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Ionic and covalent mixed-metal complexes by reaction of transition metal M-H acids (M = Mo, Mn, Fe, Co) with [Ir(PMe₃)₄CH₃] or [Rh(PMe₃)₃CH₃] and structurally related Rh-M and Ir-M heterobimetallics (M = Mn, Fe, Ru)

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Dedicated to Professor Dr. Pierre Braunstein.

Abstract

Treatment of $[Ir(PMe_3)_4CH_3]$ with equimolar quantities of the carbonyl hydrides $[M(CO)_nH]$ (M = Mn, Co; n = 5, 4) or $[CpM(CO)_nH]$ (M = Mo, Fe; n = 3, 2) resulted in clean protonation of the d⁸ substrate producing *cis*- $[Ir(PMe_3)_4(H)(CH_3)][X]$, where X⁻ = $[Mn(CO)_5]^-$ (1), $[Co(CO)_4]^-$ (2), $[CpMo(CO)_3]^-$ (3), and $[CpFe(CO)_2]^-$ (4), respectively. Combination of $[Rh(PMe_3)_3CH_3]$ with $[Mn(CO)_5H]$ furnished $[(Me_3P)_3Rh(\mu-CO)_2Mn(CO)_3PMe_3]$ (5), which was also isolated from the salt elimination reaction between $[Rh(PMe_3)_4]Cl$ and $Na[Mn(CO)_5]$. $[(Me_3P)_2Rh(\mu-CO)_2Fe(PMe_3)Cp]$ (6), $[(Me_3P)_3Ir(\mu-CO)_2Fe(P-Me_3)Cp]$ (7), and $[(Me_3P)_3Ir(\mu-CO)_2Ru(PMe_3)Cp]$ (8) were obtained similarly by reacting $[Rh(PMe_3)_4]Cl$ or $[Ir(PMe_3)_4]Cl$ with the potassium salts $K[CpM(CO)_2]$ (M = Fe, Ru). The crystal structure analysis of 3 demonstrates that in the solid state the hexacoordinate $[Ir(PMe_3)_4(H)(CH_3)]^+$ cation and its $[CpMo(CO)_3]^-$ counterion exist as well-separated ion pairs. The structures of 5-8 comprise $(Me_3P)_nRh$ (n = 3, 2) or $(Me_3P)_3Ir$ groups attached to $Mn(CO)_3PMe_3$ or $M(PMe_3)Cp$ fragments (M = Fe, Ru) by doubly carbonyl-bridged metal–metal bonds of normal length: Rh–Mn, 2.6695(14); Rh–Fe, 2.5748(6); Ir–Fe, 2.6470(7); Ir–Ru, 2.7348(14) Å.

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1. Introduction

While E–H acids of the main group elements with bond polarities as disparate as C–H and Cl–H are well known for their aptitude to oxidatively add to coordinatively unsaturated complexes of e.g., Rh(I), Ir(I) or Pt(0) [1], analogous M–H additions of Brønsted-acidic transition metal hydrides [2] are less well documented. Combination of acidic metal carbonyl hydrides or dihydrides, [M(CO)_nH_m] or [CpM(CO)_nH_m], with lowvalent metal complexes [L_nM'X] typically leads to metal-metal-bonded heterobimetallics with concomitant loss of HX. Illustrative examples include the formation of [CpW(CO)₃Re(CO)₃(diars)], [CpM(CO)(µ- $CO_2M'(PPh_3)_2$] (M = Cr, Mo, W; M' = Rh, Ir) or $[CpMo(CO)_3Co(CO)_4]$ in the reactions occurring between the M-H acids $[CpM(CO)_3H]$ [3] and either $[Re(CO)_3(diars)OCH_3]$ [4], $[Rh_2(PPh_3)_4(\mu-OH)_2]$ [5a], $[Ir(CO)(PPh_3)_2CH_3]$ [6], or $[Co(CO)_4X]$ (X = Co(CO)_4, Mn(CO)₄PBu₃) [7]. 'Neutralization' of the dinuclear palladium hydroxide $[Pd_2(PPh_3)_2(C_6H_5)_2(\mu-OH)_2]$ by acidic transition metal hydrides, [CpM(CO)₃H], similarly afforded heterotrimetallic clusters, [Pd2(PPh3)2- $(C_6H_5)_2(\mu-OH)(\mu-CO)_2(\mu_3-CO)MCp]$ (M = Cr, Mo, W), along with water [5b]. The obvious inference to be drawn for the isolation of M-H addition products is that the use of coordinatively unsaturated substrate

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complexes which have no X ligands and/or form particularly strong metal-to-hydrogen bonds might lead to stable complexes directly resulting from $[M(CO)_n H_m]$ or $[CpM(CO)_n H_m]$ oxidative addition. That this is correct is evident from the smooth formation of [CpRe(CO)₂(µ-H)Pt(PPh₃)₂H] [8] and [CpMo- $(CO)_{3}Pt(PPh_{3})_{2}H$ [9] from $[Pt(C_{2}H_{4})(PPh_{3})_{2}]$ and either [CpRe(CO)₂H₂] or [CpMo(CO)₃H]. Moreover, treatment of the iridium chelate complex [Ir{t-BuP(CH₂CH₂CH₂PPh₂)₂Cl] with equimolar [CpM- $(CO)_{3}H$ (M = Mo, W) leads to clean protonation of the d^8 substrate producing [Ir{t-BuP(CH₂CH₂CH₂- PPh_2)₂{(H)(Cl)][CpM(CO)₃], as shown in a previous communication from this laboratory [10]. The latter reaction, which at least in part is driven by the distinct stability of hydridoiridium(III) complexes, appears to depend critically on the electron richness of the Ir(I) substrate complex: While no reaction whatsoever occurs between either [CpMo(CO)₃H] or [CpW(CO)₃H] and trans-[Ir(CO)(PPh₃)₂Cl] [6], proton transfer from the Mo-H or the W-H bond to iridium can be induced readily by substituting additional P donor groups for CO as has been demonstrated for the [Ir{t-BuP(CH₂CH₂CH₂PPh₂)₂Cl/[CpM(CO)₃H] systems investigated earlier [10] and is confirmed further for several [Ir(PMe₃)₄CH₃]/[M(CO)_nH] (M = Mn, Co; n =5, 4) and $[Ir(PMe_3)_4CH_3]/[CpM(CO)_nH]$ (M = Mo, Fe; n = 3, 2) pairs to be described below. For comparative purposes, the reactivity of the methylrhodium compound [Rh(PMe₃)₃CH₃] toward [Mn(CO)₅H] was also studied, as were some salt elimination reactions of Na[Mn(CO)₅] and K[CpM(CO)₂] (M = Fe, Ru) with [Rh(PMe₃)₄]Cl and [Ir(PMe₃)₄]Cl, respectively.

2. Experimental

2.1. General remarks

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. — NMR: JEOL FT-JNM-GX 270 and JEOL FT-JNM-EX 270 (269.9 MHz for ¹H and 109.4 MHz for ³¹P) at 20 ± 2 °C; spectra referenced versus SiMe₄ as internal or versus H₃PO₄ as external standard (downfield positive).—IR: Mattson Polaris.

Published procedures were used for the synthesis of the starting materials PMe_3 [11], $[Ir(PMe_3)_4]Cl$ [12], $[Rh(PMe_3)_4]Cl$ [13], $[Ir(PMe_3)_4CH_3]$ [14], $[Rh(PMe_3)_3 CH_3]$ [15], $Na[Mn(CO)_5]$ [16], $[Ph_3PNPPh_3][Mn(CO)_5]$ [17], $[Ph_3PNPPh_3][Co(CO)_4]$ [18], $[CpMo(CO)_3H]$ [19], and $K[CpM(CO)_2]$ (M = Fe, Ru) [20,21].

2.2. Metal complexes

2.2.1. $[Ir(PMe_3)_4(H)(CH_3)][Mn(CO)_5]$ (1)

A solution of [Mn(CO)₅H], generated by treating $[Ph_3PNPPh_3][Mn(CO)]_5$ (435 mg, 0.59 mmol) with the stoichiometrically required amount of CF₃SO₃H in 30 ml of pentane [22], was filtered over Celite and subsequently condensed in vacuo onto a nitrogen-cooled frozen mixture of [Ir(PMe₃)₄CH₃] (210 mg, 0.41 mmol) and $n-C_5H_{12}$ (10 ml). Warming to ambient temperature with stirring caused the formation of a pale yellow solution together with a colorless precipitate, which was filtered off and thoroughly washed with pentane. Crystallization from acetonitrile/diethyl ether at -20 °C afforded 75 mg (26%) of 1 as colorless to pale yellow needles.—IR (Nujol): 1869, 1905 (CO), 2035 (IrH) cm⁻¹; (CH₃CN): 1850, 1898 cm⁻¹ (CO). $^{-1}$ H NMR (CD₃CN): $\delta = -13.31$ (dq, trans-²J(P,H) = 138, $cis^{-2}J(P,H) = 20$ Hz; IrH; hydride-to-methyl coupling not resolved), -0.01 (ddq; ${}^{3}J(H,H) \cong 1$, trans-³-J(P,H) = 4, $cis^{-3}J(P,H) = 8$ Hz; IrCH₃), 1.44 (d, $^{2}J(P,H) = 8$ Hz; 1 P(CH₃)₃), 1.59 (X₉AA'X'₉-t, $\Sigma J(P,H) = 7$ Hz; 2 P(CH₃)₃, mutually *trans*), 1.65 (d, ${}^{2}J(P,H) = 8$ Hz; 1 P(CH₃)₃). $-{}^{31}P\{{}^{1}H\}$ NMR (DMFd₇): $\delta = -67.9$, -67.3 (*ABX*₂ m, *cis*-²*J*(P_A, P_B) = 18 Hz; 2 P(CH₃)₃, trans to H and CH₃), -52.6 (ABX₂ t, $|cis^2 J(P_A, P_X) + cis^2 J(P_B, P_X)| = 38$ Hz; 2 P(CH₃)₃, mutually trans).—Anal. Found: C, 30.38; H, 6.17. Calc. for C₁₈H₄₀IrMnO₅P₄ (707.52): C, 30.56; H, 5.70%.

2.2.2. $[Ir(PMe_3)_4(H)(CH_3)][Co(CO)_4]$ (2)

A procedure analogous to that for **1** was employed, using 435 mg (0.61 mmol) of $[Ph_3PNPPh_3][Co(CO)_4]$ together with 50.0 µl of triflic acid in petroleum ether (10 ml) and 185 mg (0.36 mmol) of $[Ir(PMe_3)_4CH_3]$ in 10 ml of petroleum ether, frozen at -196 °C, as starting materials; colorless microcrystals (from acetonitrile/ diethyl ether); yield 96 mg (39%).—IR (CH₃CN): 1890 cm⁻¹ (CO):—The cation exhibited ¹H and ³¹P{¹H} NMR spectra identical with that of **1**.—*Anal*. Found: C, 29.46; H, 6.14. Calc. for C₁₇H₄₀CoIrO₄P₄ (683.55): C, 29.87; H, 5.90%.

2.2.3. $[Ir(PMe_3)_4(H)(CH_3)][CpMo(CO)_3](3)$

A solution of 115 mg (0.47 mmol) of [CpMo(CO)₃H] in 30 ml of petroleum ether was added dropwise to a vigorously stirred solution of 245 mg (0.48 mmol) of [Ir(PMe₃)₄CH₃] in 20 ml of the same solvent. The product, which separated from solution as a colorless precipitate, was collected by filtration and re-dissolved in 10 ml of acetonitrile. Addition of diethyl ether followed by cooling to -20 °C furnished the complex as pale yellow needles; yield 115 mg (32%).—IR (CH₃CN): 1775, 1899 cm⁻¹ (CO).—¹H NMR (CD₃CN): $\delta = 5.06$ (s; C₅H₅); NMR data of the cation matched those of **1** and **2**.—*Anal.* Found: C, 33.28; H, 6.48. Calc. for $C_{21}H_{45}IrMoO_3P_4$ (757.59): C, 33.29; H, 5.99%.

2.2.4. $[Ir(PMe_3)_4(H)(CH_3)]/CpFe(CO)_2]$ (4)

[CpFe(CO)₂H] was generated by adding a 0.92 ml aliquot of a stock solution made up of 1.0 ml of glacial acetic acid and 0.2 ml of thiophenol in 29 ml of petroleum ether to 115 mg (0.53 mmol) of K[CpFe(CO)₂] suspended in 20 ml of petroleum ether [23]. The resulting mixture was filtered over Celite and the filtrate was condensed onto a frozen solution of 245 mg (0.48 mmol) of $[Ir(PMe_3)_4CH_3]$ in petroleum ether (5 ml), as described for 1. After warming to room temperature (r.t.), the product precipitated from the reaction mixture as an orange solid, which was collected by filtration and washed with petroleum ether (3×5) ml); yield 200 mg (60%).—IR (CH₃CN): 1790, 1865 (CO) cm⁻¹.—¹H NMR (CD₃CN): 4.46 (s; C₅H₅); ¹H and ${}^{31}P{}^{1}H$ NMR spectra of the cation were as given for 1.—Anal. Found: C, 35.01; H, 6.79. Calc. for C₂₀H₄₅FeIrO₂P₄ (689.54): C, 34.84; H, 6.58%.

2.2.5. $[(Me_3P)_3Rh(\mu-CO)_2Mn(CO)_3PMe_3]$ (5)

- I) A filtered hydrocarbon solution of $[Mn(CO)_5H]$, resulting from the addition of 180 µl (2.05 mmol) of CF₃SO₃H, diluted with 15 ml of pentane, to a suspension of 1.56 g (2.07 mmol) of [Ph₃PNPPh₃][Mn(CO)]₅ in 15 ml of petroleum ether [22], was condensed onto 165 mg (0.48 mmol) of [Rh(PMe₃)₃CH₃] frozen in petroleum ether (15 ml) by cooling with liquid nitrogen. The mixture was then slowly warmed to 25 °C, filtered over Celite, and concentrated to a residual volume of 5 ml. Standing at -20 °C induced the deposition of complex 5 as yellow rhombs containing n-hexane of crystallization, $5 \cdot 1/2C_6H_{14}$; yield 180 mg (58%).
- II) An equimolar mixture of Na[Mn(CO)₅] (220 mg, 1.01 mmol) and [Rh(PMe₃)₄]Cl (450 mg, 1.01 mmol) in 50 ml of THF was stirred for 5 min at r.t. Removal of the volatiles in vacuo left a semi-solid residue, which was re-dissolved in 60 ml of petro-leum ether. Filtration over Celite followed by concentration of the filtrate to 10 ml and standing at -20 °C furnished 510 mg (78%) of yellow crystalline $5 \cdot 1/2C_6H_{14}$.

IR (THF): 1718, 1745, 1870, 1895, 1962 cm⁻¹ (CO).—¹H NMR (C₆D₆): $\delta = 1.03$ (d, ²*J*(P,H) = 5 Hz; 1 P(CH₃)₃), 1.07 (d, ²*J*(P,H) = 9 Hz; 3 P(CH₃)₃).—³¹P{¹H} NMR (C₆D₆): $\delta = -28.1$ (d, ¹*J*(Rh,P) = 147 Hz; RhP); 14.3 (br s; MnP).—*Anal.* Found: C, 37.51; H, 6.89. Calc. for C₁₇H₃₆MnO₅P₄Rh· 1/2C₆H₁₄ (645.27): C, 37.23; H, 6.72%.

2.2.6. $[(Me_3P)_2Rh(\mu-CO)_2Fe(PMe_3)Cp]$ (6)

The preparation was carried out as described for **5** (method II) by treating 450 mg (1.01 mmol) of [Rh(PMe₃)₄]Cl with 220 mg (1.02 mmol) of K[CpFe(CO)₂] in THF for 5 min at ambient conditions. Crystallization of the filtered and evaporated reaction mixture from *n*-hexane at -20 °C furnished the heterobimetallic complex as black–green columns; yield 380 mg (70%).—IR (THF): 1673, 1712 cm⁻¹ (CO).—¹H NMR (THF-d₈): $\delta = 1.06$ (d, ²*J*(P,H) = 7 Hz; 1 P(CH₃)₃), 1.20 (d, ²*J*(P,H) = 7 Hz; 2 P(CH₃)₃), 4.40 (s, C₅H₅).—*Anal.* Found: C, 37.48; H, 6.62. Calc. for C₁₆H₃₂FeO₂P₃Rh (508.09): C, 37.82; H, 6.35%.

2.2.7. $[(Me_3P)_3Ir(\mu-CO)_2Fe(PMe_3)Cp]$ (7)

535 mg (1.00 mmol) of [Ir(PMe₃)₄]Cl and 235 mg (1.09 mmol) of K[CpFe(CO)₂] were combined in THF (40 ml) for 30 min at r.t. The resulting dark green reaction mixture was evaporated to dryness and the remaining solids were extracted into a total of 30 ml of petroleum ether. Filtration of the combined extracts over Celite followed by partial evaporation of the filtrate and cooling to -20 °C gave 455 mg (67%) of 7 as shiny crystals which had a distinct black-green luster in reflected light and a red color in transmitted light. -IR (THF): 1645, 1685 cm⁻¹ (CO). $-^{1}H$ NMR $(C_6D_6): \delta = 1.00 \text{ (d, } {}^2J(P,H) = 8 \text{ Hz}; 1 P(CH_3)_3), 1.27$ $(d, {}^{2}J(P,H) = 7 Hz; 3 P(CH_{3})_{3}), 4.37 (s, C_{5}H_{5}). - {}^{31}P$ NMR (C₆D₆): $\delta = -63.5$ (s; IrP), 44.8 (s, FeP).—*Anal.* Found: C, 33.36; H, 6.22. Calc. for C₁₉H₄₁FeIrO₂P₄ (673.45): C, 33.88; H, 6.14%.

2.2.8. $[(Me_3P)_3Ir(\mu-CO)_2Ru(PMe_3)Cp](8)$

The synthesis followed the procedure outlined before, using 175 mg (0.33 mmol) of [Ir(PMe₃)₄]Cl and 85 mg (0.33 mmol) of K[CpRu(CO)₂] in 25 ml of THF; red crystals (from pentane); yield 55 mg (23%).—IR (THF): 1651, 1688 cm⁻¹ (CO).—¹H NMR (C₆D₆): $\delta = 1.15$ (d, ²*J*(P,H) = 9 Hz; 1 P(CH₃)₃), 1.26 (d, ²*J*(P,H) = 7 Hz; 3 P(CH₃)₃), 4.29 (s, C₅H₅).—³¹P NMR (C₆D₆): $\delta =$ -67.6 (s; IrP), 21.4 (s, FeP).—*Anal.* Found: C, 31.26; H, 5.95. Calc. for C₁₉H₄₁IrO₂P₄Ru (718.67): C, 31.75; H, 5.75%.

2.3. X-ray structure determinations

Single crystals of the salt-like complex 3 (size $0.60 \times 0.20 \times 0.15$ mm) were grown from acetonitrile; the specimens used for the structure analyses of $5 \cdot 1/2C_6H_{14}$ (size $0.35 \times 0.35 \times 0.25$ mm), 6 (size $0.35 \times 0.30 \times 0.30$ mm), 7 (size $0.40 \times 0.40 \times 0.40$ mm), and 8 (size $0.50 \times 0.50 \times 0.40$ mm) were selected from samples that had been recrystallized from petroleum ether. Diffraction measurements were made at -70 ± 2 °C ($5 \cdot 1/2C_6H_{14}$, 6, 7) and at 20 ± 2 °C (3, 8) on Siemens P4 (3, 7, 8) and Philips PW 1100 ($5 \cdot 1/2C_6H_{14}$, 6)

diffractometers using graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å): orientation matrix and unit cell parameters from the setting angles of at least 20 machine-centered medium-angle reflections; collection of the diffraction intensities by $\omega - 2\theta$ scans; data corrected for absorption by ψ scans [24]; 3: $T_{\min} =$ 0.2450, $T_{\text{max}} = 0.4656$; $5 \cdot 1/2C_6H_{14}$: $T_{\text{min}} = 0.6786$, $T_{\text{max}} = 0.7533;$ **6**: $T_{\text{min}} = 0.5940,$ $T_{\text{max}} = 0.6356;$ **7**: $T_{\min} = 0.0736, \ T_{\max} = 0.0966; \ \mathbf{8}: \ T_{\min} = 0.0412, \ T_{\max} =$ 0.1031. The structures were solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing the WINGX package [25] and the relevant programs (SIR-97 [26], SHELXL-97 [27], ORTEP-3 [28], PARST-95 [29]) implemented therein. Carbon-bound hydrogen atoms were included in the final structural models assuming ideal geometry and using appropriate riding models. The position of the hydride ligand in structure 3 was inferred by means of the potential energy minimization procedure of XHYDEX [30]. During subsequent refinement, the Ir-H distance was fixed at 1.6 A in order to maintain a reasonable coordination geometry. The C_5H_5 ligand of complex 3 displayed twofold rotational disorder about the normal to the ring plane, which was accounted for by assigning the respective carbon atoms split occupancies of 0.5 each and treating the disordered rings as idealized pentagons of variable metrics [27]. According to the U'_{ii} s of several of the PMe₃ carbon atoms, rotational disorder about the Ir-P bonds of structure 3 was suggested for these ligands, too, but was ignored during refinement. The C atoms of the trimethylphosphine group attached to rhodium via phosphorus atom P4 in structure $5 \cdot 1/2C_6H_{14}$ were similarly found to be rotationally disordered over two sites, and in this case the disorder was resolved with occupancies of 0.55 and 0.45 for the particular carbon positions. The *n*-hexane of solvation was located on Wyckoff position 2b of the monoclinic $P2_1/n$ cell.—3: $C_{21}H_{45}IrMoO_3P_4$ (757.59); orthorhombic, $P2_12_12_1$, a = 9.729(2), b =15.387(4), c = 19.979(4) Å, V = 2991(1) Å³, Z = 4, $d_{\text{calc}} = 1.682 \text{ g cm}^{-3}$, μ (Mo K α) = 5.096 mm⁻¹; $2.04 \le \Theta \le 27.07^\circ$, 4698 reflections ($-12 \le h \le 8, 0 \le$ $k \le 19, 0 \le l \le 25$) collected (including 797 Friedel pairs), 4503 unique ($R_{int} = 0.0344$); wR = 0.1324 for all data and 317 parameters, R = 0.0542 for 2008 intensities $I > 2\sigma(I)$, $GooF = 0.865. - 5 \cdot 1/2C_6H_{14}$: $C_{17}H_{36}MnO_5$ - $P_4Rh \cdot 1/2C_6H_{14}$ (645.27); monoclinic, $P2_1/n$, a =18.046(2), b = 9.544(1), c = 19.474(4) Å, $\beta = 115.77(3)^{\circ}$, V = 3020.5(8) Å³, Z = 4, $d_{calc} = 1.419$ g cm⁻³, μ (Mo $K\alpha$) = 1.201 mm⁻¹; $3.29 \le \Theta \le 24.04^{\circ}$, 5508 reflections $(-20 \le h \le 18, \ 0 \le k \le 10, \ 0 \le l \le 22)$ collected, 4750 unique ($R_{int} = 0.0631$); wR = 0.0934 for all data and 318 parameters, R = 0.0432 for 2611 intensities $I > 2\sigma(I)$, GooF = 0.921. —6: C₁₆H₃₂FeO₂P₃Rh (508.09); monoclinic, $P2_1/n$, a = 13.123(2), b = 11.229(1), c = 15.609(3) Å, $\beta = 109.97(2)^{\circ}, V = 2161.8(7) \text{ Å}^3, Z = 4, d_{\text{calc}} = 1.561 \text{ g} \text{ cm}^{-3}, \mu(\text{Mo K}\alpha) = 1.661 \text{ mm}^{-1}; 3.08^{\circ} \le \Theta \le 24.06^{\circ},$ 3882 reflections $(-15 \le h \le 14, 0 \le k \le 12, 0 \le l \le 17)$ collected, 3392 unique ($R_{int} = 0.0726$); wR = 0.0510 for all data and 217 parameters, R = 0.0260 for 2681 $I > 2\sigma(I)$, GooF = 0.953.7: intensities $C_{19}H_{41}FeIrO_2P_4$ (673.45); monoclinic, P_{21}/n , a =9.237(2), b = 17.926(3), c = 15.960(3) Å, $\beta = 93.05(2)^{\circ}$, V = 2639.0(9) Å³, Z = 4, $d_{calc} = 1.695$ g cm⁻³, μ (Mo K α) = 5.842 mm⁻¹; 1.71 $\leq \Theta \leq 27.06^{\circ}$, 7739 reflections $(-11 \le h \le 3, 0 \le k \le 22, -20 \le l \le 20)$ collected, 5771 unique ($R_{int} = 0.0339$); wR = 0.0525 for all data and 256 parameters, R = 0.0237 for 4240 intensities $I > 2\sigma(I)$, GooF = 0.818. —8: $C_{19}H_{41}IrO_2P_4Ru$ (718.67); monoclinic, $P2_1/n$, a = 9.383(4), b = 18.127(10), c = 16.044(6) Å, $\beta = 93.01(4)^{\circ}$, V = 2725(2) Å³, Z = 4, $d_{calc} = 1.752$ g cm⁻³, μ (Mo K α) = 5.679 mm⁻¹; 1.70 $\leq \Theta \leq 27.06^{\circ}$, 9159 reflections $(-12 \le h \le 12, -23 \le k \le 0, -20 \le$ $l \le 7$) collected, 5984 unique ($R_{int} = 0.0551$); wR =0.0801 for all data and 256 parameters, R = 0.0332 for 4688 intensities $I > 2\sigma(I)$, GooF = 0.924.

3. Results

The methyliridium(I) complex [Ir(PMe₃)₄CH₃] [14] underwent clean transformation into [Ir(P- $Me_{3}_{4}(H)(CH_{3})[M(CO)_{n}]$ (M = Mn, n = 5: 1; M = Co, n = 4: 2) and [Ir(PMe₃)₄(H)(CH₃)][CpM(CO)_n] (M = Mo, n = 3: 3; M = Fe, n = 2: 4), respectively, when combined with the corresponding carbonyl hydrides $[M(CO)_nH]$ or $[CpM(CO)_nH]$ in 1:1 stoichiometry (Scheme 1). To facilitate isolation of the products, the reactions were conducted in hydrocarbon solution, from which the salt-like complexes precipitated as analytically pure samples. The NMR data of 1-4 (see Section 2) were consistent with the *cis* hydridomethyl structure of the $[Ir(PMe_3)_4(H)(CH_3)]^+$ cation shown in Scheme 1 and, in fact, corresponded in all respects with those



Scheme 1. Oxidative addition of transition metal M-H acids to $[Ir(PMe_3)_4CH_3]$.

previously described by Thorn for the complex salts $[Ir(PMe_3)_4(H)(CH_3)]X(X^- = BF_4^-, PF_6^-)$, which were isolated from oxidative addition of either HBF₄ or HPF₆ to $[Ir(PMe_3)_4CH_3]$ in pyridine or diethyl ether [14].

The formulation of 1-4 as ionic complexes was further confirmed by their conductance values in CH₃CN ($\Lambda = 87$ and $83 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$ for 3 and 4, respectively) as well as by an X-ray structure determination of 3. The orthorhombic unit cell of space group $P2_12_12_1$ contains four $[Ir(PMe_3)_4(H)(CH_3)]^+$ cations accompanied by four well-separated [CpMo(CO)₃]⁻ anions. As evidenced from the interligand bond angles (Fig. 1), the octahedral coordination geometry about iridium is considerably distorted by the steric demand of the four PMe₃ groups and the small size of the hydride ligand. The Ir-P distances, 2.341(4)-2.354(4) Å, reveal no significant dependence on the nature of the trans ligand and fall within the range from 2.31 to 2.38 Å typically spanned by Ir^{III}-PMe₃ bonds opposite to Ir-H, $Ir-sp^3$ -C, or Ir-P in *cis*-octahedral $[Ir(PMe_3)_4$ -(H)(X)⁺ cations (X = CH₂OH, OH, OCH₃, SH) [31– 33]. Large thermal motion of the carbon atoms (see Section 2) caused unrealistic shortening of the Ir-CH₃ bond to an uncorrected value of 2.04(2) Å. Corrected for riding motion [34], the Ir-C bond length was calculated [29] as 2.11(2) Å, close to the 2.123(6)-2.192(7) Å observed for $d(Ir-sp^3-C)$ in other six-coordinate PMe₃-substituted alkyl iridium(III) complexes [32,35-



Fig. 1. Molecular structure of **3** showing the twofold disorder of the C_5H_5 ring (H atoms of Cp and PMe₃ ligands omitted). Selected interatomic distances (Å) and angles (°) for cation: Ir–P1, 2.347(4); Ir–P2, 2.341(4); Ir–P3, 2.342(4); Ir–P4, 2.354(4); Ir–C21, 2.04(2); Ir–H, 1.6 (H position calculated and fixed [30]). P1–Ir–P2, 161.35(15); P1–Ir–P3, 95.59(14); P1–Ir–P4, 96.60(15); P2–Ir–P3, 94.01(15); P2–Ir–P4, 97.68(15); P3–Ir–P4, 97.95(16); P1–Ir–C21, 87.1(7); P2–Ir–C21, 80.7(6); P3–Ir–C21, 169.6(7); P4–Ir–C21, 91.6(7); P1–Ir–H1, 83(2); P2–Ir–H1, 82(1); P3–Ir–H1, 85(2); P4–Ir–H1, 177(2); C21–Ir–H1, 85(2). Anion: Mo–C1, 1.95(2), Mo–C2, 1.89(2); Mo–C3, 1.88(2); C1–O1, 1.19(2), C2–O2, 1.22(2), C3–O3, 1.20(2); Mo-c3, 1.88(2); C1–O1, 1.19(2); Mo···centroid(C4a–C8a), 2.08(2). C1–Mo–C2, 87.6(7); C1–Mo–C3, 85.1(7); C2–Mo–C3, 91.0(6); Mo–C1–O1, 175.8(14); Mn–C2–O2, 177.2(13); Mn–C3–O3, 173.9(15).

38]. The $[CpMo(CO)_3]^-$ counterion adopts piano stool geometry, as expected [39].

In the reactions leading to compounds 1-4, the metal base [Ir(PMe)₄CH₃] interacts with the transition metal M–H acids [M(CO)_nH] and [CpM(CO)_nH]¹ in the same way as with strong mineralic acids such as HBF₄ or HPF₆ [14] to yield [Ir(PMe₃)₄(H)(CH₃)]⁺ as its conjugate acid in a transformation that may be considered to involve oxidative addition of a proton to iridium(I). The clean formation of the products isolated from these oxidative addition reactions mirrors the remarkable stability of *cis*-alkyl(hydrido)iridium(III) species showing no tendency to release alkane by reductive elimination as has been noticed for a number of related examples described before [14,32,40].

A different situation is encountered if the methylrhodium(I) complex $[Rh(PMe_3)_3CH_3]$ [15] is chosen as a substrate. This complex interacts with $[Mn(CO)_5H]$ in petroleum ether by liberation of methane and concomitant formation of a Rh–Mn bond. In addition, trimethylphosphine is partially transferred from rhodium to manganese, producing $[(Me_3P)_3Rh(\mu CO)_2Mn(CO)_3PMe_3]$ (5), accompanied by unidentified by-products. In a more straightforward fashion, heterobinuclear complex 5 is obtained by a salt elimination reaction occurring between $[Rh(PMe_3)_4]Cl$ [13] and Na[Mn(CO)₅] (Scheme 2).

The molecular structure of the 34 VE complex **5** (Fig. 2) reveals two coordinatively saturated metal centers linked by a doubly carbonyl-bridged metal-metal bond. The four-membered RhC₂Mn metallaheterocycle is folded along the Rh-Mn vector, the dihedral angle between the two Rh(μ -CO)Mn planes being 122.4(3)°. The coordination geometries about manganese and rhodium are approximately octahedral (Mn) and close to square-pyramidal (Rh), if metal-metal bonding is ignored. Due to the strong *trans* influence of carbonyl ligands, the Rh-PMe₃ bonds facing the CO bridges in the basal plane of the pyramid are considerably elon-



Scheme 2. Formation of [(Me₃P)₃Rh(µ-CO)₂Mn(CO)₃PMe₃].

¹ $pK_a(MeCN, 25 \circ C) = 19.4, 15.1, 13.9, and 8.4 for [CpFe(CO)_2H], [Mn(CO)_5H], [CpMo(CO)_3H], and [Co(CO)_4H], respectively [3].$



Fig. 2. Molecular structure of 5 showing the rotational disorder of one rhodium-bonded PMe3 ligand (H atoms omitted). Selected bond lengths (Å) and angles (°): Rh-Mn, 2.6695(14); Rh-P2, 2.415(2); Rh-P3, 2.324(2); Rh-P4, 2.413(2); Rh-C1, 1.984(6); Rh-C2, 2.011(8); Mn-P1, 2.312(2); Mn-C1, 2.045(6); Mn-C2, 2.076(8); Mn-C3; 1.798(8); Mn-C4, 1.790(8); Mn-C5, 1.796(8); C1-O1, 1.204(6); C2-O2, 1.190(8); C3-O3, 1.172(8); C4-O4, 1.160(7); C5-O5, 1.163(8). P2-Rh-P3, 97.54(7); P2-Rh-P4, 99.91(7); P3-Rh-P4, 101.15(6); P2-Rh-C1, 86.0(2); P2-Rh-C2, 162.7(2); P3-Rh-C1, 99.5(2); P3-Rh-C2, 98.1(2); P4-Rh-C1, 157.6(2); P4-Rh-C2, 84.3(2); P1-Mn-C1, 82.9(2); P1-Mn-C2, 83.1(2); P1-Mn-C3, 178.8(2); P1-Mn-C4, 89.2(2); P1-Mn-C5, 91.2(2); C1-Mn-C2, 81.0(3); C1-Mn-C3, 97.7(3); C1-Mn-C4, 90.4(3); C1-Mn-C5, 168.1(3); C2-Mn-C3, 98.2(3); C2-Mn-C4, 169.1(3); C2-Mn-C5, 88.1(3); C3-Mn-C4, 89.6(3); C3-Mn-C5, 88.5(3); C4-Mn-C5, 99.8(3); Rh-C1-Mn, 83.0(2); Rh-C2-Mn, 81.5(3); Rh-C1-O1, 138.7(5); Rh-C2-O2, 139.6(5); Mn-C1-O1, 138.3(4); Mn-C2-O2, 138.8(5); Mn-C3-O3, 170.6(6); Mn-C4-O4, 179.3(7); Mn-C5-O5, 177.1(6).

gated (2.413(2) and 2.415(2) Å) in comparison with the distance between rhodium and the apically coordinated phosphine (2.324(2) Å). The length of the Rh-Mn linkage, 2.669(1) Å, is almost identical with that measured $[Cp(i-Pr_3P)Rh(\mu-CO)(\mu-C=$ for CH₂)Mn(CO)Cp] (2.667(1) Å) [41]. In contrast to the also latter complex and at variance with $[(C_5Me_5)Rh(CO)(\mu-CO)_2Mn(CO)Cp]$ [42], featuring distinctly unsymmetric $Rh(\mu-CX)_2Mn$ frameworks (X = O, CH₂) as a consequence of the different 18/16 valence electron configurations of the two metal atoms, the bridging carbonyl ligands of 5 are arranged in an essentially symmetric fashion. Thus, the angles Rh-C-O and Mn–C–O, 138.3(4)–139.6(5) Å, are identical within experimental error, and the values obtained for $d(Mn-\mu-CO)$, 2.045(6) and 2.076(8) Å, differ only slightly from the corresponding distances between the μ -CO groups and rhodium, 1.984(6) and 2.011(8) Å. We, therefore, regard $[(Me_3P)_3Rh(\mu-CO)_2Mn(CO)_3PMe_3]$ as a covalently bonded heterometallic complex with a [17+ 17]-electron configuration rather than an [18+16]electron species with the metals linked by $18 \rightarrow 16$ VE donor bonds of order one [41,42].

When the $[Rh(PMe_3)_4]^+$ cation was combined with $[CpFe(CO)_2]^-$ in place of $[Mn(CO)_5]^-$ as a substituting nucleophile, heterobimetallic [(Me₃P)₂Rh(µ-CO)₂Fe(P-Me₃)Cp] (6) was produced as a result of metal-metal bond formation, phosphine loss and partial transfer of PMe₃ from rhodium to iron (Scheme 3). A perspective view of the molecule is given in Fig. 3. The Rh(µ-CO)₂Fe core possesses a butterfly conformation with a Rh(μ -CO)Fe interplanar dihedral angle of 157.3(2)°. Although most of the differences in the M-µ-CO separations (Rh-C1, 1.996(3); Rh-C2, 2.014(3); Fe-C1, 1.869(3); Fe-C2, 1.925(3) Å) can savely be allotted to the smaller size of the iron atom, there appears to be some asymmetry in the carbonyl bridges to such an extent that the CO ligand bonded through C1 interacts stronger with Fe than with Rh, while the opposite is true for the carbonyl group linked to the two metals via C2. This finding arises from the larger Fe-C1-O1 angle, $142.1(2)^{\circ}$, compared with the value of $134.9(2)^{\circ}$ measured for Rh-C1-O1 and, by similar reasoning, from the smaller angle Fe–C2–O2, $135.5(2)^{\circ}$, set against the Rh-C2-O2 angle of $141.9(2)^{\circ}$. In full agreement with this view, the Rh-P1 bond *trans* to C2, 2.3160(9) Å, is slightly longer than the Rh-P2 linkage opposite C1 (2.3023(10) Å). The complex may therefore be looked upon as a [15+17]-electron compound composed of a 15 VE {Rh(PMe₃)₂CO} fragment and a 17 VE {CpFe(P-Me₃)CO} moiety, both tied together by a Rh-Fe single bond. Within the P2RhC2 framework, the four-coordinate surroundings of the formal 16-electron metal center (Rh-Fe bonding neglected) deviates considerably from planarity, as evidenced from the angle between the normals to the two planes defined by the P1-Rh-P2



Scheme 3. Reactions of $[Rh(PMe_3)_4]^+$ and $[Ir(PMe_3)_4]^+$ cations with $[CpM(CO)_2]^-$ (M = Fe, Ru).



Fig. 3. Molecular structure of **6**. Selected interatomic distances (Å) and angles (°): Rh–Fe, 2.5748(6); Rh–P1, 2.3160(9); Rh–P2, 2.3023(10); Rh–C1, 1.996(3); Rh–C2, 2.014(3); Fe–P3, 2.1695(11); Fe–C1, 1.869(3); Fe–C2, 1.925(3); Fe···centroid(C3–C7), 1.736(4). P1–Rh–P2, 98.68(3); P1–Rh–C1, 86.16(9); P1–Rh–C2, 160.84(11); P2–Rh–C1, 151.47(11); P2–Rh–C2, 92.45(10); P3–Fe–C1, 89.09(11); P3–Fe–C2, 88.52(11); P3–Fe···centroid(C3–C7), 125.2(2); C1–Fe–C2, 98.42(13); C1–Fe···centroid(C3–C7), 123.4(2); C2–Fe···centroid(C3–C7), 122.7(2); Rh–C1–Fe, 82.97(12); Rh–C2–Fe, 82.06(13); Rh–C1–O1, 134.9(2); Rh–C2–O2, 141.9(2); Fe–C1–O1, 142.1(2); Fe–C2–O2, 135.5(2).

and C1-Rh-C2 fragments, $32.6(2)^{\circ}$, which is much larger than the limiting value of 0° for planar coordination. A comparison of the Rh–Fe distance, 2.5748(6) Å, with previous data is difficult, since there are only few structurally characterized RhFe heterobimetallics containing carbonyl-bridged but otherwise unsupported Rh-Fe linkages. In any case, the metal-metal bond length determined for 5 is much shorter than the Rh–Fe separations in [(Ph₂PC₂H₄PPh₂)Rh(µ-C₇H₇)(µ-CO)Fe- $(CO)_2$ (2.762(2) Å [43]) and also significantly shorter than the bonds found in $[(Me_3P)_2Rh(\mu-PBu_2^t)(\mu-PBu_2^t)]$ CO)Fe(CO)₂PMe₃] (2.665(1) Å [44]), [(Ph₃P)Rh(CO){ μ - $P(C_6H_{11}-cyclo)_2\}(\mu-CO)Fe(CO)_2(PPh_3)_2]$ (2.660(1) Å [45]), or $[(RC_5H_4)Fe(\mu-Ph_2PCH_2PPh_2)(\mu-CO)_2RhX_2]$ $(R = H, CH_3; X = Cl, I; average d(Rh-Fe), 2.612 Å$ [46,47]), even though in the latter cases metal-metal bonding is supported by bridging mono- or bidentate phosphorus ligands in addition to CO.

In compound **6** the iron atom achieves a formal 18electron state, while rhodium rests in a coordinatively unsaturated 16-electron environment. The coordinatively saturated [17+17]-electron analogs of RhMn complex **5** with both the Group 9 and the Group 8 metal in the 18-electron state, $[(Me_3P)_3Ir(\mu-CO)_2M(P-Me_3)Cp]$, where M = Fe (7) or Ru (8), were isolated if [Ir(PMe_3)_4]Cl [12] and the respective carbonyl metalate were allowed to interact in 1:1 stoichiometry in THF. The basic structural feature of the two isostructural complexes is a central Ir(μ -CO)₂M core with four-

membered IrC₂M rings which adopt distinctly folded conformations (dihedral angle between the two Ir(µ-CO)M planes, $133.0(2)^{\circ}$ in 7 and $127.7(2)^{\circ}$ in 8, respectively). As evidenced from the metal-µ-CO distances and angles given in the legends to Figs. 4 and 5, the CO bridges show an only small degree of asymmetry, being slightly bent toward the iron and, respectively, ruthenium center. Disregarding the bond to Fe or Ru, the coordination geometry about iridium can be approximated by a distorted square pyramid with the phosphorus atoms P1 and P3 and the carbon atoms of the CO bridges in basal positions. In line with the bonding pattern displayed by [(Me₃P)₃Rh(µ-CO)₂- $Mn(CO)_{3}PMe_{3}$ (vide supra), the lengths of the Ir-PMe₃ linkages opposite the trans bond-weakening carbonyl ligands are considerably longer than the bond between iridium and the phosphine located in the apex of the pyramid: d(Ir-P1) and d(Ir-P3), 2.345(1)-2.351(2) Å; d(Ir-P2), 2.270(2) Å for both compounds. The Ir-Fe separation found for 7, 2.6470(7) Å, matches the range from 2.5672(9) to 2.7178(9) Å reported for several other carbonyl-bridged dinuclear IrFe complexes [48-50]. The Ir-Ru bond in molecule 8, 2.735(1) Å, is much shorter than the 2.8091(3)-2.8892(9) Å recently reported [51] for $[IrH(CO)(\mu-Ph_2PCH_2PPh_2)_2(\mu-CO)Ru(CO)_2]$ and two related cations, [Ir(CO)(µ-Ph₂PCH₂PPh₂)₂(µ-CO)(µ- $(CH_2)Ru(CO)_2$ ⁺ and $[Me_3PIr(CO)(\mu-Ph_2PCH_2PPh_2)_2$ - $(\mu$ -CH₂)Ru(CO)₂]⁺, but compares reasonably well with



Fig. 4. Molecular structure of 7. Selected interatomic distances (Å) and angles (°): Ir–Fe, 2.6470(7); Ir–P1, 2.3445(12); Ir–P2, 2.2699(12); Ir–P3, 2.3462(12); Ir–C1, 2.037(4); Ir–C2, 2.044(4); Fe–P4, 2.1651(16); Fe–C1, 1.921(4); Fe–C2, 1.927(4); Fe···centroid(C3–C7), 1.745(5). P1–Ir–P2, 98.72(4); P1–Ir–P3, 94.89(4); P2–Ir–P3, 101.89(4); P1–Ir–C1, 160.80(12); P1–Ir–C2, 84.12(12); P2–Ir–C1, 98.80(13); P2–Ir–C2, 108.19(13); P3–Ir–C1, 89.13(12); P3–Ir–C2, 149.71(13); P4–Fe–C1, 85.76(14); P4–Fe–C2, 83.57(14); P4–Fe···centroid(C3–C7), 122.1(2); C1–Fe–C2, 89.3(2); C1–Fe···centroid(C3–C7), 128.7(2); C2–Fe···centroid(C3–C7), 131.9(2); Ir–C1–Fe, 83.9(2); Ir–C2–Fe, 83.5(2); Ir–C1–O1, 140.1(3); Ir–C2–O2, 139.3(3); Fe–C1–O1, 135.9(3); Fe–C2–O2, 136.7(3).



Fig. 5. Molecular structure of **8**. Selected interatomic distances (Å) and angles (°): Ir–Ru, 2.7348(14); Ir–P1, 2.347(2); Ir–P2, 2.270(2); Ir–P3, 2.351(2); Ir–C1, 2.033(6); Ir–C2, 2.037(6); Ru–P4, 2.253(2); Ru–C1, 2.032(6); Ru–C2, 2.049(6); Ru ·· centroid(C3–C7), 1.935(7). P1–Ir–P2, 99.72(6); P1–Ir–P3, 95.21(6); P2–Ir–P3, 102.87(7); P1–Ir–C1, 160.1(2); P1–Ir–C2, 84.0(2); P2–Ir–C1, 98.4(2); P2–Ir–C2, 104.5(2); P3–Ir–C1, 88.8(2); P3–Ir–C2, 152.4(2); P4–Ru–C1, 83.8(2); P4–Ru–C2, 82.3(2); P4–Ru ·· centroid(C3–C7), 122.4(3); C1–Ru–C2, 83.2(2); C1–Ru ·· centroid(C3–C7), 131.6(3); C2–Ru ·· centroid(C3–C7), 135.3(3); Ir–C1–Ru, 84.6(2); Ir–C2–Ru, 84.0(2); Ir–C1–O1, 140.2(4); Ir–C2–O2, 140.0(5); Ru–C1–O1, 135.1(4); Ru–C2–O2, 135.8(5).

distances of 2.6985(7) and 2.7727(9) Å, previously found for the Ir(μ -CO)Ru building blocks of two tetranuclear IrRu₃ clusters [52].

4. Discussion

This study has shown that [Ir(PMe₃)₄CH₃] as an electron-rich methyliridium(I) compound interacts with a number of transition metal hydrides in a similar way previously observed for [Ir{(t-BuP(CH₂CH₂as CH₂PPh₂)₂Cl] [10], yielding ionic *cis*-alkyl(hydrido)iridium(III) products, $[Ir(PMe_3)_4(H)(CH_3)]X$ (X⁻ = $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$, $[CpMo(CO)_3]^-$, [CpFe- $(CO)_2]^-$) by oxidative addition of a proton to iridium(I). In these reactions, the hydrido complexes behave as acids [2,3], similar to HCl or HBF₄, which on combination with [Ir{t-BuP(CH₂CH₂CH₂PPh₂)₂}Cl] or [Ir(PMe₃)₄CH₃] afford [Ir{t-BuP(CH₂CH₂CH₂- $PPh_{2}_{2}(H)(Cl)$ [10] and $[Ir(PMe_{3})_{4}(H)(CH_{3})]BF_{4}$ [14], respectively. The existence of the oxidative addition product [Ir(PMe₃)₄(H)(CH₃)]⁺ as a *cis* hydridomethyl compound showing no propensity to reductively eliminate methane is in accord with the outstanding stability of six-coordinate iridium(III) hydrides. The methylrhodium(I) compound [Rh(PMe₃)₃CH₃], on the other hand, does not give [Rh(PMe₃)₃(H)(CH₃)][Mn(CO)₅] on com-

bination with [Mn(CO)₅H] but rather affords $[(Me_3P)_3Rh(\mu-CO)_2Mn(CO)_3PMe_3]$ as a result of methane ejection accompanied by metal-metal bond formation. An important difference between the observed $[Ir(PMe_3)_4(H)(CH_3)]^+$ cation and the presumed $[Rh(PMe_3)_3(H)(CH_3)]^+$ complex is that the former is saturated (18 VE) while the latter is unsaturated (16 VE). Reductive elimination frequently requires initial dissociation of a σ -donor ligand. Hence, the proclivity of the alkyl(hydrido)rhodium(III) complex to release methane most probably originates from its coordinative unsaturation, which is expected to increase the rate of elimination [53]. A more direct route to $[(Me_3P)_3Rh(\mu CO_{2}Mn(CO_{3}PMe_{3}]$ involves the salt elimination reaction of [Rh(PMe₃)₄]Cl with Na[Mn(CO)₅]. Formation of doubly carbonyl-bridged metal-metal bonds and partial transfer of trimethylphosphine from rhodium or iridium to the heterometal giving $[(Me_3P)_nM(\mu-CO)_2M'(P (PMe_3)Cp$ with n = 2 (M = Rh; M' = Fe) or 3 (M = Ir; M' = Fe, Ru) are also common features of several substitution reactions carried out between tetrakis(trimethylphosphine)rhodium cations and –iridium $[M(PMe_3)_4]^+$ and carbonyl(cyclopentadienyl)ferrate and $-ruthenate anions [CpM'(CO)_2]^{-}$.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre CCDC Nos. 183055 (**3**), 183056 ($5 \cdot 1/2C_6H_{14}$), 183057 (**6**), 183058 (**7**), and 183059 (**8**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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