obtained from $\theta$ values for 15 reflections are $a$ = 15.447 (3), $b$ = 10.908 (3), $c$ = 17.603 (4) Å, $\beta$ = 106.08 (2)°. The calculated density is $d_{\text{calcd}}$ = 1.770 g/cm$^3$ for $Z$ = 4. The space group, derived from systematic absent reflections, is $P2_1/c$.

Intensity data were collected by the $\omega$ scan technique. Lorentz-polarization effects and empirical absorption were corrected ($\mu$ = 46.1 cm$^{-1}$). The absorption correction was based on $\psi$ scan measurements for nine reflections with $\chi$ near 270°. After averaging of equivalent reflections, a total of 4471 independent reflections was obtained of which the 3410 reflections with $I(khl) - 1.96\sigma(I(hkl))$ were used in the subsequent calculations.

The structure was solved by a combination of Patterson and difference Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located in difference Fourier maps. They were not refined; their contributions to $F_c$ were taken into account in the least-squares calculations, however. Scattering factors for neutral atoms were applied. The calculations were done on a Nova 1200 computer using the Syntex XTL program package. The final $R$ values are $R(F)$ = 0.046 and $R_\omega(F)$ = 0.045. Final non-hydrogen atom coordinates are listed in Table IV.

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**Registry No.** **1a**, 72465-79-3; **1b**, 61202-59-3; **2a**·3CH$_2$Cl$_2$, 89362-83-4; **2b**, 89302-66-9; **3a**, 89302-67-0; **3b**, 89302-68-1; **6b**, 89321-17-5; **7b**, 89302-69-2; **8a**, 72465-75-9.

**Supplementary Material Available:** Tables listing anisotropic temperature parameters, atomic coordinates, and structure factors (22 pages). Ordering information is given on any current masthead page.

# Binuclear Tungsten-Iridium Acyl Hydrides, Carbene Hydrides, and Related Complexes. Crystal and Molecular Structures of $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ and $WIrH(\mu\text{-}PPh_2)_2\{C(OMe)Ph\}(CO)_4(PPh_3)$

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Reaction of Li[W(CO)$_5$(PPh$_2$)] with *trans*-IrCl(CO)(PPh$_3$)$_2$ yields the binuclear complex WIr($\mu$-PPh$_2$)(CO)$_6$(PPh$_3$)$_2$ (**1**) which has been spectroscopically characterized. Complex **1** reversibly adds H$_2$ and CO at the Ir center concomitant with reversible dissociation of the W-Ir bond. Reaction of Li[W(CO)$_4$(PPh$_2$H)(PPh$_2$)] with *trans*-IrCl(CO)(PPh$_3$)$_2$ gives the new complex WIrH($\mu$-PPh$_2$)$_2$(CO)$_5$(PPh$_3$) (**2**) which has been structurally characterized. Complex **2** crystallizes in the space group $P2_1/n$ with $a$ = 11.416 (2) Å, $b$ = 19.129 (5) Å, $c$ = 20.673 (3) Å, $\beta$ = 100.78 (2)°, $V$ = 4435 (2) Å$^3$, and $Z$ = 4. The structure was refined to $R$ = 0.0332 and $R_w$ = 0.0347 for the 5433 reflections with $F_o^2 > 3\sigma(F_o)^2$. The W and Ir atoms are separated by 2.876 Å and bridged by two $\mu$-PPh$_2$ ligands. The Ir atom is further coordinated by H (located and refined), PPh$_3$, and one CO, and the W center is ligated by four additional CO's. Complex **2** reacts with PhLi and MeLi to give acyl-hydride derivatives [Li(THF)$_x$][WIrH($\mu$-PPh$_2$)$_2$(CO)$_4$(PPh$_3$){C(O)R}] (R = Ph (**6a**), Me (**6b**)) with the acyl ligand terminally bound to W and the hydride on Ir. These in turn react with [(CH$_3$)$_3$O]BF$_4$ to give the carbene-hydride complexes WIrH($\mu$-PPh$_2$)$_2$(CO)$_4$(PPh$_3$){C(OCH$_3$)R} (R = Ph (**7a**), Me (**7b**)) which have been characterized spectroscopically and (**7a**) by an X-ray diffraction study. The latter crystallizes in the space group $P2_1/n$ with $a$ = 18.773 (4) Å, $b$ = 20.690 (6) Å, $c$ = 12.761 (4) Å, $\beta$ = 95.56 (2)°, $V$ = 4933 (2) Å$^2$, and $Z$ = 4. Convergence for the 3408 reflections with $F_o^2 > 3\sigma(F_o)^2$ occurred to give residuals of $R$ = 0.0504 and $R_w$ = 0.0600. The carbene ligand is terminally bound to W which is further ligated by three CO's. The W-Ir bond (2.858 (1) Å) is bridged by the two PPh$_2$ ligands, and the Ir center is further coordinated by the hydride (not located), PPh$_3$, and one CO. Protonation of **6a** gives a thermally unstable binuclear hydroxycarbene complex which decomposes above 0 °C to release PhCHO. Complex **2** also reacts with Li[BH(*sec*-Bu)$_3$] to give the dihydride anion [WIrH$_2$($\mu$-PPh$_2$)$_2$(CO)$_5$(PPh$_3$)]$^-$ which was spectroscopically characterized. The methyl complex WIrCH$_3$($\mu$-PPh$_2$)$_2$(CO)$_5$(PPh$_3$) (**3**) results from the reaction of Li$_2$[W(CO)$_4$(PPh$_2$)$_2$] with *trans*-IrCl(CO)(PPh$_3$)$_2$ followed by treatment with CF$_3$SO$_3$CH$_3$. Spectroscopic data for **3** imply a structure analogous to **2** with the CH$_3$ ligand bound to Ir.

In our continuing exploration of the chemistry of heterobimetallic complexes,[2] we sought to link together metals with substantially different chemical properties. Particularly interesting would be complexes which combine metals from the left of the transition series (groups 4-6) with Rh and Ir, because of the facility with which these latter metals undergo oxidative-addition/reductive-elimination reactions and because of their catalytic relevance. Tungsten-iridium complexes would seem to be an attractive beginning since these third-low metals should yield stable derivatives amenable to characterization. Furthermore, only a few complexes containing these two

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[1] (a) The Pennsylvania State University. (b) University of Delaware.

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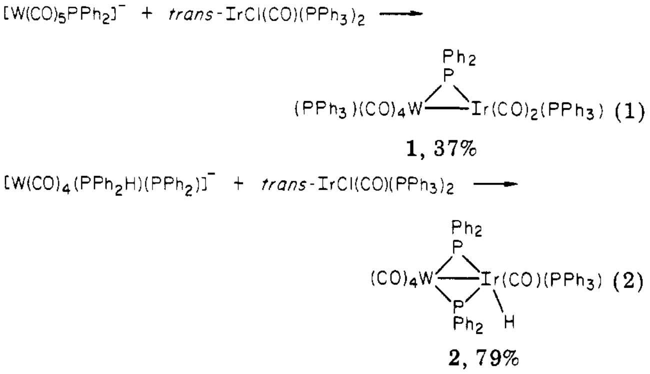
metals have been previously reported, and their chemistry has not been extensively explored.[3]

Described herein are two new sets of binuclear WIr complexes which have one and two phosphido bridges, respectively. The starting point for these studies are the new complexes $WIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ (**1**) and $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (**2**) which were respectively prepared by reactions 1 and 2.[4] Details of the synthesis and characterization of these complexes, including a complete X-ray diffraction study of **2**, are given herein. Complex **1** reversibily adds $H_2$ and CO to give fully characterized derivatives, and from complex **2** a series of novel binuclear acyl–halide and carbene–hydride complexes have been obtained. These have been spectroscopically characterized, and a full X-ray structural analysis of the carbene–hydride complex $WIrH(\mu\text{-}PPh_2)_2(CO)_4(PPh_3)\{C(OMe)Ph\}$ has been completed. The preparation and characterization of a methyl analogue of **2**, $WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (**3**), is also described.



**1**, 37%

**2**, 79%

## Experimental Section

**General.** $W(CO)_5(PPh_2H)$[5] and *trans*-$IrCl(CO)(PPh_3)_2$[6] were prepared by literature procedures. $[CH_3CO][SbCl_6]$ was obtained from Columbia Organic Chemical Co. Solvents and liquid chemicals were dried by standard methods, and all reactions were carried out under a prepurified $N_2$ atmosphere with standard Schlenk techniques. Mass spectra were recorded on a Kratos MS9/50 mass spectrometer operated in either the electron impact (EI) or fast atom bombardment (FAB) mode. IR spectra were obtained on a Perkin-Elmer Model 580 grating IR spectrophotometer using 0.5-mm NaCl IR cells or in KBr disks. NMR spectra were recorded on Bruker WP-200, Bruker WM-360, or JEOL PFT-100 spectrometers. $^{31}P$ NMR spectra are referenced to external 85% $H_3PO_4$ with downfield chemical shifts reported as positive. $Cr(acac)_3$ (1.0 mol %) was added to all $^{13}C$ NMR samples as a shiftless relaxation agent.[7]

**Preparation of $W(CO)_4(PPh_2H)_2$.** This complex[8a] was made by appropriate modification of the literature procedure for the corresponding $PPh_3$ complex.[8b] $W(CO)_6$ (5 g, 14.2 mmol) and $PPh_2H$ (5 mL) in 30 mL of toluene were placed in a 3-oz Fischer & Porter glass pressure reaction bottle under $N_2$ and were heated to 160 °C for 2 days with periodic venting to remove the released CO. The vessel was cooled and the solvent removed under vacuum. The residue was dissolved in $CH_2Cl_2$ and hexane was added until $W(CO)_4(PPh_2H)_2$ began to precipitate. After standing for 1 h in a laboratory freezer, the precipitate was filtered and washed with hexane in air. This gave off-white crystals of $W(CO)_4(PPh_2H)_2$ in 52.6% yield (4.98 g). Spectroscopic data for the complex prepared in this manner are identical to those reported.[8a]

**Preparation of $[WIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2]$ (1).** Methyllithium (1.3 M, 0.49 mL, 0.64 mmol) in $Et_2O$ was added via syringe to a tetrahydrofuran (THF, 30 mL) solution of $W(CO)_5PPh_2H$ (0.3269 g, 0.640 mmol) and *trans*-$IrCl(CO)(PPh_3)_2$ (0.5041 g, 0.647 mmol) at 22 °C. The resultant orange solution was stirred for 1 h, the solvent removed in vacuo, and the product extracted with 30% $CH_2Cl_2$/hexane. Chromatography was conducted on alumina with 30% $CH_2Cl_2$/hexane as eluant. A colorless band containing unreacted $W(CO)_5(PPh_2H)$ eluted first, followed by a yellow band containing $[WIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2]$ which was isolated in 36.8% yield (0.295 g, 0.235 mmol) following solvent evaporation. A yellow-brown band was observed at the top of the column that did not elute. Anal. Calcd for $C_{54}H_{40}IrO_6P_3W$: C, 51.73; H, 3.22. Found. C, 51.61; H, 3.41. **1**: IR $\nu_{CO}$ ($CH_2Cl_2$) 2022 w, 1975 m, 1925 s, 1893 s cm$^{-1}$; MS, *m/e* (FAB) 1254 ($M^+$), 1226 ($M^+ - CO$), 1198 ($M^+ - 2CO$), 1170 ($M^+ - 3CO$), 1142 ($M^+ - 4CO$), 1114 ($M^+ - 5CO$).

**Preparation of $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (2).** Methyllithium (1.3 M, 0.99 mL, 1.29 mmol) in $Et_2O$ was added via syringe to a THF solution (50 mL) of *cis*-$W(CO)_4(PPh_2H)_2$ (0.862 g, 1.29 mmol) and *trans*-$IrCl(CO)(PPh_3)_2$ (0.998 g, 1.28 mmol) at 22 °C. The resultant red-orange solution was stirred for 30 min, the solvent removed in vacuo, and the product extracted into 1:2 $CH_2Cl_2$/hexane. Chromatography was conducted on silica gel with 1:2 $CH_2Cl_2$/hexane as eluant. A colorless band containing $PPh_3$ elutes first, followed by a red-orange band containing $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (**2**), which was isolated as an orange solid in 78.8% yield (1.159 g; 1.01 mmol) by evaporation of solvent. Anal. Calcd for $C_{47}H_{36}IrO_5P_3W$: C, 49.10; H, 3.16. Found: C, 49.12; H, 3.21. **2**: IR $\nu_{CO}$ ($CH_2Cl_2$) 2035 s, 1980 m, 1933 s, 1912 s cm$^{-1}$; MS, *m/e* (FAB) 1149 ($M^+$), 1121 ($M^+ - CO$), 1093 ($M^+ - 2CO$), 1065 ($M^+ - 3CO$), 1037 ($M^+ - 4CO$), 1009 ($M^+ - 5CO$).

**Preparation of $WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (3).** *n*-Butyllithium (1.6 M, 0.420 mL, 0.673 mmol) in hexane was added via syringe to a $Et_2O$ solution of *cis*-$W(CO)_4(PPh_2H)_2$ (0.214 g, 0.320 mmol) while the solution was stirred at 0 °C. The resultant yellow solution was added via transfer needle to a toluene solution of *trans*-$IrCl(CO)(PPh_3)_2$ (0.250 g, 0.320 mmol) at room temperature. The solution became dark red after stirring for 1 h. $CF_3SO_3CH_3$ (76 $\mu$L, 0.673 mmol) was added to the red solution which then lightened in color. The solvent was removed in vacuo, and the residue was extracted with $Et_2O$ until the extracts were colorless. The ether extracts were combined and concentrated, and reddish microcrystals of **3** precipitated upon standing (0.205 g, 0.176 mmol, 55% yield). **3**: IR $\nu_{CO}$ ($CH_2Cl_2$) 2033 s, 2003 m, 1933 s, 1912 s cm$^{-1}$; $^1H$ NMR (benzene-$d_6$, 22 °C) $\delta$ 0.57 (dt, $J_{^{31}P-^1H}$ = 10.3 Hz, 7.88 Hz). Anal. Calcd for $C_{48}H_{38}IrO_5P_3W$; C, 49.53; H, 3.27. Found: C, 49.82; H, 3.53.

**Reaction of 1 with $H_2$.** Exposure of a benzene-$d_6$ solution of **1** (0.050 g, 0.040 mmol) to $H_2$ (1 atm) resulted in an immediate color change from orange to yellow as the product $WIrH_2(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ (**4**) formed in ~90% yield (observed by $^{31}P$ NMR). Removal of the $H_2$ atmosphere by several freeze–pump–thaw cycles quantitatively regenerated $WIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$. **4**: IR $\nu_{CO}$ ($CH_2Cl_2$) 2062 w, 2010 m, 1897 sh, 1873 s cm$^{-1}$.

**Reaction of 1 with CO.** Exposure of a benzene-$d_6$ solution of **1** (0.030 g, 0.024 mmol) to CO (1 atm, 22 °C) resulted in an immediate change in color of the solution from orange to yellow as the product $WIr(\mu\text{-}PPh_2)(CO)_7(PPh_3)_2$ (**5**) formed in ~89% yield (observed by $^{31}P$ NMR) as a mixture of two isomers. Removal of CO by successive freeze–pump–thaw cycles or $N_2$ purge resulted in quantitative regeneration of $WIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$. **5**: IR $\nu_{CO}$ ($CH_2Cl_2$) 2012 w, 1983 s, 1875 s cm$^{-1}$.

**Preparation of $[Li(THF)_x][WIrH(\mu\text{-}PPh_2)_2\{C(O)Ph\}(CO)_4(PPh_3)]$ (6a).** Phenyllithium (1.85 M, 0.45 mL, 0.83 mmol) in cyclohexane/$Et_2O$ was added via syringe to a THF solution

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(5 mL) of **2** (0.500 g, 0.435 mmol) at 22 °C. The solution was stirred for 1 h, the solvent reduced to 2 mL in vacuo, and petroleum ether was added to precipitate $[Li(THF)_x][WIrH(\mu\text{-}PPh_2)_2\{C(O)Ph\}(CO)_4(PPh_3)]$ (**6a**) as an orange microcrystalline solid. This very air-sensitive product was filtered, washed with three 10-mL aliquots of petroleum ether, and dried in vacuo to give **4a** in 96.8% yield (0.55 g, 0.42 mmol). **6a**: IR $\nu_{CO}$ (THF) 1985 s, 1945 s, 1905 s, 1851 s, 1580 w cm$^{-1}$; $^{13}C$ NMR (22 °C, acetone-$d_6$) $\delta$ 286.1 ($C$(O)$CH_3$).

**Preparation of $[Li(THF)_x][WIrH(\mu\text{-}PPh_2)_2\{C(O)CH_3\}(CO)_4(PPh_3)]$ (6b).** Methyllithium (1.3 M, 0.60 mL, 0.78 mmol) in $Et_2O$ was added via syringe to a THF solution (5 mL) of **2** (0.500 g, 0.436 mmol) at 22 °C. The solution was stirred for 1 h, and the solvent was reduced to 2 mL in vacuo. Petroleum ether (30 mL) was added, and $[Li(THF)_x][IrW(H)(\mu\text{-}PPh_2)_2\{C(O)CH_3\}(CO)_4(PPh_3)]$ (**6b**) precipitated as an orange powder. The very air-sensitive product was filtered, washed with three 10-mL aliquots of petroleum ether, and dried in vacuo to give **6b** in 94.7% yield (0.513 g, 0.413 mmol). **6b**: IR $\nu_{CO}$ (THF) 1982 s, 1943 s, 1902 s, 1852 s, 1581 w cm$^{-1}$; $^{13}C$ NMR (22 °C, acetone-$d_6$) $\delta$ 284.7 ($C$(O)$CH_3$).

**Preparation of $WIrH(\mu\text{-}PPh_2)_2\{C(OCH_3)Ph\}(CO)_4(PPh_3)$ (7a).** $[(CH_3)_3O][BF_4]$ in acetone solution (1 mL) was added to an acetone solution (2 mL) of **6a** (0.100 g, 0.077 mmol) at 22 °C. The solution was stirred for 1 h and the solvent removed in vacuo. The product was redissolved in 1:2 $CH_2Cl_2$/hexane and chromatographed on silica gel. Red-orange and orange fractions of **2** and $WIrH(\mu\text{-}PPh_2)_2\{C(OCH_3)Ph\}(CO)_4(PPh_3)$ (**7a**) eluted in that order. Removal of solvent from the orange fraction resulted in the isolation of **7a** as a microcrystalline orange solid (0.039 g, 0.032 mmol, 41.3%). Anal. Calcd for $C_{54}H_{44}IrO_5P_3W$: C, 52.22; H, 3.57. Found: C, 52.53; H, 3.80. **7a**: IR $\nu_{CO}$ (hexane) 2012 w, 1968 m, 1938 s, 1920 m cm$^{-1}$; $^{13}C$ NMR (22 °C, benzene-$d_6$) $\delta$ 298.4 (dd, $C$(OCH$_3$)Ph, $J_{^{13}C-^{31}P}$ = 7.6 Hz, 9.1 Hz, $J_{^{13}C-^{183}W}$ = 123.8 Hz); MS, *m/e* (FAB) 1242 ($M^+$), 1214 ($M^+ - CO$), 1186 ($M^+ - 2CO$), 1158 ($M^+ - 3CO$), 1130 ($M^+ - 4CO$).

**Preparation of $WIrH(\mu\text{-}PPh_2)_2\{C(OCH_3)CH_3\}(CO)_4(PPh_3)$ (7b).** Complex **7b** was prepared in exactly the same manner as **7a** by adding $[(CH_3)_3O]BF_4$ to **6b**, and it was isolated as an orange powder in 56.8% yield. **7b**: IR $\nu_{CO}$ (hexane) 2007 w, 1970 m, 1926 s, 1916 s, 1903 s cm$^{-1}$.

**Reaction of 6a with $CF_3COOH$.** $CF_3COOH$ (0.005 mL, 0.065 mmol) was added via syringe to an acetone-$d_6$ solution (1 mL) of **6a** (0.030 g, 0.022 mmol) at −40 °C in an NMR tube fitted with a rubber septum. The $^{31}P\{^1H\}$ and $^1H$ NMR spectra were immediately recorded and both showed only resonances attributable to $WIrH(\mu\text{-}PPh_2)_2\{C(OH)Ph\}(CO)_4(PPh_3)]$ (**8**). Complex **8** is stable in solution up to 5 °C, but further warmup to 22 °C results in formation of **2** and benzaldehyde (observed by $^1H$ NMR and IR spectroscopy).

**Reaction of 2 with K[BH(*sec*-Bu)$_3$].** K[BH(*sec*-Bu)$_3$] (0.044 mL, 0.044 mmol) in THF was added via syringe to a THF-$d_8$ solution (1 mL) of **2** (0.0507 g, 0.044 mmol) at 22 °C in an NMR tube fitted with a rubber septum. After 48 h, the $^{31}P\{^1H\}$ NMR spectrum displayed resonances for **2** and resonances assigned to $[K(THF)_x][WIrH_2(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)]$ (**9**) (35% conversion by $^{31}P$ NMR integration). No attempt was made to isolate this complex.

**Attempted Reaction of 2 with $H_2$/CO.** $H_2$ (1 atm) was admitted to an acetone-$d_6$ solution (1 mL) of **2** (0.030 g, 0.022 mmol) at room temperature in an NMR tube via a rubber septum. The $^{31}P\{^1H\}$ and $^1H$ NMR spectra were immediately recorded and both showed only resonances attributable to **2**. A benzene-$d_6$ solution (1 mL) of **2** (0.030 g, 0.022 mmol) was added to a Fischer & Porter reaction vessel and pressurized to 90 psig of CO. The solution was stirred at 22 °C for 8 h. The pressure was reduced to 1 atm of CO and the solution transferred to an NMR tube fitted with a rubber septum under a CO atmosphere. The $^{31}P\{^1H\}$ NMR spectrum was recorded and showed only resonances attributable to **2**. A similar reaction in a Parr Model 4753 pressure reactor under 1150 psig of CO at 180 °C for 4 h also gave no detectable reaction as observed by IR spectroscopy of the depressurized solution.

**Attempted Reaction of 2 with $C_2H_4$.** Complex **2** (0.1250 g, 0.1090 mmol) was dissolved in 25 mL of toluene in a Parr Model 4753 pressure reactor and pressurized to 1100 psig with ethylene. No reaction occurred upon stirring at 120–180 °C and 6 h. Irradiation of a glass pressure vessel containing **2** and 80 psig ethylene with an ultraviolet lamp ($\lambda > 300$ mm) for 30 min also gave no reaction.

**Thermolysis of $[WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)]$ (3).** Complex **3** (44.5 mg, 0.0382 mmol) in 20 mL of toluene was heated at reflux for 45 min, during which time the color changed from red to dark red. IR and NMR data obtained on this solution showed the formation of $WIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)(PPh_2Me)$ (**10**). IR (toluene) $\nu_{CO}$ 2012 w, 1970 m, 1920 s, br cm$^{-1}$.

**Preparation of $[WIrCl(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)]$ (11).** $[CH_3CO][SbCl_6]$ (25 mg, 0.068 mmol) was added to a $CH_2Cl_2$ solution of **2** (78 mg, 0.068 mmol) at room temperature. The resulting dark orange solution was stirred for 3 h, the solvent removed in vacuo, and the residue taken up into 5 mL of acetone. Unreacted $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ precipitated upon standing at −10 °C and was removed. Very dark red crystals of **11** precipitated upon standing overnight. These crystals were washed twice with 5 mL of ether to yield **11** in 24% yield (19 mg, 0.016 mmol). Anal. Calcd for $C_{47}H_{35}ClIrO_5P_3W$: C, 47.66; H, 2.98. Found C, 47.85; H, 3.31. IR $\nu_{CO}$ 2045 vs, 2020 s, 1950 vs, 1927 vs cm$^{-1}$.

**X-ray Structure Determination of 2 and 7a.** Crystals of both **2** and **7a** suitable for X-ray diffraction studies were grown by slow diffusion of petroleum ether into saturated $CH_2Cl_2$ solutions of the respective complexes. Diffraction data on both compounds were collected as previously described,[9] with pertinent crystal and intensity data given in Table I. All data were converted to $|F_o|$ values following correction for absorption (empirical $\Psi$-scan technique) and for $Lp$ effects. In both cases systematic absences uniquely defined the monoclinic space groups as $P2_1/n$: $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. A learned-profile procedure was used in the initial data processing to improve the precision in the measurement of weak reflections.

**$WIrH(\mu\text{-}PPh_2)_2(CO)_5(CO)_5(PPh_3)$ (2).** The structure was solved by locating the W and Ir atoms from a Patterson map. A difference map phased on these atoms revealed the locations of all remaining non-hydrogen atoms. Following refinement to convergence for a model which included anisotropic thermal parameters for all non-hydrogen atoms and phenyl ring hydrogen atoms located in fixed, idealized positions ($d$(C–H) = 0.96 Å), the hydride atom H(Ir) was located and refined isotropically. Refinement was by a blocked-cascade, least-squares method to a minimum value of $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$); $w^{-1} = \sigma^2(F) + gF^2$; $g$ was fixed at 0.001. A final difference map revealed only a diffuse background (highest peak = 0.65 $e^-$ Å$^{-3}$). Final positional parameters are collected in Table II.

**$WIrH(\mu\text{-}PPh_2)_2\{C(OMe)Ph\}(CO)_4(PPh_3)$ (7a).** The direct-methods routine SOLV ($R_{min} = 1.8$, $R_{ref} = 0.75$) provided the W and Ir atom locations, and subsequent difference Fourier syntheses phased on these atoms provided all non-hydrogen atom locations. Attempts to locate the hydride hydrogen atom failed. The final refinement process included anisotropic refinement of all non-hydrogen atoms and fixed, idealized hydrogen atom contributions. The hydride ligand was placed in the structure using the H–Ir distance (1.60 Å) and coordination site found in **2** but it was not refined. A final difference map showed no chemically resonable peaks; the highest peak of 0.92 e$^-$ Å$^{-3}$ was located 0.91 Å from the Ir atom followed by a diffuse background at the 0.5–0.7 e$^-$ Å$^{-3}$ level. Final positional parameters are collected in Table III. During all calculations the analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i\Delta f''$ terms. The residuals are defined as $R_f = \sum|\Delta|/\sum|F_o|$ and $R_{wf} = \sum(|\Delta|w^{1/2})/(\sum|F_o|w^{1/2})$. Thermal parameters, tables of bond lengths and bond angles, and the structure factors for **2** and **7a** are included in the supplementary material. Selected bond lengths and angles for **2** and **7a** are given in Tables IV and V, respectively.

## Results

**Synthesis of $WIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ (1), $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (2), and $WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (3).** In earlier work we had shown that the phosphido-bridged FeIr complex $FeIr(\mu\text{-}PPh_2)(CO)_5$-

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[9] Fultz, W. C.; Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 860.

Table I. Crystal and Intensity Data for $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (2) and $WIrH(\mu\text{-}PPh_2)_2(CO)_4(PPh_3)\{C(OCH_3)Ph\}$ (7a)

| | 2 | 7a |
|---|---|---|
| formula | $WIrP_3C_{47}H_{36}O_5$ | $WIrP_3C_{53}H_{44}O_5$ |
| cryst system | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 11.416 (2) | 18.773 (4) |
| $b$, Å | 19.129 (5) | 20.690 (6) |
| $c$, Å | 20.673 (3) | 12.761 (4) |
| $\beta$, deg | 100.78 (2) | 95.56 (2) |
| $V$, Å$^3$ | 4435 (2) | 4933 (2) |
| $Z$ | 4 | 4 |
| mol wt | 1149.7 | 1229.9 |
| $\rho$(calcd), g cm$^{-3}$ | 1.721 | 1.656 |
| temp, °C | 23 | 23 |
| cryst dimens, mm | 0.10 × 0.15 × 0.25 | 0.05 × 0.12 × 0.28 |
| radiation | graphite-monochromatized Mo Kα (λ = 0.710 73 Å) | |
| diffractometer | Nicolet R3 | Nicolet R3 |
| abs coeff, cm$^{-1}$ | 57.83 | 52.1 |
| scan speed, deg/min | variable, 3.0–15.0 | fixed, 3.0 |
| 2θ scan range, deg | 3° ≤ 2θ ≤ 48° | 4° ≤ 2θ ≤ 42° |
| scan technique | 2θ/θ | 2θ/θ |
| data collected | $\pm h,+k,+l$ | $\pm h,+k,+l$ |
| unique data | 6975 reflctns (7727 collected) | 4398 reflctns (4970 collected) |
| unique data with $(F_{obsd})^2 > 3\sigma(F_{obsd})^2$ | 5433 | 3408 |
| std reflctns | 3/97 (no decay) | 3/97 (no decay) |
| weighting factor | 0.001 (fixed) | 0.006 (fixed) |
| $R_F$ | 0.0332 | 0.0504 |
| $R_{wF}$ | 0.0347 | 0.0600 |
| GOF | 0.920 | 1.238 |

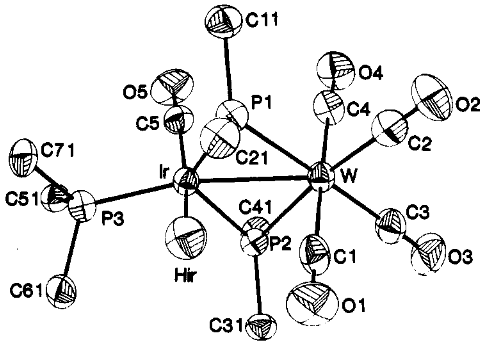
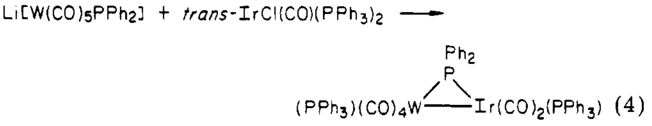


**Figure 1.** An ORTEP drawing of $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (2). Only one phenyl carbon atom is shown for each phenyl ring bonded to P.

$(PPh_3)_2$ readily results from the reaction of $[Fe(CO)_4PPh_2]^-$ with *trans*-$IrCl(CO)(PPh_3)_2$.[2a] An analogous phosphido-bridged WIr complex can be prepared by use of the appropriate phosphidotungstate reagent, $[W(CO)_5PPh_2]^-$ [10] (eq 3 and 4). This methodology can also be extended to

$$W(CO)_5PPh_2H + BuLi \rightarrow Li[W(CO)_5PPh_2] + BuH \quad (3)$$



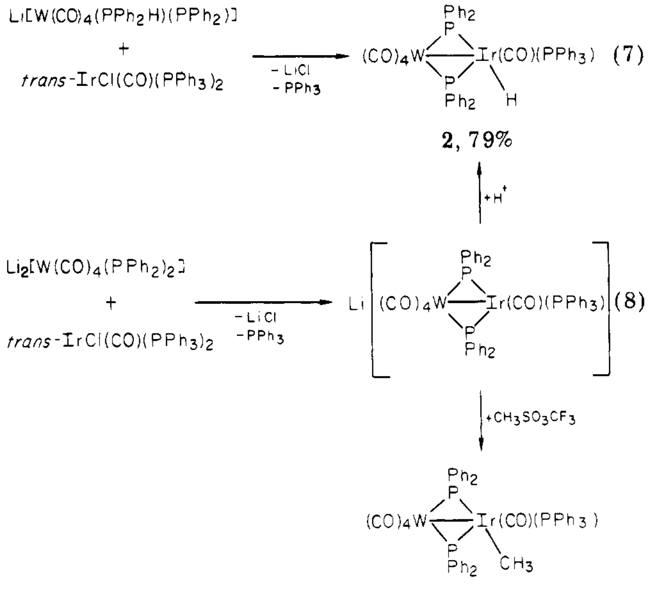
1, 37%

the preparation of bis(phosphido)-bridged complexes by using the cis-disubstituted W precursor complex *cis*-$W(CO)_4(PPh_2H)_2$.[8] By controlling the reaction stoichiometry, one or both protons can be removed from this complex (eq 5 and 6). Reaction of these phosphido reagents with

$$cis\text{-}W(CO)_4(PPh_2H)_2 + BuLi\ (1\ equiv) \rightarrow cis\text{-}Li[W(CO)_4(PPh_2H)(PPh_2)] + BuH \quad (5)$$

$$cis\text{-}W(CO)_4(PPh_2H)_2 + 2BuLi \rightarrow cis\text{-}Li_2[W(CO)_4(PPh_2)_2] + 2\ BuH \quad (6)$$

*trans*-$IrCl(CO)(PPh_3)_2$ leads to the bis(phosphido)hydrido complex 2 (eq 7) and to the anionic complex $[WIr(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)]^-$ (eq 8). The latter complex is extremely reactive and could not be isolated. However, protonation leads directly to 2, and methylation gives the analogous methyl complex 3.



3, 55%

The formation of 1 involves displacement of halide from Ir by the nucleophilic phosphido ligand on W. Also occurring during the synthesis is exchange of $PPh_3$ and CO between the two metals. The latter apparently involves initial dissociation of $PPh_3$ from Ir and then substitution for CO on W. Similar $PPh_3$ migration from Ir and Rh to Fe was observed during the syntheses of the $FeIr(\mu\text{-}PPh_2)$ and $FeRh(\mu\text{-}PPh_2)$ complexes described in ref 2a. Although not as extensively investigated, we have also observed that $[Mo(CO)_5PPh_2]^-$ works equally well as $[W(CO)_5PPh_2]^-$ in these syntheses. For example, a $MoIr(\mu\text{-}$

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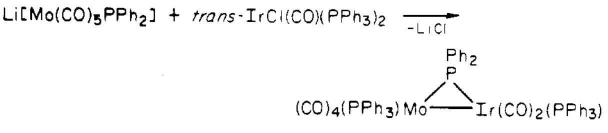
[10] Treichel, P. M.; Douglas, W. M.; Dean, W. K. *Inorg. Chem.* **1972**, *11*, 1615.

**Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)\{C(OCH_3Ph)\}$ (2)**

| atom | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|
| W | 185 (1) | 8822 (1) | 783 (1) | 36 (1) |
| Ir | −767 (1) | 7508 (1) | 1121 (1) | 34 (1) |
| P(1) | 576 (2) | 7595 (1) | 422 (1) | 37 (1) |
| P(2) | −1149 (2) | 8552 (1) | 1602 (1) | 41 (1) |
| P(3) | −1082 (2) | 6460 (1) | 1578 (1) | 40 (1) |
| O(1) | 3034 (5) | 7372 (4) | 81 (3) | 81 (3) |
| O(2) | 2356 (5) | 8582 (3) | 1965 (3) | 81 (3) |
| O(3) | 2101 (6) | 9244 (3) | −62 (3) | 79 (3) |
| O(4) | −1946 (6) | 9144 (3) | −395 (3) | 69 (2) |
| O(5) | 12 (6) | 10395 (3) | 1214 (3) | 60 (2) |
| C(1) | −2189 (7) | 7441 (4) | 459 (4) | 48 (3) |
| C(2) | 1566 (7) | 8665 (4) | 1549 (4) | 51 (3) |
| C(3) | 1391 (7) | 9093 (4) | 238 (4) | 52 (3) |
| C(4) | −1184 (7) | 9002 (4) | 28 (4) | 48 (3) |
| C(5) | 76 (7) | 9824 (4) | 1055 (4) | 49 (3) |
| C(11) | −2661 (7) | 8904 (4) | 1528 (4) | 52 (3) |
| C(12) | −3178 (8) | 8989 (5) | 2071 (5) | 66 (4) |
| C(13) | −4356 (9) | 9207 (5) | 1995 (5) | 79 (4) |
| C(14) | −5019 (9) | 9340 (6) | 1391 (7) | 91 (5) |
| C(15) | −4532 (11) | 9239 (9) | 851 (7) | 139 (8) |
| C(16) | −3350 (9) | 9020 (7) | 920 (5) | 111 (6) |
| C(21) | −499 (7) | 8707 (4) | 2460 (4) | 49 (3) |
| C(22) | −211 (10) | 8168 (5) | 2894 (4) | 88 (5) |
| C(23) | 331 (12) | 8265 (7) | 3544 (5) | 115 (6) |
| C(24) | 619 (9) | 8923 (6) | 3759 (5) | 87 (5) |
| C(25) | 330 (11) | 9503 (7) | 3352 (6) | 95 (5) |
| C(26) | −242 (9) | 9394 (5) | 2701 (4) | 76 (4) |
| C(31) | 2115 (6) | 7302 (4) | 631 (4) | 43 (3) |
| C(32) | 2907 (7) | 7442 (5) | 222 (5) | 69 (4) |
| C(33) | 4079 (9) | 7238 (6) | 374 (6) | 92 (5) |
| C(34) | 4468 (8) | 6854 (6) | 916 (5) | 94 (5) |
| C(35) | 3721 (8) | 6716 (5) | 1349 (5) | 80 (4) |
| C(36) | 2538 (7) | 6931 (4) | 1204 (4) | 62 (3) |
| C(41) | 124 (6) | 7279 (4) | −424 (3) | 40 (3) |
| C(42) | 600 (9) | 6672 (4) | −617 (4) | 73 (4) |
| C(43) | 203 (11) | 6393 (5) | −1239 (5) | 87 (5) |
| C(44) | −667 (9) | 6719 (5) | −1667 (5) | 79 (4) |
| C(45) | −1154 (10) | 7305 (6) | −1482 (4) | 90 (4) |
| C(46) | −747 (9) | 7598 (5) | −865 (4) | 77 (4) |
| C(51) | −1778 (7) | 5805 (4) | 986 (4) | 44 (3) |
| C(52) | −1452 (8) | 5776 (4) | 381 (4) | 60 (3) |
| C(53) | −1891 (9) | 5260 (5) | −68 (4) | 73 (4) |
| C(54) | −2699 (9) | 4781 (5) | 72 (5) | 81 (4) |
| C(55) | −3016 (10) | 4798 (5) | 674 (5) | 97 (5) |
| C(56) | −2589 (8) | 5309 (4) | 1123 (5) | 71 (4) |
| C(61) | 278 (7) | 6015 (4) | 1985 (4) | 47 (3) |
| C(62) | 898 (9) | 6276 (4) | 2570 (4) | 70 (4) |
| C(63) | 1965 (9) | 5958 (5) | 2882 (5) | 84 (4) |
| C(64) | 2393 (9) | 5390 (5) | 2589 (5) | 83 (4) |
| C(65) | 1783 (8) | 5140 (5) | 2026 (5) | 75 (4) |
| C(66) | 732 (8) | 5438 (4) | 1712 (4) | 61 (3) |
| C(71) | −2000 (7) | 6474 (4) | 2214 (4) | 48 (3) |
| C(72) | −1883 (9) | 6003 (4) | 2715 (4) | 75 (4) |
| C(73) | −2584 (12) | 6026 (6) | 3185 (5) | 102 (6) |
| C(74) | −3384 (11) | 6549 (6) | 3180 (5) | 96 (5) |
| C(75) | −3541 (9) | 7033 (5) | 2671 (6) | 89 (5) |
| C(76) | −2835 (7) | 7005 (5) | 2200 (4) | 63 (3) |
| H(Ir) | 365 (82) | 7514 (39) | 1711 (42) | 76 (29) |

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

$PPh_2$) complex analogous to **1** was prepared by reaction 9.[11]



(9)

(34%)

**Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $WIrH(\mu\text{-}PPh_2)_2(CO)_4(PPh_3)\{C(OCH_3)Ph\}$ (7a)**

| atom | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|
| Ir | 2415 (1) | 1181 (1) | 9823 (1) | 61 (1) |
| W | 3102 (1) | 1563 (1) | 8018 (1) | 61 (1) |
| Ph(1) | 2555 (3) | 502 (2) | 8445 (4) | 65 (2) |
| Ph(2) | 2930 (3) | 2194 (2) | 9642 (4) | 67 (2) |
| P(3) | 2263 (3) | 711 (2) | 11404 (4) | 71 (2) |
| O(1) | 903 (6) | 1681 (6) | 9434 (10) | 116 (6) |
| O(2) | 4675 (6) | 1335 (6) | 9106 (10) | 119 (6) |
| O(3) | 3490 (8) | 710 (6) | 6131 (10) | 132 (7) |
| O(4) | 1644 (6) | 1914 (6) | 6674 (10) | 121 (7) |
| O(5) | 3599 (6) | 2921 (5) | 7681 (8) | 92 (6) |
| C(1) | 1496 (9) | 1477 (8) | 9573 (13) | 82 (8) |
| C(2) | 4089 (8) | 1403 (7) | 8747 (12) | 78 (8) |
| C(3) | 3337 (10) | 1080 (10) | 6830 (13) | 120 (10) |
| C(4) | 2164 (8) | 1783 (7) | 7229 (13) | 78 (8) |
| C(5) | 3569 (10) | 2314 (8) | 7334 (15) | 90 (9) |
| C(6) | 3998 (11) | 3458 (8) | 7268 (16) | 174 (14) |
| C(10) | 4025 (11) | 2235 (9) | 6374 (16) | 94 (10) |
| C(11) | 3640 (13) | 2219 (10) | 5349 (16) | 117 (12) |
| C(12) | 4048 (13) | 2163 (10) | 4503 (17) | 149 (14) |
| C(13) | 4777 (15) | 2087 (14) | 4713 (20) | 165 (16) |
| C(14) | 5098 (15) | 2076 (14) | 5699 (22) | 155 (16) |
| C(15) | 4741 (11) | 2123 (12) | 6548 (19) | 165 (15) |
| C(20) | 3084 (13) | −242 (8) | 8714 (12) | 66 (9) |
| C(21) | 2750 (11) | −801 (12) | 8988 (15) | 89 (10) |
| C(22) | 3162 (14) | −1353 (9) | 9259 (16) | 107 (12) |
| C(23) | 3888 (13) | −1347 (11) | 9246 (19) | 109 (12) |
| C(24) | 4207 (11) | −812 (12) | 8986 (16) | 97 (11) |
| C(25) | 3822 (11) | −263 (9) | 8704 (14) | 79 (10) |
| C(30) | 1837 (9) | 207 (7) | 7511 (13) | 82 (8) |
| C(31) | 1981 (12) | −115 (8) | 6595 (14) | 99 (10) |
| C(32) | 1434 (16) | −309 (11) | 5846 (18) | 134 (14) |
| C(33) | 726 (15) | −185 (12) | 5987 (23) | 140 (15) |
| C(34) | 563 (12) | 140 (11) | 6853 (21) | 119 (13) |
| C(35) | 1100 (10) | 345 (8) | 7582 (15) | 96 (10) |
| C(40) | 3729 (9) | 2421 (11) | 10516 (14) | 64 (9) |
| C(41) | 4007 (11) | 2030 (10) | 11267 (17) | 91 (10) |
| C(42) | 4624 (14) | 2174 (13) | 11868 (17) | 114 (13) |
| C(43) | 4986 (13) | 2753 (17) | 11656 (22) | 133 (19) |
| C(44) | 4709 (14) | 3154 (14) | 10923 (22) | 127 (16) |
| C(45) | 4114 (12) | 3002 (10) | 10323 (15) | 90 (10) |
| C(50) | 2373 (10) | 2919 (8) | 9688 (18) | 64 (8) |
| C(51) | 1968 (10) | 3149 (10) | 8791 (15) | 78 (10) |
| C(52) | 1518 (11) | 3672 (10) | 8820 (18) | 94 (11) |
| C(53) | 1482 (12) | 3985 (11) | 9726 (22) | 109 (13) |
| C(54) | 1861 (12) | 3780 (11) | 10646 (17) | 95 (11) |
| C(55) | 2297 (11) | 3245 (10) | 10633 (17) | 93 (11) |
| C(60) | 1862 (10) | 1203 (9) | 12355 (14) | 88 (9) |
| C(61) | 1527 (15) | 974 (12) | 13160 (19) | 193 (17) |
| C(62) | 1189 (20) | 1309 (15) | 13847 (29) | 272 (25) |
| C(63) | 1253 (15) | 1974 (13) | 13834 (22) | 182 (17) |
| C(64) | 1611 (13) | 2264 (10) | 13090 (16) | 150 (14) |
| C(65) | 1913 (13) | 1858 (8) | 12344 (15) | 132 (12) |
| C(70) | 3090 (10) | 412 (10) | 12110 (17) | 69 (9) |
| C(71) | 3503 (14) | −39 (11) | 11654 (16) | 100 (11) |
| C(72) | 4167 (13) | −248 (11) | 12123 (21) | 107 (12) |
| C(73) | 4399 (14) | −8 (14) | 13054 (23) | 119 (14) |
| C(74) | 4024 (17) | 454 (12) | 13505 (21) | 125 (15) |
| C(75) | 3360 (12) | 641 (10) | 13083 (21) | 93 (11) |
| C(80) | 1708 (9) | −17 (8) | 11377 (14) | 76 (8) |
| C(81) | 1150 (10) | −77 (9) | 10618 (16) | 107 (10) |
| C(82) | 707 (12) | −635 (12) | 10570 (20) | 124 (16) |
| C(83) | 801 (14) | −1093 (13) | 11308 (22) | 124 (17) |
| C(84) | 1328 (11) | −1051 (10) | 12085 (19) | 184 (14) |
| C(85) | 1792 (13) | −524 (12) | 12118 (18) | 135 (16) |
| H(Ir) | 3251 (10) | 1086 (43) | 10173 (65) | 35 (30) |

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

The synthesis of **2** presumably involves the sequence of reactions shown in eq 10. Establishment of the first phosphido bridge presumably occurs by displacement of halide as in the preparation of **1**. The second phosphido bridge can then form by oxidative addition of the P–H bond of the $W\text{–}PPh_2H$ ligand to Ir, a reaction which also

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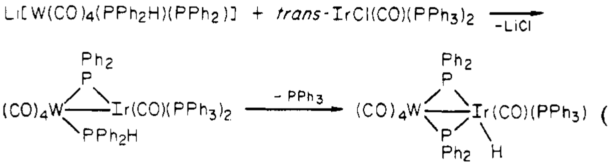
[11] Breen, M. J. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1982.

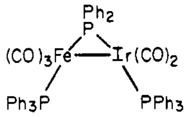


(10)

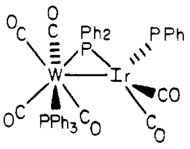
conveniently places a hydride on this metal.

**Characterization of Complexes 1–3.** These new complexes were spectroscopically characterized and the structure of 2 was established by an X-ray diffraction study (see below). The $^{31}P\{^1H\}$ and $^1H$ NMR spectral data for all the new complexes described herein are listed in Table VI; IR and mass spectral data are given in the Experimental Section. In discussions of the $^{31}P$ NMR data, bridging $\mu$-PPh$_2$ ligands will be denoted by $P_\mu$ and the terminal PPh$_3$ ligands will have a subscript corresponding to the metal to which they are bound, i.e., $P_W$ and $P_{Ir}$.

Complex 1 is similar to FeIr($\mu$-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ which has been structurally characterized.[2a]



The $^{31}P\{^1H\}$ spectrum of 1 shows a resonance at δ 112.3 (dd) attributable to the $\mu$-PPh$_2$ ligand; its downfield position implies the presence of a metal–metal bond, in accordance with other literature correlations.[12] Two separate resonances are observed for the terminal PPh$_3$ ligands; the lack of coupling between them implies that these ligands are bound to different metals. The relatively small size of the $^{31}P_\mu$–$^{31}P_M$ coupling constants implies that both of the PPh$_3$ ligands are cis to the phosphido bridge, and the structure drawn below is suggested.



1

An ORTEP drawing of 2 is shown in Figure 1; the solution spectral data are consistent with this structure. The two $\mu$-PPh$_2$ ligands are equivalent and appear at δ 132.8 (d) in its $^{31}P$ NMR spectrum, showing coupling to the terminal PPh$_3$ on Ir. The downfield position of the $\mu$-PPh$_2$ resonance is consistent with the presence of a W–Ir bond in 2 (2.876 Å). The hydride ligand appears in the $^1H$ NMR spectrum at δ −13.2 as a doublet of triplets coupling to all three $^{31}P$ nuclei.

The $^{31}P\{^1H\}$ NMR (Table VI) and IR spectra of the methyl complex 3 are sufficiently similar to 2 so as to imply similar structures for the two complexes. A comparison of the IR spectra of 2 and 3 with that of (CO)$_4$W($\mu$-PPh$_2$)$_2$Pt(PPh$_3$)[13] is shown in Figure 2; the only significant difference is the band at 1980 cm$^{-1}$ in the spectrum of 2 which shifts to 2003 cm$^{-1}$ in the spectrum of 3 and is completely absent in the spectrum of the PtW complex. This band is logically attributed to the CO on Ir which is trans to H in 2, apparently trans to CH$_3$ in 3, and not present in the PtW compound. The methyl ligand appears as a doublet of triplets at δ −0.57 in the $^1H$ NMR spectrum of 3 and does not show $^{183}W$ satellites. The structure

Table IV. Selected Bond Lengths (Å) in WIrH($\mu$-PPh$_2$)$_2$(CO)$_5$(PPh$_3$) (2) and WIrH($\mu$-PPh$_2$)$_2$(CO)$_4$(PPh$_3$){C(OCH$_3$)Ph} (7a)

| bond | 2 | 7a |
|---|---|---|
| W-Ir | 2.8764 (6) | 2.858 (1) |
| W-P1 | 2.528 (2) | 2.507 (5) |
| W-P2 | 2.534 (2) | 2.496 (5) |
| Ir-P1 | 2.302 (2) | 2.286 (5) |
| Ir-P2 | 2.308 (2) | 2.328 (5) |
| Ir-P3 | 2.273 (2) | 2.283 (5) |
| Ir-C1 | 1.922 (7) | 1.83 (2) |
| W-C2 | 2.037 (7) | 2.02 (2) |
| W-C3 | 2.004 (9) | 1.90 (2) |
| W-C4 | 2.022 (7) | 2.00 (2) |
| W-C5 | 2.007 (8) | 2.02 (2) |
| C1-O1 | 1.130 (9) | 1.19 (2) |
| C2-O2 | 1.135 (9) | 1.16 (2) |
| C3-O3 | 1.15 (1) | 1.23 (2) |
| C4-O4 | 1.144 (9) | 1.18 (2) |
| C5-O5 | 1.15 (1) | 1.33 (2) |
| C5-C6 | | 1.47 (2) |
| C5-C10 | | 1.57 (3) |
| Ir-H | 1.60 (8) | 1.60 |

Table V. Selected Bond Angles (deg) in WIrH($\mu$-PPh$_2$)$_2$(CO)$_5$(PPh$_3$) (2) and WIrH($\mu$-PPh$_2$)$_2$(CO)$_4$(PPh$_3$){C(OCH$_3$)Ph} (7a)

| angle | 2 | 7a |
|---|---|---|
| Ir-W-P1 | 49.9 (1) | 49.9 (1) |
| Ir-W-P2 | 50.0 (1) | 51.0 (1) |
| Ir-W-C2 | 87.4 (2) | 92.8 (5) |
| Ir-W-C3 | 133.9 (2) | 130.8 (6) |
| Ir-W-C4 | 93.7 (2) | 91.4 (5) |
| Ir-W-C5 | 136.1 (2) | 144.0 (5) |
| P1-W-P2 | 99.8 (1) | 100.9 (2) |
| P1-W-C2 | 86.5 (2) | 97.6 (5) |
| P1-W-C3 | 84.0 (2) | 81.0 (6) |
| P1-W-C4 | 94.8 (2) | 87.1 (4) |
| P1-W-C5 | 173.1 (2) | 166.0 (5) |
| P2-W-C2 | 85.7 (2) | 83.7 (5) |
| P2-W-C3 | 172.3 (2) | 174.0 (5) |
| P2-W-C4 | 94.4 (3) | 97.0 (5) |
| P2-W-C5 | 86.1 (2) | 93.1 (5) |
| C2-W-C3 | 87.9 (3) | 90.4 (7) |
| C2-W-C4 | 178.6 (3) | 175.1 (6) |
| C2-W-C5 | 90.2 (3) | 84.7 (7) |
| C3-W-C4 | 92.0 (3) | 88.8 (7) |
| C3-W-C5 | 89.8 (3) | 85.2 (8) |
| C4-W-C5 | 92.0 (3) | 90.3 (7) |
| W-Ir-P1 | 57.2 (1) | 57.0 (1) |
| W-Ir-P2 | 57.3 (1) | 56.4 (1) |
| W-Ir-C1 | 101.1 (2) | 105.0 (5) |
| W-Ir-P3 | 165.5 (1) | 159.2 (1) |
| W-Ir-H | 83.7 (29) | 75.7 (29) |
| P1-Ir-P2 | 114.2 (1) | 113.4 (2) |
| P1-Ir-P3 | 120.1 (1) | 116.8 (2) |
| P1-Ir-C1 | 97.5 (3) | 104.4 (5) |
| P1-Ir-H | 86.6 (36) | 87.5 (30) |
| P2-Ir-P3 | 121.7 (1) | 124.1 (2) |
| P2-Ir-C1 | 99.3 (2) | 94.3 (5) |
| P2-Ir-H | 81.7 (29) | 74.6 (31) |
| C1-Ir-H | 174.9 (33) | 166.4 (30) |
| C1-Ir-P3 | 93.4 (2) | 95.8 (5) |
| P3-Ir-H | 81.8 (29) | 84.5 (29) |
| Ir-P1-W | 72.7 (1) | 73.0 (1) |
| Ir-P2-W | 72.9 (1) | 72.6 (1) |
| W-C5-O5 | | 126.0 (13) |
| W-C5-C10 | | 123.3 (12) |
| C5-O5-C6 | | 127.0 (14) |
| O5-C5-C10 | | 110.4 (15) |

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[12] (a) Petersen, J. L.; Stewart, R. P., Jr. *No. Inorg. Chem.* **1980**, *19*, 186. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 1963. (c) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27. (d) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

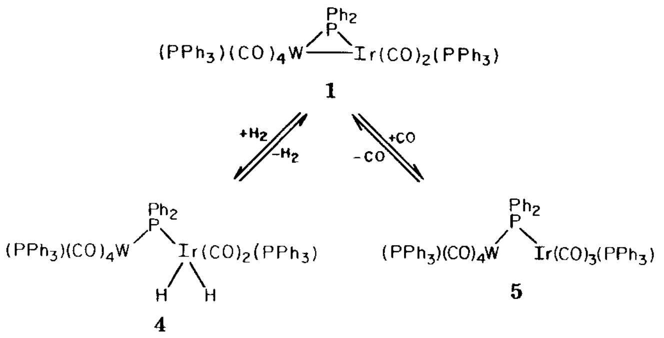
[13] (a) Morrison, E. D.; Harley, A. D.; Marcelli, M. A.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C., submitted for publication in *Organometallics*. (b) Harley, A. D. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1983.

Table VI. $^{31}P$ and $^{1}H$ NMR Spectral Data

| complex | $^{31}P$ | | | | | $^{1}H$ | |
|---|---|---|---|---|---|---|---|
| | $\delta(\mu\text{-}PPh_2)$ | $\delta(M\text{-}PPh_3)$ | $J_{^{31}P_\mu-^{31}P_M}$ | $J_{^{31}P_\mu-^{31}P_\mu}$ | $J_{^{31}P-^{183}W}$ | $\delta(H)$ | $J_{^{1}H-^{31}P}$ |
| $WIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$, 1 | 112.3 dd | 19.3 d (M = Ir) | 39.1 (M = Ir) | | *a* | | |
| | | 25.8 d (M = W) | 6.0 (M = W) | | | | |
| $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$, 2 | 132.8 d | 27.0 t | 43.3 | | 145.7 | −13.2 dt | 18.7, 15.2 |
| $WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$, 3 | 136.6 d | 25.6 t | 60.1 | | 167.0 | | |
| $WIrH_2(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$, 4 | −55.8 dd | 1.0 d (M = Ir) | 157.6 (M = Ir) | | 344.0 ($P_W$) | −8.06 dd | |
| | | 32.2 d (M = W) | 55.1 (M = W) | | | | |
| $WIr(\mu\text{-}PPh_2)(CO)_7(PPh_3)_2$, 5a | −54.8 dd | −3.0 d (M = Ir) | 121.1 (M = Ir) | | 260.2 ($P_\mu$) | | |
| | | 30.3 d (M = W) | 58.3 (M = W) | | 385.8 ($P_W$) | | |
| $WIr(\mu\text{-}PPh_2)(CO)_7(PPh_3)_2$, 5b | −56.7 dd | −1.2 d (M = Ir) | 127.6 (M = Ir) | | *a* | | |
| | | 25.3 d (M = W) | 27.7 (M = W) | | *a* | | |
| $[WIrH(\mu\text{-}PPh_2)_2\{C(O)Ph\}(CO)_4(PPh_3)]^-$, 6a | 111.9 dd | 21.4 dd | 52.2 | 132.9 | 149.6 | −13.2 ddd | 17.1, 18.3, 18.9 |
| | 87.2 dd | | 3.0 | 132.9 | 218.5 | | |
| $[WIrH(\mu\text{-}PPh_2)_2\{C(O)Me\}(CO)_4(PPh_3)]^-$, 6b | 111.8 dd | 20.8 dd | 51.5 | 138.1 | 157.9 | −13.2 ddd | 17.8, 18.6, 18.6 |
| | 85.7 dd | | 5.8 | 138.1 | 217.1 | | |
| $WIrH(\mu\text{-}PPh_2)_2\{C(OMe)Ph\}(CO)_4(PPh_3)$, 7a | 119.3 dd | 22.6 dd | 48.4 | 136.2 | 103.6 | −13.0 ddd | 16.4, 16.4, 17.9 |
| | 97.7 dd | | 2.2 | 136.2 | 190.6 | | |
| $WIrH(\mu\text{-}PPh_2)_2\{C(OMe)Me\}(CO)_4(PPh_3)$, 7b | 122.4 dd | 22.6 dd | 55.9 | 145.4 | 118.1 | −13.1 ddd | 17.7, 18.4, 21.7 |
| | 96.6 dd | | 2.6 | 145.4 | 191.9 | | |
| $WIrH(\mu\text{-}PPh_2)_2\{C(OH)Ph\}(CO)_4(PPh_3)$, 8 | 113.4 dd | 24.3 d | 26.1 | 128.8 | *a* | −12.8 ddd | 15.3, 17.1, 18.9 |
| | 61.5 d | | *a* | 128.8 | *a* | | |
| $[WIrH_2(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)]^-$, 9 | −97.6 dd | 11.2 dd | 210.5 | 48.8 | *a* | −7.45 m | *a* |
| | −140.5 dd | | 10.7 | 48.8 | *a* | −12.46 m | *a* |
| $WIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)(PPh_2Me)$, 10 | 71.9 dd | 30.9 (M = Ir) | 175.7 | | *a* | | |
| | | −9.02 (M = W) | 24.0 | | 257.0 ($P_W$) | | |
| $WIrCl(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$, 11 | 137.8 d | 19.3 t | 59.2 | | 171.0 | | |
| $MoIr(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ [b] | 133.3 dd | 50.0 d (M = Mo) | 29.5 (M = Mo) | | *a* | | |
| | | 17.9 d (M = Ir) | 160.5 (M = Ir) | | | | |

[a] Not resolved. [b] Reference 11.

### Scheme I



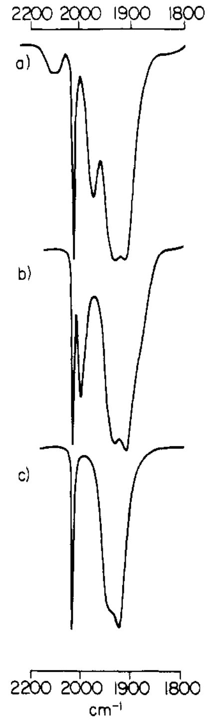
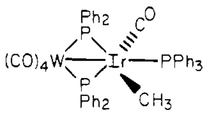


**Figure 2.** A comparison of the IR spectra of (a) $WIrH(\mu-PPh_2)_2(CO)_5(PPh_3)$ (**2**), (b) $WIrCH_3(\mu-PPh_2)_2(CO)_5(PPh_3)$ (**3**), and (c) $WPt(\mu-PPh_2)_2(CO)_4(PPh_3)$.

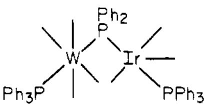
drawn below is suggested for **3**, based on the determined structure of **2**.



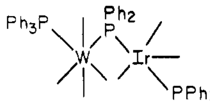
**3**

**Reactions of 1 and 2 with $H_2$ and CO.** Although **2** does not react with $H_2$ nor with CO under the conditions given in the Experimental Section, complex **1** reversibly adds both $H_2$ and CO under 1 atm pressure of these gases (Scheme I). Exposure of toluene solutions of **1** to $H_2$ results in an immediate reaction to give the dihydride complex **4**; removal of the $H_2$ atmosphere regenerates **1**. Complex **4** was not isolated but was thus spectroscopically characterized in solution. Its $^1H$ NMR spectrum shows a single resonance in the hydride region at $\delta$ −8.06 (dd) without $^{183}W$ satellites, implying that both hydrides are on Ir. The $^{31}P$ NMR spectrum, Table VI, shows separate resonances for the two terminal $PPh_3$ ligands, only one of which shows $^{183}W$ satellites, and an *upfield* resonance at $\delta$ −55.8 (dd) for the $\mu$-$PPh_2$ ligand. The upfield position argues for the *absence* of a W–Ir bond,[12] as expected since complex **1** is coordinatively saturated and the metal–metal bond in **1** must break during the addition process. The $^{31}P$–$^{31}P$ coupling constants given in Table VI suggest that both $PPh_3$ ligands are trans to the $\mu$-$PPh_2$ ligand in **4**, in contrast to the geometry of **1**.

An exactly analogous reaction occurs with CO (Scheme I). Exposure of toluene solutions of **1** to CO gives an immediate reaction to form the CO adduct **5**. This reaction readily and quantitatively reverses upon removal of the CO atmosphere. $^{31}P$ NMR data (Table VI) imply that **5** forms as a mixture of two isomers with the major isomer **5a** obtained in ~90% yield and the minor isomer **5b** in ~10% yield, determined on the basis of relative $^{31}P$ NMR intensities. The $^{31}P$ NMR data for the two complexes are similar, with slight chemical shift differences but with a significant difference in the $^{31}P_\mu$–$^{31}P_W$ coupling constants. Each shows distinct resonances for the $PPh_3$ ligands on the separate metals and an upfield resonance attributed to the $\mu$-$PPh_2$ ligand. As before, the upfield positions of these resonances argue for the absence of W–Ir bonds in these coordinatively saturated CO adducts.[12] The only significant difference in the spectral data for the two isomers is the magnitude of the $^{31}P_\mu$–$^{31}P_W$ coupling constants. The major isomer **5a** shows a much larger value (58.3 Hz) for $J_{^{31}P_\mu-^{31}P_W}$ than does the minor isomer **5b** (27.7 Hz), and we thus suggest that in **5a** both $PPh_3$ ligands are trans to the phosphido bridge whereas in **5b** the $PPh_3$ on W is cis to the $\mu$-$PPh_2$ ligand.

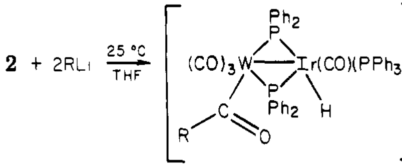


**5a**



**5b**

**Reaction of 2 with MeLi and PhLi To Give the Binuclear Acyl–Hydride Complexes 6a,b.** New acyl-hydride complexes were prepared by stirring THF solutions of **2** with a 2-fold excess of RLi (R = Me,Ph) for 1 h at 22 °C (eq 11). These complexes were precipitated as $Li(THF)_x^+$ salts from THF solution by the addition of petroleum ether and isolated as orange microcrystalline solids in ~90% yield.



(11)

**6a**, R = Ph
**6b**, R = $CH_3$

The presence of the acyl ligands in **6a** and **6b** is respectively indicated by weak acyl $\nu_{CO}$ vibrations at 1580 and 1581 cm⁻¹ and $^{13}C$ NMR resonances at $\delta$ 286.1 and 284.7. The $^{13}C$ NMR spectra of these complexes were not sufficiently resolved to allow observation of $^{13}C$–$^{183}W$ coupling or to fully discern the $^{13}C$–$^{31}P$ coupling. Either of these would have been sufficient to determine to which metal the acyl carbon is bound. However, the spectroscopic and structural data for the carbene complexes which derive from **6a** and **6b** (see below) clearly indicate that the carbene ligands are attached to W, and a similar bonding of the acyl carbons is implied. The $^{13}C$ NMR chemical shifts of the acyl carbons of **6a** and **6b** imply that these ligands are terminally bound to just one metal rather than bridging between the two metals. Further downfield chemical shifts are generally observed for bridging acyl complexes.[14] Also, the acyl carbon chemical shifts of **6a** and **6b** are similar to the $\delta$ 273.3 chemical shift of the acetyl ligand of $[Fe_2(\mu-PPh_2)_2(CO)_5\{C(O)CH_3\}]^-$ for which an X-ray structure showed this ligand to be bound to just one Fe atom.[15] Furthermore, a bridging acyl ligand would require displacement of the metal–metal bond in forming **6a,b** which is not indicated by the downfield $^{31}P$ NMR chemical shifts of the $\mu$-$PPh_2$ ligands of these complexes, Table VI.

The $^1H$ NMR spectra of **6a** and **6b** both show a single hydride resonance at $\delta$ −13.2 (ddd) (Table VI). The cou-

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(14) (a) Mann, B. E.; Taylor, B. F. "$^{13}C$ NMR Data for Organometallic Compounds"; Academic Press: London, 1981. (b) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.

(15) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Rose-Munch, F. *J. Am. Chem. Soc.* **1977**, *99*, 7381.

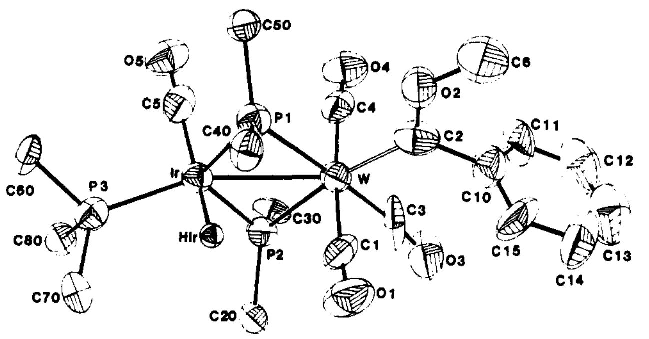


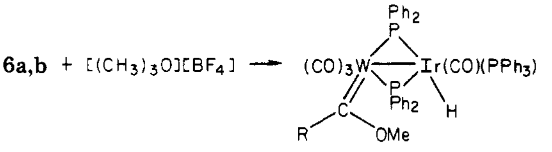
**Figure 3.** An ORTEP drawing of WIrH($\mu$-PPh$_2$)$_2$(CO)$_4$(PPh$_3$){C(OCH$_3$)Ph} (**7a**). Only one phenyl carbon atom is shown for each phenyl ring bonded to P.

pling to all three phosphorus nuclei implies that the hydride is still attached to Ir, as also does the lack of $^{183}$W satellites on these resonances. The $^{31}$P{$^1$H} NMR spectra of **6a** and **6b** (Table VI) are consistent with the suggested structures, each showing two downfield resonances for inequivalent $\mu$-PPh$_2$ ligands and a separate resonance for the Ir–PPh$_3$ ligand.

The acyl–hydride complexes **6a** and **6b** appear indefinitely stable in room-temperature solutions. However, when **6a** was maintained at 60 °C in acetone solution it slowly decomposed over a period of 4 days to give mainly the parent compound **2** and minor amounts of other unidentified products. In acetone solution maintained at 95 °C in a sealed flask, complex **6b** decomposed within 1 h to yield mainly **2**. The fate of the acyl ligands in these decomposition reactions was not determined, but the IR and $^1$H NMR spectra of the decomposed solutions showed no evidence of aldehyde formation.

In contrast to the clean derivative chemistry of **2** with PhLi, complex **1** does not react with PhLi, even when stirred for prolonged periods with an excess of this reagent.

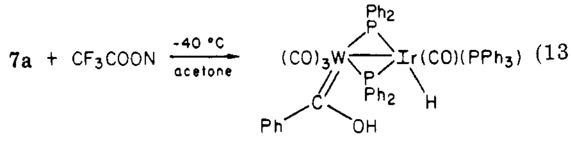
**Synthesis and Characterization of the Binuclear Carbene–Hydride Complexes 7a,b.** Methylation of the acyl complexes **6a** and **6b** with [(CH$_3$)$_3$O][BF$_4$] leads to the formation of the binuclear carbene–hydride complexes **7a** and **7b** (eq 12). These complexes were isolated as air-stable, red-orange microcrystalline solids in moderate yields. They have been characterized spectroscopically, and **7a** was fully characterized by a complete single-crystal X-ray diffraction study (see below). The latter shows the carbene ligand to be attached to W, trans to one $\mu$-PPh$_2$ ligand and cis to the other, with the hydride located on Ir. An ORTEP drawing is given in Figure 3. The spectral similarity between **7a** and **7b** argues for similar structures for the two compounds. The $^{31}$P and $^1$H NMR data, Table VI, are consistent with the structure determined for **7a**. The $^{13}$C NMR spectrum of **7a** shows a carbene resonance at $\delta$ 298.4 (dd) which couples to the two $\mu$-PPh$_2$ ligands, but not to the Ir–PPh$_3$ ligand, and which shows $^{183}$W satellites.



(12)

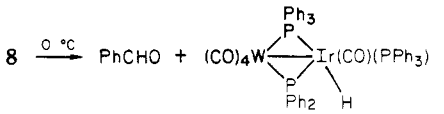
7a, R = Ph (41%)
7b, R = Me (57%)

**Protonation of 6a To Give the Binuclear Hydroxycarbene–Hydride Complex 8.** Addition of CF$_3$COOH to an acetone solution of **6a** at −40 °C yields the hydroxycarbene–hydride complex **8** (eq 13). This reaction is slow at −40 °C, but warmup to −10 °C resulted in complete reaction within 10 min. However, complex **8** is not stable above 0 °C and decomposes to yield benzaldehyde and **2** as primary products (eq 14). The $^1$H NMR spectrum of a solution of **8** warmed to 25 °C showed a resonance at $\delta$ 10.04 characteristic of benzaldehyde; the $^{31}$P NMR spectrum of this solution showed only resonances attributable to **2**. Complex **2** must derive by scavenging of CO by a coordinatively unsaturated intermediate initially formed upon aldehyde elimination. Hydroxycarbene complexes are known to be particularly unstable, and their decomposition to yield aldehydes is well-documented.[16]



(13)

8



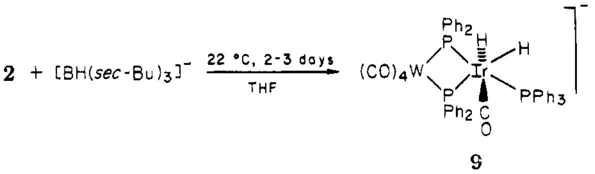
(14)

2

Complex **8** could not be isolated due to its thermal instability. It was therefore characterized primarily on the basis of its $^{31}$P{$^1$H} and $^1$H NMR spectral properties. The spectroscopic data are consistent with the structure drawn in eq 13 in which the carbene and hydride ligands are bound in a fashion similar to those ligands in the fully characterized **7a**. The similar $^{31}$P NMR spectra of **7a** and **8**, Table VI, are in accord with this proposal. The $^1$H NMR spectrum of **8** expectedly shows a hydride resonance at $\delta$ −12.8 ddd which couples to all three phosphorus nuclei but which does not show $^{183}$W satellites, consistent with its assignment to a terminal hydride on Ir. Also observable in the $^1$H NMR spectrum of **8** is a weak, broad resonance at $\delta$ 6.53 (s) which is tentatively assigned to the –O*H* resonance of the hydroxy–carbene ligand.

**Reactions of 1 and 2 with [BHR$_3$]$^-$ Reagents.** Complex **1** slowly reacts with K[BH(O-*i*-Pr)$_3$] to give a complex mixture of products. When these reagents were combined in THF solution at 25 °C and the reaction monitored by $^1$H NMR spectroscopy, a resonance appeared in the metal formyl region at $\delta$ 14.8 (dd) ($J_{^{31}\mathrm{P}-^1\mathrm{H}}$ = 8.5, 93.8 Hz) in addition to seven metal hydride resonances in the $\delta$ −10 to −14 region, with the more intense resonances observed at $\delta$ −11.0 (dd) and −12.7 (br, m). The relative intensity ratio between the formyl and hydride resonances was approximately 1:300. The formyl resonance slowly decreased in intensity with time, concomitant with the appearance of a new weak formyl resonance at $\delta$ 15.7 (m). The $^1$H NMR data clearly indicate the formation of at least two different formyl complexes, but, owing to the complexity of the reaction and the large number of hydride products, this chemistry was not further investigated.

In contrast, the bis(phosphido)-bridged complex **2** reacts smoothly with K[BH(*sec*-Bu)$_3$] to yield the dihydride complex **9**, eq 15, in which one hydride has added to Ir and



(15)

9

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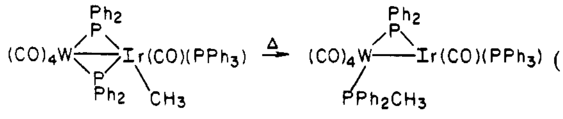
(16) (a) Fischer, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156. (b) Fischer, E. O.; Measbol, A., *Ibid.* **1967**, *100*, 2445.

displaced the W–Ir bond. This reaction proceeds very slowly, and after 2 days the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed ~35% conversion to **9**. No efforts were made to isolate a pure sample of **9**, and it was spectroscopically characterized in solution.

The $^1H$ NMR spectrum of **9** showed two equal intensity complex multiplets centered at $\delta$ −7.45 (m) and −12.46 (m), implying the presence of two nonequivalent hydride ligands. In the fully $^1H$ decoupled $^{31}P$ NMR spectrum, three doublet of doublets were observed at $\delta$ 11.2, −97.6, and −140.5. The $\delta$ 11.2 (dd) resonance is attributed to the $PPh_3$ on Ir, and it couples to the two $\mu$-$PPh_2$ ligands. The resonances at $\delta$ −97.6 and −140.5 are assigned to the nonequivalent $\mu$-$PPh_2$ ligands which couple to each other and to $PPh_3$ on Ir. The upfield positions of the $\mu$-$PPh_2$ resonances imply that there is no direct W–Ir bond in **9**.[12] Selective decoupling of the protons in the $\delta$ 0–10 region from the $^{31}P$ nuclei showed that each of the three phosphorus nuclei couple to two nonequivalent hydride ligands. The $\mu$-$PPh_2$ resonance at $\delta$ −140.5 couples weakly to one hydride ($J_{^1H-^{31}P} \simeq 10.2$ Hz) and strongly to the second ($J_{^1H-^{31}P} \simeq 81.4$ Hz), indicating that it is cis to one and trans to the other. The second $\mu$-$PPh_2$ resonance at $\delta$ −97.6 shows equivalent coupling to both hydrides with $J_{^1H-^{31}P} \simeq$ 7.1 Hz, indicating that both hydrides are cis to this $\mu$-$PPh_2$ ligand. The resonance at $\delta$ 11.2 due to the $PPh_3$ on Ir shows coupling to both hydrides with $J_{^{31}P-^1H} \cong 10$ Hz, again implying that both hydrides are cis to the $PPh_3$ ligand and also implying that both are bound to Ir. Thus, the $^{31}P$ NMR data imply the overall geometry shown in eq 15 for **9**.

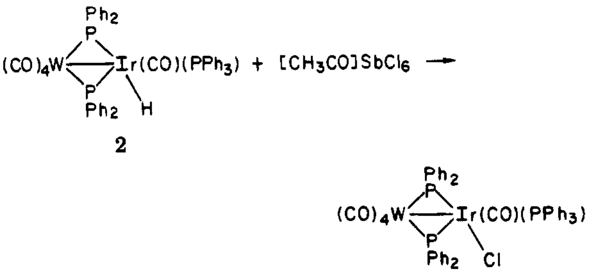
**Thermolysis of $WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$.** Although the hydride complex $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ is stable up to ~180 °C, the methyl complex $WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ undergoes the elimination reaction shown in eq 16 when heated to 110 °C. This reaction involves coupling of the methyl ligand with one of the $\mu$-$PPh_2$ ligands to give a terminal $PPh_2Me$ ligand on W. Complex **10** proved too unstable to isolate in pure form from the reaction mixture, but it was characterized spectroscopically. Its IR spectrum shows only terminal $\nu_{CO}$ bands and its $^{31}P\{^1H\}$ NMR spectrum, Table VI, shows the expected resonances for each of the three phosphorus nuclei. The $PPh_2CH_3$ resonance at $\delta$ −9.02 (d) shows $^{183}W$ satellites, indicating its location on W. The $CH_3$ group of this ligand shows a $^1H$ NMR doublet at $\delta$ 1.84 with $J_{^1H-^{31}P} = 7.2$ Hz. Exposure of solutions of **10** to CO (1 atm) gave an orange solution which showed IR bands at 2010 w, 1980 m, 1930 s, and 1880 s cm$^{-1}$, similar to those of **1** and suggesting the formation of the isostructural compound $(CO)_4(PPh_2Me)\overline{W(\mu\text{-}PPh_2)Ir}(CO)_2(PPh_3)$.



(16)

**10**

**Preparation of $WIrCl(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$.** In an attempt to prepare a binuclear WIr acyl complex with the acyl ligand on Ir, the anionic complex $[WIr(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)]^-$ was allowed to react with $[CH_3CO]SbCl_6$.[17] However, the product of this reaction proved not to be an acyl complex but rather the chloro complex **11**. We subsequently found that this complex derives directly from **2** as shown in eq 17. Acetaldehyde and $SbCl_5$ are presumably other products of this reaction, but no attempt was made to identify them. The IR and $^{31}P$ NMR spectral data (Table VI) for **11** are sufficiently similar to those of **2** and **3** so as to imply analogous structures for the three complexes.



(17)

**2**

**11** (24%)

**Discussion of the Crystal Structures of $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (2) and $WIrH(\mu\text{-}PPh_2)_2(CO)_4(PPh_3)\{C(OCH_3)Ph\}$ (7a).** ORTEP drawings of **2** and **7a** are shown in Figures 1 and 3, respectively, and important bond angles and distances are given in Tables IV and V. The structures are quite similar, differing in the substitution of a carbene ligand in **7a** for a tungsten carbonyl in **2**. The hydride ligand in **2** was located and refined whereas that in **7a** was not found. It was placed in **7a** in a coordination position analogous to that established for **2**, as indicated by the remainder of the geometry about Ir in **7a** which closely parallels that of **2**. Neglecting the W atom, in both molecules the coordination geometry about Ir is roughly trigonal bipyramidal with the three phosphorus atoms in the trigonal plane and with the hydride trans to CO in an axial position. In this regard the molecule resembles the trigonal-bipyramidal structure established for $RhH(CO)(PPh_3)_3$.[18] The six P–Ir–P angles in the two structures average 118.4° with a maximum deviation from the expected 120° value of 6.6°. Likewise the axial–equatorial angle for the refined atoms average 92.8° with a maximum deviation from the expected 90° value of 14.4°.

Neglecting for the moment the Ir atom, we find that the coordination geometry about W is essentially octahedral, with the two $\mu$-$PPh_2$ ligands in cis positions. As expected for an octahedral structure, the 24 cis L–W–L angles for the two structures average 90.1° with the maximum deviation being the larger angles between the cis-($\mu$-$PPh_2$) ligands in **2** (+10.9°) and **7a** (+9.8°). The six trans L–W–L angles average 173.2° with a maximum deviation of 14° from the expected 180° value.

The $WIr(\mu\text{-}PPh_2)_2$ cores of the two molecules are essentially planar with dihedral angles between the W–P1–Ir and W–P2–Ir planes equal to 7.8° and 2.8° for **2** and **7a**, respectively. The W–Ir distances of **2** (2.876 Å) and **7a** (2.858 (1) Å) clearly indicate a significant degree of metal–metal interaction and are within the range expected for direct single W–Ir bonds. In the only other WIr complexes whose structures have been determined, the W–Ir bonds average 2.824 Å in $WIr_3Cp(CO)_{11}$ and 2.835 Å in $W_2Ir_2Cp_2(CO)_{10}$.[3a]

The carbene ligand in **7a** is trans to one of the $\mu$-$PPh_2$ ligands and cis to the other. Importantly, it is directed away from the Ir atom and the hydride ligand on that metal. The dihedral angle between the plane defined by the carbene ligand (C5–C6–C10) and the $WIrP_2$ plane is 13.2°.

A priori, there are several possible descriptions of these molecules if one wishes to assign oxidation states. As-

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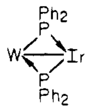
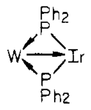
[17] Olah, G. A.; Kuhn, S. J.; Tolgyesi, W. S.; Baker, E. B. *J. Am. Chem. Soc.* **1962**, *84*, 2733.

[18] LaPlaca, S. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1963**, *85*, 3501.

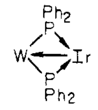
suming that there are three anionic ligands (H, $2PPh_2$), a total metal oxidation state of +3 must be accounted for. Consider molecule **2** which could be described as having a direct covalent single metal–metal bond between $d^5$-W(I) and $d^7$-Ir(II) centers (**2a**), a polar donor–acceptor bond between $d^6$-W(0) and $d^6$-Ir(III) centers (**2b**), or a polar donor–acceptor bond in the opposite direction between $d^4$-W(II) and $d^8$-Ir(I) centers (**2c**). On the basis of coordination geometries, description **2c** appears most resonable. Trigonal-bipyramidal Ir(I) and octahedral W(II) are reasonable geometries for these metal oxidation states. In **2c**, a filled d orbital on Ir could donate an electron pair into an empty $t_{2g}$ orbital on W(II) to achieve 18 valence electrons at the latter metal.



W(I) Ir(II)
2a



W(0) Ir(III)
2b



W(II) Ir(I)
2c

A sensitive probe of metal oxidation states is often the $\nu_{CO}$ stretching frequencies of coordinated CO's; low oxidation state complexes typically show lower energy $\nu_{CO}$ vibrations. The IR data for complex **2** appear to favor description **2a**. For example, the $\nu_{CO}$ stretch for the Ir-bound CO in **2** is at 1980 cm$^{-1}$, midway between the CO vibrations of the Ir(I) complex $IrH(CO)(PPh_3)_3$ (1930 cm$^{-1}$[19]) and the Ir(III) complex $IrHCl_2(CO)(PPh_3)_2$ (2024 cm$^{-1}$[20]). Likewise, the $\nu_{CO}$ vibrations attributed to the $W(CO)_4$ portion of **2** at 2035, 1933, and 1912 cm$^{-1}$ are higher in energy than the corresponding vibrations of the W(0) precursor complex $W(CO)_4(PPh_2H)_2$ at 2020 s, 1917 sh, 1905 vs, and 1893 sh cm$^{-1}$, implying partial oxidation of the W center in complex **2**.

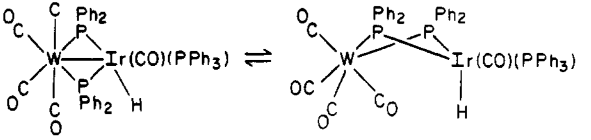
Since the available data are conflicting and do not allow a definitive choice to be made between **2a**, **2b**, and **2c**, it appears best to view the molecule as a hybrid of the three descriptions **2a**–**2c** since, in any case, electron density within the molecule can be easily redistributed through the bridging $\mu$-$PPh_2$ ligands.

## Discussion

One of the more important aspects of this work is the demonstration of the versatility of the "bridge-assisted" synthetic method for bringing different metals together to yield binuclear complexes. As illustrated by the preparation of **1**, **2**, and **3**, one can control the number of bridging phosphido ligands introduced and also the nature of the auxiliary ligands placed on Ir (H in **2**, $CH_3$ in **3**) by appropriate choice of the precursor complex. Oxidative addition of the PH bond of a coordinated $PPh_2H$ ligand across a second metal, as in the synthesis of **2** from $[W(CO)_4(PPh_2H)(PPh_2)]^-$, should be a generally useful way to introduce the important hydride functionality into binuclear compounds. In preliminary work we have shown that $[Fe(CO)_3(PPh_2H)(PPh_2)]^-$ can also be used in analogous reactions. For example, the latter reagent with *trans*-$IrCl(CO)(PPh_3)_2$ forms the hydride complex $(CO)_3Fe(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3)$.[21]

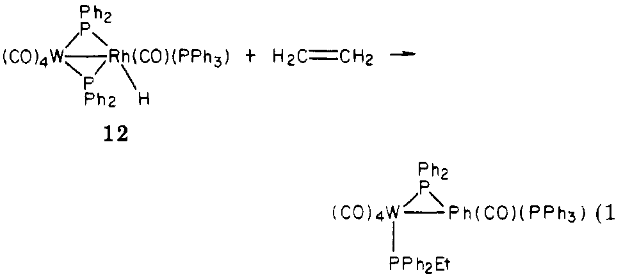
This study also illustrates the utility of the bridging phosphido ligands for maintaining complex integrity. In the reactions of **1** with $H_2$ and CO, for example, there is no evidence for disruption of the binuclear complex even though the W–Ir bond is readily, but reversibly, cleaved by these reagents. The phosphido bridge keeps the two metal centers tied together even when left in the presence of $H_2$ and CO for prolonged periods.

The bis(phosphido)-bridged complex **2** is remarkably unreactive toward $H_2$ and CO. Even heating to 180 °C for 4 h under 1500 psig of CO pressure gave no detectable decomposition nor reaction. Unlike complex **1**, **2** will not even reversibly bind $H_2$ or CO. Reversible addition of $H_2$ and CO to the Ir center concomitant with breaking the W–Ir bond, analogous to the chemistry of **1**, could occur, but it does not. Why does **2** not add CO and $H_2$ whereas **1** does? The lack of reactivity of **2** may be due to the rigidity of the $M_2(\mu\text{-}P)_2$ core. Since **2** is coordinatively saturated, for it to react with $H_2$ or CO, a preequilibrium would presumably have to be established in which the W–Ir bond was broken so as to generate an open coordination site for these reagents to add. Such would likely involve bending of the planar $WIr(\mu\text{-}PPh_2)_2$ core, eq 18, and the activation for this process could be sufficiently large so as to precluded its occurence in the temperature range studied.



(18)

As noted in the Experimental Section, **2** also fails to react with $C_2H_4$. In other work, we have shown that the analogous WRh complex **12** does react with this reagent to give the interesting conversion shown in eq 19.[21] This reaction likely proceeds via the intermediacy of a binuclear WRh–ethyl complex. A reaction analogous to eq 19 does not occur with **2**, again implying that an open coordination site to which $C_2H_4$ could add is not readily achieved with this complex. However, once an alkyl group is established on the Ir center, as with the methyl complex $WIrCH_3(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$ (**3**) bridge elimination does occur under fairly mild conditions to give the mono(phosphido)-bridged complex **10** having a $PPh_2CH_3$ ligand on W. We have seen this type of bridge-elimination reaction in our earlier study of phosphido-bridged cobalt carbonyls,[22] and its occurrence will surely limit the utility of phosphido-bridged compounds in catalysis.



12

(19)

Another surprising feature of the chemistry reported herein is the stability of the acyl–hydride and carbene–hydride complexes which result from **2**. A priori, one might have anticipated that coupling of the acyl ligand with the hydride would readily occur to yield an aldehyde from **6**.[15] Hydride migration to the carbene ligand in **7** could also conceivably occur to give an alkyl complex. However, neither of these transformations were observed. It could be argued that the disposition of the carbene ligand in **7** away from the Ir–hydride ligand (Figure 3), and presum-

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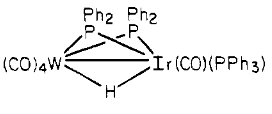
(21) Shulman, P. M.; Geoffroy, G. L., unpublished observations.
(22) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.

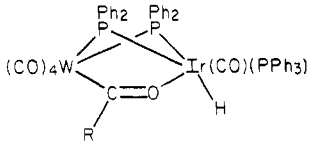
ably a similar ligand arrangement in the acyl–hydride complexes **6**, could account for the stability of these derivatives. Another reasonable explanation is that for aldehyde elimination to be facilitated or for hydride migration to the carbene ligand to occur, the hydride and organic ligands must be simultaneously attached to the same metal at some point in the reaction. Migration of hydride to W appears more reasonable than carbene or acyl migration to Ir, but there is apparently no tendency for either of these to occur. The W center in these derivatives is coordinatively saturated and hydride migration apparently cannot occur without ligand loss on W. The crystal structure of **2** in which the hydride was located and refined clearly shows that the hydride is terminally bound to Ir with no interaction with W.

It is significant that even though interesting acyl, carbene, and hydride ligands can be separately placed on the W and Ir centers in **2** and its derivatives, these ligands steadfastly refuse to interact even under forcing conditions. As noted above this may be due to the relative inertness of the third-row metals in these complexes and/or due to the steric constraints imposed by the two phosphido bridges. It is also interesting to note that none of these ligands in **2**, **6**, and **7** interact simultaneously with both metals even though bridging structures such as **13**, **14**, and **15** do not appear unreasonable on any obvious grounds.

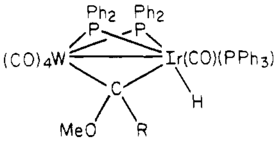
Future work in this program will focus on complexes containing more reactive first- and second-row metals as well as further studies of compounds possessing only one sterically demanding phosphido bridge.



**13**



**14**



**15**

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**Supplementary Material Available:** Listings of anisotropic temperature factors, structure factors, and bond angles (63 pages). Ordering information is given on any current masthead page.

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# X-ray Crystal Structure for Two Disilenes

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*Received November 28, 1983*

The synthesis and X-ray crystal structures of tetramesityldisilene, **1a**, and *trans*-1,2-di-*tert*-butyl-1,2-dimesityldisilene, **1b**, are reported. The silicon–silicon bond lengths, 216.0 pm for **1a** and 214.3 pm for **1b**, are consistent with silicon–silicon double bonding in these molecules. The two silicon atoms and four attached carbons in **1b** are coplanar, but **1a** has a distorted structure with moderate anti pyramidalization at the silicon atoms. The differences in molecular geometry and the question of aryl–silicon conjugation are discussed. Crystals of **1a** are tetragonal of space group $I4_1/a$; crystals of **1b** are triclinic of space group $P\bar{1}$.

Following the recent synthesis of kinetically stable compounds with silicon–carbon[1] and silicon–silicon double bonds,[2] a structural chemistry of tricoordinate silicon is beginning to emerge.[3,4] The disilenes, as silicon counterparts of olefins, have attracted the attention of chemists for over 60 years.[5] These long sought species were proposed in 1968 as transient species in the pyrolysis of disilabicyclooctadienes,[6] and since that time considerable evidence has been presented for disilenes as reaction intermediates.[5,7] The first stable disilene, tetramesityldisilene, was synthesized in 1981 by photolysis of a polysilane precursor.[2a] The stability of this compound is attributed to the prevention of bimolecular condensations by the sterically large mesityl rings. This and other similar molecules have been subsequently synthesized by our group and others with use of a variety of methods.[2]

The spectroscopic properties and chemical reactivity of tetramesityldisilene are characteristic of a genuinely doubly bonded compound. The $\sigma$–$\pi$ nature of the silicon–silicon

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[‡] J.M., University of Utah. M.J.F., M.J.M., K.J.H., and R.W., University of Wisconsin.

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