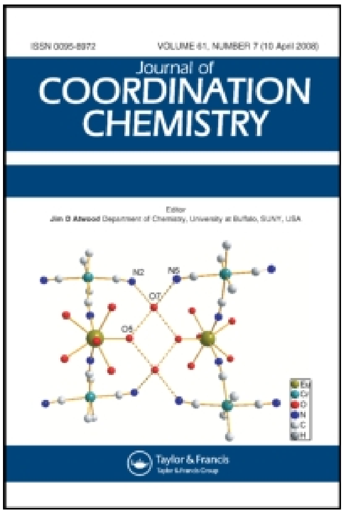

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Mononuclear Complexes of Cr(II) and Fe(II) with Terminal -SH Groups. Synthesis and X-Ray Crystal Structures of *trans*-M(SH)$_2$(dmpe)$_2$ (M = Cr, Fe; dmpe = 1,2-Bis(Dimethylphosphino)Ethane)

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To cite this Article Arif, Atta M. , Hefner, John G. , Jones, Richard A. and Koschmieder, Stefan U.(1991) 'Mononuclear Complexes of Cr(II) and Fe(II) with Terminal -SH Groups. Synthesis and X-Ray Crystal Structures of *trans*-M(SH)$_2$(dmpe)$_2$ (M = Cr, Fe; dmpe = 1,2-Bis(Dimethylphosphino)Ethane)', Journal of Coordination Chemistry, 23: 1, 13 — 19

To link to this Article: DOI: 10.1080/00958979109408238

URL: http://dx.doi.org/10.1080/00958979109408238

J. Coord. Chem. 1991, Vol. 23, pp. 13–19
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MONONUCLEAR COMPLEXES OF Cr(II) AND Fe(II) WITH TERMINAL –SH GROUPS. SYNTHESIS AND X-RAY CRYSTAL STRUCTURES OF *trans*-$M(SH)_2(dmpe)_2$ (M = Cr, Fe; dmpe = 1,2-BIS(DIMETHYLPHOSPHINO)ETHANE)

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(Received July 12, 1990)

The reaction of two equivalents of NaSH with $MCl_2(dmpe)_2$ (M = Cr, Fe,) at $-78°C$ gives *trans*-$M(SH)_2(dmpe)_2$ (M = Cr, (**1**), 30%; Fe, (**2**) 98%). The complexes have been characterized spectroscopically, and the *trans* geometry has been confirmed by single crystal X-ray diffraction studies. Crystal data (**1**): $C_{12}H_{34}CrP_4S_2$, $M = 418.42$, monoclinic, $P2_1/n$, $a = 8.857$ (1), $b = 12.719$ (2), $c = 9.648$ (1) Å, $\beta = 92.14(1)°$, $U = 1086.2$ (5) Å, $D_c = 1.279\,g\,cm^{-3}$, $Z = 2$, $\lambda(MoK_\alpha) = 0.71073$ Å, (graphite monochromator), $\mu(MoK_\alpha) = 9.80\,cm^{-1}$. Methods: MULTAN, difference Fourier, full-matrix least-squares. Refinement of 1149 reflections ($I > 3\sigma(I)$) out of 1901 unique observed reflections ($3.0° < 2\theta < 48.0°$) gave R and R_w values of 0.092 and 0.096, respectively. Crystal data (**2**): $C_{12}H_{34}FeP_4S_2$, $M = 422.28$, monoclinic, $P2_1/n$, $a = 8.834$ (2), $b = 12.594$ (2), $c = 9.532$ (2) Å, $\beta = 90.66$ (2)°, $U = 1060.3$ (5) Å^3, $D_c = 1.323\,g\,cm^{-3}$, $Z = 2$, $\lambda(MoK_\alpha) = 0.71073$ Å, (graphite monochromator), $\mu(MoK_\alpha) = 11.87\,cm^{-1}$. Methods: same as for (**1**). Refinement of 1178 reflections ($I > 3\sigma$ (I)) out of 2086 unique observed reflections ($2.0° < 2\theta < 50.0°$) gave R and R_w values of 0.056 and 0.059, respectively.

Keywords: X-ray, chromium, iron, phosphine, SH, complex

INTRODUCTION

Mononuclear terminally bonded-SH complexes of the d-block transition metals are relatively rare.[1] Routes to such complexes are sometimes complex since reactions involving H_2S or HS^- can lead to polymeric or cluster species which contain bridging SH^- or S^{2-}. In order to prepare soluble, mononuclear complexes with terminally bound –SH groups, we have investigated the reactions of NaSH with a variety of metal halide starting materials in the presence of phosphines. We report here the syntheses and X-ray crystal structures of the complexes *trans*-$M(SH)_2(dmpe)_2$ (M = Cr, Fe; dmpe = 1,2-bis(dimethylphosphino)ethane).

RESULTS AND DISCUSSION

The reaction of *trans*-$MCl_2(dmpe)_2$ with NaSH in methanol at $-78°C$ gives good yields of the mononuclear *trans*-$M(SH)_2(dmpe)_2$ complexes (M = Cr (**1**), Fe (**2**)). The *trans* geometry is no doubt favoured on steric grounds since it minimizes the

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electronically unfavourable close contact of the sulfur lone pairs that would occur in a *cis* product.

$Cr(SH)_2(dmpe)_2$ (1)

This red, crystalline, hexane-soluble complex is formed in *ca* 30% yield and is air-stable for several hours in the solid state. (1) is paramagnetic ($\mu_{eff} = 2.78$ B. M., Evans' Method[2]) corresponding to two unpaired electrons per Cr(II), d^4 ion. The IR spectrum contains a weak ν_{S-H} band at $2563\,cm^{-1}$. Interestingly, the order of addition of reagents is critical to this reaction since reaction of $CrCl_2$ with NaSH in methanol at −78°C followed by the addition of dmpe results in the novel Cr_3, mixed valence cluster $Cr_3(\mu_3-S)_2(\mu_2-S)_3(dmpe)_3$, which we recently described.[3]

$Fe(SH)_2(dmpe)_2$ (2)

(2) is a purple, crystalline diamagnetic complex. The ^1H NMR contains a multiplet to high field ($\delta - 7.02$, quintet $^3J_{P-H} = 7.5$ Hz) which is assigned to the Fe–S*H* protons. The IR stretch of the SH groups appears as a peak at $2550\,cm^{-1}$ (med.).

X-Ray Structures of (1) and (2)

Both (1) and (2) crystallize in the monoclinic space group $P2_1/n$ with similar unit cell dimensions. The metal lies at a crystallographically imposed centre of inversion in both complexes [(1): $x = 1$, $y = 0$, $z = 1$; (2): $x = 1$, $y = 0$, $y = 0.5$]. The coordination geometry about all three complexes may best be described as octahedral with the –SH groups in *trans* positions. An ORTEP view of (1) is shown in Figure 1.

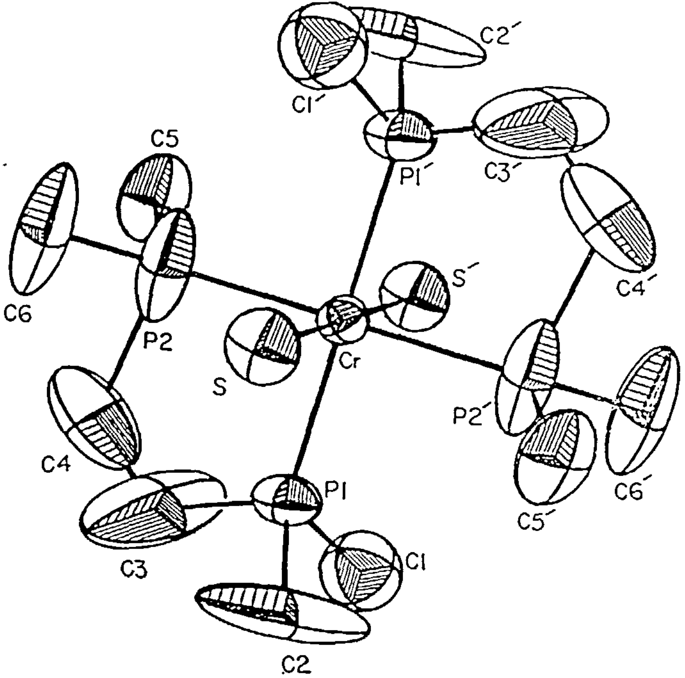

FIGURE 1 ORTEP view of (1) showing the atomic numbering scheme. The atomic numbering scheme for (2) is similar.

TABLE I
Crystal data and Refinement Parameters.

	(1)	(2)
Colour	ruby red	purple
Habit	prism	cube
Max. dimension (mm)	0.25 × 0.25 × 0.20	0.28 × 0.28 × 0.25
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	8.857(1)	8.834(2)
b (Å)	12.719(2)	12.594(2)
c (Å)	9.648(1)	9.532(2)
β (deg)	92.14(1)	90.66(2)
U (Å^3)	1086.2(5)	1060.3
Molecules per unit cell	2	2
Formula	$C_{12}H_{34}CrP_4S_2$	$C_{12}H_{34}FeP_4S_2$
M	418.42	422.28
D (calc, gcm^{-3})	1.279	1.323
μ (calc, cm^{-1})	9.80	11.87
Radiation (Å)	MoK$_\alpha$, 0.71073	MoK$_\alpha$, 0.71073
Scan technique	ω/2θ	ω/2θ
Scan width	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
Range of indices	$+h$, $+k$, $\pm l$	$+h$, $+k$, $\pm l$
2θ range (deg)	3.0 to 48.0	2.0 to 50.0
No. reflections measured	1901	2086
Standard reflections:		
intensity	$3\ 2\ 3,\ \bar{4}\ 1\ 3$	$1\ 5\ 4,\ 1\ \bar{1}\ 8$
orientation	$4\ 2\ 2,\ \bar{4}\ \bar{1}\ 3$	$\bar{3}\ 4\ 5,\ 4\ \bar{1}\ 6$
Decay of standards	1.0%	<0.1%
Min. % transmission	94.85	90.58
Max. % transmission	99.96	99.93
Av. % transmission	97.34	96.98
No. reflections used ($I > 3\sigma(I)$)	1149	1178
No. parameters varied	86	86
Data/parameter ratio	13.36	8.73
Shift to error ratio	8.39	0.594
E.s.d of an observation of unit weight	2.71	1.68
R	0.092	0.056
R_w	0.096	0.059

TABLE II
Table of bond lengths in Å for $Cr(SH)_2(dmpe)_2$, (1)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cr	S	2.391(4)	Cr	P(1)	2.359(4)
Cr	P(2)	2.329(5)	P(1)	C(1)	1.84(2)
P(1)	C(2)	1.80(2)	P(1)	C(3)	1.67(3)
P(2)	C(4)	2.14(3)	P(2)	C(5)	1.84(2)
P(2)	C(6)	1.71(2)	C(3)	C(4)	1.36(4)

Numbers in parentheses are estimated standard deviations.

The key M–P and M–S bond lengths are slightly different for the two compounds although they all fall within normal limits. Thus for (**1**) Cr–P (av.) = 2.344(5) Å and Cr–S = 2.391(4) Å; for (**2**), these values are Fe–P (av.) = 2.222(2) Å and Fe–S = 2.356(2) Å. The shorter metal ligand distances in (**2**) probably reflect the decreasing radius for the M^{2+} ion which occurs with increasing atomic number. Positional and structural data for the complexes are listed in Tables II to VII.

TABLE III

Table of bond angles in degrees for Cr(SH)$_2$(dmpe)$_2$, (**1**)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S	Cr	P(1)	89.4(1)	S	Cr	P(2)	89.0(2)
P(1)	Cr	P(2)	86.4(2)	Cr	P(1)	C(1)	120.8(8)
Cr	P(1)	C(2)	119.7(9)	Cr	P(1)	C(3)	114.(1)
C(1)	P(1)	C(2)	98.(1)	C(1)	P(1)	C(3)	102.(1)
C(2)	P(1)	C(3)	97.(1)	Cr	P(2)	C(4)	101.7(8)
Cr	P(2)	C(5)	120.8(6)	Cr	P(2)	C(6)	130.1(9)
C(4)	P(2)	C(5)	99.(1)	C(4)	P(2)	C(6)	90.(1)
C(5)	P(2)	C(6)	104.(1)	P(1)	C(3)	C(4)	120.(2)
P(2)	C(4)	C(3)	117.(2)				

Numbers in parentheses are estimated standard deviations.

TABLE IV

Table of positional parameters for Cr(SH)$_2$(dmpe)$_2$, (**1**)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
Cr	0.000	0.000	0.500	2.90(5)
S	1.1771(5)	0.1340(3)	0.4443(4)	5.15(9)
P(1)	0.8676(4)	0.1235(3)	0.6315(4)	4.43(8)
P(2)	1.1424(6)	−0.0342(4)	0.7028(5)	8.7(1)
C(1)	0.664(3)	0.108(2)	0.658(2)	8.1(6)*
C(2)	0.866(3)	0.260(2)	0.581(3)	16.5(8)
C(3)	0.938(4)	0.141(3)	0.793(2)	28.3(9)
C(4)	1.049(4)	0.076(2)	0.844(2)	15(1)
C(5)	1.116(2)	−0.156(1)	0.800(2)	7.2(4)
C(6)	1.321(2)	0.007(2)	0.753(2)	12.0(6)

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

TABLE V

Table of bond lengths in Å for Fe(SH)$_2$(dmpe)$_2$, (**2**)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe	S(1)	2.356(2)	Fe	P(1)	2.228(2)
Fe	P(2)	2.211(3)	P(1)	C(1)	1.882(13)
P(1)	C(2)	1.809(14)	P(1)	C(3)	1.757(15)
P(2)	C(4)	1.93(2)	P(2)	C(5)	1.809(11)
P(2)	C(6)	1.729(13)	C(3)	C(4)	1.36(3)

Numbers in parentheses are estimated standard deviations.

TABLE VI
Table of bond angles in degrees for $Fe(SH)_2(dmpe)_2$, (2)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S(1)	Fe	P(1)	89.43(9)	S(1)	Fe	P(2)	89.22(9)
P(1)	Fe	P(2)	86.72(9)	Fe	P(1)	C(1)	120.1(5)
Fe	P(1)	C(2)	122.9(6)	Fe	P(1)	C(3)	110.4(7)
C(1)	P(1)	C(2)	96.6(8)	C(1)	P(1)	C(3)	99.7(8)
C(2)	P(1)	C(3)	104.(1)	Fe	P(2)	C(4)	107.9(5)
Fe	P(2)	C(5)	122.2(4)	Fe	P(2)	C(6)	124.6(6)
C(4)	P(2)	C(5)	99.8(6)	C(4)	P(2)	C(6)	93.8(9)
C(5)	P(2)	C(6)	102.2(8)	P(1)	C(3)	C(4)	121.(1)
P(2)	C(4)	C(3)	114.(1)				

Numbers in parentheses are estimated standard deviations.

TABLE VII
Table of positional parameters for $Fe(SH)_2(dmpe)_2$, (2)

Atom	x/a	y/b	z/c	$B(\text{Å}^2)$
Fe	0.000	0.000	1.000	2.70(2)
S(1)	0.8199(3)	0.1278(2)	1.0664(3)	5.11(5)
P(1)	1.1198(3)	0.1238(2)	0.8766(3)	4.70(5)
P(2)	0.8651(3)	−0.0315(2)	0.8077(3)	5.71(6)
C(1)	1.116(2)	0.266(1)	0.935(2)	11.1(5)
C(2)	1.320(1)	0.118(1)	0.841(2)	19.3(6)
C(3)	1.036(2)	0.137(2)	0.710(1)	21.8(6)
C(4)	0.920(2)	0.073(1)	0.669(1)	15.3(6)
C(5)	0.888(1)	−0.1516(9)	0.706(1)	7.1(3)
C(6)	0.673(1)	−0.007(2)	0.790(2)	18.5(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)^*[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos\ \text{gamma})^*B(1,2) + ac(\cos\ \text{beta})^*B(1,3) + bc(\cos\ \text{alpha})^*B(2,3)]$.

EXPERIMENTAL

General

All reactions were performed under oxygen-free nitrogen or in vacuum. Microanalyses were by the Schwartkopf Microanalytical Laboratory, Woodside, NY. Methanol and ethanol were dried over magnesium turnings and distilled from the magnesium alkoxide under nitrogen prior to use. Toluene was distilled from sodium under nitrogen. Hexane was distilled from sodium benzophenone ketyl under nitrogen before use. Dmpe (1,2-bis(dimethylphosphino)ethane) was prepared by the literature method.[4] $CrCl_2$ was prepared from chromous acetate[5] by reaction with dry HCl gas in THF at 0°C. NaSH was prepared by the literature method.[6] *Instruments*: IR: Perkin-Elmer 1330, NMR: Varian EM-390 (^1H, 90 MHz), FT-80 (^{31}P, 32.384 MHz), Bruker WM-90 (^{31}P, 36.43 MHz), Nicolet NT-200 (^1H and ^{31}P). 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 temperatures and are referenced to Me_4Si (δ 0.0, ^1H) or 85% (aq.) H_3PO_4 (δ 0.0 ^{31}P). ESR data were recorded on a Varian E-9 EPR spectrometer.

Preparation of trans-*Cr(SH)$_2$(dmpe)$_2$ (1)*

A solution of $CrCl_2(dmpe)_2$[7] (0.20 g, 1.63 mmol) in methanol (40 cm^3) was cooled to −78°C and a solution of NaSH (1.56 cm^3 of a 2.09 M methanol solution, 2 equiv.) was added slowly. A bright orange colour developed immediately, and which became more brown on slowly warming the mixture to room temperature. The solution was stirred an additional 12 h at room temperature. Volatile materials were then removed under vacuum. The residue was extracted into hexane (2 × 3 cm^3). The resulting yellow-orange solution was filtered and reduced in volume (*ca* 40 cm^3) by evaporation under vacuum. Cooling (−20°C) gave ruby-red prisms of (1). Yield 0.20 g (30%). M.p.: the complex appears to decompose slightly at 143–145°C, and the remaining material does not melt below 360°C; $\mu_{eff} = 2.78$ B. M. (Evans' Method).[2] IR (nujol mull), 2953 m, 2890 s, 2794 w, 2563 w, 1410 s, 1285 m, 1269 s, 1226 w, 1094 v.br. m, 985 w, 924 br.s., 882 m, 855 w, 799 v.br.w, 746 w, 720 m, 691 m, 626 s, 565 m, 446 m, 372 m, 332 m (cm^{-1}). Microanalysis: calcd. for $C_{12}H_{34}CrP_4S_2$: C, 29.06; H, 8.13%. Found: C, 28.83; H, 8.01%.

Preparation of trans-*Fe(SH)$_2$(dmpe)$_2$ (2)*

A solution of $FeCl_2$ (0.25 g, 1.97 mmol) in methanol (40 cm^3) was cooled to −78°C and excess dmpe (0.66 cm^3, 4.10 mmol) was added to give a violet suspension. NaSH (1.88 cm^3 of a 2.09 M solution in MeOH) was added slowly at −78°C to give a deep red-violet solution. The solution was allowed to warm to room temperature and stirred an additional four hours at which point it was deep purple in colour. Volatile materials were removed under vacuum, and the purple residue was washed with hexane (15 cm^3) and dried under vacuum. The residue was extracted into toluene (40 cm^3), the resulting solution filtered and reduced in volume to *ca* 25 cm^3. Cooling (−20°C) gave large purple cubes of (2). Yield 0.80 g, (98%). M.p.: the complex appears to decompose at 167–168°C, and the remaining residue melts at 211–214°C with further decomposition. IR: 2960 m, 2965 m, 2893 s, 2798 w, 2550 m, 1414 s, 1286 m, 1270 s, 1226 m, 118 w, 1064 m, 985 w, 920 br.s, 881 m, 832 s, 791 m, 728 s, 691 s, 637 s, 452 m, 382 m, 342 w (cm^{-1}). NMR: ^1H (C_6D_6) δ 1.67 m, 8H, $-CH_2$, δ 1.24 d, 24H, $-CH_3$, $^2J_{H-H} = 3$Hz, δ − 7.02, pent, 2H, −SH. $^{31}P\{^1H\}$ δ 59.10, s. Microanalysis: calcd. for $C_{12}H_{34}FeP_4S_2$: C, 34.18; H, 8.12; P, 29.34%. Found C, 33.98; H, 7.95; P, 29.47%.

X-Ray Experimental

Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated MoK_α radiation. Data were collected by the ω/2θ scan technique at 23 ± 2°C. Details of the standard data collection methods are as described in reference 8. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package "SDP PLUS."[9] Crystals of (1) and (2) were mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 24.0° and 26.0°. The two compounds are isostructural and the monoclinic space group $P2_1/n$

was uniquely determined by the systematic absences $h\,0\,l, h + 1 = 2n + 1; 0\,k\,0, k = 2n + 1$, and $h\,0\,0, h = 2n + 1, 0\,0\,l, l = 2n + 1$). Details of crystal data parameters and other relevant information are collected in Table I. The data for each structure were corrected for Lorentz and Polarization effects and also for absorption using an empirical ψ scan method (program EAC). The structures were solved by direct methods (MULTAN)[10] and successive cycles of difference Fourier maps followed by least-squares refinement.

For (1): Hydrogen atoms were not located, and all non-hydrogen atoms were refined anisotropically. Unit weights were used throughout the course of the refinement. The maximum peak in the final difference Fourier map had a height of 0.714 e Å^{-3} and was located 1.836 Å from P(1).

For (2): Hydrogen atoms were located but not refined, and all non-hydrogen atoms were refined anisotropically. Unit weights were used throughout the course of the refinement. The maximum peak in the final difference Fourier map had a height of 0.664 e Å^{-3} and was located 2.230 Å from Fe.

ACKNOWLEDGEMENTS

We thank the Robert A. Welch Foundation (F-816), the National Science Foundation and the Texas Advanced Technology Research Project for financial support. R. A. J. thanks the Alfred P. Sloan Foundation for a Fellowship (1985–89).

SUPPLEMENTARY MATERIAL

Tables of thermal parameters and observed and calculated structure factors for (1) and (2) are available from R. A. J.

REFERENCES

1. See for example: B.H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, **14**, 322 (1975) and references therein.
2. D.F. Evans, *J. Chem. Soc. (A)*, 2003 (1959).
3. A.M. Arif, J.G. Hefner and R.A. Jones, *J. Am. Chem. Soc.*, **108**, 1701 (1986).
4. E.H. Uhing and A.D.F. Toy, *Proc. Int. Conf. Phosphorus Chem., ACS Symp. Ser.*, **171**, 333 (1981); R.J. Burt, J. Chatt, W. Hussain and G.J. Leigh, *J. Organomet. Chem.*, **182**, 203 (1979).
5. H.S. Booth, (Ed.)"*Inorganic Synthesis*" Vol. I, (McGraw-Hill, New York, 1939), p. 122.
6. J. Keinber, (Ed.) "Inorganic Synthesis" Vol. 7, (McGraw-Hill, New York, 1963), p. 128.
7. G.S. Girolami, J.E. Salt, J.G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Am. Chem. Soc.*, **105**, 5954 (1983).
8. R.A. Jones and T.C. Wright, *Organometallics*, **2**, 1842 (1983).
9. SDP Plus (4th ed., 1981), B.A. Frenz and Associates, College Station, Texas 77840.
10. G. Germain, P. Main, and M.M. Woolfson, *Acta/Crystallogr., Sect.* **A27**, 368 (1971).