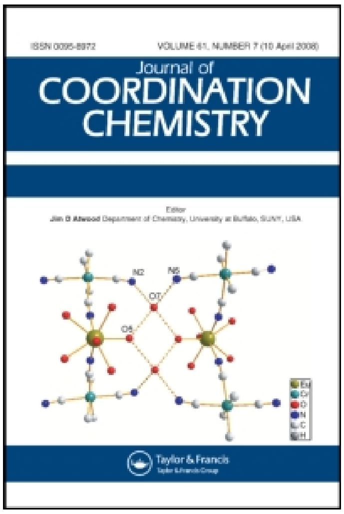


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND X-RAY STRUCTURE OF $[Ni(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2(Ni\text{-}Ni)$, SPONTANEOUS LOSS OF CO TO GIVE THE ASYMMETRIC TRICARBONYL $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$

Atta M. Arif[a]; Richard A. Jones[a]; Stuart T. Schwab[a]
[a] Department of Chemistry, University of Texas at Austin, Austin, Texas, U.S.A.

To cite this Article Arif, Atta M. , Jones, Richard A. and Schwab, Stuart T.(1987) 'SYNTHESIS AND X-RAY STRUCTURE OF $[Ni(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$(Ni-Ni), SPONTANEOUS LOSS OF CO TO GIVE THE ASYMMETRIC TRICARBONYL $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$', Journal of Coordination Chemistry, 16: 1, 51 — 57
To link to this Article: DOI: 10.1080/00958978708079805
URL: http://dx.doi.org/10.1080/00958978708079805

J. Coord. Chem. 1987, Vol. 16 p. 51-57
Photocopying permitted by license only

SYNTHESIS AND X-RAY STRUCTURE OF $[Ni(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$(Ni-Ni), SPONTANEOUS LOSS OF CO TO GIVE THE ASYMMETRIC TRICARBONYL $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$

ATTA M. ARIF, RICHARD A. JONES*, and STUART T. SCHWAB
Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

(Received May 23, 1986)

Reaction of t-Bu_2PCl with $Na_2[Ni_6(CO)_{12}]$ (2:1) in THF at −78°C yields $[Ni(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (1) in 65% yield. The structure of (1) as determined by X-ray crystallography consists of two Ni atoms (Ni-Ni = 2.509 (2) Å) bridged by two di-tertbutylphosphido groups. Each Ni also bears two terminal CO ligands and has a roughly tetrahedral coordination geometry. The complex slowly loses CO ($t_{1/2} \approx 24h$ in C_6D_6 ambient temperature) to give the thermodynamically stable tricarbonyl complex $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$ in which one Ni now bears a single CO ligand and the other retains two.

Crystal data (1): $C_{20}H_{36}Ni_2O_4P_4$, $M = 519.88$, monoclinic, $C2/m$, $a = 13.646$ (2), $b = 11.861$ (2), $c = 8.712$ (3) Å, $\beta = 117.97$ (2)°, $U = 1245.3$ (5) Å^3, $Z = 2$, $D_c = 1.386$ g cm^{-3}. Methods: MULTAN, difference Fourier, full-matrix least-squares. Refinement on 913 reflections ($I > 3\sigma(I)$) out of 1153 unique observed reflections ($3° < 2\theta < 50°$) gave R and R_w values of 0.030 and 0.033, respectively.

Keywords: Nickel, phosphide, carbonyl, dimer, complex.

INTRODUCTION

We have shown that bulky phosphido ligands can dramatically affect the coordination geometries, stoichiometries, and reactivities of transition metal complexes.[1] As part of our studies, we recently described the synthesis and structures of a number of ditertbutylphosphido complexes of Ni(I).[2] An intriguing observation in these studies was the predominance of asymmetric species such as $(CO)Ni(\mu\text{-}t\text{-}Bu_2P)_2Ni(CO)_2$, (**2**), and $(PMe_3)Ni(\mu\text{-}t\text{-}Bu_2P)_2Ni(CO)_2$, (**3**), in which one Ni bears one two-electron donor while the other has two. (Scheme). We were unable to prepare the symmetrical tetracarbonyl species $[Ni(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$, (**1**), by exposure of (**2**) to high pressures of CO and assumed that it is unstable due to steric congestion around the metal centers. We have now discovered that (**1**) can be synthesized but by a completely different route to those employed previously. (**1**) is actually quite stable in the solid state but slowly loses CO in solution to give the tricarbonyl $(CO)Ni(\mu\text{-}t\text{-}Bu_2P)_2Ni(CO)_2$, (**2**). We assumed that this slow extrusion of CO occurred in order to relieve steric strain since the analogous diphenylphosphido complex $[Ni(\mu\text{-}Ph_2P)(CO)_2]_2$[3] is quite stable. However careful examination of the X-ray structure reveals no short nonbonded intramolecular contacts. The reasons for facile CO loss are therefore still unknown. We describe here the synthesis, characterization and structure of (**1**).

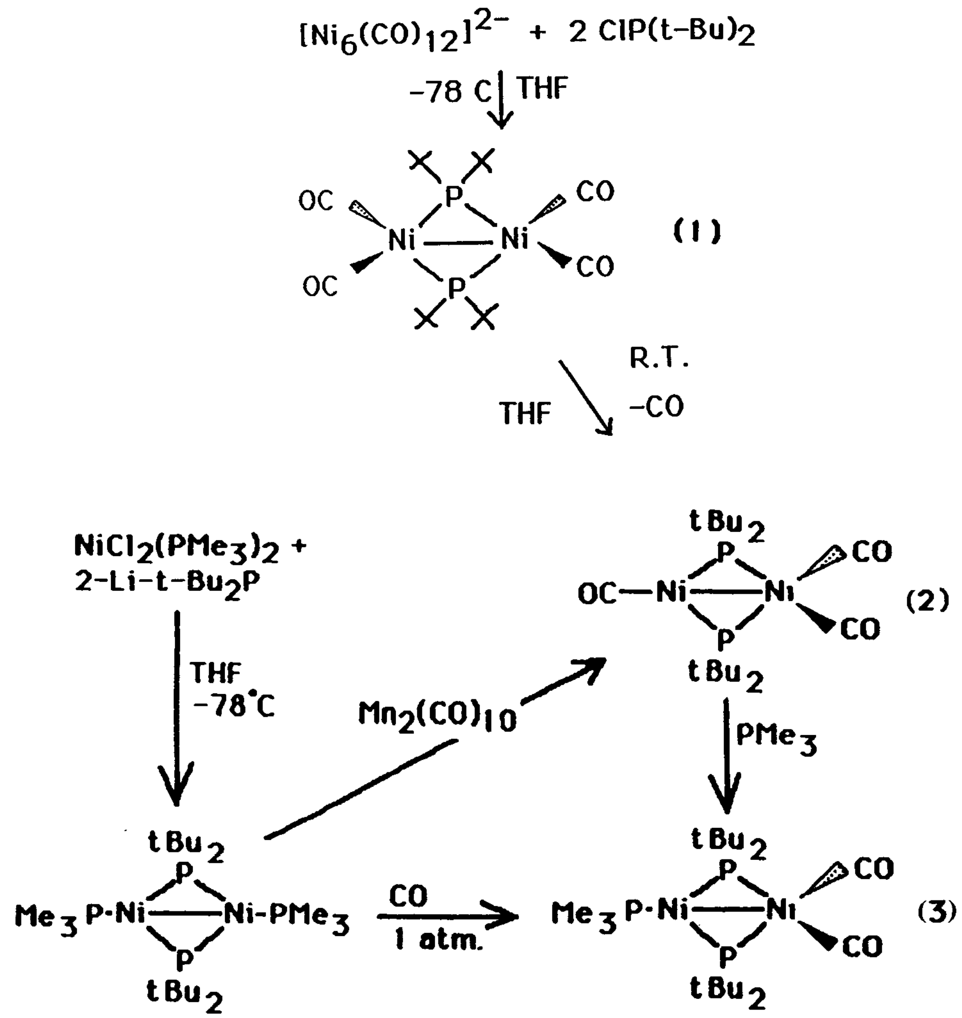
EXPERIMENTAL

All manipulations were performed under nitrogen or in vacuum. Hexane and THF

---

*Author for correspondence.

Scheme



were dried over sodium benzophenone and distilled under nitrogen before use. Melting points were in sealed tubes under nitrogen (1 atm) and are uncorrected. Instruments: I.R., Perkin-Elmer 1330; NMR, Varian EM-390 (^{1}H, 90 MHz), Varian FT-80 (^{31}P, 32.384 MHz). Bu$^t_2$PCl[4] and Na$_2$[Ni$_6$(CO)$_{12}$][5] were prepared by the literature methods.

Synthesis of [Ni(μ-t-Bu$_2$P)(CO)$_2$]$_2$ (**1**)

An excess of *t*-Bu$_2$PCl (0.18 cm^3, 1.12 mmol) was added to a solution of Na$_2$[Ni$_6$(CO)$_{12}$] (0.17 g, 0.23 mmol) in THF (100 cm^3) at −78°C. The deep red solution was allowed to warm to room temperature over *ca* 5 hours and volatile materials were removed under vacuum. The red-brown residue was extracted into hexane (2 × 20 cm^3), the solution filtered, and the volume reduced under vacuum (*ca* 15 cm^3). Cooling (−35°C, 12 hours) gave deep red-brown crystals of (**1**). They were collected and dried under vacuum.

TABLE I
Crystal Data for [Ni(μ-t-Bu$_2$P)(CO)$_2$]$_2$ (**1**).

Description of Crystal	(1)
Colour	red-brown
Habit	rhombohedral
Max. crystal dimension (mm)	0.30 × 0.25 × 0.22
Unit Cell	
Crystal system	monoclinic
Space group	*C2/m*
Unit cell parameters:	
a(Å)	13.646(2)
b(Å)	11.861(2)
c(Å)	8.712(3)
β(deg)	117.97(2)
U(Å^3)	1245.3(5) Å^3
Molecules per unit cell	2
Formula	$C_{20}H_{36}Ni_2O_4P_2$
Molecular weight (g.mol^{-1})	519.88
Calculated density (g.cm^{-3})	1.386
μ-calc. (cm^{-1})	16.66
Data Collection	
Radiation (Å)	MoK$_\alpha$(0.71073)
Scan technique	$\theta/2\theta$
Scan width (deg)	0.8 + *0.35 tan* θ
Range of indices	0 → 16, 0 → 14, -10 → 10
2θ range (deg)	3°-50°
No. reflections measured	1153
Standard reflections:	
intensity	5 3 2, 6 4 $\bar{4}$
orientation	5 5 1, 6 2 $\bar{5}$
Decay of standards	0.3%
Min. % transmission	99.36
Max. % transmission	99.93
Average % transmission	98.60
Agreement factor for averaged reflections	
F(obs)	0.02
intensity	0.009
Structure Determination	
No. reflections used ($I > 3\sigma(I)$)	913
No. parameters varied	127
Data/parameter ratio	7.2
Shift to error ratio	2.52
E.s.d. of an observation of unit weight	3.46
R	0.030
R_w	0.033

Yield 0.08g, (65%). M.p. 144–146°C. I.R. (THF solution, KBr cells):- 2010 s, 1985 m, (cm^{-1}) (Nujol mull), 2000 s, 1970 s, 1365 s, 1165 s, 955 vw, 930 w, 880 w, 805 m, 740 vw, 725 w, 595 m, 580 m, 520 vw, 490 m, 455 m, 450 s, 425 m, 330 vw (cm^{-1}). NMR ^{1}H (C_6D_6, ambient temperature), δ 1.20 (apparent triplet J = 5 Hz), ^{31}P{^{1}H} (C_6D_6, ambient temperature), δ 375.0 s. Microanalysis: Calcd. for $C_{20}H_{36}Ni_2O_4P_2$; C 46.21, H 6.98%. Found C 45.99, H 6.59%.

X-Ray Experimental Methods

Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphitemonochromated MoK_α radiation. Data were collected by the $\theta/2\theta$ scan technique at 23 ± 2°C. Details of the standard data collection methods are as described in reference 6. All calculations were performed on a PDP 11/44 computer using the software package SDP-PLUS.[7] A crystal of (**1**) was mounted in a thin walled glass capillary tube under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 24° and 28°. Systematic absences indicated a choice of space groups *C*2, *Cm*, or *C*2/*m*. *C*2/*m* was chosen on the basis of subsequent successful refinement. Details of crystal data parameters and other relevant information are collected in Table I. Bond lengths, angles, and positional parameters are given in Tables II, III and IV, respectively. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction was made using a psi scan method (Program EAC). The structure was solved and refined by direct methods (MULTAN)[8] followed by successive cycles of least-squares refinements followed by difference Fourier maps. A non-Poisson contribution weighting scheme was used in the least squares refinement with an experimental instability factor $P = 0.07$.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located and refined with isotropic thermal parameters. The highest peak in the final difference Fourier was 0.3 e Å^{-3} located 1.04 Å from Ni.

RESULTS AND DISCUSSION

Synthesis

The reaction of excess *t*-Bu$_2$PCl with Na$_2$[Ni$_6$(CO)$_{12}$][5] results in a deep red solution from

TABLE II
Bond Distances (Å) for (**1**).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ni1	Ni1′	2.509(2)						
Ni1	P1	2.204(1)	C3	C4	1.502(5)	C5	H6	0.83(4)
Ni1	C1	1.780(4)	C3	C5	1.556(7)	C6	H7	1.02(4)
Ni1	C2	1.786(7)	C3	C6	1.516(7)	C6	H9	0.98(5)
P1	C3	1.888(4)	C4	H1	0.92(4)	C6	H8	0.95(4)
O1	C1	1.130(5)	C5	H4	1.03(5)			
O2	C2	1.131(9)	C5	H5	0.97(5)			

Numbers in parentheses are estimated standard deviations.

TABLE III
Bond Angles (deg) for (**1**).

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
P1	Ni1	C1	110.5(1)	C4	C3	C5	104.1(4)	H5	C5	H6	117(4)
P1	Ni1	C2	108.55(7)	C4	C3	C6	108.0(3)	C3	C6	H7	103(2)
C1	Ni1	C2	108.1(3)	C5	C3	C6	112.6(4)	C3	C6	H9	107(3)
Ni1	P1	C3	119.8(1)	C3	C4	H1	111(2)	C3	C6	H8	110(2)
Ni1	C1	O1	172.5(6)	C3	C5	H4	75(3)	H7	C6	H9	102(3)
Ni1	C2	O2	173.6(4)	C3	C5	H5	105(3)	H7	C6	H8	118(4)
P1	C3	C4	108.8(3)	C3	C5	H6	123(4)	H9	C6	H8	114(4)
P1	C3	C5	109.8(2)	H4	C5	H5	88(4)				
P1	C3	C6	113.0(3)	H4	C5	H6	69(4)				
P1	Ni1	P1′	110.6(2)								

Numbers in paretheses are estimated standard deviations.

TABLE IV
Positional Parameters for (**1**).

Atom	x/a	y/b	z/c	B(Å^2)
Nil	0.40104(5)	0.500	0.47207(8)	3.00(1)
P1	0.500	0.6528(1)	0.500	2.92(3)
O1	0.1945(3)	0.500	0.1486(6)	6.7(1)
O2	0.3250(3)	0.500	0.7334(5)	7.3(1)
C1	0.2785(4)	0.500	0.2680(7)	4.4(1)
C2	0.3605(4)	0.500	0.6395(7)	4.8(1)
C3	0.4659(3)	0.7450(3)	0.3047(4)	4.17(9)
C4	0.4194(4)	0.6724(4)	0.1448(5)	5.6(1)
C5	0.5746(4)	0.7940(5)	0.3150(6)	7.5(1)
C6	0.3811(4)	0.8355(4)	0.2791(6)	7.6(1)
H1	0.406(3)	0.714(3)	0.048(4)	5(1)*
H2	0.348(3)	0.354(4)	0.117(5)	7(1)*
H3	0.542(3)	0.608(4)	0.852(5)	7(1)*
H4	0.538(3)	0.861(4)	0.343(5)	9(1)*
H5	0.552(3)	0.827(4)	0.202(5)	8(1)*
H6	0.620(3)	0.829(4)	0.400(5)	9(1)*
H7	0.312(3)	0.790(3)	0.257(4)	6(1)*
H9	0.359(4)	0.870(5)	0.165(6)	11(2)*
H8	0.411(3)	0.887(4)	0.373(5)	8(1)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivlent thermal parameter defined as: $4/3\ [a^2.B(1,1) + b^2.B(2, 2) + c^2.B(3, 3) + ab(\cos\alpha).B(1, 2) + ac(\cos\beta).B(1, 3) + b.\ c(\cos\alpha).B(2, 3)]$

which dark red crystalline $[Ni(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$, (**1**), may be isolated in good yield. Recently, Power and coworkers have employed a similar route with $RPCl_2$ species for the synthesis of transition metal cluster complexes such as $Ni_5(CO)_6[(Me_3Si)_2CH\ P = PCH(SiMe_3)_2]_2Cl$ involving P=P double bonds.[10] The lower nuclearity of (**1**) is no doubt due to the increased steric demands of the t-Bu_2P unit *vs* $(Me_3Si)_2CHP$.

The IR spectrum of (1) in THF shows two strong peaks (ν(CO)) at 2010 and 1975 cm^{-1} and the ^1H NMR (C_6D_6) is an apparent triplet (δ 1.20, J = 5.0 Hz). In solution, the complex slowly loses CO to give the asymmetric tricarbonyl complex $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$ (**2**). Thus, the $^{31}P\ \{^1H\}$ NMR spectrum of freshly made solutions shows a single sharp resonance which is shifted well downfield (δ 375.0 s) indicative of a phosphido group which bridges a metal-metal bond.[11] After several hours at room temperature, a new peak at δ 312.52 appears in the spectrum which corresponds to $Ni_2(\mu\text{-}t\text{-}Bu_2P)(CO)_3$, (**2**). The process of CO loss from (**1**) cannot be reversed under high pressures of CO (50 atm).

X-Ray Crystal Structure of (**1**)

A view of the molecule is shown in Figure 1. The overall molecular geometry consists of two Ni atoms linked by a single Ni-Ni bond and bridged by two ditertbutylphosphido ligands. Each Ni bears two terminal CO ligands in a nearly perfect tetrahedral coordination geometry. The molecule is therefore isostructural with $[Ni(\mu\text{-}Ph_2P)(CO)_2]_2$[3] and $[Ni(\mu\text{-}t\text{-}Bu_2As)(CN(p\text{-}tol))_2]_2$.[12] There is a crystallographically imposed mirror plane containing the Ni atoms and which is perpendicular to a two-fold axis passing through the two P atoms. Thus, the molecule contains a center of inversion at the midpoint of the Ni-Ni bond, and the central Ni_2P_2 core is rigorously planar. The Ni-Ni distance of 2.509 (2) Å is typical for a Ni-Ni single bond between two 18-electron Ni atoms.[12] The coordination geometry about the Ni atom is virtually tetrahedral. Thus, C(1) - Ni(1) - C(2)

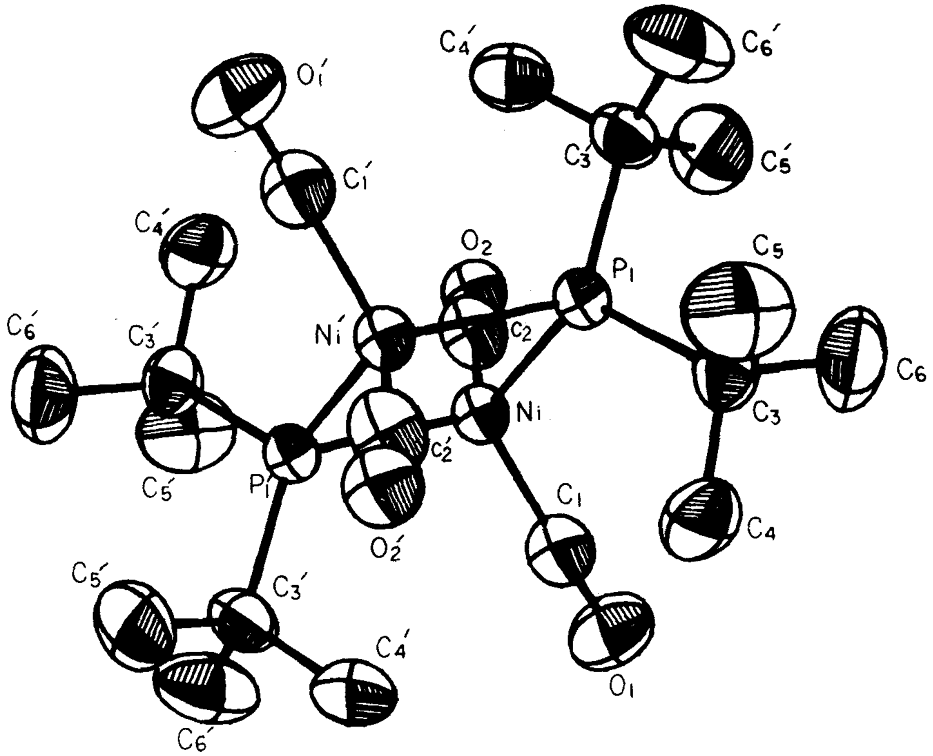


FIGURE 1 An ORTEP view of (1). Hydrogen atoms have been omitted for clarity.

= 108.1 (3)°, P(1) - Ni(1) - C(1) = 110.5 (1), P(1) - Ni(1) - C(2) = 108.55 (7), and P(1) - Ni(1) - P(1)′ = 110.6 (2)°. The Ni-P distance of 2.204 (1) Å is slightly less than the analogous distances found in $Ni_2(\mu\text{-}t\text{-}Bu_2P)_3(CO)_3$(2) (2.238 (2) and 2.242 (3) Å).[2] Ironically, there appear to be no particularly short intramolecular contacts which would support the suggestion of CO loss in order to relieve steric strain. Thus the shortest nonbonded distance within the molecule is 2.60(5) Å between H(2) and C(1). The question of why facile CO loss occurs in this system therefore remains unanswered.

ACKNOWLEDGEMENTS

We thank the Robert A. Welch Foundation (F-816), The Texas Advanced Technology Research Program, and the National Science Foundation (CHE-8517759) for support. R.A.J. thanks the Alfred P. Sloan Foundation for a fellowship (1985-87).

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of thermal parameters and observed and calculated structure factors have been deposited with the editor and are available upon request.

REFERENCES

1. See for example: A.M. Arif, R.A. Jones, S.T. Schwab and B.R. Whittlesey, *J. Amer. Chem. Soc.*, **108,** 1703 (1986); J.G. Gaudiello, T.C. Wright, R.A. Jones and A.J. Bard, *J. Amer. Chem. Soc.*, **107,** 888 (1985), and references therein.
2. R.A. Jones, A.L. Stuart, J.L. Atwood and W.E. Hunter, *Organometallics*, **2,** 874 (1983).
3. J.A.J. Jarvis, R.H.B. Mais, P.G. Owston and D.T. Thompson, *J. Chem. Soc. A.*, 1867 (1970).
4. H. Hoffman and P. Schellenbeck, *Chem. Ber.*, **99,** 1134 (1966); K. Issleib and F. Krech, *J. Organometal. Chem.* **13,** 283 (1968).
5. G. Longoni, P. Chini, A. Cavaleri, *Inorg. Chem.*, **15,** 3025 (1976).
6. R.A. Jones and T.C. Wright, *Organometallics*, **2,** 1842 (1983).
7. SDP-PLUS, B.A. Frenz and Associates, College Station, Texas, 77840, 4th Edition 1981.
8. G. Germain, P. Main and M.M. Woolfson, *Acta Cryst.*, **A27,** 368 (1971).
9. P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least squares refinement. The function minimized was $w(F_0 - F_c)^2$ where $w = 4(F_0)^2/[\Sigma(F_0)^2]^2$, where $[\Sigma(F_0)^2]^2 = [S^2(C + R^2B) + \{P(F_0)^2\}^2]/Lp^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count and Lp is the Lorentz-polarization factor.
10. M.M. Olmstead and P.P. Power, *J. Amer. Chem. Soc.*, **106,** 1495 (1984).
11. Downfield shifts in the σ 50–200 ppm range in the ^{31}P NMR of Ph_2P groups bridging metal-metal bonds have been noted by several groups of workers: P.E. Garrou, *Chem. Rev.*, **81,** 229 (1981); A.J. Carty, *Adv. Chem. Ser.*, **196,** 163 (1982); P.E. Kreter and D.W. Meek, *Inorg. Chem.*, **22,** 319 (1983); A.D. Harley, G.J. Guskey and G.L. Geoffroy, *Organometallics*, **2,** 53 (1983). Similar downfield shifts have been noted for -*t*-Bu_2P complexes: see refs. 1, 2 and 6.
12. R.A. Jones and B.R. Whittlesey, *Inorg. Chem.*, **25,** 852 (1986).