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Organometallic Iridium Complexes with Glucose Based Phosphite Ligands

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Abstract: New organometallic iridium compounds with phosphorus modified glucose ligands containing isopropylidene protection group or bearing uracil, thymine, and 5-fluorouracil (3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranoside, 3,5,6-bicyclophosphite-1-β-D-glucofuranosyluracil, 3,5,6-bicyclophosphite-1-β-D-glucofuranosylthymine, 3,5,6-bicyclophosphite-1-β-D-glucofuranosyl-5-flurouracil) were prepared. The structure of the new complexes was confirmed by the spectroscopic technique (^{1}H, ^{31}P{^{1}H} NMR) and mass spectrometry, and purity by elemental analysis. The molecular structure of the complex with the isopropylidene protection group was established by the X-ray analysis. The antiproliferative activity of the new iridium compounds was evaluated against several cancer cell lines of human origin, and all compounds showed low toxicity independent of the pyrimidine base nature, attached to the sugar unit.

Keywords: iridium complexes; phosphite ligands; antiproliferative activity

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1. Introduction

Many types of malignant tumors are successfully treated with platinum-based compounds, but their use is partly complicated by known side effects (nephrotoxicity, neurotoxicity, anemia, tachycardia, vision decrease, problem with the food intake, and vomiting) and primary or acquired resistance [1–3]. Currently, the preparation of antitumor compounds based on other metals different from platinum is the major trend in the field of antitumor metal-based drugs [4–9]. Iridium base compounds recently received considerable attention as a very likely alternative to platinum antineoplastic drugs [10–14] and some iridium complexes have higher antitumor activity in vitro than cisplatin [10].

Organophosphorus compounds are a well-known class of biologically active molecules that have several clinical applications including those against glaucoma, cardiovascular diseases and fungal and viral infections. The organophosphorus compounds were one of the first classes of compounds to be considered as chemotherapeutic substances used to treat a wide range of cancer types and are still utilized for the treatment of several types of cancer as well as cardiovascular disease, fungal and viral infections. Anticancer organophosphates were introduced into clinical practice in the late 1950s. Nowadays, cyclophosphamide, ifosfamide, or thiotepa (Figure 1) are clinically approved antitumor agents [15–18].

The combination of phosphorus containing ligands (phosphines, phosphonates, and phosphites) with metals of the platinum group is one way to overcome the limitations of clinical platinum drugs. i.e by providing a tunable platform in terms of structural modifications as well as a targeted approach. Platinum(II) complexes with aminomethyl phosphonic ligands showed activity against bone malignancies [19]. The PTA (1,3,5-triaza-7-phosphatricyclo-[3.3.1.1]decane) ligand coordinated to organometallic Ru(II)-arene systems resulted in selective antimetastatic activity [20]. A number of Pt, Ru, and Au complexes

with phosphorus ligands are active against cisplatin resistant tumors. Auranofin, which is used in the clinic to treat rheumatic arthritis, also shows significant anticancer activity [21].

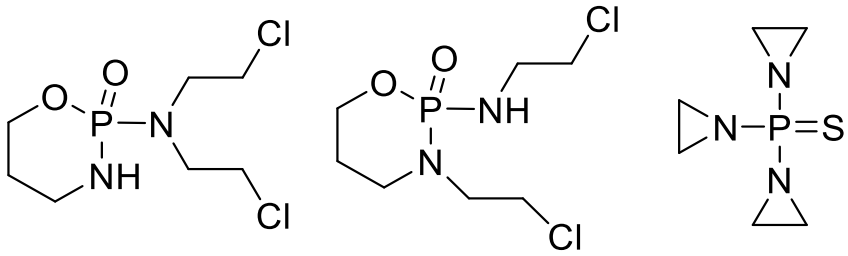
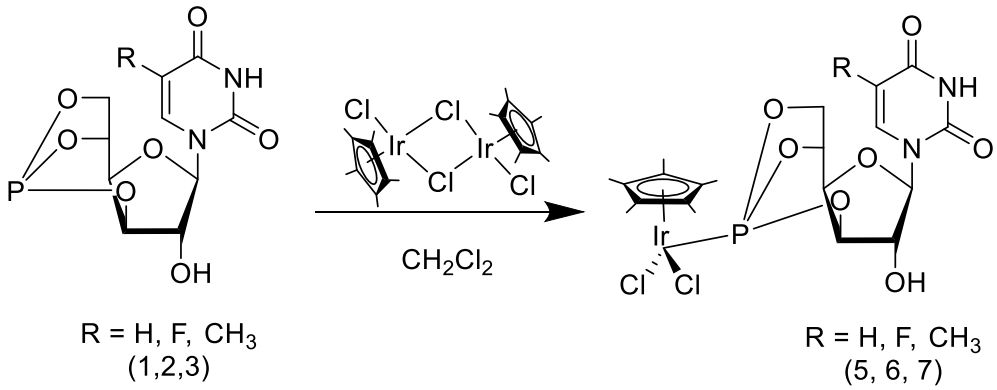


Figure 1. Cyclophosphamide (**left**), ifosfamide (**middle**), thiotepa (**right**).

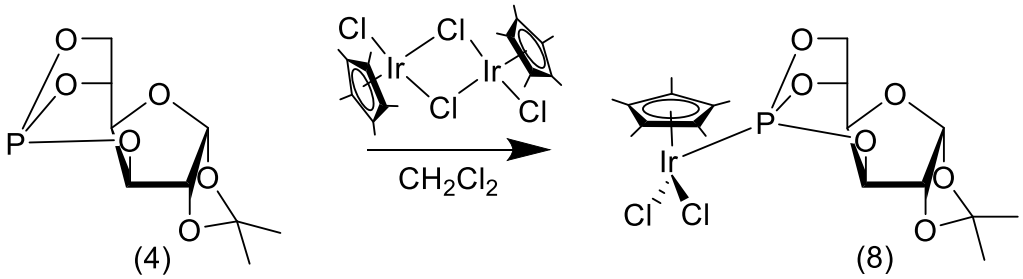
Carbohydrate chemistry joins organic chemistry with medicinal chemistry and biology, because of the role that carbohydrates play in glycobiology, in antiinfective therapy as units of antibiotics, antitumors, and antiviral agents [22]. The addition of a carbohydrate moiety to a metal-binding ligand leads to reduced toxicity, and to improved solubility and molecular targeting. Carbohydrate ligands can be used for building a well-defined binding environment and improving the stability of the complexes. The carbohydrate unit remains pendant and can lead to an interaction with carbohydrate transporters in the cell [23]. Moreover, there are several organic compounds in clinical use as anticancer agents possessing a sugar moiety, e.g., the DNA strand break-inducing compound bleomycin [24], the alkylating agent glufosfamide [25], and the DNA intercalator doxorubicin [26]. Earlier, we showed that a combination of the phosphite ligands based on the glucose moiety with organometallic ruthenium center gives a new class of antiproliferative compounds capable to tune antiproliferative anti-angiogenic and antiviral activities [27–30]. In the present work, we prepared new organometallic iridium complexes with phosphite ligands based on the glucose and bearing the uracil, thymine, 5-fluoro uracil residues, or isopropylidene protecting group and studied their antiproliferative activity against several human cancer cell lines.

2. Results and Discussion

New organometallic iridium(III) compounds **5**–**8** were prepared by the treatment of corresponding phosphites **1**–**4** with an iridium dimer (Schemes 1 and 2) at room temperature in methylene chloride. Pure complexes were isolated by precipitation out of the reaction mixture with the diethyl ether.



Scheme 1. Synthesis of Ir(III) complexes.



Scheme 2. Synthesis of Ir(III) complex **8**.

The structure of the resulting complexes **5**–**8** was confirmed by the spectroscopic technique (^{1}H, ^{31}P{^{1}H} NMR) and mass spectrometry, and purity by elemental analysis. In the ^{31}P{^{1}H} NMR spectra complexes **5**–**8**, only one singlet signal was observed with characteristic downfield shifts compared to uncoordinated ligands from ca. 119–120 ppm to 98–99 ppm. In the ^{1}H NMR spectra complexes **5**–**8** only minor shifts for protons were observed in comparison to the uncoordinated ligands **1**–**4**. Additionally, signals corresponding to the methyl groups in the Cp-star fragment are now present in the spectra. Electrospray ionization did not result in the formation of protonated species, but analysis of the recorded mass spectra revealed signals assigned as $[M + Na]^+$ in the positive and $[M + Cl]^-$ in the negative ionization modes. Isotopic distributions in these ion clusters clearly indicate the presence of Iridium, which was proven by plotting the simulated mass spectra of expected ion species and comparing them with experimental data. Thus, the molecular formulas of all the obtained compounds were confirmed (Figure 2).

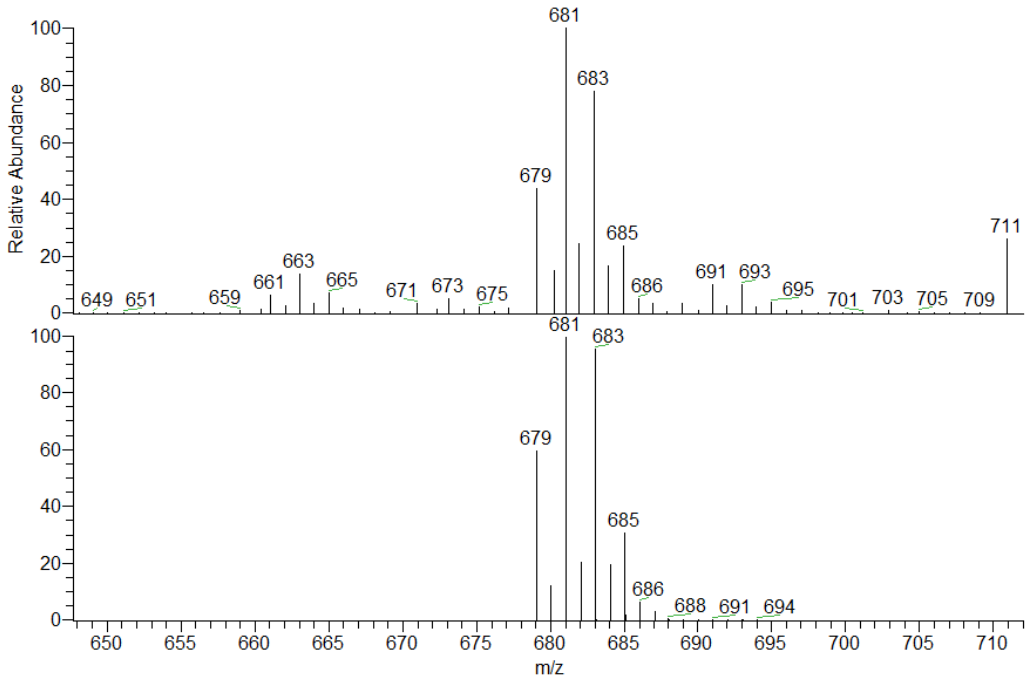


Figure 2. Experimental (**bottom**) and calculated (**up**) distribution for complex **8** $[M + Cl]^-$.

Via the recrystallization of compound **8** from a mixture of diethyl ether and methylene chloride, we obtained orange crystals suitable for XRD (Figure 3, Tables 1 and 2).

XRD of complex **8** has shown that the basic bond lengths and valence angles are almost identical to those of the trialkyl and triaryl phosphite iridium complexes [31]. The bond lengths and angles in complex **8** are close to the expected ones. The phosphorus atom is characterized by the distorted tetrahedral configuration with the variation of bond angles in the range of 96.2(5)–122.1(4)° (Table 1). The maxima value is observed for one of the

O-P-Ir angles and is clearly the consequence of steric repulsion. The analysis of crystal packing has revealed that all contacts correspond to normal Van-der-Waals interactions such as weak Cl . . . .H and H . . . H ones. The absence of specific interactions is clearly the reason for pentamethyl cyclopentadienyl ring libration. The Ir-P bond length in structure **8** is 2.209(3)Å whereas in the complexes mentioned above it is 2.24 A. Similar Ir-Cp(centroid) distance also remains unchanged and is equal to 1.84 Å in 8 and 1.83 and 1.85 Å according to the literature data [31]. The geometry of the ligand is also close to the expected one. The P-O bond length is 1.58 Å. The six-membered P1O2O3C3C4C5 ring is characterized by the slightly distorted chair conformation with the deviation of P1 and C4 atoms. The five-membered PO2C2 cycle is characterized by the envelope conformation with the deviation of the O3.

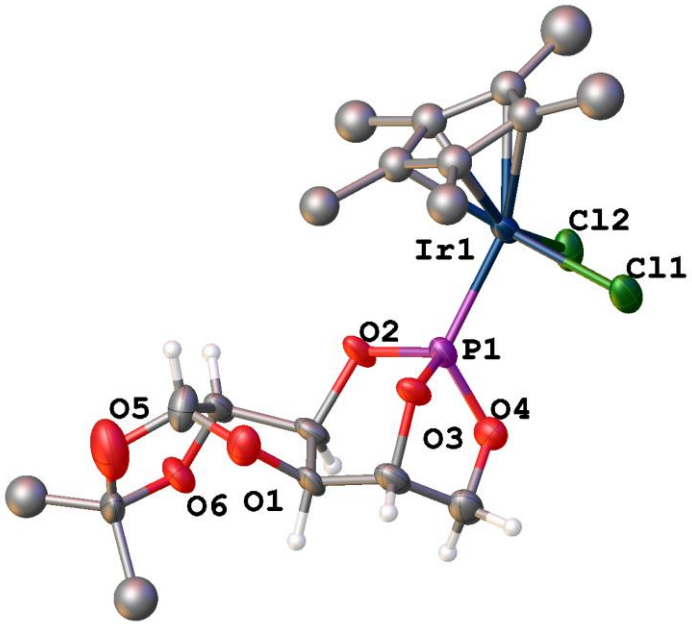


Figure 3. Molecular structure of **8**.

Table 1. Selected bond lengths (Å) and bond angles (°) for **8**.

Ir(1)-Cl(1)	2.392(3)	O(3)-C(5)	1.460(15)
P(1)-O(2)	1.586(9)	O(4)-C(6)	1.447(16)
P(1)-O(4)	1.587(10)	O(5)-C(1)	1.344(19)
P(1)-O(3)	1.587(10)	O(6)-C(7)	1.422(18)
O(1)-C(1)	1.425(18)	O(6)-C(2)	1.419(16)
O(1)-C(4)	1.456(18)		
P(1)-Ir(1)-Cl(1)	89.68(12)	O(6)-C(2)-C(3)	107.9(11)
O(2)-P(1)-O(4)	103.4(6)	O(6)-C(2)-C(1)	104.9(11)
O(2)-P(1)-O(3)	103.2(5)	C(3)-C(2)-C(1)	105.2(12)
O(4)-P(1)-O(3)	96.2(5)	O(2)-C(3)-C(4)	112.9(10)
O(2)-P(1)-Ir(1)	113.4(3)	O(2)-C(3)-C(2)	107.0(10)
O(4)-P(1)-Ir(1)	122.1(4)	C(4)-C(3)-C(2)	102.0(10)
O(3)-P(1)-Ir(1)	115.7(4)	O(1)-C(4)-C(3)	106.2(11)
C(1)-O(1)-C(4)	108.6(12)	O(1)-C(4)-C(5)	109.0(12)
C(3)-O(2)-P(1)	117.7(8)	C(3)-C(4)-C(5)	114.2(10)
C(5)-O(3)-P(1)	105.4(8)	O(3)-C(5)-C(6)	102.8(10)
C(6)-O(4)-P(1)	110.9(10)	O(3)-C(5)-C(4)	109.2(10)
C(1)-O(5)-C(7)	111.1(15)	C(6)-C(5)-C(4)	110.7(13)
C(7)-O(6)-C(2)	110.4(12)	O(4)-C(6)-C(5)	105.3(11)
O(5)-C(1)-O(1)	116.8(15)	O(6)-C(7)-C(8)	122(2)
O(5)-C(1)-C(2)	103.9(15)	O(6)-C(7)-O(5)	103.1(11)
O(1)-C(1)-C(2)	107.9(13)	C(8)-C(7)-O(5)	95(2)

Table 2. Crystallographic data for **8**.

Identification Code	8	Z(Z′)	4(1)
Difractomer	Bruker D8 Quest with Photon III detector	Density (calculated)	1.930
Wavelength, Å	0.71072	Absorption coefficient	63.46
Empirical formula	C19H28Cl2IrO6P	F(000)	1264
Formula weight	646.48	θ range for data collection	1.89 to 30.6
Temperature, K	122	Reflections collected	34,785
Crystal system	Orthorhombic	Independent reflections	6832 [R(int) = 0.0979]
Space group	P212121	Observed reflections	5483
Unit cell dimensions		Completeness to θ max, %	99.7
a (Å)	9.8274(7)	Goodness-of-fit on F2	0.920
b (Å)	14.4958(10)	Final R indices [I > 2sigma(I)]	R1 = 0.0510, wR2 = 0.1325
c (Å)	15.6169(11)	R indices (all data)	R1 = 0.0711, wR2 = 0.1479
Volume	2224.7(3)	Largest diff. peak and hole	2.200 and −1.515 e.Å −3

Stability is a highly important parameter for the selection of compounds as drug candidates. Previously, we showed the direct correlation between hydrolytic stability and activity of Ru and Os complexes with the glucose phosphate ligands [32–34]. Stability in the water solutions complexes **5**–**8** was studied by menace ^{31}P NMR spectroscopy. First, we employed DMSO-d^6 to prepare the stock solutions and then added water to obtain working solutions for the ^{31}P NMR spectra measurements. In contrast to the previously studied complexes, new iridium compounds **5**–**8** showed high stability in the water solution at least for 24 h.

It is known from the literature that the coordination of toxic metal center to a glucose containing ligands in some cases leads to loss or reduction of antiproliferative activity [27,29,34]. For complexes **5**–**8** and clinically used cisplatin, the concentration of half-maximal inhibition (IC_{50}) was examined against cancer cell lines of human origin: colon carcinoma SW480, breast carcinoma MCF7, lung adenocarcinoma A549, and colon carcinoma HCT116 using MTT assay. As was the case for similar Ru complexes, coordination of glucose phosphate ligands to the organometallic Ir center led to a significant decrease of the antiproliferative activity for compounds **5**–**8** (IC_{50} > 100, Table 3), even compared to the starting dimer [35]. We found that the antiproliferative activity of Ir complexes **5**–**8** does not depend on the presence and type of nucleobase (uracil, thymine) or 5-fluorouracil incorporated in compounds.

Table 3. Antiproliferative activity of **5**–**8** and cisplatin against human cancer cells.

Cell Lines	IC_{50}, μM				
	5	**6**	**7**	**8**	**Cisplatin**
HCT116	>100	>100	>100	>100	13 ± 4
A549	>100	>100	>100	>100	13 ± 3
SW480	>100	>100	>100	>100	6.0 ± 0.3
MCF7	>100	>100	>100	>100	30 ± 9

3. Conclusions

Thus, new representatives of organometallic iridium compounds containing phosphite ligands based on the glucose moiety with uracil, thymine, and 5-fluorouracil residues, as well as with an isopropylidene protecting group(3,5,6-bicyclophosphite-1,2-*O*-isopropylidene-α-D-

glucofuranoside, 3,5,6-bicyclophosphite-1-β-D-glucofuranosyluracil, 3,5,6-bicyclophosphite-1-β-D-glucofuranosylthymine, 3,5,6-bicyclophosphite-1-β-D-glucofuranosyl-5-flurouracil ligands) were obtained. We observed that the coordination of these glucose phosphite ligands to the cytotoxic metal core can allay toxicity, thus presenting a potentially useful tool in drug design.

4. Materials and Methods

Commercially available compounds and solvents were used as obtained from vendors. Solvents were purified and deoxygenated before use [36]. ^{1}H and ^{31}P NMR spectra were recorded in DMSO-d6 using the following instrument: Bruker AMX-400 with working frequencies of 400.1 (^{1}H) and 161.9 MHz (^{31}P{^{1}H}). The chemical shifts at the NMR spectra were reported using the δ scale. The ^{1}H NMR shifts are given relative to the residual solvent signal; the ^{31}P NMR shifts are reported relative to 85% H_3PO_4. Elemental analysis was carried out on a Vario Micro Cube Elementar analyzer. Mass-spectrometry analysis was performed using TSQ Endura (Thermo Fisher Scientific, Waltham, MA, USA) instrument with an electrospray ionization source (ESI). The methanol solution of each compound was introduced through a syringe pump directly into the ion source at 5–10 μL/min. Mass spectra were acquired in both positive and negative modes. The system was controlled by the Xcalibur software (Thermo Xcalibur 3.0.63, Thermo Scientific, Waltham, MA, USA), which was also used for data collection and data processing. The ion transfer tube temperature was set to 275 °C, vaporizer temperature to 40 °C. Sheath and Aux gases were 6 and 5 units, while Sweep gas wasn't used at all. Spray voltage was 3.4 and 2.5 kV for positive and negative modes correspondingly. The triple quadrupole mass spectrometer was operated in full scan mode with the first two quadrupoles working at full transmittance. The spectra were recorded during 30 s in the m/z range 150–1400. Melting points were determined with a Stuart Scientific SMP3 apparatus and are uncorrected.

4.1. Dichloro(1,2,3,4,5-pentamethylcyclopenta-1,3-diene)-[1-(3,5,6-bicyclophosphite-β-D-glucofuranosyl)uracil]iridium(III) (5)

A solution of Di-μ-chloro-bis[chloro(pentamethylcyclopentadienyl) iridium(III)] (105.3 mg, 0.13 mmol) in dry methylene chloride (10.0 mL) was slowly added to a suspension of 3,5,6-bicyclophosphite-1-β-D-glucofuranosyluracil (80.5 mg, 0.27 mmol) in dry methylene chloride (10.0 mL) at the room temperature. The reaction mixture was stirred at room temperature for twelve hours. The solvent was removed under vacuum, the dry product was dissolved in dry acetone (5.0 mL), precipitated with ether, and dried under vacuum. Yield 87 mg (46%), mp. > 208 °C. NMR^{1}H (400.1 MHz, $(CD_3)_2SO$, δ): 11.39 (s, 1H, NH), 7.77 (d, 1H, J = 8.1 Hz, H-7), 6.24 (s, 1H, H-1), 5.95 (d, J = 2.3 Hz, 1H, OH), 5.58 (d, 1H, J = 2.2 Hz, H-8), 5.14 (m, 1H, H-5), 4.78 (t, 1H, J = 9.6 Hz, H-6), 4.64 (s, 1H, H-2), 4.23 (t, 1H, J = 3.1 Hz, H-6), 4.14–4.03 (m, 2H, H-3,4), 1.71–1.52 (m, 15H, Cp). NMR ^{31}P {^{1}H} (161.98 MHz, $(CD_3)_2SO$, δ): 99.2. Found (%): C, 33.24; H, 3.69; N, 4.12. $C_{19}H_{25}O_7N_2PIrCl_2$. Calculated (%): C, 33.12; H, 3.63; N, 4.07. MS (ESI): m/z 710 $[M + Na]^+$.

4.2. Dichloro(1,2,3,4,5-pentamethylcyclopenta-1,3-diene)-[1-(3,5,6-bicyclophosphite-β-D-glucofuranosyl)thymine]iridium(III) (6)

A solution of di-μ-chloro-bis[chloro (pentamethylcyclopentadienyl) iridium(III)] (98.8 mg, 0.13 mmol) in dry methylene chloride (10.0 mL) was slowly added to a suspension of 3,5,6-bicyclophosphite-1-β-D-glucofuranosylthymine (80.0 mg, 0.25 mmol) in dry methylene chloride (10.0 mL) at the room temperature. The reaction mixture was stirred at room temperature for twelve hours. The solvent was removed under vacuum, the dry product was dissolved in dry acetone (5.0 mL), precipitated with ether, and dried under vacuum. The pure substance was isolated by column chromatography on Silica Gel (as liquid phase dry acetone was used). Yield 84 mg (47%), mp. > 209 °C.

NMR ^{1}H (400.1 MHz, $(CD_3)_2SO$, δ.): 11.43 (s, 1H, NH), 7.37 (s, 1H, H-7), 5.91 (s, 1H, H-1), 5.74 (d, 1H, J = 2.2 Hz, OH), 5.14 (m, 1H, H-5), 4.77 (t, 1H, J = 10.1 Hz, H-6), 4.63 (d, 1H, J = 3.4 Hz, H-2), 4.38 (s, 1H, H-3), 4.22 (dt, 1H, J = 9.0, 4.5 Hz, H-6), 4.10 (s, 1H, H-4),

1.88 (s, 3H, H-11), 1.75–1.67 (m, 15H, Cp). NMR ^{31}P {^{1}H} (161.98 MHz, $(CD_3)_2SO$, δ.): 98.5. Found (%): C, 33.07; H, 3.86; N, 3.88. $C_{20}H_{27}O_7N_2PIrCl_2$. Calculated (%): C, 34.18; H, 3.84; N, 3.98. MS (ESI): *m*/*z* 724 $[M + Na]^+$.

4.3. Dichloro(1,2,3,4,5-pentamethylcyclopenta-1,3-diene)-[1-(3,5,6-bicyclophosphite-β-D-glucofuranosyl)-5-fluorouracil]iridium(III) (7)

A solution of from di-μ-chloro-bis[chloro (pentamethylcyclopentadienyl) iridium(III)] (98.8 mg, 0.13 mmol) in dry methylene chloride (10.0 mL) was added to a suspension of 3,5,6-bicyclophosphite-1-(5-fluorouracil)-β- D-glucofuranosil (80 mg, 0.25 mmol) in dry methylene chloride (10.0 mL) at room temperature. The reaction mixture was stirred at room temperature for twelve hours. The solvent was removed under vacuum, and the dry product was dissolved in acetone (5.0 mL), precipitated with ether, and dried under vacuum. The pure substance was isolated by column chromatography on Silica Gel (as liquid phase dry acetone was used). Yield 84 mg (47%), mp. > 195 °C.

NMR^{1}H (400.1 MHz, $(CD_3)_2SO$, δ): 11.85 (s, 1H, NH), 8.46 (d, 1H, J = 7.0 Hz, H-7), 8.01 (s, 1H, H-1), 6.01 (d, J = 1.9 Hz, 1H, OH), 5.89–5.12 (m, 2H, H-8, H-5), 5.07 (m, 1H, H-6), 4.79–3.97 (m, 4H,H-2, H-3, H-4, H-6), 1.74–1.61 (m, 15H, Cp). NMR^{31}P {^{1}H} (161.98 MHz, $(CD_3)_2SO$, δ): 98.3. Found (%): C, 32.30; H, 3.42; N, 3.93. $C_{19}H_{24}O_7N_2PIrCl_2F$. Calculated (%): C, 32.33; H, 3.40; N, 3.90. MS (ESI): *m*/*z* 728 $[M + Na]^+$.

4.4. Dichloro(1,2,3,4,5-pentamethylcyclopenta-1,3-diene)-[1-(3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranoside]iridium(III) (8)

A solution of from di-μ-chloro-bis[chloro (pentamethylcyclopentadienyl) iridium(III)] (98.8 mg, 0.13 mmol) in dry methylene chloride (10.0 mL) was added to a suspension of 3,5,6-bicyclophosphite-1,2-*O*-isopropylidene-α-D-glucofuranoside (80 mg, 0.25 mmol) in dry methylene chloride (10.0 mL) at the room temperature. The reaction mixture was stirred at room temperature for 12 h. The solvent was removed under vacuum, and the dry product was dissolved in acetone (5.0 mL), precipitated with ether, and dried under vacuum. The pure substance was isolated by column chromatography on Silica Gel (as liquid phase dry acetone was used). Yield 84 mg (47%), mp. > 195 °C.

NMR ^{1}H (400.1 MHz, $(CD_3)_2SO$, δ): 6.04 (s, 1H, H-1), 5.13 (m, 1H, H-5), 4.79–4.65 (m, 3H, H-6, H-6, H-2), 4.42 (m, 1H, H-3), 2.48 (m, 6H, 2CH3). NMR ^{31}P {^{1}H} (161.98 MHz, (CD3)2SO, δ): 98.3. Found (%): C, 35.40; H, 4.26; $C_{19}H_{28}O_6PIrCl_2$. Calculated (%): C, 35.29; H, 4.33; MS (ESI): m/z 681 $[M + Cl]^-$.

4.5. Structure Determination

Well-shaped single crystals of compound 8 were selected from the reaction product. The single crystal diffraction data were measured using a Bruker D8 Quest diffractometer (Bruker, Karlsruhe, Germany) equipped with a CMOS detector (MoKα, λ = 0.71073 Å) at 122 K. Data were corrected for absorption effects using semiempirical methods implemented in SADABS (2016/2) [37]. The crystal structure was solved by the intrinsic phase methods, which gave the positions of all atoms with the exception of the Cp* ligand. Difference Fourier syntheses in Shelxt (SHELXL-2018/3) gave the positions of Cp* atoms [38]. The detailed analysis of atomic displacement parameters as well as the presence of additional peaks near methyl groups were interpreted as the disorder of Cp* due to slight libration around the Ir-Cp(centroid) axis. The refinement of two conformations was performed with equal occupancies. Due to the proximity of the carbon atom positions of two positions of the Cp* rings, the refinement was performed with the restraints on the atomic displacement and positional parameters using a number of constraints and restraints. H-atoms were positioned geometrically and refined as riding atoms with relative isotropic displacement parameters. Experimental and crystallographic information is given in Table 1. Further details of the crystal structures may be obtained from the Cambridge Crystallographic Data Centre by quoting the CCDC number 2236574 or from supplementary information.

4.6. Cells and In Vitro Antiproliferative Assays

The human HCT116 colorectal carcinoma, A549 non-small cell lung carcinoma, MCF7 breast adenocarcinoma, and SW480 colon adenocarcinoma cell lines were obtained from the European collection of authenticated cell cultures (ECACC; Salisbury, UK). All cells were grown in a DMEM medium (Gibco™, Ireland) supplemented with 10% fetal bovine serum (Gibco™, Brasilia Brazil). The cells were cultured in an incubator at 37 °C in a humidified 5% CO_2 atmosphere and were sub-cultured 2 times a week. The effect of the investigated compounds on cell proliferation was evaluated using a common MTT assay. The cells were seeded in 96-well tissue culture plates («TPP», Trasadingen, Switzerland) at a 1×10^4 cells/well in 100 μL of the medium. After overnight incubation at 37 °C, the cells were treated with the solution of compounds 6–8 in DMEM in the concentration range of 0 to 200 μM. Cisplatin was used as a standard. After 72 h of treatment, the solution was removed, and a freshly diluted MTT solution (100 μL, 0.5 mg/mL in cell medium) was added to the wells, and the plates were further incubated for 50 min. Subsequently, the medium was removed, and the formazan product was dissolved in 100 μL of DMSO. The number of living cells in each well was evaluated by measuring the absorbance at 570 nm using the «Zenith 200 rt» microplate reader (Biochrom, Cambridge, UK).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11030124/s1. CIF data file.

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Data Availability Statement: All data are available upon request.

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