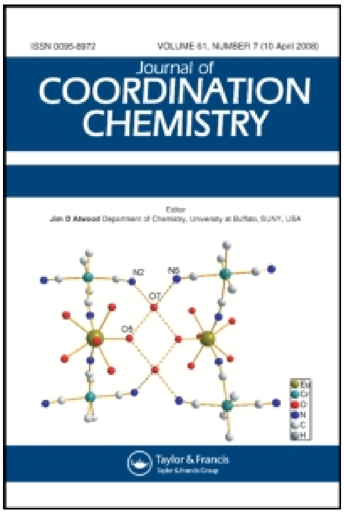

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CHELATING PROPERTIES OF THE ANIONIC IRIDIUM(III) COMPLEX $(\eta^5\text{—}C_5Me_5)IrCl(PO(OMe)_2\}_2]^-$, SYNTHESIS OF BI—AND TRINUCLEAR DERIVATIVES

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CHELATING PROPERTIES OF THE ANIONIC IRIDIUM(III) COMPLEX (η^5—C_5Me_5)IrCl{PO(OMe)$_2$}$_2$]$^-$. SYNTHESIS OF BI— AND TRINUCLEAR DERIVATIVES

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The synthesis and properties of new neutral complexes of the type [(η^5—C_5Me_5)IrX{PO(OMe)$_2$}{P(OH)(OMe)$_2$}] (X═Cl, I) and their thallium derivatives. [(η^5—C_5Me_5)IrX{PO(OMe)$_2$}$_2$Tl] are described. The potentially bidentate or terdentate ligand being the anionic complex [(η^5—C_5Me_5)IrCl{PO(OMe)$_2$}$_2$]$^-$ has been studied. It reacts with metal ions and with some organometallic fragments to yield trinuclear or binuclear complexes. Spectroscopy data for the isolated complexes are discussed.

Keywords: Iridium(III); alkylphosphonates; synthesis; binuclear; trinuclear

INTRODUCTION

Transition metal complexes containing simultaneously a secondary phosphonate and secondary phosphite groups in a *cis* arrangement present a symmetrical hydrogen system $L_n\underline{MP(OR)_2O\cdots H\cdots OP}(OR)_2$ (R═Me, Et or Ph) where the hydrogen bonded proton can easily be removed to form an anionic *bis*(phosphonate) complex; this can act as a bidentate chelating ligand through the oxygen atoms.[1–4] When these compounds contain additionally a halogen as an ancillary ligand, for example in the anions [(η^5—C_5Me_5)RhI{PO(OMe)$_2$}]$^-$, [(η^6—C_6Me_6)RuCl{PO(OMe)$_2$}]$^-$ and [(η^6—*p*—$MeC_6H_4Pr^i$)RuI{PO(OMe)$_2$}]$^-$, they can act as terdentate ligands with the halogens atom as one of

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the donors, forming a large variety of bi- or trimetallic derivatives. In some cases these compounds only act as bidentade *O, O*–donor ligands probably due to the labile halogen donor site.[5–7]

In this article we report the synthesis and characterization of mononuclear compounds of general formula $[(\eta^5\text{—}C_5Me_5)IrX\{P(OH)(OMe)_2\}\{PO(OMe)_2\}]$ (X═Cl, I) and their thallium derivatives $[(\eta^5\text{—}C_5Me_5)IrX\{PO(OMe)_2\}_2Tl]$. We also report the coordination properties of the anionic complex $[(\eta^5\text{—}C_5Me_5)IrCl\{PO(OMe)_2\}_2]^-$ (hereafter abbreviated as L⁻) in reactions with metals to form trinuclear compounds of formula ML_2 (M ═ Mg^{2+}, Zn^{2+}, Cu^{2+}) and with some organometallic fragments to give binuclear compounds of formula [LRh(cod)], $[LMCl(\eta^5\text{—}C_5Me_5)]$ and $[LM(\eta^5\text{—}C_5Me_5)]PF_6$ [M═Rh(III), Ir(III)].

EXPERIMENTAL

C and H analyses were carried out with Heraeus Mikro Standard and Perkin-Elmer 240B microanalysers. IR spectra were recorded on a Perkin Elmer 567 spectrophotometer (4000–200 cm^{-1}) using KBr pellets. Visible spectra were recorded on a Perkin Elmer Lamda 3 spectrophotometer. Conductivities were measured in *ca* 5×10^{-4} *M* nitrometane solutions using a WTW LF-521 conductimeter. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian XL100 and Bruker AC200 instruments. Chemical shifts are reported relative to $SiMe_4$ and 85% H_3PO_4 in D_2O (positive shifts downfield), respectively.

All reactions were carried out in Schlenk tubes under purified nitrogen. Reagent grade solvents were dried, distilled and stored under nitrogen. The starting complexes $[(\eta^5\text{—}C_5Me_5)IrCl\{PO(OMe)_2\}_2]Na \cdot 0.4NaI$, $[\{Rh(\mu\text{—}Cl)(cod)\}_2]$ and $[\{\eta^5\text{—}C_5Me_5)MCl(\mu\text{—}Cl)\}_2]$ (M═Rh, Ir) were prepared by published procedures.[8-10]

Preparation of Complexes

$[(\eta^5\text{—}C_5Me_5)IrCl\{PO(OMe)_2\}\{P(OH)(OMe)_2\}]$ (1)

To a solution of $[(\eta^5\text{—}C_5Me_5)IrCl\{PO(OMe)_2\}]Na \cdot 0.4NaI$ (500 mg) in water (10 cm^3) was added dropwise a solution of 10% H_2SO_4 to pH 3; a yellow solid formed. The mixture was stirred for 5 min and then extracted with CH_2Cl_2 (2 x 25 cm^3). Evaporation of the organic solvent give a solid which was dried *in vacuo*. The yellow complex was crystallized from chloroform-hexane. Yield

374 mg (95%). Anal.: calcd. for $C_{14}H_{28}ClIrO_6P_2$: C, 28.89; H, 4.85%. Found: C, 29.00; H, 5.05%. ^1H NMR ($CDCl_3$): δ 11.07 (s, br, OH), 3.80 [vt, OCH_3, $^3J(PH)$ = 11 Hz], 3.66 [vt, OCH_3, $^3J(PH)$ = 11 Hz] and 1.80 [t, C_5Me_5, $^3J(PH)$ = 3 Hz] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.25 (s) ppm. IR (KBr): ν(P=O), 1010 cm^{-1}.

[(η^5—C_5Me_5)IrI{PO(OMe)$_2$}{P(OH)(OMe)$_2$}] (2)

To a suspension of complex **1** (0.256 mg, 0.38 mmol) in water (15 cm^3) was added the stoichiometric amount of NaOH (22.2 mg, 0.38 mmol). The resulting solution was treated with excess NaI (1.2 g) and the mixture stirred at room temperature for 14 h. Aqueous 10% H_2SO_4 was added dropwise to pH3 and then mixture extracted with CH_2Cl_2 (2 x 25 cm^3). The organic layer was washed with water, dried with $MgSO_4$ and evaporated to dryness. Yellow crystals were obtained from chloroform-hexane. Yield 289 mg (97%). Anal.: calcd. for $C_{14}H_{28}IIrO_6P_2$: C, 22.97; H, 4.19%. Found: C, 24.22; H, 4.65%. ^1H NMR ($CDCl_3$): δ 10.20 (s, br, OH), 3.76 [vt, OCH_3, $^3J(PH)$ = 11 Hz], 3.64 [vt, OCH_3, $^3J(PH)$ = 12 Hz] and 1.98 [t, C_5Me_5, $^3J(PH)$ = 2.9 Hz] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$: δ 57.39 (s) ppm. IR (KBr): ν(P=O), 1010 cm^{-1}.

[(η^5—C_5Me_5)IrX{PO(OMe)$_2$}$_2$Tl] [X=Cl (3), *I* (4)*]*

To a solution of complex **1** or **2** (0.86 mmol) in benzene (30 cm^3) was added the stoichiometric amount of thallium acetylacetonate (280 mg, 0.86 mmol). The resulting mixture was stirred for 15 h at room temperature and evaporated to dryness under vacuum. The complexes were crystallized as yellow crystals from chloroform-hexane. For (3) yield 674 mg (92%). Anal.: calcd. for $C_{14}H_{27}ClIrO_6P_2Tl$: C, 21.41; H, 3.46%. Found: C, 21.62; H, 4.00%. ^1H NMR ($CDCl_3$): δ 3.65 [vt, OCH_3, $^3J(PH)$ = 10 Hz], 3.59 [vt, OCH_3, $^3J(PH)$ = 10 Hz] and 1.76 [t, C_5Me_5, $^3J(PH)$ = 3 Hz] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.45 (s) ppm. IR (KBr): ν (P=O), 1010 cm^{-1}. For (4), yield: 679 mg (90%). Anal.: calcd. for $C_{14}H_{27}IIrO_6P_2Tl$: C, 19.18; H, 3.10%. Found: C, 18.99; H, 3.00%. ^1H NMR ($CDCl_3$): δ 3.70 [vt, OCH_3, $^3J(PH)$ = 10 Hz], 3.58 [vt, OCH_3, $^3J(PH)$ = 10 Hz] and 1.91 [t, C_5Me_5, $^3J(PH)$ = 2.8 Hz] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.56 (s) ppm. IR (KBr): ν(P=O), 1005 cm^{-1}.

[{(η^5—C_5Me_5)IrCl{PO(OMe)$_2$}$_2$}$_2$M] [M = Mg^{2+} (5), *Zn^{2+}* (6), *Cu^{2+}* (7)*]*

To a solution of complex [(η^5—C_5Me_5)IrCl{PO(OMe)$_2$}$_2$]Na · 0.4NaI (200 mg) in water (10 cm^3) was added an excess of the corresponding metallic salt

($MgSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, 200 mg) in aqueous solution. Immediately a yellow solid was formed and which was extracted with CH_2Cl_2 (20 cm^3). The organic layer was washed with water and evaporated to dryness. The complexes were crystallized from dichloromethane-hexane. For (**5**) yellow crystals, yield: 143 mg (89%). Anal.: calcd. for $C_{28}H_{54}Cl_2Ir_2MgO_{12}P_4$: C, 28.35; H, 4.59%. Found: C, 27.94; H, 4.80%. ^1H NMR ($CDCl_3$): δ 3.64 [vt, OCH_3, $^3J(PH)$ = 11 Hz], 3.60 [vt, OCH_3, $^3J(PH)$ = 11 Hz] and 1.75 [t, C_5Me_5, $^3J(PH)$ = 3 Hz] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.48 (s) ppm. IR (KBr): ν (P═O), 1005 cm^{-1}. For (**6**), yellow crystals, yield 151 mg (91%). Anal.: calcd. for $C_{28}H_{54}Cl_2Ir_2O_{12}P_4Zn$: C, 27.28; H, 4.43%. Found: C, 27.40; H, 4.48%. ^1H NMR ($CDCl_3$): δ 3.68 [vt, OCH_3, $^3J(PH)$ = 12 Hz], 3.61 [vt, OCH_3, $^3J(PH)$ = 11 Hz] and 1.75 [t, C_5Me_5, $^3J(PH)$ = 2.5 Hz] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.50 (s) ppm. IR (KBr): ν(P═O), 1005 cm^{-1}. For (**7**), yellow-green crystals, yield: 133 mg (80%). Anal.: calcd. for $C_{28}H_{54}Cl_2CuIr_2O_{12}P_2$: C, 27.44; H, 4.44%. Found: C, 27.72; H, 4.30%. IR (KBr): ν(P═O), 1000 cm^{-1}.

[(η^5—C$_5$Me$_5$)IrCl{PO(OMe)$_2$}$_2$Rh(cod)] (8)

A solution of complex **3** (200 mg, 0.254 mmol) in dichloromethane (10 cm^3) was treated with [{Rh(μ—Cl)(cod)}$_2$] (63 mg, 0.127 mmol). The mixture was stirred for 30 min and the TlCl formed was filtered off through kieselguhr. The filtrate was evaporated to dryness and yellow crystals were obtained from dichloromethane-pentane. Yield 180 mg (90%). Anal.: calcd. for $C_{32}H_{39}ClIrO_6$ PRh : C, 33.36; H, 4.96%. Found: C, 33.80; H, 4.65%. ^1H NMR ($CDCl_3$): δ 3.80 (s, br, CH) 3.57 [vt, OCH_3, $^3J(PH)$ = 11 Hz], 3.50 [vt, OCH_3, $^3J(PH)$ = 11 Hz], 2.49 (m, CH_2), 1.76 [t, C_5Me_5, $^3J(PH)$ = 2.5 Hz] and 1.54 (m, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.05 [d, $^2J(RhP)$ = 3.2 Hz) ppm.

[(η^5—C$_5$Me$_5$)IrCl{PO(OMe)$_2$}$_2$MCl(η^{5}C$_5$Me$_5$)] [M═Rh (9), *Ir* (10)*]*

A solution of complex **3** (120 mg, 0.152 mmol) in methanol (20 cm^3) was treated with the stoichiometric amount of [{η^5—C$_5$Me$_5$)MCl(μ—Cl)}$_2$] [M═Rh (47 mg, 0.076 mmol); Ir (61 mg, 0.076 mmol)]. After 1 h with stirring, the TlCl formed was filtered off through kieselguhr and the solution evaporated to dryness. The solid residue was crystallized from dichloromethane-hexane. For (**9**) orange-yellow crystals, yield 78 mg (60%). Anal.: calcd. for $C_{24}H_{42}Cl_2IrO_6P_2Rh$: C, 33.73; H, 4.95%. Found: C, 33.37; H, 4.73%. ^1H NMR ($CDCl_3$): δ 3.54 [vt, OCH_3, $^3J(PH)$ = 11 Hz], 3.57 [vt, OCH_3, $^3J(PH)$ = 11.5 Hz], 1.73 [t, C_5Me_5, $^3J(PH)$ = 2.8 Hz] and 1.68 (s, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 69.36 (s, br) ppm. Λ_M = 53 ohm^{-1} cm^2mol^{-1}.

For (**10**), yellow crystals, yield; 74 mg(70%). Anal.: calcd. for $C_{24}H_{42}ClF_6Ir_2O_6P_3$: C, 30.60; H, 4.49%. Found: C, 31.00; H, 4.72%. ^1H NMR ($CDCl_3$): δ 3.60 [vt, OCH_3, $^3J(PH)$ = 11.5 Hz], 3.55 [vt, OCH_3, $^3J(PH)$ = 11.5 Hz] 1,75 [t, C_5Me_5, $^3J(PH)$ = 2.8 Hz] and 1.58 (s, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 76.1 (s, br) ppm. Λ_M = 50 ohm^{-1} cm^2 mol^{-1}.

[(η^5—C_5Me_5)IrCl{PO(OMe)$_2$}$_2$M($\eta^5C_5Me_5$)]PF_6 [M═Rh (**11**), *Ir* (**12**)*]*

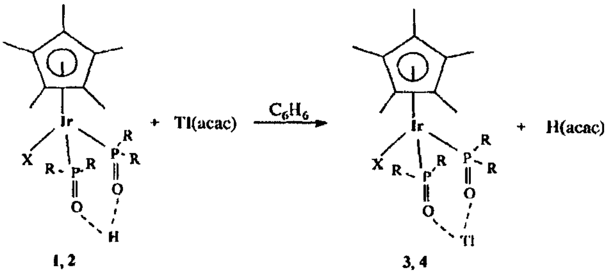
To solution of complex **9** or **10** (0.05 mmol) in methanol was added excess $NaPF_6$ (15 mg, 0.09 mmol) in aqueous solution. The complexes that precipitated were filtered, washed with water, dried *in vacuo* and crystallized from acetone-hexane. For (**11**), orange-yellow crystals, yield: 107 mg (73%). Anal.: calcd. for $C_{24}H_{42}ClF_6IrO_6P_3Rh$: C, 29.89; H, 4.39%. Found: C, 29.82; H, 4.67%. ^1H NMR ($CDCl_3$): δ 3.63 [vt, OCH_3, $^3J(PH)$ = 11 Hz], 3.58 [vt, OCH_3, $^3J(PH)$ = 11.5 Hz], 1.76 [t, C_5Me_5, $^3J(PH)$ = 2.8 Hz] and 1.68 (s, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 69.17 (s) ppm. IR (KBr): ν(P═O) 1020 cm^{-1}; ν(PF_6^-), 840 and 560 cm^{-1}. Λ_M = 94 ohm^{-1} cm^2 mol^{-1}. For (**12**) orange-yellow crystals, yield: 74 mg (70%). Anal.: calcd. for $C_{24}H_{42}ClF_6Ir_2O_6P_3$: C, 27.36; H, 4.02%. Found: C, 27.15; H, 4.30%. ^1H NMR ($CDCl_3$): δ 3.61 [vt, OCH_3, $^3J(PH)$ = 11.5 Hz], 3.52 [vt, OCH_3, $^3J(PH)$ = 11.5 Hz], 1.80 [t, C_5Me_5, $^3J(PH)$ = 2.8 Hz] and 1.62 (s, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 76.60 (s) ppm. IR (KBr): ν(P═O), 1025 cm^{-1}; ν (PF_6^-), 840 and 560 cm^{-1}. Λ_M = 98 ohm^{-1} cm^2 mol^{-1}.

RESULTS AND DISCUSSION

The mononuclear complex [(η^5—C_5Me_5)IrCl{PO(OMe)$_2$}$_2$]Na · 0.4NaI reacts with HCl in benzene solution or with H_2SO_4 in aqueous solution to give the protonated species [(η^5—C_5Me_5)IrCl{PO(OMe)$_2$}{P(OH)(OMe)$_2$}] (**1**). When the reaction was carried out with sulphuric acid in aqueous solution, the isolated complex contains variable quantities of the iodide compound [(η^5—C_5Me_5)IrI{PO(OMe)$_2$}{P(OH)(OMe)$_2$}] (**2**), due to slow halogen exchange. Consequently, in order to obtain **1** as a pure sample using this method, it is necessary to extract the complex with dichloromethane immediately after addition of sulphuric acid.

This halogen metathetic reaction is faster using the starting sodium derivative in aqueous solution. Thus, addition of a slight excess of NaI to this solution gives complete halogen exchange, generating *in situ* the anionic complex [(η^5—C_5Me_5)IrI{PO(OMe)$_2$}$_2$]$^-$, which reacts with sulphuric acid to give **2**.

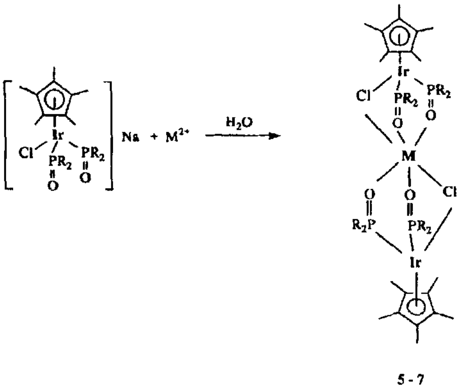
Both protonated complexes **1** and **2**, react with Tl(acac) in benzene solution, giving the corresponding thallium derivatives [(η^5—C_5Me_5)IrX{PO(OMe)$_2$}$_2$Tl] [X═Cl (**3**), I (**4**)] (Scheme 1).



SCHEME 1 (R═OMe).

All complexes were isolated as stable solids and characterized by elemental analyses and IR and NMR spectroscopy. In particular, the IR spectra show the presence of ν(P═O) bands in the range 1005–1010 cm^{-1}. ^{1}H NMR spectra are consistent with the proposed formulations, showing a triplet for the C_5Me_5 ligand and the characteristic pattern of two virtual triplets with a slight difference in coupling constants due to the presence of two pairs of non-isochronous OMe groups.[6] The ^{31}P NMR decoupled spectra of **1** and **3** show the expected singlet resonances for the phosphonate groups (see Experimental).

The anionic complex L$^-$(═[(η^5—C_5Me_5)IrCl{PO(OMe)$_2$}$_2$]$^-$) reacts with bivalent main group or transition metals and with organometallic fragments, giving trinuclear or binuclear complexes. Thus, the complex NaL · 0.4 NaI reacts in aqueous solution with salts of Mg^{2+}, Zn^{2+} or Cu^{2+}, generating the trinuclear complexes ML$_2$ [M═Mg (**5**), Zn (**6**), Cu (**7**)] (Scheme 2).



SCHEME 2 (R═OMe).

^{1}H NMR spectra of the diamagnetic complexes **5** and **6** are virtually identical with that of the sodium salt NaL, suggesting an similar behaviour of these compounds where the central metal ion is octahedrally coordinated with the anionic ligand L$^-$ acting as an *O,O,Cl*—— tripodal ligand. These coordination properties are different to those shown by the related rhodium complex [(η^5—C_5Me_5)RhI{$PO(OMe)_2$}$_2$]$^-$; this reacts with Mg^{2+} in aqueous solution, giving the trinuclear complex [(η^5—C_5Me_5)RhI{$PO(OMe)_2$}$_2$]$_2$ $Mg(H_2O)_2$. In this case the anionic ligand acts as an *O,O*——donor ligand due to the labile iodide site.[6]

The paramagnetic compound 7 exhibits an effective magnetic moment of 1.78 B.M. (measured at 25°C by the Evans method[11]). The visible spectrum in $CHCl_3$ shows a non-symmetric band centred at 13,793 cm^{-1} ($\varepsilon \approx 14$ M^{-1} cm^{-1}) as expected for a six-coordinate geometry at the metal centre, probably with a *trans* arrangement of chlorine atoms.[5]

On the other hand, the thallium derivative LTI (**3**) react, with the binuclear complex [{RhCl(cod)}$_2$] in dichloromethane solution, forming the thallium chloride and the corresponding heterobimetallic complex [LRh(cod)] (**8**). The ^{1}H NMR spectrum shows the expected triplet for C_5Me_5, two virtual triplets for the phosphonate groups and three multiplets for the coordinated cod ligand, in the required intensity ratios, supporting the proposed formulation. The ^{31}P{^{1}H} NMR spectrum shows a doublet resonance at δ 55.05 ppm with a rhodium-phosphorus coupling of 3.2 Hz. In this complex the environment of Rh(I) is probably square-planar with the anionic ligand acting as an *O ,O*—donor ligand. Bubbling of carbon monoxide through a dichloromethane solution of this complex causes displacement of the coordinated diolefin and the formation of the dicarbonyl complex [$LRh(CO)_2$]. The infrared spectrum of the solution shows strong ν(CO) absorptions at 1965 and 2060 cm^{-1}, characteristic of a *cis* arrangement of carbonyl groups.[12] Similar results were obtained by reaction of **3** with the binuclear complex [{$RhCl(CO)_2$}$_2$]. Unfortunately, the carbonyl complex could not be isolated in the solid state as a pure compound.

Complex **3** reacts in mol ratio 2:1 with the binuclear complex [{(η^5—C_5Me_5)MCl_2}$_2$] by cleavage of the chloride bridges to yield orange-yellow solids. In these compounds the organometallic fragment has a strong tendency to obey the 18-electron rule and the compounds can be formulated as [LMCl(η^5—C_5Me_5)], with the ligand acting as a bidentate *O,O*——donor or as [LM(η^5—C_5Me_5)]Cl [M==Rh(**9**), Ir(**10**)], with the ligand acting as a terdentate *O,O,Cl*——donor. ^{1}H NMR spectra of these complexes show two virtual triplets for the phosphonate groups and singlet and triplet resonances for the C_5Me_5 groups, where the C_5Me_5 ligand bond to the iridium atom which in turn is bonded to the phosphorus atoms, resonates at lower field than the C_5Me_5 ligand bonded to the other metal centre. At room temperature the ^{31}P{^{1}H} NMR spectra in chloroform consist of a broad signals centered at δ 69.36 and 76.10 ppm, respectively. With cooling at −35°C, these appear as sharp signals at δ 70.84 and 77.22 ppm, respectively. At 60°C only broad signals were observed. Similar results were obtained using deuterated nitromethane solutions. The molar conductivities nitromethane, in the range 50–53 ohm^{-1} cm^{2} mol^{-1}, are slightly lower than those proposed for 1:1 electrolytes (75–95 ohm^{-1} cm^{2} mol^{-1}).[13]

On the other hand, **9** and **10** react in methanolic solution with aqueous $NaPF_6$ to give the cationic complexes $[LM(\eta^5—C_5Me_5)]PF_6$ [M═Rh (**11**), Ir (**12**)], where the anionic ligand L^- acts as a terdentate *O,O,Cl*— donor. These complexes were isolated as microcrystalline solids and behave as 1:1 electrolytes in nitromethane solution (94–98 ohm^{-1} cm^{2} mol^{-1}). ^{1}H NMR spectra of the complexes in deuterated chloroform show a very similar pattern those of the starting compounds. $^{31}P\{^1H\}$ NMR spectra in chloroform at room temperature show a single resonance at δ 69.17 and 76.60 ppm for **11** and **12**, respectively.

The similar chemical shifts in the ^{1}H and $^{31}P\{^1H\}$ NMR spectra suggest that L^- in **9** and **10**, acts as tripodal ligand at low temperature and the complexes can be formulated as cationic compounds, $[LM(\eta^5—C_5Me_5)]Cl$. When the temperature increases, the phosphorus nuclei become non-equivalent and the broad resonances in the $^{31}P\{^1H\}$ NMR spectra are possibly due to partial formation of the neutral form $[LMCl(\eta^5—C_5Me_5)]$ in chloroform solution at room temperature. The lower values of molar conductivities are in agreement with this proposition.

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