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# Formation of a Heterobimetallic Compound by Reductive Elimination of $CH_4$ and Oxidative Cleavage of an Aryl–Phosphorus Bond in Reaction of *trans*-MeIr(CO)[P(*p*-tolyl)$_3$]$_2$ with HMoCp(CO)$_3$: Crystal and Molecular Structures of CpMo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(*p*-tolyl)[P(*p*-tolyl)$_3$](CO)$_2$(*Mo–Ir*) and CpMo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(H)[P(*p*-tolyl)$_3$](CO)$_2$(*Mo–Ir*)

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Reaction of HMoCp(CO)$_3$ with *trans*-MeIr(CO)[P(*p*-tolyl)$_3$]$_2$ results in quantitative elimination of $CH_4$ and formation of a heterobimetallic complex, Cp(CO)$_2$Mo[$\mu$-P(*p*-tolyl)$_2$]Ir(*p*-tolyl)[P(*p*-tolyl)$_3$](CO)$_2$, by activation of the phosphorus–carbon bond. This complex has been fully characterized, including by X-ray crystallography. Cp(CO)$_2$Mo[$\mu$-P(*p*-tolyl)$_2$]Ir(*p*-tolyl)[P(*p*-tolyl)$_3$](CO)$_2$(*Mo–Ir*) crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (No. 14) with $a$ = 13.108 (5) Å, $b$ = 11.892 (5) Å, $c$ = 30.165 (11) Å, $\beta$ = 102.52 (3)°, $V$ = 4590 (3) Å$^3$, and $Z$ = 4. Diffraction data (Mo K$\alpha$, $2\theta$ = 5–45°) were collected with a Siemens R3m/V diffractometer and the structure was refined to $R$ = 7.68% and $R_w$ = 6.05% for all 6023 reflections ($R$ = 3.62%, $R_w$ = 4.63% for those 3586 reflections with $F_o > 6.0\sigma(F_o)$). The molecule contains a molybdenum–iridium bond (Mo–Ir = 2.976 (2) Å), which is bridged by a $\mu$-P(*p*-tolyl)$_2$ ligand (Mo–P = 2.412 (3) and Ir–P = 2.376 (3) Å). The molybdenum atom is bonded to an $\eta^5$-$C_5H_5$ ligand (Mo–C = 2.306 (11)–2.377 (11) Å) and two terminal carbonyl ligands (Mo–CO = 1.937 (10)–1.942 (15) Å); the iridium atom is bonded to mutually trans carbonyl ligands (Ir–CO = 1.899 (14)–1.907 (12) Å) and mutually cis P(*p*-tolyl)$_3$ and $\sigma$-(*p*-tolyl) ligands (Ir–P = 2.355 (3) and Ir–C(ipso) = 2.168 (10) Å). The heterobimetallic complex is surprisingly unreactive to CO, $CH_3I$, and PhC≡CPh; however, reaction with $H_2$ causes elimination of toluene and formation of a trihydride and a monohydride. Both have been separated and fully characterized. These hydrides are fluxional at room temperature and appear to be reactive. The monohydride, CpMo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(H)[P(*p*-tolyl)$_3$](CO)$_2$(*Mo–Ir*), crystallizes in the centrosymmetric orthorhombic space group *Pbca* (No. 61) with $a$ = 12.934 (2) Å, $b$ = 23.890 (3) Å, $c$ = 26.615 (3) Å, $V$ = 8224 (2) Å$^3$, and $Z$ = 4. The structure was refined to $R$ = 8.18% and $R_w$ = 6.56% for all 5390 reflections ($R$ = 3.41%, $R_w$ = 3.59% for those 2861 reflections with $F_o > 6.0\sigma(F_o)$). This molecule has Mo(1)–Ir(1) = 2.957 (1) Å and a bridging $\mu$-P(*p*-tolyl)$_2$ ligand associated with Mo–P = 2.391 (3) and Ir–P = 2.334 (3) Å. The molybdenum atom is bonded to an $\eta^5$-$C_5H_5$ ligand (Mo–C = 2.283 (14)–2.383 (15) Å) and two terminal carbonyl ligands (Mo–CO = 1.940 (13)–1.953 (14) Å); the iridium atom is now bonded to mutually cis carbonyl ligands (Ir–CO = 1.899 (13)–1.912 (15) Å) and mutually cis P(*p*-tolyl)$_3$ and hydride ligands (Ir–P = 2.333 (3) Å and Ir–H = 1.67 (9) Å).

The formation of heterobimetallic complexes between metal centers of different chemical reactivity continues to be an active area of investigation.[1–9] Many of these complexes contain bridging phosphido groups[3] or are combinations of early and late transition metals where reactivity differences should be maximized.[4] Very few of the prepared heterobimetallic complexes involve a coordinatively unsaturated metal center.[5–9] Reaction of *trans*-Rh(CO)(PEt$_3$)$_2$Cl with NaCo(CO)$_4$ resulted in the formation of *trans*-(PEt$_3$)$_2$(CO)RhCo(CO)$_4$, a complex having an unsaturated center and an unsupported Rh–Co bond.[5] Studies of the reactivity of this complex were precluded by heterolytic fission of the Rh–Co bond, giving Co(CO)$_4^-$. Similar reactions of CpMo(CO)$_3^-$, CpW(CO)$_3^-$, and Mn(CO)$_5^-$ with *trans*-Pt(PR$_3$)$_2$(R)(Cl) (R = H, Me, Ph) led to unsaturated heterobimetallic complexes.[6]

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$$\mathrm{CpMo(CO)_3^- + \textit{trans}\text{-}Pt(PPh_3)_2(H)(Cl) \rightarrow (PPh_3)_2HPt\text{-}MoCp(CO)_3 + Cl^-} \quad (1)$$

$$\mathrm{CpW(CO)_3^- + \textit{trans}\text{-}Pt(PPh_3)_2(H)(Cl) \rightarrow (PPh_3)_2HPt\text{-}WCp(CO)_3 + Cl^-} \quad (2)$$

$$\mathrm{Mn(CO)_5^- + \textit{trans}\text{-}Pt(PPh_3)_2(H)(Cl) \rightarrow (PPh_3)_2Pt(\mu\text{-}H)(\mu\text{-}CO)Mn(CO)_4 + Cl^-} \quad (3)$$

The reactivity of the platinum center in these heterobimetallic complexes was not explored.[6] The unsaturated heterobimetallic complex $CoRh(CO)_7$ (prepared in situ by cluster degradation) reacts with $H_2$ to give mononuclear hydrides, which then condense to $Rh_4(CO)_{12}$ and $Co_2(CO)_8$.[7]

Another approach to heterobimetallic complexes has involved oxidative addition of a metal hydride to an unsaturated metal center.[8] Reaction of $CpRe(CO)_2H_2$ with *trans*-$Ir(CO)(PPh_3)_2Cl$ led to $CpRe(CO)_3$, $H_2Ir(CO)(PPh_3)_2Cl$, and $H_2Ir(PPh_3)_3Cl$.

$$\mathrm{CpRe(CO)_2H_2 + \textit{trans}\text{-}Ir(CO)(PPh_3)_2Cl \rightarrow CpRe(CO)_3 + H_2IrL(PPh_3)_2Cl} \quad (4)$$

$$\mathrm{L = CO, PPh_3}$$

The suggestion was made that this reaction occurs through a heterobimetallic intermediate involving oxidative addition of the rhenium–hydride bond to the iridium(I) center.[8] A stable heterobimetallic complex was formed by reaction of $CpRe(CO)_2H_2$ with $Pt(PPh_3)_2(C_2H_4)$.[8]

$$\mathrm{CpRe(CO)_2H_2 + Pt(PPh_3)_2(C_2H_4) \rightarrow C_2H_4 + Cp(CO)_2(H)Re\text{-}Pt(H)(PPh_3)_2} \quad (5)$$

The hydride ligands were shown to be fluxional and could be transferred to alkenes or alkynes.[8] Very interesting complexes, $Cp_2Ta(CH_2)_2M$ (M = Ir or Pt complex), have been reported.[9] The iridium complex was shown to be active in the hydrogenation, isomerization, and hydrosilylation of alkenes.[9] There have also been reports on heterobimetallic complexes containing an unsaturated copper center, but the presence of semibridging carbonyls may hinder potential reactions; no reactions were reported.[10] Thus, while a few heterobimetallic complexes containing an unsaturated metal center have been prepared, the possible reactivity of the unsaturated center is largely unexplored.

Over the last several years our group has examined a number of reactions of *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ that lead to methyl–hydrogen, methyl–oxygen, methyl–carbon, and methyl–silicon bond formation.[11] In this manuscript we report on the reaction of *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ with metal hydrides, especially $HMoCp(CO)_3$, to eliminate $CH_4$ and form new heterobimetallic complexes.

## Experimental Section

All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Beckman 4240 or a Mattson Polaris Fourier-transform infrared spectrophotometer using 0.5-mm NaCl solution cells. $^1H$ and $^{31}P$ NMR spectra were recorded on a Varian VXR-400 spectrometer; $^{13}C$ spectra were recorded on a Varian Gemini-300. The $^{31}P$ spectra reported are proton decoupled and referenced to $H_3PO_4$. Gas chromatographic detection of $CH_4$ was accomplished on a Varian 2440-FID chromatograph equipped with a Porapak Q column.

Gases—$H_2$ (Matheson), CO (Linde), $^{13}CO$ (99%, ICON Stable Isotopes), and HCl (Matheson)—were used as received. Methyl iodide (Mallinckrodt) was purified on an activated alumina column prior to use. Diphenylacetylene (98%, Aldrich) and $P(p\text{-tolyl})_3$ (Strem) were used as received. $IrCl_3{\cdot}xH_2O$ was obtained from Johnson Matthey and used as received. $Cp_2Mo_2(CO)_6$ was purchased from Strem Chemical; $Cp_2W_2(CO)_6$ was prepared by adaptation of the literature procedure.[12] The complexes *trans*-$Ir(CO)(Cl)[P(p\text{-tolyl})_3]_2$ and *trans*-$CH_3Ir(CO)[P(p\text{-tolyl})_3]_2$ were prepared as previously described.[11a]

The hydrides, $HMCp(CO)_3$, M = Mo, W, were prepared from $Cp_2M_2(CO)_6$ as described in the literature.[12] The NMR and infrared spectra are in good agreement with literature values. M = Mo: IR ($Et_2O$) 2026 (s), 1939 (s) cm$^{-1}$; $^1H$ NMR ($C_7D_8$) 4.53 (s), −5.48 (s) ppm. M = W: IR ($C_7H_8$) 2020 (s), 1926 (vs) cm$^{-1}$; $^1H$ NMR ($C_7D_8$) 4.54 (s) and −7.27 (d) ($J_{W-H}$ = 36 Hz) ppm. $HMoCp(CO)_3$ was $^{13}CO$ enriched as follows: 0.188 g of $HMoCp(CO)_3$ was dissolved in 3 mL of $Et_2O$ in a glass reaction vessel fitted with a vacuum adaptor. The solution was degassed (3× freeze–pump–thaw) on a vacuum line and $^{13}CO$ (1 atm) added. After stirring for 48 h the ether was removed by vacuum. The infrared spectrum showed new bands ($\nu_{CO}$) at lower frequencies consistent with $^{13}CO$ enrichment >75%. The $^{13}C$ NMR spectrum contained one resonance at 228 (s) ppm.

**Preparation of $CpMo(CO)_2[\mu\text{-}P(p\text{-tolyl})_2]Ir(p\text{-tolyl})[P(p\text{-tolyl})_3](CO)_2$ (1A).** A solution of 0.345 g (0.409 mmol) of *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ in 5 mL of toluene was prepared in an inert atmosphere glovebox. The molybdenum hydride $HMoCp(CO)_3$ (0.104 g, 0.433 mmol) was added to the yellow-orange solution and the mixture was stirred. The color changed to reddish purple in 10 min. The solution was stirred overnight. The toluene was removed by vacuum to leave an oily solid. $Et_2O$ was added and removed by vacuum to leave a reddish orange solid. Hexanes were added and the insoluble orange solid was collected by filtration. The yield was 0.29 g (0.27 mmol), 66%. The infrared spectrum in $Et_2O$ showed absorptions at 2059 (w), 1997 (vs), 1925 (s), and 1843 (m) cm$^{-1}$. The $^1H$ NMR ($C_7D_8$) spectrum showed resonances at 6.7–7.6 (m), 4.90 (s, 5 H), 2.19 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), and 2.00 (s, 9 H) ppm; the $^{31}P$ ($C_7D_8$) NMR spectrum was −6.08 (d) ($J_{P-P}$ = 18.3 Hz) and 91.46 (d) ppm ($J_{P-P}$ = 18.3 Hz); and the $^{13}C$ NMR spectrum in the carbonyl region was 243.5 (d) ($J_{P-C}$ = 28.0 Hz), 241.4 (s), 183.6 (m), and 181.9 (m) ppm. Microanalysis (Oneida Research Services) confirmed the formulation. Calcd: C, 57.04; H, 4.38; P, 5.48; Ir, 17.89; Mo 8.95. Obsd: C, 56.95; H, 4.43; P, 5.61; Ir, 18.37; Mo, 8.71. X-ray quality crystals were grown by slow evaporation of $Et_2O$.

**Formation of $Cp(CO)_2W[\mu\text{-}P(p\text{-tolyl})_2]Ir(p\text{-tolyl})[P(p\text{-tolyl})_3](CO)_2$ (1B).** A procedure similar to that for the Mo analogue was followed. The reaction was stirred for 48 h. After removal of the toluene, hexanes were added and the solution was filtered. The yield was 0.085 g (0.073 mmol), 42%. IR ($Et_2O$) 1998 (s), 1919 (vs), 1843 (m); $^1H$ NMR ($C_6D_6$) 6.7–7.6 (m), 4.91 (s, 5 H), 2.02 (s, 3 H), 1.99 (s, 3 H), 1.98 (s, 3 H), 1.937 (s, 9 H) ppm; $^{31}P$ NMR ($C_6D_6$) −17.6 (d) ($J_{P-P}$ = 20.7 Hz), 55.2 (d) ($J_{P-P}$ = 20.7 Hz) (coupling of this resonance to tungsten, $J_{P-W}$ = 265 Hz, was also observed).

**Reaction of 1A with $H_2$.** A solution of 0.195 g of **1A** in 3 mL of $Et_2O$ was placed in a glass reaction vessel equipped with a vacuum adaptor and degassed (3× freeze–pump–thaw) and 1 atm of $H_2$ added. The solution was stirred for 24 h during which the solution changed from maroon to burnt orange. The $Et_2O$ was removed by vacuum giving an orange solid. This orange solid appears to be composed of two products that could be separated by solubility/crystallization or column chromatography. The spectra and assignments will be described under Results and Discussion. Toluene was quantitatively eliminated in this reaction (by NMR integration).

**Reaction of 1B with $H_2$.** A very similar procedure to that for the molybdenum analogue was followed for 0.034 g of **1B** in 2 mL of toluene. After $H_2$ addition the reaction was stirred for

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**Table I. Details of Data Collection for the X-ray Structural Study of ($\eta^5$-$C_5H_5$)Mo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(*p*-tolyl)[P(*p*-tolyl)$_3$](CO)$_2$(*Mo–Ir*) (1A) and ($\eta^5$-$C_5H_5$)Mo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(H)[P(*p*-tolyl)$_3$](CO)$_2$(*Mo–Ir*) (2)**

| | 1A | 2 |
|---|---|---|
| cryst data | | |
| empirical formula | $C_{51}H_{47}IrMoO_4P_2$ | $C_{44}H_{26}IrMoO_4P_2$ |
| color, habit | bright red cryst | red |
| cryst size, mm | 0.3 × 0.35 × 0.4 | 0.3 × 0.3 × 0.3 |
| cryst syst | monoclinic | orthorhombic |
| space group | $P2_1/n$ (No. 14) | *Pbca* (No. 61) |
| unit cell dimens | | |
| *a*, Å | 13.108 (5) | 12.934 (2) |
| *b*, Å | 11.892 (5) | 23.890 (3) |
| *c*, Å | 30.165 (11) | 26.615 (3) |
| $\beta$, deg | 102.52 (3) | 90 |
| vol, Å$^3$ | 4590 (3) | 8224.0 (16) |
| *Z* | 4 | 8 |
| fw | 1074.0 | 968.7 |
| density (calcd), Mg/m$^3$ | 1.554 | 1.565 |
| abs coeff, mm$^{-1}$ | 3.262 | 3.633 |
| *F*(000) | 2136 | 3768 |
| diffractometer used | Siemens R3m/V | |
| radiatn | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) | |
| temp, K | 298 | |
| monochromator | highly oriented graphite cryst | |
| 2$\theta$ range | 5.0–45.0° | |
| scan type | $\omega$ | |
| scan speed | constant; 2.00 deg/min in $\omega$ | |
| scan range ($\omega$) | 0.80° | |
| bkgd measmt | stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of total scan time | |
| std rflns | 3 measd every 97 rflns | |
| index ranges | $0 \le h \le 14$,<br>$0 \le k \le 12$,<br>$-32 \le l \le 31$ | $0 \le h \le 13$,<br>$0 \le k \le 25$,<br>$-28 \le l \le 28$ |
| rflns collected | 6694 | 11675 |
| indep rflns | 6023 ($R_{int}$ = 1.25%) | 5390 ($R_{int}$ = 1.37%) |
| obsd rflns | 6023 ($F > 0.3\sigma(F)$) | 5390 ($F > 0.3\sigma(F)$) |
| abs correctn | semiempirical | |

48 h. The product was separated as for the molybdenum analogue.

**Collection of X-ray Diffraction Data for CpMo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(*p*-tolyl)[P(*p*-tolyl)$_3$](CO)$_2$ (1A).** A bright red, approximately equidimensional (0.30 × 0.35 × 0.40 mm) crystal was aligned on a Siemens R3m/V diffractometer. Attempts to collect data via the preferred coupled $\theta$ (crystal)–2$\theta$ (counter) scan were abandoned because of some overlap of adjacent reflections. This problem was essentially eliminated by use of an "$\omega$-scan". Details of data collection appear in Table I.

The systematic absences *h*0*l* for $h + l = 2n + 1$ and 0*k*0 for $k = 2n + 1$ uniquely define the centrosymmetric monoclinic space group $P2_1/n$ (No. 14). 6694 reflections were collected and corrected for Lorentz and polarization effects and for absorption. Data were merged ($R_{int}$ = 1.25%) to a unique set of 6023 independent reflections with $F_o > 0.3\sigma(|F_o|)$.

**Solution and Refinement of the Crystal Structure for 1A.** All crystallographic calculations were carried out on a VAX3100 workstation with use of the Siemens SHELXTL PLUS program set. The analytical scattering factors for neutral atoms were corrected for the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. The structure was solved by a combination of direct methods and difference Fourier techniques. Refinement led to convergence ($(\Delta/\sigma)_{max}$ = 0.001) with *R* = 7.68%, $R_w$ = 6.05%, and GOF = 0.89 for 6023 reflections and 533 variables (*R* = 3.62% and $R_w$ = 4.63% for those 3586 reflections with $F_o > 6.0\sigma(F_o)$).

All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the phenyl rings were included in calculated positions with *d*(C–H) = 0.96 Å.[13] A final difference Fourier synthesis showed features only in the range 1.03 to –0.83 e$^-$/Å$^3$. Final atomic coordinates of 1A appear in Table II.

**Table II. Final Atomic Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters (Å$^2$ × 10$^3$) for ($\eta^5$-$C_5H_5$)Mo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(*p*-tolyl)[P(*p*-tolyl)$_3$](CO)$_2$(*Mo–Ir*)**

| | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|
| Ir(1) | 3064 (1) | 2009 (1) | 898 (1) | 35 (1) |
| Mo(1) | 3633 (1) | 4126 (1) | 1420 (1) | 42 (1) |
| P(1) | 2834 (2) | 103 (2) | 689 (1) | 38 (1) |
| P(2) | 3489 (2) | 2246 (2) | 1700 (1) | 37 (1) |
| C(3) | 4460 (10) | 1965 (10) | 816 (4) | 57 (5) |
| O(3) | 5269 (7) | 1896 (8) | 739 (3) | 78 (4) |
| C(4) | 1657 (9) | 2323 (8) | 933 (3) | 43 (4) |
| O(4) | 808 (6) | 2519 (7) | 937 (3) | 63 (3) |
| C(1) | 4671 (9) | 4165 (9) | 1985 (4) | 47 (4) |
| O(1) | 5271 (7) | 4180 (7) | 2330 (3) | 71 (4) |
| C(2) | 4910 (10) | 4149 (10) | 1192 (5) | 65 (5) |
| O(2) | 5696 (8) | 4264 (9) | 1080 (3) | 87 (4) |
| C(11) | 2626 (9) | 2824 (8) | 242 (3) | 42 (4) |
| C(12) | 3218 (10) | 3654 (10) | 114 (4) | 61 (5) |
| C(13) | 2823 (12) | 4338 (11) | −261 (4) | 72 (6) |
| C(14) | 1847 (14) | 4192 (12) | −522 (5) | 80 (7) |
| C(15) | 1262 (11) | 3358 (11) | −404 (4) | 68 (5) |
| C(16) | 1625 (10) | 2655 (10) | −29 (4) | 58 (5) |
| C(17) | 1392 (13) | 4957 (14) | −916 (5) | 112 (8) |
| C(21) | 2419 (7) | 2061 (8) | 1996 (3) | 37 (3) |
| C(22) | 2256 (8) | 2824 (9) | 2313 (3) | 45 (4) |
| C(23) | 1358 (9) | 2781 (9) | 2492 (3) | 49 (4) |
| C(24) | 618 (8) | 1961 (9) | 2365 (3) | 42 (4) |
| C(25) | 813 (9) | 1135 (10) | 2059 (3) | 52 (4) |
| C(26) | 1697 (8) | 1209 (9) | 1883 (4) | 49 (4) |
| C(27) | −370 (9) | 1958 (11) | 2540 (4) | 64 (5) |
| C(31) | 4568 (8) | 1535 (8) | 2073 (3) | 38 (4) |
| C(32) | 5583 (9) | 1684 (9) | 2014 (4) | 55 (5) |
| C(33) | 6429 (9) | 1101 (10) | 2271 (4) | 52 (4) |
| C(34) | 6279 (8) | 348 (10) | 2604 (4) | 51 (4) |
| C(35) | 5263 (9) | 210 (9) | 2672 (4) | 50 (4) |
| C(36) | 4449 (9) | 782 (8) | 2413 (4) | 48 (4) |
| C(37) | 7168 (10) | −365 (11) | 2870 (4) | 76 (6) |
| C(41) | 2487 (8) | −256 (8) | 83 (3) | 38 (4) |
| C(42) | 2996 (9) | 267 (9) | −209 (4) | 50 (4) |
| C(43) | 2875 (10) | −116 (11) | −658 (4) | 61 (5) |
| C(44) | 2261 (9) | −1028 (10) | −805 (4) | 53 (4) |
| C(45) | 1711 (10) | −1537 (11) | −516 (4) | 63 (5) |
| C(46) | 1838 (8) | −1172 (9) | −68 (3) | 46 (4) |
| C(47) | 2142 (11) | −1440 (13) | −1291 (4) | 88 (6) |
| C(51) | 3984 (8) | −774 (8) | 862 (3) | 39 (4) |
| C(52) | 4647 (8) | −614 (9) | 1290 (3) | 39 (4) |
| C(53) | 5467 (8) | −1298 (8) | 1447 (4) | 45 (4) |
| C(54) | 5729 (8) | −2164 (9) | 1196 (4) | 49 (4) |
| C(55) | 5085 (9) | −2340 (10) | 765 (4) | 62 (5) |
| C(56) | 4232 (9) | −1649 (10) | 614 (4) | 56 (5) |
| C(57) | 6638 (9) | −2932 (10) | 1361 (5) | 73 (5) |
| C(61) | 1841 (7) | −592 (8) | 926 (3) | 36 (4) |
| C(62) | 2058 (8) | −1409 (9) | 1266 (3) | 44 (4) |
| C(63) | 1291 (9) | −1850 (10) | 1464 (4) | 54 (4) |
| C(64) | 279 (10) | −1540 (10) | 1332 (4) | 55 (5) |
| C(65) | 23 (8) | −777 (10) | 978 (4) | 57 (5) |
| C(66) | 788 (8) | −300 (9) | 778 (4) | 45 (4) |
| C(67) | −565 (10) | −1986 (12) | 1549 (5) | 84 (6) |
| C(71) | 2689 (10) | 5509 (10) | 1705 (5) | 63 (5) |
| C(72) | 1935 (9) | 4808 (9) | 1414 (5) | 60 (5) |
| C(73) | 2087 (9) | 4943 (10) | 979 (4) | 58 (5) |
| C(74) | 2920 (10) | 5683 (10) | 981 (5) | 65 (5) |
| C(75) | 3303 (10) | 6030 (9) | 1426 (5) | 60 (5) |

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

**Collection of X-ray Diffraction Data for CpMo(CO)$_2$[$\mu$-P(*p*-tolyl)$_2$]Ir(H)[P(*p*-tolyl)$_3$](CO)$_2$ (2).** Data were collected in a similar fashion to that described for 1A, by use of the $\omega$-scan technique. Details of data collection appear in Table I.

The systematic absences 0*kl* for $k = 2n + 1$, *h*0*l* for $l = 2n + 1$, and *hk*0 for $h = 2n + 1$ uniquely define the centrosymmetric orthorhombic space group *Pbca* (No. 61). A total of 11675 reflections were collected. This represented two symmetry-equivalent octants (*hkl* and $hk\bar{l}$). These data were merged ($R_{int}$

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[13] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

**Table III. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å$^2 \times 10^3$) for $(\eta^5\text{-}C_5H_5)Mo(CO)_2[\mu\text{-}P(p\text{-tolyl})_2]Ir(H)[P(p\text{-tolyl})_3](CO)_2\text{-}(Mo\text{-}Ir)$**

| | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|
| Ir(1) | 1216 (1) | 1055 (1) | 923 (1) | 62 (1) |
| Mo(1) | 1651 (1) | 1842 (1) | 92 (1) | 68 (1) |
| H(1) | 1680 (70) | 569 (37) | 531 (34) | 81 (30) |
| P(3) | 1341 (2) | 405 (1) | 1574 (1) | 63 (1) |
| P(4) | 2739 (2) | 1551 (1) | 770 (1) | 57 (1) |
| O(11) | 251 (8) | 1920 (4) | 1623 (4) | 130 (5) |
| O(12) | −651 (8) | 669 (6) | 320 (5) | 158 (6) |
| O(21) | −242 (8) | 2470 (4) | 540 (4) | 125 (5) |
| O(22) | 2708 (8) | 2979 (4) | 271 (4) | 109 (4) |
| C(11) | 639 (10) | 1604 (6) | 1356 (5) | 90 (6) |
| C(12) | 28 (12) | 812 (6) | 556 (5) | 101 (6) |
| C(21) | 459 (11) | 2218 (5) | 390 (5) | 88 (6) |
| C(22) | 2323 (11) | 2553 (6) | 224 (5) | 84 (5) |
| C(31) | 1578 (9) | 729 (5) | 2185 (4) | 67 (4) |
| C(32) | 2380 (11) | 1108 (5) | 2237 (4) | 89 (5) |
| C(33) | 2578 (12) | 1372 (6) | 2690 (5) | 93 (6) |
| C(34) | 1964 (11) | 1269 (5) | 3102 (5) | 87 (5) |
| C(35) | 1171 (10) | 901 (6) | 3056 (5) | 93 (6) |
| C(36) | 967 (9) | 626 (5) | 2609 (5) | 79 (5) |
| C(37) | 2214 (13) | 1576 (7) | 3602 (5) | 129 (8) |
| C(41) | 155 (8) | −6 (5) | 1664 (4) | 70 (5) |
| C(42) | −778 (9) | 278 (6) | 1635 (5) | 83 (5) |
| C(43) | −1702 (13) | −24 (8) | 1698 (5) | 101 (7) |
| C(44) | −1694 (13) | −593 (8) | 1795 (5) | 99 (7) |
| C(45) | −778 (15) | −868 (7) | 1816 (5) | 114 (8) |
| C(46) | 170 (11) | −577 (5) | 1756 (5) | 88 (6) |
| C(47) | −2723 (12) | −897 (7) | 1880 (6) | 143 (8) |
| C(51) | 2319 (9) | −129 (4) | 1516 (4) | 64 (4) |
| C(52) | 3116 (10) | −222 (5) | 1859 (4) | 77 (5) |
| C(53) | 3840 (10) | −616 (5) | 1766 (5) | 82 (5) |
| C(54) | 3833 (9) | −961 (5) | 1352 (5) | 74 (5) |
| C(55) | 3023 (10) | −888 (5) | 1032 (5) | 76 (5) |
| C(56) | 2290 (8) | −481 (4) | 1109 (4) | 60 (4) |
| C(57) | 4675 (11) | −1406 (5) | 1268 (5) | 99 (6) |
| C(61) | 3209 (9) | 2010 (4) | 1263 (4) | 68 (4) |
| C(62) | 2647 (12) | 2468 (5) | 1416 (5) | 85 (5) |
| C(63) | 3012 (12) | 2782 (6) | 1830 (6) | 107 (7) |
| C(64) | 3923 (11) | 2685 (5) | 2095 (5) | 87 (5) |
| C(65) | 4462 (11) | 2233 (5) | 1915 (5) | 84 (5) |
| C(66) | 4145 (9) | 1901 (5) | 1511 (4) | 79 (5) |
| C(67) | 4289 (13) | 2996 (5) | 2552 (5) | 114 (6) |
| C(71) | 3901 (7) | 1165 (4) | 611 (4) | 54 (4) |
| C(72) | 4079 (8) | 615 (4) | 757 (4) | 64 (4) |
| C(73) | 5026 (9) | 352 (5) | 655 (4) | 76 (5) |
| C(74) | 5797 (9) | 625 (6) | 403 (4) | 71 (5) |
| C(75) | 5616 (9) | 1165 (5) | 256 (4) | 77 (5) |
| C(76) | 4680 (9) | 1428 (5) | 354 (4) | 70 (4) |
| C(77) | 6855 (10) | 323 (7) | 298 (5) | 107 (6) |
| C(81) | 749 (13) | 1530 (9) | −621 (5) | 113 (8) |
| C(82) | 1414 (15) | 1096 (7) | −492 (5) | 100 (7) |
| C(83) | 2400 (15) | 1275 (8) | −531 (5) | 104 (7) |
| C(84) | 2361 (14) | 1835 (8) | −696 (5) | 103 (7) |
| C(85) | 1342 (16) | 1999 (8) | −741 (5) | 107 (7) |

= 1.37%) to a unique set of 5390 independent data with $F_o > 0.3\sigma(|F_o|)$.

**Solution and Refinement of the Crystal Structure of 2.** Refinement was carried out as for **1A** (vide supra), leading to convergence with $R = 8.18\%$, $R_w = 6.56\%$, and GOF = 0.94 for 5390 reflections and 499 variables ($R = 3.41\%$ and $R_w = 3.59\%$ for those 2861 reflections with $F_o > 6.0\sigma(F_o)$).

All non-hydrogen atoms were refined anisotropically, the coordinates for the hydride ligand were refined and hydrogen atoms of the phenyl rings were included in calculated positions. A final difference Fourier synthesis showed features in the range 0.96 to −0.70 e$^-$/Å$^3$.

Final atomic coordinates for **2** appear in Table III.

## Results and Discussion

Binuclear reductive eliminations of carbon–hydrogen bonds have been demonstrated for several stoichiometric reactions and suggested for catalytic reactions.[14] The key step in these reductive elimination reactions was generation of an open coordination site on the alkyl complex.[15] The square-planar iridium complex *trans*-MeIr(CO)[P(*p*-tolyl)$_3$]$_2$, which has an open coordination site, readily undergoes bimolecular reductive elimination of $CH_4$ with a variety of transition-metal hydrides.

$$trans\text{-MeIr(CO)[P(}p\text{-tolyl)}_3]_2 + \text{HM} \rightarrow [\text{MIr(CO)[P(}p\text{-tolyl)}_3]_2] + \text{CH}_4 \quad (6)$$

$$\text{M} = \text{CpMo(CO)}_3,\ \text{CpW(CO)}_3,\ \text{Cp}_2\text{Nb(CO)},\ \text{HOs(CO)}_4,\ \text{Re(CO)}_5$$

These reactions almost certainly occur through oxidative addition of the metal–hydride bond to the 16-electron iridium center. Such a step has been observed for hydrogen sources as disparate as HCl and $HSiMe_2Ph$.[11] Reductive elimination of methane would lead to *trans*-MIr(CO)[P(*p*-tolyl)$_3$]$_2$. However, subsequent reactions preclude isolation of this heterobimetallic product. Formation of $H_3$Ir(CO)[P(*p*-tolyl)$_3$]$_2$ in reactions with HRe(CO)$_5$, $H_2Os(CO)_4$, and HNbCp$_2$(CO) indicates that multiple oxidative additions are occurring at the iridium center. However, for the more sterically hindered hydrides HMoCp(CO)$_3$ and HWCp(CO)$_3$, only one oxidative addition of the hydride occurs and $CH_4$ is produced stoichiometrically. The possible products, Cp(CO)$_3$M′Ir(CO)[P(*p*-tolyl)$_3$]$_2$, are not stable and undergo oxidative addition of a phosphorus–carbon bond producing Cp(CO)$_2$M′[$\mu$-P(*p*-tolyl)$_2$]Ir(*p*-tolyl)(CO)$_2$[P(*p*-tolyl)$_3$] (1) [M′ = Mo (**1A**) or W (**1B**)]. Note that these compounds are isomers of Cp(CO)$_3$M′Ir(CO)[P(*p*-tolyl)$_3$]$_2$, but rearrangement has produced a structure with an 18e$^-$ configuration at each metal center.

The presence of four CO absorptions indicates the low symmetry of the bimetallic complexes. The absorption for **1A** at 1843 (m) cm$^{-1}$ suggests that, in solution, a bridging or semibridging carbonyl is present. The $^{13}$C NMR also shows the presence of four different carbonyl groups. One of the carbonyl resonances is a doublet ($J = 28.0$ Hz) from CO coupling to phosphorus. On the basis of comparison to mononuclear complexes, we assign the two resonances at ~240 ppm to carbonyls on molybdenum and the two at ~180 ppm to carbonyls on iridium. The $^{31}$P spectrum (−6.08 (d), 91.46 (d)) is diagnostic of a P(*p*-tolyl)$_3$ and a phosphide bridging between two metals that are connected by a metal–metal bond.[17,18] The relatively small coupling constant, $J_{P\text{-}P} = 18$ Hz, is consistent with a cis orientation of the phosphine and phosphide.[19] The $^1$H NMR spectrum shows the presence of four different tolyl groups. The

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(14) (a) Hoxmeier, R. J.; Blickensderfer, J. R.; Kaesz, H. D. *Inorg. Chem.* **1979**, *18*, 3453. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447. (c) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619. (d) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. (e) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (f) Ruszczyk, R. J.; Huang, B. L.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *299*, 205.

(15) (a) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150. (b) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33. (c) Wegman, R. M. *Organometallics* **1986**, *5*, 707.

(16) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1982; p 298.

(17) (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163 and references therein. (b) Grushin, V. V.; Vymentis, A. B.; Yanovsky, A. I.; Sturchkov, Y. T.; Vol'pin, M. E. *Organometallics* **1991**, *10*, 48. (c) McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543. (d) Brown, S. C.; Evans, J.; Smart, L. E. *J. Chem. Soc., Chem. Commun.* **1980**, 1021.

(18) Garrou, P. *Chem. Rev.* **1981**, *81*, 229 and references therein.

(19) (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163. (b) Rosenberg, S.; Lockledge, S. P.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 2517.

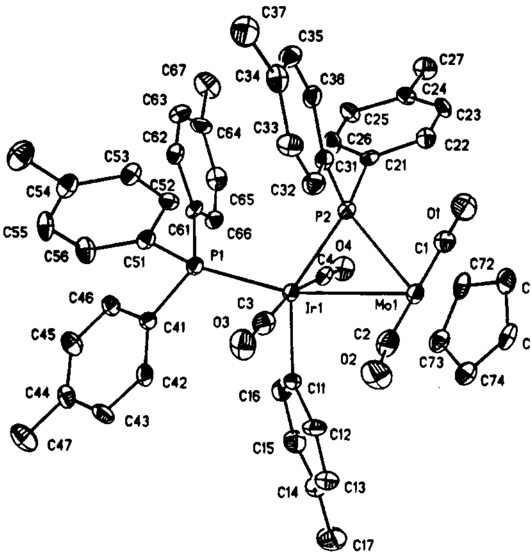

**Figure 1.** Labeling of non-hydrogen atoms in $(\eta^5\text{-}C_5H_5)Mo(CO)_2[\mu\text{-}P(p\text{-tolyl})_2]Ir(p\text{-tolyl})[P(p\text{-tolyl})_3](CO)_2$(*Mo-Ir*) (**1A**).

2.00 (s) ppm resonance is assigned to the $P(p\text{-tolyl})_3$ ligand; the two resonances at 2.04 (s) and 2.05 (s) are assigned to the two tolyl groups on the phosphide ligand; the 2.19 (s) is assigned to the tolyl ligand bound to iridium. Integration is consistent with these assignments. Spectra for complex **1B** were analogous except that the $^{31}P$ spectrum also shows coupling to W.

Microanalysis and spectroscopic analysis provide data on the composition of **1A** and **1B** in solution, but to confirm the structure we grew X-ray quality crystals and determined the solid-state structure of **1A**.

**Structure of $Cp(CO)_2Mo[\mu\text{-}P(p\text{-tolyl})_2]Ir(p\text{-tolyl})[P(p\text{-tolyl})_3](CO)_2$(*Mo-Ir*) (1A).** The crystal consists of discrete molecular units separated by normal van der Waals distances; there are no abnormally short intermolecular contacts.

Figure 1 shows the labeling of non-hydrogen atoms. Selected interatomic distances and angles appear in Table IV.

The heterobimetallic molecule consists of a $CpMo(CO)_2$ and an $Ir(p\text{-tolyl})[P(p\text{-tolyl})_3](CO)_2$ fragment, which are linked via a direct molybdenum–iridium linkage (Mo(1)–Ir(1) = 2.976 (2) Å) and a bridging di(*p*-tolyl)phosphide ligand (Mo(1)–P(2) = 2.412 (3) Å, Ir(1)–P(2) = 2.376 (3) Å, and ∠Ir(1)–P(2)–Mo(1) = 76.9 (1)°); see Figure 2.

The molybdenum atom has the "four-legged piano stool" coordination geometry typical of $CpMo(CO)_3X$ (and related) species.[20] Individual $Mo\text{-}C(\eta^5\text{-}C_5H_5)$ distances range from Mo(1)–C(75) = 2.306 (11) Å to Mo(1)–C(73) = 2.377 (11) Å, while C–C distances are 1.377 (20)–1.438 (16) Å (average = 1.406 Å). The two terminal carbonyl ligands are linked to the central molybdenum atom by Mo(1)–C(1) = 1.937 (10) Å and Mo(1)–C(2) = 1.942 (15) Å, with ∠Mo(1)–C(1)–O(1) = 178.1 (11)° and ∠Mo(1)–C(2)–O(2) = 173.0 (11)°.

**Table IV. Selected Interatomic Distances (Å) and Angles (deg) for 1A**

| | | | |
|---|---|---|---|
| (A) Distances within Ir(1)–P(2)–Mo(1) Core | | | |
| Ir(1)–Mo(1) | 2.976 (2) | Mo(1)–P(2) | 2.412 (3) |
| Ir(1)–P(2) | 2.376 (2) | | |
| (B) Distances around Mo(1) | | | |
| Mo(1)–C(1) | 1.937 (10) | Mo(1)–C(73) | 2.377 (11) |
| Mo(1)–C(2) | 1.942 (15) | Mo(1)–C(74) | 2.349 (12) |
| Mo(1)–C(71) | 2.333 (13) | Mo(1)–C(75) | 2.306 (11) |
| Mo(1)–C(72) | 2.366 (12) | | |
| (C) Distances around Ir(1) | | | |
| Ir(1)–P(1) | 2.355 (3) | Ir(1)–C(3) | 1.899 (14) |
| Ir(1)–C(11) | 2.168 (10) | Ir(1)–C(4) | 1.907 (12) |
| (D) P–C Distances | | | |
| P(1)–C(41) | 1.834 (10) | P(2)–C(21) | 1.833 (11) |
| P(1)–C(51) | 1.814 (10) | P(2)–C(31) | 1.815 (10) |
| P(1)–C(61) | 1.815 (11) | | |
| (E) C–O Distances | | | |
| C(1)–O(1) | 1.162 (13) | C(3)–O(3) | 1.137 (17) |
| C(2)–O(2) | 1.159 (18) | C(4)–O(4) | 1.139 (15) |
| (F) Angles within Ir(1)–P(2)–Mo(1) Core | | | |
| Mo(1)–Ir(1)–P(2) | 52.1 (1) | Ir(1)–P(2)–Mo(1) | 76.9 (1) |
| Ir(1)–Mo(1)–P(2) | 51.0 (1) | | |
| (G) Selected Angles around Mo(1) | | | |
| Ir(1)–Mo(1)–P(2) | 51.0 (1) | P(2)–Mo(1)–C(1) | 78.9 (3) |
| Ir(1)–Mo(1)–C(1) | 122.2 (3) | P(2)–Mo(1)–C(2) | 106.0 (4) |
| Ir(1)–Mo(1)–C(2) | 87.8 (4) | C(1)–Mo(1)–C(2) | 79.4 (5) |
| (H) Angles around Ir(1) | | | |
| Mo(1)–Ir(1)–P(1) | 163.5 (1) | P(1)–Ir(1)–C(11) | 101.0 (3) |
| Mo(1)–Ir(1)–P(2) | 52.1 (1) | P(2)–Ir(1)–C(3) | 96.6 (3) |
| Mo(1)–Ir(1)–C(3) | 87.3 (4) | P(2)–Ir(1)–C(4) | 86.4 (3) |
| Mo(1)–Ir(1)–C(4) | 86.6 (3) | P(2)–Ir(1)–C(11) | 146.5 (3) |
| Mo(1)–Ir(1)–C(11) | 95.2 (3) | C(3)–Ir(1)–C(4) | 169.4 (5) |
| P(1)–Ir(1)–P(2) | 112.0 (1) | C(3)–Ir(1)–C(11) | 88.0 (5) |
| P(1)–Ir(1)–C(3) | 90.5 (4) | C(4)–Ir(1)–C(11) | 83.9 (4) |
| P(1)–Ir(1)–C(4) | 97.7 (3) | | |
| (I) Mo–C–O and Ir–C–O Angles | | | |
| Mo(1)–C(1)–O(1) | 178.1 (11) | Ir(1)–C(3)–O(3) | 175.0 (10) |
| Mo(1)–C(2)–O(2) | 173.0 (11) | Ir(1)–C(4)–O(4) | 177.5 (9) |

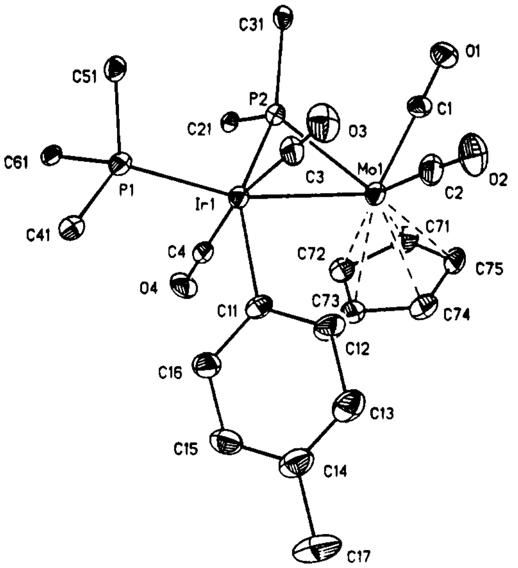

**Figure 2.** Central portion of the binuclear molecule **1A**. (Only the ipso carbons of P-bonded tolyl groups are shown.) Note the mutually trans carbonyls on Ir(1).

The iridium atom is in a distorted octahedral environment, the smallest cis angle being ∠Mo(1)–Ir(1)–P(2) = 52.1 (1)°; trans angles are Mo(1)–Ir(1)–P(1) = 163.5 (1)°, C(3)–Ir(1)–C(4) = 169.4 (5)°, and P(2)–Ir(1)–C(11) = 146.5 (3)°. The two mutually trans carbonyl ligands are associated with the Ir–CO bond lengths Ir(1)–C(3) = 1.899 (14) Å and Ir(1)–C(4) = 1.907 (12) Å and the Ir–C–O angles Ir(1)–C(3)–O(3) = 175.0 (10)° and Ir(1)–C(4)–O(4) = 177.5 (9)°. The tri-*p*-tolylphosphine ligand is associated with a bond length of Ir(1)–P(1) = 2.355 (3) Å; Ir–P–C(ipso) angles are all expanded from the regular tetrahedral value (109.5°), with Ir(1)–P(1)–C(41) = 118.8 (3)°, Ir(1)–P(1)–

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[20] Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197.

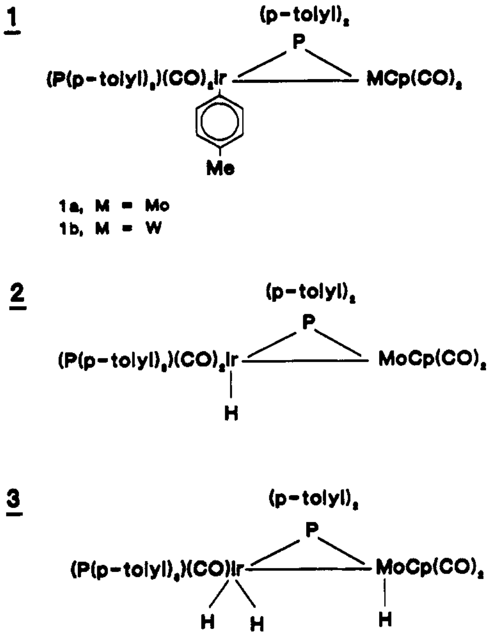

Figure 3. Complexes 1, 2, and 3.

C(51) = 115.2 (3)°, and Ir(1)–P(1)–C(61) = 113.2 (3)°. The $\sigma$-(*p*-tolyl) ligand is linked to iridium through the bond Ir(1)–C(11) = 2.168 (10) Å. This is similar to previously described iridium–carbon $\sigma$-bond lengths.[21]

The structure of 1A, with two CO ligands on iridium and molybdenum, a terminal P(*p*-tolyl)$_3$, a bridging P(*p*-tolyl)$_2$, a $\sigma$-bonded tolyl, and a Cp on molybdenum, is completely consistent with that predicted from spectroscopic studies.

Orthometalation of unsaturated complexes containing phosphine ligands producing an 18e$^-$ complex has often been observed.[16] Activation of a phosphorus–carbon bond is much less common.[17] Carty has demonstrated the addition of a phosphorus–carbon bond of $PPh_2C{\equiv}CPh$ to produce the phosphide, acetylide complex.[17a] Both phosphorus–carbon and carbon–hydrogen activation were observed in conversion of $PPh_3$ to a diphenylphosphido and an *o*-phenylene ligand.[17b,c] Thermolysis of $Os_3(CO)_{11}PPh_2R$ produced a $\mu_3$-PR and coordinated benzyne.[17d] A review describing catalyst deactivation by phosphorus–carbon bond cleavage has appeared.[18] The extra stability resulting from a phosphide ligand bridging the bimetallic complex may be responsible for the less commonly observed phosphorus–carbon activation in formation of 1A. In formation of the complex, a CO ligand is transferred from molybdenum to iridium. When $HMoCp(^{13}CO)_3$ is used, 1A has $^{13}CO$ scrambled throughout as shown by $^{13}C$ NMR.

**Reactivity of 1A.** The heterobimetallic complex is stable toward air and water in solution and in the solid state. 1A is also unreactive toward CO, $CH_3I$, and $PhC{\equiv}CPh$. This low reactivity is consistent with both centers having 18e$^-$ and also being sterically hindered. The Ir center is six-coordinate and the Mo center is seven-coordinate.

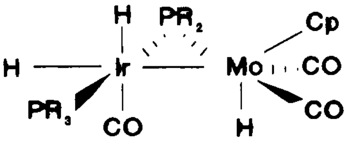

Figure 4. Suggested geometry for $Cp(CO)_2(H)M[\mu\text{-}P(p\text{-tolyl})_2]Ir(CO)(H)_2[P(p\text{-tolyl})_3]$ (3).

Reaction of 1A with $H_2$ occurs under ambient conditions in 24 h producing 1 equiv of toluene.

$$1A + H_2 \rightarrow \text{toluene} + \underset{2}{Cp(CO)_2Mo[\mu\text{-}P(p\text{-tolyl})_2]Ir(H)(CO)_2[P(p\text{-tolyl})_3]} + \underset{3}{Cp(CO)_2(H)Mo[\mu\text{-}P(p\text{-tolyl})_2]Ir(H)_2(CO)[P(p\text{-tolyl})_3]} \qquad (7)$$

There appear to be two heterobimetallic hydride complexes formed (compounds 2 and 3 in a 1:3 ratio); there is a small amount of $H_3Ir(CO)[P(p\text{-tolyl})_3]_2$ formed, but no evidence for other mononuclear products (such as $HMoCp(CO)_3$, $HIr(CO)_2[P(p\text{-tolyl})_3]_2$, or $HIr(CO)[P(p\text{-tolyl})_3]_3$ etc.) formed in this reaction. Schematics for 1, 2, and 3 are shown in Figure 3. At room temperature broad resonances are observed in the $^1H$ and $^{31}P$ NMR spectra for 2 and 3. The broad resonances sharpen at low temperatures (–50 °C), indicating fluxional behavior. The dominant product, 3, has three hydride resonances (–7.6 (s), –12.6 (t) ($J_{P-H}$ = 19 hz), –13.1 (m) ppm) that integrate 1:1:1 at –60 °C. The $^{31}P$ NMR spectrum shows two doublets [–6.5 (d) and 115.4 (d) ppm ($J_{P-P}$ = 216 Hz)], similar to the spectrum for 1A, indicating the presence of $P(tolyl)_3$ on the iridium and a $P(tolyl)_2$ bridging the two metals. The large P–P coupling indicates a trans orientation of phosphide and phosphine. The apparent triplet in the $^1H$ NMR spectrum at –12.6 ppm must arise from nearly equal coupling to two different phosphorus centers.[22] The multiplet at –13.1 ppm appears to be two overlapping doublets as expected from dissimilar phosphorus atoms. The lack of coupling to the hydride at –7.6 ppm and the chemical shift are strong indications that this hydride is bound to Mo. When the analogous reaction of $H_2$ with 1B is accomplished, the resonance at –7.2 ppm shows satellites due to tungsten coupling ($J_{W-H}$ = 19 Hz). Thus the product, 3, appears to be $Cp(CO)_2(H)Mo[\mu\text{-}P(p\text{-tolyl})_2]Ir(H)_2(CO)[P(p\text{-tolyl})_3]$. The suggested geometry is shown in Figure 4. At –40 °C the resonances are beginning to broaden and by –20 °C the resonances at –7.5 and –13.1 ppm are more broadened than the resonance at –12.6 ppm. This continues to 25 °C where the resonances at –7.5 and –13.1 ppm have disappeared leaving only the broadened –12.6 ppm resonance. This type of pairwise exchange is consistent with a doubly hydride-bridged intermediate allowing exchange. Representative $^1H$ NMR spectra are shown in Figure 5. The infrared spectrum indicates that, in solution, a bridging or semibridging CO is present (in $Et_2O$: 2090 (w), 1945 (vs), 1871 (s) cm$^{-1}$).

The minor product when the reaction is run under 1 atm of $H_2$ becomes dominant when the reaction is carried out with 1 atm of a 1:1 mix of CO and $H_2$. This product also appears to contain a bridging CO in solution (IR ($Et_2O$): 2119 (w), 2029 (m), 1915 (vs), 1843 (s)). A single hydride is observed for this complex, broad at room temperature, but sharpening at –60 °C to a triplet at –12.4 (t) ppm ($J_{P-H}$ = 16 Hz). The $^{31}P$ NMR spectrum is also broad at room

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[21] (a) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91–164; see, especially, pp 145–147. (b) Churchill, M. R.; Fettinger, J. C.; Janik, T. S.; Rees, W. M.; Thompson, J. S.; Tomazewski, S.; Atwood, J. D. *J. Organomet. Chem.* **1987**, *323*, 233. (c) Fettinger, J. C.; Rees, W. M.; Churchill, M. R.; Atwood, J. D. *J. Organomet. Chem.* **1987**, *319*, 411. (d) Churchill, M. R.; Fettinger, J. C.; Rees, W. M.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *301*, 99. (e) Rees, W. M.; Churchill, M. R.; Li, Y. G.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162.

[22] Very similar coupling from different phosphines leading to an apparent triplet has been previously observed.[23]

[23] Clark, H. C.; Goel, A. B.; Wong, C. S. *J. Organomet. Chem.* **1980**, *190*, C101.

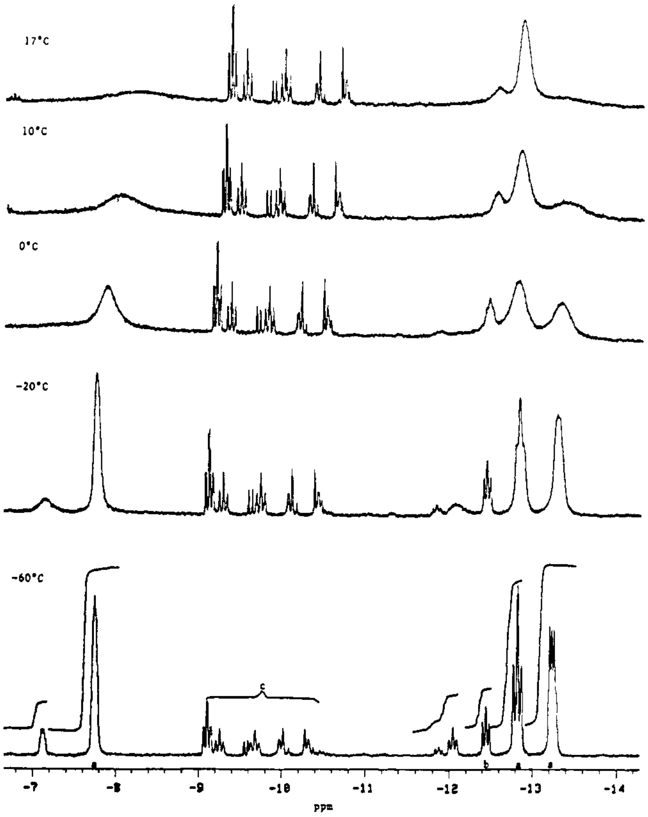

**Figure 5.** $^1H$ NMR spectra of the hydride region for reaction of **1A** with $H_2$ at various temperatures showing the collapse of two of the resonances, consistent with pairwise exchange. The resonances labeled a are from the heterobimetallic trihydride **3**. The resonance labeled b is from the heterobimetallic monohydride **2**. The resonances labeled c are from the *fac*- and *mer*-$Ir(H)_3(CO)[P(p\text{-tolyl})_3]_2$. The spectrum at -60 °C is recorded at 40% of the other temperatures. The resonances not labeled are not consistently observed.

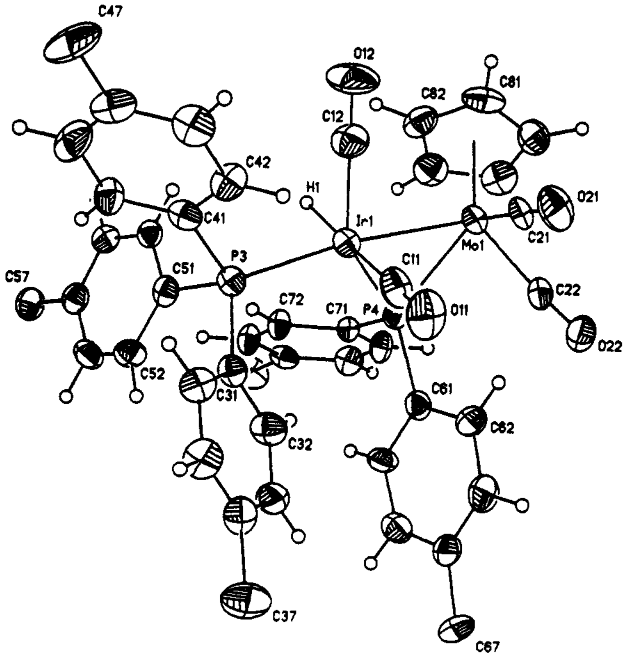

**Figure 6.** Labeling of atoms in $Cp(CO)_2Mo[\mu\text{-}P(p\text{-tolyl})_2]Ir(CO)_2(H)[P(p\text{-tolyl})_3]_2$ (**2**).

Table V. Selected Interatomic Distances (Å) and Angles (deg) for 2

| | | | |
|---|---|---|---|
| (A) Distances within Ir(1)-P(4)-Mo(1) Core | | | |
| Ir(1)-Mo(1) | 2.957 (1) | Mo(1)-P(4) | 2.391 (3) |
| Ir(1)-P(4) | 2.334 (3) | | |
| (B) Distances around Mo(1) | | | |
| Mo(1)-C(21) | 1.953 (14) | Mo(1)-C(83) | 2.348 (17) |
| Mo(1)-C(22) | 1.940 (13) | Mo(1)-C(84) | 2.288 (14) |
| Mo(1)-C(81) | 2.347 (15) | Mo(1)-C(85) | 2.283 (14) |
| Mo(1)-C(82) | 2.383 (15) | | |
| (C) Distances around Ir(1) | | | |
| Ir(1)-H(1) | 1.67 (9) | Ir(1)-C(11) | 1.899 (13) |
| Ir(1)-P(3) | 2.333 (3) | Ir(1)-C(12) | 1.912 (15) |
| (D) P-C Distances | | | |
| P(3)-C(31) | 1.827 (11) | P(4)-C(61) | 1.815 (11) |
| P(3)-C(41) | 1.837 (12) | P(4)-C(71) | 1.814 (10) |
| P(3)-C(51) | 1.803 (11) | | |
| (E) C-O Distances | | | |
| C(11)-O(11) | 1.152 (17) | C(21)-O(21) | 1.160 (17) |
| C(12)-O(12) | 1.133 (18) | C(22)-O(22) | 1.141 (16) |
| (F) Angles within Ir(1)-P(4)-Mo(1) Core | | | |
| Mo(1)-Ir(1)-P(4) | 52.1 (1) | Ir(1)-P(4)-Mo(1) | 77.5 (1) |
| Ir(1)-Mo(1)-P(4) | 50.4 (1) | | |
| (G) Selected Angles around Mo(1) | | | |
| Ir(1)-Mo(1)-P(4) | 50.4 (1) | P(4)-Mo(1)-C(21) | 106.9 (4) |
| Ir(1)-Mo(1)-C(21) | 80.7 (4) | P(4)-Mo(1)-C(22) | 81.6 (4) |
| Ir(1)-Mo(1)-C(22) | 120.4 (4) | C(21)-Mo(1)-C(22) | 83.0 (6) |
| (H) Angles around Ir(1) | | | |
| Mo(1)-Ir(1)-P(3) | 165.0 (1) | P(3)-Ir(1)-H(1) | 88.6 (30) |
| Mo(1)-Ir(1)-P(4) | 52.1 (1) | P(4)-Ir(1)-C(11) | 95.0 (4) |
| Mo(1)-Ir(1)-C(11) | 95.1 (4) | P(4)-Ir(1)-C(12) | 138.0 (4) |
| Mo(1)-Ir(1)-C(12) | 87.9 (4) | P(4)-Ir(1)-H(1) | 86.6 (31) |
| Mo(1)-Ir(1)-H(1) | 84.6 (30) | C(11)-Ir(1)-C(12) | 101.7 (6) |
| P(3)-Ir(1)-P(4) | 114.2 (1) | C(11)-Ir(1)-H(1) | 177.8 (36) |
| P(3)-Ir(1)-C(12) | 103.5 (4) | | |
| (I) Mo-C-O and Ir-C-O Angles | | | |
| Mo(1)-C(21)-O(21) | 175.0 (11) | Ir(1)-C(11)-O(11) | 176.7 (11) |
| Mo(1)-C(22)-O(22) | 175.8 (11) | Ir(1)-C(12)-O(12) | 177.0 (13) |

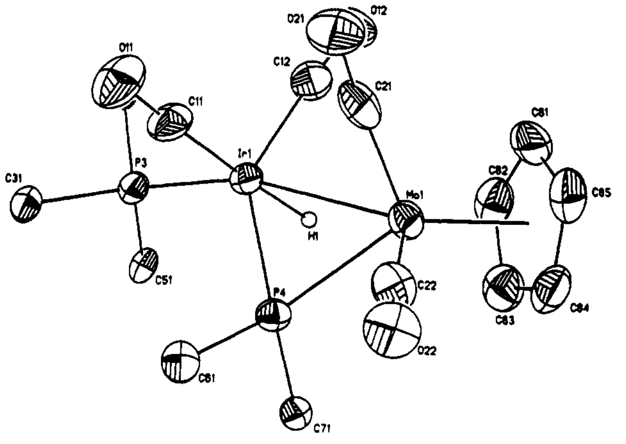

**Figure 7.** Central portion of the binuclear molecule **2**. Note the mutually cis carbonyls on Ir(1). (Compare with Figure 2).

temperature and is not fully resolved at -60 °C (-0.81 (br) and 123.2 (br) ppm). However, the chemical shifts indicate a phosphine and a phosphide bridge. Thus two isomers of product **2** must be present with one in a sufficiently small concentration that it cannot be identified. The process that interconverts the two must be quite rapid. These spectroscopic data for compound **2** are consistent with the observed structure for $Cp(CO)_2Mo[\mu\text{-}P(p\text{-tolyl})_2][\mu\text{-}CO]Ir(H)(CO)[P(p\text{-tolyl})_3]$.

**Structure of $Cp(CO)_2Mo[\mu\text{-}P(p\text{-tolyl})_2]Ir(H)[P(p\text{-tolyl})_3](CO)_2$(*Mo-Ir*) (2).** The crystal consists of discrete molecular units separated by normal van der Waals distances; there are no abnormally short distances. Figure 6 shows the labeling of atoms in this molecule. Selected distances and angles appear in Table V.

The molecule consists of a $CpMo(CO)_2$ and an $Ir(H)[P(p\text{-tolyl})_3](CO)_2$ fragment, which are linked via a direct molybdenum–iridium bond (Mo(1)–Ir(1) = 2.957 (1) Å) and by a bridging di-*p*-tolyl phosphide ligand (Mo(1)–P(4) = 2.391 (3), Ir(1)–P(4) = 2.334 (3) Å and ∠Ir(1)–P(4)–Mo(1) = 77.5 (1)°); see Figure 7.

The geometry about molybdenum is similar to that in **1A**. Individual Mo–C($\eta^5$-$C_5H_5$) distances range from Mo(1)–C(85) = 2.283 (14) Å to Mo(1)–C(82) = 2.383 (15) Å, while C–C distances are 1.349 (27)–1.409 (25) Å (average = 1.383 Å). The two terminal carbonyl ligands are linked to molybdenum by Mo(1)–C(21) = 1.953 (14) Å and Mo(1)–C(22) = 1.940 (13) Å, with ∠Mo(1)–C(21)–O(21) = 175.0 (11)° and ∠Mo(1)–C(22)–O(22) = 175.8 (11)°.

The iridium atom is in a distorted octahedral environment, the smallest cis angle being ∠Mo(1)–Ir(1)–P(4) = 52.1 (1)°; trans angles are Mo(1)–Ir(1)–P(3) = 165.0 (1)°, C(11)–Ir(1)–H(1) = 177.8 (36)°, and P(4)–Ir(1)–C(12) = 138.0 (4)°. The two carbonyl groups are in a mutually cis juxtaposition with Ir(1)–C(11) = 1.899 (13) Å and Ir(1)–C(12) = 1.912 (15) Å. (Compare to structure of **1A** where the carbonyl ligands are mutually trans.) Ir–C–O angles in the present structure are Ir(1)–C(11)–O(11) = 176.7 (11)° and Ir(1)–C(12)–O(12) = 177.0 (13)°. Other dimensions of interest include Ir(1)–P(3) = 2.333 (3) Å and the refined Ir(1)–H(1) distance of 1.67 (9) Å.

**Conversions between 2 and 3.** Compounds **2** and **3** interconvert in the presence of $H_2$ or CO.

$$\mathbf{2} + H_2 \rightarrow \mathbf{3} + CO$$

$$\mathbf{3} + CO \rightarrow \mathbf{2} + H_2$$

Reaction of **2** with $H_2$ is fairly slow with completion occurring in 24 h at room temperature. The reaction of **3** with CO is considerably more rapid (completion in 1 h at room temperature). The more rapid reaction of **3** with CO and the formation of **2** under preparative conditions ($[H_2]$ = 1 atm, [CO] = $10^{-3}$ atm) are consistent with preferential binding of CO.

**Reaction of 1A with HCl.** The molybdenum complex **1A** reacts quite rapidly with HCl, producing, primarily, $CpMo(CO)_3Cl$ and $Ir(CO)(Cl)_2(H)[PH(p\text{-tolyl})_2][P(p\text{-tolyl})_3]$. The molybdenum product is identified by its Cp resonance at 5.28 (s) ppm in the $^1H$ NMR spectrum and its IR spectrum. The iridium product is identified by its similarity to $Ir(CO)(Cl)_2(H)[P(p\text{-tolyl})_3]_2$. The mixed phosphine product has two doublets in the $^{31}P$ spectrum, −2.7 (d) and −28.3 (d) ppm ($J_{P-P}$ = 354 Hz). Both are consistent with terminal phosphines and the coupling indicates a trans stereochemistry. The $^1H$ NMR spectrum contains a single hydride resonance at −16.2 (t) ppm ($J_{P-H}$ = 11 Hz), arising from nearly equal coupling to two different $^{31}P$ nuclei. The net reaction is

$$Cp(CO)_2Mo[\mu\text{-}P(p\text{-tolyl})_2]Ir(CO)_2(p\text{-tolyl})[P(p\text{-tolyl})_3] + 3HCl \rightarrow PhCH_3 + CpMo(CO)_3Cl + Ir(CO)(Cl)_2(H)[PH(p\text{-tolyl})_2][P(p\text{-tolyl})_3]$$

We have not attempted the reaction of **1B** with HCl.

**Summary of Reactions of 1A.** The relatively slow reaction of **1A** and **1B** with $H_2$ may indicate that CO dissociation precedes $H_2$ addition. Changing the product ratio in the presence of CO certainly suggests a role for CO dissociation. On the basis of the stability of 16$e^-$ complexes of iridium and ease of CO dissociation from 18$e^-$ complexes, we tentatively suggest CO dissociation from iridium. Oxidative addition of $H_2$ and reductive elimination of toluene leads to a hydride complex that can react with CO to produce the monohydride product **2** or with $H_2$ to produce the trihydride product **3**. In the reaction with $H_2$, **3** is formed in 80–95% yield. The presence of 1:1 $CO/H_2$ gives predominantly the monohydride product. Reaction with HCl is considerably more rapid and probably occurs by initial protonation of the phosphide bridge.

## Conclusion

The reactions reported in this manuscript demonstrate that *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ can oxidatively add transition-metal–hydride bonds and, through reductive elimination of $CH_4$, generate heterobimetallic complexes. The 16-electron iridium center in a heterobimetallic complex retains its reactivity. The center formed after reductive elimination of methane, $[Cp(CO)_3Mo\text{–}Ir(CO)[P(p\text{-tolyl})_3]_2]$, is sufficiently reactive to activate the phosphorus–tolyl bond. The resulting complex, **1A**, is stable except for addition of a hydrogen source. Addition of $H_2$ evidently requires dissociation of CO; the resulting 16-electron center oxidatively adds $H_2$, then reductively eliminates toluene, and oxidatively adds $H_2$ (unless CO is present). Reaction with HCl is much more rapid and probably involves initial protonation of the phosphide bridge. The heterobimetallic hydrides are fluxional; the trihydride undergoes pairwise exchange of a hydride on each metal. The reactivity and ease of transfer between metal centers make these heterobimetallic hydrides interesting candidates for catalysis.

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**Registry No.** **1A**, 136115-67-8; **1B**, 136115-68-9; **2**, 136115-69-0; **3**, 136115-70-3; *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$, 121617-18-3; $HMoCp(CO)_3$, 12176-06-6.

**Supplementary Material Available:** Tables of complete bond lengths, complete bond angles, anisotropic thermal parameters, and calculated H atom positions for both **1A** and **2** (11 pages); structure factor tables for **1A** and **2** (42 pages). Ordering information is given on any current masthead page.