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(η^5-Pentamethylcyclopentadienyl)iridium(III) Complexes with η^2-N,O and η^2-P,S Ligands

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Chloro(η^5-pentamethylcyclopentadienyl)(η^2-pyridine-2-carboxylato)iridium(III) [Ir(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl] (**2**) and chloro(η^5-pentamethylcyclopentadienyl)[η^2-2-(diphenylphosphanyl)thiophenolato]iridium(III) [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Cl] (**3**) were prepared and their structures determined by single-crystal X-ray diffraction analysis. Complex **2** crystallizes in the orthorhombic space group *Pbca*. The number of molecules per unit cell is eight, whereas **3** crystallizes in the orthorhombic space group $Pna2_1$ and the number of molecules per unit cell is four. The coordination of the η^2-bound ligands in **2** and **3** leads to chelate bite angles N–Ir–O(2) and P–Ir–S of 77.0(2)° and 82.42(7)°, respectively. The iridium atoms in **2** and **3** are chiral and both enantiomers are present in the unit cell. The substitution of the chloro ligand in **3** affords hydrido(η^5-pentamethylcyclopentadienyl)-[η^2-2-(diphenylphosphanyl)thiophenolato]iridium(III) [Ir($\eta^5$$C_5Me_5$)($\eta^2$-2-$Ph_2PC_6H_4S$)H] (**4**) and methyl($\eta^5$-pentamethylcyclopentadienyl)[η^2-2-(diphenylphosphanyl)thiophenolato]iridium(III) [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Me] (**5**), respectively, in good yields. The $^{31}P\{^1H\}$ NMR resonances of **4** (δ = 33.9 ppm) and **5** (δ = 35.8 ppm) prove unambiguously that the 2-(diphenylphosphanyl)thiophenolato ligand still remains η^2-coordinated.

Introduction

The chemistry of (η^5-pentamethylcyclopentadienyl)iridium(III) complexes has been extensively investigated during the last few decades.[1] However, there are only a few compounds that contain anionic η^2-coordinated ligands (η^2-A,B), of which α-amino acid complexes are the best-known examples.[2,3] The main aspect of research in this field is focused on the chiral-at-metal behavior of the isolated complexes. However, in general, the diastereoselectivity is low and, due to the configurational instability at the metal center, epimerization reactions occur in solution.[4] Pyridine-2-carboxylic acid is an analog to amino acids and is commercially available. Examples of η^2-coordinated pyridine-2-carboxylato ligands (η^2-N,O) applied in organoiridium chemistry are [Ir(η^5-C_5Me_5)(η^2-N,O)(OH_2)]$^+$ and [Ir(η^5-C_5Me_5)(η^2-N,O)]$_3$(ClO_4)$_3$, although they were structurally not characterized.[5]

Stable thiolato complexes have for some time also been of special interest. Dimeric iridium(I) complexes with bridging thiolato ligands, for example, have been intensely examined for their catalytic activity in hydroformylation reactions.[6] However, the elimination of the free thiol by reaction with dihydrogen has proved problematic. Chelating phosphanyl-thiolate ligands, like the 2-(diphenylphosphanyl)thiophenolato ligand (η^2-P,S), have been introduced to ensure retention of the thiolate. Accordingly, the two compounds [Ir(η^2-P,S)$(Cl)_2$($PMePh_2$)$_2$] and [Ir(η^2-P,S)$_3$]·0.75CH_2Cl_2 have been observed.[7] In addition, an increased stability due to the chelate effect has been observed for the iridium(I) complex [Ir(η^2-P,S)(CO)(PPh_3)].[8]

A particular objective of our research in organoiridium chemistry is the synthesis of stable monomeric complexes with a defined reaction center that allows further reactions. Thus, these compounds are useful as starting materials in the search for new applications in preparative chemistry as well as in catalysis. We present here the syntheses, characterizations, and crystal-structure analyses of the thus far unknown chloro(η^5-pentamethylcyclopentadienyl)iridium(III) complexes [Ir(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl] (**2**) and [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Cl] (**3**), which contain η^2-coordinated pyridine-2-carboxylato (η^2-N,O) and 2-(diphenylphosphanyl)thiophenolato (η^2-P,S) ligands, respectively. The substitution of the chloro ligand in **3** by a hydride ion and a methyl group are described too, and the analytical data are given.

Results and Discussion

The reaction of di-μ-chlorobis[chloro(η^5-pentamethylcyclopentadienyl)iridium(III)] [Ir_2(η^5-C_5Me_5)$_2$(μ-Cl)$_2$$Cl_2$] (**1**) with sodium pyridine-2-carboxylate in methanol or sodium 2-(diphenylphosphanyl)thiophenolate in tetrahydrofuran gives the orange crystalline compounds chloro(η^5-pentamethylcyclopentadienyl)(η^2-pyridine-2-carboxylato)iri-

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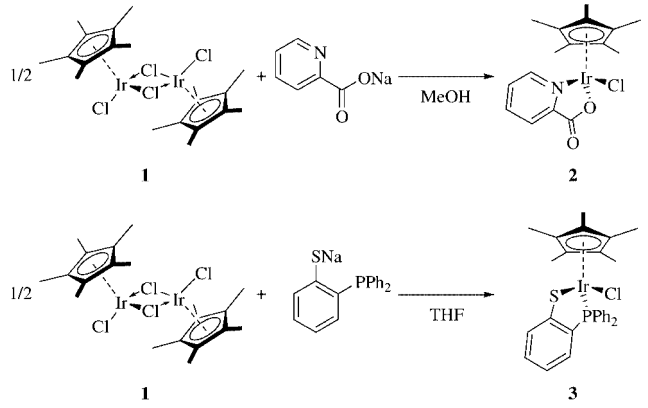
dium(III) [Ir(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl] (**2**) in 89% yield and chloro(η^5-pentamethylcyclopentadienyl)[η^2-2-(diphenylphosphanyl)thiophenolato]iridium(III) [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Cl] (**3**) in 72% yield, respectively (Scheme 1).



Scheme 1.

The resonances of the protons of the η^5-C_5Me_5 groups appear in the ^{1}H NMR spectrum of **2** as a singlet (δ = 1.63 ppm, 15 H) and that of **3** as a doublet (δ = 1.56 ppm, $J_{H,P}$ = 2.2 Hz, 15 H). In the ^{13}C NMR spectrum of **2**, the resonances of the η^5-C_5Me_5 ring carbon atoms are found at δ = 84.9 ppm and those of the methyl groups at δ = 8.3 ppm. The corresponding resonances of compound **3** are observed at δ = 92.9 ppm (d, $J_{C,P}$ = 3 Hz) and δ = 8.2 ppm (d, $J_{C,P}$ = 1 Hz). The ^{31}P{^{1}H} NMR spectrum of **3** shows a resonance at δ = 30.4 ppm, which is strongly shifted downfield ($\Delta\delta$ = 43.5 ppm) in comparison to the free phosphane (δ = –13.1 ppm).[9]. This is in agreement with the coordination shift typical for the ^{31}P NMR resonances of five-membered rings.[10]

The bands at $\tilde{\nu}$ = 253 and 267 cm^{-1} in the IR spectra of **2** and **3** can be assigned to the absorptions of the Ir–Cl stretching modes.

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a saturated solution of **2** in dichloromethane. Compound **2** crystallizes in the orthorhombic space group *Pbca*. Figure 1 shows the molecular structure of [Ir(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl] (**2**) together with selected bond lengths and angles. The Ir–Cl [239.97(15) pm] and Ir–N [208.8(7) pm] bonds are shorter than in the L-prolinato complex [Ir(η^5-C_5Me_5)(L-ProO)Cl] [Ir(1)–Cl(1) = 241.7(2), Ir(2)–Cl(2) = 240.6(3), Ir(1)–N(1) = 212.8(7), and Ir(2)–N(2) = 213.1(7) pm],[2] which is probably due to the π-acceptor properties of the pyridine ring in **2**. The coordination of the η^2-bound pyridine-2-carboxylate leads to an N–Ir–O(2) bond angle of 77.0(2)°, which is similar to that of 77.7(1)° in the corre-

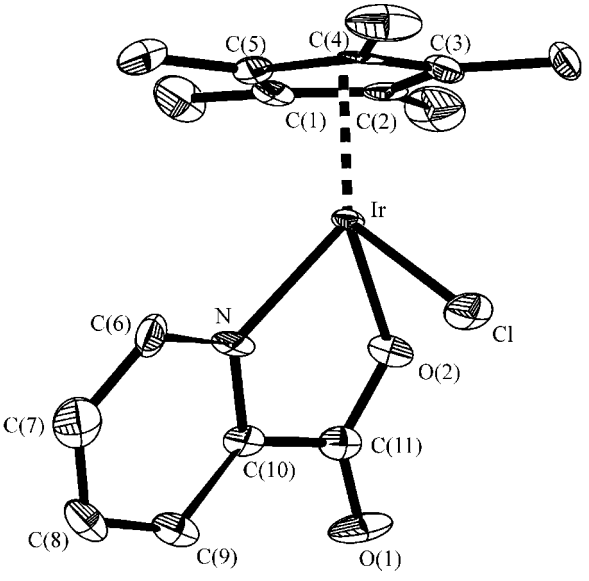


Figure 1. Molecular structure of [Ir(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl] (**2**) with 50% probability ellipsoids and the labelling scheme; selected bond lengths [pm] and angles [°]: Ir–Cl 239.97(15), Ir–N 208.8(7), Ir–O(2) 210.1(5), O(1)–C(11) 122.5(9), O(2)–C(11) 127.9(10); C(1)–Ir–C(2) 37.2(3), C(1)–Ir–C(3) 64.8(3), C(1)–Ir–Cl 160.8(3), C(2)–Ir–C(3) 39.2(3), C(2)–Ir–Cl 129.8(2), C(3)–Ir–Cl 96.92(19), C(4)–Ir–C(1) 66.2(3), C(4)–Ir–C(2) 65.5(3), C(4)–Ir–C(3) 39.1(3), C(4)–Ir–C(5) 39.2(3), C(4)–Ir–Cl 96.16(17), C(5)–Ir–C(1) 40.8(3), C(5)–Ir–C(2) 65.5(2), C(5)–Ir–C(3) 65.7(3), C(5)–Ir–Cl 128.03(18), C(11)–O(2)–Ir 117.7(4), N–Ir–C(1) 111.7(3), N–Ir–C(2) 144.5(3), N–Ir–C(3) 166.1(3), N–Ir–C(4) 127.0(3), N–Ir–C(5) 102.5(3), N–Ir–Cl 84.55(15), N–Ir–O(2) 77.0(2), O(1)–C(11)–O(2) 125.2(7), O(2)–Ir–C(1) 107.9(3), O(2)–Ir–C(2) 95.4(2), O(2)–Ir–C(3) 116.9(2), O(2)–Ir–C(4) 156.0(2), O(2)–Ir–C(5) 146.9(2), O(2)–Ir–Cl 85.02(14).

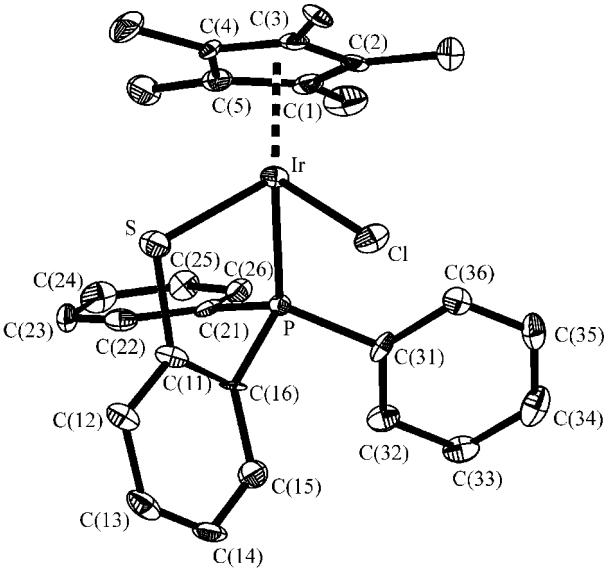


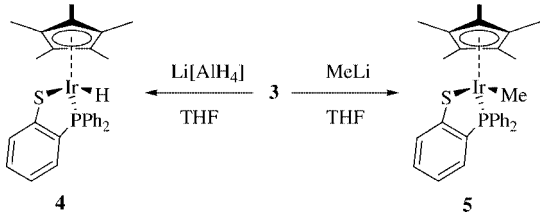
Figure 2. Molecular structure of [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Cl] (**3**) with 50% probability ellipsoids and the labelling scheme; selected bond lengths [pm] and angles [°]: Ir–Cl 241.93(18), Ir–P 227.32(18), Ir–S 238.0(2); C(1)–Ir–C(3) 63.7(3), C(1)–Ir–C(4) 64.0(3), C(1)–Ir–Cl 126.9(2), C(1)–Ir–P 103.2(2), C(1)–Ir–S 143.0(2), C(2)–Ir–C(1) 37.6(3), C(2)–Ir–C(3) 38.2(3), C(2)–Ir–C(4) 63.0(3), C(2)–Ir–Cl 95.1(2), C(2)–Ir–P 127.0(2), C(2)–Ir–S 150.3(2), C(3)–Ir–Cl 94.5(2), C(3)–Ir–P 165.1(2), C(3)–Ir–S 112.3(2), C(4)–Ir–C(3) 37.1(3), C(4)–Ir–Cl 125.7(2), C(4)–Ir–P 145.7(2), C(4)–Ir–S 90.67(18), C(5)–Ir–C(1) 38.9(3), C(5)–Ir–C(2) 64.3(3), C(5)–Ir–C(3) 64.5(3), C(5)–Ir–C(4) 39.2(3), C(5)–Ir–Cl 157.9(2), C(5)–Ir–P 110.4(2), C(5)–Ir–S 104.5(2), P–Ir–Cl 88.02(6), P–Ir–S 82.42(7), S–Ir–Cl 89.45(8).

sponding rhodium(III) complex [Rh(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl].[11]

Slow cooling of a hot solution of **3** in toluene gave single crystals suitable for X-ray diffraction analysis. Compound **3** crystallizes in the orthorhombic space group *Pna*2_1. Figure 2 shows the molecular structure of [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Cl] (**3**) together with selected bond lengths and angles. In comparison with [Ir(Cl)$_2$(η^2-2-$Ph_2PC_6H_4S$)(PMePh_2)$_2$] [Ir–P(1) = 236.1(1), Ir–S = 240.1(1), Ir–Cl(1) = 238.42(9), Ir–Cl(2) = 237.36(9) pm; P–Ir–S = 81.06(3)°][7] the Ir–P [227.32(18) pm] and Ir–S [238.0(2) pm] bonds are shorter and the Ir–Cl bond [241.93(18) pm] is longer. The deviation from 90°, with a P–Ir–S bond angle of 82.42(7)°, is of the same order of magnitude and is not as clear as that in **2**. The geometry in both **2** and **3** can be described as pseudo-octahedral coordination of the iridium atom in which the η^5-C_5Me_5 group occupies three *fac* coordination sides. The metal coordination sphere is completed by an η^2-coordinated ligand and a chlorine atom (the bond angles at the iridium atom are listed in the captions of Figures 1 and 2). In each case, the iridium atom is chiral and both enantiomers are present in the unit cell.

Substitution Reactions

Substitution of the chloro ligand by a hydride ion or a methyl group was achieved successfully only for **3**. Thus, the reaction of [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Cl] (**3**) with $LiAlH_4$ or MeLi in tetrahydrofuran results, after removal of the solvent and subsequent extraction with hexane, in the corresponding hydrido complex hydrido(η^5-pentamethylcyclopentadienyl)[η^2-2-(diphenylphosphanyl)thiophenolato]iridium(III) [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)H] (**4**) in 91% yield and the methyl compound methyl(η^5-pentamethylcyclopentadienyl)[η^2-2-(diphenylphosphanyl)-thiophenolato]iridium(III) [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)-Me] (**5**) in 87% yield, respectively (Scheme 2).



4 5

Scheme 2.

The resonances of the protons of the η^5-C_5Me_5 groups in the ^{1}H NMR spectrum of **4** appear, due to the coupling to the iridium-bound hydrido ligand, as a doublet of doublets (δ = 1.62 ppm, $^4J_{H,P}$ = 2.0, $^4J_{H,H}$ = 0.8 Hz, 15 H) and those of **5** as a doublet (δ = 1.57 ppm, $^4J_{H,P}$ = 1.9 Hz, 15 H). The resonances of the hydrido ligand in **4** and of the methyl group in **5** are observed as doublets at high field at δ = –15.37 (d, $^2J_{H,P}$ = 36.0 Hz, 1 H) and –0.22 ppm (d, $^3J_{H,P}$ = 6.1 Hz, 3 H), respectively. In the ^{13}C NMR spectrum of **4**, the resonance of the η^5-C_5Me_5 ring carbon atoms is found at δ = 93.2 ppm (d, $J_{C,P}$ = 3.1 Hz) and that of the methyl groups at δ = 9.1 ppm (d, $J_{C,P}$ = 0.8 Hz). The corresponding resonances of compound **5** appear at δ = 92.8 (d, $J_{C,P}$ = 3.3 Hz) and 8.20 ppm (d, $J_{C,P}$ = 1.0 Hz). The resonance of the methyl group bound to the iridium atom is observed at δ = –17.4 ppm (d, $J_{C,P}$ = 8.4 Hz). The ^{31}P{^{1}H} NMR spectrum of **4** shows a resonance at δ = 33.9 ppm whereas that of **5** appears at δ = 35.8 ppm. In comparison to the free ligand (δ = –13.1 ppm),[9] this strong downfield shift is good evidence that the 2-(diphenylphosphanyl)thiophenolato ligand still remains η^2-coordinated.

In the IR spectrum of **4**, the band at $\tilde{\nu}$ = 2102 cm^{-1} is characteristic of absorptions of the Ir–H stretching modes.[12]

Conclusions

The cleavage of the chloro bridges in [Ir$_2$(η^5-C_5Me_5)$_2$(μ-Cl)$_2$Cl$_2$] (**1**) by η^2-A,B ligands affords stable monomeric chelate complexes. Thus, the reactions of **1** with pyridine-2-carboxylate and 2-(diphenylphosphanyl)thiophenolate yield [Ir(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl] (**2**) and [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Cl] (**3**), respectively. The X-ray diffraction analyses show that the geometry of both complexes can be described as pseudo-octahedral coordination of the iridium atom in which the η^5-C_5Me_5 group occupies three *fac* coordination sides. In each case the complex is chiral at the iridium atom and both enantiomers are present in the unit cell. The complexes [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)H] (**4**) and [Ir(η^5-C_5Me_5)(η^2-2-$Ph_2PC_6H_4S$)Me] (**5**) are easily accessible by substitution of the chloro ligand in **3**. According to the ^{31}P NMR spectra, the 2-(diphenylphosphanyl)thiophenolato ligand remains η^2-coordinated in both compounds. The hydrido complex **4** and the methyl compound **5** are useful derivatives for further investigations.

Experimental Section

General Remarks: Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under dry nitrogen, using standard Schlenk techniques. NMR spectra were recorded using a Bruker Avance 200, a Bruker MSL 400, or a Bruker Avance 500 spectrometer and referenced to the resonances of the residual protons in [D_6]DMSO, $CDCl_3$, or C_6D_6. ^{1}H NMR: external standard TMS. ^{13}C NMR: external standard TMS. ^{31}P NMR: external standard 85% H_3PO_4. Infrared spectra were recorded with a BIO-RAD Digilab FTS 7 spectrometer. [Ir$_2$(η^5-C_5Me_5)$_2$(μ-Cl)$_2$Cl$_2$] (**1**) [13] and 2-$Ph_2PC_6H_4SH$[9] were prepared by literature methods. All other materials used in the syntheses were reagent grade chemicals and used without further purification.

[Ir(η^5-C_5Me_5)(η^2-C_5H_4N-2-CO_2)Cl] (2): A mixture of **1** (0.80 g, 1.00 mmol), C_5H_4N-2-CO_2H (0.26 g, 2.12 mmol), and NaOEt (0.12 g, 2.22 mmol) in methanol (70 mL) was heated under reflux for 3 h and finally filtered hot through Celite. The solution was concentrated under reduced pressure to 20 mL. The resulting orange crystalline solid was filtered off, washed with diethyl ether (2 × 10 mL), and dried in vacuo (0.85 g, 89%). M.p. 270 °C (decomp.). $C_{16}H_{19}ClIrNO_2$ (485.00): calcd. C 39.62, H 3.95, Cl 7.31, N 2.89; found C 39.59, H 4.01, Cl 7.39, N 2.96. IR (CsI): $\tilde{\nu}$ = 253

(Ir–Cl) cm^{-1}. ^1H NMR (500.13 MHz, [D$_6$]DMSO): δ = 8.77 (d, J = 6.0 Hz, 1 H, $C_5H_4NCO_2$), 8.12 (t, J = 5.0 Hz, 1 H, $C_5H_4NCO_2$), 7.90 (d, J = 8.0 Hz, 1 H, $C_5H_4NCO_2$), 7.75 (t, J = 7.0 Hz, 1 H, $C_5H_4NCO_2$), 1.63 (s, 15 H, C_5Me_5) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 171.7 ($C_5H_4NCO_2$), 150.5 ($C_5H_4NCO_2$), 150.3 ($C_5H_4NCO_2$), 139.6 ($C_5H_4NCO_2$), 129.1 ($C_5H_4NCO_2$), 126.2 ($C_5H_4NCO_2$), 84.9 (C_5Me_5), 8.3 (C_5Me_5) ppm. EIMS (70 eV): *m*/*z* (%) = 485 (40) [M], 449 (60) [M – H – Cl], 362 (100) [M – C_5H_4N-2-CO_2 – H].

[Ir(η⁵-C_5Me_5)(η²-2-$Ph_2PC_6H_4S$)Cl] (3): A solution of 2-$Ph_2PC_6H_4SH$ (0.59 g, 2.00 mmol) in THF (30 mL) together with surplus sodium (approx. 200 mg) was stirred at room temperature until the evolution of hydrogen ceased. After filtration, the filtrate was added dropwise to a solution of **1** (0.80 g, 1.00 mmol) in THF (30 mL). The reaction mixture was stirred for an additional 3 h and, subsequently, the solvent was removed under reduced pressure. The residue was crystallized from dichloromethane/diethyl ether (1:4). The reddish crystals obtained accordingly were filtered off and dried in vacuo (0.95 g, 72%). M.p. 325 °C. $C_{28}H_{29}ClIrPS$ (656.24): calcd. C 51.25, H 4.45, P 4.72; found C 50.64, H 4.47, P 4.31.[14] IR (CsI): $\tilde{\nu}$ = 267 (Ir–Cl) cm^{-1}. ^1H NMR (500.13 MHz, $CDCl_3$): δ = 7.97 (m, 2 H, $Ph_2PC_6H_4S$), 7.62 (dd, ^1J = 7.9, ^2J = 3.4 Hz, 1 H, $Ph_2PC_6H_4S$), 7.49 (m, 3 H, $Ph_2PC_6H_4S$), 7.28 (m, 5 H, $Ph_2PC_6H_4S$), 7.13 (t, ^1J = 8.2 Hz, 1 H, $Ph_2PC_6H_4S$), 6.99 (t, ^1J = 7.4 Hz, 1 H, $Ph_2PC_6H_4S$), 6.72 (t, ^1J = 7.4 Hz, 1 H, $Ph_2PC_6H_4S$), 1.56 (d, $^4J_{H,P}$ = 2.2 Hz, 15 H, C_5Me_5) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 155.5 (d, $J_{C,P}$ = 23.4 Hz, $Ph_2PC_6H_4S$), 136.2 (d, $J_{C,P}$ = 52.9 Hz, $Ph_2PC_6H_4S$), 135.8 (d, $J_{C,P}$ = 10.6 Hz, $Ph_2PC_6H_4S$), 134.8 (d, $J_{C,P}$ = 70.6 Hz, $Ph_2PC_6H_4S$), 132.0 (d, $J_{C,P}$ = 3.7 Hz, $Ph_2PC_6H_4S$), 131.7 (d, $J_{C,P}$ = 9.5 Hz, $Ph_2PC_6H_4S$), 131.2 (d, $J_{C,P}$ = 2.7 Hz, $Ph_2PC_6H_4S$), 130.7 (d, $J_{C,P}$ = 2.6 Hz, $Ph_2PC_6H_4S$), 130.0 (d, $J_{C,P}$ = 2.6 Hz, $Ph_2PC_6H_4S$), 128.8 (d, $J_{C,P}$ = 10.4 Hz, $Ph_2PC_6H_4S$), 128.1 (d, $J_{C,P}$ = 10.9 Hz, $Ph_2PC_6H_4S$), 128.0 (d, $J_{C,P}$ = 10.2 Hz, $Ph_2PC_6H_4S$), 126.1 (d, $J_{C,P}$ = 58.5 Hz, $Ph_2PC_6H_4S$), 122.1 (d, $J_{C,P}$ = 7.6 Hz, $Ph_2PC_6H_4S$), 92.9 (d, $^2J_{C,P}$ = 3 Hz, C_5Me_5), 8.2 (d, $^3J_{C,P}$ = 1.0 Hz, C_5Me_5) ppm. ^{31}P NMR (202.46 MHz, $CDCl_3$): δ = 30.4 (s, Ir*P*) ppm. EIMS (70 eV): *m*/*z* (%) = 656 (8) [M], 621 (100) [M – Cl].

[Ir(η⁵-C_5Me_5)(η²-2-$Ph_2PC_6H_4S$)H] (4): A solution of **3** (0.66 g, 1.01 mmol) in THF (20 mL) was treated with $LiAlH_4$ (0.04 g, 1.05 mmol), stirred at room temperature for 12 h, and subsequently filtered through Celite. The solvent was removed from the filtrate under reduced pressure and the resulting residue was extracted with hexane (2 × 60 mL). The removal of the solvent from the combined extracts in vacuo afforded the title compound as a yellow powder (0.57 g, 91%). M.p. 240 °C (decomp.). $C_{28}H_{30}IrPS$ (621.79): calcd. C 54.09, H 4.86; found C 53.71, H 4.80. IR (CsI): $\tilde{\nu}$ = 2102 (Ir–H) cm^{-1}. ^1H NMR (500.13 MHz, C_6D_6): δ = 7.99 (dd, ^1J = 11.5, ^1J = 8.1 Hz, 2 H, $Ph_2PC_6H_4S$), 7.91 (dd, ^1J = 8.1, ^2J = 3.5 Hz, 1 H, $Ph_2PC_6H_4S$), 7.21 (m, 3 H, $Ph_2PC_6H_4S$), 7.11 (m, 3 H, $Ph_2PC_6H_4S$), 6.93 (m, 3 H, $Ph_2PC_6H_4S$), 6.76 (t, ^1J = 7.0 Hz, 1 H, $Ph_2PC_6H_4S$), 6.57 (t, ^1J = 7.0 Hz, 1 H, $Ph_2PC_6H_4S$), 1.62 (dd, $^4J_{H,P}$ = 2.0, $^4J_{H,H}$ = 0.8 Hz, 15 H, C_5Me_5), –15.37 (d, $^2J_{H,P}$ = 36.0 Hz, 1 H, Ir*H*) ppm. ^{13}C NMR (125.77 MHz, C_6D_6): δ = 160.8 (d, $J_{C,P}$ = 26.9 Hz, $Ph_2PC_6H_4S$), 138.0 (d, $J_{C,P}$ = 46.9 Hz, $Ph_2PC_6H_4S$), 135.4 (d, $J_{C,P}$ = 62.7 Hz, $Ph_2PC_6H_4S$), 135.3 (d, $J_{C,P}$ = 69.5 Hz, $Ph_2PC_6H_4S$), 134.6 (d, $J_{C,P}$ = 11.2 Hz, $Ph_2PC_6H_4S$), 132.2 (d, $J_{C,P}$ = 3.7 Hz, $Ph_2PC_6H_4S$), 131.6 (d, $J_{C,P}$ = 10.5 Hz, $Ph_2PC_6H_4S$), 129.9 (d, $J_{C,P}$ = 2.5 Hz, $Ph_2PC_6H_4S$), 129.3 (d, $J_{C,P}$ = 2.4 Hz, $Ph_2PC_6H_4S$), 128.7 (d, $J_{C,P}$ = 2.4 Hz, $Ph_2PC_6H_4S$), (127.8, 127.7, 127.5 overlaps from C_6D_6), 120.4 (d, $J_{C,P}$ = 7.2 Hz, $Ph_2PC_6H_4S$), 93.2 (d, $^2J_{C,P}$ = 3.1 Hz, C_5Me_5), 9.1 (d, $^3J_{C,P}$ = 0.8 Hz, C_5Me_5) ppm. ^{31}P NMR (202.46 MHz, C_6D_6): δ = 33.9 (s, Ir*P*) ppm. EIMS (70 eV): *m*/*z* (%) = 622 (100) [M], 607 (50) [M – H – CH_2].

[Ir(η⁵-C_5Me_5)(η²-2-$Ph_2PC_6H_4S$)Me] (5): A solution of **3** (0.26 g, 0.40 mmol) in THF (10 mL) was treated with MeLi (0.30 mL, 0.48 mmol, 1.6 M in hexane), stirred at room temperature for 12 h, and subsequently filtered through Celite. The solvent was removed from the filtrate under reduced pressure and the resulting residue was extracted with hexane (2 × 40 mL). The removal of the solvent from the combined extracts in vacuo resulted in the title compound as a yellow powder (0.22 g, 87%). M.p. 240 °C (decomp.). $C_{29}H_{32}IrPS$ (635.82): calcd. C 54.78, H 5.07; found C 54.71, H 5.02. ^1H NMR (200.13 MHz, $CDCl_3$): δ = 7.64 (m, 1 H, $Ph_2PC_6H_4S$), 7.46 (m, 5 H, $Ph_2PC_6H_4S$), 7.24 (m, 5 H, $Ph_2PC_6H_4S$), 6.95 (m, 2 H, $Ph_2PC_6H_4S$), 6.70 (m, 1 H, $Ph_2PC_6H_4S$), 1.57 (d, $^4J_{H,P}$ = 1.9 Hz, 15 H, C_5Me_5), –0.22 (d, $^3J_{H,P}$ = 6.1 Hz, 3 H, Ir*Me*) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 157.6 (d, $J_{C,P}$ = 26.2 Hz, $Ph_2PC_6H_4S$), 137.7 (d, $J_{C,P}$ = 50.1 Hz, $Ph_2PC_6H_4S$), 133.9 (d, $J_{C,P}$ = 3.2 Hz, $Ph_2PC_6H_4S$), 133.0 (d, $J_{C,P}$ = 9.7 Hz, $Ph_2PC_6H_4S$), 131.8 (d, $J_{C,P}$ = 10.7 Hz, $Ph_2PC_6H_4S$), 128.3 (d, $J_{C,P}$ = 10.7 Hz, $Ph_2PC_6H_4S$), 120.7 (d, $J_{C,P}$ = 6.9 Hz, $Ph_2PC_6H_4S$), 92.8 (d, $^2J_{C,P}$ = 3.3 Hz, C_5Me_5), 8.2 (d, $^3J_{C,P}$ = 1.0 Hz, C_5Me_5), –17.4 (d, $J_{C,P}$ = 8.4 Hz, IrMe) ppm. ^{31}P NMR (202.46 MHz, $CDCl_3$): δ = 35.8 (s, Ir*P*) ppm. EIMS (70 eV): *m*/*z* (%) = 636 (10) [M], 621 (100) [M – CH_3], 607 (5) [M – CH_3–CH_2].

X-ray Crystallographic Study: The single crystals were mounted on a glass fiber in a frozen drop of paraffin. Diffraction data were collected with a STOE AED2 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). The crystal structures were solved by direct methods using SHELXS-97[15] and refined with SHELXL-97[16] against F^2 on all data by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at fixed positions (Table 1). CCDC-272324 (**2**) and -272325 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for **2** and **3**.

	2	**3**
Empirical formula	$C_{16}H_{19}ClIrNO_2$	$C_{28}H_{29}ClIrPS$
Formula mass [g mol^{-1}]	484.97	656.19
Temperature [K]	203(2)	133(2)
Wavelength λ [pm]	71.073	71.073
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	$Pna2_1$
a [pm]	1429.4(3)	1655.0(3)
b [pm]	1457.9(4)	1019.6(2)
c [pm]	1468.1(5)	1456.3(3)
Volume [nm^3]	3.0595(14)	2.4574(8)
Z	8	4
Absorption coefficient [mm^{-1}]	8.906	5.707
F(000)	1856	1288
Reflections collected	5382	31373
Independent reflections	2691 (R_{int} = 0.1867)	7149 (R_{int} = 0.1654)
Data/restraints/parameters	2691/339/189	5681/1/296
Goodness-of-fit on F^2	1.065	1.081
Final *R* indices [$I > 2\sigma(I)$]	0.0462, 0.1169	0.0399, 0.0924
Largest diff. peak/hole [e Å^{-3}]	2.130/–3.595	7.323/–1.967

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[1] J. K. O'Connor, *Sci. Synth.***2002**, *1*, 617–744.
[2] R. Krämer, K. Polborn, H. Wanjek, I. Zahn, W. Beck, *Chem. Ber.* **1990**, *123*, 767–778.
[3] K. Severin, R. Bergs, W. Beck, *Angew. Chem.* **1998**, *110*, 1722–1743; *Angew. Chem. Int. Ed.* **1998**, *37*, 1634–1654.
[4] H. Brunner, A. Köllnberger, T. Burgmeister, M. Zabel, *Polyhedron* **2000**, *19*, 1519–1526.
[5] T. Poth, H. Paulus, H. Elias, C. Dücker-Benfer, R. van Eldik, *Eur. J. Inorg. Chem.* **2001**, 1361–1369.
[6] M. T. Pinillos, A. Elduque, L. A. Oro, *Inorg. Chim. Acta* **1990**, *178*, 179–183.
[7] J. R. Dilworth, C. Lu, J. R. Miller, Y. Zheng, *J. Chem. Soc., Dalton Trans.* **1995**, 1957–1964.
[8] L. Dahlenburg, K. Herbst, M. Kühnlein, *Z. Anorg. Allg. Chem.* **1997**, *623*, 250–258.
[9] E. Block, G. Ofori-Okai, J. Zubieta, *J. Am. Chem. Soc.* **1989**, *111*, 2327–2329.
[10] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229–266.
[11] A. P. Abbott, G. Capper, D. L. Davies, J. Fawcett, D. R. Russell, *J. Chem. Soc., Dalton Trans.* **1995**, 3709–3713.
[12] C. B. Cooper, D. F. Shriver, S. Onaka, *Adv. Chem. Ser.* **1978**, *167*, 232–247.
[13] J. W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* **1969**, *91*, 5970–5977.
[14] The slight deviations from the calculated values are attributable to traces of the used solvents, which were found in the ^{1}H NMR spectrum.
[15] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[16] G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Analysis*, Institut für Anorganische Chemie der Universität Göttingen, **1998**.

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