by sublimation at reduced pressure at 90 °C and stored in a drybox.

GPC data were collected by using a Waters GPC system consisting of a set of ultrastyragel columns of 100, 500, $10^4$, and $10^6$ Å that were standardized by using polystyrene and an ultraviolet (254 nm) detector. The carrier solvent was tetrahydrofuran. Data reduction was carried out with Perkin-Elmer/Nelson Analytical GPC chromatography software on an IBM AT computer system.

All NMR data were collected on either a Varian XL-200 NMR spectrometer or a Varian EMT-390 NMR spectrometer using deuterated benzene as the solvent and tetramethylsilane as the internal standard. The standard IR data were collected on a Beckman 4240 infrared spectrometer. The mass spectra and GC data were collected on a Hewlett-Packard 5790 GC/MS system using a split column injector leading to two columns: one a 12.5-m capillary column for flame ionization detection and the other a 25-m capillary column for mass detection. Standard injection volumes of 0.02 $\mu$L were used.

The GC/FT-IR analyses were carried out as follows. For each analysis, 1.0 $\mu$L of the neat sample was injected into a Hewlett-Packard 5890A gas chromatograph coupled to a Hewlett-Packard 5965A IRD, an FT-IR spectrometer dedicated for gas chromatography. The chromatographic conditions for the separations were as follows: a 15 m × 0.32 mm i.d. 1.0 $\mu$m film DB-5 column (J&W) Scientific) with a flow rate of 3 mL/min Helium, operated at a 30/1 split ratio, temperature programmed from 150 to 285 °C at 10 °C/min. To facilitate resolutions and/or elution of high boiling components, one sample was also analyzed by using a temperature program to 70–260 °C at 10 °C/min. The injection temperature was 250 °C, and the temperature of the interface and light pipe was 300 °C for all analyses. The HP 5965A IRD utilized a 120 mm × 1 mm i.d. light pipe and a narrow band MCT detector. FT-IR spectral data were recorded at 8 cm$^{-1}$ resolution. A Gram-Schmidt reconstruction produced a total response chromatogram for each run, and collected spectra were ratioed against background spectra to produce transmittance spectra from 4000 to 750 cm$^{-1}$ for each component.

**Preparation of $C_4H_9SiH_3$.** Although this material is known in the literature, we believe that the following represents an improved synthesis. A 1000-mL three-neck round-bottom flask was equipped with a reflux condenser and a pressure equalizing dropping funnel. The flask was charged with 300 mL of dry diglyme, and 22.8 g (0.60 mol) of $LiAlH_4$, and this mixture was stirred under an Ar atmosphere while 152.3 g (0.79 mol) of $n$-$C_4H_9SiCl_3$ was added over a period of 2 h. When the addition was complete, stirring was continued for 1 h. Fractional distillation directly from the reaction mixture gave the desired product $n$-$C_4H_9SiH_3$, 62.6 g (89.9% yield). Spectral analysis agreed with literature values.[9]

**Polymerization of $n$-$C_4H_9SiH_3$.** The following is a representative procedure used for the $Cp_2ZrMe_2$-catalyzed polymerization of $n$-$C_4H_9SiH_3$. In a 50-mL Schlenk tube was added 4.59 g (0.052 mol) of $n$-$C_4H_9SiH_3$ and 5.0 mL of dry toluene. This solution was freeze–thaw degassed under reduced pressure and allowed to warm to room temperature under an Ar atmosphere. The above mixture was then stirred while 0.2 g ($8.0 \times 10^{-4}$ mol, 1.5 mol %) of $Cp_2ZrMe_2$ was added as a solution in 0.5 mL of dry toluene. The reaction immediately turned light yellow, and after 5 min mild gas evolution had begun and the color had intensified. After 1 h the gas evolution was strong, and the solution had turned to a dark orange color. After 3 h the gas evolution began to slow. After 24 h the reaction ceased. The mixture was analyzed by GC, and then all volatile components were removed at reduced pressure, and the nonvolatile materials were taken up in 10 mL of hexane and exposed to air by bubbling air through the stirred solution for 5 min. The yellow hexane mixture was then passed through a Florosil column (10 cm × 2 cm) to remove the Zr species giving 2.52 g (56%) of a clear, water white oil.

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# Transition-Metal Derivatives of the Cyclopentadienyl Phosphine Ligands. 3. New Pathways to Polymetallic Complexes

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A series of new derivatives of heterodifunctional ligands have been synthesized starting from lithium (diphenylphosphino)- or ((diphenylphosphino)ethyl)cyclopentadienide and from ((diphenylphosphino)cyclopentadienyl)- or ((dimethylphosphino)cyclopentadienyl)thallium. These are monometallic (**1**, **2**, and **4**) and heterobimetallic molybdenum(0), tungsten(0), rhodium(I), and iridium(I) complexes (**3**) together with dissymmetric (**5**) and symmetric (**6**) homobimetallic rhodium(I) and iridium(I) complexes. They have been fully characterized by their spectroscopic data (including phosphorus–rhodium and phosphorus–tungsten coupling constant measurements) and by electron-impact mass spectroscopy. Interestingly, the synthesis of the bimetallic compounds involves a novel pathway beginning with steps of coordination of the phosphorus extremity of the bifunctional ligands. Of special interest are the compounds $L_2Rh(\eta^5\text{-}C_5H_4)Ph_2PRhCl(PPh_3)L$ (**5**), which associate one 18-electron and one 16-electron site, and the compounds $[M(\eta^5\text{-}C_5H_4)PR_2(CO)]_2$ (M = Rh, Ir; R = Ph, Me) (**6**), which associate two 18-electron sites. Complex **6a** (M = Rh; R = Ph) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell of dimensions $a$ = 9.475 (1) Å, $b$ = 9.527 (1) Å, $c$ = 9.145 (1) Å, $\alpha$ = 99.80 (1)°, $\beta$ = 109.86 (1)°, $\gamma$ = 90.36 (1)°, and $V$ = 763.2 (3) Å$^3$. Least-squares refinement leads to a value of 0.032 for the conventional $R$ index for 2938 reflections having $I > 3\sigma(I)$. The dinuclear molecule consists of two "Rh(CO)" moieties bridged by two (diphenylphosphino)cyclopentadienyl ligands that are in a mutual head-to-tail arrangement, and the large Rh–Rh separation, 4.3029 (6) Å, precludes any metal–metal interaction.

## Introduction

The preparation of polymetallic complexes is a major tool in the main fields of application of coordination chemistry, namely, catalysis, materials, or biomimetic studies.

It enlightens the growing interest on accurate ligands, leading to prefer, in a specific attempt to control synthetic processes, heterodifunctional ligands rather than symme-

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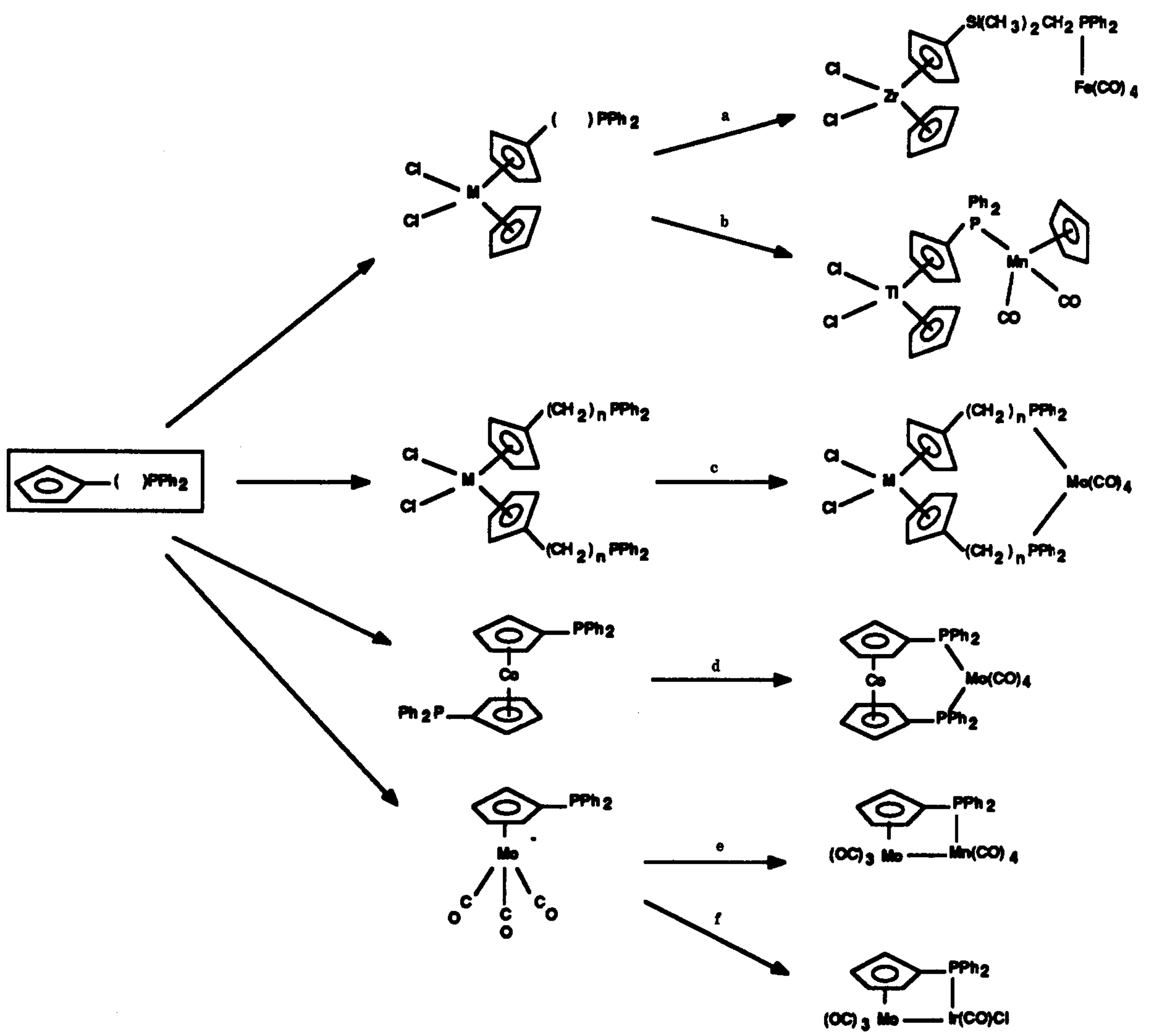

**Figure 1.** The previously known routes to the heterobimetallic complexes of bidifunctional ligands containing tertiary phosphine and cyclopentadienide (or -yl) functionalities: (a) from ref 3; (b) from ref 4a; (c) from ref 7 and 8; (d) from ref 9; (e) from ref 6a; (f) from ref 6b.

tric difunctional ligands such as, for example, the widely used bis(diphenylphosphino)methane.[1]

With this respect, the heterodifunctional ligands containing a cyclopentadienide or cyclopentadienyl ring, directly linked either to a phosphine group as in lithium(diphenylphosphino)cyclopentadienide[2] or in (diphenylphosphino)cyclopentadienyl)thallium[3] or by a molecular chain as in (dimethyl((diphenylphosphino)methyl)silyl)cyclopentadienide[4] and ((diphenylphosphino)ethyl)cyclopentadienide[5] anions have received significant attention in the last 10 years. Examples of their ability to join two different metallic centers have been described.[3,4,6-9]

Taking advantage from the difference of reactivity between the two functionalities, the synthetic way adopted so far has been to bind first the cyclopentadienide or cyclopentadienyl moiety to one "of the" transition metals, thus producing metallo ligand derivatives which may then act as a monodentate or chelating bidentate phosphorus ligand (Figure 1).

This leads to three kinds of heterobimetallic complexes, depending on the mode of association of the metallic centers, namely: through a single heterodifunctional bridging ligand (a and b), through two heterodifunctional ligands, in a "head-to-head" relative disposition (c and d), and through a single heterodifunctional bridging ligand together with a single metal–metal bond (e and f).

In the course of our research program concerning the use of the homo- and heterodimetallic species in activation and homogeneous catalysis, we have developed two new high-yield routes leading to new polymetallic complexes, as shown on Figures 2 and 3.

In this paper, we report the synthesis and characterization of new heterobimetallic (**3a–g**), monometallic (**4a–c**), dissymmetric homobimetallic (**5a–c**), symmetric homobimetallic (**6a–c**), and trimetallic (**7a**) species. The homobimetallic complex **6a** has been characterized by crystal

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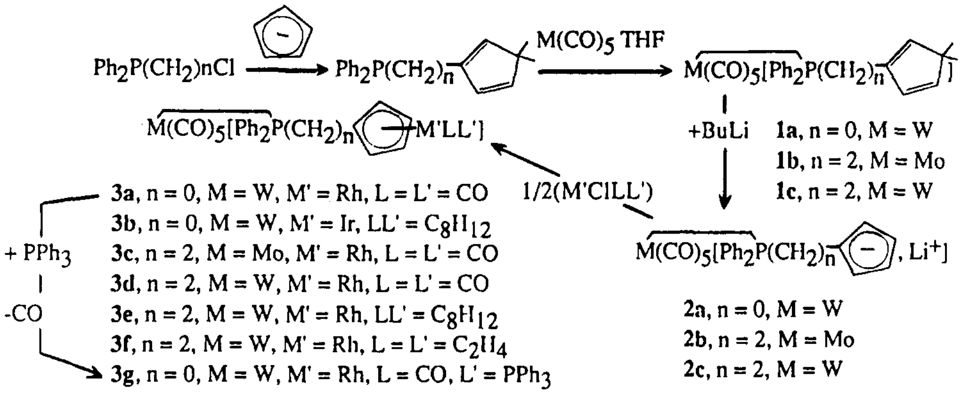

**Figure 2.** The alternative synthetic method to heterobimetallic compounds, using prior coordination of the phosphorus atom ligands.

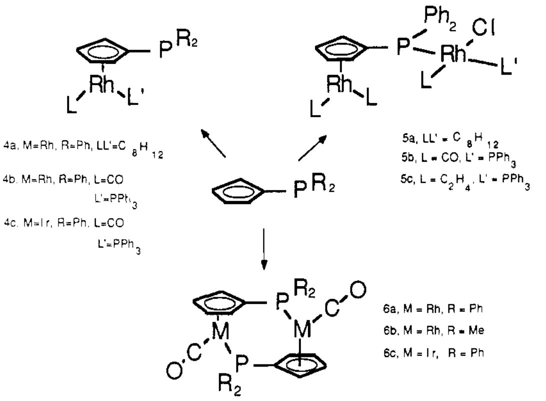

**Figure 3.** Preparation of new simply or doubly bridged homodimetallic $d^8$–$d^8$ complexes.

structure determination. The formation mechanism of type **6** complexes is discussed.

## Experimental Section

**General Remarks.** All reactions and manipulations were routinely performed under nitrogen or argon atmosphere in Schlenk-type glassware. All solvents were appropriately dried and deoxygenated prior to use. Tetrahydrofuran (THF), diethyl ether, and toluene were purified before use by distillation from sodium benzophenone. Microanalyses were performed by the Service de Microanalyses du Laboratoire de Chimie de Coordination du CNRS. Mass spectra were recorded on a Varian MAT 311 A. Infrared spectra of hexane or dichloromethane solutions were recorded by using a Perkin-Elmer Model 225 grating spectrometer. The spectra were calibrated with water vapor lines in the carbonyl stretching region. $^1$H NMR spectra were obtained at 90 MHz on a Bruker WH 90 FT instrument and/or at 250 MHz on a Bruker WM 250 FT spectrometer. Chemical shifts were referenced to internal tetramethylsilane. $^{13}$C NMR spectra were obtained at 62.9 MHz on a Bruker WM 250 FT spectrometer. $^{31}$P NMR spectra were obtained at 36.4 MHz on a Bruker WH 90 FT spectrometer and/or at 101.1 MHz on a Bruker WM 250 FT spectrometer, and chemical shifts were referenced to external $H_3PO_4$.

**Preparation of the Compounds.** (Diphenylphosphino)cyclopentadiene,[2] ((diphenylphosphino)ethyl)cyclopentadiene,[5] and ((diphenylphosphino)cyclopentadienyl)thallium[3] were prepared according to published procedures.

The starting materials $Mo(CO)_5(THF)$ and $W(CO)_5(THF)$ were prepared from $Mo(CO)_6$ and $W(CO)_6$, respectively, according to a published procedure.[10] $Rh_2Cl_2(CO)_4$,[11] $Rh_2Cl_2(CO)_2(PPh_3)_2$,[12] $Rh_2Cl_2(C_2H_4)_4$,[13] $Rh_2Cl_2(C_8H_{12})_2$,[14a] $Ir_2Cl_2(C_8H_{12})_2$,[14b] and Vaska's complex *trans*-$IrCl(CO)(PPh_3)_2$[15] were routinely prepared according to published procedures.

We prepared the ((dimethylphosphino)cyclopentadienyl)thallium compound by adapting the method described[3] for the phenyl analogue.

**$W(CO)_5[Ph_2P(C_5H_5)]$ (1a).** Into a nitrogen-purged 150-mL Schlenk tube, equipped with a magnetic stirrer and mercury overpressure valve, containing a suspension of thin sodium balls (0.33 g) in tetrahydrofuran (15 mL) was slowly added freshly distilled cyclopentadiene (1.2 mL, 14.5 mmol). This mixture was stirred at room temperature until total consumption of sodium (3 h). To the resulting colorless solution, previously cooled to −78 °C, was added dropwise chlorodiphenylphosphine. Stirring was maintained for an additional 30 min at room temperature.

The resulting solution was added to a solution of freshly prepared $W(CO)_5(THF)$ (15 mmol) in tetrahydrofuran (450 mL). The initial deep yellow solution turned immediately light yellow. After 10 min of stirring, the solvent was removed under vacuum, leading to a yellow crude solid. This solid was extracted by toluene (30 mL), producing a yellow solution. The solvent was removed under vacuum and the solid so obtained washed several times with ethanol (3 × 10 mL) and dried, yielding 2.8 g (4.88 mmol, 32%) of **1a**. Anal. Calcd for $C_{22}H_{15}O_5PW$: C, 47.87; H, 3.18. Found: C, 47.71; H, 3.32. Electron-impact MS (70 eV), *m/e* 574 ($M^+$) plus fragment ions corresponding to successive loss of five CO groups.

**$Mo(CO)_5[Ph_2P(CH_2)_2(C_5H_5)]$ (1b).** To a suspension of sodium (0.67 g) in tetrahydrofuran (40 mL) was slowly added freshly distilled cyclopentadienine (3.3 mL, 40 mmol). The resulting mixture was stirred at room temperature for 3 h. To the resulting colorless solution, previously cooled to −78 °C, was slowly added (1-chloroethyl)diphenylphoshine (3.0 g, 12.07 mmol) in tetrahydrofuran (30 mL). Stirring was maintained for an additional 2 h at room temperature. The solvent then was removed under vacuum, and the solid residue so obtained was extracted by 50 mL of petroleum ether. Removal of petroleum ether under vacuum produced 2.14 g (7.70 mmol, 64%) of $Ph_2P(CH_2)_2(C_5H_5)$ as a pale yellow oil.

To a deep yellow solution containing 4.64 mmol of freshly prepared $Mo(CO)_5(THF)$, in tetrahydrofuran (400 mL), was added a solution containing a slight excess of $Ph_2P(CH_2)_2(C_5H_5)$ (1.3 g, 4.68 mmol) in tetrahydrofuran (20 mL). The solution turned immediately light yellow. The solvent was removed under vacuum, producing a yellow crude solid. Yellow crystals of **1b** were obtained by crystallization upon slowly cooling an $Et_2O/CH_3OH$ (1/1) solution of the crude solid. Anal. Calcd for $C_{24}H_{19}O_5PMo$: C, 56.05; H, 3.72. Found: C, 56.14; H, 3.98.

**$W(CO)_5[Ph_2P(CH_2)_2(C_5H_5)]$ (1c).** This compound was prepared by using the procedure described above for **1b**, by addition of a solution containing 0.79 g of $Ph_2P(CH_2)_2(C_5H_5)$ in tetrahydrofuran (15 mL) to an equimolar amount of $W(CO)_5(THF)$ in tetrahydrofuran, followed by evaporation of the solvent. **1c** was obtained as a pure solid by crystallization from an $Et_2O/CH_3OH$ solution of the crude yellow product. Anal. Calcd for

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$C_{24}H_{19}O_5PW$: C, 47.87; H, 3.18. Found: C, 47.71; H 3.32.

**$W(CO)_5[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)_2]$ (3a).** To a solution of **1a** (0.574 g, 1 mmol) in tetrahydrofuran (20 mL) maintained at −78 °C was added dropwise 0.6 mL of butyllithium in hexane (106.3 mg $L^{-1}$, 1.06 mmol). The solution turned orange-yellow, and, after 30 min of stirring, a solution of $Rh_2Cl_2(CO)_4$ (0.184 g, 0.47 mmol) in tetrahydrofuran (10 mL) was added. The resulting solution, which immediately turned brown red, was slowly warmed to room temperature. This solution was filtered through a column of Celite. The solvents were then partially removed under vacuum until a volume of 3 mL. Petroleum ether (25 mL) was gradually added to precipitate the product **3a** as a red-brown solid (600 mg, 0.82 mmol, 82%). Anal. Calcd for $C_{24}H_{14}O_7PRhW$: C, 39.30; H, 1.90. Found: C, 39.62; H, 1.88. Electron-impact MS: *m/e* 732 ($M^+$) plus fragment ions corresponding to successive loss of seven CO groups.

**$W(CO)_5[Ph_2P(\eta^5\text{-}C_5H_5)Ir(\eta^4\text{-}C_8H_{12})]$ (3b).** A pure form of **3b** was obtained as a deep red solid by the procedure described above for **3a**, in similar yield, using $Ir_2Cl_2(\eta^4\text{-}C_8H_{12})_2$ as a source of the $Ir(\eta^4\text{-}C_8H_{12})$ fragment. Anal. Calcd for $C_{30}H_{26}O_5PIrW$: C, 41.24; H, 2.99. Found: C, 40.90; H, 2.90. Electron-impact MS: *m/e* 873 ($M^+$) plus fragment ions corresponding to the successive loss of five CO groups. The parent ion $M^+$ exhibits a typical pattern constituted of nine principal peaks from *m/e* 870 to *m/e* 879, consistent with the presence of one W atom (four isotopes (natural abundance): $^{182}W$ (26.4), $^{183}W$ (14.4), $^{184}W$ (30.6), and $^{186}W$ (28.4)) and one Ir atom (two isotopes: $^{191}Ir$ (37.4) and $^{193}Ir$ (62.6)).

**$W(CO)_5[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)(PPh_3)]$ (3g).** To a solution of **3a** (366 mg, 0.5 mmol) in toluene (10 mL) was added a solution of triphenylphosphine (0.5 mmol) in toluene. The resulting mixture was maintained at 70 °C overnight under stirring. A red-orange precipitate slowly formed. This precipitate was allowed to settle out and the mother liquor decanted. The red-orange product was washed with toluene and dried under vacuum (300 mg, 0.31 mmol, 62%). Anal. Calcd for $C_{41}H_{29}O_6P_2RhW$: C, 50.93; H, 3.02. Found: C, 50.76; H, 2.96.

**$Ph_2P(\eta^5\text{-}C_5H_4)Rh(\eta^4\text{-}C_8H_{12})$ (4a).** To a solution of $Rh_2Cl_2(C_8H_{12})_2$ (200 mg, 0.41 mmol) in tetrahydrofuran (10 mL) was added a large excess of $Ph_2P(C_5H_4)^-$, $Li^+$ (800 mg, 3.12 mmol) in tetrahydrofuran (10 mL). The resulting solution was stirred at room temperature for 18 h. The solution then was filtered, and the solvent was removed under vacuum. The resulting yellow solid was washed successively with methanol and pentane and dried under vacuum, yielding 200 mg (0.43 mmol, 53%) of **4a**. Anal. Calcd for $C_{25}H_{26}PRh$: C, 65.23; H, 5.69. Found: C, 65.01; H, 5.72.

**$RhCl(\eta^4\text{-}C_8H_{12})[Ph_2P(\eta^5\text{-}C_5H_4)Rh(\eta^4\text{-}C_8H_{12})]$ (5a).** To a suspension of $Rh_2Cl_2(C_8H_{12})_2$ (720 mg, 1.46 mmol) in toluene (20 mL) was added a slight excess of $Ph_2P(C_5H_4)^-,Li^+$ (400 mg, 1.56 mmol) in tetrahydrofuran (10 mL). The mixture was stirred at room temperature for 1.5 h and then filtered through a glass frit, and the solvent was removed under vacuum. The resulting yellow crude product was washed successively with ethanol (20 mL) and pentane (4 × 50 mL) and dried under vacuum producing 412 mg (0.58 mmol, 42%) of **5a**. Anal. Calcd for $C_{33}H_{38}ClPRh_2$: C, 56.07; H, 5.42. Found: C, 56.04; H, 5.50. Electron-impact MS, *m/e* 707 ($M^+$).

**Formation and Identification in Solution of $RhCl(CO)(PPh_3)[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)_2]$ (5b).** To a solution of $Ph_2P(C_5H_4)^-,Li^+$ (120 mg, 0.47 mmol) in tetrahydrofuran (20 mL), cooled to −78 °C, was added dropwise a solution of $Rh_2Cl_2(CO)_4$ (170 mg, 0.44 mmol) in tetrahydrofuran (10 mL). The mixture was stirred at −78 °C for 10 min, and triphenylphosphine (115 mg, 0.44 mmol) in tetrahydrofuran (2 mL) then was added. The resulting red-orange solution was slowly warmed to room temperature. The $^{31}P\{^1H\}$ NMR spectrum of a sample of this solution indicated the total consumption of the starting salt and the quantitative formation of a new compound. This compound was identified as the title product, **5b**, by $^{31}P\{^1H\}$ NMR and IR ($\nu$(CO)) spectra (see text).

**Formation and Identification in Solution of $RhCl(C_2H_4)(PPh_3)[Ph_2P(\eta^5\text{-}C_5H_4)Rh(C_2H_4)_2]$ (5c).** To a solution of $Ph_2P(C_5H_4)^-,Li^+$ (275 mg, 1.07 mmol) in tetrahydrofuran (15 mL) was added a suspension of $Rh_2Cl_2(C_2H_4)_4$ (425 mg, 1.09 mmol) in tetrahydrofuran (10 mL) at −78 °C. This solid rapidly dissolved, and the solution turned red-orange within a few minutes. Triphenylphosphine 290 mg, 1.10 mmol) then was added, and the solution was stirred for an additional 10 min at room temperature. The solvent then was evaporated under vacuum, producing a red-orange residue that was extracted with toluene (10 mL). The addition of pentane (15 mL) to the red toluene solution led to the formation of a red-orange precipitate. The precipitate was allowed to settle out overnight at −78 °C, and the mother liquor decanted. The red-orange product was washed with pentane and dried under vacuum. It was identified as the title product, **5c**, by $^{31}P\{^1H\}$ NMR (see text).

**$Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)(PPh_3)$ (4b) and $[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)]_2$ (6a). Method A.** $Ph_2P(C_5H_4)^-,Li^+$ (153 mg, 0.60 mmol) was added to a stirred suspension of $Rh_2Cl_2(CO)_2(PPh_3)_2$ (200 mg, 0.47 mmol) in toluene (10 mL) at 0 °C. The resulting mixture was progressively warmed to 80 °C. The suspension dissolved within 10 min, and an orange precipitate slowly formed. After 10 h, the mixture was cooled to room temperature. The precipitate was allowed to settle out, and the mother liquor decanted. The orange product was washed several times with methanol (2 × 5 mL) and dried under vacuum, yielding 115 mg (0.15 mmol, 32%) of **6a**. Anal. Calcd for $C_{36}H_{28}O_2P_2Rh_2$: C, 56.85; H, 3.71. Found: C, 56.95; H, 4.10. Electron-impact MS: *m/e* 760 ($M^+$) plus fragment ions corresponding to successive loss of two CO groups.

In another experiment, using quite similar initial conditions, the mixture or $Ph_2P(C_5H_4)^-,Li^+$ and $Rh_2Cl_2(CO)_2(PPh_3)_2$ in toluene was heated at 80 °C for 1 h only and then cooled to room temperature. The orange precipitate so formed was separated and treated as above, yielding 60 mg (17%) of pure **6a**. The filtrate was evaporated under vacuum leading to an orange crude solid. IR ($\nu$(CO)), $^{31}P\{^1H\}$ NMR, and MS experiments run on this material indicated the presence of free triphenylphosphine and some traces of **6a** together with another compound identified as the monometallic species **4b**. Electron-impact MS: *m/e* 642 ($M^+$) plus fragment ion corresponding to the loss of one CO group.

Attempts to isolate a pure analytical sample of **4b** failed. Moreover, redissolution of the crude solid containing **4b** in toluene, followed by heating at 80 °C for an additional 10 h, led to the quantitative transformation of the monometallic species **4b** into the bimetallic one **6a**, which slowly precipitated as an orange-yellow solid.

**Method B.** A mixture of $Ph_2P(C_5H_4)^-,Li^+$ (270 mg, 1.05 mmol) and $Rh_2Cl_2(CO)_4$ (200 mg, 0.52 mmol) in toluene (20 mL) was heated at 80 °C. An orange-yellow precipitate slowly appeared, and after 3 h, the mixture was cooled to room temperature. The precipitate was collected upon filtration of the mother liquor, washed with methanol, and dried under vacuum, yielding 250 mg of pure **6a** (0.32 mmol, 63%).

**Method C.** To a solution of $Rh_2Cl_2(CO)_4$ (112 mg, 0.29 mmol) in tetrahydrofuran (20 mL) was added a slight excess of freshly prepared $Ph_2P(C_5H_4)Tl$ (300 mg, 0.66 mmol). The resulting solution immediately turned red while a pale yellow precipitate of TlCl appeared. The Ir ($\nu$(CO), $CH_2Cl_2$) spectrum of this red solution exhibits three absorption bands at 2044 (s), 1980 (s), and 1946 (s) $cm^{-1}$, indicating the total consumption of the starting rhodium complex. During 10 h of magnetic stirring, the initial red solution slowly turned orange. This is accompanied, on the IR spectra, by the total disappearance of the $\nu$(CO) bands at 2044 and 1980 $cm^{-1}$ and formation of a single compound having a CO absorption band at 1946 $cm^{-1}$. The solution then was filtered, and the solvent was removed under vacuum. The orange-yellow residue so obtained was successively washed with toluene and pentane and dried under vacuum, yielding 198 mg of pure **6a** (0.26 mmol, 90%). Pure orange crystals of **6a** could be obtained upon slow cooling of a saturated toluene solution of **6a** from 50 to −20 °C.

**$[Me_2P(\eta^5\text{-}C_5H_4)Rh(CO)]_2$ (6b).** A suspension of freshly prepared $(CH_3)_2P(C_5H_4)Tl$ (280 mg, 0.85 mmol) in tetrahydrofuran (100 mL) was added to a yellow solution of $Rh_2Cl_2(CO)_4$ (145 mg, 0.37 mmol) in tetrahydrofuran (10 mL). The initial yellow solution immediately turned red-orange. The IR spectrum ($\nu$(CO), hexane) run on a sample of this solution indicated the total consumption of the starting rhodium material and the formation of a compound having two absorption bands of equal intensities at 2046 and 1980 $cm^{-1}$. This mixture was heated at 60 °C. Progressively, it darkened while a brown precipitate appeared. Monitored by IR spectroscopy, this evolution is accompanied by the slow disappearance of both bands at 2046 and 1980 cm$^{-1}$ and the concomitant growing of a new one at 1954 cm$^{-1}$. After a reaction time of 5 h, the mixture was cooled to room temperature and the solvent was removed under vacuum, producing a brown residue. This residue was extracted with chloroform/hexane (1/10), yielding an orange-yellow solution. Evaporation of the solvents produced 160 mg of **6b** as an orange solid (67%). Analytical pure **6b** was obtained by chromatography through an alumina column which was eluted by dichloromethane/hexane. Anal. Calcd for $C_{16}H_{20}O_2P_2Rh_2$: C, 37.53; H, 3.94. Found: C, 37.38; H, 3.95.

**$Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)$ (4c), $[Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)]_2$ (6c), and $IrCl(CO)[Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)]_2$ (7a).** An excess of freshly prepared $Ph_2P(C_5H_4)^-,Li^+$ (240 mg, 0.94 mmol) was added to a stirred suspension of *trans*-$IrCl(CO)(PPh_3)_2$ (600 mg, 0.77 mmol) in toluene (15 mL) at room temperature. The suspension progressively dissolved, leading to an orange solution. The orange solution was heated at 70 °C for 1 h. An orange precipitate progressively formed. This precipitate was separated from the orange mother liquor. It was washed several times with methanol (2 × 5 mL) and with diethyl ether (5 mL) and dried under vacuum, producing (89 mg, 0.095 mmol, 12.3%) of the dimetallic compound **6c**. Anal. Calcd for $C_{36}H_{28}P_2O_2Ir_2$: C, 46.05; H, 3.01. Found: C, 45.88; H, 2.62. Electron-impact MS: *m/e*, three principal peaks at 936, 938, and 940 (M$^+$), consistent with the presence of two natural isotopes for the iridium element, plus fragment ions corresponding to the loss of two CO groups.

The orange filtrate was evaporated under vacuum leading to a yellow solid that was analyzed as containing free triphenylphoshine together with another iridium species. The purification from triphenylphosphine was performed by chromatography on neutral Alumina III, the product being eluted by a mixture 25/75 of dichloromethane–hexane. The solution was evaporated, and the remaining pale yellow solid was then dried under vacuum, yielding 395 mg of the monometallic species **4c** (0.50 mmol, 70%). Anal. Calcd for $Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)\cdot 0.25CH_2Cl_2$ ($C_{36.25}H_{29.5}OP_2IrCl_{0.5}$): C, 57.82; H, 3.95. Found: C, 58.01; H, 4.02. Electron-impact MS: *m/e*, two principal peaks at 730 and 732 (M$^+$) plus fragment ion corresponding to the loss of one CO group.

The distribution of both monometallic, **4c**, and bimetallic, **6c**, species is independent of the reaction time. When the starting orange solution was heated for 10 h instead of 1 h, similar quantities of **4c** and **6c** were cropped. Moreover, the transformation of **4c** into **6c** was not observed even after a toluene solution of **4c** was heated for 10 h.

In another experiment, $Ph_2P(C_5H_4)^-,Li^+$ (173 mg, 0.68 mmol) was added to a slight excess of *trans*-$IrCl(CO)(PPh_3)_2$ (600 mg, 0.77 mmol) in toluene (15 mL). As above, the mixture was heated at 70 °C for 1 h, leading to the formation of an orange precipitate of **6c**. This compound was separated from the mother liquor, affording 75 mg of pure **6c** (0.08 mmol, 10%). Pentane (5 mL) was added to the filtrate, producing a yellow precipitate. This precipitate was allowed to settle out, and the mother liquor was decanted. Spectrographic experiments indicated that the mother liquor contained essentially free triphenylphosphine together with **6c**. The yellow precipitate was washed with petroleum ether and dried under vacuum yielding 10 mg of a pure trimetallic species **7a** (0.006 mmol). Anal. Calcd for $C_{73}H_{58}O_3P_4Ir_3$: C, 52.08; H, 3.44. Found: C, 51.76; H, 3.71.

**X-ray Structure Determination of 6a. Collection and Reduction of X-ray Data.** Crystals of **6a** suitable for diffraction measurements were obtained by slow cooling of a saturated hot toluene solution (50 °C). The selected crystal, an orange plate, was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Crystals belong to the triclinic system, space group $P\bar{1}$. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data is given in Table I. A total of 3511 independent reflections were recorded at a $2\theta$(Mo) maximum of 55° by procedures described elsewhere.[17] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Data reduction then was performed,[18] and absorption corrections[19] were made on 2938 reflections having $I > 3\sigma(I)$ ($\mu = 12$ cm$^{-1}$, calculated transmission range 0.77–0.93).

**Table I. Crystal Data and Details of Data Collection for 6a**

| | |
|---|---|
| Crystal Data | |
| formula | $C_{36}H_{28}O_2P_2Rh_2$ |
| fw | 760.4 |
| cryst system | triclinic |
| space group | $P\bar{1}$ |
| $a$, Å | 9.475 (1) |
| $b$, Å | 9.527 (1) |
| $c$, Å | 9.145 (1) |
| $\alpha$, deg | 99.80 (1) |
| $\beta$, deg | 109.86 (1) |
| $\gamma$, deg | 90.36 (1) |
| $V$, Å$^3$ | 763.2 (3) |
| $Z$ | 1 |
| $F(000)$ | 380 |
| $D$(calcd), g cm$^{-3}$ | 1.654 |
| cryst size, mm | 0.450 × 0.125 × 0.075 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 12.0 |
| Data Collection | |
| temp, °C | 20 |
| radiatn | Mo K$\alpha$ ($\lambda$ = 0.71073 Å), graphite monochromatized |
| $\theta$(min–max), deg | 1.5–27.5 |
| scan mode | $\omega$–$2\theta$ |
| scan range, deg | 0.80 + 0.35 tan $\theta$ |
| scan speed, deg min$^{-1}$ | 1.1–10.1 |
| receiving aperture, mm | 4.0 × 4.0 |
| takeoff angle, deg | 3.5 |
| collected reflctns | 3511($\pm h,\pm k,l$) |

**Table II. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses for 6a**

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Rh | 0.53763 (4) | 0.27708 (3) | 0.45197 (4) |
| C(1) | 0.4369 (6) | 0.1250 (5) | 0.2990 (5) |
| O(1) | 0.3790 (5) | 0.0264 (4) | 0.2063 (4) |
| C(2) | 0.7113 (4) | 0.4722 (4) | 0.5299 (4) |
| C(3) | 0.7579 (5) | 0.3630 (4) | 0.4333 (5) |
| C(4) | 0.7850 (5) | 0.2422 (5) | 0.5077 (6) |
| C(5) | 0.7610 (5) | 0.2755 (5) | 0.6547 (6) |
| C(6) | 0.7074 (5) | 0.4128 (4) | 0.6655 (5) |
| P | 0.3248 (1) | 0.3448 (1) | 0.4889 (1) |
| C(7) | 0.3105 (5) | 0.3326 (4) | 0.6822 (5) |
| C(8) | 0.1795 (5) | 0.3654 (5) | 0.7142 (5) |
| C(9) | 0.1706 (6) | 0.3542 (5) | 0.8619 (6) |
| C(10) | 0.2878 (6) | 0.3080 (5) | 0.9722 (6) |
| C(11) | 0.4180 (7) | 0.2734 (6) | 0.9414 (6) |
| C(12) | 0.4281 (6) | 0.2852 (5) | 0.7948 (5) |
| C(13) | 0.1478 (5) | 0.2471 (4) | 0.3534 (5) |
| C(14) | 0.0464 (5) | 0.3028 (5) | 0.2341 (5) |
| C(15) | −0.0846 (6) | 0.2223 (6) | 0.1293 (6) |
| C(16) | −0.1074 (6) | 0.0819 (6) | 0.1488 (6) |
| C(17) | −0.0084 (6) | 0.0272 (5) | 0.2682 (7) |
| C(18) | 0.1212 (6) | 0.1068 (5) | 0.3712 (6) |

**Structure Solution and Refinement.** The structure was solved[20] by the heavy-atom method. Successive difference Fourier maps and least-squares refinement cycles revealed the positions of all non-hydrogen atoms that were refined anisotropically. Hydrogen atoms were all located on a difference Fourier map. They were included in calculations in constrained geometry (C–H = 0.97 Å), with a fixed isotropic temperature factor, $U_H$ = 0.06 Å$^2$.

The atomic scattering factors used were those proposed by Cromer and Waber[21] with anomalous dispersion effects.[22]

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**Table III. Infrared Data for Complexes 1–7**[a]

| | | |
|---|---|---|
| $W(CO)_5[Ph_2P(C_5H_5)]$ | **1a** | 2070 m, 1946 sh, 1938 vs |
| $Mo(CO)_5[Ph_2P(CH_2)_2(C_5H_5)]$ | **1b** | 2071 m, 1951 sh, 1943 vs |
| $W(CO)_5[Ph_2P(CH_2)_2(C_5H_5)]$ | **1c** | 2070 m, 1946 sh, 1936 vs |
| $Mo(CO)_5[Ph_2P(CH_2)_2(C_5H_4)^-Li^+]$ | **2b** | 2071 m, 1934 vs[b] |
| $W(CO)_5[Ph_2P(CH_2)_2(C_5H_4)^-Li^+]$ | **2c** | 2072 m, 1936 vs[b] |
| $W(CO)_5[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)_2]$ | **3a** | 2072 m, 2057 m, 1999 m, 1945 sh, 1940 vs |
| $W(CO)_5[Ph_2P(\eta^5\text{-}C_5H_4)Ir(\eta^4\text{-}C_8H_{12})]$ | **3b** | 2072 m, 1946 sh, 1938 vs |
| $Mo(CO)_5[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)_2]$ | **3c** | 2073 m, 2044 m, 1979 m, 1952 sh, 1944 vs |
| $W(CO)_5[Ph_2P(CH_2)_2(\eta^5\text{-}C_5H_4)Rh(CO)_2]$ | **3d** | 2077 m, 2044 m, 1980 m, 1948 sh, 1935 vs |
| $W(CO)_5[Ph_2P(CH_2)_2(\eta^5\text{-}C_5H_4)Rh(\eta^4\text{-}C_8H_{12})]$ | **3e** | 2069 m, 1946 sh, 1936 vs |
| $W(CO)_5[Ph_2P(CH_2)_2(\eta^5\text{-}C_5H_4)Rh(C_2H_4)_2]$ | **3f** | 2071 m, 1946 sh, 1936 vs |
| $W(CO)_5[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)(PPh_3)]$ | **3g** | 2068 m, 1954 m, 1945 sh, 1938 vs |
| $Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)(PPh_3)$ | **4b** | 1956 |
| $Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)$ | **4c** | 1948 (1928[b]) |
| $RhCl(CO)(PPh_3)[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)_2]$ | **5b** | 2049 s, 1989 s, 1980 s (2048 s, 1983 s, 1970 s[b]) |
| $[Ph_2P(\eta^5\text{-}C_5H_4)Rh(CO)]_2$ | **6a** | 1946[b] |
| $[Me_2P(\eta^5\text{-}C_5H_4)Rh(CO)]_2$ | **6b** | 1954 (1940[b]) |
| $[Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)]_2$ | **6c** | 1934[b] |
| $IrCl(CO)[Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)]_2$ | **7a** | 1952 m, 1929 s[b] |

[a] $\nu(CO)$, $cm^{-1}$ in hexane solutions. [b] In dichloromethane solutions.

Scattering factors for the hydrogen atoms were taken from Stewart et al.[23] The final full-matrix least-squares refinement converged to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.032$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.036$ with unit weights. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 0.99$ with $n = 2938$ observations and $m = 190$ variables.

An analysis of variance showed no unusual trends. In the last cycle of refinement the shifts for all parameters were less than $0.1\sigma$ (mean value $0.03\sigma$). A final difference Fourier map showed a residual electron density of 1 e/Å$^3$ near the Rh atom. The final fractional atomic coordinates are listed in Table II.

## Results

Infrared (CO stretching) and $^{31}P$ NMR data for the new complexes are given in Tables III and IV.

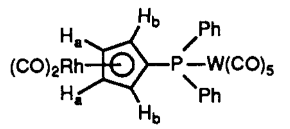
**Heterobimetallic d$^8$–d$^6$ Complexes 3.** As expected, the phosphines $Ph_2P(CH_2)_2(C_5H_5)^-$ and $Ph_2P(C_5H_5)^-$ react easily and quantitatively with $Mo(CO)_5(THF)$ or $W(CO)_5(THF)$ to yield the substitution products **1a–c**. The infrared spectra in the CO stretching vibration range of these products are quite similar to those observed for $M(CO)_5(PPh_3)$ (M = Mo,W)[24] and are consistent with molecular structures in which the local symmetry surrounding the metal is $C_{4v}$. Moreover, in the $^{31}P\{^1H\}$ NMR spectra of **1a** and **1c**, the occurrence of two satellite peaks symmetrically disposed from the central singlet is an obvious indication of direct P–W bonds[25] ($^1J(P\text{–}^{183}W) = 210.3$ Hz for **1a** and 251.5 Hz for **1c**).

The reaction of **1a**, **1b**, and **1c** with equimolar amounts of butyllithium leads quantitatively to the cyclopentadienyl derivatives **2a–c**. These reactions do not affect the local symmetry around the metals, as indicated by the similarity between the IR spectra of the initial compounds and of the products.

The cyclopentadienyl derivative **2a** may then act as a metallo ligand species. Following the experimental methods previously described for the syntheses of $(\eta^5\text{-}C_5H_5)M'LL'$ (M′ = Rh, L = L′ = CO;[26a] M′ = Ir, LL′ = $\eta^4\text{-}C_8H_{14}$[14b]), it reacts readily and quantitatively with half amounts of chloro-bridged dinuclear rhodium or iridium complexes $[M'(\mu\text{-Cl})LL']_2$, leading to the heterobimetallic complexes $W(CO)_5[Ph_2P(CH_2)_n(\eta^5\text{-}C_5H_4)M'LL']$ (**3a** and **3b**). The new complexes **3a** and **3b** were isolated in the solid state and identified and characterized by elemental analyses, by mass spectra, and by IR ($\nu$(CO)) and $^{31}P\{^1H\}$ and $^1H$ NMR spectroscopy. They are quite soluble in common organic solvents. The electron-impact mass spectrum of **3b** exhibits, for the parent ion, a typical isotopic pattern constituted of nine principal peaks from *m/e* 870 to *m/e* 879, as expected for a compound containing one tungsten (four main isotopes: $^{182}W$, $^{183}W$, $^{184}W$, and $^{185}W$) and one iridium (two isotopes: $^{192}Ir$ and $^{194}Ir$) atoms. Moreover, the mass spectrum of **3b** exhibits five isotopic patterns due to the successive loss of five CO groups. The IR spectra of all these heterobimetallic commpounds exhibit the characteristic three absorption $\nu$(CO) bands due to the $Mo(CO)_5$ fragments. Moreover, superimposed characteristic absorption bands, separated by ca. 60–65 $cm^{-1}$, due to the $Rh(CO)_2$ fragment, are observed for **3a** and compare well with those reported for $(\eta^5\text{-}C_5H_5)Rh(CO)_2$.[26a]

The $^{31}P\{^1H\}$NMR spectra of **3a** and **3b** are consistent with the binding of the phosphorus extremity of the heterodifunctional ligand to the tungsten atoms, as in the precursors **1a** and **1c**. They indeed exhibit in each case a singlet with two satellite peaks due to the presence of $^{183}W$, the $^1J(P\text{–}^{183}W)$ coupling constants being in the range 240–250 Hz.

The $^1H$ NMR spectrum of **3a** consists of a seven-line and a four-line pattern of equal intensity at 5.76 and 5.33 ppm for the two sets of protons $H_a$ and $H_b$ of the cyclopentadienyl ligand (at 90 as well as at 250 MHz). The problem of the multiplicity of these signals has been resolved by a combination of homo- and heteronuclear ($^1H\text{-}\{^{31}P\}$) irradiation experiments. Selective irradiation of $H_b$ signal at 5.33 ppm together with noise-decoupled $^{31}P$ transforms the multiplet at 5.76 ppm into a doublet with a spacing of 1.0 Hz whereas selective irradiation of $H_a$ signal at 5.76 ppm together with noise-decoupled $^{31}P$ transforms the quadruplet at 5.33 ppm into a singlet.



$^1J(H_a\text{–}H_b) = 2.1$ Hz, $^3J(H_a\text{–}P) = 1.0$ Hz, $^2J(H_b\text{–}P) = 2.3$ Hz, and $J(H_a\text{–}Rh) = 1.0$ Hz.

The apparent equivalence of both $H_a$ protons and both $H_b$ protons is consistent with a plane of symmetry in the molecule shown above.

We have shortly looked over the reaction of **3a** with triphenylphosphine. It leads quantitatively to **3g** in which the added triphenylphosphine is coordinated to the rhodium metal atom as shown by $^{31}P$ NMR spectra ($J(P\text{–}Rh) = 197.1$ Hz). Moreover, the phosphorus extremity of the bridging ligand is bonded to the tungsten atom with a coupling constant of 247.1 Hz, a value quite close to that observed for the starting material **3a**. Therefore, in this

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Table IV. $^{31}P$ NMR Data for Complexes 1–6[a]

| | $\delta(^{31}P)$ | $J(P-^{183}W)$ | $J(P-Rh)$ | $J(P-P')$ |
|---|---|---|---|---|
| $W(CO)_5[Ph_2P(C_5H_5)]$ (**1a**) | +4.92 | 241.2 | | |
| $W(CO)_5[Ph_2P(CH_2)_2(C_5H_5)]$ (**1c**) | +13.20 | 210.3 | | |
| $W(CO)_5[Ph_2P(\eta^5-C_5H_4)Rh(CO)_2]$ (**3a**) | +3.75 | 251.5 | | |
| $W(CO)_5[Ph_2P(\eta^5-C_5H_4)Ir(\eta^4-C_8H_{12})]$ (**3b**) | +3.31 | 248.6 | | |
| | +2.58 | 247.1 | | |
| $W(CO)_5[Ph_2P(\eta^5-C_5H_4)Rh(CO)(PPh_3)]$ (**3g**) | | | | |
| | +51.44 (d) | | 197.1 | |
| | −21.20 (s) | | | |
| $Ph_2P(\eta^5-C_5H_4)Rh(CO)(PPh_3)$ (**4b**) | | | | |
| | +52.28 (d) | | 198.0 | |
| | −20.56 (s) | | | |
| $Ph_2P(\eta^5-C_5H_4)Ir(CO)(PPh_3)$ (**4c**) | | | | |
| | +16.08 (s) | | | |
| $Ph_2P(\eta^5-C_5H_4)Rh(\eta^4-C_8H_{12})$ (**4a**) | −13.90 (s) | | | |
| $RhCl(\eta^4-C_8H_{12})[Ph_2P(\eta^5-C_5H_4)Rh(\eta^4-C_8H_{12})]$ (**5a**) | +16.80 | 151.5 | | |
| | +18.23 (dd) | | 123.5 | |
| $RhCl(CO)(PPh_3)[Ph_2P(\eta^5-C_5H_4)Rh(CO)_2]$ (**5b**) | | | | 130 |
| | +27.83 (dd) | | 103.0 | |
| | +21.46 (dd) | | 161.0 | |
| $RhCl(C_2H_4)(PPh_3)[Ph_2P(\eta^5-C_5H_4)Rh(C_2H_4)_2]$ (**5c**) | | | | 130 |
| | +34.07 (dd) | | 130.0 | |
| $[Ph_2P(\eta^5-C_5H_4)Rh(CO)]_2$ (**6a**) | +41.08 (AA′XX′) | | 200.0 | |
| $[Me_2P(\eta^5-C_5H_4)Rh(CO)]_2$ (**6b**) | +4.24 (AA′XX′) | | 183.3 | |
| $[Ph_2P(\eta^5-C_5H_4)Ir(CO)]_2$ (**6c**) | +4.54 (s) | | | |

[a] In $CD_2Cl_2$; values in ppm; $J$ values in Hz.

reaction, the 18-electron rhodium site appears more reactive toward substitution than the 18-electron tungsten site.

The above synthetic procedure used for **3a** and **3b** may be extended to the complexes of general formula $M(CO)_5[Ph_2P(CH_2)_n(\eta^5-C_5H_4)M'LL']$ (M = Mo or W) (**3c–f**) (Figure 2) using $Rh_2Cl_2(C_8H_{12})_2$ and $Rh_2Cl_2(C_2H_4)_4$ as sources for the fragments $Rh(CO)_2$, $Rh(C_8H_{12})$, and $Rh(C_2H_4)_4$. They were identified by comparison of their IR ($\nu$(CO)) spectra with those of 3a and 3b (Table III).

**The Dissymmetrical Homobimetallic d$^8$–d$^8$ Complexes 5.** The cyclopentadienide ligand $Ph_2P(C_5H_4)^-,Li^+$ reacts quantitatively with an equivalent amount of the dinuclear square-planar rhodium complex $Rh_2Cl_2(C_8H_{12})_2$ to yield **5a**. This product associates a 16e rhodium(I) center, in a square-planar environment, to a 18e rhodium(I) center via the phosphorus and the cyclopentadienyl extremities of the bridging difunctional ligand, respectively. The binding of the phosphorus to the rhodium(I) square-planar center is clearly demonstrated by a $^1J$(P–Rh) coupling constant of 151.5 Hz on the $^{31}P$ NMR spectrum instead of, e.g., 200 Hz for a binding to a 18e rhodium(I) center (vide supra).

Interestingly, when a large exess of lithium (diphenylphosphino)cyclopentadienide is used, the monometallic species **4a** is obtained. The $^{31}P\{^1H\}$ spectrum of **4a** exhibits a singlet at −13.90 ppm indicative of a noncoordinated tertiary phosphine.

According to the experimental methods described, addition of $Rh_2Cl_2(CO)_4$ or $Rh_2Cl_2(C_2H_4)_4$ to an equimolar amount of $Ph_2P(C_5H_4)^-,Li^+$, followed by the addition of an equimolar amount of triphenylphosphine leads quantitatively to **5b** or **5c**, respectively. As in the case of **5a**, the $^{31}P\{^1H\}$ NMR spectra of these two compounds indicate unambiguously the binding of the phosphorus extremity of the difunctional ligand to square-planar rhodium(I) centers, the $^1J$(P–Rh) coupling constants being in the range 120–160 Hz. Moreover, in both cases, as indicated by a $^2J$(P–P) coupling constant of 130 Hz, triphenylphosphine adds to the same rhodium(I) center in a relative trans position to the phosphorus moiety of the ligand.

**The Symmetrical Homobimetallic Complexes 6.** The symmetrical dirhodium complex **6a**[16] was obtained by addition of lithium (diphenylphosphino)cyclopentadienide or ((diphenylphosphino)cyclopentadienyl)thallium to half the amount of the dinuclear complexes $Rh_2Cl_2(CO)_2(PPh_3)_2$ or $Rh_2Cl_2(CO)_4$. Similarly, **6b** was obtained from ((dimethylphosphino)cyclopentadienyl)thallium. The iridium analogue **6c** was obtained by addition of lithium (diphenylphosphino)cyclopentadienide to equimolar amount of *trans*-$IrCl(CO)(PPh_3)_2$.

These new complexes were fully characterized by mass spectroscopy, IR($\nu$(CO)), and $^{31}P\{^1H\}$, $^1H$, and $^{13}C\{^1H\}$ NMR spectroscopy and by X-ray crystal structure determination of **6a**.

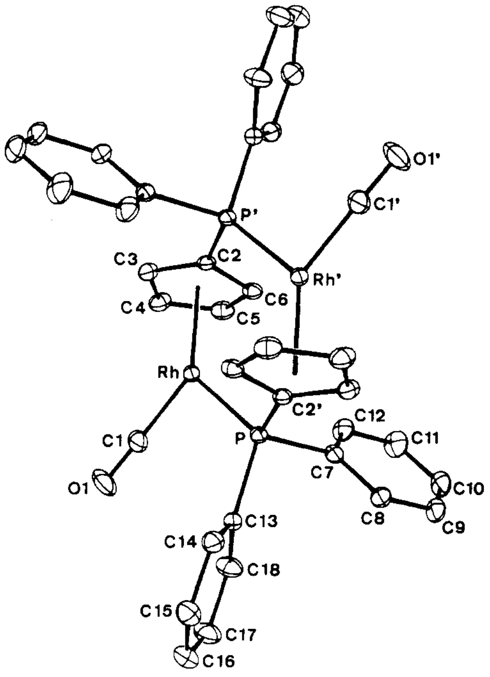

**Figure 4.** A perspective representation of **6a**.

**Description of the Crystal and Molecular Structure of 6a.** Figure 4 shows a perspective view of the molecule with the atom numbering scheme. Selected interatomic distances and angles are given in Table V. The dinuclear molecule consists of two "Rh(CO)" moieties

**Table V. Bond Lengths (Å) and Angles (deg) for 6a with Estimated Standard Deviations in Parentheses**

| | | | |
|---|---|---|---|
| Rh–C(1) | 1.831 (4) | C(1)–O(1) | 1.144 (5) |
| Rh–C(2) | 2.321 (4) | Rh–C(5) | 2.294 (4) |
| Rh–C(3) | 2.307 (5) | Rh–C(6) | 2.248 (3) |
| Rh–C(4) | 2.263 (5) | Rh–P | 2.237 (1) |
| Rh–C(1)–O(1) | 177.0 (4) | C(2)–Rh–P | 109.7 (1) |
| C(1)–Rh–C(2) | 148.0 (2) | C(3)–Rh–C(4) | 36.1 (2) |
| C(1)–Rh–C(3) | 115.6 (2) | C(3)–Rh–C(5) | 60.2 (2) |
| C(1)–Rh–C(4) | 105.7 (2) | C(3)–Rh–C(6) | 60.8 (2) |
| C(1)–Rh–C(5) | 126.7 (2) | C(3)–Rh–P | 143.0 (1) |
| C(1)–Rh–C(6) | 162.7 (2) | C(4)–Rh–C(5) | 36.4 (2) |
| C(1)–Rh–P | 91.5 (2) | C(4)–Rh–C(6) | 60.7 (2) |
| C(2)–Rh–C(3) | 35.7 (1) | C(4)–Rh–P | 159.5 (1) |
| C(2)–Rh–C(4) | 60.3 (1) | C(5)–Rh–C(6) | 36.1 (2) |
| C(2)–Rh–C(5) | 60.6 (2) | C(5)–Rh–P | 123.6 (1) |
| C(2)–Rh–C(6) | 37.2 (2) | C(6)–Rh–P | 100.0 (1) |
| C(2)–C(3) | 1.420 (6) | C(6)–C(2)–C(3) | 106.4 (3) |
| C(3)–C(4) | 1.417 (7) | C(2)–C(3)–C(4) | 108.5 (4) |
| C(4)–C(5) | 1.422 (8) | C(3)–C(4)–C(5) | 108.9 (4) |
| C(5)–C(6) | 1.406 (6) | C(4)–C(5)–C(6) | 107.5 (4) |
| C(6)–C(2) | 1.460 (6) | C(5)–C(6)–C(2) | 108.6 (4) |
| Rh–C(2)–C(3) | 71.6 (2) | Rh–C(2)–C(6) | 68.7 (2) |
| Rh–C(3)–C(4) | 70.2 (3) | Rh–C(3)–C(2) | 72.7 (3) |
| Rh–C(4)–C(5) | 73.0 (3) | Rh–C(4)–C(3) | 73.7 (3) |
| Rh–C(5)–C(6) | 70.2 (2) | Rh–C(5)–C(4) | 70.6 (2) |
| Rh–C(6)–C(2) | 74.1 (2) | Rh–C(6)–C(5) | 73.8 (2) |
| P–C(2)′-C(3)′ | 130.5 (4) | P–C(2)′–C(6)′ | 122.9 (3) |
| P–C(2)′ | 1.804 (4) | P–C(7) | 1.841 (5) |
| | | P–C(13) | 1.841 (4) |
| Rh–P–C(2)′ | 113.7 (2) | C(2)′–P–C(7) | 103.8 (2) |
| Rh–P–C(7) | 116.4 (1) | C(2)′–P–C(13) | 102.6 (2) |
| Rh–P–C(13) | 117.3 (1) | C(7)–P–C(13) | 101.1 (2) |
| C(7)–C(8) | 1.394 (7) | C(13)–C(14) | 1.374 (6) |
| C(8)–C(9) | 1.404 (8) | C(14)–C(15) | 1.406 (6) |
| C(9)–C(10) | 1.357 (7) | C(15)–C(16) | 1.404 (9) |
| C(10)–C(11) | 1.385 (9) | C(16)–C(17) | 1.360 (8) |
| C(11)–C(12) | 1.400 (8) | C(17)–C(18) | 1.389 (6) |
| C(12)–C(7) | 1.375 (6) | C(18)–C(13) | 1.405 (7) |
| P–C(7)–C(8) | 120.9 (3) | P–C(13)–C(14) | 123.1 (3) |
| P–C(7)–C(12) | 119.8 (4) | P–C(13)–C(18) | 117.1 (3) |
| C(12)–C(7)–C(8) | 119.3 (4) | C(18)–C(13)–C(14) | 119.7 (4) |
| C(7)–C(8)–C(9) | 120.0 (4) | C(13)–C(14)–C(15) | 121.2 (5) |
| C(8)–C(9)–C(10) | 120.1 (5) | C(14)–C(15)–C(16) | 117.9 (5) |
| C(9)–C(10)–C(11) | 120.6 (5) | C(15)–C(16)–C(17) | 121.0 (4) |
| C(10)–C(11)–C(12) | 119.7 (5) | C(16)–C(17)–C(18) | 121.0 (5) |
| C(11)–C(12)–C(7) | 120.4 (5) | C(17)–C(18)–C(13) | 119.2 (4) |

bridged by two (diphenylphosphino)cyclopentadienyl groups which are in a mutual head-to-tail arrangement. The large rhodium–rhodium separation of 4.3029 (6) Å precludes any metal–metal interaction.

The geometry around each rhodium atom strongly resembles that around the iridium atom in ($\eta^5$-$C_5H_5$)Ir(CO)($PPh_3$).[27] The cyclopentadienyl ring center Cp and the atoms P and C(1) are in a planar triangular arrangement around the central metal atom, and the C(1)–Rh–P angle of 91.5 (2)° compares with the C(O)–Ir–P angle observed in ($\eta^5$-$C_5H_5$)Ir(CO)($PPh_3$), i.e. 89.2 (3)°.

As shown in Table VI, some pertinent planes may be conveniently used to describe the overall geometry of **6a**. The geometry of the (diphenylphosphino)cyclopentadienyl group in **6a** is very similar to that mentioned in other dinuclear complexes containing such a bridging ligand, e.g. Fe[($\eta^5$-$C_5H_4$)$PPh_2$]$_2$Pd$Cl_2$,[28] Fe[($\eta^5$-$C_5H_4$)$PPh_2$]$_2$Rh($\eta^4$-$C_7H_8$),[29] $(CO)_4$Mo[($\eta^5$-$C_5H_4$)$PPh_2$]Zr$Cl_2$,[8] $(CO)_4$Mn–Mo$(CO)_3$[($\eta^5$-$C_5H_4$)$PPh_2$],[6a] Cl(CO)Ir–Mo$(CO)_3$[($\eta^5$-$C_5H_4$)$PPh_2$],[6b] or in the trinuclear complex [Co[($\eta^5$-$C_5H_4$)$PPh_2$]$_2$][Mo$(CO)_5$]$_2$.[30]

**Table VI. Least-Squares Planes of the Form *Ax* + *By* + *Cz* + *D* = 0 for 6a**

| plane | atoms | *A* | *B* | *C* | *D* |
|---|---|---|---|---|---|
| 1 | C(2)C(3)C(4)C(5)C-(6) | –0.8316 | –0.2754 | –0.4824 | +7.3671 |
| 2 | Rh, P, C(1), Cp[a] | 0.1007 | 0.7254 | –0.6810 | 0.8350 |
| 3 | Rh, Rh′, Cp, Cp′ | 0.3918 | 0.2735 | –0.8785 | 1.3908 |
| 4 | Rh, P′, Cp | 0.4913 | –0.0296 | –0.8705 | 1.5793 |

Distances of Atoms from Planes, Å

1 C(2), –0.015 (4); C(3), 0.002 (5); C(4), 0.020 (5); C(5), –0.033 (5); C(6), 0.025 (4); Rh, 1.9383 (4); P′, –0.182 (1)
2 Rh, 0.0006 (3); P, –0.001 (1); C(1), –0.042 (5); Cp, –0.043 (4)
3 P, –0.951 (1)
4 P, –1.338 (1)

Dihedral Angles

| planes | angle, deg | planes | angle, deg |
|---|---|---|---|
| 1,2 | 87.4 | 2,3 | 33.3 |
| 1,3 | 88.7 | 3,4 | 18.4 |

[a] Cp is the center of the cyclopentadienyl ring.

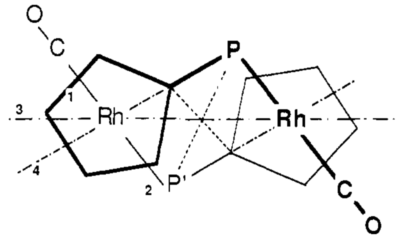

**Figure 5.** A schematic view of **6a**. The notations 2, 3, and 4 refer to the traces of planes considered in Table VI.

The cyclopentadienyl ring is slightly distorted from the corresponding least-squares plane [C(2),C(3),C(4),C(5),C(6)]. The rhodium atom distance to the cyclopentadienyl ring least-squares plane is 1.9383 (4) Å, and the rhodium–carbon (cyclopentadienyl) distances lie in the range 2.248–2.321 Å with a mean value of 2.287 (4) Å. It is of interest to note that these values are somewhat larger than those reported for monometallic rhodium cyclopentadienyl systems.[31] A relatively large deviation of the P′ atom out of the cyclopentadienyl ring least-squares plane to which it is attached is observed. The P′ atom is indeed bent up by 0.182 Å from this plane, toward the Rh′ atom.

The $\nu$(CO) abbsorption band of **6a** and **6c** compares well with those of ($\eta^5$-$C_5H_5$)Rh(CO)($PPh_3$) and ($\eta^5$-$C_5H_5$)Ir(CO)($PPh_3$), i.e. 1957 and 1947 cm$^{-1}$ (hexane), respectively.[32] The $^{31}P\{^1H\}$ NMR spectra of complexes **6a–c** reveal equivalent phosphorus nuclei. Further, the typical AA′XX′ (X = X′ = Rh) resonance pattern observed for **6a** and **6b** is consistent with a symmetrical molecular structure.

More significantly, the $^{13}C\{^1H\}$ spectrum of **6a** exhibits three signals for the cyclopentadienyl ring carbons: two doublets of equal intensities at 108.86 and 95.25 ppm with respective doublet spacings of 53.0 and 10.2 Hz and one singlet of half intensity at 87.80 ppm. Similarly, the $^1H$ NMR spectra of **6a–c** exhibit, for the four hydrogen atoms of the cyclopentadienyl ring, two signals that appeared in each case as ill-resolved second-order multiplets (at 90 MHz as well as at 250 MHz) (centered at 5.68 and 5.56

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ppm for **6a**, 5.56 and 5.45 ppm for **6b**, and 5.75 and 5.49 ppm for **6c**).

As shown on Figure 5, the molecule **6a** is, in the solid state, centrosymmetric; however, these NMR data clearly indicate that, at the NMR time scale, complexes **6** contain, in addition to a center of symmetry, a plane of symmetry and a 2-fold axis ($C_{2h}$ group). This situation is quite different to what is observed in the crystalline state and should be interpreted in *terms of intramolecular wagging of the molecular geometry around a mean plane.* In that case, this interconversion should be of low activation energy, the $^1$H NMR spectra being unchanged in the temperature range −70 to +30 °C (at 250 MHz).

## Summary and Conclusion

The potentiality of the cyclopentadienyl (or cyclopentadienide) phosphine as an assembling ligand is interestingly exemplified by the above results.

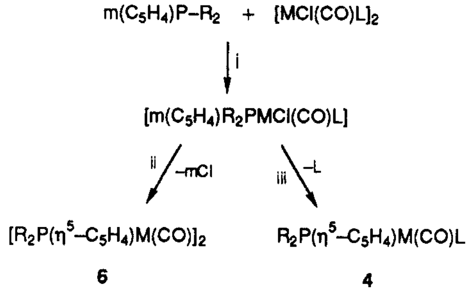
Table I, which briefly reviews the literature, shows that the synthesis of heterobimetallic derivatives of this type of ligand starts in all the cases with a reaction of the cyclopentadienyl (or cyclopentadienide) extremity of the phosphine. On the contrary (Figure 2), the synthesis of the heterobimetallic $d^8$–$d^6$ complexes **3** illustrates a new alternative approach, involving as a first step the coordination of the phosphorus extremity.

Concerning the homobimetallic complexes, our syntheses summed up in Figure 3 could suggest first steps involving the coordination of the cyclopentadienide end of the ligand. Nevertheless, our preliminary observations[16] on the reaction

$$\tfrac{1}{2}[\mathrm{RhCl(CO)(PPh_3)}]_2 \xrightarrow[-70\ ^\circ\mathrm{C},\ -\mathrm{LiCl}]{\mathrm{LiC_5H_4PPh_2}} \mathbf{4b} + \mathbf{6a} + 2\mathrm{PPh_3} \quad (1)$$

make doubtful this simple conclusion. Indeed, after 15 min of reaction time, the $^{31}$P NMR spectra recorded at the same temperature clearly show, following the total consumption of the rhodium starting materials and of the heterodifunctional ligand, the formation of five major intermediates together with *free* triphenylphosphine. For all these intermediates, the values of the phosphorus–rhodium coupling constants[33] are unambiguous indications of the coordination of the phosphorus on a 16-electron rhodium(I) atom in a square-planar configuration. Actually, a mixture of mono- and binuclear 16-electron rhodium species is usually observed in such type of reaction of a phosphine ligand with a chloro-bridged complex, $[\mathrm{RhL_2Cl}]_2$.[11] This leads us to consider that the series of intermediates observed in the present study is similar to such a mixture of species.

Therefore, it was assumed that *the first step of (1) consists of the coordination of the phosphorus end of the ligand* and that *it is followed*, for each intermediate, by a nucleophilic attack by the cyclopentadienide free extremity of the ligand with further elimination of chloride. Therefore a more complete pathway can be proposed for the preparation of the three compounds **6a**–**6c**.



m = Li, Tl; M = Rh

This hypothesis has now been confirmed by monitoring by $^{31}$P NMR the reaction for M = Rh, L = CO, R = Me, and m = Tl. In that case, signals successively appear at room temperature at $\delta$ −12.31 ($J$(P–Rh) = 117.6 Hz), −12.74 ($J$(P–Rh) = 119.8 Hz), and −14.35 ppm ($J$(P–Rh) = 121.3 Hz) attributed, with respect to the phosphorus–rhodium coupling values, to 16-electron rhodium(I) species (presumably mononuclear $\mathrm{RhCl(CO)_2[P(C_5H_4Tl)Me_2]}$, dinuclear *cis*- and *trans*-$\mathrm{[RhCl(CO)(P(C_5H_4Tl)Me_2]_2)}$, and then at $\delta$ −5.46 ($J$(P–Rh) = 186.8 Hz) attributed to an unidentified 18-electron intermediate. Finally, all the previous compounds transform slowly to **6b**.

Accurate details on reactions ii and iii are difficult to reach owing to the heterogeneity of the reactional system. We can nevertheless notice that in the case of the rhodium compounds, **4b** transforms easily into **6a** while in the case of the iridium compounds, **4c** and **6c** form simultaneously; still, in contrast with the rhodium case, the transformation of one of the complexes into the other is not observed. Finally the isolation of a compound $\mathrm{Ir(CO)Cl[Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)]_2}$ (**7a**),[16] ascertains the possibility of intermediate formation of 16-electron compounds in such system.

**Registry No.** **1a**, 122470-22-8; **1b**, 122470-23-9; **1c**, 122470-24-0; **2b**, 122470-25-1; **2c**, 122470-26-2; **3a**, 122470-27-3; **3b**, 122470-28-4; **3c**, 122470-29-5; **3d**, 122470-30-8; **3e**, 122470-31-9; **3f**, 122470-32-0; **3g**, 122470-33-1; **4a**, 122470-34-2; **4b**, 106520-04-1; **4c**, 106500-77-0; **5a**, 122470-35-3; **5b**, 122470-36-4; **5c**, 122470-37-5; **6a**, 106500-79-2; **6b**, 122470-38-6; **6c**, 106500-78-1; **7a**, 106520-03-0; $\mathrm{W(CO)_5(THF)}$, 36477-75-5; $\mathrm{C_5H_5Na}$, 4984-82-1; $\mathrm{Ph_2P(CH_2)_2(C_5H_5)}$, 122470-20-6; $\mathrm{Mo(CO)_5(THF)}$, 53248-43-4; $\mathrm{Rh_2Cl_2(CO)_4}$, 14523-22-9; $\mathrm{IrCl_2(\eta^4\text{-}C_8H_{12})_2}$, 12112-67-3; $\mathrm{Rh_2Cl_2(C_8H_{12})_2}$, 12092-47-6; $\mathrm{Ph_2P(C_5H_4)^-Li^+}$, 83272-80-4; $\mathrm{Rh_2Cl_2(C_2H_4)_4}$, 12081-16-2; $\mathrm{Rh_2Cl_2(CO)_2(PPh_3)_2}$, 34676-63-6; $\mathrm{Ph_2P(C_5H_4)Tl}$, 85320-10-1; $\mathrm{(CH_3)_2P(C_5H_4)Tl}$, 122470-21-7; *trans*-$\mathrm{IrCl(CO)(PPh_3)_2}$, 15318-31-7; chlorodiphenylphosphine, 1079-66-9; (1-chloroethyl)diphenylphosphine, 73576-89-3.

**Supplementary Material Available:** Tables of fractional coordinates, hydrogen atom positional and thermal parameters, anisotropic thermal parameters, bond lengths and angles, interatomic distances, and least-squares planes (6 pages); a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[33] Four of these intermediates were characterized by single doublets centered at 35.6 ($J$(P–Rh) = 120 Hz), 33.3 ($J$(P–Rh) = 120 Hz), 31.2 ($J$(P–Rh) = 127 Hz), and 26.3 ppm ($J$(P–Rh) = 120 Hz). One intermediate is characterized by two doublets of doublets of equal intensity, centered at 23.56 ($J$(P–Rh) = 120 Hz, $J$(P–P) = 55 Hz) and 23.14 ppm ($J$(P–Rh) = 119 Hz, $J$(P–P) = 55 Hz), respectively. Owing to the thermal sensitivity of the complicated mixture, the study of its conversion to **4b** and **6a** has not been tackled.