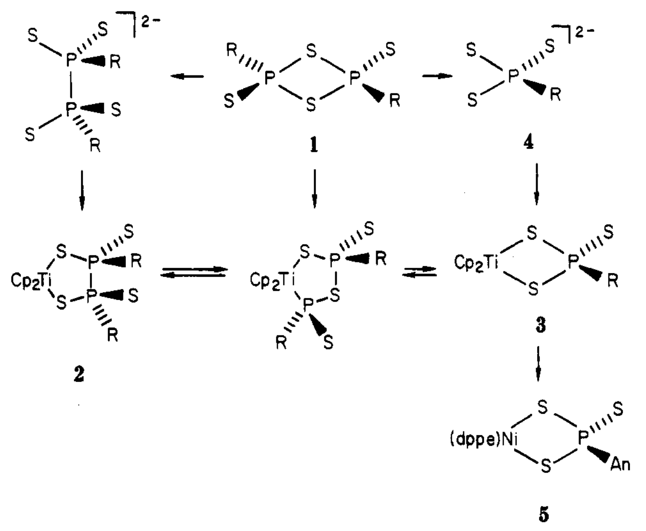
Organometallics **1984**, *3*, 1199–1204

Scheme IV



$CpRhC_2S_4(PMe_3)$ as reported by Werner.[38] Gafney and Ibers have shown that a similar type I ligand in $Ru(CO)_2(PPh_3)_2(\eta^2\text{-}COS)$ reacts with an excess of COS to yield a type III chelate, $Ru(CO)_2(PPh_3)_2(S_2CO)$.[39] The results presented in this paper provide examples of the facile interconversions of a type II to a type III chelate, by the expulsion of an RPS moiety from a type II chelate. Most likely the insertion of PhPS into the type III chelate **3a** is an example of the conversion of a head-to-tail type II chelate into its symmetrical head-to-head isomer, **2a**. Head-to-head couplings of heterocumulenes have only previously been observed for bimetallic systems.[40,41] These results are summarized in Scheme IV.

Acknowledgment. This research was supported by the National Science Foundation (CHE-81-06781), and we also thank the donors to the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. S. R. Wilson for his assistance with the crystallography. Dr. Mark Draganjac was helpful in working up the crystallographic data. High-field NMR spectra were obtained through the NSF Midwest Regional NMR center (CHE 79-16100).

Registry No. **1a**, 90412-95-6; **1b**, 90412-96-7; **1c**, 90412-97-8; **2a**, 90432-13-6; **2b**, 90412-98-9; **2c**, 90412-99-0; **3a**, 90413-00-6; **3b**, 90413-01-7; **3c**, 90432-14-7; **4**, 90412-94-5; **5**, 90413-02-8; **6**, 90413-04-0; $Cp_2Ti(CO)_2$, 12129-51-0; Cp_2TiCl_2, 1271-19-8; $(MeCp)_2TiCl_2$, 1271-19-8; $(MeCp)_2Ti(CO)_2$, 90413-05-1.

Supplementary Material Available: Tables of thermal parameters and all hydrogen atom parameters of **3a** and structure factors (16 pages). Ordering information is given on any current masthead page.

---

(38) Werner, H.; Kolb, O.; Feser, R. *J. Organomet. Chem.* **1980**, *191*, 283–93.

(39) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2860–4.

(40) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 4278–80.

(41) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921–2.

Reactions of Crowded Secondary Phosphines with $(\eta^3\text{-}2\text{-}XC_3H_4)M(1,5\text{-}COD)$ (X = H or Me and M = Rh or Ir)

Brendan D. Murray and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

Received February 13, 1984

A series of rhodium(I) and iridium(I) phosphine complexes have been prepared by treating $(\eta^3\text{-}2\text{-}XC_3H_4)M(\eta^4\text{-}1,5\text{-}COD)$ (where X = H or Me and M = Rh or Ir) with di-*tert*-butylphosphine, dicyclohexylphosphine, and bis[bis(trimethylsilyl)methyl]phosphine. Intermediates have been isolated that involve various degrees of substitution by the phosphines as well as the product of an unusual rearrangement involving the $PH\{CH(SiMe_3)_2\}_2$ ligand. ^{31}P and ^1H NMR, GC/MS, and X-ray methods were used to identify the products of these reactions. Many of the complexes react with hydrogen and readily hydrogenate simple olefins. The molecular structures of $(\eta^3\text{-}2\text{-}MeC_3H_4)Rh[PH(C_6H_{11})_2]_2$, **2**, $(\eta^4\text{-}1,5\text{-}COD)Rh(\eta^3\text{-}2\text{-}MeC_3H_4)[PH(t\text{-}Bu)_2]$, **3**, and $(\eta^4\text{-}1,5\text{-}COD)Ir(\eta^3\text{-}2\text{-}MeC_3H_4)[PH(t\text{-}Bu)_2]$, **5**, have been determined by X-ray diffraction. The crystal data at 140 K are as follows. **2**: $a = 10.637$ (2) Å, $b = 12.242$ (2) Å, $c = 12.453$ (3) Å, $\alpha = 104.88$ (2)°, $\beta = 94.962$ (2)°, $\gamma = 111.57$ (2)°, $Z = 2$, space group $P1$ (No. 2). **3**: $a = 9.130$ (2) Å, $b = 9.821$ (3) Å, $c = 12.262$ (4) Å, $\alpha = 105.13$ (3)°, $\beta = 99.34$ (2)°, $\gamma = 105.70$ (3)°, $Z = 2$, space group $P1$. **5**: $a = 9.151$ (2) Å, $b = 9.778$ (2) Å, $c = 12.304$ (3) Å, $\alpha = 104.77$ (2)°, $\beta = 99.34$ (2)°, $\gamma = 106.05$ (1)°, $Z = 2$, space group $P1$. Complex **2** is essentially square planar. Complexes **3** and **5** are both square pyramidal with the phosphine occupying the axial position. In **3** the Rh–P distance is 2.457 (1) Å while the Ir–P distance in **5** is 2.402 (3) Å. These distances are much greater than the values reported for similar structures containing smaller phosphines and phosphites as the axial ligand.

Introduction

The reactions of $[(\eta^4\text{-}1,5\text{-}COD)Rh(\eta^3\text{-}2\text{-}XC_3H_4)]$ (where X = H or Me) with various types of phosphines and phosphites have been examined in a number of recent publications.[1-4] The addition of small phosphorus ligand(s) has resulted in the loss of the COD group to produce some interesting four- and five-coordinate complexes. These complexes characteristically have the phosphorus ligands arranged in a cis geometry.

---

(1) Murray, B. D.; Olmstead, M. M.; Power, P. P. *Organometallics* **1983**, *2*, 1700.

(2) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134.

(3) Fryzuk, M. D. *Inorg. Chim. Acta* **1981**, *54*, L265.

(4) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

0276-7333/84/2303-1199$01.50/0

We recently reported the high-yield synthesis and X-ray crystal structure of a unique cyclometalated rhodium(I) phosphine complex 1 derived from $[(\eta^4\text{-1,5-COD})\text{Rh}(\eta^3\text{-2-MeC}_3\text{H}_4)]$ and bis[bis(trimethylsilyl)methyl]phosphine.[1] We now describe more detailed studies of this system and the analogous iridium system involving the less sterically demanding dicyclohexyl- and di-*tert*-butylphosphines. The reaction mechanisms are discussed, and the X-ray structures of several of the products are described.

Experimental Section

All manipulations were carried out in a Vacuum Atmospheres Co. HE-43-2 Dri-Lab, in a conventional vacuum system or by using modified Schlenk tube techniques under a nitrogen or argon atmosphere. All solvents were freshly distilled from drying agents and degassed three times immediately before use. $[(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Rh(1,5-COD)}]$,[5] $[(\eta^3\text{-C}_3\text{H}_5)\text{Ir(1,5-COD)}]$,[6] $[\{\text{IrCl(1,5-COD)}\}_2]$,[7] $\text{Sn(2-MeC}_3\text{H}_4)_4$,[8] $\text{PH}\{\text{CH(SiMe}_3)_2\}_2$,[9] PH($t$-Bu)$_2$,[10] PhLi and PhLi (containing LiBr),[11,12] and (2-methylallyl)magnesium chloride[8] were prepared by standard literature methods. Dicyclohexylphosphine (Strem), tetraallyltin (Alfa), and $\text{Sn(2-MeC}_3\text{H}_4)_4$ were vacuum distilled immediately prior to use. Melting points were determined in capillaries sealed under argon.

^{1}H NMR spectra were recorded on a NT-500, NT-360, or NT-200 spectrometer. ^{31}P NMR spectra were obtained on a NT-200 spectrometer operating at 81 MHz. Positive phosphorus chemical shifts were measured downfield from 85% H_3PO_4. GC/MS data were obtained on a Finnigan 3200 equipped with a 30-m column. Microanalyses were performed by the Analytical Laboratory at the University of California, Berkeley, and at U.C. Davis.

$(\eta^4\text{-1,5-COD})\overline{\underline{\text{Rh}}\text{(PH[CH((SiMe}_3\text{)SiMe}_2)_2\text{CH}}\text{])}$, 1. $\text{PH}\{\text{CH(SiMe}_3)_2\}_2$ (2.64 g) was added to a bright yellow hexane solution (30 mL) of $[(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Rh(1,5-COD)}]$ (1.00 g) at 25 °C. The stirred solution was warmed to 65 °C for 2 h, and then the volatiles were removed in vacuo. Hexane (20 mL) was added, and the orange solution was filtered through a Celite-padded, medium-porosity filter. The volume was reduced and cooled to −30 °C to yield large yellow crystals that were collected by filtration, washed with cold pentane (−60 °C), and then dried under vacuum: 80% yield; mp 182 °C; ^{1}H NMR (200 MHz, C_6D_6, ppm, 22 °C) 5.00, 4.26 (br s, 4 H, CHCOD), 4.12 (d of d, 1 H, $^1J_{\text{P-H}} = 292.3$ Hz, $^3J_{\text{PH-CH}} = 5.5$ Hz, PH), 2.18, 1.98 (br m, 8 H, CH_2COD) 0.49, 0.40 (s, 12 H, SiMe_2), 0.30 (s, 18 H, SiMe_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, C_6D_6, ppm, 22 °C) −15.2 (d, $^1J_{\text{Rh-P}} = 152.3$ Hz). Anal. Calcd for $\text{C}_{21}\text{H}_{46}\text{PRhSi}_4$: C, 46.30; H, 8.51. Found: C, 46.3; H, 8.6.

$(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Rh[PH(C}_6\text{H}_{11})_2]_2$, 2. $\text{PH(C}_6\text{H}_{11})_2$ (0.75 g) was added to $[(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Rh(1,5-COD)}]$ (0.50 g) in hexane (25 mL). The solution darkened to orange after 12 h. The volatiles were removed under vacuum. Hexane (10 mL) was added, and the solution was filtered and cooled to −30 °C. Yellow crystals were collected, washed with cold pentane, and dried under vacuum: 89% yield; mp 123–124 °C; ^{1}H NMR (360 MHz, C_6D_6, ppm, 21 °C) 4.14 (d of t, 2 H, $^1J_{\text{P-H}} = 307.6$ Hz, $J_{\text{P-CH}} = 5.0$ Hz, PH), 3.38 (s, 2 H, CH-syn), 2.27 (d, 2 H, $^3J_{\text{P}} = 6.5$ Hz, CH-anti), 1.80 (d, 3 H, $^3J_{\text{Rh}} = 1.9$ Hz, Me), 1.85, 1.30 (br m, 44 H, C_6H_{11}); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, C_6D_6, ppm, 23 °C) 46.2 (d, $^1J_{\text{Rh-P}} = 185.6$ Hz). Anal. Calcd for $\text{C}_{28}\text{H}_{53}\text{P}_2\text{Rh}$: C, 60.64; H, 9.63. Found: C, 60.6; H, 9.5.

$(\eta^4\text{-1,5-COD})\text{Rh}(\eta^3\text{-2-MeC}_3\text{H}_4)[\text{PH}(t\text{-Bu})_2]$, 3. PH($t$-Bu)$_2$ (0.55 g) was added to a hexane solution (30 mL) of $[(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Rh(1,5-COD)}]$ (0.50 g) at 30 °C. The bright yellow solution darkened immediately to orange-red and was left to stir for 12 h. The volatiles were removed in vacuo, and fresh hexane (25 mL) was added. After the mixture was filtered, concentrated, and cooled to −30 °C, large colorless crystals were obtained in 83% yield: mp 100–102 °C; ^{1}H NMR (360 MHz, C_7D_8, ppm, 21 °C) 4.11 (br s, CHCOD), 2.91 (d, $^1J_{\text{P-H}} = 261.2$ Hz, PH), 2.27, 2.14, 2.03 (br m, CH_2COD and 2-MeC_3H_4); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, C_7D_8, ppm, 25 °C) 67.06 (br s), −80 °C, 82.88 (d, $^1J_{\text{Rh-P}} = 109.0$ Hz, $^1J_{\text{P-H}} = 281.1$ Hz). Anal. Calcd for $\text{C}_{20}\text{H}_{38}\text{PRh}$: C, 58.24; H, 9.28. Found: C, 58.0; H, 9.2.

$(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Rh}[\text{PH}(t\text{-Bu})_2]_2$, 4. PH($t$-Bu)$_2$ was added to a toluene solution (25 mL) of **3** (0.50 g) at 25 °C. The light yellow solution was heated to 80 °C for 1 h. The solutiom darkened to yellow-orange during this period. The volatiles were removed in vacuo, and after the previously described workup a yellow powder was obtained in 80% yield. The product also can be obtained by simply heating a toluene solution of 3 to 80 °C without adding any free phosphine: mp 100 °C (darkens); ^{1}H NMR (360 MHz, C_7D_8, ppm, 80 °C) 4.19 (d, 1 H, $^1J_{\text{P-H}} = 307.0$ Hz, PH), 3.48 (s, 2 H, CH-syn), 2.07 (d, 2 H, $^3J_{\text{P}} = 6.2$ Hz, CH-anti), 1.69 (d, 3 H, $^3J_{\text{Rh}} = 1.9$ Hz, Me), 1.32, 1.26 (d, 36 H, $J = 12.4$ Hz, t-Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, C_7D_8, ppm, 25 °C) 92.79 (d, $^1J_{\text{Rh-P}} = 187.1$ Hz). Anal. Calcd for $\text{C}_{20}\text{H}_{45}\text{P}_2\text{Rh}$: C, 53.33; H, 10.07. Found: C, 53.1; H, 10.0.

$(\eta^4\text{-1,5-COD})\text{Ir}(\eta^3\text{-2-MeC}_3\text{H}_4)[\text{PH}(t\text{-Bu})_2]$, 5. Tetramethylallyltin (0.26 g) was added to PhLi (3.2 mmol) in diethyl ether (30 mL) and stirred for 30 min at 25 °C. The SnPh_4 was filtered off, and the yellow brown solution was added dropwise to a chilled (−78 °C) suspension of $[\{\text{IrCl(COD)}\}_2]$ (1.00 g) in Et_2O (20 mL) over a period of 30 min. After an additional 30 min, PH(t-Bu)$_2$ (1.00 g) was added and the contents were stirred for 2 h. The mixture was warmed to 25 °C slowly and stirred for 12 h. The solution was filtered to remove LiCl, and then the volatiles were removed in vacuo to yield an orange solid that was extracted with hexane. The solution was filtered, concentrated, and cooled to −30 °C to give colorless crystals in 62% yield. The product may be contaminated with a small percentage of $[\text{IrX(COD)}\{\text{PH}(t\text{-Bu})_2\}]$ (X = Cl or Br), if the correct quantity of organolithium is not used. The impurity can be removed by recrystallization: mp 159–160 °C; ^{1}H NMR (500 MHz, C_6D_6, ppm, 25 °C) 3.71, 3.43 (br s, 4 H, CHCOD), 3.29 (br d, $^1J_{\text{P-H}} = 317.1$ Hz, PH), 2.47 (d, 2 H, $^3J_{\text{P}} = 6.0$ Hz, CH), 2.41, 2.25, 2.20 (br s, 10 H, CH and CH_2COD), 1.82 (br s, 3 H, Me), 1.17 (d, 18 H, $J = 12.0$ Hz, t-Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, C_6D_6, ppm, 22 °C) 62.27 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{38}\text{IrP}$: C, 47.88, H, 7.63. Found: C, 47.6, H, 7.5.

$(\eta^4\text{-1,5-COD})\text{Ir}(\eta^3\text{-C}_3\text{H}_5)[\text{PH}(t\text{-Bu})_2]$, 6. A chilled suspension (−78 °C) of $[\{\text{IrCl(COD)}\}_2]$ (1.00 g) in Et_2O (30 mL) was treated with allyllithium (3.2 mmol) in Et_2O (25 mL) and PH(t-Bu)$_2$ (1.00 g) in the manner described for **5**. After workup, colorless crystals were obtained in 56% yield: mp 129–132 °C; ^{1}H NMR (200 MHz, C_6D_6, ppm, 23 °C) 4.80 (m, 1 H, CH-allyl), 3.62, 3.41 (overlapping br s, 4 H, CHCOD), 3.51 (br d, 1 H, $^1J_{\text{P-H}} = 311.5$ Hz, PH), 2.21, 2.05 (overlapping br m, 10 H, CH-syn and CH_2COD), 1.45 (d of d, 2 H, CH-anti), 1.16 (d, 18 H, $J = 12.2$ Hz, t-Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, C_6D_6, ppm, 21 °C) 58.12 (br s). Anal. Calcd for $\text{C}_{19}\text{H}_{36}\text{IrP}$: C, 46.79; H, 7.44. Found: C, 46.5; H, 7.2.

Structure Solution and Refinement

All X-ray data were collected with a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device, using a procedure described earlier.[13] Further details are in Table I.

All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors, including anomalous scattering, were from ref 14. The three structures were solved by Patterson heavy-atom methods, phasing difference electron density maps in consecutive steps.

Large, well-shaped, yellow single crystals of $[(\eta^3\text{-2-MeC}_3\text{H}_4)\text{Rh(PH(C}_6\text{H}_{11})_2)_2]$, **2**, were obtained from a concentrated hexane

---

(5) Only freshly prepared bright yellow crystals were used. Older samples gave lower yields.[2]

(6) Muetterties, E. L.; Tau, K. D.; Kirner, J. F.; Harris, T. V.; Stark, J.; Thompson, M. R.; Day, V. W. *Organometallics* **1982**, *1*, 1562.

(7) Crabtree, R. H.; Quirk, J. M.; Felken, H.; Fillebeen-Kahn, T. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.

(8) O'Brien, S.; Fishwick, M.; McDermott, B. *Inorg. Synth.* **1972**, *13*, 73. 3-Chloro-2-methylpropene (Aldrich) was substituted for allyl chloride.

(9) Power, P. P. Ph.D. Thesis, University of Sussex, 1977.

(10) Fild, M.; Stelzer, O.; Schmutzler, R. *Inorg. Synth.* **1973**, *14*, 4.

(11) Gilman, H.; Summers, L.; Leeper, R. W. *J. Org. Chem.* **1952**, *17*, 630.

(12) Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5320.

(13) Hope, H.; Nichols, B. *Acta Crystallogr., Sect. B* **1981**, *B37*, 158.

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England 1962; Vol. 3.

Table I. Crystallographic Data and Summary of Intensity Data Collection and Structure Refinement for 2, 3, and 5

	2	3	5
formula	$C_{28}H_{53}P_2Rh$	$C_{20}H_{38}PRh$	$C_{20}H_{38}PIr$
fw, g·mol^{-1}	554.58	412.40	501.70
cryst system	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, K	140	140	140
a, Å	10.637 (2)	9.130 (2)	9.151 (2)
b, Å	12.242 (2)	9.821 (3)	9.778 (2)
c, Å	12.453 (3)	12.262 (4)	12.304 (3)
α, deg	104.88 (2)	105.13 (3)	104.77 (2)
β, deg	94.962 (2)	99.34 (2)	99.34 (2)
γ, deg	111.57 (2)	105.70 (3)	106.05 (1)
V, Å^3	1427.7	989.2	990.5
Z	2	2	2
d_{calcd} (140 K), g·cm^{-3}	1.29	1.38	1.68
cryst size, mm	0.50 × 0.32 × 0.17	0.50 × 0.45 × 0.25	0.53 × 0.39 × 0.16
radiatn graphite monochromated	Mo Kα (λ = 0.710 69 Å)	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 69 Å)
μ, cm^{-1}	7.1	78.5	72.3
scan speed, deg·min^{-1}	30	60	30
scan type	ω	ω	ω
scan range, deg	1.3	1.5	2.1
ω background offset, deg	1.2	1.3	1.7
2θ limits, deg	0–50	0–140	0–50
abs correctn	yes	yes	yes
no. of data measured	5000	3678	3491
no. of reflns used in LS ($F > 6\sigma(F)$)	4458	3436	3175
no. of parameters	492	218	218
R	0.023	0.068	0.057
R_w ($w = 1/\sigma^2(\lvert F_o \rvert)$)	0.023	0.076	0.060
GOF	1.02	1.06	1.41

Table II. Atomic Coordinates (Esd's) for the Non-Hydrogen Atoms in 2

atom	10^4x	10^4y	10^4z
Rh	2529 (1)	3537 (1)	1919 (1)
P(1)	1241 (1)	2055 (1)	2575 (1)
P(2)	2031 (1)	2323 (1)	129 (1)
C(1)	3323 (3)	5073 (2)	3496 (2)
C(2)	4296 (3)	5210 (2)	2797 (2)
C(3)	3930 (3)	5243 (2)	1697 (2)
C(4)	5631 (3)	5093 (3)	3136 (2)
C(5)	2183 (2)	1694 (2)	3656 (2)
C(6)	3443 (3)	1524 (2)	3262 (2)
C(7)	4286 (3)	1294 (3)	4167 (2)
C(8)	3408 (3)	187 (3)	4504 (2)
C(9)	2157 (3)	356 (3)	4899 (3)
C(10)	1306 (3)	584 (3)	3996 (3)
C(11)	−266 (2)	2160 (2)	3171 (2)
C(12)	152 (2)	3128 (2)	4336 (2)
C(13)	−1113 (2)	3227 (2)	4791 (2)
C(14)	−2011 (2)	3493 (2)	3959 (2)
C(15)	−2425 (3)	2535 (2)	2795 (2)
C(16)	−1167 (2)	2439 (2)	2343 (2)
C(17)	3504 (2)	2173 (2)	−487 (2)
C(18)	3108 (3)	1271 (2)	−1691 (2)
C(19)	4372 (3)	1192 (3)	−2150 (2)
C(20)	5250 (3)	875 (2)	−1366 (2)
C(21)	5648 (3)	1771 (3)	−163 (2)
C(22)	4377 (3)	1825 (2)	293 (2)
C(23)	1056 (3)	2625 (3)	−983 (2)
C(24)	−324 (3)	2580 (3)	−699 (2)
C(25)	−1119 (3)	2879 (3)	−1589 (3)
C(26)	−278 (3)	4102 (3)	−1749 (2)
C(27)	1080 (3)	4123 (4)	−2056 (3)
C(28)	1893 (3)	3852 (3)	−1156 (3)

Table III. Atomic Coordinates (Esd's) for the Non-Hydrogen Atoms in 3

atom	10^4x	10^4y	10^4z
Rh	2827 (1)	−16 (1)	2138 (1)
P	2945 (2)	2172 (2)	2171 (1)
C(1)	1240 (7)	1164 (7)	2739 (6)
C(2)	353 (7)	−361 (7)	2111 (6)
C(3)	−273 (8)	−1459 (11)	2716 (10)
C(4)	833 (10)	−1913 (13)	3388 (10)
C(5)	2531 (8)	−1242 (7)	3384 (6)
C(6)	3448 (8)	277 (9)	4013 (5)
C(7)	2795 (10)	1369 (13)	4707 (7)
C(8)	1614 (13)	1796 (10)	4048 (7)
C(9)	2190 (7)	−716 (6)	221 (5)
C(10)	2536 (7)	−1847 (6)	635 (5)
C(11)	4098 (7)	−1424 (6)	1331 (6)
C(12)	1355 (8)	−3317 (6)	418 (5)
C(13)	4482 (7)	3815 (7)	1845 (6)
C(14)	3954 (9)	4684 (8)	2862 (7)
C(15)	3098 (8)	3130 (7)	779 (6)
C(16)	5812 (9)	4905 (9)	1592 (9)
C(17)	6926 (7)	2787 (7)	3141 (6)
C(18)	6838 (11)	3590 (9)	4469 (6)
C(19)	7289 (7)	1363 (8)	3238 (6)
C(20)	8309 (9)	3774 (11)	2927 (9)

solution. After the crystals were removed from the Schlenk tube, they were protected from air contamination by a layer of hydrocarbon oil. A large crystal was cut to a suitable size, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream (140 K). Final lattice parameters were determined by a least-squares refinement of 20 reflections ($\theta > 15°$) accurately centered on the diffractometer. Although the precise stoichiometry was unknown initially, the correct structure was found and subsequently refined by least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms. The data were corrected for absorption. All of the 53 atoms were detected in a difference electron density map; their sites compared well with the coordinates calculated according to carbon hybridization. The 53 hydrogen atoms were allowed to refine isotropically, and the refinement converged with $R = 0.023$ for the 4458 reflections used.

The structures of 3 and 5 were solved by the procedure described above. While the crystals used were of good quality, we were unable to locate the H atoms bound to phosphorus in 3 and 5. All of the other H atoms were included in the refinement with fixed group geometry. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The refinements converged with $R = 0.068$ for 3 and $R = 0.057$ for 5. The final atomic coordinates for the non-hydrogen atoms in 2, 3, and 5 are listed in Tables II, III, and IV, respectively.

Description of Structures

The structure of 2 is illustrated in Figure 1. The complex contains a coordinatively unsaturated rhodium(I)

Table IV. Atomic Coordinates (Esd's) for the Non-Hydrogen Atoms in 5

atom	10^4x	10^4y	10^4z
Ir	2861 (1)	20 (1)	2151 (1)
P	4931 (3)	2154 (3)	2145 (2)
C(1)	3476 (13)	388 (15)	4002 (10)
C(2)	2568 (14)	−1162 (14)	3417 (9)
C(3)	904 (16)	−1838 (19)	3508 (15)
C(4)	−290 (15)	−1559 (17)	2646 (14)
C(5)	407 (13)	−427 (18)	2110 (13)
C(6)	1235 (12)	1129 (12)	2724 (7)
C(7)	1477 (20)	1679 (20)	4031 (11)
C(8)	2834 (17)	1458 (21)	4693 (12)
C(9)	4177 (13)	−1343 (11)	1407 (8)
C(10)	2600 (13)	−1833 (13)	660 (9)
C(11)	2262 (14)	−675 (13)	260 (9)
C(12)	1381 (15)	−3341 (13)	452 (12)
C(13)	6907 (13)	2776 (14)	3196 (11)
C(14)	6872 (20)	3646 (18)	4426 (12)
C(15)	7276 (14)	1346 (15)	3241 (12)
C(16)	8254 (15)	3738 (21)	2863 (15)
C(17)	4414 (14)	3802 (13)	1874 (10)
C(18)	5760 (17)	4947 (16)	1635 (16)
C(19)	3042 (14)	3120 (14)	785 (10)
C(20)	3883 (16)	4622 (15)	2899 (11)

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

(a) Bond Distances

Rh-P(1)	2.229 (1)	Rh-C(1)	2.181 (2)
Rh-C(2)	2.142 (2)	P(1)-C(5)	1.847 (3)
P(1)-HP(1)	1.311 (20)	C(1)-C(2)	1.400 (4)

(b) Bond Angles

P(1)-Rh-P(2)	95.2 (1)	C(1)-Rh-C(3)	67.6 (1)
C(5)-P(1)-C(11)	103.7 (1)	C(11)-P(1)-HP(1)	96.4 (12)
C(1)-C(2)-C(3)	119.4 (3)	C(1)-C(2)-C(4)	120.1 (3)

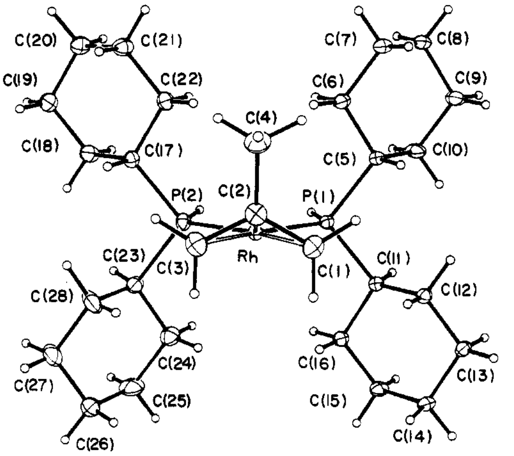


Figure 1. Computer-generated perspective diagram of 2.

atom bound to two phosphorus atoms and a η^3-bonded 2-methylallyl group. The geometry at Rh is near square planar, with the Rh, P(1), P(2), H(P1), and H(P2) atoms and the centers of the C(1)–C(2) and C(2)–C(3) bonds being almost coplanar. The methyl group (C(4)) is bent out of the C(1), C(2), C(3) plane by 5° toward the Rh atom. The cyclohexyl groups are in the expected chair conformation and permit excellent screening of the metal center. The average Rh–C(allyl) distance is 2.166 (2) Å. Table V contains some selected bond distances and angles for 2.

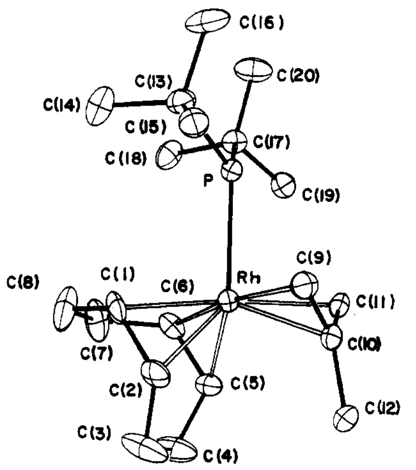


Figure 2. Computer-generated perspective diagram of 3. The hydrogen atoms have been omitted for clarity.

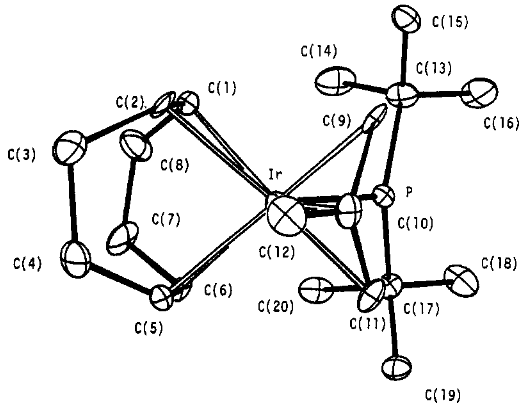


Figure 3. Computer-generated perspective diagram of 5. The hydrogen atoms have been omitted for clarity.

Table VI. Selected Bond Distances (Å) and Angles (deg) for 3

(a) Bond Distances

Rh-P	2.457 (1)	Rh-C(9)	2.198 (5)
P-C(17)	1.893 (6)	C(1)-C(2)	1.425 (8)
C(10)-C(12)	1.477 (8)	C(17)-C(18)	1.532 (10)

(b) Bond Angles

C(1)-Rh-C(5)	91.2 (3)	C(9)-Rh-C(11)	66.3 (3)
C(10)-Rh-C(11)	38.5 (2)	C(13)-P-C(17)	111.5 (3)

The structures of 3 and 5 are illustrated in Figures 2 and 3. Both structures display square-pyramidal geometry with the η^3-allylic group spanning a basal edge and a di-*tert*-butylphosphine occupying the axial position. The structures resemble the complex (η^3-C_3H_5)Ir(η^4-COD)[P(OCH_3)$_3$].[6] The complexes 3 and 5 crystallize with similar cell dimensions but exhibit some different bond distances and angles. All of the Rh–ligand distances in 3 are longer than the corresponding Ir–ligand distances in 5. The most striking structural feature of 3 and 5 is the metal–phosphine distance. The Rh–P distance is 2.457 (1) Å, and the Ir–P distance is 2.402 (3) Å. These metal to phosphorus distances are much longer than the Ir–P distance of 2.276 (2) Å in (η^3-C_3H_5)Ir(η^4-COD)[P(OCH_3)$_3$].[6] The average Rh–C(COD) distance is 2.189 (7) Å compared to the average Ir–C(COD) distance of 2.169 (13) Å. The average Rh–C(allyl) distance is 2.172 (6) Å compared to 2.165 (11) Å the for Ir system. There are many close intermolecular contacts in 3 and 5 supporting the view that these systems exist in low-energy conformations in the solid state.[6]

In 5 the methyl group is bent 4° out of the C(9), C(10), C(11) plane toward Ir. The Ir–C(12) distance is 3.181 (16) Å. The methyl group in 3 is nearly coplanar with the C(9), C(10), C(11) plane. The Rh–C(12) distance is 3.149 (10) Å. The dihedral angle between the plane defined by the olefinic carbons and the allylic carbons C(9), C(10), C(12)

Table VII. Selected Bond Distances (Å) and Angles (deg) for 5

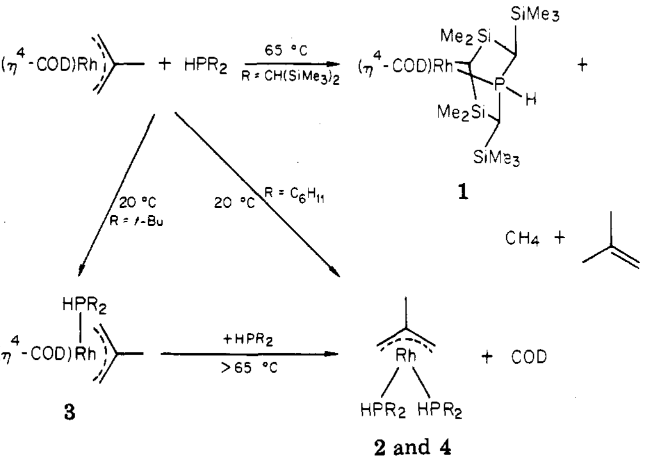
(a) Bond Distances

Ir-P	2.402 (3)	Ir-C(11)	2.179 (10)
P-C(17)	1.891 (14)	C(1)-C(2)	1.397 (16)
C(10)-C(12)	1.513 (16)	C(17)-C(19)	1.534 (15)

(b) Bond Angles

C(1)-Ir-C(5)	91.4 (5)	C(9)-Ir-C(11)	67.4 (5)
C(10)-Ir-C(11)	38.6 (5)	C(13)-Ir-C(17)	111.7 (5)

Scheme I



is 21.0° in 3 and 18.1° in 5. Steric crowding and the increased stability of [(η^3-2-MeC_3H_4)Rh(COD)] compared to [(η^3-2-Me-C_3H_4)Ir(COD)] may be responsible for the longer metal–phosphorus distance. [(η^3-2-MeC_3H_4)Ir(η^4-1,5-COD)] forms a very thermally stable molecule upon ligation of the σ-donating phosphine. Tables VI and VII contain some selected bond distances and angles for 3 and 5, respectively.

Results and Discussion

The products of the reaction of [(η^4-1,5-COD)Rh(η^3-2-MeC_3H_4)], 7, with secondary phosphines in hexane are related to the steric bulk of the phosphine employed. The cone angles of the secondary phosphines increase in the order $PH(C_6H_{11})_2$ < PH(*t*-Bu)$_2$ < PH{CH($SiMe_3$)$_2$}$_2$.[15,16] This order is consistent with the ease of adding the phosphine to 7. Two equivalents of dicyclohexylphosphine react with 7 at 20 °C to give 2 and free COD in high yield. When the more sterically demanding di-*tert*-butylphosphine is used under identical conditions, complex 3 is obtained in high yield and only a very small amount of the bis(phosphine) product 4 is produced. Upon warming to higher temperatures 4 and free COD are produced in high yield. The largest phosphine PH{CH($SiMe_3$)$_2$}$_2$ does not react with 7 at 20 °C. The product of the reaction of PH{CH($SiMe_3$)$_2$}$_2$ with 7 at 65 °C in hexane are complex 1, methane, and isobutene (see Scheme I). We believe the large steric bulk of PH{CH($SiMe_3$)$_2$}$_2$ prohibits the formation of the bis(phosphine) complex.

The production of 1 and 2 probably arises via an intermediate similar to 3. The five-coordinate intermediate undergoes a Lewis base promoted loss of the COD group when a cis product (2 and 4) is possible. If the formation of a cis product is sterically forbidden, bond activation may occur when a thermodynamically favored ring cyclization reaction is possible. The close approach of a $SiMe_3$ group may initiate a γ-H abstraction[17,18] reaction with the subsequent production of C_4H_8, CH_4, and 1. The drive to form the new bonds is assisted by the increased entopy of the products and the ease at which the volatile products can be removed. Scheme I illustrates the differences in reactivity of the secondary phosphines employed in this work.

The extent of the reaction of 7 with the phosphines can be monitored easily by ^{1}H and ^{31}P NMR. The ^{31}P{^{1}H} spectra of 2 displays a narrow temperature-independent doublet at 46.2 ppm ($^1J_{Rh-P}$ = 185.6 Hz). The $^1J_{Rh-P}$ coupling constant is similar to those reported for analogous Rh(I) systems containing the 2-MeC_3H_4 moiety. The ^{1}H NMR spectra contains a pair of downfield triplets due to the hydrogen atoms bound to phosphorus and two broad overlapping multiplets due to the cyclohexyl groups. The methylallyl group displays a singlet at 3.38 ppm due to the syn protons, a doublet at 2.27 ppm due to the anti protons coupled to phosphorus, and a doublet at 1.80 ppm due to coupling between the methyl hydrogens and the metal center (^{103}Rh, 100% natural abundance, $I = ^1/_2$). The NMR data for 2 support a rigid symmetrical η^3-2-MeC_3H_4 group with very slow η^3-η^1 interconversions.

When 2 equiv of PH(*t*-Bu)$_2$ are added to 7 at 25 °C, three peaks appear in the ^{31}P{^{1}H} spectra. The primary species in solution that exhibits a broad singlet at 67.06 ppm is 3. A temperature-independent doublet at 92.79 ppm (J_{Rh-P} = 187.1 Hz) is due to 4. The broad singlet is very temperature-dependent, and upon cooling to −80 °C it collapses to a well-resolved doublet at 82.88 ppm ($^1J_{Rh-P}$ = 109.0 Hz). No free phosphine can be seen in the spectra. Variable-temperature ^{1}H NMR reveals that the COD and methylallyl groups of 3 are fluxional in solution. Upon warming to 80 °C in toluene only the doublet due to 4 remains in the ^{31}P{^{1}H} spectrum. If colorless crystalline 3 is dissolved in toluene at 20 °C, the solution turns light yellow due to the slow formation of the bis(phosphine) complex 4. The ^{1}H NMR spectra at 80 °C in C_7D_8 reveals the presence of free COD, isobutene, and 4. The ^{1}H NMR of 4 is very similar to the ^{1}H NMR spectra of 2.

The analogous iridium systems [(η^4-1,5-COD)Ir(η^3-2-XC_3H_4)] (where X = H or Me) have received much less attention. To date only the interactions of P(OMe_3)$_3$ and PH(*t*-Bu)$_2$ with [(η^4-1,5-COD)Ir(η^3-C_3H_5)] have been reported.[1,6] The development of these systems is hampered by their low thermal stability when compared to their rhodium analogues. While the rhodium complexes can be sublimed slightly above room temperature, the iridium species are best prepared in situ and reacted at subambient temperatures. The lower yield of the iridium products is probably due to the inability to purify the precursor and the fact that the formation of [IrX(COD)(phosphine)] (whee X = Cl or Br) as a side product occurs.[15] When [(η^4-1,5-COD)Ir(η^3-2-XC_3H_4) solutions are treated with 2 equiv of PH{CH($SiMe_3$)$_2$}$_2$], two products are obtained in near equal yields. These are the complexes [IrBr(COD)(PH{CH($SiMe_3$)$_2$}$_2$)] and (η^4-1,5-COD)Ir(η^3-2-X-C_3H_4)[PH{CH($SiMe_3$)$_2$}$_2$], 8. The crystal structure of [IrBr(COD)(PH{CH($SiMe_3$)$_2$}$_2$] is similar to that of [RhCl(COD)(PCl{CH($SiMe_3$)$_2$}$_2$].[15] We are currently attempting to obtain suitable crystals of (η^4-1,5-COD)Ir(η^3-2-MeC_3H_4)[PH{CH($SiMe_3$)$_2$}$_2$] for an X-ray crystal determination. This complex is the iridium analogue of the proposed five-coordinate intermediate in the reaction

---

(15) Murray, B. D.; Hope, H.; Hvoslef, J.; Power, P. P. *Organometallics* **1984**, *3*, 657.

(16) Tolman, C. *Chem. Rev.* **1977**, *77*, 313.

(17) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.

(18) Planalp, R. P.; Andersen, R. A. *Organometallics* **1983**, *2*, 1675.

of **7** with PH{CH(SiMe$_3$)$_2$}$_2$. The complex (η^4-1,5-COD)Ir(PH{CH((SiMe$_3$)SiMe$_3$)$_2$CH}), **10**, can be prepared in low yield by treating **8** with excess PH{CH(SiMe$_3$)$_2$}$_2$ in refluxing hexane. The ^{31}P spectrum of **10** in toluene-d_8 at 60 °C exhibits a singlet at −17.56 ppm ($^1J_{\text{P-H}}$ = 301 Hz). A smaller singlet in the ^{31}P spectrum at −13.75 ppm ($^1J_{\text{P-H}}$ = 338 Hz) is due to [IrCl(COD)(PH{CH(SiMe$_3$)$_2$}$_2$)]. This upfield shift of 3.8 ppm for **10** is similar to the 5.0 ppm upfield shift of **1** when compared to [RhCl(COD)(PH{CH(SiMe$_3$)$_2$}$_2$)].[15] The ^{1}H (200 MHz, benzene-d_6) spectrum of **10** shows no resonances due to the 2-methylallyl group and is similar to that of **1**. The $^1J_{\text{P-H}}$ coupling constant of 301 Hz is slightly larger than the 292 Hz obtained for **1** but is much less than the 338 Hz obtained for pure **9**. The similar solubilities of **9** and **10** have complicated our attaining **10** in high purity.

The use of halide-free PhLi[12] results in the production of **8** and [IrCl(COD)(PH{CH(SiMe$_3$)$_2$}$_2$)], **9**, but does not afford higher product yields. The origin of the bromine in [IrBr(COD)(PH{CH(SiMe$_3$)$_2$}$_2$)] is due to the presence of LiBr in the PhLi.[12] The conversion of [{IrCl(COD)}$_2$] to [{IrBr(COD)}$_2$] in polar solvents is well-known. The use of halide-rich alkyl- and aryllithiums can have a pronounced effect on systems sensitive to halide exchange.

The reaction of [(η^4-1,5-COD)Ir(η^3-2-XC$_3$H$_4$)] (where X = H or Me) with 1 or 2 equiv of di-*tert*-butylphosphine produce (η^4-1,5-COD)Ir(η^3-2-XC$_3$H$_4$)[PH(t-Bu)$_2$] in moderate yield. The conversion of the mono(phosphine) complexes into bis(phosphine) complexes does not occur readily at room temperature even in the presence of excess phosphine. This is in sharp contrast to the formation of (η^4-1,5-COD)Ir(η^1-C$_3$H$_5$)[P(OMe)$_3$]$_2$ when 2 equiv of the small phosphite P(OMe)$_3$ are reacted with [(η^4-1,5-COD)Ir(η^3-C$_3$H$_5$)].[6]

Muetterties and co-workers have shown the iridium trimethyl phosphite complexes derived from [(η^4-1,5-COD)Ir(η^3-C$_3$H$_5$)] perform a number of catalytic processes.[6] We have examined the ability of some of our new complexes to react with hydrogen and simple olefins. The complex [(η^4-1,5-COD)Ir(η^3-2-MeC$_3$H$_4$)[PH(t-Bu)$_2$], **5**, reacts readily at 20 °C with hydrogen in hexane to yield C$_4$H$_8$, C$_4$H$_{10}$, cyclooctane, and at least one hydridoiridium complex. Benzene or hexane solutions of **5** treated with 1 atm of hydrogen also convert 1-hexene into hexane (in >85% yield) in less than 2 h. Complex **5** did not catalyze the hydrogenation of benzene or toluene. Similar reactions were observed when solutions of **6** were used. These reactions differ from the simple thermal production of COD and C$_4$H$_8$ that occurs upon heating solutions of **3**, in that the hydrogenated products are not observed when hydrogen is not added.

Hexane solutions of **2** react with 3 atm of hydrogen very slowly, but at 65 °C the yellow solution darkens to a deep red, with the production C$_4$H$_8$. Similar reactions with smaller phosphines have produced multinuclear hydrides.[19-21] We are currently attempting to fully characterize the metal complexes formed in these reactions.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-8116355), U.C. Davis NMR Facility, and a generous loan of rhodium chloride by Johnson Matthey, Inc. B.D.M. wishes to thank U.C. Davis for a generous graduate research award.

Registry No. **1**, 87451-18-1; **2**, 90624-03-6; **3**, 90624-04-7; **4**, 90624-05-8; **5**, 90624-06-9; **6**, 90624-07-0; **7**, 81177-96-0; **9**, 89178-77-8; **10**, 90624-08-1; [{IrCl(COD)}$_2$], 12112-67-3; PH{CH(SiMe$_3$)$_2$}$_2$, 83436-92-4.

Supplementary Material Available: Tables of bond distances and angles, structure factors, and calculated positional and thermal parameters (40 pages). Ordering information is given on any current masthead page.

---

(19) Fryzuk, M. D. *Organometallics* **1982**, *1*, 408.

(20) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185.

(21) Fryzuk, M. D. *Can. J. Chem.* **1983**, *61*, 1347.