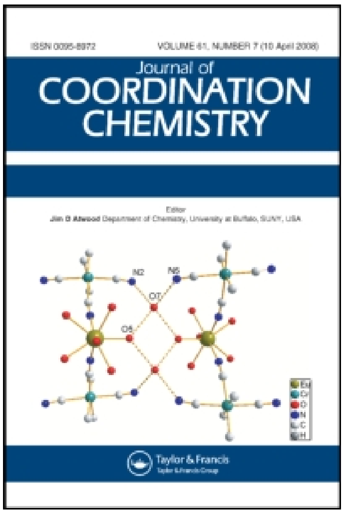

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND STRUCTURE OF A HETEROBIMETALLIC Fe-Ni PHOSPHIDO BRIDGED COMPLEX; X-RAY CRYSTAL STRUCTURE OF $(PMe_3)(CO)_3Fe(\mu\text{-t-Bu}_2P)Ni(PMe_3)Cl$, (Fe-Ni)

Atta M. Arif[a]; Don J. Chandler[a]; Richard A. Jones[a]
[a] Department of Chemistry, The University of Texas at Austin, Austin, Texas, U.S.A.

To cite this Article Arif, Atta M. , Chandler, Don J. and Jones, Richard A.(1988) 'SYNTHESIS AND STRUCTURE OF A HETEROBIMETALLIC Fe-Ni PHOSPHIDO BRIDGED COMPLEX; X-RAY CRYSTAL STRUCTURE OF $(PMe_3)(CO)_3Fe(\mu\text{-t-Bu}_2P)Ni(PMe_3)Cl$, (Fe-Ni)', Journal of Coordination Chemistry, 17: 1, 45 — 51

To link to this Article: DOI: 10.1080/00958978808078446

URL: http://dx.doi.org/10.1080/00958978808078446

J. Coord. Chem. 1988, Vol. 17, pp. 45–51
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND STRUCTURE OF A HETEROBIMETALLIC Fe-Ni PHOSPHIDO BRIDGED COMPLEX; X-RAY CRYSTAL STRUCTURE OF $(PMe_3)(CO)_3Fe(\mu\text{-t-}Bu_2P)Ni(PMe_3)Cl$, (Fe-Ni)

ATTA M. ARIF, DON J. CHANDLER and RICHARD A. JONES*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

(Received January 5, 1987; in final form June 11, 1987)

Reaction of $Fe(CO)_3(t\text{-}Bu_2PH)(t\text{-}Bu_2PLi)$ with $NiCl_2(PMe_3)_2$ gives the heterobimetallic ditertbutylphosphido bridged complex $(PMe_3)(CO)_3Fe(\mu\text{-}t\text{-}Bu_2P)Ni(PMe_3)Cl$, (Fe-Ni), (**1**), (55%). The Fe atom bears three terminal CO groups and a PMe_3 ligand in a roughly trigonal-bipyramidal geometry. The Fe-PMe_3 ligand is *trans* to the $\mu\text{-}t\text{-}Bu_2P$ group. The Ni atom is roughly planar with the Cl atom *trans* to the $\mu\text{-}t\text{-}Bu_2P$ unit. Crystal data: (**1**) $C_{17}H_{36}ClFeNiO_3P_3$, $M = 531.4$ monoclinic, space group $P2_1/c$ (No. 14), $a = 17.363$ (1) Å, $b = 11.383$ (2) Å, $c = 13.308$ (2) Å, $\beta = 104.60$ (1)°, $U = 2545.1$ (5) $Å^3$, $D_c = 1.387\ g\ cm^{-3}$, $Z = 4$, $\mu(MoK_\alpha) = 16.2\ cm^{-1}$. Refinement of 1979 reflections ($I > 3\sigma(I)$) out of 3537 unique observed reflections ($2° < 2\theta < 46°$) gave R and R_w values of 0.062 and 0.070 respectively. Data/parameter ratio 8.4, hydrogen atoms not located, $\lambda(MoK_\alpha) = 0.71073$ Å, (graphite monochromator); methods: MULTAN, difference Fourier, full-matrix least squares; all non-hydrogen atoms anisotropic.

Keywords: phosphide, iron, nickel, complex, structure

INTRODUCTION

The chemistry of heterobimetallic transition metal complexes is currently of considerable interest.[1] In particular, synthesis of phosphido bridged bimetallic compounds is being investigated since the bridge may serve to maintain structural integrity in the event of metal-metal bond cleavage. A number of phosphido bridged heterobimetallic complexes have been synthesized[2]; we have recently reported a number of such species employing the sterically demanding di-tert-butyl phosphide unit.[3] We report here the synthesis of the phosphido bridged, Fe-Ni complex $(CO)_3(PMe_3)Fe(\mu\text{-}t\text{-}Bu_2P)Ni(PMe_3)Cl$, (Fe-Ni).

RESULTS AND DISCUSSION

Reaction of one equivalent of $(CO)_3Fe(t\text{-}Bu_2PH)(t\text{-}Bu_2PLi)$ (generated *in situ*) with one equivalent of $NiCl_2(PMe_3)_2$ gives dark red (**1**) in *ca* 55% yield. The compound is stable to the atmosphere for short periods when in the solid state, but decomposes rapidly in solution. (**1**) is diamagnetic and its ^{31}P NMR spectrum is reasonably diagnostic. Thus at 32.38 MHz the spectrum shows a downfield triplet (δ 225.1) attributable to a di-tert-butyl phosphide bridging a metal-metal bond.[4] This is

---

* Author for correspondence.

probably an overlapping doublet of doublets due to very similar J_{P-P}'s between each of the terminal phosphines and the bridging phosphide. In addition there are two sets of doublets (δ 40.4 and δ-14.6) which are assigned to two terminal phosphines bound to different metals.

The ^1H NMR shows three distinct doublets in a ratio of 2:1:1 indicating the presence of one Bu^t_2P group and two PMe_3 groups. A PMe_3 group is transferred from Ni to Fe during the course of the reaction and Bu^t_2PH is eliminated from Fe. We have observed similar transformations in the formation of other heterobimetallic t-Bu_2P bridged complexes. The precise reasons for these transfers are not well understood at present.

It was thought that the Cl on the Ni atom in (**1**) would provide a useful leaving group for a variety of salt elimination reactions to give cluster expansion products or replacement to give alkyl or other derivatives. This, however, has proven surprisingly difficult since (**1**) is recovered essentially quantitatively from reactions with phenyl acetylide, allyl-MgBr, MeLi, $[(CO)_3Fe(P\text{-}Bu^t_2H)(P\text{-}Bu^t_2)]^-$, $[(MeCp)Mn(CO)_2(P\text{-}Bu^t_2)]^-$, and $[(CO)_5Cr(P\text{-}Bu^t_2)]^-$. Reaction with t-Bu_2PLi gave only $(CO)_3Fe(PMe_3)_2$ (identified by ^{31}P and ^1NMR and mass spectrometry) in about 15% yield as the only isolated product.

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

Molecules of (**1**) crystallize from hexane in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Other crystallographic data are given in Table I and an ORTEP diagram of the molecule is shown in Figure 1. The molecule has a triangular Fe-P-Ni core with the phosphide bridging an Fe-Ni single bond of 2.521 (1) Å. This is similar to those found in several other Fe-Ni compounds (Fe-Ni = 2.44 (1) Å,[5] 2.453 (1) Å,[6] and 2.460 (1) Å[7]).

The geometry about the iron, if the metal-metal bond is ignored, is best described as a trigonal bipyramid. The P(1)-Fe-P(2) angle of 173.47(8)° is reasonably close to 180°. Each of the CO ligands which occupy the equatorial sites are only distorted from the ideal P-Fe-C angle of 90° by a maximum of 7.8°. There is a significant distortion, however, in the C(2)-Fe-C(3) angle (131.4(3)°) which is bisected by the Fe-Ni bond. It seems likely that steric effects are largely responsible for this distortion.

The geometry around the nickel atom including the metal-metal bond is best described as a distorted square plane. The Cl-Ni-P(3) angle of 90.79(8)° fits the criteria very well, while the P(1)-Ni-P(3) angle of 111.16 (8)° is more indicative of a tetrahedral geometry. The P(1)-Ni-Cl angle at 156.25(9)° is intermediate but suggests a more square planar than tetrahedral character. More complete listings of bond lengths and angles are given in Tables II and III, and final positional parameters are listed in Table IV.

EXPERIMENTAL

All reactions were performed under oxygen-free nitrogen or under vacuum. Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Hexane and THF were dried over sodium and distilled from sodium benzophenone ketyl under nitrogen before use. $NiCl_2(PMe_3)_2$[8] and $(CO)_3Fe(Bu^t_2PH)_2$[9] were prepared by the literature procedures. Melting points were measured in sealed capillaries under nitrogen (1 atm.) (uncorrected). *Instruments*: IR, Perkin Elmer 1330; NMR, Varian EM-390 (^1H, 90 MHz), FT-80 (^{31}P, 32.384 MHz), Bruker WM-90 (^{31}P,

TABLE I
Crystal Structure Parameters for (**1**)

Description	(**1**)
Colour	dark red
Habit	prism
Max. Dim. (mm)	0.28 × 0.27 × 0.25
Unit Cell	
Crystal System	monoclinic
Space Group	$P2_1/c$
Unit Cell Parameters	
a (Å)	17.363 (1)
b (Å)	11.383 (2)
c (Å)	13.308 (2)
α (deg.)	90
β (deg.)	104.60 (1)
γ (deg.)	90
U (Å^3)	2545.1 (5)
Z	4
Formula	$C_{17}H_{36}ClFeNiO_3P_3$
M	531.4
Density (calc.) g cm^{-3}	1.387
μ (calc.) cm^{-1}	16.2
Radiation (Å)	MoK$_\alpha$ (0.71073)
Scan Technique	$\theta/2\theta$
Scan Width (deg.)	$0.8 + 0.35 \tan \theta$
Range/Indices (h,k,l)	$-18 \rightarrow 18$; $0 \rightarrow 12$; $0 \rightarrow 14$
2θ Range (deg.)	2° to 46°
No. Reflections measured	3537
Standard reflections	
intensity	$4\,\bar{5}\,2$, $6\,\bar{4}\,\bar{4}$
orientation	$1\,\bar{1}\,7$, $3\,\bar{4}\,\bar{6}$
Decay of Standards	7.3%
Min. % Transmission	82.49%
Max % Transmission	99.78%
Average % Transmission	91.94%
Agreement Factor for Averaged reflections	
(*F obs.*)	0.035
(*Int.*)	0.032
Structure Determination	
Reflections used $\{I > 3\sigma(I)\}$	1979
Parameters varied	235
Data/Parameter ratio	8.4
Shift to error ratio	2.554
E.S.D. of an observation of unit wt.	4.32
R	0.062
R_w	0.070

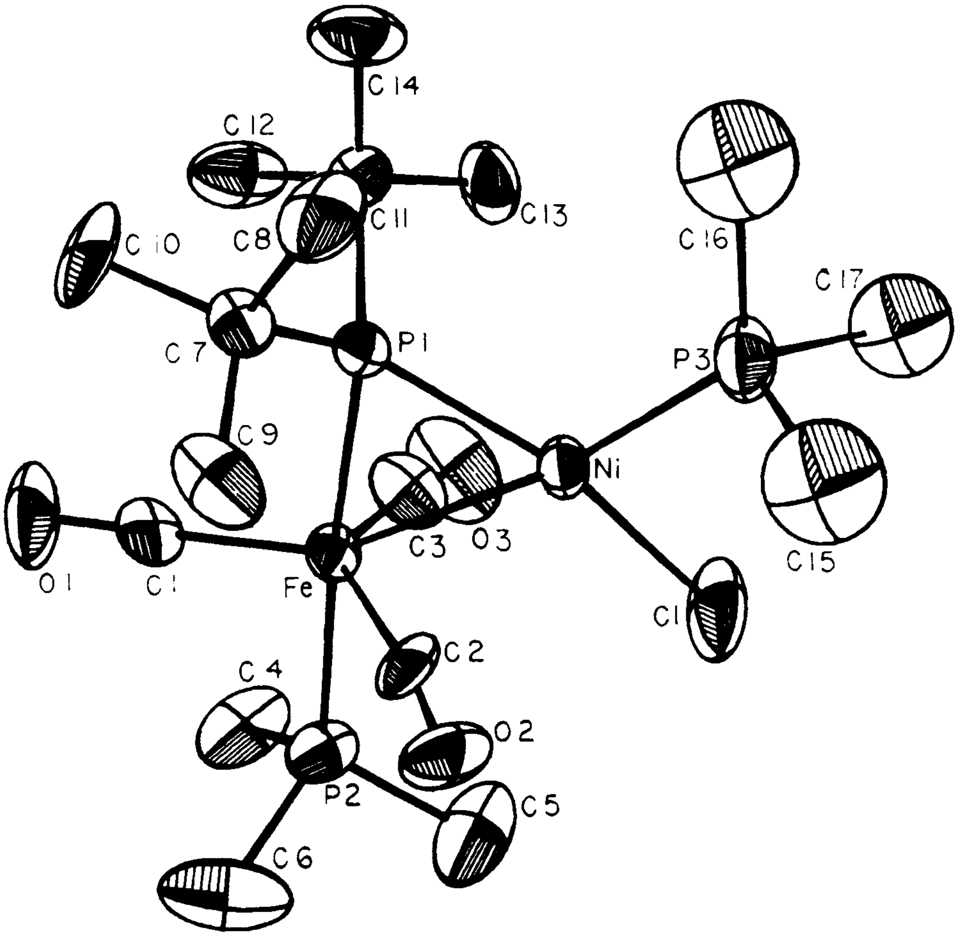

FIGURE 1 ORTEP view of (**1**) showing the atom labeling scheme.

TABLE II
Selected Bond Lengths (Å) for (**1**)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe	Ni	2.521(1)	P1	C11	1.895(7)
Fe	P1	2.238(2)	P2	C4	1.843(8)
Fe	P2	2.225(2)	P2	C5	1.765(9)
Fe	C1	1.772(7)	P2	C6	1.78(1)
Fe	C2	1.821(7)	P3	C15	1.80(1)
Fe	C3	1.796(8)	P3	C16	1.850(9)
Ni	Cl1	2.192(2)	P3	C17	1.87(1)
Ni	P1	2.140(2)	01	C1	1.155(8)
Ni	P3	2.173(2)	02	C2	1.126(7)
Ni	C2	2.318(7)	03	C3	1.127(8)
P1	C7	1.910(6)			

Numbers in parentheses are estimated standard deviations.

36.43 MHz). IR spectra were as nujol mulls (KBr plates) or in solution (matched KBr or CaF_2 cells). NMR spectra were recorded in C_6D_6 at ambient temperature (unless otherwise stated) and are referenced to Me_4Si (δ 0.0, ^1H) and 85% H_3PO_4 (aq) (δ 0.0, ^{31}P, downfield is positive).

Preparation of $(CO)_3(PMe_3)Fe(\mu\text{-}t\text{-}Bu_2P)Ni(PMe_3)Cl$ (**1**)

A solution of n-BuLi(0.40 cm^3 of 2.41 M in hexane, 0.96 mmol) was added to a solution of $Fe(CO)_3(t\text{-}Bu_2PH)_2$ (0.41 g, 0.96 mmol) in THF (40 cm^3) at −78°C. The yellow solution was allowed to warm to 10°C over 30 minutes, then cooled to −78°C and added dropwise to a solution of $NiCl_2(PMe_3)_2$ (0.27 g, 0.96 mmol) in THF (40 cm^3) at −78°C. The resulting dark green solution was allowed to warm to room temperature (over 2h) during which time the colour gradually changed to dark red. Volatile materials were then removed under vacuum and the solid extracted into hexane (2 x 25 cm^3). The solution was filtered, and the volume reduced under vacuum (*ca* 20 cm^3). Cooling (−20°C) gave dark red crystals of (**1**) after 24 h. They were collected and dried under vacuum. Yield: 0.28 g (55%); m.p.: 160–162°C (dec.); ^1H NMR: δ 1.51, s, (18H, μ-*t*-*Bu*$_2$P), δ 1.39, d, $J_{P-H} = 2.7$ Hz (9H, P*Me*$_3$), δ 1.21, d, $^2J_{P-H} = 9.0$ Hz (9H, P*Me*$_3$). $^{31}P\{^1H\}$ (in THF): δ 225.1, t, $^2J_{P-P} = 24.6$ Hz (μ-*t*-Bu$_2$*P*), δ 40.4, d, $^2J_{P-P} = 25.6$ Hz (*P*Me$_3$), δ −14.6, d, $^2J_{P-P} = 26.3$ Hz, (*P*Me$_3$). IR (nujol mull): 1957 s, 1900 s, 1878 s, (cm^{-1}). Microanalysis: calcd. for $C_{17}H_{36}ClFeNiO_3P_3$: C, 38.42; H, 6.83; P, 17.49%; found: C, 37.95; H, 6.82; P, 17.10%.

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

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Ni	Fe	P1	53.04(5)	Fe	P1	C7	116.9(2)
Ni	Fe	P2	121.95(7)	Fe	P1	C11	118.6(2)
Ni	Fe	C1	145.3(2)	Ni	P1	C7	123.8(2)
Ni	Fe	C2	62.1(2)	Ni	P1	C11	115.1(2)
Ni	Fe	C3	85.4(2)	C7	P1	C11	108.4(3)
P1	Fe	P2	173.47(8)	Fe	P2	C4	112.7(3)
P1	Fe	C1	93.1(2)	Fe	P2	C5	117.7(4)
P1	Fe	C2	90.4(2)	Fe	P2	C6	116.6(4)
P1	Fe	C3	97.8(2)	Fe	C1	01	178.6(7)
P2	Fe	C1	91.1(2)	Fe	C2	Ni	74.0(3)
P2	Fe	C2	83.2(2)	Fe	C2	O2	171.1(6)
P2	Fe	C3	85.4(2)	Ni	C2	O2	114.4(5)
C1	Fe	C2	117.9(3)	Fe	C3	O3	171.7(7)
C1	Fe	C3	109.4(3)	Ni	P3	C15	111.1(4)
C2	Fe	C3	131.4(3)	Ni	P3	C16	125.3(3)
Fe	Ni	Cl1	102.07(7)	Ni	P3	C17	111.0(4)
Fe	Ni	P1	56.67(5)				
Fe	Ni	P3	166.86(7)				
Fe	Ni	C2	44.0(2)				
Cl1	Ni	P1	156.25(9)				
Cl1	Ni	P3	90.79(8)				
Cl1	Ni	C2	90.2(2)				
P1	Ni	P3	111.16(8)				
P1	Ni	C2	80.9(2)				
P3	Ni	C2	134.7(2)				
Fe	P1	Ni	70.29(5)				

Numbers in parentheses are estimated standard deviations.

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

Atom	x/a	y/b	z/c	B(Å^2)
Fe	0.7887(1)	−0.1302(2)	0.8127(2)	2.20(4)
Ni	0.7810(1)	0.0904(1)	0.8240(1)	2.39(3)
Cl1	0.8936(2)	0.1453(4)	0.7920(4)	6.7(1)
P1	0.6820(2)	−0.0232(3)	0.8193(3)	2.20(7)
P2	0.9028(2)	−0.2228(4)	0.8199(3)	3.33(9)
P3	0.7516(2)	0.2719(4)	0.8488(3)	3.70(9)
O1	0.7089(7)	−0.3521(9)	0.833(1)	5.8(3)
O2	0.8879(5)	−0.028(1)	1.0048(7)	4.2(2)
O3	0.7924(7)	−0.095(1)	0.5970(8)	6.8(3)
C1	0.7411(8)	−0.265(1)	0.826(1)	3.0(3)
C2	0.8465(7)	−0.059(1)	0.930(1)	2.9(3)
C3	0.7852(9)	−0.106(1)	0.678(1)	3.9(4)
C4	0.8930(9)	−0.337(1)	0.720(1)	5.3(4)
C5	0.984(1)	−0.138(2)	0.805(2)	6.8(5)
C6	0.946(1)	−0.300(2)	0.937(2)	7.6(6)
C7	0.6375(7)	−0.050(1)	0.935(1)	2.6(3)
C8	0.5987(8)	0.061(1)	0.965(1)	4.2(4)
C9	0.7041(9)	−0.080(1)	1.025(1)	4.5(4)
C10	0.5776(8)	−0.151(1)	0.910(1)	4.8(4)
C11	0.5974(8)	−0.011(1)	0.698(1)	3.7(4)
C12	0.5729(9)	−0.131(2)	0.649(1)	5.5(4)
C13	0.630(1)	0.062(1)	0.620(1)	4.8(4)
C14	0.5233(9)	0.050(2)	0.717(2)	5.6(5)
C15	0.809(1)	0.325(2)	0.973(2)	13.5(7)
C16	0.651(1)	0.328(2)	0.843(2)	8.4(7)
C17	0.774(2)	0.370(2)	0.747(2)	14.2(7)

Numbers in parentheses are estimated standard deviations.

X-Ray Experimental

Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated MoK$_\alpha$ radiation. Data for the unit cell determination were collected by the $\omega/2\theta$ scan technique at 23 ± 2°C. Details of the standard data collection methods were similar to those outlined in reference [10]. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package "SDP-PLUS," (B. A. Frenz and Associates, College Station, Texas 77840, 4th Edition, 1981). 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 vetween 24.0° and 26.0°. The space group $P2_1/c$ was uniquely determined by systematic absences. Details of crystal data parameters and other relevant information are collected in Table I. Key bond lengths and angles are in Tables II and III respectively and positional parameters in Table IV. Data were corrected for Lorentz and polarization effects and an anisotropic decay correction was applied. No absorption correction was applied since none was deemed necessary. The structure was solved by direct methods (MULTAN)[11] and 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 $P = 0.06$.[12] All atoms were refined anisotropically and hydrogen atoms were not located. The highest peak in the final difference Fourier was 0.46 eÅ^{-3}. Scattering factors were taken from reference [13]. Complete tables of bond lengths and angles and thermal parameters and observed and calculated structure factors for (**1**) have been deposited with the editor and are available upon request.

ACKNOWLEDGEMENTS

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

REFERENCES

1. For recent reviews in this area, see the following: D.A. Roberts and G.L. Geoffroy, *Comprehensive Organometallic Chemistry*, Chap. 40; G. Wilkinson, F.G.A. Stone and E.W. Abel, Eds. (Pergamon Press, New York, 1982); M.I. Bruce, *J. Organomet. Chem.*, **283**, 339 (1985).
2. See for example: M. Miller and H. Vahrenkamp, *Chem. Ber.*, **116**, 2322 (1983); M.J. Breen, M.R. Duttera, G.L. Geoffroy, G.C. Novotnak, D.A. Roberts, P.M. Shulman and G.R. Steinmetz, *Organometallics*, **1**, 1008 (1982); R.J. Haines, A.L. Du Preez and C.R. Nolte, *J. Organomet. Chem.*, **55**, 199 (1973); B.C. Benson, R. Jackson, K.K. Joshi and D.T. Thompson, *J. Chem. Soc., Chem. Comm.*, 1506 (1968); M.J. Breen and G.L. Geoffroy, *Organometallics*, **1**, 1437 (1982); R.T. Baker and T.H. Tulip, *Organometallics*, **5**, 839 (1986) and references therein.
3. See for example: R. A. Jones, J.G. Lasch, N.C. Norman, A.L. Stuart, T.C. Wright and B.R. Whittlesey, *Organometallics*, **3**, 114 (1984); D.J. Chandler, R.A. Jones, A.L. Stuart and T.C. Wright, *Organometallics*, **3**, 1830 (1984) and references therein.
4. Downfield shifts in the δ 50-200 range in the ^{31}P NMR of the Ph_2P groups bridging metal-metal bonds have been noted by several groups of workers. See for example: P.E. Garrou, *Chem. Rev.*, **81**, 229 (1981); A.J. Carty, *Adv. Chem. Ser.* No. 196, 163 (1982); P.E. Kreter and D. 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 μ-*t*-Bu_2P complexes (see ref. 3).
5. B.L. Burnett and C. Kruger, *Cryst. Struct. Commun.*, **2**, 347 (1973).
6. M.I. Bruce, J.R. Rodgers, M.R. Snow and F.S. Wong, *J. Organomet. Chem.*, 1982, **240**, 299 (1982).
7. W. Petz, C. Kruger and R. Goddard, *Chem. Ber.*, **112**, 3413 (1979).
8. K.A. Jensen, P.H. Nielsen and C.T. Petersen, *Acta Chem. Scand.*, **17**, 1115 (1963).
9. A.M. Arif, D. J. Chandler and R.A. Jones, *Organometallics* **6**, 506 (1987).
10. R.A. Jones, and T.C. Wright, *Organometallics*, **2**, 1842 (1983).
11. G. Germain, P. Main and M.M. Wolfson, *Acta Cryst.*, **A27**, 368 (1971).
12. P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = 4(F_o)^2/[\Sigma(F_o)^2]^2$, where $[\Sigma(F_o)^2]^2 = [S^2(C + R^2B) + \{P(F_o)^2\}^2/Lp^2$, 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.
13. *International Tables for X-Ray Crystallography* (Kynoch Press, Birmingham, England, 1974) Vol. 4.