$[Cp^*Ir\{P(O)(OMe)_2\}_3]^-$, an iridium(III) phosphonate complex acting as a chelating oxygen ligand: synthesis and coordination chemistry

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Abstract

The anionic iridium complex $[(C_5Me_5)Ir\{P(O)(OMe)_2\}_3]^-$ (L^-) has been prepared as sodium salt from the corresponding trimethyl phosphite complex $[(C_5Me_5)Ir\{P(OMe)_3\}_3](ClO_4)_2$. L^- reacts with metal ions M^{2+} to give ML_2. With $[PtMe_3]_2SO_4 \cdot 4H_2O$ in water and with $[\{RhCl(cod)\}_2]$, cod = 1,5-cyclooctadiene, in cyclohexane solution the air-stable heterobimetallic complexes $[LPtMe_3]$ and $[LRh(cod)]$ are formed. The rhodium complex $[(C_5Me_5)Rh\{P(O)(OMe)_2\}_3]^-$ (L'^-) similarly gives $[L'PtMe_3]$ and $[L'Rh(cod)]$. $[LRh(cod)]$ and $[L'Rh(cod)]$ react with CO gas (1 atm.) to yield $[LRh(CO)_2]$ and $[L'Rh(CO)_2]$. Partial decarbonylation of these dicarbonyl complexes at room temperature leads to the tetranuclear complexes $[L'Rh(\mu\text{-}CO)_3RhL'](Rh\text{-}Rh)$ and $[LRh(\mu\text{-}CO)_3RhL](Rh\text{-}Rh)$.

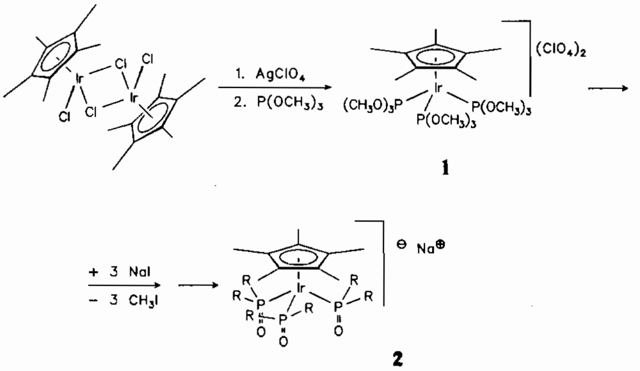
Introduction

Anions of the type $R_2P{=}O$ have a pronounced tendency to coordinate metal ions through phosphorus and oxygen. Many di-, tri-, tetra- and pentanuclear complexes with phosphoryl units bridging the metal ions have been described [1]. Especially interesting are soft–soft and hard–soft combinations of metal ions bridged by P=O groups. Several metal complexes of the iron, cobalt and nickel triad bearing $R_2P{=}O$ ligands are known to be active catalyst components [2, 3]. In the present contribution we describe the synthesis and some coordination chemistry of $[Cp^*Ir\{P(O)(OMe)_2\}_3]^-$, $Cp^* = C_5Me_5$, an iridium(III) phosphonate complex. It is the so far missing member in the series of half sandwich complexes of the general composition $[(C_5R_5)M\{P(O)(R')_2\}_3]^-$, M = Co [1e], Rh [4], Ir.

Results and discussion

The dinuclear complex $[Cp^*IrCl_2]_2$ reacts with silver salts of non-coordinating, bulky anions $A = PF_6^-$, ClO_4^- in acetone to give the solvate species $[Cp^*Ir(Me_2CO)_3]^{2+}$ [5]. The coordinated acetone is easily displaced by trimethylphosphite with formation of the compounds $[Cp^*Ir\{P(OMe)_3\}_3]A_2$. With $A = PF_6^-$, this salt was obtained only in poor yield due to partial decomposition of the anion and formation of the cationic hydride complex $[Cp^*IrH\{P(OMe)_3\}_2]^+$ [6]. However, with perchlorate as counterion the desired dicationic complex was isolated as $[Cp^*Ir\{P(OMe)_3\}_3](ClO_4)_2$ (**1**) in high yield.

Compound **1** reacts in acetone solution with sodium iodide. Thereby each of the three trimethylphosphite ligands is transformed into a dimethylphosphonate ligand via a Michaelis–Arbuzov type reaction [7] to give the sodium salt **2** (Scheme 1).



Scheme 1.

Compound **2** is an off-white solid that is stable in air and soluble without decomposition in water and polar organic solvents. The proposed structure (see Scheme 1) follows from the NMR spectra and the comparison with the known rhodium complex $Na[Cp^*Rh\{P(O)(OMe)_2\}_3]$. The three isochronous phosphorus nuclei give rise to a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 38.7 ppm. The ^1H NMR spectrum shows a symmetrical multiplet with a broad central

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component and two sharp outer signals at δ 3.50 ppm (^3J(POCH) = 11 Hz) for the methoxy protons. It is the X part of an $[AX_3X'_3]_3$ spin system. The signal of the five ring methyls occurs as a quartet at δ 1.88 ppm (^4J(PRhCCH) = 2.7 Hz).

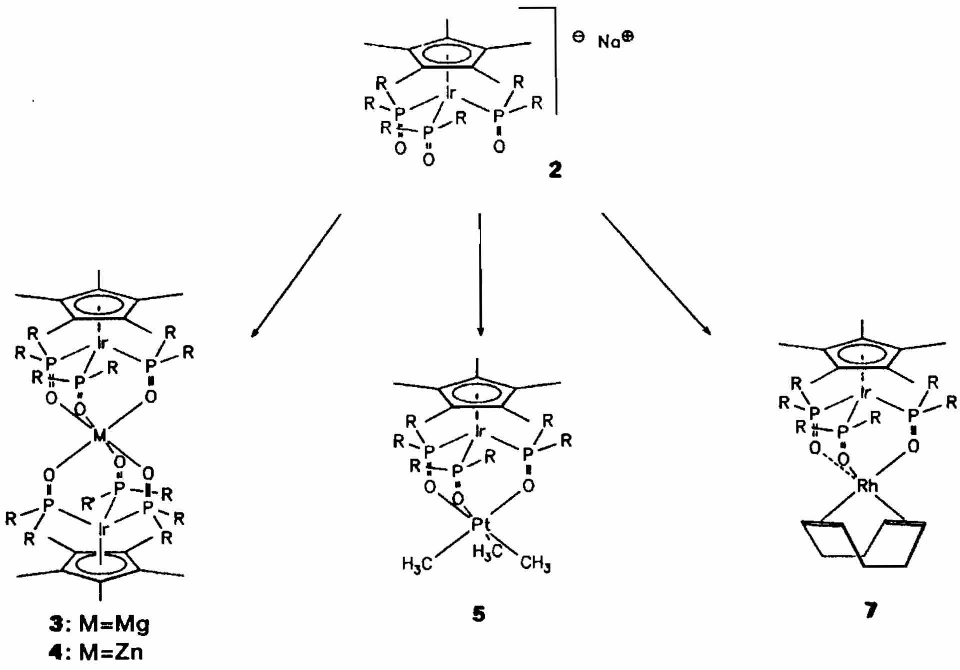
The anion $[Cp^*Ir\{P(O)(OMe)_2\}_3]^-$ (hereafter abbreviated as L^-) behaves as a strong tris-chelating oxygen ligand. The sodium salt **2**, for example, reacts with divalent metals in aqueous solutions to form neutral compounds of the type ML_2, $M^{2+} = Mg^{2+}$ (**3**), Zn^{2+} (**4**). Their ^1H NMR spectra are virtually identical with that of the sodium salt **2**.

In addition we have found that complex **2** reacts with the platinum(IV) complex $[PtMe_3]_2SO_4 \cdot 4H_2O$ in water and with the rhodium(I) compound $[\{RhCl(cod)\}_2]$, cod = 1,5-cyclooctadiene, in cyclohexane solution to give the air-stable heterobimetallic complexes $[LPtMe_3]$ (**5**) and $[LRh(cod)]$ (**7**), respectively (see Scheme 2).

The ^1H NMR spectrum of **5** is in accord with the proposed structure. The platinum bonded methyl protons are isochronous. They give rise to a pseudo triplet at δ 1.02 ppm with a ^{195}Pt–^1H coupling constant $^2J = 79$ Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 48.3 with satellites ($^2J = 32.3$ Hz) due to ^{195}Pt–^{31}P coupling. This indicates that the anionic complex L^- acts as a C_{3v} symmetrical oxygen ligand giving an octahedral coordination at the platinum centre. The geometry is probably very similar to the one in the complex $[(C_5H_5)Co\{P(O)(OEt)_2\}_3PtMe_3]$, the crystal structure of which has been determined recently [8]. The ^1H NMR spectrum of complex **7** shows three broad multiplets characteristic of η^4-coordinated cyclooctadiene-1,5. The signals of the coordinated ligand L^- indicate local C_{3v} symmetry. This could mean a coordination number five species undergoing fast Berry pseudorotation. Alternatively, **7** could be a square planar rhodium complex with L acting as a bidentate ligand where the coordinated and the non-coordinated P=O oxygen donors interchange rapidly on the NMR time scale. Since we have not been successful with growing crystals suitable for an X-ray determination we do not know the instantaneous structure of **7**.

The sodium salt of the anionic rhodium complex $L'^- = [Cp^*Rh\{P(O)(OMe)_2\}_3]^-$ that we prepared earlier [4] reacts with $[PtMe_3]_2SO_4 \cdot 4H_2O$ and $[\{RhCl(cod)\}_2]$ under the same conditions to give the analogous heterobimetallic complexes $[L'PtMe_3]$ (**6**) and $[L'Rh(cod)]$ (**8**), respectively. The NMR spectra data are collected in Table 1.

The diolefin complexes **7** and **8** react with carbon monoxide gas at atmospheric pressure. Bubbling CO through a cyclohexane or dichloromethane solution of these complexes causes immediate displacement of the coordinated cyclooctadiene and the formation of the dicarbonyl complexes $[LRh(CO)_2]$ or $[L'Rh(CO)_2]$. The IR spectra show as expected two strong ν(CO) absorptions at 1990, 2070 (cyclohexane) and 1990, 2080 (dichloromethane) cm^{-1}, respectively. However, our attempts failed to isolate these carbonyl complexes in pure form. Upon evaporation of the solvent the two carbonyl bands disappear and a new ν(CO) absorption



Scheme 2.

TABLE 1. NMR data[a] (δ (ppm) J (Hz))

Complex	Solvent	^{1}H NMR		^{31}P{^{1}H} NMR
		C_5Me_5 (^4J(PH))	OCH_3 (^3J(PH))	
1	CD_3NO_2	2.07q (4.0)	4.05vq (12)	60.0s
2	$(CD_3)_2CO$	1.88q (2.7)	3.58m (11)	38.7s
3	$CDCl_3$	1.85q (2.5)	3.75m (11)	37.3s
4	$CDCl_3$	1.83q (2.7)	3.59m (11)	43.0s
5[b]	$CDCl_3$	1.87q (2.7)	3.63m (11)	48.3pt (^2J(PtOP) = 32.4)
6[c]	$CDCl_3$	1.79q (3.7)	3.58m (11)	99.4dxpt (^1J(RhP) = 180,8; ^2J(PtOP) = 25.2)
7[d]	$CDCl_3$	1.86q (2.6)	3.68m (11)	40.7d (^2J(RhOP) = 2.9)
8[e]	$CDCl_3$	1.80q (4.0)	3.70m (11)	96.2dxd (^1J(RhP) = 185,8; ^2J(RhOP) = 2.8)
9	$CDCl_3$	1.78q (3.7)	3.60m (11)	93.1dxvm (^1J(RhP) = 180,7; ^2J(RhOP) = 0.97; ^1J(RhRh) ≈ 2; ^3J(RhPORh) ≈ 0.5)

[a] s = singlet; d = doublet; t = triplet; m = multiplet; vq = virtual quartet; pt = pseudo triplet. [b] Pt–Me: δ 1.02 (pt, ^2J(PtCH) = 79 Hz). [c] Pt–Me: δ 1.00 (pt, ^2J(PtCH) = 78 Hz). [d] cod: δ 1.58 (d, br, CH_2); 2.40 (s, br, CH_2); 4.20 (m, CH). [e] cod: δ 1.60 (d, br, CH_2); 2.44 (s, br, CH_2); 3.80 (m, CH, partially masked by OMe signal).

located at 1835 cm^{-1} grows in. It belongs to a thermally stable product that could be isolated. We have observed a similar behaviour with $[(C_5H_5)Co\{P(O)(OEt)_2\}_3Rh(CO)_2]$. There we have been able to determine the crystal structure of the product [9].

Based on the elemental analyses and the comparison of the IR and ^{1}H NMR spectra it seems clear that the partial decarbonylation of the dicarbonyl complexes described here leads to the same type of compound, namely the tetranuclear complexes [LRh(μ-CO)$_3$RhL] and [L′Rh(μ-CO)$_3$RhL′] (**9**). In these linear molecules all three phosphoryl oxygen donor atoms are coordinated to rhodium and the central rhodium–rhodium bond is triply bridged by CO ligands. The ^{31}P NMR spectrum of **9** is very complex due to extensive spin–spin coupling of the four rhodium and six phosphorus nuclei giving rise to an $[A[X]_3C]_2$ D_{3h} spin system. The coupling constants that could be extracted from the spectra are given in Table 1.

Conclusions

In this communication we have described the heaviest member in the series of tris-chelating oxygen ligands of the type $[CpM\{P(O)R_2\}_3]^-$, M = Co, Rh, Ir. This gives us now the opportunity to compare, for example, their inertness in catalytic processes, electronic properties and the redox chemistry in this triad. With cobalt and rhodium complexes high kinetic inertness is confined to the oxidation state +III. Iridium complexes on the other hand have a much higher tendency to be inert in different oxidation states. Preliminary cyclovoltammetric measurements have shown that the iridium–rhodium complex **7** undergoes a reversible redox process at *c.* +0.16 V. It seems to be a rhodium centered process. Whether L$^-$ (**2**) is able to act as a redox active ligand in other complexes remains to be seen.

Experimental

Elemental analyses were made with a Heraeus Mikro Standard microanalyser. IR spectra were recorded on a Perkin-Elmer 567 spectrometer using Nujol mulls between polyethylene disks or hexane solutions between KBr plates. Conductivities were measured in *c.* 5×10^{-4} M acetone solutions with a WTW-LF 521 conductometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on Varian XL-100 and Bruker WP80 instruments, and the chemical shifts are given in ppm relative to Me_4Si and external 85% H_3PO_4, respectively. $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot 3H_2O$ were obtained from Degussa. The starting complexes $[\{Cp^*MCl_2\}_2]$ (M = Rh, Ir) [5], $[Me_3Pt]_2SO_4 \cdot 4H_2O$ [10] and $[\{RhCl(cod)\}_2]$ [11] were prepared according to published procedures. All manipulations were carried out under purified nitrogen in Schlenk type glassware. Reagent-grade solvents were dried, distilled and stored under a nitrogen atmosphere. The analytical results, yields, and colours of the isolated complexes are collected in Table 2.

Synthesis of $[Cp^*Ir\{P(OMe)_3\}_3](ClO_4)_2$ (1)

300 mg (0.37 mmol) of the iridium complex $[\{Cp^*IrCl_2\}_2]$ and 313 mg (1.5 mmol) of silver perchlorate in acetone (20 ml) were stirred for 10 min at room temperature in the absence of light. The precipitated silver chloride was removed by filtration through cellulose and the resulting solution was stirred with 420 mg (3.39 mmol) of trimethylphosphite. After 30 min diethyl ether was added to precipitate a white solid which was washed with diethyl ether and dried *in vacuo*. The product was recrystallized from acetone/diethyl ether.

Synthesis of $Na[Cp^*Ir\{P(O)(OMe)_2\}_3]$ (2)

To a solution of 300 mg (0.33 mmol) of complex **1** in acetone (5 ml) was added a large excess of NaI. The mixture was stirred at room temperature for 35 h. The solvent was removed under reduced pressure and the solid residue was washed with n-hexane to

TABLE 2. Analytical results, colours, yields and IR data for the isolated complexes

Complex	Colour	Found (calc.) (%)		Yield (%)	IR data $\nu(P{=}O)$ (cm^{-1})
		C	H		
1[a]	white	25.76 (25.40)	4.98 (4.71)	85	
NaL (**2**)[b]	pale yellow	28.02 (28.36)	5.39 (4.91)	87	1165
MgL_2 (**3**)	pale yellow	28.11 (28.82)	5.07 (4.99)	60	1115
ZnL_2 (**4**)	pale yellow	27.33 (27.96)	4.84 (4.84)	65	1100
$LPtMe_3$ (**5**)	white	25.43 (25.50)	4.80 (4.73)	64	1115
$L'PtMe_3$ (**6**)	white	28.55 (28.33)	5.38 (5.26)	72	1110[c]
LRh(cod) (**7**)	yellow	32.80 (33.00)	5.98 (5.24)	80	1100
L'Rh(cod) (**8**)	yellow	37.17 (37.13)	6.00 (5.84)	81	1100[c]
$[L'Rh(\mu\text{-}CO)_3RhL']$ (**9**)	yellow	29.71 (29.60)	4.44 (4.68)	70	1100[c]

[a] $\Lambda_M = 248\ \Omega^{-1}\ cm^2\ mol^{-1}$ (acetone). [b] $\Lambda_M = 160\ \Omega^{-1}\ cm^2\ mol^{-1}$ (acetone). [c] $\nu(P{=}O)$ (NaL') = 1168 cm^{-1}.

eliminate 4-hydroxy-4-methylpentan-2-one which is formed in an appreciable amount by aldol condensation of acetone. Finally the product was extracted with dichloromethane. The solution obtained was evaporated to dryness and the solid residue was recrystallised from dichloromethane/n-hexane.

Synthesis of $[\{Cp^*Ir[P(O)(OMe)_2]_3\}_2M]$, M = Mg (3), Zn (4)

To a solution of 100 mg (0.14 mmol) of the complex **2** in 10 ml of distilled water was added a solution of a slight excess of the metal salt ($MgSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$) in 5 ml of water. The yellow precipitate that formed was filtered off, washed with water and dried *in vacuo*. The complexes were recrystallised from dichloromethane/n-hexane.

Synthesis of $[Cp^*Ir\{P(O)(OMe)_2\}_3PtMe_3]$ (5)

To a solution of the complex **2** (100 mg, 0.14 mmol) in 10 ml of distilled water was added the stoichiometric amount of $(Me_3Pt)_2SO_4$ (28 mg, 0.07 mmol) in 7 ml of water. A white solid formed immediately. The mixture was stirred for 15 min, then filtered, washed with water and dried *in vacuo*. The complex was recrystallised from chloroform/n-pentane. The analogous rhodium complex $[Cp^*Rh\{P(O)(OMe)_2\}_3PtMe_3]$ (**6**) was also prepared according to this procedure, using $Na[Cp^*Rh\{P(O)(OMe)\}_3]$ instead of **2** as starting material.

Synthesis of $[Cp^*Ir\{P(O)(OMe)_2\}_3Rh(cod)]$ (7)

A slurry of 284 mg (0.42 mmol) of complex **2** and 103 mg (0.21 mmol) of the rhodium complex $[\{RhCl(cod)\}_2]$ in 20 ml of cyclohexane was stirred for 5 days at room temperature. The solvent was evaporated under reduced pressure, the solid residue was extracted with n-pentane and filtered through cellulose. The solution was concentrated and cooled to −30 °C. A crystalline yellow solid formed that was filtered off, washed with cold n-pentane and dried *in vacuo*.

Synthesis of $[Cp^*Rh\{P(O)(OMe)_2\}_3Rh(cod)]$ (8)

A slurry of 323 mg (0.55 mmol) of $Na[Cp^*Rh\{P(O)(OMe)_2\}_3]$ and 120 mg (0.24 mmol) of $[\{RhCl(cod)\}_2]$ in distilled water (40 ml) was stirred for 5 h at 60 °C. The solid was filtered off, washed with water and dried *in vacuo*. The complex was dissolved in a minimum amount of n-pentane and cooled to −30 °C to yield yellow crystals.

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