Inorganica Chimica Acta, *86* (1984) 179–183

The Crystal and Molecular Structure of *trans*-Dichloro-, *trans*-Dimethyl-, *trans*-Bis-(hexamethylphosphoramide)tin(IV): $(CH_3)_2SnCl_2 \cdot 2O{=}P[N(CH_3)_2]_3$

ARNOLD L. RHEINGOLD

Department of Chemistry, University of Delaware, Neward, Del. 19711, U.S.A.

S. W. NG and J. J. ZUCKERMAN

Department of Chemistry, University of Delaware, Newark, Del. 19716, U.S.A.

and S. W. NG and J. J. ZUCKERMAN*

*$(CH_3)_2SnCl_2 \cdot 2O{=}P[N(CH_3)_2]_3$, f.w. = 578.08 crystallizes in the monoclinic space group, $P2_1/n$: $a = 8.417(3)$, $b = 12.880(3)$, $c = 12.139(4)$ Å, $\beta = 94.20(3)°$, $V = 1312.4(7)$ Å^3, $Z = 2$, $\rho(calcd.) = 1.462$ g cm^{-3}, Mo(K_α) $\lambda = 0.71073$ Å, $\mu = 13.22$ cm^{-1}. Anisotropic refinement of all nonhydrogen atoms converged at $R_F = 4.36\%$ using 1897 unique reflections, $I \geqslant 3\sigma(I)$. Hexamethylphosphoramide (HMPA) forms a stereochemically crowded, all-*trans-octahedral complex with dimethyltin(IV) dichloride.*

Introduction

Dimethyltin(IV) dichloride, $(CH_3)_2SnCl_2$, forms both 1:1 [1–3] and 1:2 six-coordinated complexes with donor ligands [4]. The 1:2 complexes all adopt distorted octahedral structures [5, 6]. It has been predicted that in 1:2 complexes of non-stereochemically demanding donor molecules, a *cis*-donor-molecule arrangement should be preferred, whereas crowding may cause some donor molecules to adopt a less favorable *trans*-configuration [7]. A large number of dimethyltin(IV) dichloride complexes have been prepared [4], and six containing monodentate donor molecules have been structurally confirmed by X-ray diffraction [5, 6]: the 1:2 complexes *cis*-dichloro-, *cis*-bis(dimethylsulfoxide)-, *trans*-dimethyltin(IV) [8, 9], *trans*-dichloro-, *trans*-bis-(pyridine-N-oxide)-, *trans*-dimethyltin(IV) [10], *trans*-dichloro-, *trans*-bis(hexamethylphosphoramide-, *trans*-dimethyltin(IV) [11], and *cis*-dichloro-, *cis*-bis-(dimethylformamide)-, *trans*-dimethyltin(IV), [9] and three 1:1 complexes which are actually six-coordinated in the solid state, *cis*-dichloro-, *cis*-chloro-, salicylaldehyde-, *trans*-dimethyltin(IV) [12], *cis*-dichloro-, *cis*-chloro-, diphenylcyclopropenone-, *trans*-dimethyltin(IV) [2] and *cis*-dichloro-, *cis*-chloro-, 2,6-dimethylpyridine N-oxide-, *trans*-dimethyltin(IV) [3]. In addition, the potentially chelating bis-(salicylaldehyde)ethylenediimine (salenH$_2$) bridges *trans*-dimethyl-, *trans*-dichlorotin-(IV) units by oxygen atoms to form a polymeric solid [13].

Following our interest in 1:1 complexes of dimethyltin(IV) dichloride [1–3], we used a literature receipe [14] to obtain the 1:1 complex of HMPA (hexamethylphosphoramide), but structural determination reveals an all-*trans*-1:2 octahedral structure, in agreement with a previous study [11].

Experimental

The $(CH_3)_2SnCl_2 \cdot 2HMPA$ adduct was obtained by adding HMPA (1.79 g, 10.0 mmol) to dimethyltin(IV) dichloride (2.20 g, 10.0 mmol), both in chloroform, and cooling the mixture to precipitate the title complex in 70% yield. Single crystals were obtained by the slow evaporation of a chloroform solution, mp 121.5 °C [lit. 122–123° [15]]; infrared $\nu_{asym}(Sn{-}C) = 571$ cm^{-1}; ^1H NMR ($CDCl_3$) $\delta H_3CSn = 1.12$ ppm, $|^2J(^{119}Sn{-}C{-}^1H)| = 93.8$ Hz [lit. 121.1 Hz [16]], $\delta(H_3C)_2NP = 2.50$, 2.66 ppm (doublet), $|^3J(^{31}P{-}N{-}C{-}^1H)| = 9.7$ Hz; tin-119m Mössbauer isomer shift (IS) = 1.33 ± 0.03, quadrupole splitting (QS) = 4.22 ± 0.06 mm s^{-1} [lit. IS = 1.32, QS = 4.28 [17], IS = 1.54, QS = 4.45 mm s^{-1} [18]]. A colorless, nearly spherical specimen (radius 0.15 mm) was used in the structure determination. A Nicolet R3 automated four-circle diffractometer was used to collect the diffraction data. The unit-cell parameters and orientation matrix were determined from the angular settings of 25 reflections well-distributed in reciprocal space ($25° \leqslant 2\theta \leqslant 32°$, MoK$_\alpha$ radiation). Observed systematic absences uniquely defined the monoclinic space group, $P2_1/n$. An empirical absorption correction was applied to the data based upon five ψ-scan reflections (max. trans. = 0.255; min. trans. = 0.237). Correction also was made for decay; a uniform ~7% decrease in check reflection intensity was observed during data collection. An ω-scan procedure was used to collect 2559 reflections (h, k, ±l) over the range $3° \leqslant 2\theta \leqslant$

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

50° of which 2298 reflections were unique; 1792 reflections with $I > 3\sigma(I)$ were used in solution and refinement. Agreement between averaged reflections was at the 3.49% level. The structure was solved by the trial placement of the Sn atom at the coordinates (0, 0, 0), a reasonable assumption given that $Z = 2$ and the large deviations from 1.00 for the multiplication factors required for parity group renormalization. All remaining non-hydrogen atoms were located in a subsequent difference-Fourier synthesis. After placing hydrogen atoms in idealized locations [d(C–H) = 0.96 Å, isotropic thermal parameters set equal to 1.2 times the isotropic equivalent for the carbon atom to which it was bound using an updated riding model], and block-cascade refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms, the structure converged at the reported residual [$R_F = 4.36\%$, $R_w = 4.27\%$, GOF = 1.197, $w = [\sigma^2(F) + g(F^2)]$, $g = 0.00048$ (refined)]. The maximum least-squares shift to error in the final refinement cycle was 0.043, and the maximum and minimum heights in the final difference Fourier synthesis were 0.70 and −0.44 e $Å^{-3}$. F(000) = 596. Atomic scattering factors were obtained from the *International Tables of Crystallography*. All computer programs used are contained in the P3, SHELXTL and XP packages distributed by the Nicolet Corporation.

Results

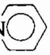
Atomic coordinates and isotropic equivalents for the thermal parameters for all non-hydrogen atoms are provided in Table I, and selected bond lengths and angles (with comparisons to a previous study and two related compounds) are provided in Table II. The molecular geometry and labelling scheme for

TABLE I. Atomic Coordinates with Esd's for $(CH_3)_2SnCl_2 \cdot 2HMPA$.

Atom	x	y	z	U(iso)
Sn	0	0	0	0.0321
Cl	0.1331(2)	−0.0357(1)	−0.2078(1)	0.0637
P	0.1372(2)	0.2557(1)	−0.0747(1)	0.0342
O	0.0487(4)	0.1682(3)	−0.0260(3)	0.0437
N(1)	0.2591(5)	0.2315(3)	−0.1693(3)	0.0454
N(2)	0.0031(5)	0.3331(3)	−0.1363(4)	0.0488
N(3)	0.2511(5)	0.3097(3)	0.0248(3)	0.0453
C(1)	0.2447(6)	−0.0326(5)	0.0280(5)	0.0578
C(11)	0.4168(7)	0.1888(5)	−0.1403(5)	0.0697
C(12)	0.2064(8)	0.2151(6)	−0.2847(5)	0.0708
C(21)	−0.1554(7)	0.3379(5)	−0.0969(5)	0.0626
C(22)	0.0504(9)	0.4297(5)	−0.1887(6)	0.0766
C(31)	0.2210(8)	0.2958(6)	0.1391(4)	0.0733
C(32)	0.3616(7)	0.3946(5)	0.0042(5)	0.0641

TABLE II. Selected Bond Distances and Angles for $(CH_3)_2SnCl_2 \cdot 2HMPA$ with Comparisons to $(CH_3)_2SnCl_2 \cdot 2DMSO$ and $(CH_3)_2SnCl_2 \cdot 2py \cdot NO$*.

	$(CH_3)_2SnCl_2 \cdot 2HMPA$[a, b]		$(CH_3)_2SnCl_2 \cdot 2DMSO$[c]	$(CH_3)_2SnCl_2 \cdot 2py \cdot NO$[d]
	Bond distances (Å)			
Sn–Cl	2.575(1)[a]	2.57(1)[b]	2.53(1), 2.49(1)	2.584(10)
Sn–O	2.231(3)[a]	2.26(2)[b]	2.31(1), 2.27(1) 2.38	2.251(16)
Sn–C	2.105(5)[a]	2.14(1)[b]	2.13(2), 2.12(2)	2.225(25)
E–O	1.496(4)			
	Bond angles (°)			
Cl–Sn–Cl′	180[a]	180[b]	95.2(3)	180
O–Sn–O′	180[a]	180[b]	83.7(5)	180
C–Sn–C	180[a]	180[b]	170.4(8)	180
Cl–Sn–O	90.8(1)[a]	89.1(5)[b]	92.0(4) 89.0(4) 174.5(3) 172.7(3)	95.6(8)
Cl–Sn–C	90.6(2)[a]	85.8(5)[b]	90.9(6) 93.8(6) 93.2(6) 94.5(6)	89.5(7)
O–Sn–C	91.7(2)[a]	89.5(6)[b]	87.0(7) 84.1(6) 92.4(7) 83.0(7)	95.6(8)
Sn–O–E	162.7(2)[a] E = P	162.7(8)[b] E = P	119.0(7), 125.2(7) E = S	117(1) E = N

*HMPA = $O{=}P[(CH_3)_2N]_3$; DMSO = $O{=}S(CH_3)_2$; py·NO = O←N  . [a]This work. [b]Ref. 11. [c]Ref. 9. [d]Ref. 10.

$(CH_3)SnCl_2 \cdot 2O{=}P[N(CH_3)_2]_3$ are given in Fig. 1, and a stereoview of the unit-cell packing is given in Fig. 2.

Discussion

As shown in Fig. 1, dimethyltin(IV) dichloride forms a discrete hexacoordinated, octahedral complex with two molecules of HMPA in an all-*trans*-structure; the presence of the tin atom at a center of symmetry imposes 180° bond angles for the *trans*-ligands. The linear C–Sn–C angles rationalize the absence of the infrared ν_{sym}(Sn–C) and the large magnitude of the Mössbauer QS value. The Cl–Sn–O, Cl–Sn–C(1) and O–Sn–C(1) bond angles [90.9(1), 90.6(2) and 91.7(2)°, respectively] reveal little distortion from an idealized octahedral geometry. The structure corresponds closely to that of *trans*-dichlorodimethyl-bis(pyridine-N-oxide) [10] which also assumes an all-*trans*-structure. No intermolecular Sn–Cl distances less than 4.0 Å are found.

A comparison of the bond parameters for the three complexes is given in Table II; several features require comment. While the Sn–Cl bond distances do not differ significantly for the three six-coordinated adducts, all are considerably longer than for the chlorine-bridged parent, $(CH_3)_2SnCl_2$, for which d(Sn–Cl) = 2.40(4) Å [19]. The Sn–C distances vary significantly among the three adducts, but curiously the *trans*-bis(HMPA) and the *cis*-bis(DMSO) adducts are similar, and the *trans*-bis(py·NO) is longer than either. The reported uncertainty in d(Sn–C) = 2.21(8) Å for $(CH_3)_2SnCl_2$ makes comparisons to the parent unreliable. The Sn–O bond distances for the two *trans*-adducts are significantly shorter than for the *cis*-complex, indicative of the reduced steric effects when the donor molecules are in *trans*-positions, but all are much longer than those found in less strained four-coordinated complexes, *e.g.*, $[(CH_3)_3Sn]_2O$, d(Sn–O) = 1.940(1) Å [20].

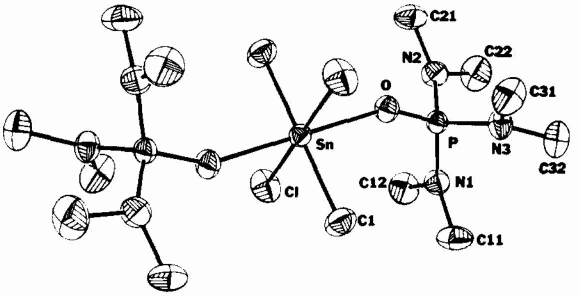


Fig. 1. Molecular geometry and labelling scheme for all-*trans* $(CH_3)_2SnCl_2 \cdot 2HMPA$.

The bis(HMPA) adduct displays a remarkably large Sn–O–P bond angle, 162.7(2)°; this angle is at the high end of the scale of previously reported values for either 1:1 or 1:2 tin adducts of oxygen-donor molecules, and may be reasonably explained as an attempt to reduce strain. Table III compares the Sn–O–E angles in non-chelated complexes of R_nSnX_{4-n} compounds where E = C, N, S and P and X = Cl, Br for which structural data are available [5, 6]. The angles fall in the general order Sn–O–P (av. 156°) > Sn–O–C (av. 129°) > Sn–O–S (av. 126°) > Sn–O–N (av. 120°). Among the E = C examples the ligands with a propensity for change dispersal show larger angles.

Acknowledgement

Our work is supported by the Office of Naval Research and by the National Science Foundation under Grant No. CHE-78-26548 (to J.J.Z.). We thank M & T Chemicals, Inc. for the donation of organotin starting materials and the Fulbright Commission for the award of a travel grant (to S.W.N.).

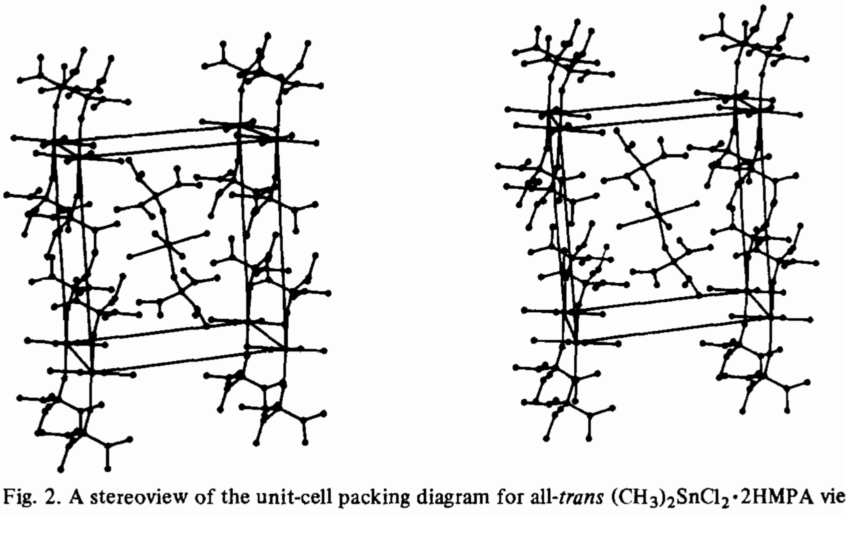


Fig. 2. A stereoview of the unit-cell packing diagram for all-*trans* $(CH_3)_2SnCl_2 \cdot 2HMPA$ viewed along the *a* axis.

TABLE III. Comparison of Sn–O–E Angles (E = C, N, S and P) in Non-chelated Complexes of R_nSnX_{4-n} (X = Cl, Br).

Compound	Sn–O–E angle (°)	Ref.
E = C		
$SnCl_4 \cdot C_{14}H_{14}N_4O_3 \cdot 2H_2O$	116.9(5)	a
$(CH_3)_2SnCl_2 \cdot 2DMF$	120(1)	b
$CH_3SnCl_3 \cdot 2DMF$	127(3)	c
$CH_3SnBr_3 \cdot DMF$	127(3)	c
$SnCl_4 \cdot C_6H_5CONHC_6H_5$ (Form I)	134.8	d
$SnCl_4 \cdot C_6H_5CONHC_6H_5$ (Form II)	132.1, 134.8	e
$[(CH_3)_2SnCl_2 \cdot OCC_2(C_6H_5)_2]_2$	132.7(2)	f
$[(CH_3)_2SnCl_2 \cdot (2\text{-}HOC_6H_4CHNCH_2\text{-})_2]_n$	133(2), 135(2)	g
$[(CH_3)_2SnCl_2 \cdot 2\text{-}HOC_6H_4CHO]_n$	134(1)	h, i, j
$(CH_3)_3SnCl \cdot (C_6H_5)_3PCHCOCH_3$	134.3(5)	k
E = N		
$(CH_3)_2SnCl_2 \cdot PyNO$	117(2)	l
$[(CH_3)_2SnCl_2 \cdot 2,6\text{-}(CH_3)_2C_5H_3NO]_2$	123.0(2)	m
E = S		
$(CH_3)_2SnCl_2 \cdot 2DMSO$	117(2), 122(2)	n
$(CH_3)_2SnCl_2 \cdot 2DMSO$	119.0(7), 125.2(7)	c
$(C_6H_5)_2SnCl_2 \cdot 2DMSO$ (Form II)	124.5(3), 133.7(3)	o
$(CH_3)_2SnBr_2 \cdot 2DMSO$	125(1)	c
$(C_6H_5)_2SnCl_2 \cdot 2DMSO$ (Form I)	126.5(2), 142.0(2)	p
$(CH_3)_2Sn_2(CH_2)Cl_4 \cdot 2DMSO$	131.1(3), 145.6(3)	q
$(CH_3)_3Sn_2(CH_2)Cl_3 \cdot DMSO$	130.6(5)	q
$Sn_2(CH_2)Cl_6 \cdot 4DMSO$	123.8(3), 128.7(3)	q
$[(C_6H_5)_3SnCl]_2 \cdot [n\text{-}C_3H_7S(O)CHCHS(O)n\text{-}C_3H_7]$	128.8(5)	r
E = P		
$(C_6H_5)_3SnCl \cdot [(C_6H_5)_2P(O)CH_2\text{-}]_2$	141.2(4)	s
$SnBr_4 \cdot 2HMPA$	147.6(6)	t
$(CH_3)_2SnBr_2 \cdot 2HMPA$	152.8(6)	c
$CH_3SnBr_3 \cdot 2HMPA$	153.0(6)	t
$(CH_3)_3SnCl \cdot HMPA$	158(1)	u
$[(C_6H_5)_3SnCl]_2 \cdot [(C_6H_5)_2P(O)CH_2\text{-}]_2$	161.8(2)	v
$(CH_3)_2SnCl_2 \cdot 2HMPA$	162.7(8)	b
$CH_3SnCl_3 \cdot 2HMPA$	164.3(8)	b
$SnCl_4 \cdot 2HMPA$	165.2(8)	b

[a] P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi and G. Predieri, *Inorg. Chim. Acta, 38*, 9 (1980). [b] Ref. 9. [c] L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin and V. S. Petrosyan, *J. Struct. Chem. (Engl. Transl.), 19*, 269 (1978). [d] T. S. Khodashova, M. A. Porai-Koshits, R. A. Slavinskaya and T. N. Sumarokova, *Koord. Khim., 7*, 301 (1981); *Chem. Abstr., 94*, 130666y (1981). [e] M. A. Porai-Koshits, T. S. Khodashova, R. A. Slavinskaya, A. E. Shalamov and T. N. Sumarakova, *Koord. Khim., 6*, 1751 (1980); *Chem. Abstr., 94*, 56294g (1981). [f] Ref. 2. [g] Ref. 13; L. Randaccio, Personal communication (1982). [h] Ref. 1. [i] M. McPartlin, Personal communication (1981). [j] Ref. 12. [k] J. Buckle, P. G. Harrison, T. J. King and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 1552 (1975). [l] Ref. 10. [m] Ref. 3. [n] Ref. 8. [o] L. Coghi, M. Nardelli, C. Pelizzi and G. Pelizzi, *Gazz. Chim. Ital., 105*, 1187 (1975). [p] L. Coghi, C. Pelizzi and G. Pelizzi, *Gazz. Chim. Ital., 104*, 873 (1974). [q] T. J. Karol, J. P. Hutchinson, J. R. Hyde, H. G. Kuivila and J. A. Zubieta, *Organometallics, 2*, 106 (1983). [r] C. A. L. Filgueras, P. R. Holland, B. F. G. Johnson and P. R. Raithby, *Acta Crystallogr., Sect. B, 29*, 2684 (1982). [s] C. Pelizzi and G. Pelizzi, *Inorg. Nucl. Chem. Lett., 16*, 451 (1980). [t] Ref. 11. [u] L. A. Aslanov, V. M. Attiya, V. M. Ionov, A. B. Permin and V. S. Petrosyan, *J. Struct. Chem. (Engl. Transl.), 18*, 884 (1977). [v] C. Pelizzi and G. Pelizzi, *J. Organomet. Chem., 202*, 411 (1980).

References

1 S. W. Ng and J. J. Zuckerman, *J. Chem. Soc., Chem. Commun.*, 475 (1982).

2 S. W. Ng, C. L. Barnes, M. B. Hossain, D. van der Helm, J. J. Zuckerman and V. G. Kumar Das, *J. Am. Chem. Soc., 104*, 5359 (1982).

3 S. W. Ng, C. L. Barnes, D. van der Helm and J. J. Zuckerman, *Organometallics, 2*, 600 (1983).

4 V. S. Petrosyan, N. S. Yashina and O. A. Reutov, *Adv. Organomet. Chem., 14*, 63 (1976).

5 J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem., 24*, 251 (1978).

6 P. J. Smith, *J. Organomet. Chem. Libr., 12*, 97 (1981).

7 R. F. Zahrobsky, *J. Am. Chem. Soc., 93*, 3313 (1971).

8 N. W. Issacs and C. H. L. Kennard, *J. Chem. Soc. A*, 1257 (1970).

9 L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin and V. S. Petrosyan, *J. Struct. Chem. (Engl. Transl.), 19*, 91 (1978).

10 E. A. Blom, B. R. Penfold and W. T. Robinson, *J. Chem. Soc. A*, 913 (1969).

11 L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin and V. S. Petrosyan, *J. Struct. Chem. (Engl. Transl.), 18*, 876 (1977).

12 D. Cunningham, I. Douek, M. J. Frazer and M. McPartlin, *J. Organomet. Chem., 90*, C23 (1975).

13 L. Randaccio, *J. Organomet. Chem., 55*, C58 (1973).

14 L. Burger, A. Vertes, A. Tzschach and H. Mech, *Radiochem. Radioanal. Lett., 5*, 335 (1970).

15 V. S. Petrosyan, N. S. Yashina and O. A. Reutov, *J. Organomet. Chem., 52*, 315 (1973).

16 V. S. Petrosyan, N. S. Yashina, V. I. Bakhmutov, A. B. Permin and O. A. Reutov, *J. Organomet. Chem., 72*, 71 (1974).

17 G. M. Bancroft, V. G. Kumar Das and K. D. Butler, *J. Chem. Soc., Dalton Trans.*, 2355 (1974).

18 V. S. Petrosyan, N. S. Yashina, S. G. Sacharov and O. A. Reutov, *J. Organomet. Chem., 52*, 333 (1973).

19 A. G. Davies, H. J. Miledge, D. C. Puxley and P. J. Smith, *J. Chem. Soc. A*, 2862 (1970).

20 L. V. Vilkov and N. A. Tarasenko, *J. Struct. Chem. (Engl. Transl.), 10*, 979 (1969).

Note added in proof:

The Sn-O-E angles in $(CH_3)_3SnCl \cdot 2,6\text{-}(CH_3)_2C_5H_3NO$ and $(C_6H_5)_2SnCl_2 \cdot 2,6\text{-}(CH_3)_2C_5H_3NO$ (E = N) are 130.6(2)° and 125.7(2)°, respectively [A. L. Rheingold, S. W. Ng and J. J. Zuckerman, *Organometallics, 3*, 233 (1984).