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A clash of cultures: metal carbonyl functionalized Werner complexes[1]

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Abstract

Reactions of $[Fe(\mathbf{1})_2][PF_6]_2$ ($\mathbf{1}$ = 4′-diphenylphosphino-2,2′:6′,2″-terpyridine) with $[M'(CO)_5(THF)]$ (M′ = Mo or W) yield $[Fe\{(\mu\text{-}\mathbf{1})M'(CO)_5\}_2][PF_6]_2$. Treatment of $[Ru(Cltpy)_2][PF_6]_2$ (Cltpy = 4′-chloro-2,2′:6′,2″-terpyridine) with the $[Ph_2P]^-$ anion gives $[Ru(\mathbf{1})_2][PF_6]_2$ which functions as a nucleophile in reactions with $[M'(CO)_5(THF)]$ (M′ = Mo or W) to yield $[Ru\{(\mu\text{-}\mathbf{1})M'(CO)_5\}_2][PF_6]_2$. The bisphosphines $[M(\mathbf{1})_2]^{2+}$ (M = Fe or Ru) can be functionalized with triosmium carbonyl clusters by treatment with $[Os_3(CO)_{11}(NCMe)]$. All new products have been characterized by ^1H-, ^{31}P-NMR and IR spectroscopies and mass spectrometry, and the electrochemical properties of the iron(II) complexes have been investigated. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Bisphosphines; Triosmium carbonyl clusters; Oligopyridines

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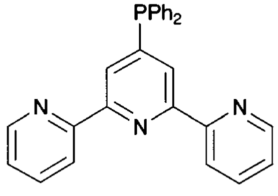
1. Introduction

Although coordination complexes and organometallic compounds individually have attractive and interesting properties, remarkably few species are known in which both motifs are incorporated into a single molecule. Such hybrid molecules are expected to possess much of the useful reactivity of both high and low oxidation state species. As part of a wider study of cluster-functionalized complexes [1–7], we have recently described a novel approach to the preparation of complexes which combine covalently-linked octahedral $[Ru(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) and $R_2C_2Co_2(CO)_6$ cluster domains [8]. In these species, the cluster units are formed in situ by reactions of coordinated alkyne-functionalized 2,2′:6′,2″-terpyridine ligands with $Co_2(CO)_8$. In a parallel study, we have prepared phosphine-functionalized tpy ligands [9] which have the potential to link hard (high oxidation state) and soft (low oxidation state) metal centres. We have already reported the synthesis of 4′-diphenylphosphino-2,2′:6′,2″-terpyridine (**1**) [9],



(**1**)

and have illustrated the effective partitioning into hard and soft metal-binding domains by preferential coordination of only the *N*,*N*′,*N*″-domain to iron(II) and the selective binding of the *P*-donor to palladium(II). However, attempts to prepare the ruthenium(II) complex $[Ru(\mathbf{1})_2]^{2+}$ resulted in oxidation of the phosphine and gave only salts containing the *N*,*N*′,*N*″-coordinated ligand 4′-$Ph_2P(O)$tpy. Since our aim was to use these complexes to link classical coordination to organometallic domains through the soft *P*-donor, the oxidation of this site was undesirable. We now report a route for the synthesis of $[Ru(\mathbf{1})_2]^{2+}$ involving the

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[1] This paper is dedicated to Professor Brian F.G. Johnson on the occasion of his 60th birthday.

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reaction of a coordinated Cltpy (Cltpy = 4′-chloro-2,2′:6′,2″-terpyridine) ligand and show that metal carbonyl-functionalized complexes can be produced from this complex and $[Fe(\mathbf{1})_2]^{2+}$ by substitution reactions with metal carbonyl derivatives containing labile ligands.

2. Experimental

2.1. General data

All reactions were carried out under dry argon or dinitrogen and all solvents were distilled before use and were oxygen-free.

NMR spectra were recorded on a Varian Gemini 300 or Bruker AC 250 spectrometer at room temperature; ^{31}P-NMR spectroscopic chemical shifts are with respect to δ 0 for 85% H_3PO_4 in D_2O. IR measurements were carried out on an ATI Mattson Genesis Series FTIR spectrometer. The MALDI-time-of-flight mass spectra (TOF-MS) were recorded on a PerSeptive Biosystems Vestec spectrometer in positive linear mode at 15 kV acceleration voltage either without a matrix or with 1,8,9-trihydroxyanthracene as matrix, and electrospray mass spectra (ES-MS) were recorded using a Finnigan Mat LCQ-mass spectrometer with acetone or acetonitrile as solvent. Electrochemical measurements were performed with an EcoChemie Autolab PGSTAT 20 potentiostat. A conventional three electrode configuration was used, with glassy carbon working and platinum bead auxiliary electrodes and an Ag/AgCl reference. For the electrochemical measurements, acetonitrile, freshly distilled from P_4O_{10}, was used as solvent. The base electrolyte was 0.1 M $[^n Bu_4N][PF_6]$, recrystallised twice from ethanol/water and thoroughly dried in vacuo over P_4O_{10}. Potentials are quoted vs. the ferrocene/ferrocenium couple ($Fc/Fc^+ = 0.0$ V), and referenced to internal ferrocene added at the end of each experiment. Photolyses were carried out using a mercury lamp (180 W, Heraeus Original Hanau Q180). For column (silica) and thin-layer plate (Kieselgel 60-PF-254) chromatographic separations the eluent was $CH_3CN:H_2O$:sat. KNO_3(aq) in volume ratios 7:0.5:1. The complexes $[Fe(\mathbf{1})_2][PF_6]_2$ [9] and $[Ru(Cltpy)_2][PF_6]_2$ [10] were prepared as described in the literature. $[Mo(CO)_6]$, $[W(CO)_6]$ (Fluka) and $[Os_3(CO)_{12}]$ (Oxkem) were used as received.

2.2. Preparation of $[Ru(\mathbf{1})_2][PF_6]_2$

An intimate mixture of KOH (2.0 g, 36 mmol) and K_2CO_3 (6.6 g, 48 mmol) was heated under reduced pressure at 120°C for 1 h. Acetonitrile (150 ml) was then added to the cooled mixture and the suspension boiled for 1 h, after which Ph_2PH (0.19 ml, 1.1 mmol) was added; the reaction mixture turned orange. After heating at reflux for a further 15 min, a solution of $[Ru(Cltpy)_2][PF_6]_2$ (480 mg, 520 μmol) in MeCN (10 ml) was added and after 5 min the mixture was poured into H_2O (200 ml) containing $[NH_4][PF_6]$ (200 mg, 1.2 mmol). An orange–red precipitate formed, was collected on celite, and was washed thoroughly with dioxygen-free water. The product was separated by column chromatography; yield of $[Ru(\mathbf{1})_2][PF_6]_2$ 484 mg (76%).

^{1}H-NMR ($CD_3C(O)CD_3$): δ 8.62 (d, J_{PH} 5.5 Hz, 4H, $H^{3'}$), 8.45 (d, J_{HH} 7.8 Hz, 4H, H^3), 7.89 (td, J_{HH} 8, 1 Hz, 4H, H^4), 7.67–7.60 (m, 12H, Ph + H^6), 7.53–7.47 (m, 12H, Ph), 7.20 (m, 4H, H^5). ^{31}P{^{1}H}-NMR ($CD_3C(O)CD_3$): δ + 4.7 (s), − 138.1 (septet, J_{PF} 708 Hz, PF_6^-). IR (KBr): 3059vw, 2935vw, 1603w, 1475w, 1413w, 1391w, 1286vw, 1162vw, 1092vw, 1029vw, 838vs(br, PF_6^-), 786m, 749m, 698m, 558s (PF_6^-) cm^{-1}. ES-MS 1081 $\{Ru(\mathbf{1})_2(PF_6)\}^+$, 936 $\{Ru(\mathbf{1})_2\}^+$, 468 $\{Ru(\mathbf{1})_2\}^{2+}$. Elem. analysis: found C, 51.3; H, 3.5; N, 6.8%; calc. for $C_{54}H_{40}F_{12}N_6P_4Ru \cdot 1.3H_2O$: C, 51.9; H, 3.4; N, 6.7%.

2.3. Preparation of $[Fe\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2][PF_6]_2$

A solution of $[Mo(CO)_6]$ (16.3 mg, 61.7 μmol) in dry THF (15 ml) was irradiated for 1 h while a stream of argon was bubbled through. A solution of $[Fe(\mathbf{1})_2][PF_6]_2$ (18.2 mg, 15.4 μmol) in dry MeCN (5 ml) was added and the mixture was kept under an argon stream for 1 h. Solvents were removed in vacuo and the product was purified by preparative TLC ($R_f = 0.95$). The product was washed through a sinter with the eluting solvent, solvent was reduced in vacuo and the purple product was precipitated by addition of $[NH_4][PF_6]$ in dioxygen-free H_2O. ^{1}H-NMR ($CD_3C(O)CD_3$): δ 8.98 (d, J_{PH} 8.8 Hz, 4H, $H^{3'}$), 8.47 (br d, J_{HH} 7.3 Hz, 4H, H^3), 8.05–7.95 (m, 8H, Ph), 7.88

Table 1
NMR spectroscopic data for $[Fe(\mathbf{1})_2]^{2+}$, $[Ru(\mathbf{1})_2]^{2+}$ and their metal carbonyl complexes and comparisons with PPh_3, $[M'(CO)_5(PPh_3)]$ (M′ = Mo or W) and $[Os_3(CO)_{11}(PPh_3)]$

Species	δ ^{31}P	$\Delta\delta = (\delta_{complex} - \delta_{ligand})$	Ref.
$[Fe(\mathbf{1})_2]^{2+}$	+4.9		[9]
$[Fe\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2]^{2+}$	+49.6	44.7	
$[Fe\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2]^{2+}$	+32.5	27.6	
$[Fe\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^{2+}$	+9.3	4.4	
$[Ru(\mathbf{1})_2]^{2+}$	+4.7		
$[Ru\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2]^{2+}$	+49.5	44.8	
$[Ru\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2]^{2+}$	+32.2	27.5	
$[Ru\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^{2+}$	+9.2	4.5	
PPh_3	−6		
$[Mo(CO)_5(PPh_3)]$	+37.5	43.5	[16]
$[W(CO)_5(PPh_3)]$	+20.6	26.6	[16]
$[Os_3(CO)_{11}(PPh_3)]$	+2.1	8.1	[21]

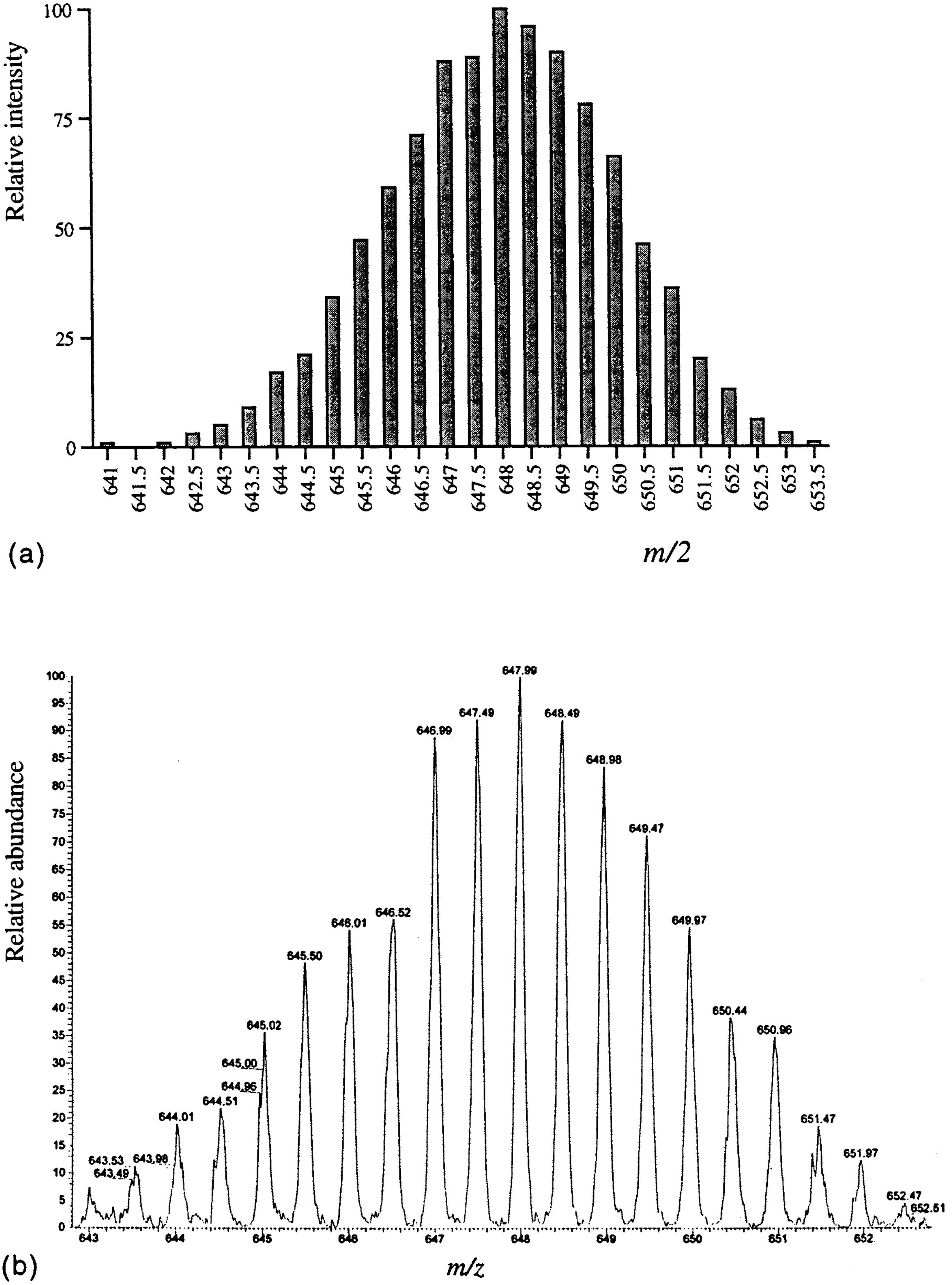
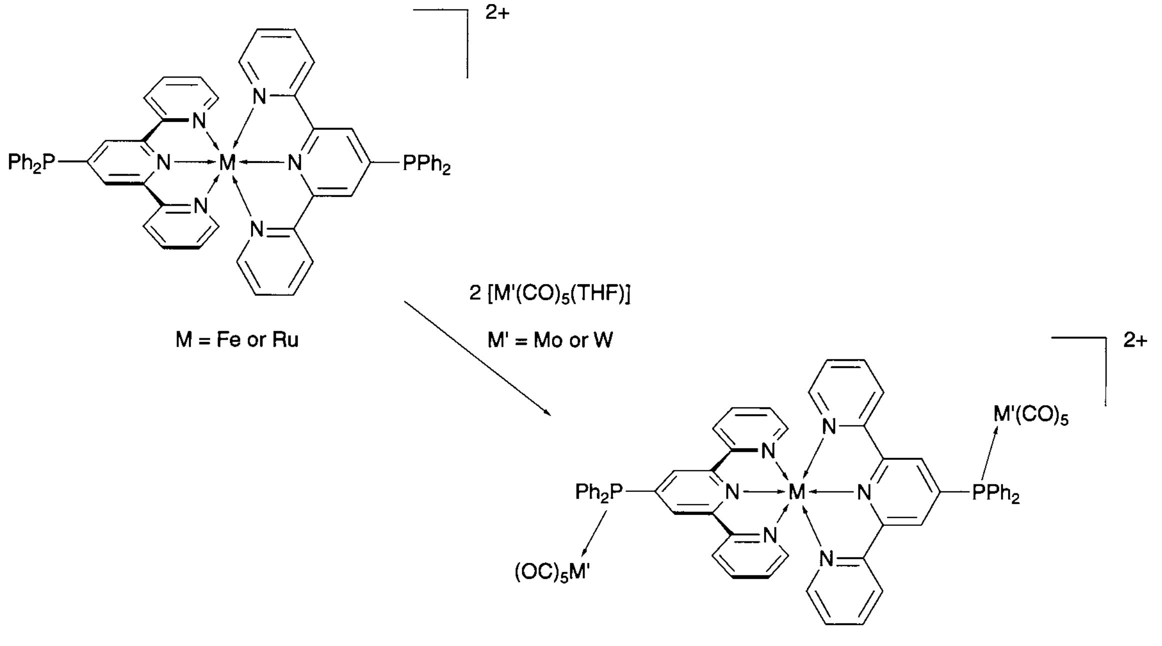


Fig. 1. (a) Calculated and (b) observed electrospray mass spectra for $[Ru\{(\mu\text{-}\mathbf{1})Mo(CO)_3\}_2]^{2+}$.



Scheme 1.

(br t, J_{HH} 7.3 Hz, 4H, H^4), 7.68–7.58 (m, 12H, Ph), 7.25 (br d, J_{HH} 6.5 Hz, 4H, H^6), 7.10 (br t, J_{HH} 7.3 Hz, 4H, H^5). $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$): $\delta + 49.6$ (s), -138.1 (septet, J_{PF} 706 Hz). IR (KBr): 2924w, 2074s (CO), 1995m sh (CO), 1937vs (CO), 1415w, 1384w, 840vs (PF_6^-), 607w, 584m, 558s (PF_6^-) cm^{-1}. TOF-MS: 1251 $\{Fe(\mathbf{1})_2Mo_2(CO)_6\}^+$, 1070 $\{Fe(\mathbf{1})_2Mo(CO)_3\}^+$, 890 $\{Fe(\mathbf{1})_2\}^+$. Insufficient material was isolated for elemental analysis.

2.4. *Preparations of* $[Fe\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2][PF_6]_2$ *and* $[Ru\{(\mu\text{-}\mathbf{1})M'(CO)_5\}_2][PF_6]_2$ *(M' = Mo or W)*

These compounds were prepared in an analogous manner and on similar scales to $[Fe\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}][PF_6]_2$. In each case, insufficient material was isolated for elemental analysis.

$[Fe\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2][PF_6]_2$ (purple): ^1H-NMR ($CD_3C(O)CD_3$): δ 8.96 (d, J_{PH} 9.3 Hz, 4H, H$^{3'}$), 8.48 (br d, J_{HH} 7.3 Hz, 4H, H^3), 8.13–8.00 (m, 8H, Ph), 7.87 (br t, 4H, H^4), 7.60–7.68 (m, 12H, Ph), 7.34 (br d, J_{HH} 4.9 Hz, 4H, H^6), 7.13 (br t, 4H, H^5). $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$): δ +32.5 (s), -138.1 (septet, J_{PF} 707 Hz). IR (KBr): 2952m, 2924s, 2854m, 2075w (CO), 1944s (CO), 1384s, 840s (PF_6^-), 558m (PF_6^-) cm^{-1}. TOF-MS: 1538 $\{Fe(\mathbf{1})_2W_2(CO)_{10}\}^+$, 1511 $\{Fe(\mathbf{1})_2W_2(CO)_9\}^+$, 1214 $\{Fe(\mathbf{1})_2W(CO)_5\}^+$, 1158 $\{Fe(\mathbf{1})_2W(CO)_3\}^+$, 890 $\{Fe(\mathbf{1})_2\}^+$, 418 $\{\mathbf{1}\}^+$.

$[Ru\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2][PF_6]_2$ (orange): ^1H-NMR ($CD_3C(O)CD_3$): δ 8.81 (d, J_{PH} 9.4 Hz, 4H, H$^{3'}$), 8.46 (br d, J_{HH} 7.4 Hz, 4H, H^3), 8.00–7.85 (m, 12H, Ph + H^4), 7.63–7.60 (m, 12H, Ph), 7.48 (br d, J_{HH} 4.9 Hz, 4H, H^6), 7.21 (br t, 4H, H^5). $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$): δ + 49.5 (s), -138.1 (septet, J_{PF} 707 Hz). TOF-MS: 1445 $\{Ru(\mathbf{1})_2Mo_2(CO)_6(PF_6)\}^+$, 1299 $\{Ru(\mathbf{1})_2Mo_2(CO)_6\}^+$. ES-MS: 648 $\{Ru(\mathbf{1})_2Mo_2(CO)_6\}^{2+}$.

$[Ru\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2][PF_6]_2$ (orange): ^1H-NMR ($CD_3C(O)CD_3$): δ 8.82 (d, J_{PH} 8.7 Hz, 4H, H$^{3'}$), 8.49 (br d, J_{HH} 7.5 Hz, 4H, H^3), 7.98–7.89 (m, 12H, Ph + H^4), 7.68–7.60 (m, 12H, Ph), 7.48 (br m, 4H, H^6), 7.21 (br t, 4H, H^5). $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$): δ +32.2 (s), -138.1 (septet, J_{PF} 708 Hz). ES-MS: 1728 $\{Ru(\mathbf{1})_2W_2(CO)_{10}(PF_6)\}^+$, 792 $\{Ru(\mathbf{1})_2W_2(CO)_{10}\}^{2+}$ with seven successive CO losses.

2.5. *Preparation of* $[Fe\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2][PF_6]_2$

$[Os_3(CO)_{11}(NCMe)]$ was prepared from $[Os_3(CO)_{12}]$ (90.8 mg, 100.2 μmol), Me_3NO (7.50 mg, 99.9 μmol) in MeCN (50 ml) according to the literature [11]. The solvent was removed, the residue redissolved in CH_2Cl_2 (40 ml). To 20 ml of this solution was added solid $[Fe(\mathbf{1})_2][PF_6]_2$ (14.78 mg, 12.5 μmol). After stirring at room temperature for 17 h, solvent was removed and the residue dried in vacuo. Separation by column chromatography, eluting first with CH_2Cl_2, and then with $CH_3C(O)CH_3$:CH_2Cl_2 (1:2) yielded 13.8 mg (39%) purple $[Fe\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2][PF_6]_2$.

^1H-NMR ($CD_3C(O)CD_3$): δ 8.94 (d, J_{PH} 10 Hz, 4H, H$^{3'}$), 8.40 (br d, J_{HH} 7.6 Hz, 4H, H^3), 7.99–7.89 (m, 12H, Ph + H^4), 7.70–7.62 (m, 12H, Ph), 7.25 (br d, J_{HH} 5 Hz, 4H, H^6), 7.10 (br t, 4H, H^5). $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$): δ +9.3 (s), -138.1 (septet, J_{PF} 708 Hz). IR (CH_2Cl_2, ν_{CO}): 2110m, 2058s, 2035s, 2020 vs, 1993m, 1980m, 1951w cm^{-1}. TOF-MS: 2791 $\{Fe(\mathbf{1})_2Os_6(CO)_{22}(PF_6)\}^+$, 2647 $\{Fe(\mathbf{1})_2Os_6(CO)_{22}\}^+$

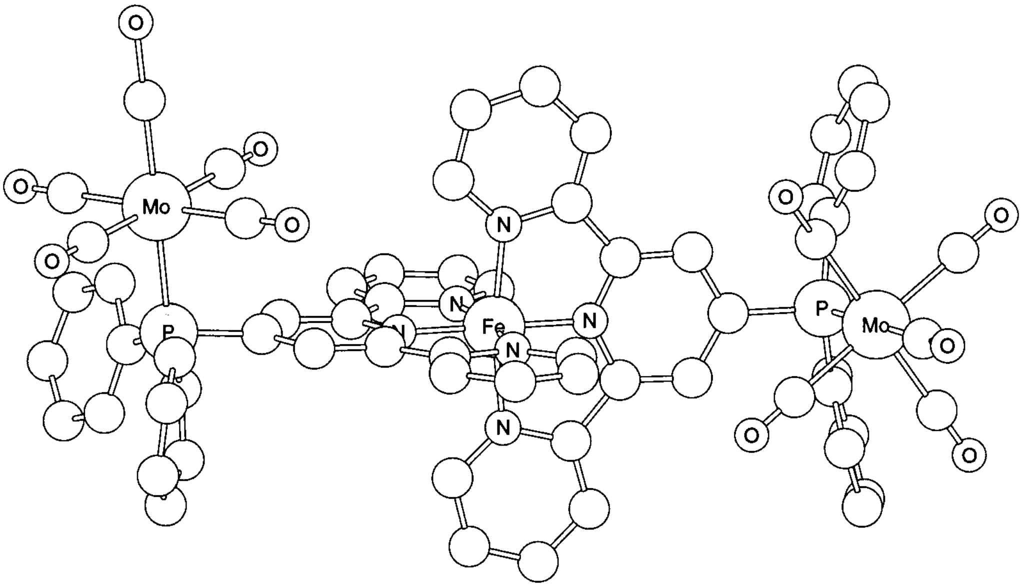


Fig. 2. Modelled structure of $[Fe\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2]^{2+}$.

with two successive CO losses, 1770 $\{Fe(\mathbf{1})_2Os_3(CO)_{11}\}^+$ with one CO loss. Elem. analysis: found C, 31.7; H, 2.1; N, 2.7%; calc. for $C_{76}H_{40}F_{12}FeN_6O_{22}Os_6P_4 \cdot 2Me_2CO \cdot 3H_2O$: C, 31.7; H, 1.9; N, 2.7%.

2.6. Preparation of $[Ru\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2][PF_6]_2$

Solid $[Ru(\mathbf{1})_2][PF_6]_2$ (15.2 mg, 12.5 µmol) was added to the second portion (20 ml) of the CH_2Cl_2 solution of $Os_3(CO)_{11}(NCMe)$ prepared above. After stirring at room temperature for 17 h, CH_2Cl_2 was removed and the residue was dried in vacuo. Separation by column chromatography, eluting first with CH_2Cl_2, and then with $CH_3C(O)CH_3$:CH_2Cl_2 (1:2) yielded 12.1 mg (32%) orange $[Ru\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2][PF_6]_2$.

^{1}H-NMR ($CD_3C(O)CD_3$): δ 8.77 (d, J_{PH} 10.3 Hz, 4H, $H^{3'}$), 8.40 (br d, J_{HH} 8.0 Hz, 4H, H^3), 7.98 (td, J_{HH} 6.3, 1.6 Hz, 4H, H^4), 7.94–7.84 (m, 8H, Ph), 7.68–7.59 (m, 12H, Ph), 7.48 (dd, J_{HH} 5.3 Hz, 4H, H^6), 7.21 (m, 4H, H^5). ^{31}P{^{1}H}-NMR ($CD_3C(O)CD_3$): δ + 9.2 (s), − 138.1 (septet, J_{PF} 708 Hz). IR (CH_2Cl_2, ν_{CO}): 2110m, 2058s, 2035s, 2020vs, 1993m, 1979m, 1950w cm^{-1}. ES-MS: 1346.5 $\{Ru(\mathbf{1})_2Os_6(CO)_{22}\}^{2+}$ with two successive CO losses. Elem. analysis: found C, 31.8; H, 2.0; N, 2.6%; calc. for $C_{76}H_{40}F_{12}N_6O_{22}Os_6P_4Ru \cdot 3Me_2CO \cdot 3H_2O$: C, 31.8; H, 2.2; N, 2.6%.

3. Results and discussion

In an earlier paper [9], we reported the synthesis of the phosphino-functionalized ligand (**1**) and illustrated the ability of the pendant phosphine moiety to coordinate to a soft metal centre during the formation of *trans*-$[PdCl_2(P\text{-}\mathbf{1})_2]$. We also reported that with iron(II), (**1**) forms the complex $[Fe(N,N',N''\text{-}\mathbf{1})_2]^{2+}$ which bears two antipodal pendant PPh_2 units. This complex can be regarded as a didentate ligand containing a rigid backbone. This ligand is capable of coordination to low oxidation state metal centres, and we now show that $[Fe(\mathbf{1})_2]^{2+}$ can coordinate to metal carbonyl units. Before detailing these reactions, we describe the preparation of $[Ru(\mathbf{1})_2]^{2+}$. Our previous attempts involved the initial isolation of (**1**) followed by reaction with ruthenium trichloride and resulted in the isolation of the oxidized product $[Ru(N,N'N''\text{-}4'\text{-}Ph_2P(O)tpy)_2]^{2+}$ [9]. We have now adopted an alternative strategy, based on that of Huttner and coworkers [12] for the conversion of chloro to diarylphosphino derivatives. The complex cation $[Ru(\text{-}Cltpy)_2]^{2+}$ [10] contains an electrophilic ligand and we have previously shown that nucleophilic substitution of the coordinated Cltpy ligand provides an extremely efficient methodology for the synthesis of novel ligands [13]. Acetonitrile solutions of $[Ru(Cltpy)_2][PF_6]_2$ reacted smoothly with $[Ph_2P]^-$ (generated in situ from KOH and PPh_2H) to give $[Ru(\mathbf{1})_2]^{2+}$ isolated after chromatographic purification as the hexafluorophosphate salt in 76% yield. Solutions of the salt are prone to oxidation to $[Ru(4'\text{-}Ph_2P(O)tpy)_2]^{2+}$ and must be handled under dioxygen-free conditions. The ^{31}P-NMR spectrum of $[Ru(\mathbf{1})_2][PF_6]_2$ was consistent with the formation of a symmetrical cationic complex; a septet characteristic of $[PF_6]^-$ and a singlet at $\delta + 4.7$ were observed in a 1:1 ratio. The shift of $\delta + 4.7$ is similar to that observed for $[Fe(\mathbf{1})_2]^{2+}$ in the same solvent ($\delta + 4.9$, $CD_3C(O)CD_3$, Table 1) [9]. The ^{1}H-NMR spectrum indicates a symmetrical species, and, in addition to the appearance of the

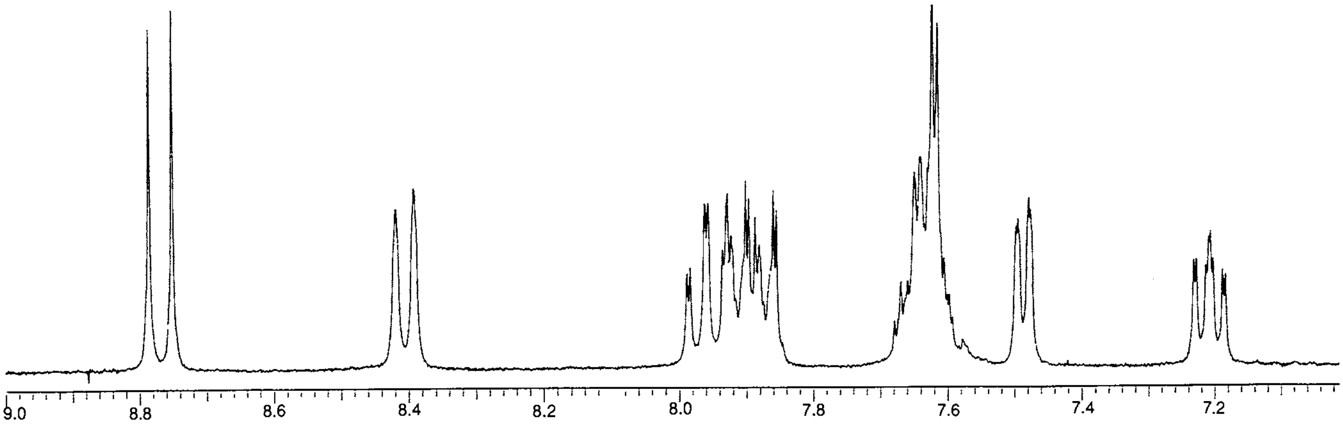


Fig. 3. The 300 MHz ^{1}H-NMR spectrum of $[Ru\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2][PF_6]_2$ in acetone-d_6 (298 K).

signals assigned to Ph groups, the diagnostic feature confirming the introduction of a PPh_2 group in each 4′-position is the appearance of the signal for $H^{3'}$ of **1** as a doublet with $^3J_{PH}$ of 5.5 Hz. The highest mass peak in the electrospray mass spectrum (*m*/*z* 1081) was consistent with the molecular ion $\{[Ru(\mathbf{1})_2][PF_6]\}^+$.

3.1. Mononuclear metal carbonyl derivatives

Our first studies of the coordinating abilities of the bisphosphines $[Fe(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{1})_2]^{2+}$ involved reactions of these cations with $M'(CO)_5$-fragments ($M' = Mo$ or W). Phosphine complexes of mononuclear Group 6 metal carbonyls are well documented [14] as are uses of the labilized complexes $[M'(CO)_5(THF)]$ and $[M'(CO)_4(THF)_2]$ [15].

The reaction of $[Fe(\mathbf{1})_2][PF_6]_2$ with a 4-fold excess of $[Mo(CO)_5(THF)]$ (generated in situ by irradiation of a THF solution of $[Mo(CO)_6]$ followed by chromatographic separation gave one major product, isolated as the purple hexafluorophosphate salt. The ^{31}P-NMR spectrum was consistent with a symmetrical product; it exhibited two signals (relative integrals 1:1) one being the characteristic septet of $[PF_6]^-$. The second signal (a singlet, $\delta + 49.6$) was significantly shifted to lower field with respect to $[Fe(\mathbf{1})_2]^{2+}$ ($\delta + 4.9$), consistent with the coordination of the phosphine. The change in chemical shift, $\Delta\delta$ (defined in Table 1) is similar to that observed in going from PPh_3 to $[Mo(CO)_5(PPh_3)]$ (Table 1) [16]. A downfield shift would also accompany oxidation of the PPh_2 groups to $P(O)Ph_2$, but a comparison with the shift of the previously reported $[Fe(tpy\text{-}4'\text{-}P(O)Ph_2)_2]^{2+}$ ($\delta + 30.1$) [9] allowed us to rule out this possibility. In the TOF mass spectrum of the new compound, the highest mass peak at *m*/*z* 1251 is assigned to $[Fe\{(\mu\text{-}\mathbf{1})Mo(CO)_3\}_2]^+$. The presence of carbonyl ligands is apparent in the IR spectrum of the product, and the pattern of ν(CO) absorptions (2074, 1995, 1937 cm^{-1}) coincides closely with those reported for $[Mo(CO)_5(PPh_3)]$ (2074, 1988, 1946 cm^{-1}) [17].

The reaction between $[Fe(\mathbf{1})_2][PF_6]_2$ and a 4-fold excess of $[W(CO)_5(THF)]$ was carried out in a similar manner to that of the molybdenum analogue. The ^{1}H- and ^{31}P-NMR spectra were in accord with a product containing a symmetrical complex cation, although ^{183}W satellites were not observed. In the ^{31}P-NMR spectrum, the observation of the phosphine resonance at $\delta + 32.5$ with a coordination shift $\Delta\delta$ of 27.6 is consistent with coordination to a $W(CO)_5$-unit; the value of $\Delta\delta$ compares well with that observed in going from PPh_3 to $[W(CO)_5(PPh_3)]$ (Table 1) [16]. The TOF-mass spectrum was consistent with a product containing the cation $[Fe\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2]^{2+}$ and showed a parent ion with subsequent CO losses. The IR spectrum showed a set of absorptions which were as expected for a $[W(CO)_5L]$ (L = phosphine) complex [17].

The compound $[Ru(\mathbf{1})_2][PF_6]_2$ reacts with $[Mo(CO)_5(THF)]$ and $[W(CO)_5(THF)]$ in a similar manner to the iron(II) analogue, and the products are formulated on the basis of spectroscopic and mass spectrometric data as $[Ru\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2][PF_6]_2$ and $[Ru\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2][PF_6]_2$, respectively. The highest mass peaks in the ES-MS corresponded to the ions $[Ru\{(\mu\text{-}\mathbf{1})Mo(CO)_3\}_2][PF_6]^+$ and $[Ru\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2]$-$[PF_6]^+$. Electrospray mass spectrometry is proving to be a valuable technique for the characterization of these complexes, and the spectra show well resolved clusters of peaks with the correct isotopomeric distribution for various singly and multiply charged ions. As a typical example, Fig. 1 shows the calculated and observed mass spectra for $[Ru\{(\mu\text{-}\mathbf{1})Mo(CO)_3\}_2]^{2+}$. In addition to a signal due to the $[PF_6]^-$ ion, the ^{31}P-NMR spectrum of $[Ru\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2][PF_6]_2$ exhibited one singlet at $\delta + 49.5$, a shift reminiscent of that observed for $[Fe\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2]^{2+}$ ($\delta + 49.6$). Similarly, the ^{31}P-NMR spectroscopic signal assigned to

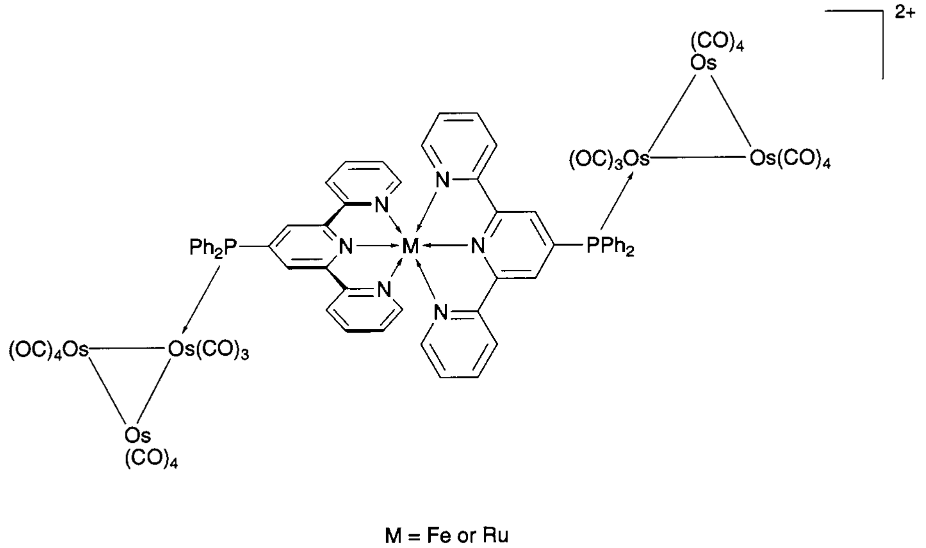


Fig. 4. Proposed structures of $[M\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^{2+}$ (M = Fe or Ru).

$[Ru\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2]^{2+}$ (δ + 32.2) is close to that of $[Fe\{(\mu\text{-}\mathbf{1})W(CO)_5\}_2]^{2+}$ (δ + 32.5) and downfield of $[Ru(\mathbf{1})_2]^{2+}$ (δ + 4.7). These changes in chemical shift upon phosphine coordination are summarized in Table 1 and, when compared with values of $\Delta\delta$ on going from PPh_3 to $[Mo(CO)_5(PPh_3)]$ or $[W(CO)_5(PPh_3)]$, give strong supporting evidence for the coordination of the *P*-donors of $[Ru(\mathbf{1})_2]^{2+}$ to the molybdenum or tungsten centres.

The structures that we propose for the cations $[M\{(\mu\text{-}\mathbf{1})M'(CO)_5\}_2]^{2+}$ (M = Fe or Ru; M′ = Mo or W) are shown in Scheme 1, and an energy-minimized, modelled[2] structure of $[Fe\{(\mu\text{-}\mathbf{1})Mo(CO)_5\}_2]^{2+}$ is illustrated in Fig. 2.

The two iron complexes are electrochemically active and have been studied by cyclic voltammetry. Acetonitrile solutions of $[Fe\{(\mu\text{-}\mathbf{1})M'(CO)_5\}_2][PF_6]_2$ exhibit a reversible iron(II)/(III) process at + 0.76 V (M′ = Mo) and + 0.79 V (M′ = W). In each case, near-reversible ligand-centred reductions at ca. − 1.4, − 1.6 and − 2.0 V are observed (all potentials versus Fc/Fc$^+$). The iron(II)/iron(III) processes are effectively independent of the metal carbonyl substituent and occur at the same potential as in the parent complex $[Fe(\mathbf{1})_2][PF_6]_2$ (+ 0.79 V) [9]. However, the coordination of the phosphine to the metal centre appears to be electronically very similar to oxidation to the phosphine oxide and the ligand-centred reductions are to significantly less negative potential than in the starting iron(II) complex (− 1.54, − 1.69 V); compare − 1.39, − 1.54 V for $[Fe(tpy\text{-}4'\text{-}P(O)Ph_2)_2][PF_6]_2$. This presumably represents a lowering of the ligand LUMO with the development of positive charge at phosphorus.

3.2. Triosmium carbonyl derivatives

Phosphine derivatives of $[Os_3(CO)_{12}]$ are well known [18,19] and a controlled method of synthesis is by the use of $[Os_3(CO)_{11}(NCMe)]$ [11,20] which contains a labile acetonitrile ligand. The addition of $[Fe(\mathbf{1})_2][PF_6]_2$ to an acetonitrile solution of $[Os_3(CO)_{11}(NCMe)]$ led to the formation of a new carbonyl-containing species as evidenced by the IR spectrum of the crude mixture. There was one major product, and its IR spectroscopic signature in the carbonyl region closely resembled that of $[Os_3(CO)_{11}(PPh_3)]$ [20] indicating that an analogous monosubstituted cluster-product had been obtained. The highest mass peaks in the TOF mass spectrum (*m*/*z* 2791 and 2647) corresponded to the ions $[Fe\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2][PF_6]^+$ and $[Fe\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^+$, respectively, providing evidence for the formation of a symmetrical product $[Fe\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^{2+}$.

That both phosphorus atoms of $[Fe(\mathbf{1})_2]^{2+}$ were involved in substitution was evident from the ^{31}P-NMR spectrum of the product which (in addition to the septet assigned to $[PF_6]^-$) exhibited one singlet at δ + 9.0, downfield of that of the free ligand. As Table 1 shows, the difference in chemical shift, $\Delta\delta$, on going from $[Fe(\mathbf{1})_2]^{2+}$ to $[Fe\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^{2+}$ is only 4.1 as compared to a significantly larger value for the mononuclear molybdenum and tungsten complexes. However, a similarly small $\Delta\delta$ value is observed in going from PPh_3 to $[Os_3(CO)_{11}(PPh_3)]$ (Table 1) [21].

A similar reaction occurs between $[Ru(\mathbf{1})_2]^{2+}$ and $[Os_3(CO)_{11}(NCMe)]$ and the product, isolated as the hexafluorophosphate salt in good yield, is formulated as $[Ru\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^{2+}$. Once again, this formulation is supported by mass spectrometric, IR and NMR spectroscopic data; the ^{1}H-NMR spectrum of the product is shown in Fig. 3. The ^{31}P-NMR spectrum is

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[2] Calculations were performed using Molecular Simulations Cerius^2 ™ software.

particularly diagnostic (Table 1). The proposed structures of $[M\{(\mu\text{-}\mathbf{1})Os_3(CO)_{11}\}_2]^{2+}$ (M = Fe or Ru) are shown in Fig. 4. To date, we have been unable to grow X-ray quality crystals of these compounds.

4. Conclusions

In this study, we have shown that the phosphine-functionalized complexes $[Fe(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{1})_2]^{2+}$ undergo substitution reactions with metal carbonyls which possess labile ligands. Our approach has allowed the preparation of metal carbonyl-functionalized coordination complexes, and we are presently extending the study to related systems.

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References

[1] D. Armspach, E.C. Constable, C.E. Housecroft, M. Neuburger, M. Zehnder, Supramol. Chem. 7 (1996) 97.

[2] D. Armspach, E.C. Constable, C.E. Housecroft, M. Neuburger, M. Zehnder, New J. Chem. 20 (1996) 331.

[3] D. Armspach, M. Cattalini, E.C. Constable, C.E. Housecroft, D. Phillips, Chem. Commun. (1996) 1823.

[4] D. Armspach, E.C. Constable, F. Diederich, C.E. Housecroft, J.F. Nierengarten, Chem. Commun. (1996) 2009.

[5] D. Armspach, E.C. Constable, C.E. Housecroft, M. Neuburger, M. Zehnder, J. Organomet. Chem. 550 (1998) 193.

[6] E.C. Constable, C.E. Housecroft, M. Cattalini, D. Phillips, New J. Chem. 22 (1998) 193.

[7] D. Armspach, E.C. Constable, F. Diederich, C.E. Housecroft, J.F. Nierengarten, Chem. Eur. J. 4 (1998) 723.

[8] E.C. Constable, C.E. Housecroft, L.A. Johnston, Inorg. Chem. Commun. 1 (1998) 68.

[9] E.C. Constable, C.E. Housecroft, M. Neuburger, A.G. Schneider, M. Zehnder, J. Chem. Soc. Dalton Trans. (1997) 2427.

[10] E.C. Constable, A.M.W. Cargill Thompson, D.A. Tocher, New J. Chem. 16 (1992) 855.

[11] J.N. Nicholls, M.D. Vargas, Inorg. Synth. 28 (1990) 232.

[12] A. Muth, O. Walter, G. Huttner, A. Asam, L. Zsolnai, Ch. Emmerich, J. Organomet. Chem. 468 (1994) 149.

[13] E.C. Constable, A.M.W. Cargill Thompson, P. Harverson, L. Macko, M. Zehnder, Chem. Eur. J. 1 (1995) 360.

[14] G.R. Dobson, I. Stolz, R.K. Sheline, Adv. Inorg. Chem. Radiochem. 8 (1966) 1.

[15] See for example: W. Strohmeier, K. Gerlach, Chem. Ber. 94 (1961) 398; W. Strohmeier, D. von Hobe, Chem. Ber. 94 (1961) 2031.

[16] S.O. Grim, D.A. Wheatland, W. McFarlane, J. Am. Chem. Soc. 89 (1967) 5573.

[17] T.A. Magee, C.N. Matthews, T.S. Wang, J.H. Wotiz, J. Am. Chem. Soc. 83 (1961) 3200.

[18] R.D. Adams, J.P. Selegue, in: E.W. Abel, F.G.A. Stone G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 4, Ch. 33, Pergamon, Oxford, 1982, p. 967.

[19] A.J. Deeming, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprensive Organometallic Chemistry II, vol. 4, Ch. 12, Pergamon, Oxford, 1995, p. 683.

[20] B.F.G. Johnson, J. Lewis, D.A. Pippard, J. Chem. Soc. Dalton Trans. (1984) 407.

[21] V.D. Alexiev, N.J. Clayden, S.L. Cook, C.M. Dobson, J. Evans, D.J. Smith, J. Chem. Soc. Chem. Commun. (1986) 938.