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# (Dimethylphosphino)- and (Diphenylphosphino)cyclopentadienyl Derivatives of Cobalt, Rhodium, and Iridium: The Crystal and Molecular Structure of Dicarbonyl{$\mu$-[($\eta^5$-cyclopentadienyl)dimethylphosphine-*P*]}-dirhodium

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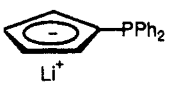
The reaction of cyclopentadienylthallium with chlorodimethylphosphine followed by thallium ethoxide has produced [(dimethylphosphino)cyclopentadienyl]thallium (**3**) in 80% yield. Reactions of **3** as well as its diphenyl analogue (**2**) with group 9 metal carbonyl halides afford new homobimetallic complexes $[M(\eta^5\text{-}C_5H_4)PR_2(CO)]_2$ (M = Co, Rh, Ir; R = $CH_3$, $C_6H_5$) (**4**, **7-10**) in good to excellent yields. These complexes possess novel cyclic, dimeric structures. The product from the reaction of **3** with $[Rh(CO)_2Cl]_2$ (**9**) has been characterized by means of a single-crystal X-ray diffraction study. **9** crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 7.188 (6), $b$ = 7.725 (6), $c$ = 8.675 (3) Å, $\alpha$ = 102.34 (5)°, $\beta$ = 96.26 (5), and $\gamma$ = 102.05°. The final $R$ value based on 1528 observed reflections was 0.036. The dimer resides on a crystallographic center of inversion. The Rh–C($\eta^5$) lengths range from 2.232 (7) to 2.303 (8) Å, and the Rh–P length is 2.233 (2) Å.

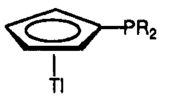
## Introduction

The preparation and properties of organometallic compounds that contain two or more metals in close proximity represent an area that has been extensively studied in recent years. These compounds are of interest as possible models for active sites in catalysts and as intermediates in organic synthesis. In addition, they may provide useful information about the surface structure of metals and clusters.[1]

One synthetic route to such complexes involves the use of the heterodifunctional phosphinocyclopentadienyl ligand, which has proved to be an excellent intermediate for the preparation of bimetallic complexes that contain two dissimilar metals. [(Diphenylphosphino)cyclopentadienyl]lithium (**1**), first prepared by Mathey and Lampin[2] and by Davidson and co-workers,[3] has been widely employed in recent years as a synthetic route to heterobimetallic complexes.[3-7] Other heterodifunctional ligands that contain a diphenylphosphino moiety connected by a short chain to a cyclopentadienyl ring have been developed by Shore and co-workers[8] and by Mathey, Poilblanc, et al.[5]



**1**



**2**: R = Ph
**3**: R = Me

Our own efforts in this area have resulted in a high yield synthesis of [(diphenylphosphino)cyclopentadienyl]thallium (**2**).[9] This useful heterodifunctional reagent, which is readily prepared from (diphenylphosphino)cyclopentadiene and thallium ethoxide and which can be conveniently stored for long periods of time, has been employed in the formation of a series of titanium–manganese heterobimetallics.[9]

In continuation of our studies on new functionally substituted cyclopentadienylmetal compounds,[10] we now report the synthesis of the new heterodifunctional reagent [(dimethylphosphino)cyclopentadienyl]thallium (**3**). Also described are reactions of **3** as well as the diphenyl analogue **2** with group 9 metal carbonyl halides, leading to a series of homobimetallic complexes that have novel cyclic, dimeric structures. An X-ray crystallographic investigation of one of the complexes that confirms their structure is also described.[11,12]

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(1) For recent reviews on bimetallic compounds, see: (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 40, p 763. (b) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207. (c) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167.

(2) Mathey, F.; Lampin, J.-P. *J. Organomet. Chem.* **1977**, *128*, 297.

(3) Rudig, A. W.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* **1978**, *17*, 2859.

(4) (a) Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1591. (b) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, *105*, 7574. (c) Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218.

(5) Leblanc, J.-C.; Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1982**, *231*, C43.

(6) Tikkanen, W.; Fujita, Y.; Peterson, J. L. *Organometallics* **1986**, *5*, 888.

(7) DuBois, D.-L.; Eigenbrot, C. W., Jr.; Miedaner, A.; Smart, J. C.; Haltiwanger, R. C. *Organometallics* **1986**, *5*, 1405.

(8) (a) Schore, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 7410. (b) Schore, N. E.; Benner, L. S.; LaBelle, B. E. *Inorg. Chem.* **1981**, *20*, 3200.

(9) Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882.

(10) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1.

(11) Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987; paper INOR 129.

(12) Since completion of this research program, we have learned of some analogous independent studies in this area, including an X-ray structural determination of **4**: (a) He, X. D.; Mainsonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* **1987**, *6*, 678. (b) Mainsonnat, A.; He, X. D.; Poilblanc, R. XIII International Conference on Organometallic Chemistry, Turin, Italy, Sept 1988; paper 15. (c) He, X. D.; De Montanzon, D.; Maisonnat, A.; Poilblanc, R. XXV International Conference on Coordination Chemistry, Nanjing, P.R.C., July 1988; paper 344.

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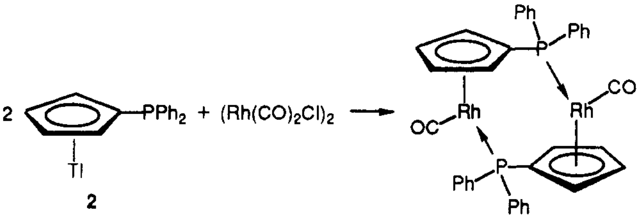
## Results and Discussion

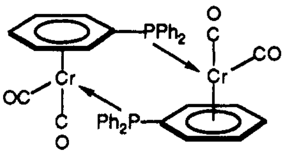
The original goal of this research program was to prepare phosphino-substituted cyclopentadienylmetal dicarbonyls ($\eta^5$-$C_5H_4PR_2$)M(CO)$_2$ (R = Me, Ph; M = Co, Rh, Ir) that could be used in the formation of heterobimetallic compounds via subsequent coordination of the unshared pair of electrons of phosphorus. However, an initial reaction between 2 equiv of **2** and dichlorotetracarbonyldirhodium in THF at room temperature did not produce the expected dicarbonyl complex but instead a slightly air-sensitive orange solid that was subsequently identified as the dimeric species [Rh($\eta^5$-$C_5H_4$)PPh$_2$(CO)]$_2$ (**4**).



2

4

The dimeric structure proposed for **4** is similar to that postulated for tetracarbonylbis{$\mu$-[($\eta^6$-phenyl)diphenylphosphine-*P*]}dichromium (**5**), whose structure was determined by X-ray crystallographic methods.[13] Elemental analysis and the $^1$H NMR spectrum of **4** were consistent with those of the proposed composition. An IR spectrum of **4** exhibited a single carbonyl stretching frequency at 1947 cm$^{-1}$, and the mass spectrum contained a molecular ion at *m/e* 760 with a relative intensity of 30% versus the (M − CO)$^+$ base peak.



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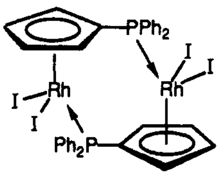
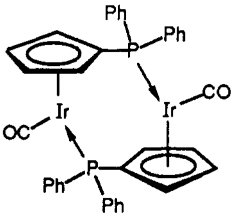


6

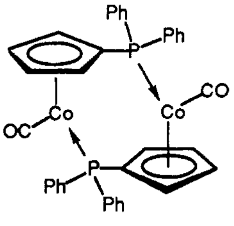
Dimeric complex **4** did not react with carbon monoxide or triphenylphosphine under either thermal or photolytic conditions. The failure of these reactions demonstrates the considerable stability of the cyclic dimeric structure. Substitution reactions on cyclopentadienylrhodium dicarbonyl complexes have been postulated by Basolo and co-workers to involve an $\eta^5$ to $\eta^3$ ring slippage as an important step in the mechanism.[14] Steric constraints imposed by the cyclic dimeric structure of **4** may prevent such ring slippage. Further, **4** is electronically analogous to CpRh(CO)(PR$_3$) complexes, and the latter are known to be less reactive than CpRh(CO)$_2$ toward substitution, since the remaining CO ligand is more firmly bonded to the metal.[14a]

Complex **4** also failed to react with an excess of iodomethane in THF at room temperature. This result is in sharp contrast to studies by Oliver and Graham,[15] who reported that the related complex CpRh(CO)(PPh$_3$) reacted with iodomethane under similar conditions to form an acyl derivative CpRh(PPh$_3$)[C(O)CH$_3$]I in good yield. Treatment of **4** with excess iodine did produce the tetraiodo complex **6** in quantitative yield, however. Complex **6** has been independently prepared in a similar manner by Poilblanc and co-workers.[12c]

The thallium reagent **2** likewise reacted with chlorotricarbonyliridium in THF solution to form an analogous dimeric iridium complex (**7**) in 62% yield as a slightly air-sensitive yellow solid. The IR spectrum of **7** exhibited a single carbonyl band at 1934 cm$^{-1}$. The corresponding cobalt dimer **8** was also prepared in 48% yield by reaction of **2** with [ICo(CO)$_n$]$_x$[16] and was isolated as an air-sensitive, red-brown powder. A single carbonyl band occurred in the IR spectrum of **8** at 1925 cm$^{-1}$. The mass spectrum of **8** contained strong peaks at *m/e* 644 and 616, corresponding to losses of one and two CO units from the molecular ion, respectively. Both **7** and **8** were also characterized by suitable elemental analyses and by their $^1$H NMR spectra.

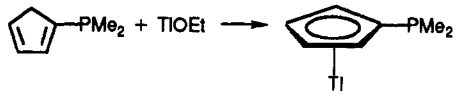


7



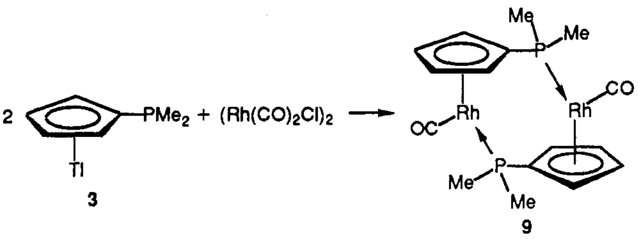
8

In order to further examine reactions of this type and to hopefully produce dimeric homobimetallic complexes that could provide more definable NMR information, we decided to examine analogous dimethylphosphino analogues. [(Dimethylphosphino)cyclopentadienyl]thallium (**3**) has not previously been reported in the literature. We found that a cold (0 °C) diethyl ether solution of (dimethylphosphino)cyclopentadiene[17] reacted with thallium ethoxide to form the thallium reagent **3** in 80% yield. The product was soluble in THF, benzene, and dichloromethane. This material was sufficiently pure for further reactions. An analytical sample could be prepared by vacuum sublimation at 80 °C, although extensive decomposition occurred. The $^1$H NMR spectrum of **3** exhibited resonances for the cyclopentadienyl ring at $\delta$ 5.98 and 5.81 ppm and a doublet at $\delta$ 1.10 ppm ($J_{H\text{-}P}$ = 2.7 Hz) assignable to the methyl protons. The $^{31}$P NMR proton-decoupled spectrum showed a singlet at $\delta$ −61.08 ppm, whereas the mass spectrum contained weak molecular ion peaks at *m/e* 330/328 whose intensities corresponded to the expected $^{205}$Tl/$^{203}$Tl isotopic abundances.



3

A reaction between 2 equiv of **3** and dichlorotetracarbonyldirhodium in THF at room temperature produced the dimeric product [Rh($\eta^5$-$C_5H_4$)PMe$_2$(CO)]$_2$ (**9**) in 91% yield. The $^1$H NMR spectrum of **9** exhibited two multiplet



3

9

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[13] Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *60*, C11.

[14] (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) Basolo, F. *Inorg. Chim. Acta* **1981**, *50*, 65. (c) Rereck, M.; Basolo, F. *Organometallics* **1983**, *2*, 372. (d) Cheong, M.; Basolo, F. *Organometallics* **1988**, *7*, 2041.

[15] Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 243.

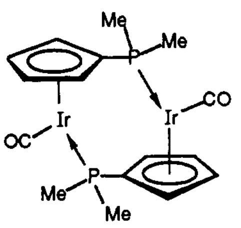
[16] Rausch, M. D.; Hart, W. P.; Macomber, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 1196.

[17] Mathey, F.; Lampin, J.-P. *Tetrahedron* **1975**, *31*, 2685.

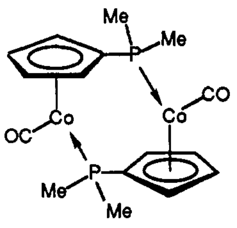
resonances for the cyclopentadienyl protons and a doublet of doublets ($J_{H\text{-}P}$ = 10 Hz, $J_{H\text{-}Rh}$ = 1.6 Hz) for the methyl protons. Similar coupling constants have been observed for the methylphosphino resonances of $CpRh(C_2H_4)PMe_3$ ($J_{H\text{-}P}$ = 9 Hz, $J_{H\text{-}R}$ = 1 Hz),[18] $CpRh(CO)PMe_3$ ($J_{H\text{-}P}$ = 10 Hz, $J_{H\text{-}Rh}$ = 1.4 Hz),[19] and $CpRh(CO)PMe_2Ph$ ($J_{H\text{-}P}$ = 9.7 Hz, $J_{H\text{-}Rh}$ = 1.6 Hz).[15] The $^{13}C$ NMR spectrum of **9** contained resonances at $\delta$ 194.2 ppm (d of d, $J_{C\text{-}Rh}$ = 87.8 Hz, $J_{C\text{-}P}$ = 25.6 Hz), assignable to the carbonyl carbon, at $\delta$ 109.1 (d of m, $J_{C\text{-}P}$ = 56.3 Hz), 93.6 (d of m, $J_{C\text{-}P}$ = 12 Hz), and 87.4 ppm (d of t, $J_{C\text{-}P}$ = 4 Hz), assignable to the cyclopentadienyl carbons, and at $\delta$ 22.1 ppm (d of d, $J_{C\text{-}P}$ = 35.9 Hz, $J_{C\text{-}Rh}$ = 2.6 Hz), assignable to the methyl carbons. The $^{31}P$ NMR spectrum of **9** exhibited a multiplet resonance at $\delta$ 2.6 ppm. Spin coupling simulation indicated the coupling constants were $J_{P\text{-}Rh}$ = 190 Hz, $J_{P\text{-}P'}$ = 11 Hz, and $J_{P\text{-}Rh'}$ = −2 Hz. The IR spectrum of **9** showed a single carbonyl stretching frequency at 1938 $cm^{-1}$, whereas the mass spectrum contained a weak molecular ion peak at *m/e* 512.

An interesting structural feature of **9** as determined by a single-crystal X-ray diffraction study (vide infra) is that the dimeric structure forms a six-membered ring of two phosphorus, two rhodium, and two carbon atoms in a chair conformation. Such a geometry would appear to cause the methyl substituents attached to a given phosphorus atom to occupy different environments and thus exhibit different chemical shifts in the NMR spectrum of **9**. This phenomenon is not observed and may be a result of rapid interconversion between the two possible chair conformations in solution, producing an averaged chemical shift of the methyl resonances. The methyl resonance is very sharp at 20 °C, suggesting that such an interconversion has a low activation energy.

In an analogous manner, a reaction between **3** and chlorotricarbonyliridium in THF solution afforded $[Ir(\eta^5\text{-}C_5H_4)PMe_2(CO)]_2$ (**10**) in 87% yield. In addition to resonances assignable to the cyclopentadienyl protons, a doublet ($J_{H\text{-}P}$ = 10.3 Hz) representing the methyl protons was observed. Iridium complex **10** should have a structure analogous to the rhodium analogue **9**, and once again there is no apparent evidence for dissimilar methyl groups, nor is there evidence of any significant broadening of the methyl resonances. The IR spectrum of **10** exhibited a single carbonyl stretching frequency at 1921 $cm^{-1}$.



**10**



**11**

Attempts to prepare and separate the final member of this series, $[Co(\eta^5\text{-}C_5H_4)PMe_2(CO)]_2$ (**11**), were largely unsuccessful. Thallium reagent **3** reacted with $[ICo(CO)_n]_x$[16] in THF to produce a brown residue after removal of the solvent. Subsequent chromatography of this product on an alumina column using benzene afforded a red band whose IR spectrum exhibited four carbonyl absorptions at 2022, 1968, 1948, and 1920 $cm^{-1}$. The carbonyl band at 1920 $cm^{-1}$ is very similar to that observed for the diphenyl analogue **8** (1925 $cm^{-1}$) and may thus result from the expected product. The other carbonyl bands were not identified. Attempts to further separate the mixture by column chromatography or by fractional crystallization were unsuccessful.

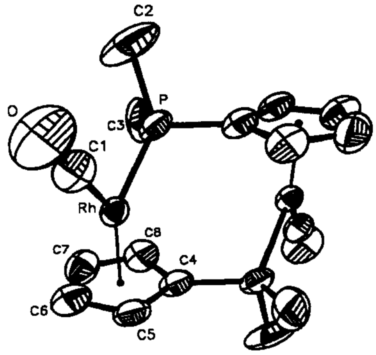


**Figure 1.** Molecular structure and atom-labeling scheme for **9**. The atoms are represented by their 50% probability ellipsoids for thermal motion.

**Table I. Bond Lengths (Å) and Angles (deg) for 9**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Rh–P | 2.233 (2) | Rh–C(1) | 1.804 (7) |
| Rh–C(4) | 2.295 (6) | Rh–C(5) | 2.283 (6) |
| Rh–C(6) | 2.279 (7) | Rh–C(7) | 2.303 (8) |
| Rh–C(8) | 2.232 (7) | Rh–Cen | 1.936 (9) |
| P–C(2) | 1.813 (9) | P–C(3) | 1.816 (9) |
| P–C(4)[a] | 1.783 (9) | O–C(1) | 1.163 (8) |
| C(4)–C(5) | 1.427 (8) | C(4)–C(8) | 1.428 (9) |
| C(5)–C(6) | 1.42 (1) | C(6)–C(7) | 1.38 (1) |
| C(7)–C(8) | 1.409 (9) | | |
| Bond Angles | | | |
| P–Rh–C(1) | 89.8 (2) | P–Rh–Cen[b] | 128.2 (3) |
| C(1)–Rh–Cen | 142.1 (7) | Rh–P–C(2) | 119.5 (3) |
| Rh–P–C(3) | 113.6 (3) | Rh–P–C(4)[a] | 112.5 (3) |
| C(2)–P–C(3) | 102.8 (4) | C(2)–P–C(4)[a] | 103.3 (4) |
| C(3)–P–C(4)[a] | 103.3 (4) | Rh–C(1)–O | 178.4 (6) |
| C(5)–C(4)–P[a] | 130.5 (4) | C(8)–C(4)–P′ | 124.5 (4) |
| C(5)–C(4)–C(8) | 105.0 (5) | C(4)–C(5)–C(6) | 108.7 (6) |
| C(5)–C(6)–C(7) | 108.6 (6) | C(6)–C(7)–C(8) | 107.8 (6) |
| C(7)–C(8)–C(4) | 109.7 (6) | | |

[a] $[x,y,z] \rightarrow [-x, -y, 1 - z]$. [b] Cen is the centroid of the cyclopentadienyl ring.

Reactions of **2** and **3** with manganese and rhenium carbonyl halides have led to both phosphinocyclopentadienyl tricarbonyl derivatives of these metals as well as dimeric products similar to **4** and **7**–**10**.[11] These results as well as other reactions of **2** and **3** will be reported in subsequent publications.

## X-ray Crystallographic Studies

The structure of **9** (Figure 1) bears a close resemblance to that of **4**.[12] Both exhibit the same connectivity, and both are positioned on a crystallographic center of inversion. Indeed, a detailed comparison of the metrical parameters shows few differences. The Rh–C(cyclopentadienyl) bond lengths in **4** range from 2.248 (3) to 2.321 (4) Å, and in **9** they range from 2.232 (7) to 2.303 (8) Å (Table I). In both **4** and **9** the rings are planar to within 0.03 Å. With **4**, the Rh–P distance is 2.237 (1) Å and the P atom resides 0.18 Å out of the plane of the cyclopentadienyl ring. With **9**, the Rh–P length is 2.233 (2) Å, although in this case the phosphorus atom is effectively coplanar with the carbon ring, lying 0.026 Å out of the plane.

## Experimental Section

All operations were carried out under an argon atmosphere by using standard Schlenk, vacuum, or glovebox techniques. The argon was dried with $MgClO_4$, molecular sieves, and $P_2O_5$, and

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[18] Werner, H.; Feser, R. *J. Organomet. Chem.* **1982**, *232*, 351.
[19] Werner, H.; Feser, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 157.

trace oxygen was removed with activated BTS catalyst. Diethyl ether and tetrahydrofuran (THF) were predried over sodium wire and distilled under argon from sodium–benzophenone ketyl radical. Pentane, hexane, dichloromethane, benzene, and toluene were distilled under argon from calcium hydride. Column chromatography was conducted under argon by using Alfa-Ventron CAMAG alumina. The alumina was heated under vacuum on a rotary evaporater to remove oxygen and water, then deactivated with 5% (by weight) argon-saturated water, and stored under argon until used. Celite was obtained from Fisher Scientific Co. and was used as received. Chlorodimethylphosphine was obtained from Strem Chemicals. Chlorodiphenylphosphine was obtained from Aldrich Chemical Co. and was distilled under argon prior to use. Thallium ethoxide was purchased from Aldrich or prepared via a literature procedure.[20] Dicobalt octacarbonyl and chlorotricarbonyliridium were obtained from Strem, whereas dichlorotetracarbonyldirhodium was prepared from rhodium trichloride hydrate and carbon monoxide by using a literature method.[21] $^1$H NMR spectra were obtained on a JEOL FX-90Q or a Varian XL-300 spectrometer. IR spectra were recorded on a Perkin-Elmer 1310 or Beckmann IR-10 spectrometer. Mass spectra were obtained on a Perkin-Elmer RMU 6L mass spectrometer at the University of Massachusetts or by Prof. H. G. Alt at the University of Bayreuth, Bayreuth, West Germany. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

**Dicarbonyl{$\mu$-[($\eta^5$-cyclopentadienyl)diphenylphosphine-*P*]}dirhodium (4).** In an argon-flushed 500-mL Schlenk flask were placed [(diphenylphosphino)cyclopentadienyl]thallium[9] (2.63 g, 5.80 mmol) and THF (200 mL). Dichlorotetracarbonyldirhodium (1.13 g, 2.90 mmol) was added, and the mixture was stirred for 18 h. The solution was filtered through a Celite plug in a Schlenk filtration apparatus, and the THF was removed from the orange solution to yield 2.08 g (94%) of **4** as an orange-brown solid. Recrystallization from dichloromethane–hexane afforded analytically pure product as orange platelets: dec >245 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.62 (m, 8 H), 7.39 (m, 12 H), 5.66 (m, 4 H), 5.55 (m, 4 H); IR ($CH_2Cl_2$) $\nu_{CO}$ 1947 cm$^{-1}$; MS *m/e* 760 ($M^+$). Anal. Calcd for $C_{36}H_{28}O_2P_2Rh_2$: C, 56.86; H, 3.71; P, 8.15. Found: C, 56.61; H, 3.73; P, 7.94.

**Tetraiodo{$\mu$-[($\eta^5$-cyclopentadienyl)diphenylphosphine-*P*]}dirhodium (6).** An 89-mg sample of **4** (0.12 mmol) was dissolved in 50 mL of THF in an argon-flushed 100-mL Schlenk flask. Solid iodine (60 mg, 0.24 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h, during which time a purple precipitate formed. The solvent was decanted, and the insoluble residue was washed twice with ethyl ether and dried to produce the product **6** in quantitative yield; dec >360 °C. No carbonyl band was observed in the IR spectrum of the product. IR (KBr): 3110 (w), 2480 (m), 2350 (vw), 1630 (w), 1475 (vw), 1430 (m), 1395 (w), 1155 (w), 1090 (m), 1050 (m), 1020 (m), 980 (m), 820 (w), 790 (m), 735 (s), 675 (s) cm$^{-1}$. Anal. Calcd for $C_{34}H_{28}I_4P_2Rh_2$: C, 33.69; H, 2.33. Found: C, 33.85; H, 2.61.

**Dicarbonyl{$\mu$-[($\eta^5$-cyclopentadienyl)diphenylphosphine-*P*]}diiridium (7).** To an argon-flushed 300-mL Schlenk flask were added [(diphenylphosphino)cyclopentadienyl]thallium[9] (1.59 g, 3.50 mmol), THF (150 mL), and chlorotricarbonyliridium (1.08 g, 3.46 mmol). The mixture was heated at reflux for 48 h with stirring. The solvent was removed from the yellow-brown solution to yield 1.01 g (62%) of a tan solid. An analytical sample was prepared by recrystallization from hot toluene to yield **7** as a yellow powder: dec >250 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.61 (m, 8 H), 7.38 (m, 12 H), 5.79 (t, 4 H), 5.51 (t, 4 H); IR ($CH_2Cl_2$) $\nu_{CO}$ 1934 cm$^{-1}$. Anal. Calcd for $C_{36}H_{28}O_2P_2Ir_2$: C, 46.05; H, 3.01. Found: C, 45.73; H, 3.24.

**Dicarbonyl{$\mu$-[($\eta^5$-cyclopentadienyl)diphenylphosphine-*P*]}dicobalt (8).** To an argon-flushed 300-mL Schlenk flask were added dicobalt octacarbonyl (0.97 g, 2.84 mmol) and THF (150 mL). Iodine (0.72 g, 2.84 mmol) was added slowly with stirring. After 3 h the green solution was transferred via a cannula to a stirred slurry of [(diphenylphosphino)cyclopentadienyl]thallium (0.64 g, 1.42 mmol) in 150 mL of THF in a 500-mL Schlenk flask at −78 °C. The red-brown solution was stirred at −78 °C for 4 h, warmed to room temperature, and stirred for 12 h. The mixture was filtered through a Celite plug, the solvent was removed, and the residue was chromatographed on an alumina column with benzene to afford a dark red band. Removal of the solvent gave 0.92 g (48%) of a red-brown solid. Several recrystallizations from toluene gave **8** as a red-brown solid: dec >170 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.90–7.15 (m, 20 H), 5.05 (m, 4 H), 4.77 (m, 4 H); IR ($CH_2Cl_2$) $\nu_{CO}$ 1925 cm$^{-1}$; MS *m/e* 644 $(M - CO)^+$. Anal. Calcd for $C_{36}H_{28}P_2O_2Co_2$: C, 64.30; H, 4.20. Found: C, 63.87; H, 4.26.

**[(Dimethylphosphino)cyclopentadienyl]thallium (3).** In an argon-flushed 300-mL Schlenk flask was placed cyclopentadienylthallium (13.96 g, 51.8 mmol). Diethyl ether (150 mL) was added, and the slurry was cooled to 0 °C. Chlorodimethylphosphine (5.0 g, 52 mmol) was added via a cannula, and the solution was stirred for 2 h at 0 °C. The ether solution was decanted from the solid thallium chloride into an argon-flushed Schlenk tube, and thallium ethoxide (12.3 g, 3.5 mL, 49.4 mmol) was added slowly with stirring. The slurry was stirred for 2 h, and the solvent was decanted. The remaining creamy white solid was washed six times with diethyl ether and dried under a high vacuum overnight to yield 13.13 g (80%) of **3** as a gray-white, air and thermally sensitive solid. This material is sufficiently pure for further reactions. An analytical sample was prepared by sublimation at 80 °C ($10^{-4}$ Torr) with extensive decomposition: $^1$H NMR (DMSO-$d_6$, external TMS) $\delta$ 5.98 (m, 2 H, $H_{2,5}$), 5.81 (m, 2 H, $H_{3,4}$), 1.10 (d, 6 H, $J_{H-P}$ = 2.7 Hz); $^{31}$P NMR (DMSO-$d_6$, external $H_3PO_4$ in $D_2O$) $\delta$ −61.08; MS *m/e* 330 (70%, $^{205}$Tl), 328 (30%, $^{203}$Tl) ($M^+$). Anal. Calcd for $C_7H_{10}PTl$: C, 25.51; H, 3.05; P, 9.40. Found: C, 25.57; H, 2.80; P, 9.21.

**Dicarbonyl{$\mu$-[($\eta^5$-cyclopentadienyl)dimethylphosphine-*P*]}dirhodium (9).** In an argon-flushed Schlenk flask were placed [(dimethylphosphino)cyclopentadienyl]thallium (1.37 g, 4.16 mmol) and THF (100 mL). Dichlorotetracarbonyldirhodium (0.80 g, 2.06 mmol) was added slowly with stirring, and the solution was stirred for 18 h. The solvent was removed, and the residue was placed on a 1.5 × 3 cm alumina plug in a Schlenk filtration apparatus. Elution with diethyl ether gave a yellow band, which yielded 0.96 g (91%) of **9** as a yellow-brown solid upon removal of the solvent. Recrystallization from diethyl ether afforded analytically pure product as orange, air-sensitive crystals suitable for X-ray crystallography: dec >235 °C; $^1$H NMR ($CDCl_3$) $\delta$ 5.55 (m, 4 H), 5.41 (m, 4 H), 1.68 (dd, 12 H, $J_{H-P}$ = 10 Hz, $J_{H-Rh}$ = 1.6 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 194.2 (dd, CO, $J_{C-Rh}$ = 87.8 Hz, $J_{C-P}$ = 25.6 Hz), 109.1 (dm, $C_1$, $J_{C-P}$ = 56.3 Hz), 93.6 (dm, $C_{2,5}$, $^2J_{C-P}$ = 12 Hz), 87.4 (dt, $C_{3,4}$, $^3J_{C-P}$ = 4 Hz), 22.1 (dd, $CH_3$, $J_{C-P}$ = 35.9 Hz, $J_{C-Rh}$ = 2.6 Hz); $^{31}$P NMR ($CDCl_3$, external $H_3PO_4$ in $D_2O$) $\delta$ 2.6 ppm (dt, $J_{P-Rh}$ = 190 Hz, $J_{P-P'}$ = 11 Hz, $J_{P-Rh'}$ = −2 Hz); IR ($CH_2Cl_2$) $\nu_{CO}$ = 1938 cm$^{-1}$; MS *m/e* 512 ($M^+$). Anal. Calcd for $C_{16}H_{20}O_2P_2Rh_2$: C, 37.52; H, 3.94. Found: C, 37.65; H, 3.94.

**Dicarbonyl{$\mu$-[($\eta^5$-cyclopentadienyl)dimethylphosphine-*P*]}diiridium (10).** In an argon-flushed 300-mL Schlenk flask were placed [(dimethylphosphino)cyclopentadienyl]thallium (1.10 g, 3.34 mmol), THF (100 mL), and chlorotricarbonyliridium (1.04 g, 3.32 mmol). The mixture was heated at reflux with stirring, cooled, and filtered through a Celite plug in a Schlenk filtration apparatus. The THF was removed to yield 0.99 g (87%) of **10** as a brown solid. The solid was placed on a 1 × 20 cm alumina column and eluted with diethyl ether under argon to produce a yellow-brown powder upon removal of the solvent. An analytical sample was prepared by recrystallization from toluene to give a yellow microcrystalline powder: dec >240 °C; $^1$H NMR ($CDCl_3$) $\delta$ 5.66 (m, 4 H), 5.34 (m, 4 H), 1.96 (d, 12 H, $J_{H-P}$ = 10.3 Hz); IR ($CH_2Cl_2$) $\nu_{CO}$ 1921 cm$^{-1}$. Anal. Calcd for $C_{16}H_{20}O_2P_2Ir_2$: C, 27.82; H, 2.93; O, 4.63. Found: C, 27.58; H, 3.05; O, 4.40.

**Attempted Preparation of Dicarbonyl{$\mu$-[($\eta^5$-cyclopentadienyl)dimethylphosphine-*P*]}dicobalt (11).** In an argon-flushed 300-mL Schlenk flask were placed dicobalt octacarbonyl (1.15 g, 3.38 mmol) and THF (75 mL). Iodine (0.86 g, 3.38 mmol) was added slowly, and the mixture was stirred for 30 min. The resulting green solution was transferred via a cannula to a −68 °C stirred suspension of [(dimethylphosphino)cyclopentadienyl]thallium (2.23 g, 6.77 mmol) in THF (75 mL) in a chloroform–dry ice slush bath. The reaction mixture was allowed to stir at −68 °C for several hours and was slowly warmed to room

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[20] Fieser, M.; Fieser, L. *Reagents for Organic Synthesis*; Wiley: New York, 1969; Vol. 2, p 407.

[21] McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

**Table II. Crystallographic Data for 9**

| | |
|---|---|
| compd | $C_{16}H_{20}O_2P_2Rh_2$ |
| mol wt | 512.12 |
| space group | $P\bar{1}$ |
| cell dimens | |
| *a*, Å | 7.188 (6) |
| *b*, Å | 7.725 (6) |
| *c*, Å | 8.675 (3) |
| $\alpha$, deg | 102.34 (5) |
| $\beta$, deg | 96.26 (5) |
| $\gamma$, deg | 102.05 (6) |
| cell *V*, Å$^3$ | 454 |
| molecules/unit cell | 1 |
| $D_{calcd}$, g/cm$^3$ | 1.88 |
| linear abs coeff, cm$^{-1}$ | 19.6 |
| radiatn | Mo K$\alpha$ |
| cryst dimens, mm | 0.4 × 0.9 × 1.0 |
| scan width, deg | 0.8 + 0.2 tan $\theta$ |
| decay of stds | <1% |
| reflctns measd | 1632 |
| $2\theta$ range, deg | 2–46 |
| reflctns obsd | 1528 |
| no. of parameters varied | 100 |
| goodness of fit | 1.11 |
| *R* | 0.036 |
| $R_w$ | 0.041 |

**Table III. Final Fractional Atomic Coordinates for 9**

| atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| Rh | –0.04511 (6) | –0.12779 (6) | 0.68580 (5) |
| C(1) | 0.1436 (9) | –0.1639 (9) | 0.8215 (8) |
| O | 0.2683 (8) | –0.1863 (9) | 0.9066 (7) |
| P | 0.1055 (2) | 0.1668 (2) | 0.7359 (2) |
| C(2) | 0.301 (1) | 0.263 (1) | 0.9029 (9) |
| C(3) | –0.054 (1) | 0.320 (1) | 0.772 (1) |
| C(4) | –0.2105 (8) | –0.2237 (8) | 0.4292 (7) |
| C(5) | –0.2164 (9) | –0.3789 (8) | 0.4947 (7) |
| C(6) | –0.3165 (9) | –0.359 (1) | 0.6278 (8) |
| C(7) | –0.3770 (9) | –0.199 (1) | 0.6444 (9) |
| C(8) | –0.3052 (9) | –0.1104 (9) | 0.5295 (8) |

temperature over a 12-h period. The red-brown solution was filtered through a Celite plug and the THF was removed. The brown residue was chromatographed on an alumina column with benzene to produce a red band. The benzene was removed, and an IR spectrum was obtained in toluene: $\nu_{CO}$ 2022, 1968, 1948, and 1920 cm$^{-1}$. Attempts to separate the mixture by column chromatography or by fractional crystallization were not successful. A satisfactory $^1$H NMR spectrum of the product could not be obtained.

**X-ray Crystal Structure Determination for 9.** Crystals were mounted in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of the angular settings for 25 carefully centered reflections ($2\theta > 36°$) are given in Table II. Data were collected by the $\theta$–$2\theta$ scan technique as described previously.[22] A summary of data collections and structure solution parameters is also given in Table II. Calculations were carried out by using the SHELX system of computer programs.[23] Structure solution was accomplished by the location of the rhodium atoms on the Patterson map, followed by the calculation of a difference Fourier map. All non-hydrogen atoms were treated with anisotropic thermal parameters. Hydrogen atoms were not located. The final value of *R* equals 0.036 and $R_w$ equals 0.041. The weighting scheme was based on unit weights. No unaccounted electron density was found on a difference Fourier map. Final values of the positional parameters are given in Table III.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters and final fractional atomic coordinates for all atoms (2 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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[22] Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. W.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

[23] SHELX, a system of computer programs for X-ray structural studies by G. M. Sheldrick, University of Cambridge, Cambridge, England, 1976.

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# Dicarbonylnitrosyl(cyclohexadienyl)rhenium Cations: Synthesis, Electrochemistry, and Nucleophilic Addition Reactions

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Grignard reagent addition to [(arene)Re(CO)$_3$]PF$_6$ (**1b**) gives the corresponding (cyclohexadienyl)Re(CO)$_3$ complexes (**2b**). When the dienyl carbons in **2b** all bear methyl substituents, treatment with NOPF$_6$ affords the nitrosyl salts [(cyclohexadienyl)Re(CO)$_2$NO]PF$_6$ (**3b**). Hydride (NaBH$_4$) adds to the ring in **3b** to give (cyclohexadiene)Re(CO)$_2$NO (**4b**) in which the hydride is situated stereospecifically endo to the metal. Other nucleophiles (CN$^-$, CH(CO$_2$Me)$_2^-$, PBu$_3$) react with **3b** to substitute a CO ligand; this also occurs with the manganese analogues **3a** when the dienyl portion of the six-membered ring is permethylated. Reduction of [(cyclohexadienyl)M(CO)$_2$NO]PF$_6$ in dichloromethane at a platinum electrode occurs at nearly the same potential for both manganese and rhenium, with the important distinction that the latter is reduced in a chemically reversible manner while the former is completely irreversible. Steady-state voltammetry at platinum disk microelectrodes shows that the first reduction of [(1,2,3,4,5-pentamethyl-6-*exo*-phenylcyclohexadienyl)Re(CO)$_2$NO]PF$_6$ is quasi-reversible in dichloromethane at electrodes in the 1–10 $\mu$m diameter range; the standard heterogeneous charge-transfer rate constant is estimated as 0.1 cm/s.

## Introduction

Coordination of cyclic $\pi$-hydrocarbons to transition metals offers the potential for ring functionalization via routes normally inaccessible in organic synthesis. Most commonly, coordination results in electrophilic activation; subsequent nucleophilic addition produces a monofunc-

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