

Heterobimetallic Di-*tert*-butylphosphido-Bridged Complexes of Cr-Ni and Cr-Rh. Synthesis and X-ray Structures of $(\text{CO})_4(\text{PMe}_3)\text{Cr}(\mu\text{-}t\text{-Bu}_2\text{P})\text{Ni}(\text{PMe}_3)\text{Cl}(\text{Cr-Ni})$ and $(\text{CO})_4(\text{PMe}_3)\text{Cr}(\mu\text{-}t\text{-Bu}_2\text{P})\text{Rh}(\text{PMe}_3)\text{CO}(\text{Cr-Rh})$

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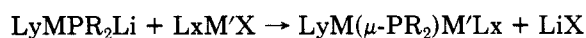
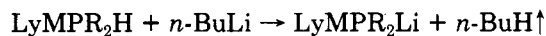
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Reaction of $(\text{CO})_5\text{CrP}(t\text{-Bu})_2\text{Li}$, prepared in situ from $(\text{CO})_5\text{CrP}(t\text{-Bu})_2\text{H}$ and $n\text{-BuLi}$ (1:1) in THF, with $\text{NiCl}_2(\text{PMe}_3)_2$ at -100°C yields $(\text{CO})_4(\text{PMe}_3)\text{Cr}(\mu\text{-}t\text{-Bu}_2\text{P})\text{Ni}(\text{PMe}_3)\text{Cl}(\text{Cr-Ni})$ (1) in 60% yield. A similar reaction with $\text{Rh}(\text{PMe}_3)_3\text{Cl}$ yields $(\text{CO})_4(\text{PMe}_3)\text{Cr}(\mu\text{-}t\text{-Bu}_2\text{P})\text{Rh}(\text{PMe}_3)\text{CO}(\text{Cr-Rh})$ (2) in 70% yield. Both 1 and 2 contain a metal-metal bond bridged by a single di-*tert*-butylphosphido ($\mu\text{-}t\text{-Bu}_2\text{P}$) unit. In both cases a PMe_3 group from the Ni and Rh starting complexes becomes bound to the Cr atom in 1 and 2, respectively. In 1 the Cr- PMe_3 group is trans to the phosphorus atom of $\mu\text{-}t\text{-Bu}_2\text{P}$ while in 2 it occupies a cis coordination site. Crystal data for 1: $\text{C}_{18}\text{H}_{36}\text{ClCrNiP}_3\text{O}_4$, $M_r = 555.56$, monoclinic, $P2_1/n$, $a = 17.682$ (2) Å, $b = 11.323$ (2) Å, $c = 13.231$ (1) Å, $\beta = 92.582$ (1)°, $U = 2646.6$ (5) Å³, $D_{\text{calcd}} = 1.394$ g cm⁻³, $Z = 4$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 14.2$ cm⁻¹, final $R = 0.0544$, $R_w = 0.0681$, from 2714 observed reflections (4683 measured). Crystal data for 2: $\text{C}_{19}\text{H}_{36}\text{CrO}_5\text{P}_3\text{Rh}$, $M_r = 592.31$, monoclinic, $P2_1/n$, $a = 8.459$ (3) Å, $b = 18.687$ (3) Å, $c = 17.113$ (2) Å, $\beta = 101.42$ (2)°, $U = 2677.1$ (1) Å³, $D_{\text{calcd}} = 1.47$ g cm⁻³, $Z = 4$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 12.0$ cm⁻¹, final $R = 0.041$, $R_w = 0.052$, from 2806 observed reflections (4854 measured).

Introduction

Metal-metal bonds between different transition metals are currently of interest in organometallic chemistry. As part of a study of the steric effects of bulky phosphido (R_2P^-) ligands¹⁻³ we have investigated the synthesis of mixed-metal dinuclear complexes where the metals are bridged by one dialkylphosphido unit. The synthetic approach used involves the in situ lithiation of a coordinated secondary phosphine followed by reaction with a complex containing a halide (see Scheme I).

Scheme I

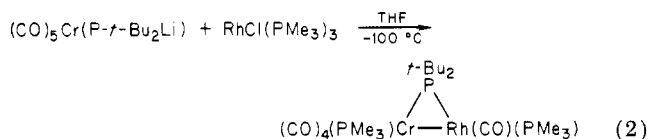
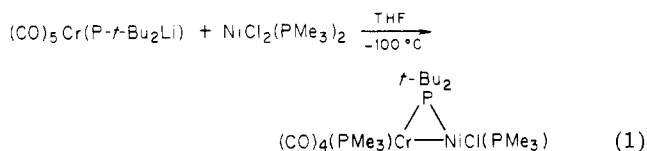


Ly, Lx = ancillary ligands; X = halide

The use of coordinated lithiated phosphines as useful intermediates in organometallic chemistry has been known for some time.⁴ More recently, for example, Geoffroy and co-workers have used this method to synthesize some interesting mixed-metal complexes of W-Ir,⁵ Fe-Rh,⁶ and Fe-Ir.⁷

With use of this general route we have synthesized two complexes that contain Cr-Ni (1) and Cr-Rh (2) bonds (see

eq 1 and 2). These complexes are the first heterodinuclear



compounds to contain the bulky bridging di-*tert*-butylphosphido ($\mu\text{-}t\text{-Bu}_2\text{P}^-$) unit.⁸ Several features of the complexes are noteworthy. The formation of both complexes is accompanied by the transfer of a PMe_3 group from the Ni or Rh starting material to the Cr atom of the product. In the solid state both 1 and 2 exist as single isomers. Although the Cr atom has virtually the same ligands in 1 and 2 (i.e., $\text{M-Cr}(\text{CO})_4(\text{PMe}_3)(\mu\text{-}t\text{-Bu}_2\text{P})$ ($\text{M} = \text{Ni, Rh}$)), the PMe_3 ligands occupy different coordination sites, being trans and cis with respect to the $\mu\text{-}t\text{-Bu}_2\text{P}$ group. The reasons for this difference in the solid state are not immediately obvious. It seems likely that different isomers are quite close in energy since in solution ³¹P NMR data indicate that both complexes exist in solution as mixtures of isomers.

We report here the synthesis, characterization, and X-ray crystal structures of 1 and 2.

Results and Discussion

$(\text{CO})_4(\text{PMe}_3)\text{Cr}(\mu\text{-}t\text{-Bu}_2\text{P})\text{NiCl}(\text{PMe}_3)(\text{Cr-Ni})$ (1). The interaction of 1 or 2 equiv of $(\text{CO})_5\text{CrP}(t\text{-Bu})_2\text{Li}$ (prepared in situ) with 1 equiv of $\text{NiCl}_2(\text{PMe}_3)_2$ in THF

(8) For other complexes containing $\mu\text{-}t\text{-Bu}_2\text{P}$ see: Schumann, H.; Neumann, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* 1981, 36B, 708 ([$\text{M}(\text{CO})_4(\mu\text{-}t\text{-Bu}_2\text{P})_2$] ($\text{M} = \text{Mn, Re}$)). Schumann, H.; Heisler, M. *Chem. Ber.* 1979, 112, 541 ($\text{Rh}_2(\text{CO})_2\text{Cl}(\text{P-}t\text{-Bu}_2)_2(\mu\text{-}t\text{-Bu}_2\text{P})$).

(1) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Rogers, R. D. *Organometallics* 1982, 1, 1721.

(2) Atwood, J. L.; Hunter, W. E.; Jones, R. A.; Wright, T. C. *Inorg. Chem.* 1982, 22, 993.

(3) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* 1982, 2, 470.

(4) See for example: Stelzer, O.; Unger, E.; Wray, V. *Chem. Ber.* 1977, 110, 3430. Hüttner, G.; Müller, H. D.; Frank, A.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 572. Treichel, P. M.; Douglas, W. M.; Dean, W. K. *Inorg. Chem.* 1972, 11, 1615.

(5) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* 1983, 105, 1069.

(6) Breen, M. J.; Geoffroy, G. L. *Organometallics* 1982, 1, 1437.

(7) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* 1982, 1, 1008.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 1 and 2

	1	2
formula	C ₁₈ H ₃₀ ClCrNiO ₄ P ₃	C ₁₈ H ₃₀ CrO ₅ P ₃ Rh
mol wt	555.56	592.31
space group	P2 ₁ /n	P2 ₁ /n
cell constants		
<i>a</i> , Å	17.682 (2)	8.459 (3)
<i>b</i> , Å	11.323 (2)	18.867 (3)
<i>c</i> , Å	13.231 (1)	17.113 (3)
β, deg	92.582 (1)	101.42 (2)
cell vol, Å ³	2646.6 (5)	2677.1 (1)
molecules/unit cell	4	4
<i>D</i> (calcd), g cm ⁻³	1.394	1.47
μ(calcd), cm ⁻¹	14.2	12.0
radiation, Å	Mo Kα, 0.710 69	Mo Kα, 0.710 69
max crystal dimens, mm	0.25 × 0.25 × 0.10	0.13 × 0.30 × 0.10
scan width, deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
std reflectns	460, 553	195, 346
decay of stds	<2%	<1%
reflectns measd	4683	4859
2θ range, deg	2.0 < 2θ < 50.0	2.0 < 2θ < 50.0
reflectns obsd	2714 (<i>I</i> > 2σ(<i>I</i>))	2806 (<i>I</i> > 3σ(<i>I</i>))
no. of parameters varied	397	262
data/parameter ratio	6.84	10.70
<i>R</i>	0.054	0.041
<i>R</i> _w	0.068	0.052

at -100 °C yields a very dark green-brown solution. The mixed-metal complex (CO)₄(PMe₃)Cr(μ-*t*-Bu₂P)NiCl(PMe₃) (1) may be isolated from this solution as a deep green crystalline material in ca. 60% yield. The complex is readily soluble in hexane and aromatic hydrocarbons and can be recrystallized from diethyl ether. It can be handled briefly in the air in the solid state but decomposes rapidly in solution when exposed to the atmosphere.

The IR spectrum shows only terminal ν_{CO} absorptions (see Experimental Section) while the ¹H NMR spectrum in C₆D₆ is a deceptively simple triplet (δ 1.08 (apparent *J*_{P-H} = 9.0 Hz)) and a doublet (δ 1.57 (*J*_{P-H} = 13.5 Hz)) which integrate in a 1:1 ratio. In contrast ³¹P{¹H} spectra indicate that a complex system is present in solution. In toluene-*d*₈ at ambient temperature the ³¹P{¹H} spectrum contains two sets of resonances. One set appears to low field and consists of two pairs of broad humps at δ 261.78, 256.53, 190.0, and 195.0 (relative to 85% H₃PO₄). These resonances can be assigned to the μ-*t*-Bu₂P group since they come to low field.⁹ To higher field there is a complex pattern of at least ten peaks that are assigned to PMe₃ resonances. The spectra are temperature dependent. On cooling all the peaks broaden slightly at -20 °C and at -80 °C they become sharp again. At this temperature the PMe₃ region remains a very complex pattern of lines while the peaks in the phosphido region now show the presence of *J*_{P-P} coupling (see Experimental Section). The spectra are very complex, and although we have not attempted a detailed analysis, they are no doubt due to a mixture of isomers being present in solution. The compound can be recovered quantitatively from the NMR solutions showing that the complex spectra are not a result of decomposition.

(9) Downfield shifts in the δ 50–200 range in the ³¹P NMR of Ph₂P groups bridging metal-metal bonds have been noted by several groups of workers. See for example: Garrou, P. E. *Chem. Rev.* 1981, 81, 229. Carty, A. J. *Adv. Chem. Ser.* 1982, No. 196, 163. Kreter, P. E.; Meek, D. W. *Inorg. Chem.* 1983, 22, 319. Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* 1983, 2, 53 and references therein. Similar downfield shifts have been noted for μ-*t*-Bu₂P complexes, see ref 1–3.

Table II. Atomic Positional Parameters for 1

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Ni(1)	0.95667 (7)	0.1665 (1)	0.2483 (1)	3.45 (2)
Cr(1)	0.03759 (8)	0.3552 (1)	0.2512 (1)	2.99 (3)
Cl(1)	0.9322 (2)	-0.0249 (2)	0.2495 (3)	5.89 (7)
P(1)	1.0791 (1)	0.1588 (2)	0.2545 (2)	3.21 (5)
P(2)	0.8298 (1)	0.2019 (2)	0.2399 (2)	4.26 (6)
P(3)	1.0053 (2)	0.5566 (2)	0.2482 (2)	4.04 (6)
O(1)	1.1471 (5)	0.4295 (8)	0.4215 (7)	7.2 (2)
O(2)	0.9281 (4)	0.3347 (7)	0.0676 (5)	5.4 (2)
O(3)	1.1510 (5)	0.4258 (8)	0.0975 (7)	7.5 (2)
O(4)	0.9278 (4)	0.3376 (7)	0.4205 (5)	5.3 (2)
CO(1)	1.1074 (5)	0.3987 (8)	0.3562 (7)	3.9 (2)
CO(2)	0.9657 (5)	0.3322 (9)	0.1406 (8)	4.2 (2)
CO(3)	1.1088 (6)	0.3959 (9)	0.1570 (9)	4.9 (3)
CO(4)	0.9658 (5)	0.3335 (9)	0.3526 (8)	4.0 (2)
C(1)	0.9487 (8)	0.609 (1)	0.136 (1)	7.5 (4)
C(2)	1.0862 (7)	0.657 (1)	0.250 (2)	11.7 (6)
C(3)	0.9490 (8)	0.613 (1)	0.3519 (9)	7.0 (3)
C(4)	1.1226 (6)	0.0938 (9)	0.3774 (9)	5.2 (3)
C(5)	1.1214 (6)	0.0906 (9)	0.1379 (9)	4.9 (2)
C(6)	0.7901 (6)	0.352 (1)	0.231 (1)	7.2 (4)
C(7)	0.7836 (6)	0.142 (1)	0.3503 (9)	5.9 (3)
C(8)	0.7819 (7)	0.129 (1)	0.1314 (9)	6.1 (3)
C(11)	1.2064 (6)	0.135 (1)	0.394 (1)	6.9 (3)
C(12)	1.0765 (8)	0.137 (1)	0.4644 (9)	6.0 (3)
C(13)	1.1211 (9)	-0.044 (1)	0.378 (1)	8.0 (4)
C(51)	1.0768 (7)	0.136 (1)	0.0438 (8)	5.6 (3)
C(52)	1.1160 (9)	-0.047 (1)	0.137 (1)	7.9 (4)
C(53)	1.2052 (7)	0.128 (1)	0.132 (1)	7.3 (4)

Table III. Selected Bond Lengths (Å) for 1^a

atom 1	atom 2	dist	atom 1	atom 2	dist
Ni(1)	Cr(1)	2.571 (1)	P(2)	C(8)	1.828 (7)
Ni(1)	Cl(1)	2.210 (2)	P(3)	C(1)	1.849 (7)
Ni(1)	P(1)	2.165 (2)	P(3)	C(2)	1.828 (7)
Ni(1)	P(2)	2.277 (2)	P(3)	C(3)	1.844 (7)
Cr(1)	P(1)	2.343 (1)	O(1)	CO(1)	1.143 (6)
Cr(1)	P(3)	2.350 (2)	O(2)	CO(2)	1.148 (7)
Cr(1)	CO(1)	1.882 (6)	O(3)	CO(3)	1.158 (7)
Cr(1)	CO(2)	1.912 (6)	O(4)	CO(1)	1.147 (6)
Cr(1)	CO(3)	1.869 (7)	C(1)	C(41)	1.561 (9)
Cr(1)	CO(4)	1.904 (6)	C(4)	C(42)	1.521 (9)
P(1)	C(1)	1.913 (6)	C(1)	C(43)	1.564 (8)
P(1)	C(5)	1.909 (6)	C(5)	C(51)	1.533 (9)
P(2)	C(6)	1.843 (7)	C(5)	C(52)	1.565 (9)
P(2)	C(7)	1.835 (7)	C(5)	C(53)	1.545 (9)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

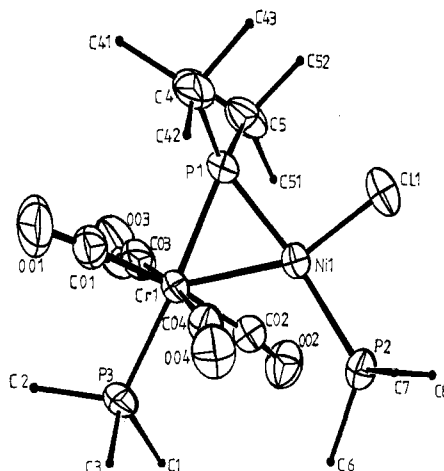


Figure 1. A view of (CO)₄(PMe₃)Cr(μ-*t*-Bu₂P)NiCl(PMe₃) (1). For clarity the methyl groups on the μ-*t*-Bu₂P and PMe₃ units are represented as sticks.

X-ray Structure of 1 (Cr-Ni). The solid-state structure of 1 has been determined by a single-crystal

Table IV. Selected Bond Angles (deg) for 1^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cr(1)	Ni(1)	Cl(1)	157.50 (6)	Cr(1)	P(1)	C(5)	120.2 (2)
Cr(1)	Ni(1)	P(1)	58.54 (4)	Cr(1)	P(1)	C(5)	112.0 (3)
Cr(1)	Ni(1)	P(2)	113.64 (5)	Ni(1)	P(2)	C(6)	122.5 (2)
Cl(1)	Ni(1)	P(1)	98.97 (6)	Ni(1)	P(2)	C(7)	111.7 (2)
Cl(1)	Ni(1)	P(2)	88.86 (6)	Ni(1)	P(2)	C(8)	112.3 (2)
P(1)	Ni(1)	P(2)	172.15 (6)	C(6)	P(2)	C(7)	102.0 (4)
Ni(1)	Cr(1)	P(1)	52.03 (4)	C(6)	P(2)	C(8)	101.9 (4)
Ni(1)	Cr(1)	P(3)	132.20 (5)	C(7)	P(2)	C(8)	104.6 (3)
Ni(1)	Cr(1)	CO(1)	125.0 (2)	Cr(1)	P(3)	C(1)	116.6 (3)
Ni(1)	Cr(1)	CO(2)	61.6 (2)	Cr(1)	P(3)	C(2)	114.5 (2)
Ni(1)	Cr(1)	CO(3)	125.9 (2)	Cr(1)	P(3)	C(3)	117.4 (2)
Ni(1)	Cr(1)	CO(4)	61.0 (2)	C(1)	P(3)	C(2)	101.9 (5)
P(1)	Cr(1)	P(3)	175.77 (6)	C(1)	P(3)	C(3)	101.2 (4)
P(1)	Cr(1)	CO(1)	92.3 (2)	C(2)	P(3)	C(3)	102.9 (5)
P(1)	Cr(1)	CO(2)	94.7 (2)	Cr(1)	CO(1)	O(1)	176.4 (6)
P(1)	Cr(1)	CO(3)	91.5 (2)	Cr(1)	CO(2)	O(2)	168.6 (5)
P(1)	Cr(1)	CO(4)	94.7 (2)	Cr(1)	CO(3)	O(3)	176.8 (6)
P(3)	Cr(1)	CO(1)	84.8 (2)	Cr(1)	CO(4)	O(4)	168.4 (5)
P(3)	Cr(1)	CO(2)	88.1 (2)	P(1)	C(4)	C(41)	110.5 (5)
P(3)	Cr(1)	CO(3)	85.4 (2)	P(1)	C(1)	C(12)	108.2 (4)
P(3)	Cr(1)	CO(1)	88.2 (2)	P(1)	C(4)	C(13)	112.3 (5)
CO(1)	Cr(1)	CO(2)	172.7 (3)	C(11)	C(4)	C(12)	109.4 (6)
CO(1)	Cr(1)	CO(3)	89.3 (3)	C(41)	C(4)	C(13)	108.4 (6)
CO(1)	Cr(1)	CO(4)	87.1 (3)	C(12)	C(1)	C(13)	107.9 (6)
CO(2)	Cr(1)	CO(3)	88.2 (3)	P(1)	C(5)	C(51)	108.3 (4)
CO(2)	Cr(1)	CO(4)	94.6 (2)	P(1)	C(5)	C(52)	112.5 (5)
CO(3)	Cr(1)	CO(4)	172.9 (3)	P(1)	C(5)	C(53)	110.2 (5)
Ni(1)	P(1)	Cr(1)	69.43 (4)	C(51)	C(5)	C(52)	107.7 (6)
Ni(1)	P(1)	C(4)	114.3 (2)	C(51)	C(5)	C(53)	108.9 (6)
Ni(1)	P(1)	C(5)	114.4 (2)	C(52)	C(5)	C(53)	109.3 (6)
Cr(1)	P(1)	C(4)	119.7 (2)				

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

X-ray diffraction study. Crystal data and the summary of intensity data collection parameters for 1 are given in Table I. Atomic positional parameters and selected bond lengths and angles for 1 are given in Tables II, III, and IV, respectively. A view of the molecule with the atom numbering scheme is shown in Figure 1. The structure consists of a central Cr(μ -*t*-Bu₂P)Ni core in which a Cr–Ni single bond (2.571 (1) Å) is bridged by one *t*-Bu₂P unit. The Cr–Ni distance can be compared to that found in (CO)₄Cr(μ -PMe₂)₂Ni(CO)₂¹⁰ (2.655 (2) Å). The bridging phosphido unit is notably asymmetric with the bond to Ni being considerably shorter than that to Cr (Ni(1)–P(1) and Cr(1)–P(1) are 2.165 (2) vs. 2.343 (1) Å, respectively). In other respects the geometry of the bridging phosphido unit appears to be quite normal. The angle subtended at P(1) is 69.43 (4)° which lies in the range normally found for R₂P[–] units bridging a metal–metal bond.¹¹ The coordination geometry of Ni is a distorted square plane with a terminal PMe₃ ligand roughly trans to the phosphorus atom of the μ -*t*-Bu₂P unit (P(1)–Ni(1)–P(2) = 172.15 (6)°). The distortions in the angles subtended at Ni are possibly due to the different sizes of the groups attached to it (see Table IV). The Cr atom is seven-coordinate including the metal–metal bond. The structure can be viewed as a Ni atom capping one face of the octahedron formed by the four roughly coplanar CO units which are cis to the mutually trans PMe₃ ligand and bridging phosphido group. The overall capped octahedral structure is not uncommon for monomeric Cr(II) seven-coordinate complexes.¹² Thus the P(3)–Cr(1)–P(1) angle is 175.77 (6)°, and the P(3)–Cr(1)–Ni(1) angle is 132.20 (5)°. The four carbonyls are

all bent slightly away from the bridging *t*-Bu₂P unit (P(3)–Cr–CO average value 86.6 (2)°) which is no doubt due to the presence of two large substituents (the Ni and μ -*t*-Bu₂P moieties) on that side of the molecule vs. PMe₃ on the other side.

Several reasonable electron counting schemes can be employed to describe the molecule. If one considers the μ -*t*-Bu₂P group as a three-electron donor, then it could be viewed as supplying one electron to Cr and two to Ni. A single 2c–2e Cr–Ni bond to which each metal contributes one electron would formally give a seven-coordinate, 18-electron Cr(II) atom bonded to a four-coordinate, 16-electron Ni(II) species.

(CO)₄(PMe₃)Cr(μ -*t*-Bu₂P)Rh(CO)(PMe₃)(Cr–Rh) (2). The reaction of (CO)₅Cr(P-*t*-Bu₂Li) with RhCl(PMe₃)₃¹³ in THF at –100 °C yields (CO)₄(PMe₃)Cr(μ -*t*-Bu₂P)Rh(CO)(PMe₃) (2) which can be isolated in ca. 70% yield. This deep red crystalline material is air stable in the solid state for several days but decomposes rapidly in solution when exposed to the atmosphere.

The formation of 2 is accompanied by the transfer of a PMe₃ ligand from Rh to Cr as found for 1. In addition the Rh atom now bears a terminal CO ligand which must have come from the Cr atom. The actual mechanism by which 2 is formed is at present unknown. As for 1, ³¹P{¹H} NMR spectra show a mixture of isomers present in solution. The resonances observed clearly show *J*_{P–P} and *J*_{Rh–P} coupling. At 25 °C in C₆D₆ there are two major resonances observed in the phosphido region which both appear as doublets of doublets of doublets: δ 258.69, (*J*_{Rh–P} = 187.86 Hz, *J*_{P–P} = 106.58, 21.83 Hz) and δ 179.29 (*J*_{Rh–P} = 180.69 Hz, *J*_{P–P} = 85.66, 33.32 Hz). Although these resonances can be assigned to the μ -*t*-Bu₂P groups of two isomers, the

(10) Fischer, K.; Vehrenkamp, H. *Z. Anorg. Allg. Chem.* 1981, 475, 109.

(11) Angles in the range 70–90° are commonly encountered for the M–P–M angle of a phosphide bridging a metal–metal bond; see ref 1–3, 5–7, and 9 and references therein.

(12) See for example: Drew, M. G. B. *Prog. Inorg. Chem.* 1977, 23, 67.

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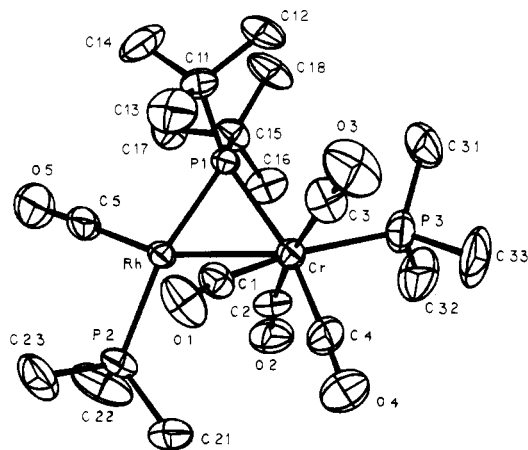


Figure 2. A view of (CO)₄(PMe₃)Cr(μ -*t*-Bu₂P)RhCO(PMe₃) (2).

Table V. Atomic Positional Parameters for 2

atom	x	y	z	B, Å ²
Rh	0.44297 (7)	0.07936 (3)	0.74261 (3)	2.59 (1)
Cr	0.6424 (1)	0.18253 (6)	0.71303 (6)	2.80 (2)
P(1)	0.5963 (2)	0.1443 (1)	0.8434 (1)	2.44 (4)
P(2)	0.2868 (3)	0.0373 (1)	0.6236 (1)	3.55 (5)
P(3)	0.7011 (3)	0.3048 (1)	0.7330 (1)	4.74 (6)
O(1)	0.6968 (7)	0.0378 (3)	0.6491 (3)	5.3 (1)
O(2)	0.2955 (7)	0.2250 (3)	0.6514 (4)	5.6 (2)
O(3)	1.0055 (7)	0.1748 (5)	0.7599 (4)	7.6 (2)
O(4)	0.6604 (9)	0.2003 (4)	0.5426 (3)	8.3 (2)
O(5)	0.298 (1)	-0.0297 (4)	0.8310 (4)	10.6 (2)
C(1)	0.6525 (9)	0.0881 (4)	0.6793 (4)	3.4 (2)
C(2)	0.422 (1)	0.2039 (5)	0.6792 (4)	3.7 (2)
C(3)	0.868 (1)	0.1768 (5)	0.7448 (5)	4.4 (2)
C(4)	0.653 (1)	0.1959 (5)	0.6094 (5)	4.8 (2)
C(5)	0.350 (1)	0.0142 (5)	0.7985 (5)	5.4 (2)
C(11)	0.763 (1)	0.0930 (5)	0.9122 (5)	4.2 (2)
C(12)	0.903 (1)	0.1445 (5)	0.9516 (5)	5.0 (2)
C(13)	0.832 (1)	0.0394 (5)	0.8595 (6)	5.5 (2)
C(14)	0.697 (1)	0.0525 (5)	0.9783 (5)	6.1 (3)
C(15)	0.4665 (9)	0.1933 (4)	0.9066 (4)	3.6 (2)
C(16)	0.363 (1)	0.2478 (5)	0.8524 (5)	4.6 (2)
C(17)	0.347 (1)	0.1433 (5)	0.9364 (5)	5.1 (2)
C(18)	0.570 (1)	0.2338 (5)	0.9790 (5)	5.8 (2)
C(21)	0.323 (1)	0.0728 (6)	0.5289 (5)	5.8 (2)
C(22)	0.072 (1)	0.0529 (7)	0.6177 (6)	8.0 (3)
C(23)	0.301 (1)	-0.0587 (5)	0.6084 (7)	7.5 (3)
C(31)	0.793 (1)	0.3359 (5)	0.8330 (6)	7.5 (3)
C(32)	0.530 (1)	0.3668 (5)	0.7012 (7)	7.9 (3)
C(33)	0.853 (1)	0.3368 (6)	0.6766 (6)	8.3 (3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(1/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

PMe₃ region is very complex and this has prevented a detailed analysis (see Experimental Section). The IR spectrum both in solution and as a Nujol mull shows terminal ν_{CO} stretches in addition to a strong band at 1782 cm⁻¹. This may be due to a semibridging CO unit (C(1)-O(1)), which is also observed in the solid state (see X-ray discussion below).

X-ray Structure of 2 (Cr-Rh). A general view of the molecule is shown in Figure 2. Atomic positional parameters and bond lengths and angles for 2 are given in Tables V, VI, and VII, respectively. As for 1, the structure contains a (CO)₄(PMe₃)Cr(μ -*t*-Bu₂P) moiety which in this case is bound to a Rh(PMe₃)(CO) group via a Cr-Rh bond and a single bridging *t*-Bu₂P unit.

The geometry of the central Cr-P(1)-Rh core again reveals notable distortion for the μ -*t*-Bu₂P group (Cr-P(1)-Rh = 68.94 (4)°). As for 1, the Cr-P(1) bond length is considerably longer than the bond to the other transition

Table VI. Bond Distances (Å) for 2^a

atom 1	atom 2	dist	atom 1	atom 2	dist
Rh	Cr	2.689 (1)	P(2)	C(23)	1.837 (7)
Rh	P(1)	2.296 (1)	P(3)	C(31)	1.831 (8)
Rh	P(2)	2.336 (2)	P(3)	C(32)	1.861 (9)
Rh	C(1)	2.259 (6)	P(3)	C(33)	1.856 (7)
Rh	C(5)	1.827 (7)	O(1)	C(1)	1.176 (7)
Cr	P(1)	2.449 (2)	O(2)	C(2)	1.151 (7)
Cr	P(3)	2.369 (2)	O(3)	C(3)	1.144 (8)
Cr	C(1)	1.879 (7)	O(4)	C(4)	1.160 (7)
Cr	C(2)	1.884 (6)	O(5)	C(5)	1.135 (8)
Cr	C(3)	1.878 (7)	C(11)	C(12)	1.580 (8)
Cr	C(4)	1.811 (6)	C(11)	C(13)	1.544 (9)
P(1)	C(11)	1.909 (6)	C(11)	C(14)	1.554 (9)
P(1)	C(15)	1.923 (6)	C(15)	C(16)	1.535 (9)
P(2)	C(21)	1.836 (7)	C(15)	C(17)	1.540 (8)
P(2)	C(22)	1.825 (7)	C(15)	C(18)	1.569 (8)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

metal (Cr-P(1) and Rh-P(1) are 2.449 (2) vs. 2.296 (1) Å, respectively). The Cr-P(1) distance is also longer than the analogous length observed in 1 (2.343 (1) Å). The Rh-Cr distance (2.689 (1) Å) can be compared to that found in other complexes containing a single Cr-Rh bond such as CrRh(CO)₄(C₅Me₅)(C₆H₆) (Cr-Rh = 2.757 (2) Å).¹⁴ An electron counting scheme similar to that described above for 1 results in a seven-coordinate 18-electron Cr(II) atom bonded to a four-coordinate 16-electron Rh(I) atom.

There are two key differences in the structures of 1 and 2. The coordination site occupied by the Cr-PMe₃ group in 2 is virtually cis with respect to the μ -*t*-Bu₂P unit (P(3)-Cr-P(1) = 102.82 (7)°). In 1 this ligand occupies a trans position with respect to the μ -*t*-Bu₂P group. Also the CO ligand which is nearly trans to the Cr-PMe₃ unit in 2 is "semibridging" to the Rh atom while no semibridging CO's are observed in 1. The geometry observed for this unit in 2 is similar to the semibridging CO unit recently observed in CrRh(CO)₄(C₅Me₅)(C₆H₆).¹⁴ Thus the Cr-C(1)-O(1) angle (159.6 (5)°) and C(1)-Rh distance of 2.259 (6) Å in 2 are 154.4 (6)° and 2.200 (7)° in CrRh(CO)₄(C₅Me₅)(C₆H₆).¹⁴

The chemistry of these and related complexes is currently under investigation.

Experimental Section

All reactions were performed under oxygen-free nitrogen. Microanalyses were by the Schwartzkopf Microanalytical Laboratory, Woodside, NY. Hexane and THF were dried over sodium and distilled from sodium/benzophenone under nitrogen before use.

Instruments: IR, Perkin-Elmer 1330; NMR, Varian EM-390 (¹H, 90 MHz), FT-80 (³¹P, 32.384 MHz), Bruker WM-90 (³¹P, 36.43 MHz), Nicolet NT-200 (¹H and ³¹P). IR spectra were as Nujol nulls (KBr plates) or in solution (matched KBr or CaF₂ cells). NMR spectra were recorded in C₆D₆ at ambient temperature and are referenced to Me₄Si (δ 0.0, ¹H) and 85% H₃PO₄(aqueous (δ 0.0, ³¹P)). Melting points were in sealed capillaries under nitrogen (1 atm) and are uncorrected.

Cr(CO)₅(*t*-Bu₂PH). One equivalent of *t*-Bu₂PH was added to a quartz Schlenk tube containing a solution of Cr(CO)₆ (2.5 g, 11.3 mmol) in THF (130 mL). The solution was photolyzed (21 h) with a 550-W Hanovia Hg vapor lamp. Volatile materials were removed under vacuum, the yellow residue extracted into hexane (2 × 20 mL), and the solution filtered. Cooling (-20 °C) yielded pale yellow needles of Cr(CO)₅-*t*-Bu₂PH which were collected and dried under vacuum. The compound is air stable in the solid state but air sensitive in solution: yield 2.42 g, 63%;

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Table VII. Bond Angles (deg) for 2^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cr	Rh	P(1)	58.21 (4)	Cr	P(1)	C(11)	118.7 (2)
Cr	Rh	P(2)	110.46 (5)	Cr	P(1)	C(15)	125.6 (2)
Cr	Rh	C(1)	43.6 (2)	Cr(11)	P(1)	C(15)	109.3 (3)
Cr	Rh	C(5)	159.4 (2)	Rh	P(2)	C(21)	118.7 (2)
P(1)	Rh	P(2)	166.91 (6)	Rh	P(2)	C(22)	112.3 (3)
P(1)	Rh	C(1)	86.6 (2)	Rh	P(2)	C(23)	114.6 (3)
P(1)	Rh	C(5)	101.7 (2)	C(21)	P(2)	C(22)	103.5 (4)
P(2)	Rh	C(1)	88.2 (2)	C(21)	P(2)	C(23)	102.0 (4)
P(2)	Rh	C(5)	90.1 (2)	C(22)	P(2)	C(23)	104.1 (5)
C(1)	Rh	C(5)	139.4 (3)	Cr	P(3)	C(31)	119.0 (3)
Rh	Cr	P(1)	52.85 (4)	Cr	P(3)	C(32)	116.2 (3)
Rh	Cr	P(3)	143.02 (6)	Cr	P(3)	C(33)	112.9 (3)
Rh	Cr	C(1)	56.0 (2)	C(31)	P(3)	C(32)	103.6 (5)
Rh	Cr	C(2)	66.0 (2)	C(31)	P(3)	C(33)	99.9 (4)
Rh	Cr	C(3)	122.8 (2)	C(32)	P(3)	C(33)	102.9 (4)
Rh	Cr	C(4)	116.1 (2)	Rh	C(1)	Cr	80.5 (2)
P(1)	Cr	P(3)	102.82 (7)	Rh	C(1)	O(1)	120.0 (5)
P(1)	Cr	C(1)	91.5 (2)	Cr	C(1)	O(1)	159.6 (5)
P(1)	Cr	C(2)	91.0 (2)	Cr	C(2)	O(2)	169.4 (6)
P(1)	Cr	C(3)	93.1 (2)	Cr	C(3)	O(3)	176.0 (7)
P(1)	Cr	C(4)	168.9 (2)	Cr	C(4)	O(4)	176.1 (7)
P(3)	Cr	C(1)	161.0 (2)	Rh	C(5)	O(5)	175.3 (8)
P(3)	Cr	C(2)	90.1 (2)	P(1)	C(11)	C(12)	110.5 (4)
P(3)	Cr	C(3)	80.9 (2)	P(1)	C(11)	C(13)	106.9 (4)
P(3)	Cr	C(4)	87.5 (2)	P(1)	C(11)	C(14)	111.9 (5)
C(1)	Cr	C(2)	102.2 (3)	C(12)	C(11)	C(13)	108.2 (6)
C(1)	Cr	C(3)	85.9 (3)	C(12)	C(11)	C(14)	109.6 (6)
C(1)	Cr	C(4)	79.4 (3)	C(13)	C(11)	C(14)	109.6 (6)
C(2)	Cr	C(3)	170.8 (3)	P(1)	C(15)	C(16)	107.6 (4)
C(2)	Cr	C(4)	84.8 (3)	P(1)	C(15)	C(17)	112.1 (5)
C(3)	Cr	C(4)	92.6 (3)	P(1)	C(15)	C(18)	112.6 (4)
Rh	P(1)	Cr	69.94 (4)	C(16)	C(15)	C(17)	106.2 (5)
Rh	P(1)	C(11)	115.5 (2)	C(16)	C(15)	C(18)	108.3 (6)
Rh	P(1)	C(15)	112.2 (2)	C(17)	C(15)	C(18)	109.8 (5)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

mp 71–73 °C; ¹H NMR δ 3.74 (d, 1 H, ¹J_{P-H} = 296.3 Hz (PH)), 1.02 (d, 18 H, ³J_{P-H} = 13.5 Hz (t-BuP)); ³¹P{¹H} NMR δ 77.21 (in the proton-coupled spectrum a broad doublet is observed (¹J_{P-H} = 296.26 Hz); IR (hexane, CaF₂ cells) 2305 (w), 2060 (s), 1945 (s), 1915 (m) cm⁻¹. Anal. Calcd for C₁₃H₁₉CrO₅P: C, 46.16; H, 5.66. Found: C, 45.85; H, 5.59.

(CO)₄(PMe₃)Cr(μ-t-Bu₂P)NiCl(PMe₃)(Cr-Ni) (1). One equivalent of *n*-BuLi (1.09 mL of a 2.9 M hexane solution) was added to a solution containing THF (30 mL) and Cr(CO)₅-*t*-Bu₂PH (1.07 g, 3.16 mmol) at -100 °C. The Cr(CO)₅-*t*-Bu₂Li was added over a 5-min period to a solution of NiCl₂(PMe₃)₂ (0.891 g, 3.16 mmol) in THF (30 mL) at -100 °C. An immediate color change from red to brown was observed. The solution was allowed to warm to room temperature and was stirred 3 h. Volatile residues were removed from the dark green solution under vacuum. The residue was extracted into hexane (2 × 20 mL) and diethyl ether (20 mL). The solution was filtered and the volume reduced to ca. 15 mL under vacuum. Cooling (-20 °C) yielded dark green crystals of 1 after 24 h. They were collected and dried under vacuum. The compound is air stable for short periods of time in the solid state but air sensitive in solution: yield 1.05 g, 60%; mp 120–123 °C dec; ¹H NMR δ 1.57 (d, ²J_{P-H} = 13.5 Hz, 18 H (PMe₃)), 1.08 (t, ³J_{P-H} = 9 Hz, 18 H (μ-P-*t*-Bu₂)); ³¹P{¹H} (see text) at 20 °C (36.43 MHz) in PhMe-*d*₆; δ 261.8 (s), 256.5 (s), 197.0 (s), 191.0 (μ-t-Bu₂P), 19.60 (s), 5.03 (d, J_{P-P} = 36.62 Hz), -6.11 (J_{P-P} = 201.42 Hz), -10.39 (s), -14.91 (s), -18.09 (s), -23.12 (s, broad), (PMe₃); at -80 °C (PhMe-*d*₆) δ 260.61 (dd, J_{P-P} = 219.7, 18.31 Hz), 252.32 (d, J_{P-P} = 24.41 Hz), 189.24 (dd, J_{P-P} = 200.28, 36.20 Hz (μ-t-Bu₂P)), 23.12 (d, J_{P-P} = 24.41 Hz), 18.18 (d, J_{P-P} = 18.31 Hz), 6.37 (d, J_{P-P} = 36.62 Hz), -3.52 (d, J_{P-P} = 195.32 Hz), -8.54 (d, J_{P-P} = 36.62 Hz), -13.24 (s), -17.09 (s), -21.28 (s (PMe₃)); IR (Nujol mull) 1985 (s), 1940 (s), 1880–1822 (s br), 1422 (m), 1385 (w), 1290 (m), 1279 (m), 1260 (w), 1165 (m), 1017 (m), 942 (s), 860 (w), 842 (w), 802 (m), 730 (m), 675 (m), 635 (s), 600 (m), 538 (m), 485 (w), 472 (m), 420 (w) cm⁻¹; IR (hexane, KBr cells) 1995 (s), 1939 (s), 1918 (m), 1886 (s), 1830 (m) cm⁻¹; Anal. Calcd for C₁₈H₃₆ClCrNiO₄P₃: C, 38.91; H, 6.53; Cl, 6.38; P, 16.72. Found: C, 38.98; H, 6.46; Cl 6.81; P, 16.24.

(CO)₄(PMe₃)Cr(μ-t-Bu₂P)Rh(CO)(PMe₃)(Cr-Rh) (2). One equivalent of *n*-Bu Li (0.385 mL of a 2.9 M solution) was added to a solution of THF (30 mL) and Cr(CO)₅-*t*-Bu₂PH (0.378 g, 1.11 mmol) at -100 °C. The Cr(CO)₅-*t*-Bu₂Li was added over a 5-min period to a solution of RhCl(PMe₃)₃ (0.41 g, 1.11 mmol) in THF (70 mL) at -100 °C. No immediate color change was observed. The initial orange color darkened at 0 °C and turned red at room temperature. After being warmed to room temperature, the solution was stirred (4 h). Volatile materials were removed under vacuum, and the residue was extracted into hexane (2 × 10 mL). After filtration of the extract, the solution was cooled to -20 °C. Deep red crystals of 2 formed over 2 h. They were isolated and dried under vacuum: yield 0.46 g, 70%; mp 155–156 °C dec; ¹H NMR (200 MHz) δ 1.55 (d, ²J_{P-H} = 13.46 Hz, 9 H), 1.40 (d, ²J = 13.11 Hz, 9 H (PMe₃)), 1.20 (m, 18 H (μ-P-*t*-Bu₂)); ³¹P{¹H} (see text); δ 258.69 (ddd, ¹J_{Rh-P} = 187.86 Hz, J_{P-P} = 106.58, 21.83 Hz), 179.29 (ddd, ¹J_{Rh-P} = 180.69 Hz, J_{P-P} = 85.66, 33.32 Hz (μ-t-Bu₂P)), 24.82 (d, J_{P-P} = 22.05 Hz), 10.27 (d, J_{P-P} = 33.08 Hz), -2.21 (s), -6.01 (s), -8.02 (s), -11.63 (s), -12.24 (s), -13.92 (s), -18.11 (s (PMe₃)); IR (Nujol mull) 1980 (s), 1940 (s), 1870 (s br), 1782 (s), 1418 (m), 1352 (w), 1275 (m), 1252 (m), 1165 (m), 1010 (m), 935 (m), 845 (m), 790 (m), 715 (w), 660 (w), 640 (w), 615 (m), 530 (w) cm⁻¹; IR (hexane, KBr cells) 1990 (w), 1950 (s), 1930 (w), 1900 (m), 1867 (m), 1832 (w), 1782 (m) cm⁻¹. Anal. Calcd for C₁₉H₃₆CrO₅P₃Rh: C, 38.52; H, 6.07; P, 15.68. Found: C, 39.55; H, 6.07; P, 15.74.

X-ray Experimental Data. Crystals of 1 and 2, grown from hexane solutions at -20 °C, were mounted in thin-walled glass capillaries under nitrogen. Final lattice parameters were determined from 25 high angle reflections (2θ > 2θ > 30.0) carefully centered on an Enraf-Nonius CAD-4 diffractometer. Data were collected by the ω/2θ scan technique at 23 ± 2 °C. Details of crystal data and a summary of intensity data collection parameters for 1 and 2 are given in Table I. For both 1 and 2 the space group was uniquely defined by systematic absences as P2₁/n.

The data for 1 and 2 were corrected for Lorentz and polarization effects, and an absorption correction was applied by using an empirical psi scan method for both. Both structures were solved

by using standard heavy-atom methods and successive difference Fourier maps using the Enraf-Nonius software package "SDP-PLUS" (B.A. Frenz and Associates, College Station, TX 77840, 4th ed., 1981) on a PDP 11/44 computer. Scattering factors were taken from ref 15, and unit weights were used throughout. For 1 the final full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms gave final values of $R = 0.0544$ and $R_w = 0.0681$. The hydrogen atoms were either located or placed in their calculated positions with idealized geometries (C-H = 0.96 Å) with fixed isotropic thermal parameters. No chemically significant peaks were present in the final difference Fourier map which showed no features greater than $0.3 \text{ e}/\text{Å}^3$. Although data was collected out to $2\theta = 50.0^\circ$ for the crystal finally chosen for measurement, the rapid fall off in intensity meant that many high angle data were unobserved. This inevitably resulted in a lower than preferred data/parameter ratio. Nevertheless, we feel that the analysis was justified in that the molecular structure is more than adequately determined. For 2 hydrogen atoms were not located and the structure refined smoothly to give $R = 0.041$ and $R_w = 0.052$ (all atoms anisotropic).

Atomic thermal parameters and tables of observed and calculated structure factors and all bond lengths and angles for 1 and 2 are available.¹⁶

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Registry No. 1, 87555-81-5; 2, 87555-82-6; Cr, 7440-47-3; Ni, 7440-02-0; Rh, 7440-16-6.

Supplementary Material Available: Tables of atomic thermal parameters and structure factors for 1 and 2 and complete tables of atomic positional parameters and bond lengths and angles for 1 (69 pages). Ordering information is given on any current masthead page.

(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Volume 4.

(16) See paragraph at end of paper regarding supplementary material.

Synthesis and Rearrangement of (Bicyclo[2.2.1]hept-2-ene)bis(triphenylphosphine)platinum(0) Complexes

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Platinum(0) complexes of a variety of halo-substituted bicyclo[2.2.1]hept-2-ene derivatives were prepared by displacement reactions between $\text{Pt}(\text{PPh}_3)_3$ and the requisite olefins. These complexes were characterized by elemental analysis, by ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy, and, in some cases, by the dissociation of the olefin ligand in solution. The rearrangement of selected haloolefin complexes to give (bicyclo[2.2.1]hept-2-en-2-yl)haloplatinum(II) derivatives was also investigated. The ease of rearrangement, which proceeded via the insertion of the platinum atom into the vinyl carbon-halogen bond, depended upon the identity of the halogen and the stability of the precursor (haloolefin)platinum(0) complex. In order to distinguish between the cis and trans isomers of (3-bromobicyclo[2.2.1]hept-2-en-2-yl)bromobis(triphenylphosphine)platinum, we carried out a structural determination on the trans isomer by single-crystal X-ray crystallography. Compound 31 crystallized in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 16.411$ (4) Å, $b = 19.340$ (8) Å, $c = 12.434$ (5) Å, and $\beta = 106.19$ (4)°. The calculated density was $1.703 \text{ g}/\text{cm}^3$ for four molecules in the unit cell. The unweighted R factor for the structure was 0.108, and data were collected by using a variable rate ω - 2θ scan technique and graphite-monochromatized $\text{Mo K}\alpha$ radiation. After Lorentz-polarization, absorption, and background corrections, 1640 reflections with $2\theta = 0$ - 60° were observed [$F_o^2 \geq 2\sigma(F_o^2)$].

Introduction

The interaction of strained organic molecules with transition-metal substrates has introduced new dimensions into the study of strain in organic chemistry. While some transition-metal systems promote the rearrangement of strained organic molecules,² other transition-metal systems form stable complexes with inherently unstable compounds.³

Bennett and Yoshida have recently reported the stabilization of the short-lived cyclic alkynes, cycloheptyne and cyclohexyne, as the bis(triphenylphosphine)platinum(0) complexes 1 and 2, respectively.⁴ Thus, reduction of the 1,2-dibromocycloalkenes 3 and 4 with sodium amalgam in the presence of tris(triphenylphosphine)-

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