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Review

Au(III) Cyclometallated Compounds with 2-Arylpyridines and Their Derivatives or Analogues: 34 Years (1989–2022) of NMR and Single Crystal X-ray Studies

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Abstract: A review paper on Au(III) cyclometallated compounds with 2-arylpyridines (2-phenylpyridine, 2-benzylpyridine, 2-benzoylpyridine, 2-phenoxypyridine, 2-phenylsulfanylpyridine, 2-anilinopyridine, 2-(naphth-2-yl)pyridine, 2-(9,9-dialkylfluoren-2-yl)pyridines, 2-(dibenzofuran-4-yl)pyridine, and their derivatives) and their analogues (2-arylquinolines, 1- and 3-arylisoquinolines, 7,8-benzoquinoline), with 113 references. A total of 554 species, containing κ^2-N(1),C(6′)*-Au(III), or analogous moiety (i.e., chelated by nitrogen of the pyridine-like ring and the deprotonated *ortho*- carbon of the phenyl-like ring) and, thus, possessing a character intermediate between metal complexes and organometallics, studied in the years 1989–2022 by NMR spectroscopy and/or single crystal X-ray diffraction (207 X-ray structures), are described. The compounds for which biological or catalytic activity and the luminescence properties were studied are also quoted.

Keywords: Au(III) compounds; 2-phenylpyridine; cyclometallation; ^{15}N NMR; X-ray

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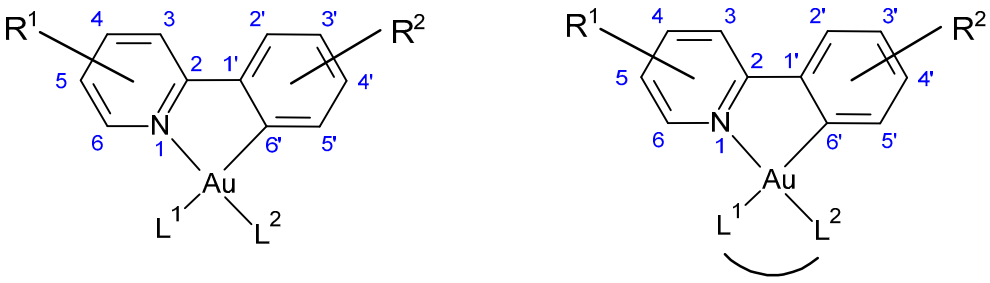
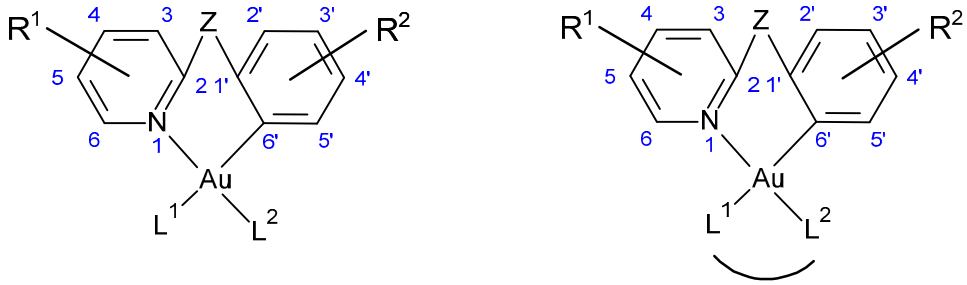
1. Introduction

The compound 2-Phenylpyridine (2ppy) is aza aromatic, which is known to coordinate transition metal ions in two alternative ways: as a monodentate N(1)-donor or a bidentate N(1),C(6′)*-chelating agent 2ppy* (2ppy* = monoanionic form of 2ppy, deprotonated in the phenyl side group at the *ortho*-carbon C(6′)*). In the latter case, it may form Au(III)-2ppy* cycloaurated compounds, which can be regarded as either complexes or organometallics (due to the presence of both gold–nitrogen and gold–carbon bonds), usually upon the presence of some other auxiliary ligands (inorganic and/or organic), which complete the square-planar (d^8) coordination sphere. The same κ^2-N(1),C(6′) coordination mode is also observed for 2ppy* derivatives containing substituents in the pyridine and/or in the phenyl ring (denoted as 2PPY*) and results in a large variety of Au(III)-2PPY* species. They are presented, together with the numbering of both aromatic rings, in a general form in Scheme 1 (L^1, L^2, and L^1L^2 denote mono- and bidentate auxiliary ligands, respectively).

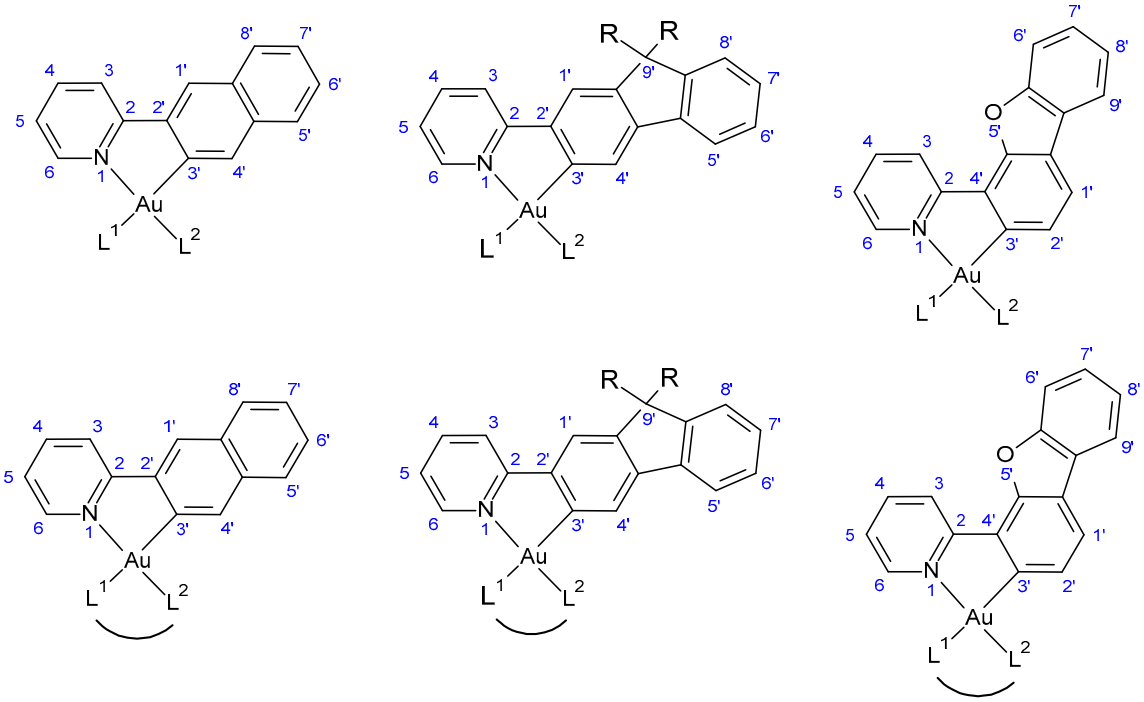


Scheme 1. Au(III)-2PPY* compounds (R^1, R^2—any substituents) with L^1, L^2 monodentate ligands (in particular—with X, Y halides) or L^1L^2 bidentate ligand.

The same κ^2-N(1),C(6′) coordination of Au(III) is observed for such analogues of 2ppy* as 2-benzylpyridine*, 2-benzoylpyridine*, 2-phenoxypyridine*, 2-phenylsulfanylpyridine*, and 2-anilinopyridine* (Scheme 2), while the similar κ^2-N(1),C(3′) one for 2-(naphth-2-yl)pyridine*, 2-(9,9-dialkylfluoren-2-yl)pyridines* and 2-(dibenzofuran-4-yl)pyridine* (Scheme 3), including their derivatives, substituted in any places of the parent heterocycles. These analogues of 2PPY*, generally named here as 2-arylpyridines* (denoted as 2ArPY*), yield many Au(III)-2ArPY* species.

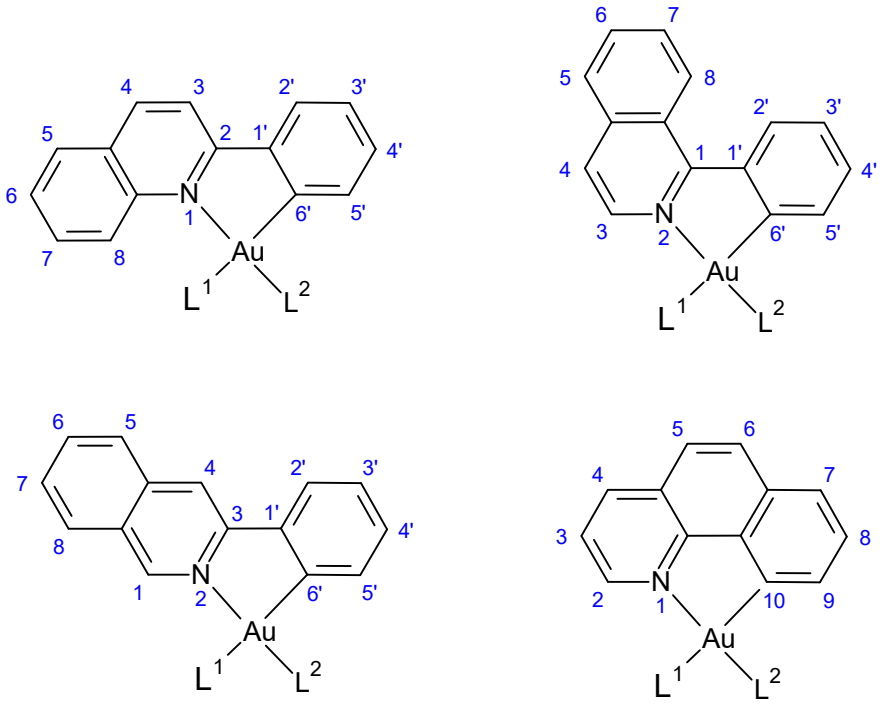


Scheme 2. Au(III)-2ArPY* compounds with 2ArPY* of the type A (Z = CH_2 in 2-benzylpyridine*, CO in 2-benzoylpyridine*, O in 2-phenoxypyridine*, S in 2-phenylsulfanylpyridine*, NH in 2-anilinopyridine*; R^1, R^2—any substituents) with L^1, L^2 monodentate ligands (in particular—with X halides) or L^1L^2 bidentate ligand.



Scheme 3. Au(III)-2ArPY* compounds with 2ArPY* of the type B (2-(naphth-2-yl)pyridine*—(**left**), 2-(9,9-dialkylfluoren-2-yl)pyridines*—(**middle**), 2-(dibenzofuran-4-yl)pyridine*—(**right**) with L^1, L^2 monodentate ligands (in particular—with X halides) or L^1L^2 bidentate ligand.

Analogous Au(III) chelation is also known for analogues of 2ArPY* containing pyridine-like ring ($PY^{\#}$, e.g., quinoline or isoquinoline) and aryl ring (Ar), linked by a single bond (in 2-arylquinolines* and 1- or 3-arylisoquinolines*) or fused (in 7,8-benzoquinoline*), together with their derivatives (denoted as $ArPY^{\#}$*). The coordination mode is generally similar, although the numbering of atoms may differ for various ring systems (usually nitrogen N(1) or N(2) in the $PY^{\#}$ moiety and the deprotonated *ortho*-carbon C(6′) or C(10) in the Ar moiety; Scheme 4)—resulting in some Au(III)-$ArPY^{\#}$* species.

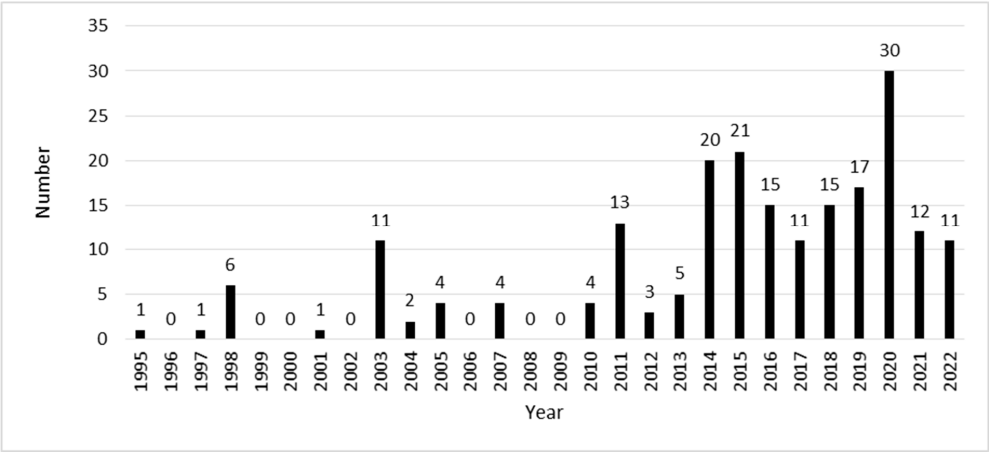


Scheme 4. Au(III)-ArPY#* compounds with 2-arylpyridines analogues: 2-phenylquinoline* (**top left**), 1-phenylisoquinoline* (**top right**), 3-phenylisoquinoline* (**bottom left**), 7,8-benzoquinoline* (**bottom right**) with L^1, L^2 monodentate ligands (in particular—with X halides) or L^1L^2 bidentate ligand (the latter case is omitted for clarity).

It must be underlined that the concerned bidentate coordination mode of 2ppy*, 2PPY*, 2ArPY*, and ArPY#* is also widely observed for many other transition metal ions; however, this review is focused on the Au(III) compounds only.

Its main aim is the summary of NMR and X-ray structural data. However, many concerned species exhibit biological (anti-tumour and/or anti-microbial) and catalytic activity, as well as luminescence (both fluorescence and phosphorescence), which allows for some practical applications; these properties were also described, at least in the most important cases.

The increasing interest in this class of Au(III) compounds can be illustrated by the numbers of molecules for which the single crystal X-ray structures were published (totally 207) every year, as presented in Scheme 5:



Scheme 5. Annual numbers of Au(III) compounds with 2ppy*, 2PPY*, 2ArPY*, and ArPY#*, for which the single crystal X-ray structures were published in the years 1995–2022.

The year-to-year fluctuations can be eliminated by calculating the numbers of molecules with the published X-ray structures for each 5-year period, as follows: 1995–1999: 8, 2000–2004: 14, 2005–2009: 8, 2010–2014: 45, 2015–2020: 79, from 2020: already 53 (in three years). This tendency clearly exhibits the growth of research intensity on the concerned compounds.

Generally, the data contained in this paper can be found in some databases, such as Reaxys or CCDC. However, their collection in one reviewing article allows the researchers to compare them and to deduce some general conclusions. In fact, it was the principal purpose of this review.

2. Reviewed Data

2.1. Au(III)-2PPY Compounds*

2.1.1. Au(III)-2PPY* Dihalides

The simplest representative of this class of chemicals is [Au(2-phenylpyridine*)Cl_2] (i.e., [Au(2ppy*)Cl_2]), described for the first time in 1989 by Constable et al. [1]. It is widely used as a precursor for the synthesis of some other Au(III)-2ppy* compounds; thus, the number of articles where it appears is really large, and the most noteworthy papers are those in which its NMR characterization was given [1–10], together with the single crystal X-ray structure (IJAQEP) [3]. Surprisingly, despite numerous reports about this dichloride [Au(2ppy*)Cl_2] species, there are no literature data on its analogues with some other halogens (F, Br, I)—although they are available for similar Au(III)-2PPY* (2PPY* ≠ 2ppy*) dihalides.

Among the dihalides having the general formula [Au(2PPY*)XY] (X, Y = F, Cl, Br, I), including [Au(2PPY*)X_2], and particularly, the most popular [Au(2PPY*)Cl_2] one, 43 (not counting [Au(2ppy*)Cl_2]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2,5,8–24].

A total of 3 of them contained 2ppy* derivatives, substituted only in the pyridine ring (R^1 = 3-methyl-, 4-*n*-propyl-, 5-*n*-butyl-) [2,10,11], while 25 had 2ppy* derivatives with substituent(s) exclusively in the phenyl ring (R^2 = 2-, 3- and 4-methyl-; 3-*n*-butyl; 4-*tert*-butyl-; 2- and 4-fluoro-; 2,4-difluoro-; 4-chloro-; 3- and 4- trifluoromethyl-; 3- and 4-methoxy-; 4-*n*-butoxy-; 3,5-dimethoxy-; 2- and 4-trifluoromethoxy-; 4-formyl-; 2-, 3- and 4-phenyl; 4-(9-bromo)-*n*-nonoxy)-; 4-(9-trimethylammonium-*n*-nonoxy)-; 4-(9-(4-methylphenylsulfonoxy)-*n*-nonoxy-) [5,8–20]. Then, 15 possessed 2ppy* derivatives substituted in both the pyridine and the phenyl ring (3-methyl-2-(2-fluorophenyl)pyridine*, 3-methyl-2-(3,4,5-trimethoxyphenyl) pyridine*, 5-carboxy-2-(4-carboxyphenyl)pyridine*, 5-ethoxycarbonyl-2-(4-ethoxycarbonylphenyl) pyridine*, 4-dimethylamino-2-(2,3,4-trifluorophenyl)pyridine*, 4-dimethylamino-2-(3-trifluoromethylphenyl)pyridine*, 4-dimethylamino-2-(4-trifluoromethoxyphenyl) pyridine*) [21–24].

All these [Au(2PPY*)XY] dihalides (Scheme 1 left, for L^1 = X and L^2 = Y) are listed in Table 1 (the 2PPY* ligands are presented as 2ppy* derivatives, variously substituted in the pyridine ring (by R^1) and/or in the phenyl ring (by R^2), so having the general formula/name of a-R^1-2-(b-R^2-phenyl)pyridine* (a = 3–6, b = 2–5)), together with the main solvents used upon the NMR studies and the CCDC reference codes for the respective single crystal X-ray structures; moreover, the biological (BIO) and catalytic (CAT) activity, as well as luminescence properties (LUM), are indicated. The same notations will be used in all other tables.

Table 1. NMR and/or X-ray studied [Au(2PPY*)XY] (in particular, [Au(2PPY*)X_2]) dihalides (2PPY* = a-R^1-2-(b-R^2-phenyl)pyridine*, where R^1 and R^2 are substituents in the pyridine ring and the phenyl ring, respectively, a = 3–6, b = 2–5; X, Y = F, Cl, Br, I).

R^1	R^2	X	Y	NMR Solvent	X-ray (CCDC)	Activity [$]
H	H	Cl	Cl	DMSO-d_6 [1–10]	IJAQEP [3]	CAT [16,17]
3-methyl	H	Cl	Cl	DMSO-d_6 [10]		
4-*n*-propyl	H	Cl	Cl	DMSO-d_6 [2]		
5-*n*-butyl	H	Cl	Cl	DMSO-d_6 [11]		
H	2-methyl	Cl	Cl	DMSO-d_6 [10]		
H	2-methyl	Br	Br		JOTQOA [12] [a]	
H	3-methyl	Cl	Cl	DMSO-d_6 [10]		
H	4-methyl	Cl	Cl	DMSO-d_6 [5,8–10,13]		CAT [17]
H	3-*n*-butyl	Cl	Cl	DMSO-d_6 [11]		
H	4-*tert*-butyl	Cl	Cl	DMSO-d_6 [10]		BIO1 [25,26]
H	2-fluoro	Cl	Cl	DMSO-d_6 [10]		
H	4-fluoro	Cl	Cl	DMSO-d_6 [10,14]	FOPBUJ [14]	
H	2,4-difluoro	Cl	Cl	DMSO-d_6 [15]	HOSHOO [16]	CAT [16]
H	4-chloro	Cl	Cl	DMSO-d_6 [17]		CAT [17]
H	3-trifluoromethyl	Cl	Cl	CD_2Cl_2 DMSO-d_6 [10,18]		
H	4-trifluoromethyl	Cl	Cl	DMSO-d_6 [10,18]		
H	3-methoxy	Cl	Cl	DMSO-d_6 [10]		
H	4-methoxy	Cl	Cl	DMSO-d_6 [17]		CAT [17]
H	4-*n*-butoxy	Cl	Cl	DMSO-d_6 [11]		
H	3,5-dimethoxy	Cl	Cl	DMSO-d_6 [10]		
H	2-trifluoromethoxy	Cl	Cl	CD_2Cl_2 [18]	MIYYUR [18]	
H	4-trifluoromethoxy	Cl	Cl	DMSO-d_6 [18]		
H	4-formyl	Cl	Cl	DMSO-d_6 [8,9]		
H	2-phenyl	Cl	Cl	DMSO-d_6 [10]		
H	3-phenyl	Cl	Cl	DMSO-d_6 [10]		
H	4-phenyl	Cl	Cl	DMSO-d_6 [10,19]		
H	4-(9-bromo-*n*-nonoxy)	Cl	Cl	$CDCl_3$ [20]		
H	4-(9-trimethylammonio-*n*-nonoxy) [1]	Cl	Cl	CD_3OD [20]		
H	4-(9-(4-methylphenylsulfonoxy)-*n*-nonoxy)	Cl	Cl	CD_2Cl_2 [20]		
3-methyl	2-fluoro	F	F	CD_2Cl_2 [21]	DAJRAK [21]	
3-methyl	2-fluoro	Cl	Cl	CD_2Cl_2 [21]	DAJQOX [21]	
3-methyl	3,4,5-trimethoxy	F	F	CD_2Cl_2 [21]	DAJREO [21]	
3-methyl	3,4,5-trimethoxy	Cl	Cl	CD_2Cl_2 [21]	DAJQUD [21]	
5-carboxy	4-carboxy	Cl	Cl	DMSO-d_6 [22,23]	GAKZUR [22] [b]	CAT [22]
5-carboxy	4-carboxy	Br	Br	DMSO-d_6 [23]	VUVLAC [23] [b]	

Table 1. *Cont.*

R^1	R^2	X	Y	NMR Solvent	X-ray (CCDC)	Activity [$]
5-carboxy	4-carboxy	I	I	DMSO-d_6 [23]	VUVKUV [23] [b]	
5-carboxy	4-carboxy	Cl [2]	I [2]	DMSO-d_6 DMF-d_7 [23]	VUVKOP [23] [b]	
5-carboxy	4-carboxy	Br [2]	I [2]	DMSO-d_6 DMF-d_7 [23]	VUVLEG [23] [b]	
5-ethoxycarbonyl	4-ethoxycarbonyl	Cl	Cl	$CDCl_3$ DMSO-d_6 [22,23]		CAT [22]
5-ethoxycarbonyl	4-ethoxycarbonyl	Br	Br	CD_2Cl_2 DMSO-d_6 [23]		
5-ethoxycarbonyl	4-ethoxycarbonyl	I	I	CD_2Cl_2 DMSO-d_6 [23]		
4-dimethylamino	2,3,4-trifluoro	Cl	Cl	CD_2Cl_2 [24]		
4-dimethylamino	3-trifluoromethyl	Cl	Cl	CD_2Cl_2 [24]		
4-dimethylamino	4-trifluoromethoxy	Cl	Cl	CD_2Cl_2 [24]		

[$] Types of activity: BIO—biological (BIO1—anti-tumour, BIO2—anti-microbial, i.e., anti-bacterial and/or anti-fungal); CAT—catalytic; LUM—luminescence (LUM1—with t > 10 μs, LUM2—with t < 10 μs). [1] this substituent is positively charged at the trimethylammonium moiety, so the whole [Au(2PPY*)Cl_2] compound is cationic (+1), appearing with the respective counterion (Br^- or *p*-$CH_3C_6H_4SO_3^-$ anion) and forming the bromide or 4-methylphenylsulfonate (tosylate) salt. [2] these mixed chloride-iodide and bromide-iodide ([Au(2PPY*)ClI], [Au(2PPY*)BrI]) compounds have *trans*(I,N) geometry. [a] monohydrate. [b] dimethyl sulfoxide solvate.

Among these [Au(2PPY*)XY] compounds, [Au(2-(4-*tert*-butylphenyl)pyridine*)Cl_2] is biologically active, revealing anti-tumour properties (against breast or lung cancer and leukemia) [25,26]. Some other [Au(2PPY*)Cl_2] dichloride species have catalytic properties (in reactions between alkynes, carbonyl compounds, and amines or imines—yielding amines, allenes, or oxazoles [16,17]—as well as between propargyl esters and styrene—yielding cyclopropane derivatives [22]).

2.1.2. Au(III)-2ppy* Compounds with Auxiliary Ligands Other Than Halides

In addition to [Au(2ppy*)Cl_2], 92 Au(III)-2ppy* compounds with various auxiliary ligands (both organic and inorganic, but not halides), having the general formula [Au(2ppy*)L^1L^2] (in case of $L^1 = L^2$, i.e., identical L ligands: [Au(2ppy*)L_2]) or [Au(2ppy*)(L^1L^2)] (in case of symmetrical LL ligands: [Au(2ppy*)(LL)]), as shown in Scheme 1 (left or right, respectively; for $R^1 = R^2 = H$), were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2,3,5–8,11,15,19,27–50]. They are listed (except for [Au(2ppy*)Cl_2], shown in Table 1) in Table 2. In case when the sum of electric charges at auxiliary ligand(s) was different from −2 (0 or −1), the concerned Au(III)-2ppy* compound was cationic (+2 or +1 charge), and the relevant anion presented in a separate column *Counterion*; otherwise (the sum of electric charges at auxiliary ligand(s) being −2), the Au(III)-2ppy* molecule was electrically neutral.

Table 2. NMR and/or X-ray studied [Au(2ppy*)L^1L^2] (in particular, [Au(2ppy*)L_2]) and [Au(2ppy*)(L^1L^2)] (in particular, [Au(2ppy*)(LL)]) compounds (L^1, L^2, L—monodentate ligands other than F, Cl, Br, I; L^1L^2, LL—bidentate ligands).

L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
CN	CN			DMSO-d_6 [27]	DUZCOS [27]		LUM2 [27]
SCN	NCS			DMSO-d_6 [28]	ILETOI [28]	*trans*(S,N)	BIO1 [28]
		ethane-1,2-dithiolate		$CDCl_3$ [2]			
		propan-1-ol-2,3-dithiolate		DMSO-d_6 [28]			BIO1 [28]
		1,4,7-trithiacyclononane-κ^3-S,S,S	$2PF_6^-$	CD_3NO_2 [5]	MOCFOB [5]		
propan-2-one-1-yl	Cl				BIGRAL [29]	*trans*(C,N)	
propan-2-one-1-yl	NO_3			DMSO-d_6 [29]	BIGREP [29]	*trans*(C,N)	
n-pentane-2,4-dione-3-yl	Cl			$CDCl_3$ [30]			
acetate	acetate			$CDCl_3$ DMSO-d_6 [3,31]	IJAQIT [3] [a] DUNCAT [31]		BIO1 [3,31]
		malonate		DMSO-d_6 [3]			BIO1 [3]
		cyclobutane-1,1-dicarboxylate		DMSO-d_6 [3]	IJAQUF [3]		BIO1 [3]
		2-thiolatepropionate		DMSO-d_6 [28]			BIO1 [28]
		2,3-dithiolatesuccinic acid		DMSO-d6 [28]			BIO1 [28]
		ethane-1-amine-2-thiolate	$B(C_6H_5)_4^-$	DMSO-d_6 [2]			
		ethane-1,2-diamine	$2ClO_4^-$	CD_3OD [32]			
		dimethylaminocarbodithioate	PF_6^-	DMSO-d_6 [2]			
		diethylaminocarbodithioate	$B(C_6H_5)_4^-$ PF_6^-	DMSO-d_6 [2,11]	MAXQOR [2]		BIO1 [11]
		di(*n*-butyl)aminocarbodithioate	PF_6^-	DMSO-d_6 [11]			BIO1 [11]
		1,1-dimethylbiguanidate	Cl^- PF_6^-	D_2O DMSO-d_6 [8,33]	REBLET [8] CEWGOE [33] [b]		BIO1 [8,33]
		2-amine-3-thiolatepropionate & 2-amine-3-thiolatepropionic acid [1A]	NO_3^-	CD_3OD [34]	LORCOM [34] [c]	*trans*(S,N)	
		2-amine-3-methyl-3-thiolatebutyrate		CD_3OD [34]	LORCEC [34] [d]	*trans*(S,N)	
		2-amine-3-methyl-3-thiolatebutyrate & 2-amine-3-methyl-3-thiolatebutyric acid [1B]	NO_3^-	CD_3OD [34]	LORCIG [34] [e]	*trans*(S,N)	

Table 2. *Cont.*

L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
trimethylphosphine	Cl		BF_4^-	CD_3COCD_3 [35]	QUNSIE [35]	*trans*(P,N)	
tricyclohexylphosphine	Cl		BF_4^-	CD_2Cl_2 [36]	IVAYUB [36] [f]	*trans*(P,N)	
trimethylsilylethynyl	trimethylsilylethynyl			CD_2Cl_2 [37]			LUM1 [37]
triisopropylsilylethynyl	triisopropylsilylethynyl			CD_2Cl_2 [15]	IZOSUM [15]		LUM2 [15]
phenyl	phenyl			$CDCl_3$ [38]	EWOJUW [38] [f]		LUM2 [38]
		1,1′-biphen-2,2′-diyl		CD_2Cl_2 [38]	EWOJOQ [38]		LUM2 [38]
phenylethynyl	phenylethynyl			$CDCl_3$ [15]	IZOSOG [15]		LUM2 [15]
4-ethylphenylethynyl	4-ethylphenylethynyl			$CDCl_3$ [37]			LUM1 [37]
4-(phenylethynyl)phenylethynyl	4-(phenylethynyl)phenylethynyl			$CDCl_3$ [15]			LUM1 [15]
		bis(2-acetylidephenyl)acetylene		DMSO-d_6 [39]			LUM1 [39]
4-fluorophenylethynyl	4-fluorophenylethynyl			CD_2Cl_2 CD_3CN [15,40]	IZOTIB [15] [f]		LUM2 [15]
pentafluorophenyl	pentafluorophenyl			$CDCl_3$ [38]			LUM2 [38]
4-trifluoromethylphenyl	4-trifluoromethylphenyl			CD_2Cl_2 [38]	EWOKAD [38] [f]		LUM2 [38]
4-trifluoromethylphenylethynyl	4-trifluoromethylphenylethynyl			CD_2Cl_2 [37]			LUM1 [37]
2,4,6-tris(trifluoromethyl)phenyl	Cl			CD_2Cl_2 [41]	GIVRIO [41]	*trans*(C,N)	LUM2 [41]
2,4,6-tris(trifluoromethyl)phenyl	I			CD_2Cl_2 [41]	GIVSOV [41]	*trans*(C,N)	LUM2 [41]
2,4,6-tris(trifluoromethyl)phenyl	CN			CD_2Cl_2 [41]	GIVSEL [41]	*trans*(C^{phenyl},N)	LUM2 [41]
2,4,6-tris(trifluoromethyl)phenyl	H_2O		$CF_3SO_3^-$	CD_2Cl_2 [42]	XOLCEI [42]	*trans*(C,N)	BIO1 [43] CAT [42] LUM1 [42]
2,4,6-tris(trifluoromethyl)phenyl	OH			CD_2Cl_2 [43]	FONDIX [43]	*trans*(C,N)	BIO1 [43]
2,4,6-tris(trifluoromethyl)phenyl	trifluoroacetate			CD_2Cl_2 [43]	FONCIW [43] [f]	*trans*(C,N)	BIO1 [43]
2,4,6-tris(trifluoromethyl)phenyl	4-fluoroaniline		$CF_3SO_3^-$	CD_2Cl_2 [42]	XOLCUY [42] [f]	*trans*(C,N^{2ppy})	CAT [42] LUM1 [42]
2,4,6-tris(trifluoromethyl)phenyl	4-phenylpyridine		$CF_3SO_3^-$	CD_2Cl_2 [42]	XOLCIM [42]	*trans*(C,N^{2ppy})	BIO1 [43] CAT [42] LUM1 [42]
2,4,6-tris(trifluoromethyl)phenyl	quinoline		$CF_3SO_3^-$	CD_2Cl_2 [42]	XOLCOS [42]	*trans*(C,N^{2ppy})	BIO1 [43] CAT [42] LUM1 [42]
2,4,6-tris(trifluoromethyl)phenyl	phenylethynyl			CD_2Cl_2 [41]	GIVSUB [41]	*trans*(C^{phenyl},N)	LUM2 [41]
2,4,6-tris(trifluoromethyl)phenyl	4-diphenylaminophenylethynyl			CD_2Cl_2 [41]			LUM2 [41]

Table 2. *Cont.*

L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
2,4,6-tris(trifluoromethyl)phenyl	trimethyl phosphite		$CF_3SO_3^-$	CD_2Cl_2 [42]	XOLDAF [42] [g]	*trans*(C,N)	CAT [42] LUM1 [42]
2,4,6-tris(trifluoromethyl)phenyl	triphenylphosphine		$CF_3SO_3^-$	CD_2Cl_2 [42]	XOLDEJ [42] [f]	*trans*(C,N)	BIO1 [43] CAT [42] LUM1 [42]
4-methoxyphenylethynyl	4-methoxyphenylethynyl			$CDCl_3$ [37]	AJOWUS [37]		LUM1 [37]
3,4,5-trimethoxyphenylethynyl	3,4,5-trimethoxyphenylethynyl			CD_2Cl_2 [15]	IZOTOH [15]		
		1,1′-biphenyl-2,2′-diolate		CD_2Cl_2 [44]			
		1,1′-binaphthyl-2-one-2′-olate-1-yl		$CDCl_3$ [45]		*R*/*S*	
		toluene-3,4-dithiolate		DMSO-d_6 [46]	HIRZIR [46]		
benzoate	benzoate			DMSO-d_6 [3]	IJAQOZ [3] [h]		BIO1 [3]
		2-thiolatebenzoate		DMSO-d_6 [28]	ILETIC [28] [i]	*trans*(S,N)	BIO1 [28,51]
		1-phenylbiguanidate	Cl^-	DMSO-d_6 [8]			BIO1 [8]
		1-(2-phenylethyl)biguanidate	PF_6^-	DMSO-d_6 [33]			BIO1 [33]
4-aminophenylethynyl	4-aminophenylethynyl			DMSO-d_6 [37]			LUM1 [37]
		L-cysteinate	1/2 Cl^- 1/2 ClO_4^-	DMSO-d_6 [28]	ILETEY [28] [g]	*trans*(S,N)	
		L-phenylalaninate	Cl^-	$CDCl_3$ [31]			BIO1 [31]
		L-methioninate	Cl^-	$CDCl_3$ [31]			BIO1 [31]
N-acetyl-L-cysteinate	Cl				AZOKUY [30]	*trans*(S,N)	
		2,2′-bipyridine	$2Cl^-$	CD_3OD [32]			
		2,3-bis(pyridin-2-yl)-6,7-dimethylquinoxaline	$2Cl^-$	CD_3CN [32]			
thiophen-2-yl	thiophen-2-yl			$CDCl_3$ [38]	EWOKEH [38]		LUM2 [38]
thiophen-2-ylethynyl	thiophen-2-ylethynyl			$CDCl_3$ [15]			
1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene	Cl		Cl^- BF_4^-	$CDCl_3$ CD_2Cl_2, CD_3COCD_3 [7,36]			CAT [7]
1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene	H_2O		$2BF_4^-$	CD_2Cl_2 [7]			
1,3-dicyclohexylimidazol-2-ylidene	Cl		BF_4^-	CD_3COCD_3 [36]	IVAZAI [36]	*trans*(C,N)	

Table 2. *Cont.*

L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene	Cl		BF_4^-	CD_2Cl_2 [36]			
1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene	Cl		BF_4^-	CD_2Cl_2 [36]			
		methylenebis(3-methyl-*1H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
		methylenebis(3-*n*-butyl-*1H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
		methylenebis(3-(3-sulfonate-*n*-propyl)-*1H*-imidazol-1-yl-2-ylidene)		D_2O [19]			LUM1 [19]
		1,2-ethylenebis(3-*n*-butyl-*1H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
		1,3-propylenebis(3-*n*-butyl-*1H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
		3,3′-bis(trifluoromethyl)-5,5′-bipyrazolate		DMSO-d_6 [6]			
		1,1-dimethylmethylenebis(3-trifluoromethylpyrazol-5-ylate)		CD_2Cl_2 [6]			
triphenylphosphine	Cl		$CF_3SO_3^-$ BF_4^-	$CDCl_3$ CD_3CN [7,36]	IVAYOV [36]	*trans*(P,N)	CAT [7]
triphenylphosphine	FBF_3		BF_4^-		IVAZEM [36] [f]	*trans*(P,N)	
triphenylphosphine	H_2O		$2BF_4^-$	CD_2Cl_2 [36]			
P(4-trifluoromethylphenyl)$_3$	Cl		BF_4^-	CD_2Cl_2 [36]			
P(4-methoxyphenyl)$_3$	Cl		BF_4^-	CD_3CN [36]			
		1,2-bis(diphenylphosphino)benzene$_2$	$2Cl^-$	$CDCl_3$ [9]			BIO1 [9]
		benzene-1-(diphenylphosphine)-2-thiolate	$B(C_6H_5)_4^-$	DMSO-d_6 [2]	MAXQIL [2]	*trans*(P,N)	
		oxybis(4-isopropoxyphenylborinate)		$CDCl_3$ [47]			
		2-((4,5-ethylenedithio)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate		DMSO-d_6 [48]	TAFJEQ [48] [j]		

Table 2. *Cont.*

L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
		2-((4,5-ethylenedithio)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate & 2-((4,5-ethylenedithio)-1,3-dithiole-2-ylidene)-1,3-dithiole-4-thione-5-thiolate [3A]	PF_6^- AsF_6^- TaF_6^-		AMEXIZ [49] YEDPUT [50] [k] YEDQAA [50] [k]		
		2-((4,5-ethylenedioxy)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate		DMSO-d_6 [50]			
		2-((4,5-ethylenedioxy)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate & 2-((4,5-ethylenedioxy)-1,3-dithiole-2-ylidene)-1,3-dithiole-4-thione-5-thiolate [3B]	BF_4^-		YEDPON [50]		
		2-(bis(*n*-decylthio)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate		$CDCl_3$ [48]			

[$] Types of activity: BIO—biological (BIO1—anti-tumour, BIO2—anti-microbial, i.e., anti-bacterial and/or anti-fungal); CAT—catalytic; LUM—luminescence (LUM1—with t > 10 µs, LUM2—with t < 10 µs). [1A–1B] These compounds contain two types of [Au(2ppy*)(L^1L^2)] species: [Au(2ppy*)(2-amine-3-thiolatepropionate)] (1A) or [Au(2ppy*)(2-amine-3-methyl-3-thiolatebutyrate)] (1B) neutral molecule and [Au(2ppy*)(2-amine-3-thiolatepropionic acid)]$^+$ (1A) or [Au(2ppy*)(2-amine-3-methyl-3-thiolatebutyric acid)]$^+$ (1B) cation, together with NO_3^- anion. [2] It is unclear whether this compound should be regarded as [Au(2ppy*)(1,2-bis(diphenylphosphino)benzene)]Cl_2 or rather [Au(2ppy[$])(1,2-bis(diphenylphosphino)benzene)Cl]Cl (2ppy[$] = monoanionic form of 2ppy, deprotonated and binding monodentately by C(2′)). [3A–3B] These compounds contain two types of [Au(2ppy*)(L^1L^2)] species: [Au(2ppy*)(2-((4,5-ethylenedithio)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate)] (3A) or [Au(2ppy*)(2-((4,5-ethylenedioxy)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate)] (3B) neutral molecule and [Au(2ppy*)(2-((4,5-ethylenedithio)-1,3-dithiole-2-ylidene)-1,3-dithiole-4-thione-5-thiolate)]$^+$ (3A) or [Au(2ppy*)(2-((4,5-ethylenedioxy)-1,3-dithiole-2-ylidene)-1,3-dithiole-4-thione-5-thiolate)]$^+$ (3B) cation, together with PF_6^-, AsF_6^-, TaF_6^- (all 3A), or BF_4^- anion. [a] monohydrate. [b] methanol solvate. [c] trihydrate. [d] dihydrate. [e] methanol solvate dihydrate. [f] dichloromethane solvate. [g] hemihydrate. [h] diethyl ether solvate. [i] sesquihydrate [j] dimethylformamide solvate. [k] chlorobenzene solvate.

Many these Au(III)-2ppy* compounds are biologically active, revealing anti-tumour properties (against various breast, cervix, colon, liver, lung, and ovarian cancers, as well as glioblastoma, leukemia, and melanoma) [3,8,9,11,28,31,33,43,51]. Some others have catalytic properties (in the hydration of alkynes to enoles [7] and photo-oxidation of benzylic amines to imines [42]). Then, a large number reveals luminescence, with lifetimes of either >10 μs [15,19,37,39,42] or <10 μs [15,27,38,41].

2.1.3. Au(III)-2PPY* Compounds with Auxiliary Ligands Other Than Halides

In addition to [Au(2PPY*)XY] (including [Au(2PPY*)X_2]) and [Au(2ppy*)L^1L^2], including [Au(2ppy*)L_2]) or [Au(2ppy*)(L^1L^2)], including [Au(2ppy*)(LL)]) compounds, 209 Au(III)-2PPY* species with various auxiliary ligands (other than halides)), having the general formulae [Au(2PPY*)L^1L^2] (in particular, [Au(2PPY*)L_2]; L^1, L^2, L ≠ F, Cl, Br, I) or [Au(2PPY*)(L^1L^2)] (in particular, [Au(2PPY*)(LL)]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2,5,8,11,12,14,15,18,19,21–27,31,37,47,52–76]; this is the most general case presented in Scheme 1 (for 2PPY* ≠ 2ppy* and L^1, L^2 ≠ F, Cl, Br, I). They are listed (except for [Au(2PPY*)XY], [Au(2ppy*)L^1L^2] and [Au(2ppy*)(L^1L^2)], already shown in Tables 1 and 2) in Table 3.

A total of 5 of them contained 2ppy* derivatives, substituted only in the pyridine ring (R^1 = 3-methyl-, 5-*n*-butyl-, 4-*tert*-butyl-, 3,5-dimethyl-) [2,11], while 137—only in the phenyl ring (2- and 4-methyl-; 3-ethyl-; 3- and 4-*n*-butyl; 4-*tert*-butyl-; 3,5-dimethyl-; 4-fluoro-; 2,4- and 3,5-difluoro-; 3-, 4- and 5-trifluoromethyl; 4-methoxy-; 4-*n*-butoxy-; 2- and 4-trifluoromethoxy-; 4-formyl; 4-nitro-; 4-phenyl-; 3,5-bis(pentafluorophenyl)-), with a predominance of the 2-(4-methylphenyl)pyridine* ligand (95 species) [5,8,11,12,14,15,18,19,25–27,31,37,47,51–66].

Then, 67 had 2ppy* derivatives with substituents in both the pyridine and the phenyl ring (2,6-bis(4-*tert*-butylphenyl)pyridine*; 3-methyl-2-(2-fluorophenyl)pyridine*; 4- and 5-methyl-2-(4-methoxyphenyl)pyridine*; 6-methyl-2-(4-methylphenyl)pyridine*; 5-*tert*-butyl-2-(4-*tert*-butylphenyl)pyridine*; 4-trifluoromethyl-2-(4-methylphenyl)pyridine*; 5-trifluoromethyl-2-(4-methoxyphenyl)pyridine*; 5-trifluoromethyl-2-(2-diphenylaminophenyl) pyridine*; 3-, 4-, and 6-methoxy-2-(4-methylphenyl)pyridine*; 5-carboxy-2-(4-carboxyphenyl) pyridine*; 5-ethoxycarbonyl-(2-(4-ethoxycarbonylphenyl)pyridine*; 4-dimethylamino-2-(2,3,4-trifluorophenyl)pyridine*; 4-dimethylamino-2-(3-trifluoromethylphenyl)pyridine*; 4-dimethylamino-2-(4-trifluoromethoxyphenyl)pyridine*; 3-nitro-2-(4-methylphenyl) pyridine*) [21–24,37,53,67–76]. Among these ligands, 2,6-bis(4-*tert*-butylphenyl)pyridine* is especially interesting because 2,6-bis(4-*tert*-butylphenyl)pyridine can chelate transition metal ions, not only in the bidentate way (κ^2-N(1),C(6′)*), but also in the tridentate mode (κ^3-N(1),C(6′)*,C(6″)*)—forming Au(III)-(2,6-bis(4-*tert*-butylphenyl)pyridine**) pincer compounds (2,6-bis(4-*tert*-butylphenyl)pyridine** = dianionic form of 2,6-bis(4-*tert*-butylphenyl)pyridine, deprotonated in both phenyl groups at the *ortho*- carbons C(6′)* and C(6″)*); however, such molecules were not included in this review.

Table 3. NMR and/or X-ray studied [Au(2PPY*)L^1L^2] (in particular, [Au(2PPY*)L_2]) or [Au(2PPY*)(L^1L^2)] (in particular, [Au(2PPY*)(LL)]) compounds (2PPY* = a-R^1-2-(b-R^2-phenyl)pyridine*, other than 2ppy*, where R^1 and R^2 are substituents in the pyridine ring and the phenyl ring, respectively, a = 3–6, b = 2–5; L^1, L^2, L—monodentate ligands other than F, Cl, Br, I; L^1L^2, LL—bidentate ligands).

R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
3-methyl	H			3-carboxy-2-thiolatepropionate		DMSO-d_6 [2]			
3-methyl	H	pyridine	acetate		ClO_4^-		MAXQEH [2]	*trans*(N,N)	
5-*n*-butyl	H			diethylaminocarbodithioate	PF_6^-	DMSO-d_6 [11]			BIO1 [11]
4-*tert*-butyl	H	acetate	acetate			$CDCl_3$ DMSO-d_6 [2]			
3,5-dimethyl	H	acetate	acetate			$CDCl_3$ [2]			
H	2-methyl	phenyl	Br				JOTROB [12]	*trans*(C,N)	
H	4-methyl	CN	CN			DMSO-d_6 [27]			LUM2 [27]
H	4-methyl	methyl	methyl			$CDCl_3$ CD_2Cl_2 [52,53]	QICNUN [52]		
H	4-methyl	methyl	Cl			CD_2Cl_2 [54]			
H	4-methyl	methyl	Br			CD_2Cl_2 [52,53]			
H	4-methyl	ethyl	Br			CD_2Cl_2 [52]			
H	4-methyl			allyl-η^3	$(CF_3SO_2)_2N^-$	CD_2Cl_2 [55]	ROVXUY [55]		
H	4-methyl	allyl	Br			CD_2Cl_2 [53,55]	ROVYAF [55]	*trans*(C,N)	
H	4-methyl	allyl	trideuteroacetonitrile		$(CF_3SO_2)_2N^-$	CD_3CN [55]			
H	4-methyl	ethynyl	ethynyl			CD_2Cl_2 [56]	LUWJUL [56]		
H	4-methyl	*n*-butylethynyl	*n*-butylethynyl			CD_2Cl_2 [56]			
H	4-methyl	*n*-butylethynyl	Br			CD_2Cl_2 [56]			
H	4-methyl			*n*-hexane-1,6-diethynyl		CD_2Cl_2 [56]			
H	4-methyl	thiacyclopentane	methyl		$CF_3SO_3^-$	CD_2Cl_2 [54]			
H	4-methyl			1,4,7-trithiacyclononane-κ^3-S,S,S	$2PF_6^-$	CD_3NO_2 [5]	MOCFIV [5]		
H	4-methyl	acetate	acetate			$CDCl_3$ CD_2Cl_2 [31,53]			BIO1 [31]
H	4-methyl	acetate	methyl			CD_2Cl_2 [54]	IDAJII [54] [a]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 CD_3CN C_6D_6 CD_3COOD CF_3COOD [52,53,57]	QICPAV [52]		
H	4-methyl	trifluoroacetate	hydroxymethyl			CD_2Cl_2 [58]			
H	4-methyl	trifluoroacetate	methoxyl			CD_2Cl_2 CD_3OD [58]			
H	4-methyl	trifluoroacetate	methoxyethyl			CD_2Cl_2 CD_3OD [58]	YIDHIF [58]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	formylmethyl			CD_2Cl_2 [59]	QEFVUV [59]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	acetate			CD_2Cl_2 [58]			
H	4-methyl	trifluoroacetate	$CH_3OCH(CH(CH_3)_2)CH_2^-$			CD_2Cl_2 [58]	YIDGIE [58]	*trans*(C,N)	

Table 3. *Cont.*

R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
H	4-methyl	trifluoroacetate	$CH_3OC(CH_3)(CH_2CH_3)CH_2^-$			CD_2Cl_2 [58]			
H	4-methyl	trifluoroacetate	$CH_3OC((CH_3)_2)CH(CH_3)^-$			CD_2Cl_2 [58]	YIDHEB [58]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CH_3OCH(CH_2CH_2CH_2CH_3)CH_2^-$			CD_2Cl_2 [58]	YIDHAX [58]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CH_3OCH(CH_2CH_2CH_3)CH(CH_3)^-$			CD_2Cl_2 [58]	YIDGOK [58]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CH_3OCH(CH_3)CH(CH_2CH_2CH_3)^-$			CD_2Cl_2 [58]	YIDGAW [58]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CH_3OCH(C_6H_5)CH_2^-$			CD_2Cl_2 [58]	YIDGUQ [58] [a]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CH_3CH_2OCH_2CH_2^-$			CD_2Cl_2 CD_3CD_2OD [58]			
H	4-methyl	trifluoroacetate	$(CH_3)_2CHOCH_2CH_2^-$			CD_2Cl_2 [58]			
H	4-methyl	trifluoroacetate	$(CH_3)_3COCH_2CH_2^-$			CD_2Cl_2 [58]			
H	4-methyl	trifluoroacetate	$CH_3COOCH_2CH_2^-$			CD_2Cl_2 CD_3COOD [58]	YIDGEA [58]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CF_3COOCH_2CH_2^-$			CD_2Cl_2 CF_3COOD [57]	FUWXIG [57]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CF_3CH_2OCH_2CH_2^-$			CD_2Cl_2 CF_3CD_2OD [57]	FUWXOM [57]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CF_3COOCH(CH(CH_3)_2)CH_2^-$			CD_2Cl_2 [58]	YIDFUP [58] [b]	*trans*(C,N)	
H	4-methyl	trifluoroacetate	$CF_3COOCH(CH_2CH_2CH_2CH_3)CH_2^-$			CD_2Cl_2 CF_3COOD [58]			
H	4-methyl	trifluoroacetate	$CF_3COOCH{=}CH^-$			CD_2Cl_2 [59]	QEFWAC [59] [c]	*trans*(C,N)	
H	4-methyl	trifluorosulfonate	methyl			CD_2Cl_2 [54]	IDAJOO [54]	*trans*(C,N)	
H	4-methyl			$HNC(CH_3)OCH_2CH_2^-$ [1]	CF_3COO^-	CD_2Cl_2 CD_3CN [60]	IPISEH [60]	*trans*(C,N)	
H	4-methyl			1,1-dimethylbiguanidate	Cl^-	DMSO-d_6 [8]			BIO1 [8]
H	4-methyl	acetonitrile	methyl		BF_4^-	CD_3CN [60]	IPISAD [60]	*trans*(C,N)	
H	4-methyl	trimethylsilylethynyl	trimethylsilylethynyl			CD_2Cl_2 [37,56]	LUWJEV [56] [a]		LUM1 [37]
H	4-methyl	trimethylsilylethynyl	Br			CD_2Cl_2 [56]			
H	4-methyl	trimethylsilylethynyl	ethynyl			CD_2Cl_2 [56]	LUWJIZ [56]	*trans*(HCC,N)	
H	4-methyl			oxybis(*n*-propylborinate)		$CDCl_3$ [47]			
H	4-methyl	phenyl	phenyl			CD_2Cl_2 [14,52]			
H	4-methyl	phenyl	Br			CD_2Cl_2 [52,53]			
H	4-methyl	2-methylphenyl	2-methylphenyl			CD_2Cl_2 [14]	FONRIL [14]		
H	4-methyl	3-methylphenyl	3-methylphenyl			CD_2Cl_2 [14]			
H	4-methyl	phenylethynyl	phenylethynyl			CD_2Cl_2 [56]	LUWJOF [56]		
H	4-methyl	phenylethynyl	Br			CD_2Cl_2 [56]	LUWKAS [56]	*trans*(C,N)	
H	4-methyl	phenylethynyl	ethynyl			CD_2Cl_2 [56]	LUWKIA [56]	*trans*(C_6H_5CC,N)	
H	4-methyl	phenylethynyl	trifluoroacetate			CD_2Cl_2 [56]			
H	4-methyl	phenylethynyl	trimethylsilylethynyl			CD_2Cl_2 [56]			
H	4-methyl	4-*n*-butylphenylethynyl	4-*n*-butylphenylethynyl			CD_2Cl_2 [37]			LUM1 [37]

Table 3. *Cont.*

R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
H	4-methyl	naphth-2-yl	naphth-2-yl			CD_2Cl_2 [14]			
H	4-methyl	naphth-1-yl	Cl			CD_2Cl_2 [14]	FONSAE [14]	*trans*(C,N)	
H	4-methyl	anthracen-2-yl	anthracen-2-yl			C_6D_6 [14]			
H	4-methyl	4-fluorophenyl	4-fluorophenyl			CD_2Cl_2 [14]	FOPCAQ [14]		
H	4-methyl	4-fluorophenyl	Cl			$CDCl_3$ [14]	FONRUX [14]	*trans*(C,N)	
H	4-methyl	2,4-difluorophenyl	2,4-difluorophenyl			CD_2Cl_2 [14]			
H	4-methyl	2,5-difluoro-3,6-dibromophenyl	2,5-difluoro-3,6-dibromophenyl			CD_2Cl_2 [61]			
H	4-methyl	4-trifluoromethylphenyl	4-trifluoromethylphenyl			CD_2Cl_2 [14]	FOPCEU [14] [a]		
H	4-methyl	4-chlorophenylethynyl	4-chlorophenylethynyl			CD_2Cl_2 [61]			
H	4-methyl	4-methoxyphenyl	4-methoxyphenyl			CD_2Cl_2 [14]			
H	4-methyl	4-methoxyphenylethynyl	4-methoxyphenylethynyl			$CDCl_3$ [37]	AJOXAZ [37]		LUM1 [37]
H	4-methyl	4-isopropoxyphenyl	4-isopropoxyphenyl			C_6D_6 [14]	FONROR [14]		
H	4-methyl			4-formylbenzene-1,2-diolate		DMSO-d_6 [62]			
H	4-methyl	4-benzoxyphenyl	4-benzoxyphenyl			CD_2Cl_2 [14]			
H	4-methyl	4-acetylphenyl	4-acetylphenyl			CD_2Cl_2 [14]			
H	4-methyl			acetophen-2,8-diyl		CD_2Cl_2 [14]	FONSEI [14] [a]	*trans*(C^{CH2},N)	
H	4-methyl			anthracene-9,10-dione-1,2-diolate		DMSO-d_6 solid phase [62]			
H	4-methyl	3-ethoksycarbonylphenyl	3-ethoksycarbonylphenyl			CD_2Cl_2 [14]			
H	4-methyl			2-thiolatebenzoate			ICUMEY [51]	*trans*(S,N)	BIO1 [51]
H	4-methyl			1-phenylbiguanidate	Cl^-	DMSO-d_6 [8]			BIO1 [8]
H	4-methyl			L-phenylalaninate	Cl^-	$CDCl_3$ [31]			BIO1 [31]
H	4-methyl			L-methioninate	Cl^-	$CDCl_3$ [31]			BIO1 [31]
H	4-methyl	3-nitrophenyl	3-nitrophenyl			CD_2Cl_2 [14]	FOPCIY [14]		
H	4-methyl			ethylene-1,2-bis(4-methylphenylsulfonylazanide)		unknown [63]			BIO1, BIO2 [63]
H	4-methyl			benzene-1,2-bis(acetylazanide)		unknown [63]			BIO1, BIO2 [63]
H	4-methyl			benzene-1,2-bis(4-methylphenylsulfonylazanide)		unknown [63]			BIO1, BIO2 [63]
H	4-methyl			sulfonebis(cyanomethyl)					BIO1 [64]
H	4-methyl			sulfonebis(benzoylmethyl)		unknown [64]			BIO1 [64]
H	4-methyl	1-benzothiophen-2-yl	1-benzothiophen-2-yl			CD_2Cl_2 [14]	FONREH [14]		
H	4-methyl	triphenylphosphine	methyl		$CF_3SO_3^-$	CD_2Cl_2 [54]	IDAJUU [54]	*trans*(C,N)	
H	4-methyl			1,2-bis(diphenylphosphino)benzene [2A]	$2Cl^-$	$CDCl_3$ [9]			BIO1 [9]
H	4-methyl			oxybis(phenylborinate)		$CDCl_3$ [47,65]			CAT [65]
H	4-methyl			oxybis(naphth-1-ylborinate)		$CDCl_3$ [47]			
H	4-methyl			oxybis(4-*tert*-butylphenylborinate)		$CDCl_3$ [47]			
H	4-methyl			oxybis(4-vinylphenylborinate)		$CDCl_3$ [47]	FUXGIQ [47] [a]		
H	4-methyl			oxybis(4-isopropoxyphenylborinate)		$CDCl_3$ [47]	FUXGAI [47]		

Table 3. *Cont.*

R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
H	4-methyl			oxybis(4-acetylphenylborinate)		$CDCl_3$ [47]	FUXGOW [47] [a]		
H	4-methyl			oxybis(thiophen-3-ylborinate)		$CDCl_3$ [47]			
H	4-methyl			oxybis(ferrocenylborinate)		$CDCl_3$ [47]	FUXGEM [47] [d]		
H	3-ethyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]			
H	3-*n*-butyl			diethylaminocarbodithioate	PF_6^-	DMSO-d_6 [11]			BIO1 [11]
H	4-*n*-butyl			diethylaminocarbodithioate	PF_6^-	DMSO-d_6 [11]			BIO1 [11]
H	4-*n*-butyl			di(*n*-butyl)aminocarbodithioate	PF_6^-	DMSO-d_6 [11]			BIO1 [11]
H	4-*tert*-butyl			dimethylaminocarbodithioate	PF_6^-	DMSO-d_6 [26]			BIO1 [26]
H	4-*tert*-butyl			diethylaminocarbodithioate	PF_6^-	DMSO-d_6 [26]	NIKHIB [26] [e]		BIO1 [26]
H	4-*tert*-butyl			di(*n*-butyl)aminocarbodithioate	SbF_6^-	CD_3CN [26]			BIO1 [26]
H	4-*tert*-butyl			(*n*-but-1,4-diyl)aminocarbodithioate	PF_6^-	CD_2Cl_2 [26]			BIO1 [26]
H	4-*tert*-butyl			N-(ethoxycarbonylmethyl)methylaminocarbodithioate	PF_6^-	DMSO-d_6 [26]			BIO1 [26]
H	4-*tert*-butyl	4-methoxyphenylethynyl	4-methoxyphenylethynyl			CD_2Cl_2 [37]			LUM1 [37]
H	4-*tert*-butyl			benzene-1-olate-2-acetylazanide		CD_2Cl_2 [25]			BIO1 [25]
H	4-*tert*-butyl			benzene-1,2-bis(acetylazanide)		CD_2Cl_2 [25]			BIO1 [25]
H	4-*tert*-butyl			benzene-1-olate-2-(N-(acridin-9-yl))azanide		CD_2Cl_2 [25]	KIGPEY [25] [a]	*trans*(N,N)	BIO1 [25]
H	4-*tert*-butyl			benzene-1-azanide-2-(N-(acridin-9-yl)azanide		CD_2Cl_2 [25]	KIGPIC [25] [a]	*trans*(NH,N)	BIO1 [25]
H	4-*tert*-butyl			*ortho*-bis(dicarboranyl)		CD_2Cl_2 [66]	WUCKUD [66] [a]		
H	3,5-dimethyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAZJED [53]		
H	4-fluoro	4-fluorophenyl	4-fluorophenyl			$CDCl_3$ [14]			
H	4-fluoro	3-ethoksycarbonylphenyl	3-ethoksycarbonylphenyl			$CDCl_3$ [14]			
H	2,4-difluoro	phenylethynyl	phenylethynyl			CD_2Cl_2 [15]			LUM2 [15]
H	2,4-difluoro			methylenebis(3-*n*-butyl-*1H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
H	2,4-difluoro			methylenebis(3-(3-sulfonate-*n*-propyl)-*1H*-imidazol-1-yl-2-ylidene)		D_2O [19]			LUM1 [19]
H	3,5-difluoro	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAYZAO [53]		
H	3-trifluoromethyl	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [18]	MIZHIP [18]		LUM2 [18]
H	3-trifluoromethyl	pentafluorophenyl	Cl			CD_2Cl_2 [18]	MIZHEL [18]	*trans*(Cl,N)	LUM2 [18]
H	3-trifluoromethyl	pentafluorophenyl	4-fluorophenylethynyl			DMF-d_7 [18]	MIZJAJ [18]	*trans*(CC,N)	LUM2 [18]
H	3-trifluoromethyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]			
H	3-trifluoromethyl	4-bis(2,4,6-trimethylphenyl)boranylphenylethynyl	pentafluorophenyl			DMSO-d_6 [18]	MIYYAX [18]	*trans*(CC,N)	LUM2 [18]
H	4-trifluoromethyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAZJAZ [53]		
H	4-trifluoromethyl			diethylaminocarbodithioate	PF_6^-	DMSO-d_6 [11]			BIO1 [11]
H	5-trifluoromethyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]			
H	4-methoxy	4-methoxyphenylethynyl	4-methoxyphenylethynyl			CD_2Cl_2 [37]			LUM1 [37]

Table 3. *Cont.*

R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
H	4-methoxy	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]			
H	4-*n*-butoxy			diethylaminocarbodithioate	PF_6^-	DMSO-d_6 [11]			BIO1 [11]
H	2-trifluoromethoxy	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [18]	MIYYEB [18] [a]		LUM2 [18]
H	2-trifluoromethoxy	pentafluorophenyl	Cl			CD_2Cl_2 [18]	MIYXOK [18]	*trans*(Cl,N)	LUM2 [18]
H	4-trifluoromethoxy	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [18]	MIZHOV [18] [a]		LUM2 [18]
H	4-trifluoromethoxy	pentafluorophenyl	Cl			CD_2Cl_2 [18]	MIYXUQ [18]	*trans*(Cl,N)	LUM2 [18]
H	4-formyl			1,2-bis(diphenylphosphino)benzene [2B]	$2Cl^-$	$CDCl_3$ [9]			BIO1 [9]
H	4-nitro	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAZJON [53]		
H	4-phenyl			methylenebis(3-*n*-butyl-*1H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
H	3,5-bis(pentafluorophenyl)	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAZCOG [53]		
5-*tert*-butyl	4-*tert*-butyl			diethylaminocarbodithioate					BIO1 [26]
6-(4-*tert*-butylphenyl)	4-*tert*-butyl			norbornane-2-ol-3-yl	SbF_6^-	CD_2Cl_2 [67]	PEZQUI [67]	*trans*(C,N)	
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	Cl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [68]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	methyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	2-methylallyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	phenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [68]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	4-*tert*-butylphenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	4-fluorophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [68]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	pentafluorophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [68]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	4-trifluoromethylphenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	4-chlorophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	4-methoxyphenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	diethyl ether	4-nitrophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	phenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	4-*tert*-butylphenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	4-fluorophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	pentafluorophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			

Table 3. *Cont.*

R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	4-trifluoromethylphenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	4-chlorophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	4-methoxyphenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dimethyl thioether	4-nitrophenyl		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [69]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	methyl	μ-H [3]		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [70]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	pentafluorophenyl	μ-H [3]		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [70]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	H	μ-H [4]		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [70]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	methyl	μ-H [4]		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [70]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	pentafluorophenyl	H			CD_2Cl_2 [71]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	pentafluorophenyl	triethylsilane		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [71]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	pentafluorophenyl	4,4,5,5-tetramethyl-1,3,2-dioxaborolane		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [71]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	adamantane-1-μ-thiolate [5]	adamantane-1-μ-thiolate [5]		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [72]	FIDBUS [72] [f]		
6-(4-*tert*-butylphenyl)	4-*tert*-butyl			$(CH_3)_3CCOCHCH_3^-$	SbF_6^-	CD_2Cl_2 [73]	KEKGEP [73] [a]	*trans*(C,N)	
6-(4-*tert*-butylphenyl)	4-*tert*-butyl			$CH_3COCHC(CH_3)_3^-$	SbF_6^-	CD_2Cl_2 [73]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	trifluoroacetate	methyl			CD_2Cl_2 [74]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	trifluoroacetate	ethyl			CD_2Cl_2 [74]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	4-fluorophenyl	trifluoroacetate			CD_2Cl_2 [74]	QEZYAX [74]	*trans*(C,N)	
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	pentafluorophenyl	trifluoroacetate			CD_2Cl_2 [74]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	thiophen-2-yl	trifluoroacetate			CD_2Cl_2 [74]			
6-(4-*tert*-butylphenyl)	4-*tert*-butyl	dibenzopyrrolate	diethyl ether		$H_2N(B(C_6F_5)_3)_2^-$	CD_2Cl_2 [72]			
3-methyl	2-fluoro	methyl	F			CD_2Cl_2 [21]	DAJRUE [21]	*trans*(C,N)	
3-methyl	2-fluoro	methyl	Br			CD_2Cl_2 [21]			
3-methyl	2-fluoro	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [21]			
3-methyl	2-fluoro	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [21]	DAJSAL [21] [g]		
3-methyl	2-fluoro	3,5-bis(trifluoromethyl)phenyl	F			CD_2Cl_2 [21]	DAJROY [21]	*trans*(C,N)	
3-methyl	2-fluoro	3,5-bis(trifluoromethyl)phenyl	Br			CD_2Cl_2 [21]	DAJRIS [21]	*trans*(C,N)	

Table 3. *Cont.*

R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
3-methyl	2-fluoro	3,5-bis(trifluoromethyl)phenyl	2,4,6-trifluorophenyl			CD_2Cl_2 [21]	DAJSEP [21]	*trans*($C^{3,5\text{-bis(trifluoromethyl)phenyl}}$,N)	
4-methyl	4-methoxy	4-methoxyphenylethynyl	4-methoxyphenylethynyl			CD_2Cl_2 [37]	AJOXIH [37] [a]		LUM1 [37]
5-methyl	4-methoxy	4-methoxyphenylethynyl	4-methoxyphenylethynyl			CD_2Cl_2 [37]	AJOXED [37] [a]		LUM1 [37]
6-methyl	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAZBOF [53]		
4-trifluoromethyl	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAYZOC [53] [a]		
5-trifluoromethyl	4-methoxy	4-methoxyphenylethynyl	4-methoxyphenylethynyl			CD_2Cl_2 [37]			LUM1 [37]
5-trifluoromethyl	2-diphenylamino	phenylethynyl	phenylethynyl			$CDCl_3$ [75]	WECYUB [75]		LUM2 [75]
3-methoxy	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAZKAA [53]		
4-methoxy	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAYZIW [53]		
6-methoxy	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAYYOB [53] [a]		
5-carboxy	4-carboxy	trifluoroacetate	trifluoroacetate			CD_3CN DMSO-d_6 [22]	GALBAA [22] [h]		CAT [22]
5-carboxy	4-carboxy	trifluorocarboxylethyl	Cl			DMSO-d_6 [23]			
5-carboxy	4-carboxy	trifluorocarboxylethyl	Br			DMSO-d_6 [23]			
5-carboxy	4-carboxy	trifluorocarboxylethyl	trifluoroacetate			DMSO-d_6 [23]			
5-ethoxycarbonyl	4-ethoxycarbonyl	N_3	N_3				PUXGUN [76]		
5-ethoxycarbonyl	4-ethoxycarbonyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 DMSO-d_6 [22]	GALBEE [22]		CAT [22]
5-ethoxycarbonyl	4-ethoxycarbonyl	trifluorocarboxylethyl	Cl			CD_2Cl_2 DMSO-d_6 [23]			
5-ethoxycarbonyl	4-ethoxycarbonyl	trifluorocarboxylethyl	Br			CD_2Cl_2 DMSO-d_6 [23]			
5-ethoxycarbonyl	4-ethoxycarbonyl	trifluorocarboxylethyl	trifluoroacetate			DMSO-d_6 [23]			
4-dimethylamino	2,3,4-trifluoro	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [24]	WASQOZ [24]		LUM2 [24]
4-dimethylamino	3-trifluoromethyl	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [24]			LUM2 [24]
4-dimethylamino	3-trifluoromethyl	4-fluorophenylethynyl	4-fluorophenylethy+nyl			CD_2Cl_2 [24]			LUM2 [24]
4-dimethylamino	4-trifluoromethoxy	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [24]			LUM2 [24]
3-nitro	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2 [53]	JAZBIZ [53] [a]		

[$] Types of activity: BIO—biological (BIO1—anti-tumour, BIO2—anti-microbial, i.e., anti-bacterial and/or anti-fungal); CAT—catalytic; LUM—luminescence (LUM1—with t > 10 μs; LUM2—with t < 10 μs). [1] This monoanionic $HNC(CH_3)OCH_2CH_2^-$ ligand chelates Au(III) by imine =NH nitrogen and terminal CH_2 carbon. [2A–2B] It is unclear whether these compounds should be regarded as [Au(2PPY*)(1,2-bis(diphenylphosphino)benzene)]Cl_2 (2PPY = 2-(4-methylphenyl)pyridine for 2A, 2-(4-formylphenyl)pyridine for 2B), or rather [Au(2PPY[$])(1,2-bis(diphenylphosphino)benzene)Cl]Cl (2PPY[$] = monoanionic form of 2PPY, deprotonated and binding monodentately by C(2′)). [3] These are dimeric compounds, in which both [Au(2,6-bis(4-*tert*-butylphenyl)pyridine*)R] (R = CH_3, C_6F_5) moieties are linked by a hydride ligand, with formation of the Au-H-Au bridge. [4] These are dimeric compounds, in which the [Au(2,6-bis(4-*tert*-butylphenyl)pyridine*)R] (R = H, CH_3) and [Au(2,6-bis(4-*tert*-butylphenyl)pyridine**)] moieties are linked by a hydride ligand, with formation of the Au-H-Au bridge. [5] This is a dimeric compound, in which both [Au(2,6-bis(4-*tert*-butylphenyl)pyridine*)] moieties are linked by two adamantane-1-thiolate ligands, with formation of two Au-S-Au bridges. [a] dichloromethane solvate. [b] chloroform solvate. [c] dichloromethane *n*-pentane solvate. [d] toluene solvate. [e] acetonitrile solvate. [f] dihydrate. [g] trihydrate. [h] trifluoroacetic acid solvate.

Many these Au(III)-2PPY* compounds are biologically active, revealing anti-tumour (against various breast, cervix, colon, liver, lung, mammary, and ovarian cancers, as well as glioblastoma, leukemia, and melanoma) [8,9,11,25,26,31,51,63,64], as well as anti-bacterial (against *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas aeruginosa*) and anti-fungal (against *Candida albicans*, *Trichophyton mentagrophytes*, and *Cladosporium resinae*) [63] properties. Some others have catalytic activity (in reactions between propargyl esters and styrene—yielding cyclopropane derivatives [22] and upon CO oxidation by air to CO_2 [65]). Then, a number of these species exhibits luminescence, with lifetimes of either >10 μs [19,37] or <10 μs [15,18,24,27,75].

2.2. Au(III)-2ArPY Compounds*

2.2.1. Au(III)-2ArPY* Dihalides

A total of 68 Au(III) dihalides with 2-arylpyridines*, other than 2PPY* (denoted as 2ArPY*), having the general formula [Au(2ArPY*)X_2] (X = F, Cl, Br, I), were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [6,9,13,16–19,30,33,40,62,77–90]. They are listed in Table 4 (by definition, it does not include [Au(2PPY*)X_2] species, shown in Table 1).

The contained 2ArPY* ligands are of two principal types: (A) containing a bridge (denoted as Z) between the pyridine and the phenyl ring (–CH_2– in 2-benzylpyridine*, –CO– in 2-benzoylpyridine*, –O– in 2-phenoxypyridine*, –S– in 2-phenylsulfanylpyridine*, –NH– in 2-anilinopyridine*; Scheme 2) and (B) having the pyridine ring linked to any aryl (but not phenyl) ring system (naphth-2-yl, 9,9-dialkylfluoren-2-yl, dibenzofuran-4-yl; Scheme 3).

There are 61 [Au(2ArPY*)X_2] molecules with 2ArPY* ligands of type A [9,13,16–18,30,33,40,62,77–89] (including 8 compounds having one or two substituents at the Z bridge, with this position being numbered as 1 of the aryl moiety: –CH_2– (6 species with 2ArPY* = 2-(1-methylbenzyl)pyridine*, 2-(1,1-dimethylbenzyl)pyridine*, 2-(1-methoxybenzyl)pyridine*, 2-(1-phenylbenzyl)pyridine*, 2-(1-carboxymethoxyiminobenzyl) pyridine* and 2-(1-benzoxyiminobenzyl)pyridine*) [17,77,83,84], or –NH– (2 species with 2ArPY* = 2-(1-methylanilino)pyridine* and 2-(1-propionylanilino)pyridine*) [40,83,89]), as well as 7 [Au(2ArPY*)X_2] molecules with 2ArPY* ligands of the type B [6,19,90].

Then, the [Au(2ArPY*)X_2] compounds with 2ArPY* of type A can be divided for those containing unsubstituted pyridine and phenyl rings (16 species) [9,13,16–18,30,33,40,62,77–87,89], substituted pyridine rings and unsubstituted phenyl rings (32 species) [83,88], as well as unsubstituted pyridine rings and substituted phenyl rings (13 species) [17,83,89], whereas those with simultaneously substituted pyridine and phenyl rings are absent. Similarly, the [Au(2ArPY*)X_2] compounds with 2ArPY* of the type B can be divided for these having no substituents in the pyridine and aryl ring (four species) [6,19,90], having substituents in the pyridine ring only (two species) [6,90] or in the aryl ring only (one species) [90], but not in both rings. Furthermore, if treating [Au(2ArPY*)X_2] molecules with 2ArPY* of the types A and B together, 20 has no substituents in both ring systems [6,9,13,16–19,30,33,40,62,77–87,89,90], while 48 is substituted either in the pyridine ring (34 examples) [6,83,88,90] or in the aryl ring (14 examples) [17,83,89,90].

A few [Au(2ArPY*)Cl_2] compounds are biologically active, revealing anti-tumour properties (against various breast, colon, kidney, lung, mammary, ovarian, pancreas, and prostate and uterus cancers, as well as leukemia) [25,30,79,83]. Some others exhibit catalytic activity (in reactions between alkynes, carbonyl compounds, and amines or imines—yielding amines, allenes, or oxazoles) [16,17].

Table 4. NMR and/or X-ray studied [Au(2ArPY*)X_2] compounds (2ArPY* ≠ 2PPY*; X = F, Cl, Br, I); R^1 and R^2 are substituents in the pyridine ring and the aryl ring, respectively.

Parent 2ArPY* Ring System	R^1	R^2	X	NMR Solvent	X-ray (CCDC)	Activity [$]
2ArPy* ligands of type A (Scheme 2)						
2-benzylpyridine*	H	H	Cl	$CDCl_3$ CD_2Cl_2 CD_3CN CD_3COCD_3 DMSO-d_6 [9,13,18,33,62,77–82]	HOSHEE [16]	BIO1 [25,79,83] CAT [16,17]
	3-methyl	H	Cl	DMSO-d_6 [83]		
	4-methyl	H	Cl	DMSO-d_6 [83]		
	5-methyl	H	Cl	CD_2Cl_2 [83]		
	6-methyl	H	Cl	DMSO-d_6 [83]		
	3-methoxy	H	Cl	DMSO-d_6 [83]		
	6-methoxy	H	Cl	CD_2Cl_2 [83]		
	3-isopropoxy	H	Cl	CD_2Cl_2 [83]		
	3-*n*-butoxy	H	Cl	CD_2Cl_2 [83]		
	3-acetomethoxy	H	Cl	CD_2Cl_2 [83]		
	H	2-methyl	Cl	CD_2Cl_2 [83]		
	H	3-methyl	Cl	DMSO-d_6 [83]		
	H	4-methyl	Cl	DMSO-d_6 [83]		
	H	4-ethyl	Cl	DMSO-d_6 [83]		
	H	4-*n*-butyl	Cl	CD_2Cl_2 [83]		
	H	4-*tert*-butyl	Cl	$CDCl_3$ [17]		CAT [17]
	H	4-*n*-hexyl	Cl	CD_2Cl_2 [83]		
	H	4-chloro	Cl	DMSO-d_6 [83]		
	H	2-methoxy	Cl	DMSO-d_6 [83]		
	H	4-phenyl	Cl	CD_2Cl_2 [83]		
	H	4-benzyl	Cl	CD_2Cl_2 [83]		
2-(1-methylbenzyl)pyridine*	H	H	Cl	$CDCl_3$ DMSO-d_6 [77]	R/S [1]	CAT [17]
2-(1,1-dimethylbenzyl)pyridine*	H	H	Cl	CD_2Cl_2 [77]	ZETYAY [77]	
2-(1-methoxybenzyl)pyridine*	H	H	Cl	DMSO-d_6 [17]		CAT [17]
2-(1-phenylbenzyl)pyridine*	H	H	Cl	DMSO-d_6 [83]		
2-(1-carboxymethoxyiminobenzyl)pyridine*	H	H	Cl	DMSO-d_6 [84]		
2-(1-benzoxyiminobenzyl)pyridine*	H	H	Cl	DMSO-d_6 [17]		CAT [17]
2-benzoylpyridine*	H	H	Cl	CD_2Cl_2 CD_3CN DMSO-d_6 [9,17,18,33,81,83–86]	PUKYAV [85]	BIO1 [30] CAT [17]
	H	H	Br	DMSO-d_6 [30]	AZOKOS [30]	
	H	H	I	DMSO-d_6 [30]		
2-phenoxypyridine*	H	H	Cl	DMSO-d_6 [9,87]	FIJZIH [87]	BIO1 [83] CAT [17]
	4-methyl	H	Cl	DMSO-d_6 [88]		
	5-methyl	H	Cl	DMSO-d_6 [88]		
	6-methyl	H	Cl	CD_2Cl_2 [88]		
	5-ethyl	H	Cl	DMSO-d_6 [88]		
	5-*n*-propyl	H	Cl	DMSO-d_6 [88]		
	5-*n*-butyl	H	Cl	CD_2Cl_2 [88]		
	5-fluoro	H	Cl	DMSO-d_6 [88]		
	5-chloro	H	Cl	DMSO-d_6 [88]		
	5-bromo	H	Cl	DMSO-d_6 [88]		
	5-iodo	H	Cl	DMSO-d_6 [88]		
	5-methoxy	H	Cl	CD_2Cl_2 [83]		
	5-methoxycarbonyl	H	Cl	CD_2Cl_2 [88]		
	5-(2-methoxycarbonylethyl)	H	Cl	$CDCl_3$ [88]		
	5-(3-acetoxy-*n*-propyl)	H	Cl	CD_2Cl_2 [88]		
	5-aminocarbonyl	H	Cl	DMSO-d_6 [88]		

Table 4. *Cont.*

Parent 2ArPY* Ring System	R^1	R^2	X	NMR Solvent	X-ray (CCDC)	Activity [$]
	5-methylaminocarbonyl	H	Cl	DMSO-d_6 [88]		
	5-dimethylaminocarbonyl	H	Cl	DMSO-d_6 [88]		
	5-cyclopentylaminocarbonyl	H	Cl	DMSO-d_6 [88]	KAGYIB [88]	
	5-acetamido	H	Cl	DMSO-d_6 [88]		
	5-(3-cyano-*n*-propyl)	H	Cl	$CDCl_3$ [88]		
	5-phenyl	H	Cl	DMSO-d_6 [88]		
	5-benzyl	H	Cl	CD_2Cl_2 [83]		
	5-benzamido	H	Cl	DMSO-d_6 [88]		
	H	4-*tert*-butyl	Cl	$CDCl_3$ [17]	IFUQUX [17]	
2-phenylsulfanylpyridine*	H	H	Cl	DMSO-d_6 [87]	FIKNOC [87]	BIO1 [83]
2-anilinopyridine*	H	H	Cl	DMSO-d_6 [9,18,87,89]	PUGMAF [89]	BIO1 [83]
	H	H	Br	DMSO-d_6 [89]		
	H	4-methyl	Cl	DMSO-d_6 [89]		
2-(1-methylanilino)pyridine*	H	H	Cl	DMSO-d_6 [83,89]		
2-(1-propionylanilino)pyridine*	H	H	Cl	$CDCl_3$ [40]		
2ArPy* ligands of type B (Scheme 3)						
2-(naphth-2-yl)pyridine*	H	H	Cl	DMSO-d_6 [19]		
2-(9,9-dimethylfluoren-2-yl)pyridine*	H	H	Cl	DMSO-d_6 [6,90]		
	4-methyl	H	Cl	CD_2Cl_2 [90]		
	4-dimethylamino	H	Cl	CD_2Cl_2 [6,90]		
	H	7-trifluoromethyl	Cl	CD_2Cl_2 [90]		
2-(9,9-di(*n*-butyl)fluoren-2-yl)pyridine*	H	H	Cl	DMSO-d_6 [19]		
2-(dibenzofuran-4-yl)pyridine*	H	H	Cl	DMSO-d_6 [6]		

[$] Types of activity: BIO—biological (BIO1—anti-tumour, BIO2—anti-microbial, i.e., anti-bacterial and/or anti-fungal); CAT—catalytic; LUM—luminescence (LUM1—with t > 10 μs, LUM2—with t < 10 μs). [1] This compound appears in two isomeric forms, i.e., enantiomers R/S.

2.2.2. Au(III)-2ArPY* Compounds with Auxiliary Ligands Other Than Halides

In addition to [Au(2ArPY*)X_2] dihalides, 108 Au(III)-2ArPY* compounds (2ArPY* ≠ 2PPY*) with various auxiliary ligands (other than halides), having the general formula [Au(2ArPY*)L^1L^2] (particularly [Au(2ArPY*)L_2]) or [Au(2ArPY*)(L^1L^2)]) (particularly [Au(2ArPY*)(LL)]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [6,9,14,18,19,25,30,31,33,39,40,45,51,62–64,75,77,79,82,85,87,89–102]. These species correspond to the most general case presented in Schemes 2 and 3 (for L^1, L^2 ≠ F, Cl, Br, I), being listed in Table 5 (by definition, it does not include the Au(III)-2ppy* and Au(III)-2PPY* molecules, shown in Tables 2 and 3). A total of 88 molecules have 2ArPY* ligands of the type A [9,14,18,25,30,31,33,40,45,51,62–64,77,79,82,85,87,89,91–101], while 20 have 2ArPY* ligands of the type B [6,19,39,75,90,102].

As many as 97 Au(III)-2ArPY* compounds contain unsubstituted (or substituted only at the Z bridge) 2ArPY* ligands [6,9,14,18,19,25,30,31,33,39,40,45,51,62–64,77,79,82,85,87,89–102] (all 88 molecules with 2ArPY* of the type A [9,14,18,25,30,31,33,40,45,51,62–64,77,79,82,85,87,89,91–101], including the predominant 2-benzylpyridine*—52 species and 9 molecules of the type B [6,19,39,90,102]).

In contrast, there are only 11 Au(III)-2ArPY* compounds with substituent(s) in the 2ArPY* ring system (except for those at the Z bridge). All these molecules are with 2ArPY* ligands of the type B [6,75,90], and eight are substituted in the pyridine ring only [6,75,90]; 1—in the aryl ring only [90], and 2—in both rings [75].

Table 5. NMR and/or X-ray studied [Au(2ArPY*)L^1L^2] (in particular, [Au(2ArPY*)L_2]) or [Au(2ArPY*)(L^1L^2)]) (in particular, [Au(2ArPY*)(LL)]) compounds (2ArPY* ≠ 2PPY*; L^1, L^2, L—monodentate ligands other than F, Cl, Br, I; L^1L^2, LL—bidentate ligands); R^1 and R^2 are substituents in the pyridine ring and the aryl ring, respectively.

Parent 2ArPY* Ring System	R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
2ArPy* ligands of type A (Scheme 2)										
2-benzylpyridine*	H	H	acetate	acetate			$CDCl_3$ [31,91]			BIO1 [31]
	H	H			*1R,2R*-cyclohexane-1,2-diamine	$2Cl^-$ $2ClO_4^-$ $2BF_4^-$	DMSO-d_6 [92] DMSO-d_6 [92] DMSO-d_6 [92]	TOFDUQ [92] TOFFAY [92] [a]		BIO1 [92]
	H	H			dimethylaminocarbodithioate	PF_6^-	CD_3CN [93]	RADKOA [93]		BIO1 [93]
	H	H			diethylaminocarbodithioate	PF_6^-	CD_3CN [93]	RADLER [93]		BIO1 [93]
	H	H			azacyclohexane-1-carbodithioate	PF_6^-	CD_3CN [93]	RADLAN [93]		BIO1 [93]
	H	H			4-(4-bromophenyl)-1,4-diazacyclohexane-1-carbodithioate	PF_6^-	CD_3CN [93]			BIO1 [93]
	H	H			4-(4-methoxyphenyl)-1,4-diazacyclohexane-1-carbodithioate	PF_6^-	CD_3CN [93]	RADKUG [93] [b]		BIO1 [93]
	H	H			4-ethoxycarbonylazacyclohexane-1-carbodithioate	PF_6^-	DMSO-d_6 [82]	OVIKOW [82]		BIO1 [82]
	H	H			4-aminocarbonylazacyclohexane-1-carbodithioate	PF_6^-	DMSO-d_6 [82]	OVILAJ [82] OVIKUC [82] [c]		BIO1 [82]
	H	H			1,1-dimethylbiguanidate	PF_6^-	DMSO-d_6 [33]	CEWGUK [33]		BIO1 [33]
	H	H			1,2-bis(ethylimine)ethane-1,2-dithiolate		$CDCl_3$ [94]			
	H	H	phenylethynyl	phenylethynyl			CD_3COCD_3 [95]			
	H	H	phenylethynyl	Cl			CD_3COCD_3 [95]	ECEGOM [95] ECEGOM 01 [95]	*trans*(C,N)	
	H	H	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [18]	MIYXIE [18]		LUM2 [18]
	H	H	4-trifluoromethylphenyl	4-trifluoromethylphenyl			$CDCl_3$ [14]			
	H	H			benzene-1,2-diolate		$CDCl_3$ [96]			BIO1, BIO2 [96]
	H	H			anthracene-9,10-dione-1,2-diolate		DMSO-d_6 solid phase [62]			
	H	H			1,1′-binaphthyl-2-one-2′-olate-1-yl		$CDCl_3$ [45]		R/S [1]	
	H	H			2-thiolatebenzoate		$CDCl_3$ [51]			BIO1 [51]
	H	H	3-ethoksycarbonylphenyl	3-ethoksycarbonylphenyl			$CDCl_3$ [14]			
	H	H			benzene-1-olate-2-acetylazanide		$CDCl_3$ [96]	BAZSEB [96]	*trans*(N,N)	BIO1, BIO2 [25,96]
	H	H			ethylene-1,2-bis(4-methylphenylsulfonylazanide)		unknown [63]			BIO1, BIO2 [63]
	H	H			benzene-1,2-bis(acetylazanide)		unknown [63]	XEWBOR [63]		BIO1, BIO2 [63]
	H	H			benzene-1,2-bis(4-methylphenylsulfonylazanide)		unknown [63]			BIO1, BIO2 [63]
	H	H	1-acetamidobenzene-2-acetylazanide	Cl				XEWBUX [63]	*trans*(N,N)	
	H	H			benzene-1-olate-2-(N-(acridin-9-yl))azanide		CD_2Cl_2 [25]			BIO1 [25]
	H	H	isatinate	isatinate			$CDCl_3$ [97]			BIO1, BIO2 [97]
	H	H	phtalimidate	phtalimidate			$CDCl_3$ [97]	SEVDON [97] [d]		BIO1, BIO2 [97]

Table 5. *Cont.*

Parent 2ArPY* Ring System	R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
	H	H	saccharinate	saccharinate			$CDCl_3$ [97]	SEVDUT [97] [e]		BIO1, BIO2 [97]
	H	H	L-phenylalaninate			Cl^-	$CDCl_3$ [31]			BIO1 [31]
	H	H			sulfonebis(cyanomethyl)					BIO1 [64]
	H	H			sulfonebis(benzoylmethyl)		unknown [64]			BIO1 [64]
	H	H			benzoylmethyl benzoyl(2-(*tert*-butylamino)ethyl) sulfone		unknown [64]	DEFGUR [64]		BIO1 [64]
	H	H			4-methylphenylsulfonyliminocarbo(phenylazanide)thiolate		$CDCl_3$ [98]			
	H	H	4-nitrophenylazanide	acetate			$CDCl_3$ [91]			
	H	H	thiophen-2-yl	thiophen-2-yl			CD_2Cl_2 [95]	ECEGAY [95]		
	H	H			2,5-bis(ethoxycarbonyl)thiophen-3,4-diolate		$CDCl_3$ [96]			BIO1, BIO2 [96]
	H	H			phenyliminocarbo(pyrrol-5-yl-1-ate)thiolate		$CDCl_3$ [99]			
	H	H			phenyliminocarbo(2,4-dimethylpyrrol-5-yl-1-ate)thiolate		$CDCl_3$ [99]	FUJHUQ [99] [d]	*trans*(S,N)	
	H	H			phenyliminocarbo(2,4-dimethyl-3-ethylpyrrol-5-yl-1-ate)thiolate		$CDCl_3$ [99]			
	H	H			4-nitrophenyliminocarbo(pyrrol-5-yl-1-ate)thiolate		$CDCl_3$ [99]			BIO1 [99]
	H	H			4-nitrophenyliminocarbo(2,4-dimethylpyrrol-5-yl-1-ate)thiolate		$CDCl_3$ [99]			
	H	H			4-nitrophenyliminocarbo(2,4-dimethyl-3-ethylpyrrol-5-yl-1-ate)thiolate		$CDCl_3$ [99]			
	H	H			2-(4-aminophenylsulfonamido)thiazol-3-yl		DMSO-d_6 [97]			
	H	H			2,2′-bipyridine		CD_3CN [100]			
	H	H			1,10-phenanthroline		CD_3CN [100]			
	H	H	triphenylphosphine	Cl		BF_4^- Cl^-	$CDCl_3$ CD_2Cl_2 DMSO-d_6 [77,85]	PUKYEZ [85] [d]	*trans*(P,N)	
	H	H			1,2-bis(diphenylphosphino)ethane	$2BF_4^-$	CD_2Cl_2 [77]			
	H	H			1,2-bis(diphenylphosphino)benzene [2A]	$2Cl^-$	$CDCl_3$ [9]	USEDOO [9] 3A,f		BIO1 [9]
	H	H	1,3,5-triazaphosphaadamantane	Cl		PF_6^-	CD_3COCD_3 [79]	QUMZIJ [79] [g]	*trans*(P,N)	BIO1 [79]
	H	H	1,2,3,4-tetraacetyl-6-thioglucose-6-yl	Cl			CD_3COCD_3 [79]			BIO1 [79]
	H	H	1,2,3,4-tetraacetyl-6-thioglucose-6-yl	1,2,3,4-tetraacetyl-6-thioglucose-6-yl			CD_3COCD_3 [79]			BIO1 [79]
2-(1-methylbenzyl)pyridine*	H	H	triphenylph osphine	Cl		BF_4^-	$CDCl_3$ [77]		R/S [1]	
	H	H			1,2-bis(diphenylphosphino)ethane	$2BF_4^-$	CD_2Cl_2 [77]		R/S [1]	
2-(1,1-dimethylbenzyl)pyridine*	H	H	triphenylphosphine	Cl		BF_4^-	$CDCl_3$ [77]			

Table 5. *Cont.*

Parent 2ArPY* Ring System	R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
2-benzoylpyridine*	H	H			2-benzoylpyridine*	BF_4^-	DMSO-d_6 [85]			
	H	H	SCN	SCN			DMSO-d_6 [30]			
	H	H	N_3	N_3			DMSO-d_6 [30]	AZOLAF [30]		
	H	H	*n*-pentane-2,4-dione-3-yl	Cl			$CDCl_3$ [30]			
	H	H			dimethylaminocarbodithioate	PF_6^-	CD_3CN [93]			BIO1 [93]
	H	H			diethylaminocarbodithioate	PF_6^-	CD_3CN [93]			BIO1 [93]
	H	H			azacyclohexane-1-carbodithioate	PF_6^-	CD_3CN [93]	RADLIV [93]		BIO1 [93]
	H	H			4-(4-bromophenyl)-1,4-diazacyclohexane-1-carbodithioate	PF_6^-	CD_3CN [93]			BIO1 [93]
	H	H			4-(4-methoxyphenyl)-1,4-diazacyclohexane-1-carbodithioate	PF_6^-	CD_3CN [93]			BIO1 [93]
	H	H			1,1-dimethylbiguanidate	PF_6^-	DMSO-d_6 [33]			BIO1 [33]
	H	H	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [18]	MIYXEA [18]		LUM2 [18]
	H	H			1,1′-binaphthyl-2-one-2′-olate-1-yl		$CDCl_3$ [45]		R/S [1]	
	H	H			1,2-bis(diphenylphosphino)benzene [2B]	$2Cl^-$	$CDCl_3$ [9]	USEDII [9] [3B]		BIO1 [9]
2-phenoxypyridine*	H	H	4-fluorophenylethynyl	4-fluorophenylethynyl			$CDCl_3$ CD_3CN [40]			
	H	H			1,1′-binaphthyl-2-one-2′-olate-1-yl		$CDCl_3$ [45]		R/S [1]	
	H	H			1,2-bis(diphenylphosphino)benzene [2C]	$2Cl^-$	$CDCl_3$ [9]	USEDEE [9] 3C,h		BIO1 [9]
2-anilinopyridine*	H	H	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [18]	MIZHUB [18] [d]		LUM2 [18]
	H	H			benzene-1,2-diolate		$CDCl_3$ [96]			BIO1, BIO2 [96]
	H	H			3,5-di(*tert*-butyl)benzene-1,2-diolate					BIO [96]
	H	H			2-thiolatebenzoate		$CDCl_3$ [51]			BIO1 [51]
	H	H	3-ethoksycarbonylphenyl	3-ethoksycarbonylphenyl			$CDCl_3$ [14]			
	H	H			anthracene-9,10-dione-1,2-diolate		DMSO-d_6 solid phase [62]			
	H	H			1,1′-binaphthyl-2-one-2′-olate-1-yl		$CDCl_3$ [45]		R/S [1]	
	H	H			sulfonebis(benzoylmethyl)		unknown [64]			BIO1 [64]
	H	H			ethylene-1,2-bis(4-methylphenylsulfonylazanide)		unknown [63]			BIO1, BIO2 [63]
	H	H			benzene-1,2-bis(acetylazanide)					BIO1, BIO2 [63]
	H	H			benzene-1,2-bis(4-methylphenylsulfonylazanide)		unknown [63]			BIO1, BIO2 [63]
	H	H			dimethyliminocarbo(phenylazanide)thiolate	$B(C_6H_5)_4^-$	DMSO-d_6 [101]	MIRLIK [101]	*trans*(S,N)	
	H	H			dicyclohexyliminocarbo(phenylazanide)thiolate	$B(C_6H_5)_4^-$	DMSO-d_6 [101]	MIRLOQ [101]	*trans*(S,N)	
	H	H			oxydiethyliminocarbo(phenylazanide)thiolate	$B(C_6H_5)_4^-$	DMSO-d_6 [101]			
	H	H	triphenylphosphine	Cl		BF_4^-	DMSO-d_6 [87]	FIKQAR [87]	*trans*(P,N)	
	H	H	tris(4-methylphenyl)phosphine	Cl		Cl^-	$CDCl_3$ [89]			
	H	H			1,2-bis(diphenylphosphino)benzene [2D]	$2Cl^-$	$CDCl_3$ [9]	USEDUU [9] [3D]		BIO1 [9]

Table 5. *Cont.*

Parent 2ArPY* Ring System	R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
2ArPy* ligands of type B (Scheme 3)										
2-(naphth-2-yl)pyridine*	H	H			methylenebis(3-*n*-butyl-1*H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
2-(9,9-dimethylfluoren-2-yl)pyridine*	H	H			bis(2-acetylidephenyl)acetylene		CD_2Cl_2 [39]			LUM1 [39]
	H	H	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [90]	MEDPOD [90] [i]		LUM1 [90]
	H	H			3,3′-bis(trifluoromethyl)-5,5′-bipyrazolate		DMSO-d_6 [6]			
	H	H			1,1-dimethylmethylenebis(3-trifluoromethylpyrazol-5-ylate)		CD_2Cl_2 [6]	QOCBES [6] [j]		LUM1 [6]
	4-methyl	H	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [90]	MEDPIX [90] [k]		LUM1 [90]
	4-dimethylamino	H	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [90]	MEDPAP [90]		LUM1 [90]
	4-dimethylamino	H			1,1-dimethylmethylenebis(3-trifluoromethylpyrazol-5-ylate)		CD_2Cl_2 [6]	QOCBUI [6]		LUM1 [6]
	H	7-trifluoromethyl	pentafluorophenyl	pentafluorophenyl			CD_2Cl_2 [90]	MEDPET [90]		LUM1 [90]
2-(9,9-di(*n*-butyl)fluoren-2-yl)pyridine*	H	H			methylenebis(3-*n*-butyl-1*H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
2-(9,9-di(*n*-hexyl)fluoren-2-yl)pyridine*	5-methyl	H	phenylethynyl	phenylethynyl			$CDCl_3$ [75]			LUM1 [75]
	5-methyl	H	3,5-bis(trifluoro)phenylethynyl	3,5-bis(trifluoro)phenylethynyl			$CDCl_3$ [75]			LUM1 [75]
	5-trifluoromethyl	H	3,5-bis(trifluoro)phenylethynyl	3,5-bis(trifluoro)phenylethynyl			$CDCl_3$ [75]			LUM1 [75]
	5-methyl	7-(4-diphenylaminophenyl)	phenylethynyl	phenylethynyl			$CDCl_3$ [75]			LUM1 [75]
	5-trifluoromethyl	7-(4-diphenylaminophenyl)	phenylethynyl	phenylethynyl			$CDCl_3$ [75]			LUM1 [75]
2-(9,9-(1,1′-biphenyl-2,2′-diyl)fluoren-2-yl)pyridine*	5-trifluoromethyl	H	3,5-bis(trifluoro)phenylethynyl	3,5-bis(trifluoro)phenylethynyl			$CDCl_3$ [75]			LUM1 [75]
2-(9,9-bis(2-hydroxyethyl)fluoren-2-yl)pyridine*	H	H	phenylethynyl	phenylethynyl			DMSO-d_6 [102]			
2-(dibenzofuran-4-yl)pyridine*	H	H			bis(2-acetylidephenyl)acetylene		CD_2Cl_2 [39]			LUM1 [39]
	H	H			1,1-dimethylmethylenebis(3-trifluoromethylpyrazol-5-ylate)		DMSO-d_6 [6]	QOCBOC [6]		LUM1 [6]
	4-dimethylamino	H			1,1-dimethylmethylenebis(3-trifluoromethylpyrazol-5-ylate)		DMSO-d_6 [6]			LUM1 [6]

[$] Types of activity: BIO—biological (BIO1—anti-tumour, BIO2—anti-microbial, i.e., anti-bacterial and/or anti-fungal); CAT—catalytic; LUM—luminescence (LUM1—with t > 10 μs, LUM2—with t < 10 μs). [1] This compound appears in two isomeric forms, i.e., enantiomers R/S. [2A–2D] It is unclear whether in the solution these compounds should be regarded as [Au(2ArPY*)(1,2-bis(diphenylphosphino)benzene)]Cl_2 (2ArPY = 2-benzylpyridine for 2A, 2-benzoylpyridine for 2B, 2-phenoxypyridine for 2C, 2-anilinopyridine for 2D) or rather [Au(2ArPY[$])(1,2-bis(diphenylphosphino)benzene)Cl]Cl (2ArPY[$] = monoanionic form of 2ArPY, deprotonated and binding monodentately by C(2′)). [3A–3D] In the solid phase, the N(1),C(2′)-chelation is observed for 2A (USEDOO), while the monodentate C(2′) coordination for 2B-2D (USEDII, USEDEE, USEDUU). [a] 1/2 chloride, 1/2 tetrafluoroborate salt. [b] diethyl ether solvate. [c] acetonitrile solvate. [d] dichloromethane solvate. [e] dichloromethane diethyl ether solvate. [f] methanol solvate. [g] acetone solvate. [h] dimethylformamide solvate. [i] diethyl ether *n*-hexane solvate. [j] *n*-pentane solvate. [k] ethyl acetate solvate.

Many above Au(III)-2ArPY* compounds are biologically active, revealing anti-tumour (against various bowel, breast, colon, lung, and mammary and ovarian cancers, as well as leukemia) [9,25,31,33,51,63,64,79,82,92,93,96,97,99], as well as anti-bacterial (against *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas aeruginosa*) and anti-fungal (against *Candida albicans*, *Trichophyton mentagrophytes*, and *Cladosporium resinae*) [63,96,97] properties. To the best of our knowledge, the catalytic activity of these species seems to be unknown, while some of them reveal luminescence, with lifetimes of either >10 μs [6,19,39,75,90] or <10 μs [18].

2.3. *Au(III)-ArPY#* Compounds*

A total of 33 Au(III) compounds with analogues of 2-arylpyridines* (e.g., 2-phenylquinoline*, 1- or 3-phenylisoquinoline* and 7,8-benzoquinoline*) and their derivatives (generally denoted as ArPY#*), with various auxiliary ligands (including halides), having the general formula [Au(ArPY#*)L^1L^2] (particularly [Au(ArPY#*)L_2], including [Au(ArPY#*)X_2]) or [Au(ArPY#*)(L^1L^2)]) (particularly [Au(ArPY#*)(LL)]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2,5,9,10,15,19,27,37,39,41,45,75,102–108]. These species are presented in Scheme 4, being listed in Table 6 (by definition, it does not include the Au(III)-2ppy*, Au(III)-2PPY*, and Au(III)-ArPY#* molecules shown in Tables 1–5).

A total of 5 compounds are [Au(ArPY#*)X_2] dihalides [2,5,9,10,15,19,104–106], while 28 molecules contain some other monodentate or bidentate ligands, revealing the general formula [Au(ArPY#*)L^1L^2] (including [Au(ArPY#*)L_2]) or [Au(ArPY#*)(L^1L^2)]) (including [Au(ArPY#*)(LL)]) [2,9,15,19,27,37,39,41,45,75,102,103,105–108].

Taking into account the type of ArPy#* molecule, these are Au(III) species (their respective numbers in parentheses) with heterocycles based on 2-phenylquinoline* (4) [2,103], 1-phenyl-, 1-(naphth-2-yl)- or 1-(9,9-di(*n*-hexyl)fluoren-2-yl)isoquinoline* (9) [10,19,27,37,39,75], 3-phenyl- or 3-(9,9-bis(2-hydroxyethyl)fluoren-2-yl)isoquinoline* (6) [45,102,103], and 7,8-benzoquinoline* (14) [5,9,10,15,41,45,103,105–108] ring systems.

Two of the above Au(III)-ArPY#* compounds are biologically active, revealing anti-tumour properties (against various breast, colon, liver, and lung and ovarian cancers, as well as melanoma) [9,102]. Some of the others have catalytic properties (in reactions between benzaldehyde, piperidine, and phenylacetylenes—yielding propargylamines—and between alkynyl alcohols and 1-methylindol—yielding substituted indols [103]—as well as upon hydroarylation reactions between diphenylacetylene and 1,3,5-trimethoxybenzene—yielding styrene derivatives [107]). Then, a number of these species exhibits luminescence, with lifetimes of either >10 μs [15,19,37,39,75] or <10 μs [27,41].

Table 6. NMR and/or X-ray studied $[Au(ArPY^{\#}*)L^1L^2]$ (in particular, $[Au(ArPY^{\#}*)L_2]$) or $[Au(ArPY^{\#}*)(L^1L^2)]$) (in particular, $[Au(ArPY^{\#}*)(LL)]$) compounds ($ArPY^{\#}* \neq$ 2PPY*, 2ArPY*; L^1, L^2, L—monodentate ligands (including F, Cl, Br, I); LL—bidentate ligands); R^1 and R^2 are substituents in the pyridine-like ring and the aryl ring, respectively.

Parent $ArPY^{\#}*$ Ring System	R^1	R^2	L^1	L^2	L^1L^2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity [$]
2-phenylquinoline*	H	H			2-phenylquinoline*	BF_4^-	DMSO-d_6 [103]	ZINHUB [103]	*trans*(C,N)	CAT [103]
	4-methoxycarbonyl	H	Cl	Cl			$CDCl_3$ [2]			
	4-methoxycarbonyl	H			dimethylaminocarbodithioate	PF_6^-	DMSO-d_6 [2]			
	4-methoxycarbonyl	H	2-(4-methoxycarbonylquinolin-2-yl)phenyl	Cl				MAXQUX [2]	*trans*(C,N)	
1-phenylisoquinoline*	H	H	Cl	Cl			DMSO-d_6 [10]			
	H	H	CN	CN			CD_2Cl_2 [27]	DUZDAF [27] DUZDAF 01 [27] DUZDAF 02 [27]		LUM2 [27]
	H	H			bis(2-acetylidephenyl)acetylene		CD_2Cl_2 [39]			LUM1 [39]
	H	H	4-methoxyphenylethynyl	4-methoxyphenylethynyl			CD_2Cl_2 [37]			LUM1 [37]
	H	4-methoxy	4-methoxyphenylethynyl	4-methoxyphenylethynyl			CD_2Cl_2 [37]	AJOXON [37] [a]		LUM1 [37]
1-(naphth-2-yl)isoquinoline*	H	H	Cl	Cl			DMSO-d_6 [19]			
	H	H			methylenebis(3-*n*-butyl-1*H*-imidazol-1-yl-2-ylidene)	$2PF_6^-$	CD_3CN [19]			LUM1 [19]
	H	H			methylenebis(3-(3-sulfonate-*n*-propyl)-1*H*-imidazol-1-yl-2-ylidene)		D_2O [19]			LUM1 [19]
1-(9,9-di(*n*-hexyl)fluoren-2-yl)isoquinoline*	H	7-(4-diphenylaminophenyl)	phenylethynyl	phenylethynyl			$CDCl_3$ [75]			LUM1 [75]
3-phenylisoquinoline*	H	H			3-phenylisoquinoline*	BF_4^-	DMSO-d_6 [103]			CAT [103]
	H	H			1,1′-binaphthyl-2-one-2′-olate-1-yl		$CDCl_3$ [45]		R/S [1]	
	H	4-*tert*-butyl	phenylethynyl	phenylethynyl			$CDCl_3$ [102]			
3-(9,9-bis(2-hydroxyethyl)fluoren-2-yl)isoquinoline*	H	H	phenylethynyl	phenylethynyl			DMSO-d_6 [102]			BIO1 [102]
	H	H	4-methylphenylethynyl	4-methylphenylethynyl			DMSO-d_6 [102]			
	H	H	4-fluorophenylethynyl	4-fluorophenylethynyl			DMSO-d_6 [102]			

Table 6. *Cont.*

Parent ArPY#* Ring System	R1	R2	L1	L2	L1L2	Counterion	NMR Solvent	X-ray (CCDC)	Geometry	Activity $
7,8-benzoquinoline*	H	H	Cl	Cl			DMSO-d_6 [5,9,10,15,104]			
	H	H	I	I			$CDCl_3$ [105,106]	EWIWUE [105]		
	H	H	*n*-butyl	Cl			$CDCl_3$ [106]			
	H	H	*n*-butyl	H_2O		SbF_6^-	CD_2Cl_2 [106]			
	H	H	trifluoroacetate	trifluoroacetate			CD_3COCD_3 [106,107]			CAT [107]
	H	H	phenyl	Br			$CDCl_3$ [106]			
	H	H	4-phenyl-*n*-butyl	Cl			$CDCl_3$ [106]	FIBRUG [106] b	*trans*(C,N)	
	H	H	4-phenyl-*n*-butyl	H_2O		SbF_6^-		FIBROA [106]	*trans*(C,N)	
	H	H	phenylethynyl	phenylethynyl			CD_2Cl_2 [15]	IZOTAT [15]		LUM1 [15]
	H	H	2,4,6-tris(trifluoromethyl)phenyl	Cl			CD_2Cl_2 [41]	GIVROU [41]	*trans*(C,N)	LUM2 [41]
	H	H			1,1′-binaphthyl-2-one-2′-olate-1-yl		$CDCl_3$ [45]		R/S [1]	
	H	H	pyridine	I		SbF_6^-	CD_3CN [105]	EWIXAL [105]	*trans*(I,N)	
	H	H			1,2-(bis(pyridin-4-yl)sulfanyl)ethene-1,2-dithiolate		CD_2Cl_2 [108]	QUVXIR [108]		
	H	H			1,2-bis(diphenylphosphino)benzene [2]	$2Cl^-$	$CDCl_3$ [9]			BIO1 [9]

$ Types of activity: BIO—biological (BIO1—anti-tumour, BIO2—anti-microbial, i.e., anti-bacterial and/or anti-fungal); CAT—catalytic; LUM—luminescence (LUM1—with t > 10 µs, LUM2—with t < 10 µs). [1] This compound appears in two isomeric forms, i.e., enantiomers R/S. [2] It is unclear whether this compound should be regarded as [Au(7,8-benzoquinoline*)(1,2-bis(diphenylphosphino)benzene)Cl]Cl (7,8-benzoquinoline$ = monoanionic form of 7,8-benzoquinoline, deprotonated and bound monodentately by C(10)). [a] dichloromethane solvate. [b] chloroform solvate.

2.4. Discussion of Single Crystal X-ray Structures

Nearly all Au(III)-2PPY* (including Au(III)-2ppy*), Au(III)-2ArPY*, and Au(III)-ArPY$^{\#}$* compounds have coordination number 4 and square-planar geometry (the only exclusions are [Au(2-phenylpyridine*)(1,4,7-trithiacyclononane-κ^3-S,S,S)]$^{2+}$ and [Au(2-(4-methylphenyl) pyridine*)(1,4,7-trithiacyclononane-κ^3-S,S,S)]$^{2+}$ in their hexafluorophosphate salts—MOCFOB, MOCFIV [5]—which exhibit coordination number 5). Thus, in cases of $L^1 \neq L^2$ or unsymmetrical L^1L^2 ligands, two geometric isomers are possible—differing in the position of both donor atoms versus the nitrogen of the pyridine (or pyridine-like) ring and the metallated carbon of the phenyl (or, more generally, aryl) ring.

In Tables 1–6, it was indicated, for molecules with the known X-ray structures, which donor atom (or the whole donor moiety) of the auxiliary ligand(s) is *trans* to the nitrogen of the pyridine (or pyridine-like) ring (column *Geometry*).

The comparison of these X-ray structures exhibits that the molecules having various elements, as donor atoms of the auxiliary ligand(s) usually adopt the following geometries:

***trans*(N,N)**, instead of *trans*(O,N) (MAXQEH [2], KIGPEY [25], BAZSEB [96]) or *trans*(Cl,N) (XEWBUX [63]);

***trans*(S,N)**, instead of *trans*(O,N) (ILETIC [28], ICUMEY [51]), *trans*(Cl,N) (AZOKUY [30]) or *trans*(N,N) (ILETOI, ILETEY [28], LORCOM, LORCEC, LORCIG [34], FUJHUQ [99], MIRLIK, MIRLOQ [101]);

***trans*(I,N)**, instead of *trans*(Cl,N) (VUVKOP [23]), *trans*(N,N) (EWIXAL [105]) or *trans*(Br,N) (VUVLEG [23]);

***trans*(C,N)**, instead of *trans*(F,N) (DAJRUE, DAJROY [21]), *trans*(O,N) (BIGREP [29], XOLCEI [42], FONDIX, FONCIW [43], IDAJII, IDAJOO [54], FUWXIG, FUWXOM [57], YIDHIF, YIDGIE, YIDHEB, YIDHAX, YIDGOK, YIDGAW, YIDGUQ, YIDGEA, YIDFUP [58], QEFVUV, QEFWAC [59], PEZQUI [67], KEKGEP [73], QEZYAX [74], FIBROA [106]), *trans*(Cl,N) (MAXQUX [2], FONSAE, FONRUX [14], BIGRAL [29], IVAZAI [36], GIVRIO, GIVROU [41], ECEGOM, ECEGOM 01 [95], FIBRUG [106]), *trans*(N,N) (XOLCUY, XOLCIM, XOLCOS [42], IPISEH, IPISAD [60], ZINHUB [103]), *trans*(Br,N) (DAJRIS [21], JOTROB [12], ROVYAF [55], LUWKAS [56]), *trans*(I,N) (GIVSOV [41]), and *trans*(P,N) (XOLDAF, XOLDEJ [42], IDAJUU [54]);

***trans*(P,N)**, instead of *trans*(F,N) (IVAZEM [36]), *trans*(Cl,N) (QUNSIE [35], IVAYUB, IVAYOV [36], QUMZIJ [79], PUKYEZ [85], FIKQAR [87]), or *trans*(S,N) (MAXQIL [2]).

Hence, generally, less electronegative (less electron-acceptor) elements are preferred to be positioned *trans* to the pyridine (or pyridine-like) nitrogen. The exception is the pair of *trans*(C,N) and *trans*(P,N), as in the X-ray structures XOLDAF, XOLDEJ, and IDAJUU, and the former geometry is preferred [42,54], although carbon is more electronegative than phosphorus.

Even more important exclusions are the X-ray structures MIZHEL, MIYXOK, and MIYXUQ, where the *trans*(Cl,N) geometry was observed, instead of the seemingly more expected *trans*(C,N) one, upon the presence of the $C_6F_5^-$ and Cl^- ligands [18]. However, it can be explained by the fact that, despite a large difference in the electronegativity of carbon and chlorine, in these molecules, there is a competition (in occupying *trans* to nitrogen position) of the pentafluorophenyl anion with the chloride one—while the former has extremely strong electron-acceptor properties, due to the presence of five fluorine atoms in the phenyl ring.

The most important structural parameters in the discussed Au(III) compounds are the Au–N and Au–C bond lengths, as well as the N–Au–C bond angles. They were usually given in original papers, but can also be deduced from the respective CIF files, which have been used as a primary source for this review. All these values, associated to the CCDC reference codes given in Tables 1–6, together with indication which elements (donor atoms) of the auxiliary ligands, are in the *trans* position, with respect to the metallated N and C atoms, which are listed in Table 7.

Table 7. Au–N and Au–C bond lengths [Å], as well as N–Au–C bond angles [°] in Au(III)-2PPY* (including Au(III)-2ppy*), Au(III)-2ArPY*, and Au(III)-ArPY$^{\#}$* compounds.

X-ray (CCDC)	Au–N	Au–C	N–Au–C	Element Trans to N	Element Trans to C
[Au(2PPY)XY] (2PPY* = a-R^1-2-(b-R^2-phenyl)pyridine*, a = 3–6, b = 2–5; X, Y = F, Cl, Br, I)*					
IJAQEP [3]	2.03(1)	1.95(2)	83.0(6)	Cl	Cl
JOTQOA [12]	2.04(1)	2.05(1)	80.9(5)	Br	Br
FOPBUJ [14]	2.037(6)	2.026(5)	81.8(2)	Cl	Cl
HOSHOO [16]	2.015(8)	2.02(1)	82.0(4)	Cl	Cl
MIYYUR [18]	2.034(5)	2.020(5)	81.3(2)	Cl	Cl
DAJRAK [21]	1.975(5)	1.967(5)	81.6(2)	F	F
DAJQOX [21]	2.036(3)	2.021(4)	80.8(1)	Cl	Cl
DAJREO [21]	1.977(3)	1.983(5)	81.2(2)	F	F
DAJQUD [21]	2.034(7) 2.031(8)	2.02(1) 2.032(9)	80.7(3) 81.0(3)	Cl	Cl
GAKZUR [22]	2.041(2)	2.025(2)	81.63(7)	Cl	Cl
VUVLAC [23]	2.066(3)	2.045(3)	81.6(1)	Br	Br
VUVKUV [23]	2.069(7)	2.05(1)	80.0(4)	I	I
VUVKOP [23]	2.08(2)	2.04(2)	82.8(6)	I	Cl
VUVLEG [23]	2.084(3)	2.028(4)	80.9(1)	I	Br
[Au(2ppy)L^{1}L^2] and [Au(2ppy*)(L^{1}L^2)] (L^1, L^2 ≠ F, Cl, Br, I)*					
DUZCOS [27]	2.051(4)	2.042(5)	81.4(2)	C	C
ILETOI [28]	2.064(6)	2.012(9)	81.4(4)	S	N
MOCFOB [5]	2.068(5)	2.057(5)	81.2(2)	S	S
BIGRAL [29]	2.111(5)	2.018(7)	81.1(2)	C	Cl
BIGREP [29]	2.114(3)	2.004(4)	81.8(2)	C	O
IJAQIT [3]	2.028(8)	2.005(8)	81.6(3)	O	O
DUNCAT [31]	2.014(5)	1.998(5)	81.4(2)	O	O
IJAQUF [3]	2.002(4)	1.999(4)	81.3(2)	O	O
MAXQOR [2]	2.06(1)	2.04(2)	82.2(5)	S	S
REBLET [8]	2.042(4) 2.036(6)	2.035(5) 2.032(7)	81.3(2) 81.5(3)	N	N
CEWGOE [33]	2.038(2)	2.021(2)	81.16(9)	N	N
LORCOM [34]	2.053(6) 2.061(6)	1.976(8) 2.022(6)	81.9(3) 79.8(3)	S	N
LORCEC [34]	2.074(4)	2.029(5)	81.6(2)	S	N
LORCIG [34]	2.083(5)	2.010(5)	81.1(3)	S	N
QUNSIE [35]	2.102(2)	2.044(3)	81.1(1)	P	Cl
IVAYUB [36]	2.119(3)	2.042(3)	80.7(1)	P	Cl
IZOSUM [15]	2.051(2)	2.052(2)	80.33(9)	C	C
EWOJUW [38]	2.111(2)	2.066(2)	80.02(7)	C	C
EWOJOQ [38]	2.125(2)	2.089(3)	79.4(1)	C	C
IZOSOG [15]	2.060(2)	2.038(2)	81.33(8)	C	C
IZOTIB [15]	2.059(2) 2.068(2)	2.039(2) 2.043(2)	80.95(9) 81.00(9)	C	C

Table 7. *Cont.*

X-ray (CCDC)	Au–N	Au–C	N–Au–C	Element Trans to N	Element Trans to C
EWOKAD [38]	2.080(4)	2.087(3)	79.8(1)	C	C
GIVRIO [41]	2.083(2)	2.018(3)	81.5(1)	C	Cl
GIVSOV [41]	2.100(3)	2.037(4)	80.9(1)	C	I
GIVSEL [41]	2.085(3)	2.038(2)	81.0(1)	C	C
XOLCEI [42]	2.076(3)	2.006(3)	82.1(1)	C	O
FONDIX [43]	2.067(3)	2.015(3)	81.6(1)	C	O
FONCIW [43]	2.077(6)	2.006(6)	82.1(2)	C	O
XOLCUY [42]	2.096(2)	2.017(2)	81.60(9)	C	N
XOLCIM [42]	2.075(4)	2.025(7)	82.5(2)	C	N
XOLCOS [42]	2.075(3)	2.016(3)	81.6(1)	C	N
GIVSUB [41]	2.086(3)	2.052(3)	80.8(1)	C	C
XOLDAF [42]	2.085(4)	2.063(5)	80.9(2)	C	P
XOLDEJ [42]	2.102(3)	2.051(3)	81.0(1)	C	P
AJOWUS [37]	2.13(3) 2.19(5)	1.95(2) 1.87(8)	82(1) 81(3)	C	C
IZOTOH [15]	2.057(1)	2.038(1)	80.89(5)	C	C
HIRZIR [46]	2.079(6)	2.035(7)	81.1(3)	S	S
IJAQOZ [3]	2.007(8)	2.001(9)	81.8(4)	O	O
ILETIC [28]	2.073(6)	1.998(8)	81.6(3)	S	O
ILETEY [28]	2.087(6) 2.095(6)	2.008(9) 2.020(9)	80.4(3) 81.2(3)	S	N
AZOKUY [30]	2.091(5) 2.088(5)	2.035(7) 2.033(7)	81.1(3) 81.1(3)	S	Cl
EWOKEH [38]	2.097(3) 2.090(3)	2.069(4) 2.051(3)	80.8(1) 80.5(1)	C	C
IVAZAI [36]	2.06(2) 2.07(2)	2.05(1) 2.03(2)	80.9(9) 82(1)	C	Cl
IVAYOV [36]	2.100(2)	2.045(2)	80.83(7)	P	Cl
IVAZEM [36]	2.092(5)	2.044(6)	82.0(2)	P	F
MAXQIL [2]	2.08(2) 2.08(2)	2.02(2) 2.04(2)	79.9(9) 79.3(9)	P	S
TAFJEQ [48]	2.063(2)	2.042(5)	80.6(2)	S	S
AMEXIZ [49]	2.070(6) 2.066(7)	2.053(7) 2.034(6)	81.1(3) 80.4(2)	S	S
YEDPUT [50]	2.08(1) 2.06(2) 1.98(2) 2.07(2)	2.09(1) 2.08(1) 2.10(2) 2.07(1)	82.0(6) 82.1(6) 79.8(7) 80.5(6)	S	S
YEDQAA [50]	2.06(1) 2.10(1) 2.09(1) 2.048(9)	2.08(1) 2.07(1) 2.08(1) 2.09(1)	81.3(4) 81.4(5) 82.1(5) 81.0(4)	S	S
YEDPON [50]	2.078(9) 2.076(9)	2.064(9) 2.055(9)	81.9(3) 80.2(3)	S	S

Table 7. *Cont.*

X-ray (CCDC)	Au–N	Au–C	N–Au–C	Element Trans to N	Element Trans to C
[Au(2PPY)L^{1}L^2] and [Au(2PPY*)(L^{1}L^2)] (L^1, L^2 ≠ F, Cl, Br, I)*					
MAXQEH [2]	2.01(2)	2.01(2)	79.5(8)	N	O
JOTROB [12]	2.12(1)	2.021(7)	80.5(3)	C	Br
QICNUN [52]	2.130(3)	2.062(3)	80.0(1)	C	C
ROVXUY [55]	2.12(2)	2.04(2)	80.9(7)	C	C
ROVYAF [55]	2.11(3)	2.02(4)	82(1)	C	Br
LUWJUL [56]	2.04	2.03	80.6	C	C
MOCFIV [5]	2.063(4)	2.043(4)	81.2(2)	S	S
IDAJII [54]	2.117(2)	2.001(2)	81.36(8)	C	O
QICPAV [52]	1.991(6)	1.995(8)	81.8(3)	O	O
YIDHIF [58]	2.09(1)	2.02(1)	81.5(4)	C	O
QEFVUV [59]	2.090(2)	2.006(3)	81.69(9)	C	O
YIDGIE [58]	2.108(7)	1.998(9)	81.6(3)	C	O
YIDHEB [58]	2.137(3)	2.012(4)	81.4(1)	C	O
YIDHAX [58]	2.117(7)	1.999(9)	81.6(3)	C	O
YIDGOK [58]	2.131(3)	2.007(3)	81.7(1)	C	O
YIDGAW [58]	2.127(3)	2.009(4)	81.5(2)	C	O
YIDGUQ [58]	2.126(2) 2.113(2)	2.010(3) 2.002(2)	81.45(9) 82.0(1)	C	O
YIDGEA [58]	2.094(8) 2.105(6)	2.014(8) 2.003(9)	81.1(3) 81.3(3)	C	O
FUWXIG [57]	2.098(2)	1.992(4)	81.8(1)	C	O
FUWXOM [57]	2.107(4)	2.006(4)	81.5(2)	C	O
YIDFUP [58]	2.110(4)	2.013(4)	81.6(2)	C	O
QEFWAC [59]	2.07(1) 2.07(1)	2.01(1) 2.01(1)	82.7(4) 81.1(5)	C	O
IDAJOO [54]	2.109(2)	1.995(2)	82.20(8)	C	O
IPISEH [60]	2.127(2)	2.019(3)	80.6(1)	C	N
IPISAD [60]	2.114	2.002	82.2	C	N
LUWJEV [56]	2.09(2)	2.05(2)	83(1)	C	C
LUWJIZ [56]	2.069(6)	2.040(7)	81.5(2)	C	C
FONRIL [14]	2.11(1)	2.08(1)	80.1(4)	C	C
LUWJOF [56]	2.283	1.845	79.9	C	C
LUWKAS [56]	2.076(7)	2.024(4)	81.4(2)	C	Br
LUWKIA [56]	2.072	2.07	81.2	C	C
FONSAE [14]	2.111(4)	2.023(4)	81.2(2)	C	Cl
FOPCAQ [14]	2.124(6) 2.114(5) 2.112(4) 2.114(4)	2.051(5) 2.065(5) 2.069(6) 2.069(6)	80.6(2) 80.3(2) 80.2(2) 79.9(2)	C	C
FONRUX [14]	2.116(3)	2.023(4)	81.1(1)	C	Cl
FOPCEU [14]	2.112(8)	2.05(1)	79.9(4)	C	C

Table 7. *Cont.*

X-ray (CCDC)	Au–N	Au–C	N–Au–C	Element Trans to N	Element Trans to C
AJOXAZ [37]	2.074(3)	2.032(3)	81.2(1)	C	C
FONROR [14]	2.115(4)	2.063(5)	80.0(2)	C	C
FONSEI [14]	2.134(4)	2.057(5)	79.6(3)	C	C
ICUMEY [51]	2.068(3)	2.010(3)	81.4(1)	S	O
FOPCIY [14]	2.112(3)	2.056(4)	80.4(1)	C	C
FONREH [14]	unknown	unknown	unknown	C	C
IDAJUU [54]	2.146(2)	2.051(2)	80.68(7)	C	P
FUXGIQ [47]	2.009(9) 2.020(9)	1.95(2) 2.04(2)	78.7(6) 85.0(6)	O	O
FUXGAI [47]	2.020(5)	1.993(7)	82.1(2)	O	O
FUXGOW [47]	2.020(3)	2.004(4)	81.7(1)	O	O
FUXGEM [47]	2.022(3)	1.994(5)	81.5(1)	O	O
NIKHIB [26]	2.061(2) 2.057(2)	2.037(3) 2.029(3)	80.6(1) 80.9(1)	S	S
KIGPEY [25]	2.028(3)	2.034(4)	81.1(1)	N	O
KIGPIC [25]	2.063(7)	2.015(6)	80.9(3)	N	N
WUCKUD [66]	2.097(2)	2.075(3)	79.4(1)	C	C
JAZJED [53]	2.000(2)	2.022(2)	81.83(8)	O	O
JAYZAO [53]	2.003(3)	2.004(5)	81.9(1)	O	O
MIZHIP [18]	2.078(2)	2.041(2)	81.11(8)	C	C
MIZHEL [18]	2.043(2)	2.045(2)	81.1(1)	Cl	C
MIZJAJ [18]	2.070(2)	2.042(2)	81.03(8)	C	C
MIYYAX [18]	2.072(3)	2.044(3)	81.3(1)	C	C
JAZJAZ [53]	2.007(2)	1.991(2)	81.82(9)	O	O
MIYYEB [18]	2.070(2)	2.049(2)	80.9(1)	C	C
MIYXOK [18]	2.024(3) 2.036(3)	2.055(4) 2.050(4)	81.1(1) 80.8(1)	Cl	C
MIZHOV [18]	2.075(3)	2.040(3)	81.0(1)	C	C
MIYXUQ [18]	2.040(3)	2.049(4)	81.1(1)	Cl	C
JAZJON [53]	2.005(2)	1.988(2)	81.63(8)	O	O
JAZCOG [53]	2.00(1)	2.02(2)	82.2(6)	O	O
PEZQUI [67]	2.180(2)	1.995(3)	81.2(1)	C	O
FIDBUS [72]	2.107(6)	2.066(8)	81.2(3)	S	S
KEKGEP [73]	2.13(1)	2.06(2)	81.8(7)	C	O
QEZYAX [74]	2.163(8)	2.014(6)	80.6(3)	C	O
DAJRUE [21]	2.08(1) 2.083(9)	1.99(1) 1.99(1)	81.6(4) 81.7(4)	C	F
DAJSAL [21]	2.076(4)	2.044(3)	81.0(2)	C	C
DAJROY [21]	2.073(6)	1.984(7)	81.7(3)	C	F
DAJRIS [21]	2.106(4)	2.027(4)	81.6(2)	C	Br
DAJSEP [21]	2.092(4)	2.058(4)	80.5(1)	C	C

Table 7. *Cont.*

X-ray (CCDC)	Au–N	Au–C	N–Au–C	Element Trans to N	Element Trans to C
AJOXIH [37]	2.065(3)	2.038(4)	81.2(1)	C	C
AJOXED [37]	2.066(3)	2.041(4)	81.0(1)	C	C
JAZBOF [53]	2.034(3) 2.033(3)	1.994(4) 1.993(4)	81.6(1) 81.7(1)	O	O
JAYZOC [53]	2.013(4) 2.008(5)	1.995(5) 2.001(5)	82.0(2) 82.1(2)	O	O
WECYUB [75]	2.060(4) 2.055(4)	2.046(5) 2.041(5)	80.8(2) 80.2(2)	C	C
JAZKAA [53]	1.997(2)	1.994(2)	81.42(9)	O	O
JAYZIW [53]	1.999(4)	2.000(5)	81.8(2)	O	O
JAYYOB [53]	2.043(2)	1.995(2)	81.23(8)	O	O
GALBAA [22]	2.008(2)	1.991(3)	81.9(1)	O	O
PUXGUN [76]	2.033(2)	2.027(2)	81.03(8)	N	N
GALBEE [22]	2.002(3) 2.007(3)	1.993(3) 1.999(4)	81.7(1) 81.7(1)	O	O
WASQOZ [24]	2.054(2)	2.047(2)	80.45(8)	C	C
JAZBIZ [53]	2.008(3)	1.996(3)	81.5(1)	O	O
[Au(2ArPY)X_2] (2ArPY* ≠ 2PPY*; X = F, Cl, Br, I)*					
HOSHEE [16]	2.06(1)	2.04(2)	87.2(6)	Cl	Cl
ZETYAY [77]	2.040(3)	2.021(5)	85.7(1)	Cl	Cl
PUKYAV [85]	2.035(5)	2.033(8)	89.6(3)	Cl	Cl
AZOKOS [30]	2.08(2) 2.09(4)	2.02(3) 2.01(3)	88(1) 88(2)	Br	Br
FIJZIH [87]	2.02(1)	2.03(2)	86.6(6)	Cl	Cl
KAGYIB [88]	2.054(5)	2.016(6)	86.6(2)	Cl	Cl
IFUQUX [17]	2.057(3)	1.992(5)	86.6(2)	Cl	Cl
FIKNOC [87]	2.061(9)	2.04(2)	88.1(5)	Cl	Cl
PUGMAF [89]	2.05(2)	2.02(2)	87.2(9)	Cl	Cl
[Au(2ArPY)L^1L^2] and [Au(2ArPY*)(L^1L^2)] (2ArPY* ≠ 2PPY*; L^1, L^2 ≠ F, Cl, Br, I)*					
TOFDUQ [92]	2.031(5) 2.046(5)	2.031(5) 2.020(6)	88.7(2) 87.7(2)	N	N
TOFFAY [92]	2.041(7) 2.028(7)	2.025(8) 2.028(7)	87.7(3) 87.1(3)	N	N
RADKOA [93]	2.070(2)	2.042(3)	88.3(1)	S	S
RADLER [93]	2.069(5)	2.061(6)	89.0(2)	S	S
RADLAN [93]	2.065(3)	2.042(3)	89.2(1)	S	S
RADKUG [93]	2.070(2)	2.046(2)	89.63(7)	S	S
OVIKOW [82]	2.12(2) 2.11(2)	2.03(2) 2.04(2)	90.0(6) 89.9(7)	S	S
OVILAJ [82]	2.067(4)	2.061(6)	88.5(2)	S	S
OVIKUC [82]	2.072(4)	2.054(3)	88.2(1)	S	S
CEWGUK [33]	2.036(2)	2.028(3)	87.9(1)	N	N

Table 7. *Cont.*

X-ray (CCDC)	Au–N	Au–C	N–Au–C	Element Trans to N	Element Trans to C
ECEGOM [95] ECEGOM 01 [95]	2.074(2) 2.085(3)	2.017(2) 2.022(3)	88.85(8) 87.6(1)	C	Cl
MIYXIE [18]	2.079(2)	2.061(3)	87.6(1)	C	C
BAZSEB [96]	2.052(6) 2.041(7)	2.005(7) 2.018(7)	89.7(3) 87.7(3)	N	O
XEWBOR [63]	2.058(3)	2.031(3)	88.1(1)	N	N
XEWBUX [63]	2.053(2)	2.012(2)	87.43(9)	N	Cl
SEVDON [97]	2.046(9)	2.04(1)	88.2(4)	N	N
SEVDUT [97]	2.040(4)	2.021(4)	89.3(2)	N	N
DEFGUR [64]	2.086(2)	2.069(2)	86.23(9)	C	C
ECEGAY [95]	2.114(3)	2.070(3)	87.0(1)	C	C
FUJHUQ [99]	2.090(5)	2.043(7)	87.1(3)	S	N
PUKYEZ [85]	2.079(9)	2.03(1)	85.8(4)	P	Cl
USEDOO [9] [1]	2.096(5)	2.100(5)	84.2(2)	P	P
QUMZIJ [79]	2.096(2) 2.100(2)	2.040(2) 2.041(2)	87.39(8) 87.27(8)	P	Cl
AZOLAF [30]	1.99(3) 1.98(4)	2.10(4) 2.10(4)	93(2) 89(2)	N	N
RADLIV [93]	2.062(2) 2.054(2)	2.042(2) 2.040(2)	90.70(8) 90.15(7)	S	S
MIYXEA [18]	2.072(3)	2.066(3)	88.5(1)	C	C
MIZHUB [18]	2.088(2)	2.068(2)	91.04(8)	C	C
MIRLIK [101]	2.071(2)	2.019(4)	89.5(1)	S	N
MIRLOQ [101]	2.068(3)	2.020(3)	90.8(1)	S	N
FIKQAR [87]	2.09(1)	2.06(1)	85.3(5)	P	Cl
MEDPOD [90]	2.074	2.053	81.3	C	C
QOCBES [6]	2.029(2) 2.035(2)	2.025(3) 2.018(3)	80.8(1) 81.1(1)	N	N
MEDPIX [90]	2.069(3)	2.045(2)	80.94(9)	C	C
MEDPAP [90]	2.075(2)	2.051(3)	80.90(9)	C	C
QOCBUI [6]	2.015(6)	2.012(5)	81.0(2)	N	N
MEDPET [90]	2.077(3)	2.039(3)	81.1(1)	C	C
QOCBOC [6]	2.035(2)	2.032(2)	81.3(1)	N	N
[Au(ArPY$^{\#}$)L^{1}L^2] and [Au(ArPY$^{\#}$*)(L^{1}L^2)] (ArPY$^{\#}$* ≠ 2PPY*, 2ArPY*)*					
ZINHUB [103]	2.175(3) 2.171(3)	2.045(4) 2.041(4)	79.4(1) 78.9(1)	C	N
MAXQUX [2]	2.223(9)	2.03(1)	81.0(4)	C	Cl
DUZDAF [27] DUZDAF 01 [27] DUZDAF 02 [27]	2.045(2) 2.06(1) 2.04(1) 2.053(4)	2.023(3) 2.036(6) 2.021(5) 2.021(5)	81.0(1) 81.5(3) 80.7(3) 80.9(2)	C	C
AJOXON [37]	2.063(2)	2.034(3)	80.6(1)	C	C
EWIWUE [105]	2.113(8)	2.055(7)	81.5(3)	I	I

Table 7. *Cont.*

X-ray (CCDC)	Au–N	Au–C	N–Au–C	Element Trans to N	Element Trans to C
FIBRUG [106]	2.141(2)	2.024(3)	82.4(1)	C	Cl
FIBROA [106]	2.141(3)	2.001(5)	82.3(2)	C	O
IZOTAT [15]	2.061(2)	2.067(2)	81.93(8)	C	C
GIVROU [41]	2.090(3)	2.004(3)	83.2(1)	C	Cl
EWIXAL [105]	2.068(7)	2.02(1)	82.8(3)	I	N
QUVXIR [108]	2.074(3)	2.070(3)	81.6(1)	S	S

[1] In analogous USEDII, USEDEE, USEDUU molecules, the monodentate C(2′) coordination was observed (see Table 5).

In the majority of cases, the Au–N bonds are longer than those of Au–C, which is well-reflected by comparison of their mean bond lengths, averaged for 206 X-ray structures (among all 207; in case of FONREH the interatomic distances could not be deduced, due to the bad quality of data), after preliminary averaging of these parameters for each Au(III) species (when two or more slightly differing, crystallographically inequivalent molecules are present in the crystal lattice): 2.072 Å versus 2.028 Å. Similarly, the range of Au–N bond lengths (1.975–2.283 Å) also corresponds to higher values than that for Au–C (1.845–2.100 Å), despite their partial overlapping.

The N–Au–C bond angles vary within a 79.2–91.0° range, with a mean value of 82.5°.

It is interesting to compare the X-ray structures of the cyclometallated [Au(2PPY*)Cl_2] and [Au(2ArPY*)Cl_2] dichlorides with the respective [Au(2PPY)Cl_3] and [Au(2ArPY)Cl_3] trichloride complexes. Such pairs of X-ray structural data are available for Au(III) compounds with 2-phenylpyridine [3,109], 2-(2,4-difluorophenyl)pyridine [16], 2-(2-trifluoromethoxyphenyl)pyridine [18], 2-benzylpyridine [16], 2-benzoylpyridine [18,85], and 2-phenylsulfanylpyridine [87,110]. In this case, the comparable parameter is the Au–N bond length, with its values being listed in Table 8.

Table 8. Au–N bond lengths [Å] in analogous [Au(2PPY*)Cl_2] or [Au(2ArPY*)Cl_2] and [Au(2PPY)Cl_3] or [Au(2ArPY)Cl_3] compounds.

2PPY or 2ArPY	[Au(2PPY*)Cl_2] or [Au(2ArPY*)Cl_2]: Au–N Bond Length	[Au(2PPY)Cl_3] or [Au(2ArPY)Cl_3]: Au–N Bond Length
2-phenylpyridine	2.03(1) IJAQEP [3]	2.035(6) YIDMAA [109]
2-(2,4-difluorophenyl)pyridine	2.015(8) HOSHOO [16]	2.047(4) HOSHUU [16]
2-(2-trifluoromethoxyphenyl)pyridine	2.034(5) MIYYUR [18]	2.041(1) MIYZEC [18]
2-benzylpyridine	2.06(1) HOSHEE [16]	2.046(3) HOSHII [16]
2-benzoylpyridine	2.035(5) PUKYAV [85]	2.053(2) MIYZAY [18]
2-phenylsulfanylpyridine	2.061(9) FIKNOC [87]	2.06(1) DUCYEI [110]

This comparison, however, does not reveal any clear relationship between the Au–N bond lengths in the respective dichloride and trichloride species. Their differences for the corresponding Au(III) compounds are of variable sign and small absolute magnitude, being statistically not significant. This is also exhibited by the overlapping of both ranges of this parameter: 2.01–2.06 Å for [Au(2PPY*)Cl_2] and [Au(2ArPY*)Cl_2] versus 2.03–2.06 Å for [Au(2PPY)Cl_3] and [Au(2ArPY)Cl_3], as well as by nearly the same mean values: 2.039 Å for [Au(2PPY*)Cl_2] and [Au(2ArPY*)Cl_2] versus 2.047 Å for [Au(2PPY)Cl_3] and [Au(2ArPY)Cl_3].

2.5. Discussion of ^{15}N NMR Spectra

In addition to the routine ^{1}H and/or ^{13}C (and, optionally, ^{19}F or ^{31}P) NMR spectra, some Au(III)-2PPY* (including Au(III)-2ppy*), Au(III)-2ArPY*, and Au(III)-ArPY$^{\#}$* compounds were studied by ^{15}N NMR [4,7,53,60,78,80,86,104]. Their ^{15}N chemical shifts (with respect to neat nitromethane), together with ^{15}N coordination shifts (i.e., differences from ^{15}N chemical shifts for free ligands), are listed in Table 9.

Table 9. ^{15}N chemical shifts (with respect to CH_3NO_2, in ppm—δ^{15N}) and ^{15}N coordination shifts (Δ^{15N}_{coord}) for [Au(2PPY*)L^{1}L^2], [Au(2PPY*)(L^{1}L^2)], [Au(2ArPY*)L^{1}L^2], [Au(2ArPY*)(L^{1}L^2)], [Au(ArPY$^{\#}$*)L^{1}L^2], [Au(ArPY$^{\#}$*)(L^{1}L^2)] compounds (L^1, L^2, L—monodentate ligands (including F, Cl, Br, I), LL—bidentate ligands; R^1 and R^2 are substituents in the pyridine (or pyridine-like) ring and the phenyl (aryl) ring, respectively.

Parent Ring System	R^1	R^2	L^1	L^2	L^{1}L^2	Counterion	NMR Solvent	^{15}N Chemical Shift	^{15}N Coordination Shift
2-phenylpyridine*			Cl	Cl			DMSO-d$_6$	−148.9 [4]	−77.0 [a]
			1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene	Cl		Cl^-	CD_3COCD_3	−147.7 [7]	−75.8 [a]
		4-methyl	methyl	methyl			CD_2Cl_2	−131.0 [53]	−56.1 [b]
		4-methyl	methyl	Br			CD_2Cl_2	−121.6 [53]	−46.7 [b]
		4-methyl	allyl	Br			CD_2Cl_2	−122.6 [53]	−47.7 [b]
		4-methyl	acetate	acetate			CD_2Cl_2	−164.4 [53]	−89.5 [b]
		4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−165.6 [53]	−90.7 [b]
		4-methyl			$HNC(CH_3)OCH_2CH_2$	CF_3COO^-	CD_2Cl_2	−129.0 [60]	−54.1 [b]
		4-methyl	phenyl	Br			CD_2Cl_2	−127.9 [53]	−53.0 [b]
		3,5-dimethyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−167.1 [53]	−94.5 [c]
		3,5-bis(pentafluorophenyl)	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−167.7 [53]	−94.7 [d]
	6-methyl	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−161.7 [53]	−88.2 [e]
	4-trifluoromethyl	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−160.4 [53]	−95.5 [f]
	3-methoxy	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−164.9 [53]	−101.0 [g]
	4-methoxy	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−187.1 [53]	−92.9 [h]
	6-methoxy	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−187.7 [53]	−66.2 [i]
	3-nitro	4-methyl	trifluoroacetate	trifluoroacetate			CD_2Cl_2	−163.9 [53]	−104.5 [j]
2-benzylpyridine*			Cl	Cl			DMSO-d^6	−151.8 [78] −154.2 [$] [80]	−90.9 [k] −93.3 [k]
2-benzoylpyridine*			Cl	Cl			DMSO-d^6	−165.0 [86]	−104.7 [l]
7,8-benzoquinoline*			Cl	Cl			DMSO-d^6	−143.3 [104]	−69.2 [m]

[$] original value (227.5 ppm) was referenced to liquid NH_3 [80] and recalculated with respect to neat CH_3NO_2 by subtracting 381.7 ppm relative shift [111]. [a] vs. 2-phenylpyridine in DMSO-d$_6$: −71.9 ppm [4]. [b] vs. 2-(4-methylphenyl)pyridine in CD_2Cl_2: −74.9 ppm [53]. [c] vs. 2-(3,5-dimethylphenyl)pyridine in CD_2Cl_2: −72.6 ppm [53]. [d] vs. 2-(3,5-bis(pentafluorophenyl)phenyl)pyridine in CD_2Cl_2: −73.0 ppm [53]. [e] vs. 6-methyl-2-(4-methylphenyl)pyridine in CD_2Cl_2: −73.5 ppm [53]. [f] vs. 4-trifluoromethyl-2-(4-methylphenyl)pyridine in CD_2Cl_2: −64.9 ppm [53]. [g] vs. 3-methoxy-2-(4-methylphenyl)pyridine in CD_2Cl_2: −63.9 ppm [53]. [h] vs. 4-methoxy-2-(4-methylphenyl)pyridine in CD_2Cl_2: −94.2 ppm [53]. [i] vs. 6-methoxy-2-(4-methylphenyl)pyridine in CD_2Cl_2: −121.5 ppm [53]. [j] vs. 3-nitro-2-(4-methylphenyl)pyridine in CD_2Cl_2: −59.4 ppm [53]. [k] vs. 2-benzylpyridine in DMSO-d$_6$: −60.9 ppm [78]. [l] vs. 2-benzoylpyridine in DMSO-d$_6$: −60.3 ppm [86]. [m] vs. 7,8-benzoquinoline in DMSO-d$_6$: δ^{15N}_{lig} = −74.1 ppm [104].

In all cases, the Au(III) coordination of 2PPY* (including 2ppy*), 2ArPY*, or ArPY$^{\#}$* leads to a large decrease of the ^{15}N NMR chemical shift of the metallated nitrogen (comparing to the parent heterocycle, measured preferably in the same solvent), reflecting a strong

^{15}N shielding phenomenon and resulting in a significant low-frequency (i.e., upfield) shift of the ^{15}N signal (thus, the Δ^{15N}_{coord} values are negative). The absolute magnitude of this effect is ca. 45–105 ppm.

In two reviews by Pazderski [112,113], the dependency was identified in that of square-planar Au(III) complexes or organometallics with aza aromatic ligands (such as azines, e.g., pyridine derivatives, etc.), and the absolute magnitude of the ^{15}N NMR coordination shift ($|\Delta^{15N}_{coord}|$) mainly reflected the type of a donor atom in the *trans* position, with respect to the Au(III)-bonded nitrogen. For example, in the two pairs of [Au^{III}LCl$_3$] and *trans*-[Au^{III}L$_2$Cl$_2$]$^+$ species, the $|\Delta^{15N}_{coord}|$ parameter for the former compound (nitrogen *trans* to Cl) was smaller than for the latter one (nitrogen *trans* to N): 84.8 ppm versus 87.2 ppm for L = pyridine, and 78.1 ppm versus 91.0 ppm for L = 4-methylpyridine [112,113].

Such observations can also be performed for some of the presently reviewed Au(III) species, when compared to the compounds containing the same cycloaurated ligand. Based on the data collected in Table 9, such a comparison is possible for the series of [Au(2-(4-methylphenyl)pyridine*)L^{1}L^2] molecules with various L^1 and L^2 ligands (methyl, allyl, phenyl, acetate, trifluoroacetate, and bromide anions). Thus, for [Au(2-(4-methylphenyl) pyridine*)(acetate)$_2$] and [Au(2-(4-methylphenyl)pyridine*)(trifluoroacetate)$_2$] (nitrogen *trans* to O), the $|\Delta^{15N}_{coord}|$ parameter is much larger than for [Au(2-(4-methylphenyl) pyridine*)(methyl)$_2$] (nitrogen *trans* to C): 89.5–90.7 ppm versus 56.1 ppm [53]. In this way, based on the ^{15}N NMR spectra only, one could assume that, in all other "unsymmetrical" [Au(2-(4-methylphenyl)pyridine*)LBr] (L = methyl, allyl, phenyl) compounds, the nitrogen atoms are positioned *trans* to C, rather than *trans* to Br, because their $|\Delta^{15N}_{coord}|$ values (46.7–53.0 ppm) are rather small and close to that of [Au(2-(4-methylphenyl)pyridine*)(methyl)$_2$] (56.1 ppm). In fact, the proposed *trans*(C,N) geometry for these three molecules was actually confirmed by the X-ray structure of [Au(2-(4-methylphenyl)pyridine*)(allyl)Br] (ROVYAF [55]), in accordance with the already mentioned preference to form *trans*(C,N), instead of *trans*(C,Br) isomers.

A more detailed discussion of this issue is difficult, due to the small number of X-ray structures, for which, the ^{15}N NMR data were also reported. They are available only for the pair of [Au(2-(4-methylphenyl)pyridine*)L$_2$] molecules (QICNUN for L = methyl and QICPAV for L = trifluoroacetate) [52], where the increase of $|\Delta^{15N}_{coord}|$ upon the $CH_3 \rightarrow CF_3COO$ ligand transition can be related to the shortening of the Au–N bond (2.130(3) Å $\rightarrow$ 1.991(6) Å; see Table 7). However, this is only one example, not allowing for general conclusions.

The analysis of the other ^{15}N NMR data exhibits that relatively large $|\Delta^{15N}_{coord}|$ parameters are observed for all [Au(2PPY*)(CF$_3$COO)$_2$] (ca. 66–105 ppm; nitrogens *trans* to O) and [Au(ArPY$^{\#}$*)Cl$_2$] (ca. 69–105 ppm; nitrogens *trans* to Cl) species, with no significant differences between both classes of molecules.

3. Applications

3.1. Biological Activity

A total of 105 reviewed compounds were studied, with respect to their biological activity [3,8,9,11,25,26,28,30,31,33,43,51,63,64,79,82,83,92,93,96,97,99,102]. Generally, all these reports concerned anti-tumour properties, but some also described anti-microbial (anti-bacterial and anti-fungal) action [63,96,97].

The anti-tumour properties of these Au(III) species against various types of cancer cells (usually of carcinoma or adenocarcinoma types, but also glioblastoma, leukemia, and melanoma), in a few cases with cytotoxic activity against some non-cancerous cells (analyzed for comparison), as well as their anti-microbial properties (indicated by footnote a), are summarized, in the order of references, in Table 10.

Table 10. Summary of biological activity studies for the reviewed Au(III) compounds.

Reference	General Formula	Auxiliary Ligand(s)	Cancer Cells	Non-Cancerous Cells
[3]	[Au(2ppy*)L_2] [Au(2ppy*)(LL)]	L = acetate, benzoate; LL = malonate, cyclobutane-1,1-dicarboxylate	leukemia MOLT-4; C2Cl2 mouse tumour	
[8]	[Au(2PPY*)(LL)]$^+$ (2PPY = 2-phenyl- and 2-(4-methylphenyl)pyridine)	LL = 1,1-dimethylbiguanidate, 1-phenylbiguanidate	breast MDA-MB 231, MDA-MB 468; lung H460	
[9]	[Au(ArPY$^{\#}$*)(LL)]$^{2+}$ (ArPY$^{\#}$ = 2-phenyl-, 2-(4-methylphenyl)-, 2-(4-formylphenyl)-, 2-benzyl-, 2-benzoyl-, 2-phenoxy- and 2-anilinopyridine; 7,8-benzoquinoline)	LL = 1,2-bis(diphenylphosphino)benzene	breast MDA-MB 231; lung H460; ovarian A2780, OVCAR8	
[11]	[Au(2PPY*)(LL)]$^+$ (2PPY = 2-phenyl-, 5-*n*-butyl-2-phenyl-, 2-(3-*n*-butylphenyl)-, 2-(4-*n*-butylphenyl)-, 2-(4-trifluoromethylphenyl)- and 2-(4-*n*-butoxyphenyl)pyridine)	LL = diethylaminocarbodithioate, di-*n*-butylaminocarbodithioate	breast MCF-7; MDA-MB-231; cervix HeLa; liver HepG2; lung NCI-H460; glioblastoma U87; melanoma B16	immortalized liver (MIHA)
[25]	[Au(2ArPY*)Cl_2] [Au(2ArPY*)(LL)] (2ArPY = 2-(4-*tert*-butylphenyl)- and 2-benzylpyridine)	LL = benzene-1-olate-2-acetylazanide, benzene-1,2-bis(acetylazanide), benzene-1-olate-2-(N-(acridin-9-yl))azanide, benzene-1-azanide-2-(N-(acridin-9-yl)azanide	breast MCF-7; lung A549; leukemia HL60	
[26]	[Au(2PPY*)(LL)] (2PPY = 2-(4-*tert*-butylphenyl)- and 2-(4-*tert*-butylphenyl)-5-*tert*-butylpyridine)	LL = dimethylaminocarbodithioate, diethylaminocarbodithioate, di(*n*-butyl)aminocarbodithioate, (*n*-but-1,4-diyl)aminocarbodithioate, N-(ethoxycarbonylmethyl) methylaminocarbodithioate	breast MCF-7, MDA-MB-231; colon HCT-116; lung A549; leukemia HL60	umbilical vein endothelial cells HUVEC
[28]	[Au(2ppy*)L^1L^2] [Au(2ppy*)(LL)]	L^1 = SCN, L^2 = NCS; LL = propan-1-ol-2,3-dithiolate, 2-thiolatepropionate, 2,3-dithiolatesuccinic acid, 2-thiolatebenzoate	leukemia MOLT-4; C2Cl2 mouse tumour	
[30]	[Au(2-benzoylpyridine*)Cl_2]		lung H358, H460; pancreas MiaPaCa	
[31]	[Au(2ArPY*)L_2] [Au(2ArPY*)(LL)]$^+$ (2ArPY = 2-phenyl-, 2-(4-methylphenyl)- and 2-benzylpyridine)	L = acetate; LL = L-phenylalaninate, L-methioninate	colon caco-2/TC7	
[33]	[Au(2ArPY*)Cl_2] [Au(2ArPY*)(LL)]$^+$ (2ArPY = 2-phenyl-, 2-benzyl- and 2-benzoylpyridine)	LL = 1,1-dimethylbiguanidate, 1-(2-phenylethyl)biguanidate	breast MDA-MB-231; ovarian A2780, A2780cis	murine hepatocytes TAMH, cardiomyocytes AC10
[43]	[Au(2ppy*)L^1L^2]$^{0/+}$	L^1 = 2,4,6-tris(trifluoromethyl)phenyl, L^2 = H_2O, OH, trifluoroacetate, 4-phenylpyridine, quinoline triphenylphosphine	cervix HeLa	lung fibroblasts MRC-5
[51]	[Au(2ArPy*)(LL)] (2ArPy = 2-phenyl-, 2-(4-methylphenyl)-, 2-benzyl- and 2-anilinopyridine)	LL = 2-thiolatebenzoate	murine leukemia P388	
[63] [a]	[Au(2ArPy*)(LL)] (2ArPy = 2-(4-methylphenyl)-, 2-benzyl- and 2-anilinopyridine)	LL = ethylene-1,2-bis(4-methylphenylsulfonylazanide), benzene-1,2-bis(acetylazanide), benzene-1,2-bis(4-methylphenylsulfonylazanide)	murine leukemia P388	
[64]	[Au(2ArPy*)(LL)] (2ArPy = 2-(4-methylphenyl)-, 2-benzyl- and 2-anilinopyridine)	LL = sulfonebis(cyanomethyl), sulfonebis(benzoylmethyl), benzoylmethyl benzoyl(2-(*tert*-butylamino)ethyl) sulfone	murine leukemia P388	
[79]	[Au(2-benzylpyridine*)Cl_2] [Au(2-benzylpyridine*)LCl]$^+$ [Au(2-benzylpyridine*)L_2]	L = 1,3,5-triazaphosphaadamantane, 1,2,3,4-tetraacetyl-6-thioglucose-6-yl	colon HCT116; lung A549; mammary MCF-7; ovarian A2780	embryonic kidney cells HEK-293T

Table 10. *Cont.*

Reference	General Formula	Auxiliary Ligand(s)	Cancer Cells	Non-Cancerous Cells
[82]	[Au(2-benzylpyridine*)(LL)]	LL = 4-ethoxycarbonylazacyclohexane-1-carbodithioate, 4-aminocarbonylazacyclohexane-1-carbodithioate	cervix HeLa; bowel HT29; ovarian A2780	
[83]	[Au(2ArPY*)Cl_2] (2ArPY = 2-benzyl, 2-phenoxy-, 2-phenylsulfanyl- and 2-anilinopyridine)		breast MDA-MB-231; colon DLD-1, HCT-116, HT29; kidney A-498, ACHN; lung A549; prostate PC-3; uterus MES-SA	
[92]	[Au(2-benzylpyridine*)(LL)]$^{2+}$	LL = *1R,2R*-cyclohexane-1,2-diamine	breast MCF7; ovarian A2780, OVCAR-8	retinal pigment epithelial cells engineered to overexpress MYC gene RPE MYC
[93]	[Au(2ArPY*)(LL)] (2ArPY = 2-benzyl- and 2-benzoylpyridine)	LL = dimethylaminocarbodithioate, diethylaminocarbodithioate, azacyclohexane-1-carbodithioate, 4-(4-bromophenyl)-1,4-diazacyclohexane-1-carbodithioate, 4-(4-methoxyphenyl)-1,4-diazacyclohexane-1-carbodithioate	breast MDA-MB-231, MDA-MB-175; ovarian A2780	retinal pigment epithelial cells engineered to overexpress NEO gene RPE-NEO; diploid lung fibroblasts MRC5
[96] [a]	[Au(2ArPy*)(LL)] (2ArPy = 2-benzyl- and 2-anilinopyridine)	LL = benzene-1,2-diolate, 3,5-di(*tert*-butyl)benzene-1,2-diolate, benzene-1-olate-2-acetylazanide, 2,5-bis(ethoxycarbonyl)thiophen-3,4-diolate	leukemia P388	
[97] [a]	[Au(2-benzylpyridine)L_2]	L = isatinate, phtalimidate, saccharinate	murine leukemia P388	
[99]	[Au(2-benzylpyridine*)(LL)]	LL = 4-nitrophenyliminocarbo(pyrrol-5-yl-1-ate)thiolate	lung A549	
[102]	[Au(3-(9,9-bis(2-hydroxyethyl)fluoren-2-yl)isoquinoline*)L_2] [b]	L = phenylethynyl	colon HCT116; liver HepG2; lung A549; melanoma A375	

[a] All compounds investigated in this paper, with respect to their anti-cancer activity, were additionally tested against some species of bacteria (*Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa*) and fungi (*Candida albicans*, *Trichophyton mentagrophytes*, *Cladosporium resinae*) [63,96,97]. [b] upon photo-activation (light irradiation).

On the basis of their biological activity, the concerned Au(III) compounds can be applied in medicine, as they are potential anti-cancer, anti-bacterial, and anti-fungal drugs.

3.2. Catalytic Activity

A total of 30 reviewed compounds were exhibited to have catalytic activity [7,16,17,22,42,65,103,107]. Their application as catalysts is summarized, in the order of references, in Table 11.

On the basis of the above catalytic activity, the concerned Au(III) compounds are applied in organic syntheses.

Table 11. Summary of catalytic activity studies for the reviewed Au(III) compounds.

Reference	General Formula	Auxiliary Ligand(s)	Reactants	Products
[7]	[Au(2ppy*)LCl]$^+$	L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, triphenylphosphine	alkynes + H_2O	enoles
[16]	[Au(2ArPY*)Cl_2] (2ArPY = 2-phenyl-, 2-(2,4-difluorophenyl)- and 2-benzylpyridine)		arylacetylenes + acyl chlorides + benzylimines	oxazoles
[17]	[Au(2ArPY*)Cl_2] (2ArPY = 2-phenyl-, 2-(4-methylphenyl)-, 2-(4-chlorophenyl)-, 2-(4-methoxyphenyl)-, 2-benzyl-, 2-(1-methylbenzyl)-, 2-(1-methoxybenzyl)-, 2-(1-benzoxyiminobenzyl)-, 2-benzoyl-, 2-phenoxy- and 2-(4-*tert*-butylphenoxy)pyridine)		terminal alkynes + aldehydes + amines	propargylic amines, allenes or oxazoles
[22]	[Au(2PPY*)L_2] (2PPY = 5-carboxy-2-(4-carboxyphenyl)- and 5-ethoxycarbonyl-2-(4-ethoxycarbonylphenyl)pyridine)	L = Cl, trifluoroacetate	propargyl esters + styrene	cyclopropane derivatives
[42]	[Au(2ppy*)L^1L^2]$^+$	L^1 = 2,4,6-tris(trifluoromethyl)phenyl, L^2 = H_2O, 4-fluoroaniline, 4-phenylpyridine, quinoline, trimethyl phosphite, triphenylphosphine	benzylic amines + O_2 (photooxidation)	benzylic imines
[65]	[Au(2-(4-methylphenyl)pyridine*)(LL)]	LL = oxybis(phenylborinate)	CO + O_2	CO_2
[103]	[Au($ArPY^{\#}$*)$_2$]$^+$ ($ArPY^{\#}$ = 2-phenylquinoline, 3-phenylisoquinoline)		(a) benzaldehyde + piperidine + phenylacetylene (b) methylethynylethanol + 1-methylindol	(a) 1-((phenylethynyl)(phenyl)methyl) piperidine (b) 3-substituted 1-methylindol
[106]	[Au(7,8-benzoquinoline*)L_2]	L = trifluoroacetate	diphenylacetylene + 1,3,5-trimethoxybenzene	styrene derivative

3.3. Luminescence

A total of 88 reviewed compounds were studied in detail, with respect to their luminescence [6,15,18,19,24,27,37–39,41,42,75,90].

An important parameter for luminescence differentiation is the lifetime, i.e., the average time that a molecule remains in an excited state prior to returning to the ground state by emitting a photon. In this review, we have arbitrarily chosen the lifetime of 10 µs as a border between long- and short-living excited forms; the former corresponds to phosphorescence, while the latter corresponds to either phosphorescence or fluorescence (it is often difficult to distinguish both phenomena: although they have different mechanisms, their identification may be ambiguous, even taking into account the fact that phosphorescence lifetimes are principally longer than the fluorescence ones).

A total of 54 reviewed compounds exhibited luminescence with lifetimes above 10 µs [6,15,19,37,39,42,75,90], while 34 exhibited luminescence with lifetimes below 10 µs [15,18,24,27,38,41,75]. The detailed data describing their chemical character, together with the maximal quantum yields (for a given group of compounds, rounded to 1%), are summarized, in the order of references, in Table 12.

Table 12. Summary of luminescence studies for the reviewed Au(III) compounds.

Reference	General Formula	Auxiliary Ligand(s)	Lifetime	Maximal Quantum Yield
[6]	[Au(2ArPY*)(LL)] (2ArPY = 2-(9,9-dimethylfluoren-2-yl)-, 4-dimethylamino-2-(9,9-dimethylfluoren-2-yl)-, 2-(dibenzofuran-4-yl)- and 4-dimethylamino-2-(dibenzofuran-4-yl)pyridine)	LL = 1,1-dimethylmethylenebis(3-trifluoromethylpyrazol-5-ylate)	>10 μs	22%
[15]	[Au(ArPY#*)L_2] (ArPY# = 2-phenyl- and 2-(2,4-difluorophenyl)pyridine; 7,8-benzoquinoline)	L = triisopropylsilylethynyl, phenylethynyl, 4-fluorophenylethynyl, 4-(phenylethynyl)phenylethynyl	>10 μs or <10 μs	11%
[18]	[Au(2ArPY*)LCl] [Au(2ArPY*)L^1L^2] (2PPY = 2-(3-trifluoromethylphenyl)-, 2-(2-trifluoromethoxyphenyl)-, 2-(4-trifluoromethoxyphenyl)-, 2-benzyl-, 2-benzoyl- and 2-anilinopyridine)	L, L^1, L^2 = pentafluorophenyl, 4-fluorophenylethynyl, 4-bis(2,4,6-trimethylphenyl)boranylphenylethynyl)	<10 μs	5%
[19]	[Au(ArPY#*)(LL)]$^{2+}$ (ArPY# = 2-phenyl-, 2-(2,4-difluorophenyl)-, 2-(4-phenylphenyl)-, 2-(naphth-2-yl)- and 2-(9,9-di(*n*-butyl)fluoren-2-yl)pyridine; 1-(naphth-2-yl)isoquinoline)	LL = methylenebis(3-methyl-1*H*-imidazol-1-yl-2-ylidene, methylenebis(3-*n*-butyl-1*H*-imidazol-1-yl-2-ylidene, methylenebis(3-(3-sulfonate-*n*-propyl)-1*H*-imidazol-1-yl-2-ylidene), 1,2-ethylenebis(3-*n*-butyl-*1H*-imidazol-1-yl-2-ylidene), 1,3-propylenebis(3-*n*-butyl-*1H*-imidazol-1-yl-2-ylidene	>10 μs	10%
[24]	[Au(2PPY*)L_2] (2PPY = 4-dimethylamino-2-(2,3,4-trifluoro)phenyl)-, 4-dimethylamino-2-(3-trifluoromethyl)phenyl)- and 4-dimethylamino-2-(4-trifluoromethoxy)phenyl)pyridine)	L = pentafluorophenyl, 4-fluorophenylethynyl	<10 μs	28%
[27]	[Au(ArPY#*)L_2] (ArPY# = 2-phenyl- and 2-(4-methylphenyl)pyridine; 1-phenylisoquinoline)	L = CN	<10 μs	26%
[37]	[Au(ArPY#*)L_2] (ArPY# = 2-phenyl-, 2-(4-methylphenyl)-, 2-(4-*tert*-butylphenyl)-, 4-methyl-2-(4-methoxyphenyl)-, 5-methyl-2-(4-methoxyphenyl)- and 5-trifluoromethyl-2-(4-methoxyphenyl)pyridine; 1-phenyl- and 1-(4-methoxyphenyl)isoquinoline)	L = trimethylsilylethynyl, 4-ethylphenylethynyl, 4-*n*-butylphenylethynyl, 4-trifluoromethylphenylethynyl, 4-methoxyphenylethynyl, 4-aminophenylethynyl	>10 μs	10%
[38]	[Au(2ppy*)L_2] [Au(2ppy*)(LL)]	L = phenyl, pentafluorophenyl, 4-trifluoromethylphenyl, thiophen-2-yl; LL = 1,1′-biphen-2,2′-diyl	<10 μs	2%
[39]	[Au(ArPY#*)(LL)] (ArPY# = 2-phenyl-, 2-(9,9-dimethylfluoren-2-yl)- and 2-(dibenzofuran-4-yl)pyridine; 1-phenylisoquinoline)	LL = bis(2-acetylidephenyl)acetylene	>10 μs	75%
[41]	[Au(ArPY#*)L^1L^2] (ArPY# = 2-phenylpyridine; 7,8-benzoquinoline)	L^1 = 2,4,6-tris(trifluoromethyl)phenyl, L^2 = Cl, I, CN, phenylethynyl, 4-diphenylaminophenylethynyl	<10 μs	39%
[42]	[Au(2ppy*)L^1L^2]$^+$	L^1 = 2,4,6-tris(trifluoromethyl)phenyl, L^2 = H_2O, 4-fluoroaniline, 4-phenylpyridine, quinoline, trimethyl phosphite, triphenylphosphine	>10 μs	18%

Table 12. *Cont.*

Reference	General Formula	Auxiliary Ligand(s)	Lifetime	Maximal Quantum Yield
[75]	$Au(ArPY^{\#}*)L_2$] ($ArPY^{\#}$ = 5-trifluoromethyl-2-(2-diphenylamino)phenyl-, 5-methyl-2-(9,9-di(*n*-hexyl)fluoren-2-yl)-, 5-trifluoromethyl-2-(9,9-di(*n*-hexyl)fluoren-2-yl)-, 5-methyl-2-(7-(4-diphenylaminophenyl)-9,9-di(*n*-hexyl)fluoren-2-yl)-, 5-trifluoromethyl-2-(7-(4-diphenylaminophenyl)-9,9-di(*n*-hexyl)fluoren-2-yl)- and 5-trifluoromethyl-2-(9,9-(1,1′-biphenyl-2,2′-diyl)fluoren-2-yl)pyridine; 1-(7-(4-diphenylaminophenyl)-(9,9-di(*n*-hexyl)fluoren-2-yl))isoquinoline)	L = phenylethynyl, 3,5-bis(trifluoro)phenylethynyl)	>10 μs or <10 μs	84%
[90]	[Au(2ArPY*)L_2] (2ArPY = 2-(9,9-dimethylfluoren-2-yl)-, 4-methyl-2-(9,9-dimethylfluoren-2-yl)-, 4-methylamino-2-(9,9-dimethylfluoren-2-yl)- and 2-(7-trifluoromethyl-9,9-dimethylfluoren-2-yl)pyridine)	L = pentafluorophenyl	>10 μs	17%

On the basis of the above luminescence properties, these Au(III) compounds can be applied in the production of organic light-emitting diodes (OLEDs).

4. Conclusions

A large numbers of reports (>100) described molecules (>500) and single crystal X-ray structures (>200) and indicated that the Au(III) compounds with 2-arylpyridines* and their derivatives or analogues are interesting from the chemical, spectroscopic, and structural viewpoints. The most popular Au(III)-2PPY* species are those with 2-phenylpyridine* and 2-(4-methylphenyl)pyridine*, while among Au(III)-2ArPY* molecules—those containing 2-benzylpyridine* ring system are the most popular.

All Au(III)-2PPY*, Au(III)-2ArPY*, and Au(III)-$ArPY^{\#}$* compounds exhibit a specific (N,C) coordination mode, alternative to classical monodentate complexation by nitrogen. Thus, these molecules contain both gold–nitrogen and gold–carbon bonds and can be regarded as either complexes or organometallics.

The coordination number 4 and the square-planar geometry are typical for Au(III) chemistry and allow, upon the presence of different monodentate ($L^1 \neq L^2$) or unsymmetrical bidentate (L^1L^2) auxiliary ligands, for the appearance of geometric isomers differing in the position of various donor atoms versus the nitrogen of the pyridine (or pyridine-like) ring or the metallated carbon of the phenyl (or aryl) ring. There is an evident preference (with a few exceptions) to form such stereomers, in which the auxiliary ligands having less electron-acceptor properties (thus, usually containing less electronegative elements as donor atoms) are *trans*-positioned to the pyridine (or pyridine-like) nitrogen.

A total of 20 Au(III)-2PPY*, Au(III)-2ArPY*, and Au(III)-$ArPY^{\#}$* compounds were studied by ^{15}N NMR. The comparison to analogous measurements for the corresponding 2PPY, 2ArPY, or $ArPY^{\#}$ reveals a ca. 45–105 ppm decrease of the chemical shift of the pyridine nitrogen. This phenomenon reflects a strong ^{15}N shielding effect at the Au(III)-bonded N atom.

About 200 Au(III)-2PPY*, Au(III)-2ArPY*, and Au(III)-$ArPY^{\#}$* compounds exhibit some specific activities, especially biological and/or catalytic, as well as luminescence properties. It opens the way for their application as anti-tumour or anti-microbial (anti-bacterial, anti-fungal) drugs and catalysts in organic syntheses, as well as materials for the production of organic light-emitting diodes. So, the wide application of these species is the reason for their intensive studies, as noted during the last few decades, as well as to write the present review.

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References

1. Constable, E.C.; Leese, T.A. Cycloaurated derivatives of 2-phenylpyridine. *J. Organomet. Chem.* **1989**, *363*, 419–424. [CrossRef]
2. Parish, R.V.; Wright, J.P.; Pritchard, R.G. Mercury(II) and gold(III) derivatives of 2-phenylpyridines and 2-phenyl-4-(methylcarboxylato)quinoline. *J. Organomet. Chem.* **2000**, *596*, 165–176. [CrossRef]
3. Fan, D.; Yang, C.T.; Ranford, J.D.; Lee, P.F.; Vittal, J.J. Chemical and biological studies of the dichloro(2-phenylpyridine)gold(III) complex and its derivatives. *Dalton Trans.* **2003**, 2680–2685. [CrossRef]
4. Pazderski, L.; Pawlak, T.; Sitkowski, J.; Kozerski, L.; Szlyk, E. 1H, 13C, 15N and 195Pt NMR studies of Au(III) and Pt(II) chloride organometallics with 2-phenylpyridine. *Magn. Reson. Chem.* **2009**, *47*, 932–941. [CrossRef] [PubMed]
5. Janzen, D.E.; Doherty, S.R.; van Derveer, D.G.; Hinkle, L.M.; Benefield, D.A.; Vashi, H.M.; Grant, G.J. Cyclometallated gold(III) complexes with a trithiacrown ligand: Solventless Au(III) cyclometallation, intramolecular gold-sulfur interactions, and fluxional behavior in 1,4,7-trithiacyclononane Au(III) complexes. *J. Organomet. Chem.* **2014**, *755*, 47–57. [CrossRef]
6. Malmberg, R.; Bachmann, M.; Blacque, O.; Venkatesan, K. Thermally Robust and Tuneable Phosphorescent Gold(III) Complexes Bearing (N^N)-Type Bidentate Ligands as Ancillary Chelates. *Chem. Eur. J.* **2019**, *25*, 3627–3636. [CrossRef] [PubMed]
7. Segato, J.; Del Zotto, A.; Belpassi, L.; Belanzoni, P.; Zuccaccia, D. Hydration of alkynes catalyzed by [Au(X)(L)(ppy)]X in the green solvent γ-valerolactone under acidfree conditions: The importance of the preequilibrium step. *Catal. Sci. Technol.* **2020**, *10*, 7757–7767. [CrossRef]
8. Kim, J.H.; Ofori, S.; Mertens, R.T.; Parkin, S.; Awuah, S.G. Water-Soluble Gold(III)–Metformin Complex Alters Mitochondrial Bioenergetics in Breast Cancer Cells. *ChemMedChem* **2021**, *16*, 3222–3230.
9. Kim, J.H.; Ofori, S.; Parkin, S.; Vekaria, H.; Sullivan, P.G.; Awuah, S.G. Anticancer gold(III)-bisphosphine complex alters the mitochondrial electron transport chain to induce in vivo tumor inhibition. *Chem. Sci.* **2021**, *12*, 7467–7479. [CrossRef]
10. Martín, J.; Gomez-Bengoa, E.; Genoux, A.; Nevado, C. Synthesis of Cyclometalated Gold(III) Complexes via Catalytic Rhodium to Gold(III) Transmetalation. *Angew. Chem. Int. Ed.* **2022**, *61*, e202116755. [CrossRef]
11. Zhang, J.J.; Ng, K.M.; Lok, C.N.; Sun, R.W.Y.; Che, C.M. Deubiquitinases as potential anti-cancer targets for gold(III) complexes. *Chem. Commun.* **2013**, *49*, 5153–5155. [CrossRef] [PubMed]
12. Wu, Q.; Du, C.; Huang, Y.; Liu, X.; Long, Z.; Song, F.; You, J. Stoichiometric to catalytic reactivity of the aryl cycloaurated species with arylboronic acids: Insight into the mechanism of gold-catalyzed oxidative C(sp2)–H arylation. *Chem. Sci.* **2015**, *6*, 288–293. [CrossRef] [PubMed]
13. Shaw, A.P.; Tilset, M.; Heyn, R.H.; Jakobsen, S. Microwave methods for the synthesis of gold(III) complexes. *J. Coord. Chem.* **2011**, *64*, 38–47. [CrossRef]
14. Maity, A.; Sulicz, A.N.; Deligonul, N.; Zeller, M.; Hunter, A.D.; Gray, T.G. Suzuki–Miyaura coupling of arylboronic acids to gold(III). *Chem. Sci.* **2015**, *6*, 981–986. [CrossRef]
15. Garg, J.A.; Blacque, O.; Venkatesan, K. Syntheses and Photophysical Properties of Luminescent Mono-cyclometalated Gold(III) cis-Dialkynyl Complexes. *Inorg. Chem.* **2011**, *50*, 5430–5441. [CrossRef]
16. von Wachenfeldt, H.; Polukeev, A.V.; Loganathan, N.; Paulsen, F.; Roese, P.; Garreau, M.; Wendt, O.F.; Stand, D. Cyclometallated gold(III) aryl-pyridine complexes as efficient catalysts for three-component synthesis of substituted oxazoles. *Dalton Trans.* **2015**, *44*, 5347–5353. [CrossRef]
17. Kung, K.K.Y.; Lo, V.K.Y.; Ko, H.M.; Li, G.L.; Chan, P.Y.; Leung, K.C.; Zhou, Z.; Wang, M.Z.; Che, C.M.; Wong, M.K. Cyclometallated Gold(III) Complexes as Effective Catalysts for Synthesis of Propargylic Amines, Chiral Allenes and Isoxazoles. *Adv. Synth. Catal.* **2013**, *355*, 2055–2070. [CrossRef]
18. Bachmann, M.; Fessler, R.; Blacque, O.; Venkatesan, K. Towards blue emitting monocyclometalated gold(III) complexes—Synthesis, characterization and photophysical investigations. *Dalton Trans.* **2019**, *48*, 7320–7330. [CrossRef]
19. Hung, F.F.; To, W.P.; Zhang, J.J.; Ma, C.; Wong, W.Y.; Che, C.M. Water-Soluble Luminescent Cyclometalated Gold(III) Complexes with cis-Chelating Bis(N-Heterocyclic Carbene) Ligands: Synthesis and Photophysical Properties. *Chem. Eur. J.* **2014**, *20*, 8604–8614. [CrossRef]
20. Jiang, J.J.; Chau, A.K.H.; Wong, M.K.; Leung, F.K.C. Controlled Supramolecular Assembly of Gold (III) Amphiphiles in Aqueous Media. *Eur. J. Inorg. Chem.* **2022**, *2022*, e202200281. [CrossRef]
21. Kumar, R.; Linden, A.; Nevado, C. Evidence for Direct Transmetalation of AuIII−F with Boronic Acids. *J. Am. Chem. Soc.* **2016**, *138*, 13790–13793. [CrossRef] [PubMed]

22. Levchenko, V.A.; Siah, H.S.M.; Oien-Odegaard, S.; Kaur, G.; Fiksdahl, A.; Tilset, M. Catalytic studies of cyclometalated gold(III) complexes and their related UiO-67 MOF. *Mol. Catal.* **2020**, *492*, 111009. [CrossRef]
23. Levchenko, V.A.; Nova, A.; Oien-Odegaard, S.; Balcells, D.; Tilset, M. Synthesis, Characterization, and Reactivity of Cyclometalated Gold(III) Dihalide Complexes in Aqua Regia. *Eur. J. Inorg. Chem.* **2020**, *2020*, 3249–3258. [CrossRef]
24. Bachmann, M.; Terreni, J.; Blacque, O.; Venkatesan, K. Rationally Designed Blue Triplet Emitting Gold(III) Complexes Based on a Phenylpyridine-Derived Framework. *Chem. Eur. J.* **2017**, *23*, 3837–3849. [CrossRef]
25. Williams, M.R.M.; Bertrand, B.; Fernandez-Cestau, J.; Waller, Z.A.E.; O'Connell, M.A.; Searcey, M.; Bochmann, M. Acridine-decorated cyclometallated gold(III) complexes: Synthesis and anti-tumour investigations. *Dalton Trans.* **2018**, *47*, 13523–13534. [CrossRef]
26. Williams, M.R.M.; Bertrand, B.; Hughes, D.L.; Waller, Z.A.E.; Schmidt, C.; Ott, I.; O'Connell, M.; Searcey, M.; Bochmann, M. Cyclometallated Au(III) dithiocarbamate complexes: Synthesis, anticancer evaluation and mechanistic studies. *Metallomics* **2018**, *10*, 1655–1666. [CrossRef]
27. Szentkuti, A.; Garg, J.A.; Blacque, O.; Venkatesan, K. Monocyclometalated Gold(III) Complexes Bearing π-Accepting Cyanide Ligands: Syntheses, Structural, Photophysical, and Electrochemical Investigations. *Inorg. Chem.* **2015**, *54*, 10748–10760. [CrossRef]
28. Fan, D.; Yang, C.T.; Ranford, J.D.; Vittal, J.J.; Lee, P.F. Synthesis, characterization, and biological activities of 2-phenylpyridine gold(III) complexes with thiolate ligands. *Dalton Trans.* **2003**, 3376–3381. [CrossRef]
29. Fan, D.; Melendez, E.; Ranford, J.D.; Lee, P.F.; Vittal, J.J. Study on carbon–hydrogen activation of ketones by Gold(III) complexes and the synthesis and characterization of two ketonylgold(III) complexes. *J. Organomet. Chem.* **2004**, *689*, 2969–2974. [CrossRef]
30. Gukathasan, S.; Parkin, S.; Black, E.P.; Awuah, S.G. Tuning Cyclometalated Gold(III) for Cysteine Arylation and Ligand-Directed Bioconjugation. *Inorg. Chem.* **2021**, *60*, 14582–14593. [CrossRef]
31. Abas, E.; Gomez-Bachiller, M.; Colom, E.; Pardina, E.; Rodríguez-Dieguez, A.; Grasa, L.; Laguna, M. Cyclometallated gold(III) complexes against colon cancer. X-ray structure of [Au(C,NPhenylpyridine)(OAc)2]. *J. Organomet. Chem.* **2020**, *920*, 121340. [CrossRef]
32. Ivanov, M.A.; Puzyk, M.V.; Balashev, K.P. Spectral Properties of 2-Phenylpyridinate Complexes of Au(III) with Diimine Ligands. *Optics Spectrosc.* **2006**, *100*, 382–385. [CrossRef]
33. Babak, M.V.; Chong, K.R.; Rapta, P.; Zannikou, M.; Tang, H.M.; Reichert, L.; Chang, M.R.; Kushnarev, V.; Heffeter, P.; Meier-Menches, S.M.; et al. Interfering with Metabolic Profile of Triple-Negative Breast Cancers Using Rationally Designed Metformin Prodrugs. *Angew. Chem. Int. Ed.* **2021**, *60*, 13405–13413. [CrossRef] [PubMed]
34. Kuwamura, N.; Hayashida, K.; Tsuge, K.; Yoshinari, N.; Konno, T. A Drastic Difference in Photoluminescent Behavior between Cysteinato and Penicillaminato Gold(III) Complexes with a Phenylpyridinato Ligand. *Chem. Lett.* **2014**, *43*, 1846–1848. [CrossRef]
35. Mayans, J.G.; Suppo, J.S.; Echavarren, A.M. Photoredox-Assisted Gold-Catalyzed Arylative Alkoxycyclization of 1,6-Enynes. *Org. Lett.* **2020**, *22*, 3045–3049. [CrossRef]
36. Tlahuext-Aca, A.; Hopkinson, M.N.; Daniliuc, C.G.; Glorius, F. Oxidative Addition to Gold(I) by Photoredox Catalysis: Straightforward Access to Diverse (C,N)-Cyclometalated Gold(III) Complexes. *Chem. Eur. J.* **2016**, *22*, 11587–11592. [CrossRef] [PubMed]
37. Au, V.K.M.; Wong, K.M.C.; Zhu, N.; Yam, V.W.W. Luminescent Cyclometalated Dialkynylgold(III) Complexes of 2-Phenylpyridine-Type Derivatives with Readily Tunable Emission Properties. *Chem. Eur. J.* **2011**, *17*, 130–142. [CrossRef]
38. Garg, J.A.; Blacque, O.; Fox, T.; Venkatesan, K. Stable and Tunable Phosphorescent Neutral Cyclometalated Au(III) Diaryl Complexes. *Inorg. Chem.* **2010**, *49*, 11463–11472. [CrossRef]
39. Malmberg, R.; Suter, D.; Blacque, O.; Venkatesan, K. Monocyclometalated (CN) Gold(III) Metallacycles: Tunable Emission and Singlet Oxygen (1O2) Generation Properties. *Chem. Eur. J.* **2021**, *27*, 14410–14417. [CrossRef]
40. Ko, H.M.; Deng, J.R.; Cui, J.F.; Kung, K.K.Y.; Leung, Y.C.; Wong, M.K. Selective modification of alkyne-linked peptides and proteins by cyclometalated gold(III) (C^N) complex-mediated alkynylation. *Bioorg. Med. Chem.* **2020**, *28*, 115375. [CrossRef]
41. Szentkuti, A.; Bachmann, M.; Garg, J.A.; Blacque, O.; Venkatesan, K. Monocyclometalated Gold(III) Monoaryl Complexes—A New Class of Triplet Phosphors with Highly Tunable and Efficient Emission Properties. *Chem. Eur. J.* **2014**, *20*, 2585–2596. [CrossRef] [PubMed]
42. Zehnder, T.N.; Blacque, O.; Venkatesan, K. Luminescent monocyclometalated cationic gold(III) complexes: Synthesis, photophysical characterization and catalytic investigations. *Dalton Trans.* **2014**, *43*, 11959–11972. [CrossRef] [PubMed]
43. Rubbiani, R.; Zehnder, T.N.; Mari, C.; Blacque, O.; Venkatesan, K.; Gasser, G. Anticancer Profile of a Series of Gold(III) (2-phenyl)pyridine Complexes. *ChemMedChem* **2014**, *9*, 2781–2790. [CrossRef] [PubMed]
44. Jiang, J.J.; Cui, J.F.; Yang, B.; Ning, Y.; Lai, N.C.H.; Wong, M.K. Chiral Cyclometalated Oxazoline Gold(III) Complex-Catalyzed Asymmetric Carboalkoxylation of Alkynes. *Org. Lett.* **2019**, *21*, 6289–6294. [CrossRef] [PubMed]
45. Cui, J.F.; Ko, H.M.; Shing, K.P.; Deng, J.R.; Lai, N.C.H.; Wong, M.K. C,O-Chelated BINOL/Gold(III) Complexes: Synthesis and Catalysis with Tunable Product Profiles. *Angew. Chem. Int. Ed.* **2017**, *56*, 3074–3079. [CrossRef]
46. Mansour, M.A.; Lachicotte, R.J.; Gysling, H.J.; Eisenberg, R. Syntheses, Molecular Structures, and Spectroscopy of Gold(III) Dithiolate Complexes. *Inorg. Chem.* **1998**, *37*, 4625–4632. [CrossRef]
47. Browne, A.R.; Deligonul, N.; Anderson, B.L.; Zeller, M.; Hunter, A.D.; Gray, T.G. Cyclometalated (boroxinato)gold(III) complexes from arrested transmetalation. *Chem. Commun.* **2015**, *51*, 15800–15803. [CrossRef]

48. Kubo, K.; Nakano, M.; Tamura, H.; Matsubayashi, G.E.; Nakamoto, M. Preparation and oxidation of polarized Au(III) complexes having both the C-deprotonated-2-phenylpyridine (ppy) and a sulfur-rich dithiolate ligand and X-ray crystal structure of [Au(η2-C,N-ppy)-(η2-S,S-C8H4S8)]·0.5DMF. *J. Organomet Chem.* **2003**, *669*, 141–148. [CrossRef]
49. Kubo, K.; Nakano, M.; Tamura, H.; Matsubayashi, G.E. X-ray Crystal Structure and Electrical Conductivity of [Au(ppy)(C8H4S8)]2[PF6] [ppy- = *C*-deprotonated 2-phenylpyridine(-); C8H4S82- = 2-{(4,5-ethylenedithio)-1,3-dithiol-2-ylidene}-1,3-dithiole-4,5-dithionate(2-)]. *Eur. J. Inorg. Chem.* **2003**, *22*, 4093–4098. [CrossRef]
50. Kubo, K.; Nakao, A.; Ishii, Y.; Kato, R.; Matsubayashi, G.E. Structures and electrical conductivities of cation radical salts based on unsymmetrical [Au(III)(C-N)(S-S)] type dithiolate complexes. *Synth. Met.* **2005**, *153*, 425–428. [CrossRef]
51. Henderson, W.; Nicholson, B.K.; Faville, S.J.; Fan, D.; Ranford, J.D. Gold(III) thiosalicylate complexes containing cycloaurated 2-arylpyridine, 2-anilinopyridine and 2-benzylpyridine ligands. *J. Organomet. Chem.* **2001**, *631*, 41–46. [CrossRef]
52. Langseth, E.; Gorbitz, C.H.; Heyn, R.H.; Tilset, M. Versatile Methods for Preparation of New Cyclometalated Gold(III) Complexes. *Organometallics* **2012**, *31*, 6567–6571. [CrossRef]
53. Hylland, K.T.; Schmidtke, I.L.; Wragg, D.S.; Nova, A.; Tilset, M. Synthesis of substituted (N,C) and (N,C,C) Au(III) complexes: The influence of sterics and electronics on cyclometalation reactions. *Dalton Trans.* **2022**, *51*, 5082–5097. [CrossRef]
54. Venugopal, A.; Shaw, A.P.; Tornroos, K.W.; Heyn, R.H.; Tilset, M. Synthesis of a Coordinatively Labile Gold(III) Methyl Complex. *Organometallics* **2011**, *30*, 3250–3253. [CrossRef]
55. Holmsen, M.S.M.; Nova, A.; Oien-Odegaard, S.; Heyn, R.H.; Tilset, M. A Highly Asymmetric Gold(III) η3-Allyl Complex. *Angew. Chem. Int. Ed.* **2020**, *59*, 1516–1520. [CrossRef] [PubMed]
56. Witzel, S.; Holmsen, M.S.M.; Rudolph, M.; Dietl, M.C.; Oien-Odegaard, S.; Rominger, F.; Tilset, M.; Hashmi, A.S.K. Simple Mercury-Free Synthesis and Characterization of Symmetric and Unsymmetric Mono- and Dialkynyl (tpy)Au(III) Complexes. *Organometallics* **2020**, *39*, 2830–2837. [CrossRef]
57. Langseth, E.; Nova, A.; Traseth, E.A.; Rise, F.; Oien, S.; Heyn, R.H.; Tilset, M. A Gold Exchange: A Mechanistic Study of a Reversible, Formal Ethylene Insertion into a Gold(III)−Oxygen Bond. *J. Am. Chem. Soc.* **2014**, *136*, 10104–10115. [CrossRef] [PubMed]
58. Holmsen, M.S.M.; Ihlefeldt, F.S.; Oien-Odegaard, S.; Langseth, E.; Wencke, Y.; Heyn, R.H.; Tilset, M. Markovnikov at Gold: Nucleophilic Addition to Alkenes at Au(III). *Organometallics* **2018**, *37*, 1937–1947. [CrossRef]
59. Holmsen, M.S.M.; Nova, A.; Balcells, D.; Langseth, E.; Oien-Odegaard, S.; Heyn, R.H.; Tilset, M.; Laurenczy, G. Trans-Mutation at Gold(III): A Mechanistic Study of a Catalytic Acetylene Functionalization via a Double Insertion Pathway. *ACS Catal.* **2017**, *7*, 5023–5034. [CrossRef]
60. Holmsen, M.S.M.; Nova, A.; Balcells, D.; Langseth, E.; Oien-Odegaard, S.; Traseth, E.A.; Heyn, R.H.; Tilset, M. Small-molecule activation at Au(III): Metallacycle construction from ethylene, water, and acetonitrile. *Dalton Trans.* **2016**, *45*, 14719–14724. [CrossRef]
61. Eppel, D.; Eryigit, A.; Rudolph, M.; Bruckner, M.; Rominger, F.; Asiri, A.M.; Hashmi, A.S.K. Mechanochemical Gold(III)-Carbon Bond Formation. *Angew. Chem. Int. Ed.* **2021**, *60*, 13636–13640. [CrossRef] [PubMed]
62. Smith, T.S.; Lane, J.R.; Mucalo, M.R.; Henderson, W. Cycloaurated gold(III) complexes derived from the functionalised catecholate ligands alizarin and 3,4-dihydroxybenzaldehyde. *Trans. Met. Chem.* **2016**, *41*, 581–589. [CrossRef]
63. Kilpin, K.J.; Henderson, W.; Nicholson, B.K. Organogold(III) complexes containing chelating bis(amidate) ligands: Synthesis, characterisation and biological activity. *Polyhedron* **2007**, *26*, 434–447. [CrossRef]
64. Henderson, W.; Nicholson, B.K.; Wilkins, A.L. Facile syntheses of four-membered aurathietane dioxide [Au–CHR-SO2-CHR] ring systems, and the first isonitrile insertion reaction into a gold(III)–carbon bond. *J. Organomet. Chem.* **2005**, *690*, 4971–4977. [CrossRef]
65. Dien, L.X.; Murayama, T.; Hung, N.T.; Truong, Q.D.; Chinh, H.D.; Yoshimura, M.; Haruta, M.; Ishida, T. Efficient non-volatile organogold complex for TiO2-supported gold cluster catalysts: Preparation and catalytic activity for CO oxidation. *J. Catal.* **2022**, *408*, 236–244. [CrossRef]
66. Chambrier, I.; Hughes, D.L.; Jeans, R.J.; Welch, A.J.; Budzelaar, P.H.M.; Bochmann, M. Do Gold(III) Complexes Form Hydrogen Bonds? An Exploration of AuIII Dicarboranyl Chemistry. *Chem. Eur. J.* **2020**, *26*, 939–947. [CrossRef] [PubMed]
67. Savjani, N.; Rosca, D.A.; Schormann, M.; Bochmann, M. Gold(III) Olefin Complexes. *Angew. Chem. Int. Ed.* **2013**, *52*, 874–877. [CrossRef]
68. Rocchigiani, L.; Fernandez-Cestau, J.; Budzelaar, P.H.M.; Bochmann, M. Arene C–H activation by gold(III): Solvent-enabled proton shuttling, and observation of a pre-metallation Au–arene intermediate. *Chem. Commun.* **2017**, *53*, 4358–4361. [CrossRef]
69. Rocchigiani, L.; Fernandez-Cestau, J.; Budzelaar, P.H.M.; Bochmann, M. Reductive Elimination Leading to C-C Bond Formation in Gold(III) Complexes: A Mechanistic and Computational Study. *Chem. Eur. J.* **2018**, *24*, 8893–8903. [CrossRef]
70. Rocchigiani, L.; Fernandez-Cestau, J.; Chambrier, I.; Hrobarik, P.; Bochmann, M. Unlocking Structural Diversity in Gold(III) Hydrides: Unexpected Interplay of cis/trans-Influence on Stability, Insertion Chemistry, and NMR Chemical Shifts. *J. Am. Chem. Soc.* **2018**, *140*, 8287–8302. [CrossRef]
71. Rocchigiani, L.; Budzelaar, P.H.M.; Bochmann, M. Heterolytic bond activation at gold: Evidence for gold(III) H–B, H–Si complexes, H–H and H–C cleavage. *Chem. Sci.* **2019**, *10*, 2633–2642. [CrossRef] [PubMed]
72. Currie, L.; Rocchigiani, L.; Hughes, D.L.; Bochmann, M. Carbon–sulfur bond formation by reductive elimination of gold(III) thiolates. *Dalton Trans.* **2018**, *47*, 6333–6343. [CrossRef] [PubMed]

73. Rocchigiani, L.; Fernandez-Cestau, J.; Agonigi, G.; Chambrier, I.; Budzelaar, P.H.M.; Bochmann, M. Gold(III) Alkyne Complexes: Bonding and Reaction Pathways. *Angew. Chem. Int. Ed.* **2017**, *56*, 13861–13865. [CrossRef] [PubMed]
74. Smith, D.A.; Rosca, D.A.; Bochmann, M. Selective Au−C Cleavage in (C∧N∧C)Au(III) Aryl and Alkyl Pincer Complexes. *Organometallics* **2012**, *31*, 5998–6000. [CrossRef]
75. Wong, B.Y.W.; Wong, H.L.; Wong, Y.C.; Au, V.K.M.; Chan, M.Y.; Yam, V.W.W. Multi-functional bis(alkynyl)gold(III) N^C complexes with distinct mechanochromic luminescence and electroluminescence properties. *Chem. Sci.* **2017**, *8*, 6936–6946. [CrossRef] [PubMed]
76. Levchenko, V.; Oien-Odegaard, S.; Wragg, D.; Tilset, M. Crystal structure of (N^C) cyclometalated AuIII diazide at 100 K. *Acta Cryst. E* **2020**, *76*, 1725–1727. [CrossRef] [PubMed]
77. Cinellu, M.A.; Zucca, A.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Santoni, M. Synthesis and Characterization of Gold(III) Adducts and Cyclometallated Derivatives with 2-Substituted Pyridines. Crystal Structure of [Au{NC5H4(CMe2C2H4)-2}Cl2]. *J. Chem. Soc. Dalton Trans.* **1995**, 2865–2872. [CrossRef]
78. Niedzielska, D.; Pawlak, T.; Bozejewicz, M.; Wojtczak, A.; Pazderski, L.; Szlyk, E. Structural and spectroscopic studies of Au(III) and Pd(II) chloride complexes and organometallics with 2-benzylpyridine. *J. Mol. Struct.* **2013**, *1032*, 195–202. [CrossRef]
79. Bertrand, B.; Spreckelmeyer, S.; Bodio, E.; Cocco, F.; Picquet, M.; Richard, P.; Le Gendre, P.; Orvig, C.; Cinellu, M.A.; Casini, A. Exploring the potential of gold(III) cyclometallated compounds as cytotoxic agents: Variations on the C^N theme. *Dalton Trans.* **2015**, *44*, 11911–11918. [CrossRef]
80. De Paiva, R.E.F.; Du, Z.; Nakahata, D.H.; Lima, F.A.; Corbi, P.P.; Farrell, N.P. Gold-Catalyzed C–S Aryl-Group Transfer in Zinc Finger Proteins. *Angew. Chem. Int. Ed.* **2018**, *57*, 9305–9309. [CrossRef]
81. Kim, J.H.; Mertens, R.T.; Agarwal, A.; Parkin, S.; Berger, G.; Awuah, S.G. Direct intramolecular carbon(sp2)–nitrogen(sp2) reductive elimination from gold(III). *Dalton Trans.* **2019**, *48*, 6273–6282. [CrossRef] [PubMed]
82. Pettenuzzo, A.; Vezzu, K.; Di Paolo, M.L.; Fotopoulou, E.; Marchio, L.; Via, L.D.; Ronconi, L. Design, physico-chemical characterization and in vitro biological activity of organogold(III) glycoconjugates. *Dalton Trans.* **2021**, *50*, 8963–8979. [CrossRef] [PubMed]
83. Zhu, Y.; Cameron, B.R.; Mosi, R.; Anastassov, V.; Cox, J.; Qin, L.; Santucci, Z.; Metz, M.; Skerlj, R.T.; Fricker, S.P. Inhibition of the cathepsin cysteine proteases B and K by square-planar cycloaurated gold(III) compounds and investigation of their anti-cancer activity. *J. Inorg. Biochem.* **2011**, *105*, 754–762. [CrossRef] [PubMed]
84. Lin, Y.; Vong, K.; Matsuoka, K.; Tanaka, K. 2-Benzoylpyridine Ligand Complexation with Gold Critical for Propargyl Ester-Based Protein Labeling. *Chem. Eur. J.* **2018**, *24*, 10595–10600. [CrossRef]
85. Fuchita, Y.; Ieda, H.; Tsunemune, Y.; Kinoshita-Nagaoka, J.; Kawano, H. Synthesis, structure and reactivity of a new six-membered cycloaurated complex of 2-benzoylpyridine [AuCl2(pcp-*C*1,*N*)] [pcp = 2-(2-pyridylcarbonyl)phenyl]. Comparison with the cycloaurated complex derived from 2-benzylpyridine. *J. Chem. Soc. Dalton Trans.* **1998**, 791–796. [CrossRef]
86. Niedzielska, D.; Pawlak, T.; Czubachowski, T.; Pazderski, L. 1H, 13C and 15N NMR studies of Au(III) and Pd(II) chloride complexes and organometallics with 2-acetylpyridine and 2-benzoylpyridine. *J. Spectrosc.* **2013**, *2013*, 982832. [CrossRef]
87. Fuchita, Y.; Ieda, H.; Kayama, A.; Kinoshita-Nagaoka, J.; Kawano, H.; Kameda, S.; Mikuriya, M. Cycloauration of 2-substituted pyridine derivatives. Synthesis, structure and reactivity of six-membered cycloaurated complexes of 2-anilino-, 2-phenoxy- and 2-(phenylsulfanyl)-pyridine. *J. Chem. Soc. Dalton Trans.* **1998**, 4095–4100. [CrossRef]
88. Zhu, Y.; Cameron, B.R.; Skerlj, R.T. Cycloauration of substituted 2-phenoxypyridine derivatives and X-ray crystal structure of gold, dichloro-[2-[[5-[(cyclopentylamino)carbonyl]-2-pyridinyl-κ*N*]oxy]phenyl-κ*C*]-, (*SP*-4-3)-. *J. Organomet. Chem.* **2003**, *677*, 57–72. [CrossRef]
89. Nonoyama, M.; Nakajima, K.; Nonoyama, K. Direct cycloauration of 2-anilinopyridine (Hanp) with tetrachloroaurate(III) and the X-ray crystal structure of [AuCl2(anp)]. *Polyhedron* **1997**, *16*, 4039–4044. [CrossRef]
90. Bachmann, M.; Blacque, O.; Venkatesan, K. Harnessing White-Light Luminescence via Tunable Singlet-and Triplet-Derived Emissions Based on Gold(III) Complexes. *Chem. Eur. J.* **2017**, *23*, 9451–9456. [CrossRef]
91. Cinellu, M.A.; Minghetti, G.; Pinna, M.V.; Stoccoro, S.; Zucca, A.; Manassero, M. Synthesis and Characterization of Mononuclear Amidogold(III) Complexes—Crystal Structure of [Au(N2C10H7(CMe2C6H4)-6](NHC6H3Me2-2,6)][PF6]—Oxidation of 4-Methylaniline to Azotoluene. *Eur. J. Inorg. Chem.* **2003**, *2003*, 2304–2310. [CrossRef]
92. Gukathasan, S.; Parkin, S.; Awuah, S.G. Cyclometalated Gold(III) Complexes Bearing DACH Ligands. *Inorg. Chem.* **2019**, *58*, 9326–9340. [CrossRef]
93. Mertens, R.T.; Parkin, S.; Awuah, S.G. Cancer cell-selective modulation of mitochondrial respiration and metabolism by potent organogold(III) dithiocarbamates. *Chem. Sci.* **2020**, *11*, 10465–10482. [CrossRef]
94. Tang, H.; Saunders, G.C.; Henderson, W. Platinum(II), palladium(II), and gold(III) complexes of dianionic, secondary dithiooxamide ligands. *J. Coord. Chem.* **2019**, *72*, 2550–2561. [CrossRef]
95. Bonsignore, R.; Thomas, S.R.; Rigoulet, M.; Jandl, C.; Pothig, A.; Bourissou, D.; Barone, G.; Casini, A. C-C Cross-Couplings from a Cyclometalated Au(III) C^N Complex: Mechanistic Insights and Synthetic Developments. *Chem. Eur. J.* **2021**, *27*, 14322–14334. [CrossRef] [PubMed]
96. Goss, C.H.A.; Henderson, W.; Wilkins, A.L.; Evans, C. Synthesis, characterisation and biological activity of gold(III) catecholate and related complexes. *J. Organomet. Chem.* **2003**, *679*, 194–201. [CrossRef]

97. Kilpin, K.J.; Henderson, W.; Nicholson, B.K. Synthesis, characterisation and biological activity of cycloaurated organogold(III) complexes with imidate ligands. *Polyhedron* **2007**, *26*, 204–213. [CrossRef]
98. Risi, M.C.; Saunders, G.C.; Henderson, W. The coordination chemistry of sulfonyl-substituted thioureas towards the d8 metal centres platinum(II), palladium(II), nickel(II) and gold(III). *Inorg. Chim. Acta* **2021**, *526*, 120506. [CrossRef]
99. Tang, H.; Saunders, G.C.; Ma, X.; Henderson, W. Pyrrole thioamide complexes of the d8 metals platinum(II), palladium(II) and gold(III). *Inorg. Chim. Acta* **2020**, *502*, 119282. [CrossRef]
100. Finagenova, G.O.; Balashev, K.P. Mixed-Ligand Cyclometalated Pd(II) and Au(III) Complexes Based on 2-Benzylpyridine. *Russ. J. Gen. Chem.* **2008**, *78*, 682–684. [CrossRef]
101. Smith, T.S.; Henderson, W.; Nicholson, B.K. Cycloaurated gold(III) complexes with monoanionic thiourea ligands. *Inorg. Chim. Acta* **2013**, *408*, 27–32. [CrossRef]
102. Luo, Y.; Cao, B.; Zhong, M.; Liu, M.; Xiong, X.; Zou, T. Organogold(III) Complexes Display Conditional Photoactivities: Evolving From Photodynamic into Photoactivated Chemotherapy in Response to O_2 Consumption for Robust Cancer Therapy. *Angew. Chem. Int. Ed.* **2022**, *61*, e202212689. [CrossRef]
103. Ko, H.M.; Kung, K.K.Y.; Cui, J.F.; Wong, M.K. Bis-cyclometallated gold(III) complexes as efficient catalysts for synthesis of propargylamines and alkylated indoles. *Chem. Commun.* **2013**, *49*, 8869–8871. [CrossRef]
104. Niedzielska, D.; Pazderski, L.; Wojtczak, A.; Kurzawa, M.; Scianowski, J.; Szlyk, E. Structural and spectroscopic studies of Au(III) chloride compounds with 7,8-benzoquinoline. *Polyhedron* **2018**, *139*, 155–171. [CrossRef]
105. Serra, J.; Parella, T.; Ribas, X. Au(III)-aryl intermediates in oxidant-free C–N and C–O cross-coupling catalysis. *Chem. Sci.* **2017**, *8*, 946–952. [CrossRef] [PubMed]
106. Serra, J.; Font, P.; Carrizo, E.D.S.; Mallet-Ladeira, S.; Massou, S.; Parella, T.; Miqueu, K.; Amgoune, A.; Ribas, X.; Bourissou, D. Cyclometalated gold(III) complexes: Noticeable differences between (N,C) and (P,C) ligands in migratory insertion. *Chem. Sci.* **2018**, *9*, 3932–3940. [CrossRef] [PubMed]
107. Blons, C.; Mallet-Ladeira, S.; Amgoune, A.; Bourissou, D. (P,C) Cyclometalated Gold(III) Complexes: Highly Active Catalysts for the Hydroarylation of Alkynes. *Angew. Chem. Int. Ed.* **2018**, *57*, 11732–11736. [CrossRef]
108. Bechu, D.; Petre, A.M.; Hosseini, M.W.; Baudron, S.A. Heterometallic coordination polymers based on homo- and heteroleptic Au(III) dithiolene complexes. *CrystEngComm* **2020**, *22*, 5760–5767. [CrossRef]
109. Zhang, X.P.; Yang, G.; Wang, L.; Ng, S.W. Trichlorido(2-phenylpyridine-κN)-gold(III). *Acta Cryst. E* **2007**, *63*, m1582. [CrossRef]
110. Mruk, J.; Pazderski, L.; Scianowski, J.; Wojtczak, A. Structural and NMR spectroscopic studies of 2-phenylsulfanylpyridine and its analogues or derivatives, and their Au(III) chloride complexes. *Inorg. Chim. Acta* **2020**, *500*, 119182. [CrossRef]
111. Marek, R.; Lycka, A. 15N NMR Spectroscopy in Structural Analysis. *Curr. Org. Chem.* **2002**, *6*, 35–66. [CrossRef]
112. Pazderski, L. 15N and 31P NMR coordination shifts in transition metal complexes with nitrogen- and phosphorus-containing heterocycles. *Annu. Rep. NMR Spectrosc.* **2013**, *80*, 33–180.
113. Pazderski, L. 15N NMR coordination shifts in transition metal complexes and organometallics with heterocycles containing nitrogen—Update for 2012–2020. *Annu. Rep. NMR Spectrosc.* **2020**, *101*, 151–284.