for 25 reflections in the range $10 < \theta < 15°$. The crystal and intensity measurement parameters obtained are summarized in Table I. Background counts were measured at both ends of the scan range with the use of a $\omega$–$2\theta$ scan, equal at each side to one-fourth of the scan range of the peak. As a check on crystal stability, three check reflections were monitored and these showed significant decay (7.5%). Therefore, a linear decay correction was applied.

Lorentz and polarization corrections were applied.[29] An empirical absorption correction based on a series of $\psi$ scans was applied to the data.[30] Relative transmission coefficients ranged from 0.685 to 0.882 with an average value of 0.778.

The structure was solved by the Patterson heavy-atom method which revealed the position of the rhenium atom. The remaining non-hydrogen atoms and the two molecules of acetonitrile were located in succeeding difference Fourier syntheses. Positions of hydrogens on the phenyl and cyclopentadienyl rings were calculated and added to the structure factor calculations, but their positions were not refined. Because the software used handled a maximum of seven scattering factor tables, the hydrogen atoms were included as $^1/_6$ occupancy carbons with fixed $B$ values of 5.0. The four highest peaks in the final difference map (0.7–1.0 e/Å$^3$) were in the vicinity of the rhenium atom (ca. 1.2 Å). The values of the atomic scattering factors were taken from the usual tabulation, and the effects of anomalous dispersion were included.[31] The $R$ factors for the final refinement were $R = 0.038$ and $R_w = 0.052$.[32]

**Acknowledgment.** We thank the Department of Energy for support of this research.

**Registry No.** 2, 80136-84-1; 4, 71763-25-2; 5, 71763-30-9; 6a, 80136-87-4; 6b, 102920-58-1; 6c, 102920-59-2; $7^+PF_6^-$, 80136-89-6; $7^+I^-$, 102920-60-5; $7^+I^-\cdot(CH_3CN)_2$, 102920-61-6; 8, 71763-18-3; 9, 80136-91-0; 10, 102940-14-7; $Ph_3C^+PF_6^-$, 437-17-2; $CH_3SCH_3$, 75-18-3; $CH_3SH$, 74-93-1; $C_6H_5SH$, 108-98-5; $C_6H_5CH_2SH$, 100-53-8.

**Supplementary Material Available:** Stereoscopic views of and tables of crystallographic data (temperature factors and torsion angles) for $7^+I^-\cdot(CH_3CN)_2$ (7 pages); a table of structure factors for $7^+I^-\cdot(CH_3CN)_2$ (9 pages). Ordering information is given on any current masthead page.

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(29) The intensity data were processed as described in *CAD4 and SDP Users Manual*; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/\mathrm{NPI})(C - 2B)$, where $K = 20.17 \times$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, $C$ = total count, and $B$ = total background count. The standard deviation in net intensity is given by $\sigma^2(I) = (K/\mathrm{NPI})[C + 4B + (pI)]$ where $p$ is a factor used to downweight intense reflections.

(30) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallog., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A, 2.2C, and 2.3.1.

(32) The function minimized is $\sum w_i||F_o| - |F_c||^2$ where $w = 1/\sigma^2(F_o)$. The weighted and unweighted residuals are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$.

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# Cationic Molybdenum(IV)- and Tungsten(IV)–Iridium(III) Complexes with Hydride and $\eta^5$:$\eta^1$-Cyclopentadienyl Bridging Ligands. Syntheses and X-ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrH(PMePh_2)_2][BPh_4]$ (M = Mo and W)

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Cations of the type $[IrH_2(\text{solvent})_2L_2]^+$ (1; L = tertiary phosphine) react readily with the hydrido complexes $[MH_2(\eta^5\text{-}C_5H_5)_2]$ (M = W (3) and M = Mo (4)) to afford the dihydrido $\eta^5$:$\eta^1$-cyclopentadienyl-bridged complexes $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrHL_2]^+$ (6, M = W, and 7, M = Mo). The structures of complex cations 6 and 7 in solutions were unambiguously established by $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy. The X-ray crystal structures of the $[BPh_4]^-$ salts of cations 6c and 7c (L = $PMePh_2$) were determined. The two compounds are isomorphous and belong to space group $Cc$; unit-cell dimensions: $a = 10.736$ (1) Å, $b = 18.872$ (2) Å, $c = 26.060$ (2) Å, $\beta = 101.43$ (1)°, $V = 5175$ (1) Å$^3$, and $Z = 4$ for [6c][$BPh_4$] and $a = 10.724$ (2) Å, $b = 18.834$ (2) Å, $c = 26.091$ (3) Å, $\beta = 101.44$ (3)°, $V = 5165$ (2) Å$^3$, and $Z = 4$ for [7c][$BPh_4$]. The structures were refined to $R = 0.045$ and 0.052, respectively. The hydride ligands in [6c][$BPh_4$] were located and refined by least squares. The geometries of the two cations are similar; the interesting difference being the metal–metal distance (W–Ir = 2.706 (1) and Mo–Ir = 2.641 (1) Å). The reaction of 3 with $[IrH_2(\text{acetone})_2(PCy_3)_2]^+$ (1e), however, follows a different well-defined stoichiometry giving 6e, $[WH_3(\eta^5\text{-}C_5H_5)_2]^+$ (11), and $[IrH_5(PCy_3)_2]$ (13e).

## Introduction

The "Lewis acid/Lewis base" coupling reaction has proved to be a very successful approach to the synthesis of heterometallic hydrido-bridged complexes[1] (eq 1). (Usually the acceptor is a cationic solvento complex). The application of this reaction has been extensively investigated in this laboratory.[1–4]

$$\underset{\text{"Lewis base"}}{L_mMH_x} + \underset{\text{"Lewis acid"}}{L'_nM'} \rightarrow \underset{x\,=\,1\text{–}3}{L_mM(\mu\text{-}H)_xM'L'_n} \quad (1)$$

In many cases the product isolated from this type of reaction is not that expected on the basis of eq 1 as, during

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(1) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

(2) Naegeli, R.; Togni, A.; Venanzi, L. M.; Albinati, A. *Organometallics* **1983**, *2*, 926.

(3) Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M.; Albinati, A. *J. Am. Chem. Soc.* **1982**, *104*, 6825.

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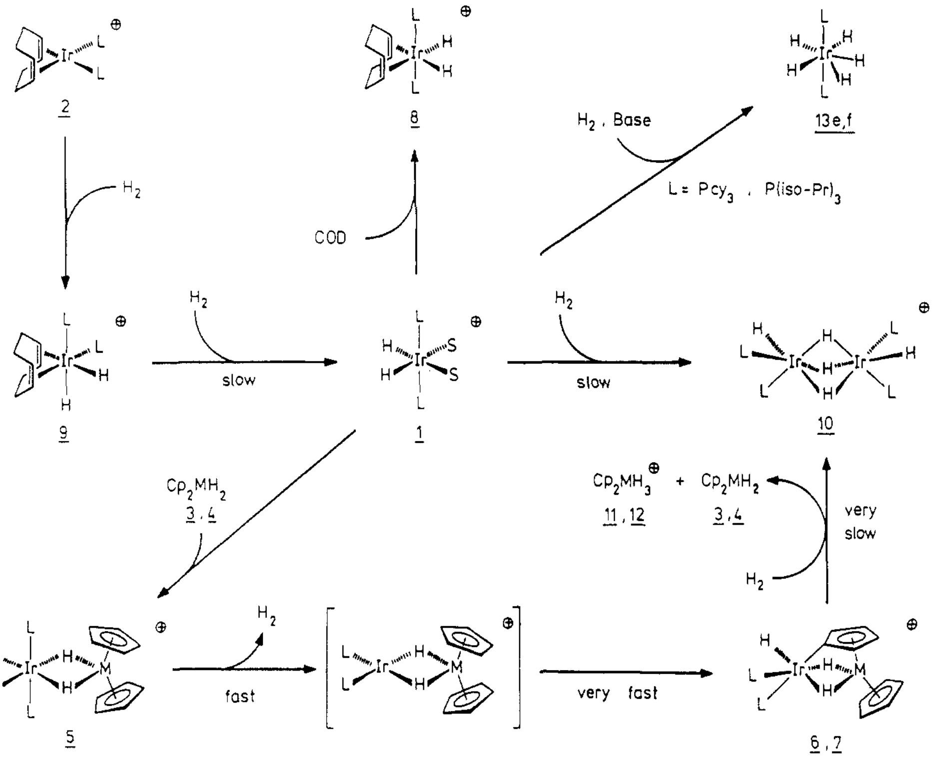
Scheme I



or after the adduct formation, further transformations take place which lead to the final product.

We report here synthetic, spectroscopic, and structural studies of a class of molybdenum(IV)- or tungsten(IV)-iridium(III) cationic complexes in which the *secondary transformation* resulted in the formation of a bridging $\eta^5$:$\eta^1$-cyclopentadienyl moiety. A preliminary account of this work has appeared earlier.[5] A similar reaction has subsequently been reported by Howarth et al.[6]

## Results and Discussion

The reactions of interest are summarized in Scheme I. Cationic complexes of the type *cis,cis,trans*-$[IrH_2(solvent)_2L_2]^+$ (**1**; L = tertiary phosphine) are well-known as alkene hydrogenation catalysts.[7] They are easily generated in situ by reacting cations of the type $[Ir(COD)L_2]^+$ (**2**; L = $PEt_3$, $PMe_2Ph$, and $PMePh_2$) with $H_2$.[8] As reported elsewhere,[5,6] cations **1** readily react, at low temperatures, with $[MH_2(\eta^5\text{-}C_5H_5)_2]$ (M = W (**3**) and M = Mo (**4**)), giving deep green solutions. Howarth et al.[6] have shown that in the case of M = W and L = $PPh_3$ the primary addition product $[(\eta^5\text{-}C_5H_5)_2M(\mu\text{-}H)_2IrH_2(PPh_3)_2]^+$ (**5d**) can be detected spectroscopically at low temperatures. This intermediate decays when the temperature is raised, giving the final cationic products $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4))IrH(PPh_3)_2]^+$ (M = W (**6**) and M = Mo (**7**)), which can be isolated as their $[PF_6]^-$ salts.

As part of a general investigation of bridged hydride formation, we have investigated the reactions of the hydrides $[MH_2(\eta^5\text{-}C_5H_5)_2]$ (M = W (**3**) and M = Mo (**4**)) with a variety of cations of the type *cis,cis,trans*-$[IrH_2(solvent)_2L_2]^+$ (**1**; L = $PEt_3$, $PMe_2Ph$, $PMePh_2$, and $PCy_3$). The yields of the bimetallic products $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4)IrHL_2]^+$ (**6** and **7**) vary considerably depending on the phosphine used, e.g., 31% for L = $PEt_3$ and 80% for L = $PMePh_2$. Furthermore, when yields are low, one can either detect or isolate significant amounts of the corresponding cations of type **8**. These differences are due to variations of the relative distributions of the species formed during the hydrogenation of the starting materials **2**. Crabtree et al.[8] have shown that during this reaction two COD-containing complexes **8** and **9** are formed and that under these experimental conditions the COD in compound **8** is not hydrogenated. Therefore, formation of the solvento complex **1** is not quantitative. Treatment of the mixture of **8** and **9** with $H_2$ for prolonged periods of time, to attempt the quantitative hydrogenation of COD, does not increase the yield of products **6** and **7**. One observes instead the formation of the homobinuclear compound of the type $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$ (**10**)[9] together with the cation $[MH_3(\eta^5\text{-}C_5H_5)_2]^+$ (M = W (**11**) and M = Mo (**12**)).[10] The stoichiometry of the reaction is given in eq 2. In this reaction the cyclopentadienyl hydrides **3** and **4** merely act as Brønsted bases.

$$2\underset{\mathbf{1}}{cis,cis,trans\text{-}[IrH_2(solvent)_2L_2]^+} + \underset{\substack{\mathbf{3},\ M = W\\ \mathbf{4},\ M = Mo}}{[MH_2(\eta^5\text{-}C_5H_5)_2]} + H_2 \rightarrow \underset{\mathbf{10}}{[L_2HIr(\mu\text{-}H)_3IrHL_2]^+} + \underset{\substack{\mathbf{11},\ M = W\\ \mathbf{12},\ M = Mo}}{[MH_3(\eta^5\text{-}C_5H_5)_2]^+} + 2solvent \quad (2)$$

Furthermore, we find that compound **6c** undergoes a further, slow reaction giving compound **10c**. This reaction indicates that, in the presence of $H_2$, the equilibria between **5** and **6** (or **7**) and those between **5** and **1** + **3** (or **4**) are reversible.

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(10) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 4854.

**Table I. $^1$H NMR Parameters of Complexes $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrHL_2]^+$: Hydride Region**[a,b]

| | W | | | | | Mo | |
|---|---|---|---|---|---|---|---|
| | $PEt_3$ (**6a**) | $PMe_2Ph$ (**6b**) | $PMePh_2$ (**6c**) | $PPh_3$[c] (**6d**) | $PCy_3$ (**6e**) | $PMePh_2$ (**7c**) | $PPh_3$[c] (**7d**) |
| $H^1$[d] | −17.6 | −17.6 | −17.4 | −16.6 | −15.0 | −14.3 | |
| $H^2$[e] | −18.9 | −19.1 | −18.6 | −18.3 | −18.5 | −17.0 | −16.9 |
| $H^3$[f] | −23.8 | −23.3 | −23.7 | −24.6 | −27.7 | −22.1 | −22.0 |
| $^2J(H^1,H^2)$ | 3.7 | | 3.7 | | | 5.1 | |
| $^2J(H^1,H^3)$ | 1 | | 1 | | | 5.1 | |
| $^2J(H^2,H^3)$ | 3.7 | | 3.1 | | | 5.1 | |
| $^1J(W,H^1)$ | 95.2 | 90.3 | 96.4 | 92.0 | 90.0 | | |
| $^1J(W,H^2)$ | 92.4 | 90.3 | 90.3 | 90.0 | 78.0 | | |
| $^2J(P^1,H^2)$ | 3.7 | | 7.3 | | | 7 | |
| $^2J(P^2,H^2)$ | 47.6 | 51.3 | 53.7 | 50.0 | 44.0 | 48.6 | 52.0 |
| $^2J(P_1,H_3)$[f] | 28.4 | 28.1 | 29.1 | 27.0 | 25.0 | 29.3 | |
| $^2J(P^2,H^3)$[f] | 16.8 | 17.1 | 17.4 | 17.0 | 18.3 | 17.8 | |

[a] Chemical shifts in ppm; coupling constants in Hz. The spectra were recorded between −30 and −40 °C. [b] The absence of a parameter in one of the columns means that the homodecoupling experiments necessary for a determination or the assignment of the appropriate resonance have not been carried out. [c] Taken from ref 6. [d] $H^1$ is not coupled to the phosphorus atoms, as verified by recording the spectrum under conditions of selective P decoupling. [e] This resonance is assigned to $H^2$ as it shows a splitting of ca. 50 Hz which is indicative of being in trans position to a phosphorus atom.[14] [f] The resonances due to $H^3$ appear as ddd or, as in the case of **7c**, as ddt patterns due to coupling to the two P atoms and $H^2$ or $H^1$ and $H^2$, respectively. The assignment of the $^2J(P,H^3)$ values follows from (a) the $^{31}P$ hydride-decoupled spectrum which allows the assignment of the resonance due to $P^2$, i.e., that in trans position to $H^2$ and (b) the $^1H$ spectrum taken under conditions of selective phosphorus decoupling. The values of $^2J(P,H^3)$ fall in the normal range for $^2J(P,H)_{cis}$ in Ir(III) complexes.[15]

It did not prove possible to isolate intermediate **5**, i.e., to prevent its further reaction to the $\eta^5{:}\eta^1$-$C_5H_4$-bridged complex **6**, even using bulkier phosphine ligands, e.g., $PCy_3$. This system, however, showed another interesting reactivity pattern: $[IrH_2(solvent)_2(PCy_3)_2]^+$ (**1e**) (generated in situ by reacting $[IrH_2Cl(PCy_3)_2]$[11] with 1 equiv of $AgBF_4$) reacts with **3**, and, although the corresponding intermediate **5e** cannot be detected, one observes that the formation of **6e** is accompanied by the simultaneous formation of pentahydride $[IrH_5(PCy_3)_2]$ (**13e**) and of the cation **11**. The stoichiometry of this reaction, which can be followed by isolating the sparingly soluble pentahydride **13e** and by NMR determination of the ratio of the products **6e** and **11** formed, is given by eq 3. The remarkable aspect

$$\underset{\mathbf{3}}{3[WH_2(\eta^5\text{-}C_5H_5)_2]} + \underset{\mathbf{1e}}{3[IrH_2(acetone)_2(PCy_3)_2]^+} \rightarrow \underset{\mathbf{6e}}{2[(\eta^5\text{-}C_5H_5)W(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrH(PCy_3)_2]^+} + \underset{\mathbf{13e}}{[IrH_5(PCy_3)_2]} + \underset{\mathbf{11}}{[WH_3(\eta^5\text{-}C_5H_5)_2]^+} \quad (3)$$

of this reaction is that the pentahydride **13e** and the cation **11** are formed in the absence of an external $H_2$ source and that the required number of hydrogen atoms (or its equivalent in the form of $H_2$ molecules) is provided by the transformation of **1e** into **6e**. A key step in the proposed pathway is the deprotonation of $[IrH_2(acetone)_2(PCy_3)_2]^+$ (**1e**) by $[WH_2(\eta^5\text{-}C_5H_5)_2]$ acting as a Brønsted base. The acidity of compounds of this type had been previously shown by Schrock and Osborn.[12] This hypothesis was tested by reacting **1e** with $H_2$ in the presence of an organic base. This experiment, as shown in eq 4, gave the expected pentahydride. The same reaction was observed when $[IrH_2(acetone)_2(P\text{-}i\text{-}Pr_3)_2]^+$ (**1f**) was used.

$$\underset{\mathbf{1e}}{[IrH_2(acetone)_2(PCy_3)_2]^+} \xrightarrow[\text{ca. }100\%]{H_2,\ NEt\text{-}i\text{-}Pr_2} \underset{\mathbf{13e}}{[IrH_5(PCy_3)_2]} \quad (4)$$

**Table II. $^1$H NMR Chemical Shifts (ppm) of the Cyclopentadienyl Hydrogen Atoms in Complexes $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrHL_2]^+$ (6a–e and 7c,d)**[a]

| complex | M | L | $\eta^5$-$C_5H_5$ | $\mu$-($\eta^5{:}\eta^1$-$C_5H_4$) |
|---|---|---|---|---|
| **6a** | W | $PEt_3$ | 5.33 (5 H) | 6.42 (1 H), 6.36 (1 H), 5.09 (2 H) |
| **6b** | W | $PMe_2Ph$ | 5.32 (5 H) | 6.32 (1 H), 5.73 (1 H), 4.45 (1 H) |
| **6c** | W | $PMePh_2$ | 4.69 (5 H) | 6.60 (1 H), 5.78 (1 H), 4.99 (1 H), 4.89 (1 H) |
| **6d**[b] | W | $PPh_3$ | 4.82 (5 H) | 6.72 (1 H), 5.02 (1 H), 4.76 (1 H), 4.53 (1 H) |
| **6e** | W | $PCy_3$ | 5.59 (5 H) | 6.50 (1 H), 6.31 (1 H), 5.57 (1 H), 5.32 (1 H) |
| **7c** | Mo | $PMePh_2$ | 4.60 (5 H) | 6.08 (1 H), 5.27 (1 H), 4.80 (1 H), 4.69 (1 H) |
| **7d**[b] | Mo | $PPh_3$ | 4.82 (5 H) | 6.29 (1 H), 5.17 (1 H), 4.22 (1 H) |

[a] Each signal appears as a singlet. [b] Data from ref 6.

**Table III. $^{31}$P NMR Parameters[a] and IR Data[b] for the Complex Cations $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrHL_2]^+$ (6a–c,e and 7c)**

| compd | M | L | $P^1$ | $P^2$ | $^2J(P^1,P^2)$ | $\nu$(Ir–$H^3$) |
|---|---|---|---|---|---|---|
| **6a** | W | $PEt_3$ | 6.2 | 4.7 | 11.8 | 2190 |
| **6b** | W | $PMe_2Ph$ | −21.0 | −28.4[c] | 14.7 | 2285 |
| **6c** | W | $PMePh_2$ | 2.1 | −7.0[c] | 11.8 | 2180 |
| **6e** | W | $PCy_3$ | 24.9 | 30.5[c] | 10.8 | 2225 |
| **7c** | Mo | $PMePh_2$ | −2.2 | 1.2 | 11.8 | 2160 |

[a] In ppm and J in Hz. [b] In $cm^{-1}$. These are broad, medium intensity bands. The absorption due to $H^1$ and $H^2$ is not apparent. [c] The $^{31}P$ hydride-coupled spectra, necessary for the assignment of the individual resonances, were not recorded.

These results were expected as Crabtree et al.[13] reported the preparation of compounds $[IrH_5L_2]$ (L = $PPh_3$, $PCy_3$, and $P\text{-}i\text{-}Pr_3$) starting either from $[Ir(COD)L_2]^+$ or $[Ir(COD)pyL]^+$, in the presence of an equivalent of L, and reacting them with $H_2$ and $NEt_3$.

On the other hand, we found that when iridium complexes of the type $[IrH_2(acetone)_2L_2]^+$, containing less bulky phosphines (L = $PEt_3$, $PMePh_2$ and $PPh_3$), were used in reaction 4, the corresponding binuclear complexes $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$ (**9**) were obtained. As the formation of these products can be described on the basis of the "donor–acceptor scheme" outlined earlier, i.e., as shown in eq 5, it can be presumed that, for smaller phosphines,

$$\underset{\mathbf{1}}{[IrH_2(solvent)_2L_2]^+} + \underset{\mathbf{15}}{[IrH_3(solvent)L_2]} \rightarrow \underset{\mathbf{10}}{[L_2HIr(\mu\text{-}H)_3IrHL_2]^+} + 3\text{solvent} \quad (5)$$

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(11) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347.

(12) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.

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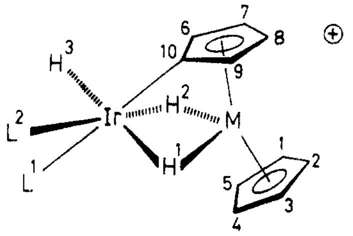
the rates of the reaction of **1** with **15** to give **10** is faster than that for the reaction of **15** with **5** to give **13**, while the converse is true for the bulkier phosphines.

The molecular structures of complexes of type **6** and **7** in solution were fully and unambiguously assigned on the basis of their $^{1}$H, $^{13}$C, and $^{31}$P NMR spectra. The general atom numbering scheme used throughout the text is that given in I. The relevant NMR parameters of these complexes are summarized in Tables I–III. The following observations are worthy of comment: (1) The high values of the $^{1}J$(W,H) coupling constants (ca. 90 Hz) suggest that the W–H interactions remain strong despite the formation of W–H–Ir bridges. (2) With the exception of the Mo compound **7c**, H$^{1}$ is not coupled to H$^{3}$, although the $^{2}J$(H,H)$_{\mathrm{trans}}$ coupling constants in iridium(III) complexes are larger than the corresponding $^{2}J$(H,H)$_{\mathrm{cis}}$ values.[14] Thus, in the case of the tungsten complexes, H$^{1}$ is significantly coupled only to H$^{2}$. However, selective homonuclear decoupling experiments, i.e., irradiation at the H$^{1}$ resonance frequency, result in a sharpening of the H$^{3}$ multiplet showing that, although not detectable, $^{2}J$(H$^{1}$,H$^{2}$) is not zero.



The resonances due to H$^{3}$ appear as ddd or, as in the case of **7c**, as ddt patterns due to coupling to the two P atoms and H$^{2}$ or H$^{1}$ and H$^{2}$, respectively. The assignment of the $^{2}J$(P,H$^{3}$) values follows from (a) the $^{31}$P hydride-decoupled spectrum which allows the assignment of the resonance due to P$^{2}$, i.e., that in transposition to H$^{2}$, and (b) the $^{1}$H spectrum taken under conditions of selective phosphorus decoupling. The values of $^{2}J$(P,H$^{3}$) fall in the normal range for $^{2}J$(P,H)$_{\mathrm{cis}}$ in Ir(III) complexes.[15] The $^{13}$C NMR spectrum of **6a** (M = W; L = PEt$_3$) (see Experimental Section) provides conclusive spectroscopic evidence for the presence of a $\mu$-($\eta^5$:$\eta^1$-C$_5$H$_4$) ligand. Thus, one observes separate resonances for the five nonequivalent C atoms, all of them appearing downfield of the resonance of the carbon of the $\eta^5$-C$_5$H$_5$ unit. The quaternary C atom, C$^{10}$, which is bound to iridium, is coupled to both phosphorus atoms whereas C$^{6}$ and C$^{9}$ are coupled to only one of the P ligands, presumably P$^{1}$. The P–C coupling for C$^{7}$ and C$^{8}$ is barely detectable. The coupling constants for C$^{10}$ are comparable with those observed by Thorn[16] in the formyl complex *cis*-[IrH(CHO)(PMe$_3$)$_4$]$^+$ where that for $^{2}J$(P,C)$_{\mathrm{trans}}$ is 83 Hz and those for $^{2}J$(P,C)$_{\mathrm{cis}}$ are 5.4 and 10 Hz, respectively.

The $^{13}$C chemical shift values of the $\eta^5$:$\eta^1$-C$_5$H$_4$-bonded moieties for several compounds are reported in the literature.[17] However, the resonance of the quaternary carbon atom has been observed only in [(PMe$_2$Ph)($\eta^5$-C$_5$H$_5$)Zr($\mu$-($\eta^5$:$\eta^1$-C$_5$H$_4$))$_2$Zr($\eta^5$-C$_5$H$_5$)(PMe$_2$Ph)] where it resonates at 190.4 ppm,[18] while in **6a** C$^{10}$ resonates at 110.3 ppm.

**Table IV. Relevant Bond Lengths (Å) and Angles (deg) for 6c and 7c (Esd's on the Last Significant Digit Are Given in Parentheses)**

| | 6c (M = W)[a] | 7c (M = Mo) |
|---|---|---|
| | Bond Lengths | |
| M–Ir | 2.706 (1) | 2.641 (1) |
| M–C(1) | 2.34 (2) | 2.33 (2) |
| M–C(2) | 2.23 (2) | 2.20 (2) |
| M–C(3) | 2.27 (2) | 2.27 (2) |
| M–C(4) | 2.37 (2) | 2.30 (2) |
| M–C(5) | 2.34 (2) | 2.34 (2) |
| M–C(6) | 2.28 (2) | 2.30 (2) |
| M–C(7) | 2.39 (2) | 2.32 (2) |
| M–C(8) | 2.34 (2) | 2.36 (2) |
| M–C(9) | 2.26 (2) | 2.24 (2) |
| M–C(10) | 2.13 (1) | 2.15 (2) |
| Ir–C(10) | 2.10 (2) | 1.98 (2) |
| Ir–P(1) | 2.321 (4) | 2.375 (4) |
| Ir–P(2) | 2.260 (4) | 2.306 (4) |
| C(1)–C(2) | 1.44 (3) | 1.40 (4) |
| C(1)–C(5) | 1.42 (4) | 1.35 (3) |
| C(2)–C(3) | 1.38 (3) | 1.37 (3) |
| C(3)–C(4) | 1.49 (3) | 1.50 (3) |
| C(4)–C(5) | 1.44 (3) | 1.43 (3) |
| C(6)–C(7) | 1.43 (3) | 1.43 (3) |
| C(6)–C(10) | 1.44 (3) | 1.47 (3) |
| C(7)–C(8) | 1.42 (3) | 1.46 (3) |
| C(8)–C(9) | 1.43 (2) | 1.43 (3) |
| C(9)–C(10) | 1.43 (3) | 1.48 (2) |
| C–C[b] | 1.44 (4) | 1.39 (3) |
| | Bond Angles | |
| M–Ir–C(10) | 50.8 (2) | 53.0 (1) |
| M–Ir–P(1) | 116.97 (8) | 118.35 (8) |
| M–Ir–P(2) | 136.23 (5) | 138.49 (5) |
| cp$^{a}$–M–cp$^{b}$ [c] | 141.9 (5) | 143.8 (4) |
| Ir–M–cp$^{a}$ | 133.4 (1) | 132.88 (9) |
| Ir–M–cp$^{b}$ | 84.9 (2) | 83.8 (1) |
| Ir–C(10)–M | 79.4 (5) | 79.2 (6) |
| Ir–C(10)–C(6) | 118.7 (8) | 120.4 (9) |
| Ir–C(10)–C(9) | 119.0 (9) | 119.7 (7) |
| P(1)–Ir–P(2) | 98.8 (1) | 96.1 (1) |
| P(1)–Ir–C(10) | 167.3 (2) | 170.9 (4) |
| P(2)–Ir–C(10) | 93.6 (4) | 93.0 (5) |
| Ir–P(1)–C(1)P(1) | 112.7 (5) | 110.5 (5) |
| Ir–P(2)–C(7)P(1) | 116.6 (5) | 116.8 (5) |
| Ir–P(1)–C(13)P(1) | 116.4 (6) | 117.3 (5) |
| Ir–P(2)–C(1)P(2) | 116.6 (5) | 115.3 (5) |
| Ir–P(2)–C(7)P(2) | 117.7 (5) | 120.1 (4) |
| Ir–P(2)–C(13)P(2) | 111.8 (6) | 111.6 (6) |
| C–P–C[b] | 103.0 (1.6) | 103.0 (8) |
| C–C–C$_{\mathrm{cp}}$[b] | 107.9 (2.3) | 107.9 (3.0) |

[a] Some relevant parameters (Å) for the H ligands (see Experimental Section) for M = W are as follows: W–H(1), 1.8 (1); W–H(2), 2.1 (1); Ir–H(1), 1.7 (1); Ir–H(2), 2.1 (1); Ir–H(3), 1.5 (1). [b] Average values. Their esd's are calculated from the formula $\sigma = (\sum(x_i - \bar{x})^2/n - 1)^{1/2}$. [c] cp$^{a}$ and cp$^{b}$ are the centroids of the $\eta^5$- and $\eta^5$:$\eta^1$-cyclopentadienyl rings respectively.

## Description of the Structures

The two compounds [**6c**][BPh$_4$] and [**7c**][BPh$_4$] are isomorphous and, as expected, show similar structural features (see Table IV). An ORTEP view of cation **6c** is shown in Figure 1.

The coordination around the iridium atom in both cations is distorted octahedral with C(10) and P(1) trans to each other. The angles P(1)–Ir–C(10), P(1)–Ir–P(2), and P(2)–Ir–C(10) are within the expected range, showing relatively small deviations from ideal geometry.

The coordination around the W atom remains pseudotetrahedral as in the case for other hydrido-bridged complexes containing **3** or **4**.[2,6]

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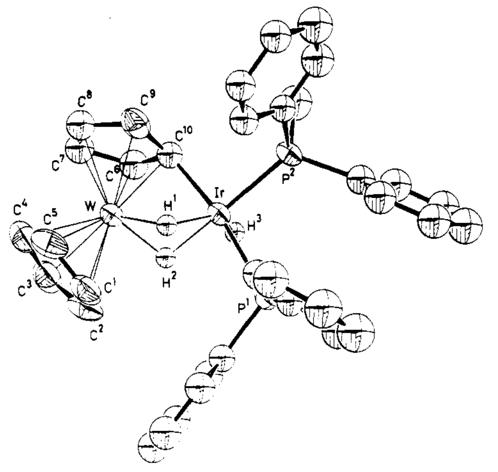

**Figure 1.** An ORTEP view of cation **6c**.

It is noteworthy that in compound **7c** the Ir–C(10) bond length is 1.98 (2) Å although the corresponding M–C distances in related compounds of metals of the second and third transition series, containing $\eta^5$:$\eta^1$-$C_5H_4$-bonded units, is in the range 2.1–2.3 Å, e.g., 2.117 (4) Å in [(CO)($\eta^5$-$C_5H_5$)Mo($\mu$-($\eta^5$:$\eta^1$-$C_5H_4$)Mo($\eta^5$-$C_5H_5$)(CO)$_2$]$^{19}$ and 2.311 (7) Å in [($\eta^5$-$C_5H_4$)Si(Me)$_2$OSi(Me)$_2$($\mu$-($\eta^5$:$\eta^1$-$C_5H_3$))$_2$Nb$_2$H$_2$]$^{2-}$ (**16**).[20] It can, therefore, be concluded that in **7c** the Ir–C interaction is strong.

The M–Ir distances in the Mo compound **7c** and in the W compound **6c** (2.641 (1) and 2.706 (1) Å, respectively) are similar to those found in complexes with two bridging hydride ligands.[1,2,21] Furthermore, in the case of [($\eta^5$-$C_5H_5$)WH($\mu$-H)($\mu$-($\eta^5$:$\eta^1$-$C_5H_4$)IrH(PPh$_3$)(diphos)] (**17**), the W–Ir distance is 3.077 (1) Å as can be expected from the presence of only one bridging hydride ligand.[6] On the other hand, one finds that in complexes bridged only by the $\eta^5$:$\eta^1$-$C_5H_4$ moiety the intermetallic separation is usually much longer, e.g., 2.960 (1) Å in [(CO)($\eta^5$-$C_5H_5$)Mo($\mu$-($\eta^5$:$\eta^1$-$C_5H_4$))Mn(CO)$_4$][22] and 3.932 (1) Å in **16**. This observation is consistent with the shortening effect on M–M distances induced by bridging hydride ligands.[23]

It should also be noted that the M–Ir distances in **6c** and **7c** are significantly different, i.e., 2.706 (1) and 2.641 (1) Å, respectively. As the Mo–C and W–C distances are comparable, one can deduce that their "radii" are also comparable. Thus, the shorter Mo–Ir distance can be taken as an indication that metal–metal interactions are stronger in **7c** than in **6c**.

In both compounds the Ir–P(1) distances are longer than the corresponding Ir–P(2) separation (see Table IV). These may be ascribed to the stronger trans influence[24] of the carbon atom which is $\sigma$-bonded to Ir as compared to the $\mu$-H atom. This observation is in agreement with the Ir–P distances found in **17**:[6] 2.397 (2) Å when trans to a terminal hydride, 2.374 (2) Å when trans to the $\sigma$-bonded carbon atom, and 2.293 (2) Å when the trans ligand is a bridging hydride.

There are also significant differences in the Ir–C(10) and Ir–P distances between the two compounds (see Table IV), and, in particular, the Ir–P bonds are shorter when the M–M distance is longer, i.e., when M = W; this could be caused by a higher electron density at the iridium atom in **7c** resulting from the stronger M–Ir interaction.

## Experimental Section

**A. Synthesis.** All operations were carried out in an atmosphere of purified nitrogen by using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. Elemental analyses were performed by the Microanalytical Section of the Swiss Federal Institute of Technology. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded at 90 and/or 250.132, 62.90, and 36.43 MHz, respectively, using Bruker FT WH 90 and Bruker WM 250 instruments. $^1$H and $^{13}$C chemical shifts are given relative to external $Me_4Si$ whereas $^{31}$P chemical shifts are relative to external 85% $H_3PO_4$. Positive values denote shifts downfield of the reference. Infrared spectra were recorded on a Beckman 4250 spectrophotometer as KBr pellets or Nujol mulls.

The compounds [Ir$_2$Cl$_2$(COD)$_2$],[25] [Ir(COD)(PMePh$_2$)$_2$][PF$_6$],[26] [IrH$_2$Cl(PCy$_3$)$_2$],[13] and [MH$_2$($\eta^5$-$C_5H_5$)$_2$] (M = Mo, W)[27] were prepared by published methods.

**[Ir(COD)(PEt$_3$)$_2$][PF$_6$].** To a stirred suspension of [Ir$_2$Cl$_2$(COD)$_2$] (250 mg, 0.3 mmol) in 50 mL of EtOH was added PEt$_3$ (1.8 mL, 1.2 mmol). The resulting deep red solution was reacted with Ag[BF$_4$] (117 mg, 0.6 mmol, in 5 mL of EtOH), and, after 15 min of stirring, AgCl was filtered off. The addition of NH$_4$[PF$_6$] (114 mg, 0.7 mmol, in 5 mL of EtOH) and the removal of part of the solvent under reduced pressure allowed the isolation of the product as a red microcrystalline solid, which was recrystallized from $CH_2Cl_2$/EtOH (348 mg, 85%). Anal. Calcd for $C_{20}H_{42}F_6IrP_3$: C, 35.24; H, 6.21. Found: C, 34.24; H, 6.28. $^{31}$P NMR (acetone-$d_6$): $\delta$(PEt$_3$) 3.18.

**[Ir(COD)(PMe$_2$Ph)][PF$_6$].** This compound was prepared as described for [Ir(COD)(PEt$_3$)$_2$][PF$_6$]; yield 80%. $^{31}$P NMR (acetone-$d_6$: $\delta$(PMe$_2$Ph) −12.31.

**[($\eta^5$-$C_5H_5$)W($\mu$-H)$_2$($\mu$-($\eta^5$:$\eta^1$-$C_5H_4$))IrH(PEt$_3$)$_2$][PF$_6$] ([6a]-[PF$_6$]).** A vigorously stirred deep red suspension of [Ir(COD)-(PEt$_3$)$_2$][PF$_6$] (539 mg, 0.79 mmol), in 25 mL of EtOH, was cooled to 0 °C, and H$_2$ was bubbled through it for 15 min. A solution of [WH$_2$($\eta^5$-$C_5H_5$)$_2$] (250 mg, 0.79 mmol), in 15 mL of EtOH, was added to the resulting clear pale yellow solution, and stirring was continued for another 30 min. The solvent was then evaporated under reduced pressure (the solution being allowed to cool off) until precipitation began. The mixture was allowed to warm up to room temperature and then cooled down to −22 °C. The green microcrystalline material formed was filtered off and recrystallized again from EtOH; yield 31%. Anal. Calcd for $C_{22}H_{42}F_6IrP_3W$: C, 29.71; H, 4.76. Found: C, 29.71; H, 4.73. $^{13}$C NMR spectral data: $\delta$ 85.5 ($\eta^5$-Cp), $\delta$ 110.3 (C$^{10}$, $^2J$(P$^1$,C$^{10}$) = 84.2 Hz, $^2J$(P$^2$,C$^{10}$) = 8.3 Hz), 95.1 (C$^6$ or C$^9$, $^3J$(P$^1$,C$^{6,9}$) = 7.4 Hz, 93.6 (C$^9$ or C$^6$, $^3J$(P$^1$,C$^{9,6}$) = 5.5 Hz), 91.2 (C$^7$ or C$^8$), 89.9 (C$^8$ or C$^7$), 20.3 and 19.8 (PCH$_2$CH, $^1J$(P,C) = 25 Hz), 8.0, 7.8 (PCH$_2$CH$_3$).

The remainder of the iridium used was in the mother liquor, mostly in the form of *cis,cis,trans*-[IrH$_2$(COD)(PEt$_3$)$_2$][PF$_6$] which could be isolated in impure form by removing more solvent under reduced pressure. $^1$H NMR (acetone-d$_6$): $\delta$ 4.40 (4 H, m, C*H*=CH), 2.45 (8 H, m, C*H$_2$*CH$_2$), 1.4 (12 H, m, PCH$_2$), 0.9 (18 H, m, CH$_3$), −14.2 (2 H, t, IrH). $^{31}$P NMR: $\delta$ −4.72. IR: $\nu$(Ir–H) 2155, 2170 cm$^{-1}$.

**[($\eta^5$-$C_5H_5$)W($\mu$-H)$_2$($\mu$-($\eta^5$:$\eta^1$-$C_5H_4$))IrHL$_2$][PF$_6$] (L = PMe$_2$Ph([6b][PF$_6$]) and L = PMePh$_2$ ([6c][PF$_6$])).** [**6b**][PF$_6$] and [**6c**][PF$_6$] were prepared as described for **6a**; yields 27% and 66%, respectively. Their characterization was based on NMR spectroscopic data (see Tables II and III).

Crystals of the [BPh$_4$] salt, suitable for X-ray diffraction, were obtained by dissolving [**6c**][PF$_6$] in $CH_2Cl_2$, adding 1.1 equiv of Na[BPh$_4$] in MeOH, and cooling the solution to 7 °C.

**[($\eta^5$-$C_5H_5$)W($\mu$-H)$_2$($\mu$-($\eta^5$:$\eta^1$-$C_5H_4$))IrH(PCy$_3$)$_2$][BF$_4$] ([6e][BF$_4$]).** A solution of [IrH$_2$Cl(PCy$_3$)$_2$][11] (247 mg, 0.31 mmol)

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**Table V. Experimental Data for the X-ray Diffraction Studies**

| compd | 6c | 7c |
|---|---|---|
| formula | $C_{60}H_{58}BP_2IrW$ | $C_{60}H_{58}BP_2IrMo$ |
| $M_r$ | 1169.27 | 1081.36 |
| crystal dimens, mm | 0.3 × 0.2 × 0.2 | 0.3 × 0.3 × 0.2 |
| cryst system | monoclinic | |
| space group | *Cc* | |
| $a$, Å | 10.736 (1) | 10.724 (2) |
| $b$, Å | 18.872 (2) | 18.834 (2) |
| $c$, Å | 26.060 (2) | 26.091 (3) |
| $\beta$, deg | 101.43 (1) | 101.44 (9) |
| $Z$ | 4 | 4 |
| $V$, Å$^3$ | 5175 (1) | 5165 (2) |
| $\rho$(calcd), g cm$^{-3}$ | 1.57 | 1.40 |
| $\mu$, cm$^{-1}$ | 49.5 | 29.1 |
| radiatn | Mo K$\bar{\alpha}$ ($\lambda$ = 0.71069 Å) | |
| measd refl | $\pm h,+k,+l$ | |
| $2\theta$ range, deg | 4.5–50.0 | 4.5–50.0 |
| scan type | $\omega/2\theta$ | |
| scan speed, deg s$^{-1}$ | 0.04 | |
| scan width | 1.1 + 0.35 tan $\theta$ | 1.0 + 0.35 tan $\theta$ |
| bkgd time | 0.5 × scan time | |
| receiving aperture | | |
| hor, mm | 1.9 + tan $\theta$ | 2.0 + tan $\theta$ |
| vert, mm | 4.0 | 4.0 |
| no. of independent data | 4736 | 4609 |
| no. of obsd data [$F_o \geq 3\sigma(F_o)$] | 4515 | 4395 |
| R[a] | 0.045 | 0.052 |
| $R_w$[b] | 0.049 | 0.057 |

[a] $R = \sum(|F_o| - |f_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

**Table VI. Final Positional Parameters for $[(\eta^5\text{-}C_5H_5)W(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrH(PMePh_2)_2]^+$ (6c)**

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ir | 0.00000 (0) | 0.18167 (3) | 0.25000 (0) |
| W | −0.05716 (7) | 0.15020 (3) | 0.14667 (3) |
| C(1) | −0.25660 (152) | 0.20125 (139) | 0.11493 (107) |
| C(2) | −0.17574 (171) | 0.20332 (117) | 0.07712 (95) |
| C(3) | −0.15557 (173) | 0.13474 (135) | 0.06197 (69) |
| C(4) | −0.21815 (197) | 0.08365 (105) | 0.09223 (75) |
| C(5) | −0.27583 (156) | 0.12854 (140) | 0.12580 (82) |
| C(6) | 0.14767 (144) | 0.18937 (96) | 0.15833 (78) |
| C(7) | 0.13292 (165) | 0.14723 (93) | 0.11174 (85) |
| C(8) | 0.10248 (172) | 0.07681 (103) | 0.12631 (83) |
| C(9) | 0.09743 (164) | 0.07242 (86) | 0.18036 (81) |
| C(10) | 0.11876 (140) | 0.14246 (78) | 0.20127 (60) |
| P(1) | −0.16675 (38) | 0.21703 (23) | 0.28874 (17) |
| P(2) | 0.16086 (37) | 0.23649 (21) | 0.30469 (17) |
| H(1) | −0.072 (16) | 0.224 (8) | 0.189 (6) |
| H(2) | −0.110 (17) | 0.127 (9) | 0.206 (6) |
| H(3) | 0.001 (16) | 0.101 (8) | 0.280 (6) |
| C(1)P(1) | −0.32318 (174) | 0.18469 (89) | 0.25294 (74) |
| C(2)P(1) | −0.34439 (192) | 0.11269 (108) | 0.25374 (83) |
| C(3)P(1) | −0.45562 (213) | 0.08348 (121) | 0.22677 (90) |
| C(4)P(1) | −0.54479 (194) | 0.12950 (113) | 0.19789 (84) |
| C(5)P(1) | −0.52267 (242) | 0.20189 (139) | 0.19519 (104) |
| C(6)P(1) | −0.41291 (200) | 0.22663 (110) | 0.22299 (84) |
| C(7)P(1) | −0.19162 (162) | 0.31067 (87) | 0.29312 (69) |
| C(8)P(1) | −0.17282 (185) | 0.35662 (97) | 0.25177 (79) |
| C(9)P(1) | −0.19490 (197) | 0.42860 (111) | 0.24802 (84) |
| C(10)P(1) | −0.23340 (249) | 0.45660 (141) | 0.29227 (107) |
| C(11)P(1) | −0.26145 (299) | 0.41953 (171) | 0.33017 (125) |
| C(12)P(1) | −0.24212 (234) | 0.34093 (123) | 0.33502 (98) |
| C(13)P(1) | −0.16635 (204) | 0.18357 (102) | 0.35232 (87) |
| C(1)P(2) | 0.22398 (161) | 0.31795 (81) | 0.27992 (69) |
| C(2)P(2) | 0.15790 (180) | 0.35225 (93) | 0.23466 (77) |
| C(3)P(2) | 0.19948 (190) | 0.41370 (107) | 0.21842 (83) |
| C(4)P(2) | 0.31913 (229) | 0.44272 (128) | 0.24700 (97) |
| C(5)P(2) | 0.38549 (239) | 0.40834 (135) | 0.29030 (103) |
| C(6)P(2) | 0.34001 (218) | 0.34604 (113) | 0.30894 (93) |
| C(7)P(2) | 0.13236 (164) | 0.26571 (91) | 0.36852 (70) |
| C(8)P(2) | 0.07950 (192) | 0.33258 (108) | 0.37338 (82) |
| C(9)P(2) | 0.05319 (259) | 0.35343 (133) | 0.42191 (110) |
| C(10)P(2) | 0.08255 (285) | 0.30788 (154) | 0.46752 (122) |
| C(11)P(2) | 0.13425 (225) | 0.23946 (129) | 0.45780 (98) |
| C(12)P(2) | 0.16230 (218) | 0.22266 (121) | 0.41255 (93) |
| C(13)P(2) | 0.30106 (210) | 0.18018 (107) | 0.32077 (90) |

in acetone (30 mL) was reacted with Ag[$BF_4$] (61 mg, 0.31 mmol). The mixture was stirred for 2 h at room temperature and the precipitated AgCl filtered off. A solution of [$WH_2(\eta^5\text{-}C_5H_5)_2$] (98 mg, 0.31 mmol) in acetone (20 mL) was added to the pale yellow solution obtained above. Removal of the solvent under reduced pressure from the resulting deep green solution resulted in the formation of a white crystalline solid. This was filtered off and identified as [$IrH_5(PCy_3)_2$] (**13e**) by its IR and $^1H$ and $^{31}P$ NMR spectra; yield 24%. MeOH (20 mL) was added to the mother liquor and the solution evaporated slowly under reduced pressure. The product formed upon cooling as olive green microcrystals; yield 20%.

**[$(\eta^5\text{-}C_5H_5)Mo(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4)IrH(PMePh_2)_2][BPh_4]$ ([7c][BPh$_4$]).** [$MoH_2(\eta^5\text{-}C_5H_5)_2$] (69 mg, 0.3 mmol) and [Ir(COD)($PMePh_2)_2$][$PF_6$] (250 mg, 0.3 mmol) were dissolved in acetone (30 mL). $H_2$ was bubbled through the red solution for 20 min. Na[$BPh_4$] (120 mg, 0.35 mmol) in MeOH (30 mL) was added to the resulting green solution which was then evaporated to half of its volume under reduced pressure. The microcrystalline product, obtained by cooling the resulting solution to −78 °C, was filtered off, washed with cold MeOH, and dried; yield: 81%. Crystals suitable for X-ray diffraction were obtained from acetone/MeOH. Anal. Calcd for $C_{60}H_{38}BP_2IrMo$: C, 63.21; H, 5.13; P, 5.43. Found: C, 63.10; H, 5.19; P, 4.32%.

**[$IrH_5(PCy_3)_2$] (13e).** $H_2$ was bubbled through a solution of 0.125 mmol of [$IrH_2(acetone)_2(PCy_3)_2$][$BF_4$] (vide supra) and 22 µl of NEt-*i*-$Pr_2$ (0.125 mmol) in 20 mL of acetone for a period of 10 min, whereupon a sparingly soluble white material was formed. The solution was concentrated under reduced pressure and cooled to 0 °C. The product was collected by filtration, washed with MeOH and $Et_2O$, and vacuum dried; yield 90 mg (95%). $^1H$ NMR ($C_6D_6$): $\delta$(H) −10.46 ($^2J$(P,H) = 12.1 Hz). $^{31}P$ ($C_6D_6$): $\delta(PCy_3)$ +31.7. IR (Nujol): $\nu$(Ir–H) 1940, 1955 cm$^{-1}$.

**[$IrH_5(P\text{-}i\text{-}Pr_3)_2$] (13f).** This complex was prepared analogously to **13e**; yield 87%. $^1H$ NMR (acetone-$d_6$): $\delta$(H) −11.32 ($^2J$(P,H) = 12.1 Hz). $^{31}P$ NMR (acetone-$d_6$): $\delta$(P-*i*-$Pr_3$) +44.7.

**X-ray Measurements.** Suitable crystals of both compounds **6c** and **7c** were obtained as [$BPh_4$]$^-$ salts as described above. They are deep green and air-stable, have a regular prismatic habit, and are isomorphous. They were mounted at a random orientation, on a glass fiber for data collection. Space group and cell constants were determined on a Nonius CAD4/SDP diffractometer, which was subsequently used for data collection. Systematic absences were consistent with space groups *Cc* or *C*2/*c*; the noncentrosymmetric space group *Cc* ($Z$ = 4) was chosen for structure solution and refinement.

Cell constants were obtained by least-squares fit of 25 high-angle reflections, for both compounds (24.0° ≤ $2\theta$ ≤ 30.0°) using the CAD4 centering routines[28] and are listed, along with crystallographic data and relevant parameters for data collection, in Table V.

Three standard reflections, evenly distributed in the reciprocal space, were used to check the stability of the crystals and of the experimental conditions and measured every 100 min.; no significant variations were detected. The orientation of the crystals were checked by measuring three standards every 220 reflections. Data were corrected for Lorentz and polarization factors, and an empirical absorption correction was applied to both sets of data using, in each case, azimuthal ($\Psi$) scans of three reflections. Transmission factors were in the range 0.90–0.99 for **7c** and 0.81–0.94 for **6c**. Data reductions and absorption corrections were carried out by using the programs of the CAD4/SDP package.[28]

Reduced data were considered as observed if $F_o \geq 3\sigma(F_o)$ while an $F_o$ = 0.0 was given to those reflections having negative net intensities.

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(28) *Enraf-Nonius Structure Determination Package, SDP*; Enraf-Nonius: Delft, 1980.

**Table VII. Final Positional Parameters for $[(\eta^5\text{-}C_5H_5)Mo(\mu\text{-}H)_2(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))IrH(PMePh_2)_2]^+$ (7c)**

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Ir | 0.00000 (0) | 0.18160 (2) | 0.25000 (0) |
| Mo | −0.05784 (11) | 0.14998 (6) | 0.14949 (5) |
| C(1) | −0.25741 (155) | 0.20033 (121) | 0.11825 (78) |
| C(2) | −0.17902 (162) | 0.20103 (102) | 0.08138 (87) |
| C(3) | −0.15743 (169) | 0.13353 (129) | 0.06504 (73) |
| C(4) | −0.21657 (173) | 0.08430 (110) | 0.09831 (79) |
| C(5) | −0.27779 (144) | 0.13140 (113) | 0.12864 (81) |
| C(6) | 0.14911 (168) | 0.18952 (103) | 0.16368 (73) |
| C(7) | 0.12719 (179) | 0.14877 (90) | 0.11630 (69) |
| C(8) | 0.10094 (152) | 0.07490 (96) | 0.12826 (74) |
| C(9) | 0.09808 (122) | 0.07378 (74) | 0.18297 (63) |
| C(10) | 0.11752 (126) | 0.14546 (76) | 0.20609 (60) |
| P(1) | −0.16664 (35) | 0.21723 (19) | 0.29229 (14) |
| P(2) | 0.16168 (33) | 0.23682 (20) | 0.30779 (15) |
| C(1)P(1) | −0.32036 (160) | 0.18332 (75) | 0.25650 (66) |
| C(2)P(1) | −0.34547 (154) | 0.11133 (90) | 0.25792 (67) |
| C(3)P(1) | −0.45891 (158) | 0.08383 (88) | 0.23175 (68) |
| C(4)P(1) | −0.54563 (175) | 0.12791 (103) | 0.20121 (75) |
| C(5)P(1) | −0.52381 (193) | 0.19944 (111) | 0.19987 (80) |
| C(6)P(1) | −0.41213 (166) | 0.22860 (93) | 0.22754 (69) |
| C(7)P(1) | −0.19505 (160) | 0.31214 (78) | 0.29585 (66) |
| C(8)P(1) | −0.17039 (157) | 0.35524 (86) | 0.25471 (66) |
| C(9)P(1) | −0.19713 (205) | 0.42730 (118) | 0.25346 (87) |
| C(10)P(1) | −0.23979 (221) | 0.45832 (131) | 0.29660 (97) |
| C(11)P(1) | −0.25830 (237) | 0.42138 (135) | 0.33654 (102) |
| C(12)P(1) | −0.24113 (183) | 0.34106 (108) | 0.33738 (78) |
| C(13)P(1) | −0.16065 (186) | 0.18478 (87) | 0.35869 (78) |
| C(1)P(2) | 0.22319 (151) | 0.31764 (70) | 0.28360 (63) |
| C(2)P(2) | 0.15900 (153) | 0.35137 (87) | 0.23970 (65) |
| C(3)P(2) | 0.20066 (159) | 0.41628 (90) | 0.22212 (68) |
| C(4)P(2) | 0.31608 (171) | 0.44325 (98) | 0.24906 (74) |
| C(5)P(2) | 0.38185 (206) | 0.40972 (115) | 0.29380 (88) |
| C(6)P(2) | 0.33949 (200) | 0.34493 (113) | 0.31056 (84) |
| C(7)P(2) | 0.13624 (152) | 0.26465 (88) | 0.37289 (65) |
| C(8)P(2) | 0.08107 (183) | 0.33204 (101) | 0.37741 (76) |
| C(9)P(2) | 0.05425 (195) | 0.35533 (110) | 0.42543 (83) |
| C(10)P(2) | 0.08151 (229) | 0.30853 (118) | 0.46775 (96) |
| C(11)P(2) | 0.13593 (189) | 0.24149 (108) | 0.46198 (81) |
| C(12)P(2) | 0.16312 (192) | 0.22232 (107) | 0.41720 (80) |
| C(13)P(2) | 0.30435 (234) | 0.17940 (106) | 0.32426 (97) |

Compound **7c** was used for the structure solution, using Patterson and Fourier methods. Both structures were refined by block-diagonal least squares, using a Cruickshank weighting scheme[29] and scattering factors taken from ref 30. Corrections for the real and imaginary parts of the anomalous dispersion[30] were also taken into account for W, Mo, Ir, and P atoms. Anisotropic temperature factors for the metals, phosphorus, and the cyclopentadienyl carbon atoms have been used. The contribution of the ligand H atoms in their calculated positions (C–H = 0.95 Å) was also taken into account but not refined.

Upon convergence Fourier differences were calculated for **6c** and **7c** with various cutoff limits (down to $(\sin\theta)/\lambda = 0.3$ Å$^{-1}$) to search for the positions for bridging and terminal hydrides. For compound **6c** three strong peaks were found in positions consistent with the presence of two bridging and one terminal hydride ligands (W–H in the range 1.8–2.1 Å). Therefore, their positions were refined by least squares. The positional parameters converged satisfactorily even though with high esd's (see Table IV). For compound **7c** the hydride positions were located by using the program HYDEX[31] which minimizes the interaction energy between the hydrides and the other ligands (M–H distances for bridging and terminal hydrides of 1.80 and 1.71 Å, respectively, were assumed). Three potential minima were found for the hydrogen positions consistent with the expected geometry.

The same energy minimization procedure applied to **6c** gave calculated hydride positions in agreement with the values obtained from the Fourier map. The handedness of the crystals of both compounds was tested at the end of the refinement by comparing the *R* factors for the two possible sets of the coordinates.[32] The positional and thermal parameters from the final refinement, giving the lowest *R*'s, for cations **6c** and **7c** are given in Tables VI and VII, respectively.

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**Registry No.** [**2a**][$PF_6$], 78355-43-8; [**2b**][$PF_6$], 102869-80-7; [**2c**][$PF_6$], 38465-86-0; **3**, 1271-33-6; 4, 1291-40-3; [**6a**][$PF_6$], 102869-74-9; [**6b**][$PF_6$], 102869-76-1; [**6c**][$PF_6$], 83210-60-0; [**6c**][$BPh_4$], 103000-78-8; [**6d**]$^+$, 83214-92-0; [**6e**][$BF_4$], 102869-78-3; [**7c**][$BPh_4$], 102920-07-0; [**7d**]$^+$, 83210-57-5; **13e**, 65231-12-1; **13f**, 53470-70-5; $Ir_2Cl_2(COD)_2$, 12112-67-3; $IrH_2Cl(PCy_3)_2$, 67420-58-0.

**Supplementary Material Available:** Tables containing final positional and thermal parameters for **6c** and **7c** and bond lengths and angles (16 pages); tables of observed and calculated structure factors for both structures (37 pages). Ordering information is given on any current masthead page.

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