

Article

Reactivity of Mononuclear and Dinuclear Gold(I) Amidinate Complexes with CS₂ and CsBr₃

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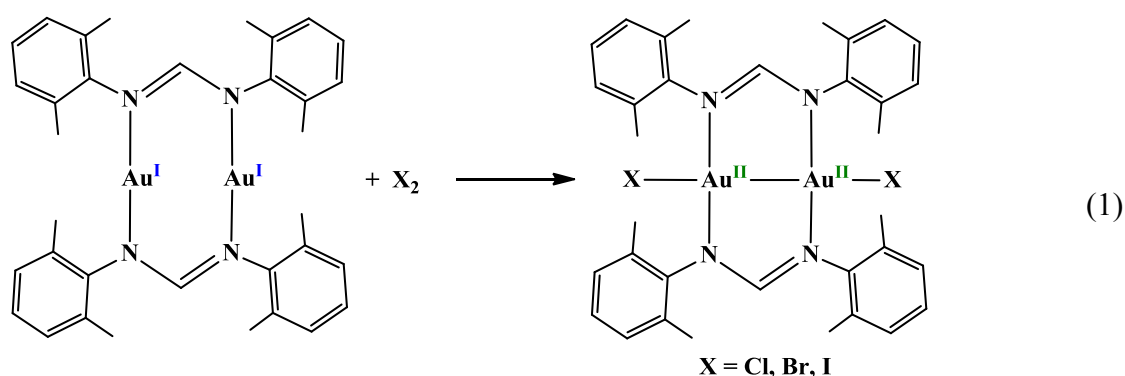
Abstract: To probe the reactivity of gold-nitrogen bonds, we have examined the insertion chemistry with carbon disulfide (CS₂) as well as oxidation with cesium tribromide (CsBr₃) with Au(I) amidinate complexes. The reaction of Ph₃PAuCl with Na[(2,6-Me₂C₆H₃N)₂C(H)] yields the mononuclear, two-coordinate gold(I) complex, Ph₃PAu[κ¹-(2,6-Me₂C₆H₃N)₂C(H)], **1**. The reactivity of **1** with CS₂ produced the mononuclear Au(I) compound, Ph₃PAu{κ¹-S₂C[(2,6-Me₂C₆H₃N)₂C(H)]}, **2**. In the case of CsBr₃ the previously reported dinuclear Au(I) complex, Au[(2,6-Me₂C₆H₃N)₂C(H)]₂, **3**, was isolated with formation of Ph₃PBr₂. We also compared the reactivity of CS₂ and CsBr₃ with **3**. Carbon disulfide insertion with **3** produces a dimeric product, Au_n[CS₂(2,6-Me₂C₆H₃NC(H)=NC₆H₃Me₂)]_n, **4**, featuring a dinuclear core with linking aurophilic interactions, making it appear polymeric in the solid state. When CsBr₃ is reacted with **3** the Au(II,II) product is obtained, Au₂[(2,6-Me₂C₆H₃N)₂C(H)]₂(Br)₂, **5**.

Keywords: gold; triphenylphosphine; insertion; carbon disulfide; oxidation

1. Introduction

The chemistry of gold is dominated by soft donor ligands due to the propensity for gold to form stronger interactions with elements such as phosphorus and sulfur. Hence, gold-nitrogen bonds are uncommon [1] and the reactivity of these bonds is relatively unexplored [2]. With the recent advances in gold amidinate chemistry [3], we sought to develop this reactivity by examining insertion and oxidative chemistry in Au(I) amidinate complexes.

Di- [4–6], tri- [4], and tetranuclear [7–10] gold amidinate complexes have been isolated, but to our knowledge, only one mononuclear gold complex has been reported [11]. However, that compound contains a protonated amidine ligand. The oxidative chemistry of dinuclear Au(I) amidinate complexes is characterized by a two-electron redox process with one-electron being produced from each Au(I) center to create Au(II,II) amidinate complexes, and maintains its dinuclear core. For example, reactions of PhICl_2 , Br_2 , and I_2 with $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C(H)}]_2$ produce $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C(H)}]_2(\text{X})_2$, $\text{X} = \text{Cl}$, Br , and I [5], respectively, Equation (1).



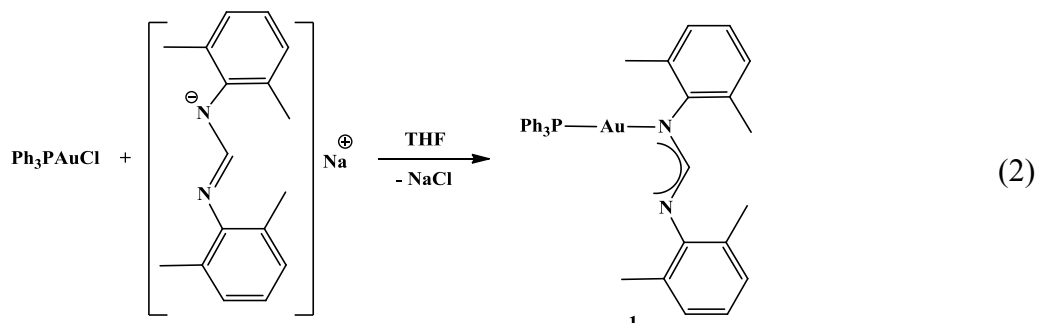
While the redox chemistry of these species has been observed, no insertion chemistry has been explored which affords the opportunity to expand to polymetallic complexes. Carbon disulfide (CS_2) was chosen due to group 11 metals' preference for soft donor atoms. The insertion chemistry of carbon disulfide with gold has been demonstrated with Au–C [12,13], Au–Cl [14], and Au–S [15] bonds.

In addition to soft donor ligands, gold chemistry is influenced by aurophilic interactions [16–18] in which the distance between two gold atoms is less than the sum of their van der Waals radii. These interactions can be quite strong and affect the coordination chemistry and chemical properties of gold [19–21].

The synthetic route to $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C(H)}]_2$ is the reaction of $(\text{tht})\text{AuCl}$ with $\text{Na}[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C(H)}]$; however, we surmised that by starting with Ph_3PAuCl , the preference for Au(I) to form two-coordinate, linear complexes would allow for the isolation of a mononuclear species. The $[\text{Ph}_3\text{PAu}]^+$ fragment can be viewed as isolobal to H^+ [22,23] and this moiety has been extensively studied [24]. We report here the synthesis of the two-coordinate, linear $\text{Ph}_3\text{PAu}[\kappa^1\text{-}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C(H)}]$ and have investigated its insertion chemistry with CS_2 as well as attempted oxidation with CsBr_3 . The analogous reactions with the dinuclear compound, $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C(H)}]_2$, were also performed for comparison.

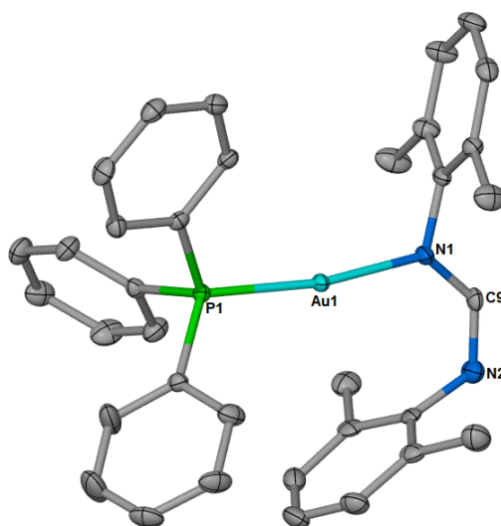
2. Results and Discussion

The amidine ligand is deprotonated with $\text{NaN}(\text{SiMe}_3)_2$ and allowed to stir for approximately one hour before addition of Ph_3PAuCl therefore we do not anticipate the formation of $\text{Ph}_3\text{PAuN}(\text{SiMe}_3)_2$ [25]. Reaction of Ph_3PAuCl with $\text{Na}[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]$ does not form the dinuclear gold product that is formed with $(\text{tht})\text{AuCl}$, Equation (2).

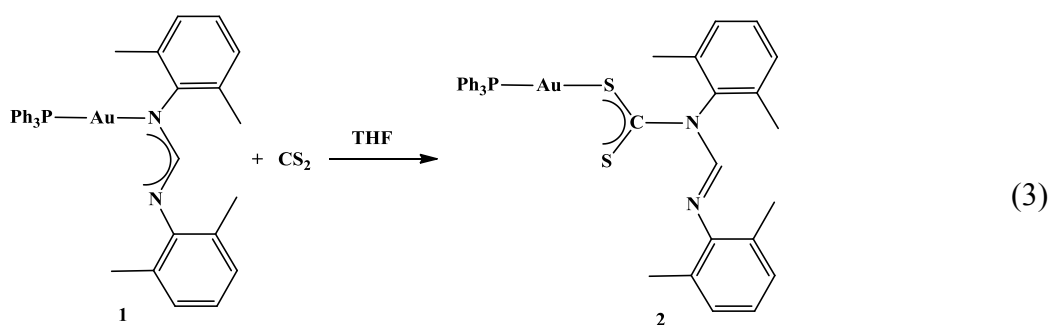


Instead, a different ^1H NMR spectrum was obtained which showed an asymmetric amidinate environment and had a ^{31}P NMR signal at 35.8 ppm in benzene- d_6 . This species is sparingly soluble in diethyl ether from which a saturated solution yielded colorless crystals suitable for X-ray diffraction analysis. The structure revealed the two-coordinate Au(I) complex, $\text{Ph}_3\text{PAu}[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]$, **1**, Figure 1. The Au–P and Au–N bond distances of 2.2297(4) and 2.0331(4) Å, respectively, are typical for a phosphine and amide coordinated to a Au(I) center, Table 1. For example, the Au–N bond lengths in $\text{IPrAuN}^i\text{Pr}_2$ [26] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and $[\text{Au}(\text{HF})(\text{HY})]\text{PF}_6$ (HF = $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})\text{C}(\text{H})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N}(\text{H}))]$; HY = diphenylmethylmethylene-substituted phosphorus ylide) are 1.967(4) and 2.069(8) Å, respectively [27].

Figure 1. Thermal ellipsoid plot of **1** shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.



We then turned our attention to the reactivity of **1**. The reaction of **1** with CS_2 produced a color change from colorless to yellow, Equation (3).



The ^1H NMR spectrum revealed an asymmetric ligand environment with two different methyl resonances and a new ^{31}P NMR resonance at 36.6 ppm. Due to the decreased solubility in arene solvents, the ^1H NMR spectrum was obtained in CDCl_3 . The proton on the formamidine backbone shifted downfield to 9.64 ppm, which is in the region observed when a localized imine bond is formed instead of a delocalized bond over the N–C–N backbone. Additional evidence of this was detected in the IR spectrum with a shift from 1605 cm^{-1} for the NCN stretch in **1** to 1646 cm^{-1} to a C=N stretch. Yellow crystals of $\text{Ph}_3\text{PAu}[\kappa^1\text{-CS}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}(\text{H})=\text{NC}_6\text{H}_3\text{Me}_2)]$, **2**, Figure 2, were obtained from a saturated diethyl ether solution, and a two-coordinate species is also observed with the insertion of CS_2 into the Au–N bond and formation of the dithiocarbamate. Similar to **1**, the Au–P bond distance is $2.2581(2)\text{ \AA}$ and the Au–S bond distance of $2.3247(2)\text{ \AA}$ is typical for Au(I) dithiocarbamates. For reference, the Au–S bond distances in $(\text{IPr})\text{Au}(\text{S}_2\text{CNET}_2)$ and $(\text{IPr})\text{Au}[\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2]$, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene, are $2.314(5)$ and $2.2999(12)\text{ \AA}$, respectively [27], and $2.312(3)\text{ \AA}$ in $\text{Ph}_3\text{PAu}(\text{indazol-1-yl dithiocarbamate})$ [28].

Table 1. Selected bond lengths (\AA) and angles ($^\circ$) for complex **4**.

Bond Distance/Angle	4
Au1–S1	2.31240(5)
Au1–S3	2.30871(5)
Au2–S2	2.2789(7)
Au2–S4	2.2888(7)
Au3–S5	2.3051(7)
Au3–S7	2.2900(7)
Au4–S6	2.2869(7)
Au4–S8	2.2996(7)
Au1–Au2	2.76154(5)
Au2–Au3	3.00745(7)
Au3–Au4	2.75717(19)
S1–C18–S2	128.6153(11)
S3–C38–S4	126.9985(11)
S4–Au2–Au3	89.8335(15)
S2–Au2–Au3	90.5685(15)

With the recent use of CsBr_3 to oxidize Au(I) to Au(III), we attempted a similar reaction with **1** [29]. Indeed, reaction of **1** with CsBr_3 is accompanied by a color change to red-brown; however, upon workup the ^1H NMR spectrum revealed the presence of the dinuclear Au(I) amidinate, $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})_2]$, **3**, as well as resonances consistent with Ph_3PBr_2 , Equation (4). Further,

the ^{31}P NMR spectrum also confirmed the phosphorus-based product as Ph_3PBr_2 [30]. The red-brown color may be due to the possible formation of $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N}_2)\text{C}(\text{H})_2(\text{Br})_2]$ which has been previously reported [5]. We rationalize that the products of this reaction result from the precipitation of CsBr , formation of the stronger P-Br bonds rather than Au-Br, and subsequent aurophilic interaction that arises.

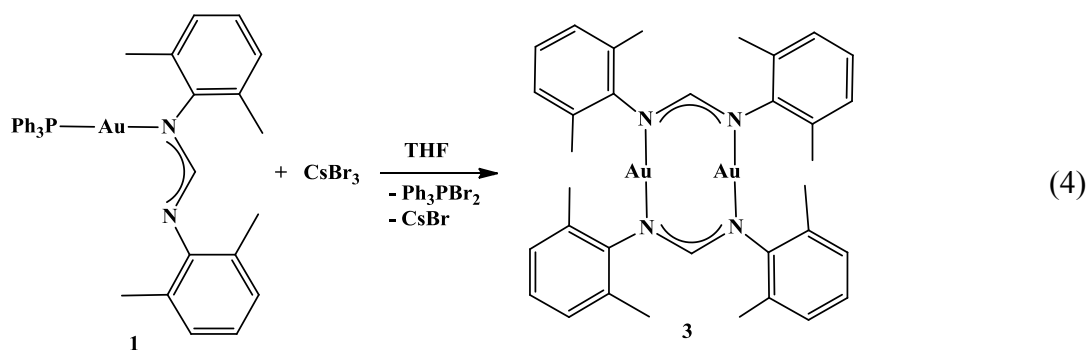
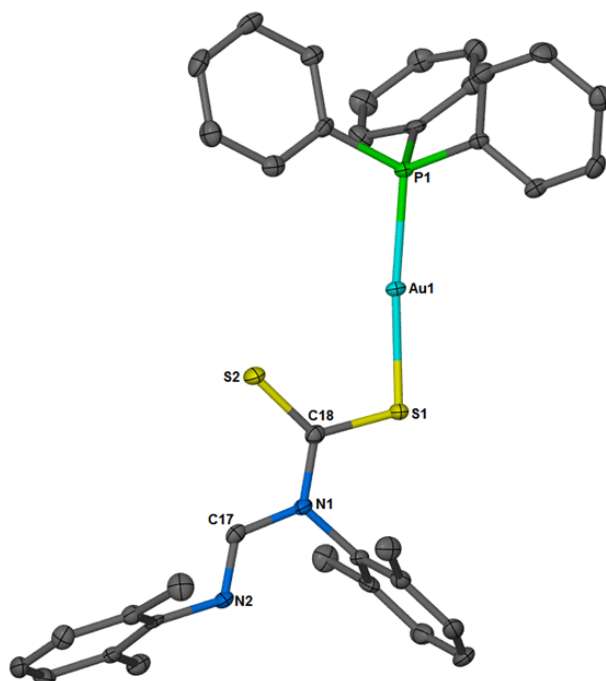


Figure 2. Thermal ellipsoid plot of **2** shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.



The reactivity of dinuclear Au(I) amidinate complex, $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N}_2)\text{C}(\text{H})_2]$, **3**, has not been reported with CS_2 or CsBr_3 and, therefore, we attempted these substrates to compare with the mononuclear species. Reaction of **3** with CS_2 in THF gave a color change to yellow, and, over time, a red solid precipitated. The ^1H NMR spectrum showed an asymmetric ligand environment with two distinct methyl resonances and a downfield shift of the formamidinate backbone proton to 9.25 ppm. The IR spectrum also revealed an imine stretch at 1648 cm^{-1} . The product is soluble in chloroform and THF, forming a yellow solution but then slowly precipitates as a red solid. Red crystals were obtained from a heated saturated THF solution and allowed to cool to room temperature, and showed the structure, $\{\text{Au}_2[\text{CS}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}(\text{H})=\text{NC}_6\text{H}_3\text{Me}_2)]_2\}_n$, **4**, Figure 3. Interestingly, **4** has a dinuclear

core, Figure 4, with one CS₂ inserting into one Au–N bond. The Au–Au bond distances within each molecule are 2.76154(5) and 2.75717(19) Å, and are much shorter than the 3.00745(7) Å aurophilic interaction that links the two dinuclear fragments, Table 1. Over time, aurophilic interactions, which have comparable strength to a hydrogen bond, start to form which could account for the solubility issues and precipitation from solution. The stacking of discrete dimeric units in the solid-state is not new in gold dithiocarbamate chemistry [28,31–35].

Figure 3. Thermal ellipsoid plot of **4** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

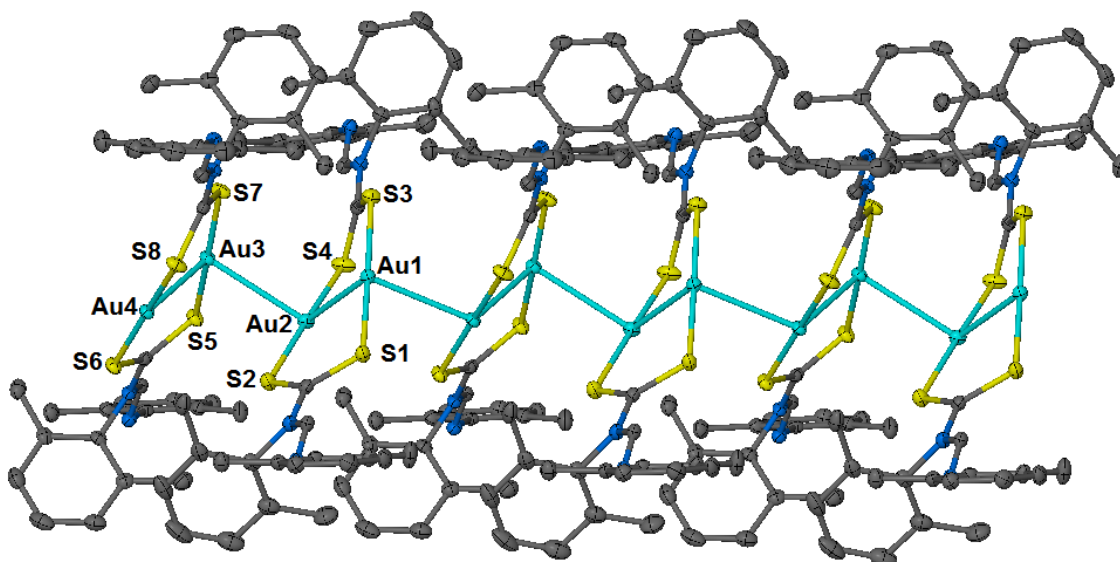
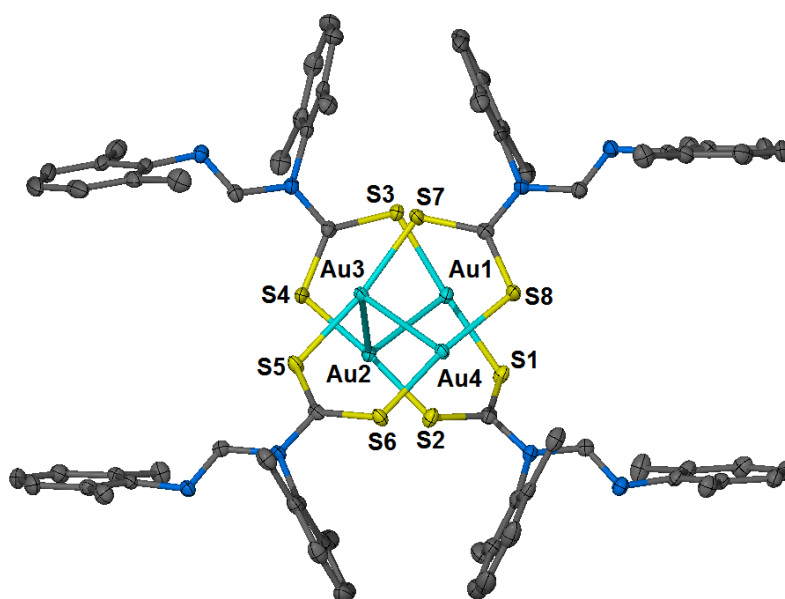


Figure 4. Thermal ellipsoid plot of two units of **4** shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.



The reaction of **3** with CsBr₃ produced a dark brown colored solution and the ¹H NMR spectrum showed the formation of the previously reported Au₂[(2,6-Me₂C₆H₃N₂)C(H)]₂(Br)₂, **5**, albeit in low

yield. While the mononuclear product afforded the oxidative addition product, **3** produces a one-electron oxidation from both metal centers yielding two Au(II) centers. This difference in reactivity demonstrates the stability of the amidinate ligand framework in the dinuclear system. Substrates such as PhNCO and CO₂ do not insert into the amidinate framework, presumably due to the stability of the dinuclear core, as well as the preference of gold for soft donor atoms, not hard atoms, such as oxygen.

3. Experimental Section

3.1. General Considerations

Even if air-stable, the syntheses described were carried out under inert atmosphere (N₂) using glove box or standard Schlenk techniques unless otherwise noted. Solvents were distilled under nitrogen and kept over drying sieves. NaN(SiMe₃)₂, anhydrous carbon disulfide (Aldrich, Milwaukee, WI, USA) and Ph₃PAuCl (Strem, Newportbury, MA, USA) were used as received. The amidine ligand, [(2,6-Me₂C₆H₃N)C(H)(2,6-Me₂C₆H₃N(H))] [36], Au₂[(2,6-Me₂C₆H₃N)₂C(H)]₂, **3** [4], and CsBr₃ [29] were prepared as previously described. Benzene-*d*₆ and chloroform-*d*₁ (Cambridge Isotope Laboratories, Tewksbury, MA, USA) were dried over molecular sieves and degassed with three freeze-evacuate-thaw cycles. All ¹H, ¹³C, and ³¹P NMR data were obtained on a 300 MHz DRX or 500 MHz DRX Bruker (Madison, WI, USA) spectrometer. Infrared spectra were recorded as KBr pellets on Perkin-Elmer (Waltham, MA, USA) Spectrum One FT-IR spectrometer.

3.2. Synthesis of Ph₃PAu[κ¹-(2,6-Me₂C₆H₃N)₂C(H)], **1**

NaN(SiMe₃)₂ (145 mg, 0.792 mmol) was added to a stirred solution of [(2,6-Me₂C₆H₃N)C(H)(2,6-Me₂C₆H₃N(H))] (200 mg, 0.792 mmol) in THF (15 mL). After 1 h, Ph₃PAuCl (391 mg, 0.791 mmol) was added and allowed to stir for 12 h. Insoluble material was removed via centrifugation and filtered through Celite. The solvent was then removed under vacuum to give yield **1** as a white powder (153 mg, 68%). Colorless X-ray quality crystals were grown overnight from a saturated diethyl ether solution at -35 °C. ¹H NMR (C₆D₆, 500 MHz): δ 7.4 (buried in multiplet, 1H, CH), 7.5 (m, PPh₃), 7.45 (m, PPh₃), 7.43 (m, PPh₃), 7.25 (t, ³J_{H-H} = 7.5 Hz, 1H, Ph), 7.07 (t, ³J_{H-H} = 7.5 Hz, 2H, Ph), 6.9 (t, ³J_{H-H} = 7.5 Hz, 1H, Ph), 6.5 (d, ³J_{H-H} = 7.5 Hz, 1H, Ph), 2.42 (s, 6H, Me), 2.17 (s, 6H, Me). ¹³C NMR (CD₃CN, 126 MHz): δ 155 (CH), 135 (Ph), 134 (PPh₃), 131 (Ph), 130 (PPh₃), 129.8 (PPh₃), 129.5 (Ph), 129 (Ph) ppm. ³¹P NMR (CDCl₃, 101MHz): δ 35.8 ppm. IR (KBr): 3060 (w, C-H), 3006 (C-H), 2961 (w (br), C-H), 2938 (m, C-H), 2904 (w (br), C-H), 1605 (s, C-N), 772 (m, P-C) cm⁻¹. Anal. Calcd. for C₃₅H₃₅N₂PAu: C, 59.16%; H, 4.82%; N, 3.94%. Found: C, 58.62%; H, 4.73%; N, 3.69%.

3.3. Synthesis of Ph₃PAu[κ¹-CS₂(2,6-Me₂C₆H₃NC(H)=NC₆H₃Me₂)], **2**

To a stirred solution of **1** (100 mg, 0.143 mmol) in THF (15 mL), excess carbon disulfide (CS₂) was added. The solution immediately turned yellow upon addition. After 1 h, the solvent was then removed under vacuum to yield **2** as a yellow powder (48 mg, 47%). Transparent yellow crystals suitable for X-ray diffraction analysis formed from a yellow solution of diethyl ether solution at -35 °C. ¹H NMR (500 MHz, CDCl₃): δ 9.64 (s, 1H, CH), 7.63–7.42 (m, 15 H, PPh₃), 7.18 (d, ³J_{H-H} = 7.6 Hz, 2H, Ph), 6.99 (d, ³J_{H-H} = 7.6 Hz, 2H, Ph), 6.87 (t, ³J_{H-H} = 7.6 Hz, 1H, Ph), 2.38 (s, 6H, Me), 2.13 (s, 6H, Me)

ppm. ^{13}C NMR (126 MHz, CDCl_3): δ 215.88 (quat), 150.65 (CH), 148.15 (Ph), 139.66 (Ph), 135.58 (Ph), 134.26–134.42 (Ph), 134.18 (Ph), 131.56 (Ph), 129.85 (Ph), 129.39 (Ph), 129.09 (Ph), 128.60 (Ph), 128.03 (Ph), 127.90 (Ph), 123.32 (Ph), 18.82 (Me), 18.00 (Me) ppm. ^{31}P NMR (101 MHz, CDCl_3): δ 36.6 ppm. IR (KBr): 3046 (w, C–H bending), 2968 (w (br), C–H bending), 2918 (w (br), C–H bending), 1646 (s, C=N stretch), 774 (m, P–C stretch) cm^{-1} . Anal. Calcd. for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{PS}_2\text{Au}$: C, 54.96%; H, 4.36%; N, 3.56%. Found: C, 54.89%; H, 4.62%; N, 3.40%.

3.4. $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]_2$, **3**, from **1** and CsBr_3

To a stirred solution of $\text{Ph}_3\text{PAu}[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]$, **1**, (100 mg, 0.141 mmol) was added CsBr_3 (52 mg, 0.141 mmol) in THF (12 mL). The solution changed from a colorless to a dark red/brown solution. Off-white precipitate crashed out after stirring for 1 h. The ^{31}P NMR spectrum of this off-white solid was identified as Ph_3PBr_2 and the ^1H NMR spectrum showed the previously reported $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]_2$, **3** [4].

3.5. Synthesis of $\text{Au}_2[\text{CS}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}(\text{H})=\text{NC}_6\text{H}_3\text{Me}_2)]_2$, **4**

To a stirred solution of **3** (114 mg, 0.128 mmol) in 15 mL of diethyl ether was added an excess amount of CS_2 (~0.1 mL). The solution color immediately changed from colorless to yellow and precipitation began. After 1 h, the solvent was removed yielding **4** as a red solid (66 mg, 45%). Red crystals suitable for X-ray diffraction analysis were obtained by heating a saturated THF solution and slowly cooling to room temperature. ^1H NMR (C_6D_6 , 500 MHz): δ 2.05 (s, 12H, Me), 2.27 (s, 12H, Me), 6.86 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 1H, Ph), 6.95 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, Ph), 7.14 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, Ph), 7.20 (m, Ph), 9.25 (s, 1H, CH). ^{13}C NMR (C_6D_6 , 500 MHz): 214.5 (CS_2), 149.0 (methine), 146.5 (quat), 140.0 (quat), 135.7 (methine), 129.5 (quat), 129.0 (Ph), 128.5 (Ph), 128 (Ph), 125.4 (quat), 19.0 (CH_3), 18.2 (CH_3). IR (KBr): 3473 (s), 3156 (s), 2947 (s), 2426 (s), 1766 (vs), 1648 (m), 1589 (s), 1384 (s), 1266 (vs), 1185 (vs), 764 (m) cm^{-1} . Elem. Anal. Calcd. for $\text{C}_{36}\text{H}_{38}\text{N}_4\text{S}_4\text{Au}_2$: C, 41.22%; H, 3.65%; N, 5.34%. Found: C, 40.75%; H, 3.78%; N, 5.09%.

3.6. Synthesis of $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]_2(\text{Br})_2$, **5**

To a stirred solution of $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]_2$ (100 mg, 0.111 mmol), **3**, in THF (10 mL), CsBr_3 (41 mg, 0.110 mmol) was added. The solution immediately turned from colorless to dark brown with the formation of a precipitate. The solution was filtered through Celite and the solvent removed under vacuum to yield **5** as a dark brown powder (40 mg, 34%). The ^1H NMR spectrum confirmed the product as the previously reported, $\text{Au}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{H})]_2(\text{Br})_2$ [5].

3.7. X-ray Crystallography Details.

A selected single crystal of **1**, **2**, and **4** was mounted on nylon cryoloops using viscous hydrocarbon oil. X-ray data collection was performed at 100(2) or 173(2) K. The X-ray data were collected on a Bruker (Madison, WI, USA) CCD diffractometer with monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) with data collection and processing using the Bruker Apex2 suite of programs [37]. The structures were solved using direct methods and refined by full-matrix least-squares methods on

F^2 using Bruker SHELEX-97 program [38]. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were added on idealized positions and not allowed to vary. Thermal ellipsoid plots were prepared by using X-seed [39] at the 50% probability level for non-hydrogen atoms. Crystal data and detail for data collection for complex **1**, **2**, and **4** is provided in Table 2.

Table 2. X-ray crystallographic data is shown for complexes **1**, **2**, and **4**.

Compound	1	2	4
CCDC deposit number	1013054	1013056	1008664
Empirical formula	C ₃₅ H ₃₄ N ₂ PAu	C ₃₈ H ₃₉ N ₂ S ₂ PO _{0.50} Au	C ₃₆ H ₃₈ N ₄ S ₄ Au ₂
Formula weight (g/mol)	710.58	823.77	2097.75
Crystal habit, color	Colorless, plate	Yellow, plate	Red, prism
Temperature (K)	173(2)	100(2)	100(2)
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
Crystal system	Triclinic	Monoclinic	Triclinic
Volume (Å ³)	2993.8(11)	7085.0(7)	3629.30(16)
<i>a</i> (Å)	10.641(2)	38.566(2)	8.3937(2)
<i>b</i> (Å)	14.542(3)	8.7877(5)	15.4728(4)
<i>c</i> (Å)	20.465(4)	27.0810(17)	29.2585(8)
α (°)	83.247(2)	90	99.1330(10)
β (°)	78.545(2)	129.4690(10)	96.0620(10)
γ (°)	75.244(2)	90	102.1610(10)
<i>Z</i>	4	8	2
Calculated density (Mg/m ³)	1.577	1.545	1.920
Absorption coefficient (mm ⁻¹)	4.993	4.346	17.373
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0236 w <i>R</i> 2 = 0.0498	<i>R</i> 1 = 0.0233 w <i>R</i> 2 = 0.0508	<i>R</i> 1 = 0.0183 w <i>R</i> 2 = 0.0427

4. Conclusions

A rare mononuclear gold(I) amidinate complex has been synthesized from reaction of Ph₃PAuCl with Na[(2,6-Me₂C₆H₃N)₂C(H)], and its reactivity explored with CS₂ and CsBr₃. Addition of CS₂ to Ph₃PAu[κ¹-(2,6-Me₂C₆H₃N)₂C(H)] results in the facile insertion into the gold-nitrogen bond to produce the dithiocarbamate species which was also found to also be two-coordinate. The reaction of CsBr₃ with Ph₃PAu[κ¹-(2,6-Me₂C₆H₃N)₂C(H)] led to the formation of Ph₃PBr₂ and the dinuclear amidinate complex, Au₂[(2,6-Me₂C₆H₃N)₂C(H)]₂. For comparison, the dinuclear gold amidinate complex was examined with CS₂ and CsBr₃. Carbon disulfide also inserted into the gold-nitrogen bonds of Au₂[(2,6-Me₂C₆H₃N)₂C(H)]₂ which maintained its dinuclear form but polymerized through aurophilic interactions between neighboring fragments in the solid-state. The CsBr₃ oxidation did occur to the form the dinuclear Au(II,II) product, Au₂[(2,6-Me₂C₆H₃N)₂C(H)]₂(Br)₂. The objective of this work was to examine the reactivity of a mononuclear gold(I) amidinate complex, which led to the comparison with the dinuclear gold(I) compound. Our results further demonstrate the tendency for gold to form aurophilic interactions as well as bonds with softer ligands, even when in a dinuclear framework.

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Author Contributions

Andrew C. Lane and Justin R. Walensky conceived and designed the synthetic experiments and wrote the manuscript. Matthew V. Vollmer assisted with experimental design and crystallography. Charles L. Barnes carried out the crystallographic analysis.

Conflicts of Interest

The authors declare no conflict of interest.

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