

Synthesis and characterization of adducts of dimethyltin(IV) dihalides (Cl, Br) with 1-hydroxymethylpyrazole. The crystal and molecular structure of dichloro(1-hydroxymethylpyrazole)dimethyltin(IV)

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Abstract

Two adducts of 1-hydroxymethylpyrazole (PzCH₂OH) with dimethyltin(IV) dihalides, SnMe₂X₂(PzCH₂OH) (X=Cl, Br), were prepared and characterized by mass, IR, Raman and NMR techniques. The crystal structure of SnMe₂Cl₂(PzCH₂OH) was determined by X-ray crystallography and refined to $R=0.053$, based on 2124 observed reflections. The compound is monoclinic, space group $P2_1/n$, with $a=9.740(2)$, $b=7.325(2)$, $c=15.983(3)$ Å and $\beta=90.27(3)^\circ$. The organic ligand is weakly bonded to Sn through the oxygen atom. The tin atom is five-coordinate trigonal bipyramidal with one Cl and the O atom in apical positions. It is reasonable to think that a similar structure is adopted by the bromine homologue.

Introduction

In previous papers [1–4] we described the preparation of diorganotin dihalide complexes with azole ligands possessing the N-H group. The antitumoral activity of those that were bioassayed, like that of other SnR₂X₂(L-L) systems [5], is limited by their low solubility in water. Since the solubility of N-H drugs is increased by replacing the N hydrogen by CH₂OH or corresponding esters [6, 7], we decided to investigate the effect of such substitution on the coordination of azole ligands to SnR₂X₂ and on the antitumoral activity of the complexes. This paper reports on the interaction of SnMe₂X₂ (X=Cl, Br) with PzCH₂OH (1-hydroxymethylpyrazole) which yielded unusual alcohol complexes, and on the crystal structure of SnMe₂Cl₂(PzCH₂OH).

Experimental

Materials

Dimethyltin dichloride and dimethyltin dibromide (Ventron) were used as supplied. Solvents were

purified by the usual methods. PzCH₂OH was prepared as described elsewhere [8].

Physical measurements

Elemental analyses were performed with a Perkin-Elmer 240B apparatus. Melting points were determined with an Electrothermal apparatus. IR spectra were recorded in Nujol mulls or KBr discs on a Perkin-Elmer 180 spectrometer and Raman spectra were obtained with a Dilor Omars spectrometer (argon ion laser, 5145 Å). Mass spectra were recorded on a Kratos MS50 TC spectrometer connected to a DS90 data system and operating under EI conditions (direct insertion probe, 70 eV, 250 °C); ions were identified by DS-90 software. Molar conductivities were determined with a WTW LF-3 conductivity meter. NMR spectra were recorded on a Bruker WM-250. ¹H chemical shifts were measured relative to the CDCl₃ resonance and referred to TMS and ¹¹⁹Sn chemical shifts were measured in CDCl₃ using tetramethyltin as external reference.

Preparation of compounds

SnMe₂Cl₂(PzCH₂OH) was obtained by adding dropwise a benzene solution of PzCH₂OH (0.1358

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g, 0.0014 mol) to a stirred solution of SnMe_2Cl_2 (0.2991 g, 0.0014 mol) in the same solvent. The white solid that immediately formed was filtered off, washed with benzene and dried under vacuum. $\text{SnMe}_2\text{Br}_2(\text{PzCH}_2\text{OH})$ was prepared similarly. When the reactions were carried out in an acceptor-donor mole ratio of 1:2, the solids obtained were again $\text{SnMe}_2\text{Cl}_2(\text{PzCH}_2\text{OH})$ and $\text{SnMe}_2\text{Br}_2(\text{PzCH}_2\text{OH})$.

Chemical analysis and mass spectra

$\text{SnMe}_2\text{Cl}_2(\text{PzCH}_2\text{OH})$: *Anal.* Found: C, 23.2; H, 3.9; N, 9.1. Calc.: C, 22.7; H, 3.8; N, 8.8%. m.p. 121 °C. The mass spectra showed peaks at m/e (ion, intensity): 68 (HPz, 18.8); 81 (PzCH₂, 24.3); 98 (PzCH₂OH, 48.6); 120 (Sn, 13.8); 155 (SnCl, 44.1); 170 (SnMeCl, 6.3); 185 (SnMe₂Cl, 83.9); 205 (SnMeCl₂, 100.0); 220 (SnMe₂Cl₂, 7.6). Other metallated peaks of higher m/e and low abundance were not identified.

$\text{SnMe}_2\text{Br}_2(\text{PzCH}_2\text{OH})$: *Anal.* Found: C, 17.7; H, 3.1; N, 7.1. Calc.: C, 17.7; H, 3.0; N, 6.9%. m.p. 108 °C. The mass spectra showed peaks at m/e (ion, intensity): 68 (HPz, 5.3); 81 (PzCH₂, 11.2); 120 (Sn, 6.7); 199 (SnBr, 40.9); 214 (SnMeBr, 1.7); 229 (SnMe₂Br, 2.9); 293 (SnMe₂Br₂, 100.0). Other metallated peaks of higher m/e and low abundance were not identified.

Conductivities

Molar conductivities in CH_3CN (10^{-3} M) were $2.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for $\text{SnMe}_2\text{Cl}_2(\text{PzCH}_2\text{OH})$ and $4.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for $\text{SnMe}_2\text{Br}_2(\text{PzCH}_2\text{OH})$.

X-ray data for $\text{SnMe}_2\text{Cl}_2(\text{PzCH}_2\text{OH})$

Crystals suitable for X-ray analysis were obtained by slow crystallization from CDCl_3 . A crystal of max. dimension 0.2 mm was selected and used for the X-ray analysis. Data collection was made with Mo $K\alpha$ radiation on a Philips PW 1100 diffractometer. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and intensity data are reported in Table 1. The crystals were stable under irradiation. Solution of the structure was achieved by Patterson and Fourier methods, alternated with cycles of least-squares refinement of the atomic parameters. All hydrogen atoms were located on the Fourier-difference maps but were generally introduced in calculated positions with fixed C-H distances and isotropic temperature factors (C-H = 0.96 Å, $U_{\text{iso}} = 0.08 \text{ \AA}^2$). Anisotropy was introduced for all non-hydrogen atoms. Refinement of scale factor, positional and thermal parameters was proceeded by minimizing the function $\sum w(\Delta F)^2$ with $w = 1$. At convergence, the largest parameter shift on the refined parameters of the non-hydrogen

TABLE 1. Crystal and intensity data for $\text{SnMe}_2\text{Cl}_2(\text{PzCH}_2\text{OH})$

Formula	$\text{C}_6\text{H}_{13}\text{Cl}_2\text{N}_2\text{OSn}$
Formula weight	339
Cell constants	
a (Å)	9.740(2)
b (Å)	7.325(2)
c (Å)	15.983(3)
β (°)	90.27(3)
V (Å ³)	1140
Density (calc.) (g cm ⁻³)	1.97
Molecules per cell, Z	4
System	monoclinic
Space group	$P2_1/n$
Absorption (Mo $K\alpha$), μ (cm ⁻¹)	28.4
Wavelength (Mo $K\alpha$), λ (Å)	0.7107
Scan method	$\theta/2\theta$
2θ limits (°)	$2^\circ < 2\theta < 50^\circ$
Scan speed (°/min)	2
Data collected	3332
Data with $I > 3\sigma(I)$	2124
Corrections applied	Lp, absorption [9]
Discrepancy factor, R	0.053

TABLE 2. Fractional coordinates and temperature factors ($\times 10^2$) for $\text{SnMe}_2\text{Cl}_2(\text{PzCH}_2\text{OH})$

atom	x	y	z	U_{eq}^a
Sn(1)	0.21442(6)	0.54893(8)	0.42994(3)	3.75
Cl(1)	0.3698(3)	0.4601(4)	0.3244(2)	6.56
Cl(2)	0.0710(3)	0.2756(4)	0.4183(2)	7.28
O(1)	0.3723(6)	0.8171(9)	0.4421(4)	4.90
N(1)	0.5426(7)	0.9501(11)	0.3554(4)	4.48
N(2)	0.6375(8)	1.0246(11)	0.4068(5)	4.98
C(1)	0.3990(8)	0.9499(15)	0.3788(6)	5.43
C(2)	0.7542(9)	0.9991(14)	0.3675(6)	5.49
C(3)	0.7383(10)	0.9082(14)	0.2924(6)	5.65
C(4)	0.5998(10)	0.8746(15)	0.2878(5)	5.38
C(5)	0.0756(9)	0.7324(14)	0.3733(6)	4.91
C(6)	0.2942(10)	0.4930(14)	0.5485(5)	3.66
H(1)	0.438(9)	0.864(13)	0.491(6)	
H(11)	0.335(1)	0.923(2)	0.325(1)	
H(12)	0.374(1)	1.083(1)	0.404(1)	
H(2)	0.852(1)	1.045(1)	0.391(1)	
H(3)	0.816(1)	0.871(1)	0.248(1)	
H(4)	0.547(1)	0.801(1)	0.239(1)	
H(51)	-0.019(1)	0.657(1)	0.373(1)	
H(52)	0.095(1)	0.784(1)	0.311(1)	
H(53)	0.068(1)	0.845(1)	0.416(1)	
H(61)	0.226(1)	0.381(1)	0.534(1)	
H(62)	0.285(1)	0.530(1)	0.614(1)	
H(63)	0.399(1)	0.452(1)	0.536(1)	

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atoms was 0.2 times the standard deviation. No significant residual of electronic density was observed in the final electron density map.

TABLE 3. Bond distances (Å) and angles (°) for SnMe₂Cl₂(PzCH₂OH). e.s.d.s. in parentheses refer to the last significant digit

Sn–Cl(1)	2.363(2)	C(1)–N(1)	1.45(1)
Sn–Cl(2)	2.448(3)	N(1)–N(2)	1.35(1)
Sn–C(5)	2.108(8)	N(2)–C(2)	1.32(1)
Sn–C(6)	2.085(7)	C(2)–C(3)	1.38(1)
Sn–O(1)	2.502(6)	C(3)–C(4)	1.37(1)
O(1)–C(1)	1.43(1)	C(4)–N(1)	1.34(1)
Sn...Cl(2 ^I)	3.916	Cl(2)...Sn ^I	3.916
O(1)...N(2 ^{II})	2.68	H(1)...N(2 ^{II})	1.97
O(1)–Sn–Cl(2)	176.8(2)	Sn–O(1)–C(1)	126.4(5)
O(1)–Sn–Cl(1)	82.9(2)	O(1)–C(1)–N(1)	111.3(7)
O(1)–Sn–C(5)	85.7(3)	C(1)–N(1)–N(2)	120.2(7)
O(1)–Sn–C(6)	81.8(3)	C(1)–N(1)–C(4)	127.9(8)
Cl(2)–Sn–Cl(1)	95.0(1)	N(1)–N(2)–C(2)	104.1(7)
Cl(2)–Sn–C(5)	97.1(3)	N(2)–C(2)–C(3)	113.0(8)
Cl(2)–Sn–Cl(6)	96.8(3)	C(2)–C(3)–C(4)	103.9(8)
Cl(1)–Sn–C(5)	106.3(3)	C(3)–C(4)–N(1)	107.2(8)
Cl(1)–Sn–C(6)	110.9(3)	C(4)–N(1)–N(2)	111.9(7)
C(5)–Sn–C(6)	138.7(4)		

Superscript codes: none = *x, y, z*; I = *x, 1 – y, 1 – z*; II = *1 – x, 2 – y, 1 – z*.

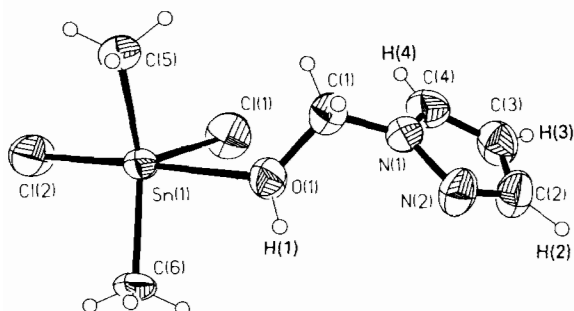


Fig. 1. Crystal structure of SnMe₂Cl₂(PzCH₂OH) with the used numbering scheme.

Form factors for the atoms were supplied internally by the SHELX program system [10]. Final atomic parameters are listed in Table 2; bond distances and angles are reported in Table 3.

Results and discussion

The crystal structure of SnMe₂Cl₂(PzCH₂OH) is shown in Fig. 1 together with the numbering scheme used. The tin atom is five-coordinated in a distorted trigonal bipyramidal arrangement with Cl(2) and O(1) as apical atoms. On the other hand two Sn...Cl contact distances of 3.916 Å, that is at the upper limit of the van der Waals radii sum [11], are present between centrosymmetric molecules in the crystal (for example between the molecule at *x, y, z* and that at $-x, 1 - y, 1 - z$), as shown in Fig. 2. On this

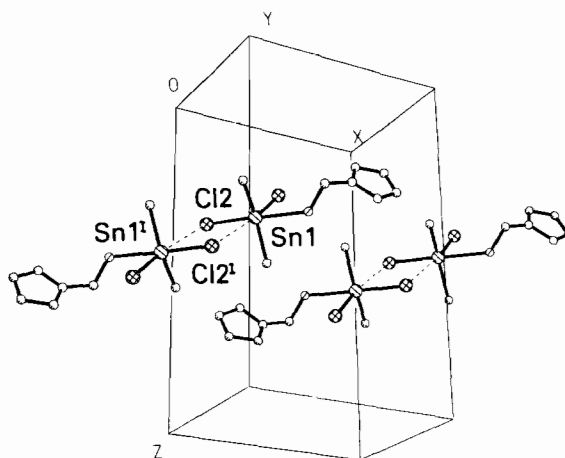


Fig. 2. Pseudo-octahedral dimeric configuration of centrosymmetric SnMe₂Cl₂(PzCH₂OH) pairs in the crystal packing.

basis the compound could be alternatively described as an incipient dimeric complex [12] with the metal atom in a distorted octahedral geometry, the sixth coordination site being filled, in a very broad sense, by the bridging Cl(2) atom of the neighbouring molecule.

Major bond angle deviations with respect to the ideal trigonal bipyramidal coordination geometry appear to be related to the different sizes of the methyl groups, Cl and O atoms. Thus in the base plane, the Me–Sn–Me angle (138.7(4)°) is larger than the Me–Sn–Cl angles (mean 108.6°), while the Cl(2)–Sn–X angles are all significantly larger (up to 15°) than the corresponding O(1)–Sn–X owing to the methyl groups being larger than chlorine and chlorine larger than oxygen. The PzCH₂ fragment seems to play no role in this distortion. The major features of this trigonal bipyramidal geometry are similar to those previously described for the 1:1 adducts of SnMe₂Cl₂ with the O-donors salicylaldehyde [13], tetramethylurea [14] and dibenzylsulfoxide [15]. As in these structures, the two Sn–Cl bonds are not equivalent, the equatorial Cl(1)–Sn bond being shorter than the apical Cl(2)–Sn bond, which is placed *trans* to the oxygen atom. This can be due also, at least in part, to the circumstance that Cl(2) is involved in the bridging contact with the Sn atom of the adjacent molecule. However, both bonds are significantly shorter than the corresponding values of about 2.60 Å found in many octahedral Sn(IV) complexes [3, 14b, 16, 17] and are also shorter than those formed in 1:1 complexes which unequivocally dimerize via Sn–Cl–Sn bridges [18]. The Sn–O distance, although shorter than in other complexes [13, 19], is much longer than the

sum of the covalent radii, and longer than those found in RCH_2OH complexes of tin [20, 21], indicating that the organic ligand is only weakly bonded to the metal atom. Moreover, the ligand oxygen is involved in a relatively short contact of 2.68 Å with the N(2) atom of a neighbouring molecule (see Table 3), which highly suggests the presence of hydrogen bonding in the crystal packing.

The bond lengths in the aromatic ring indicate that π -delocalization of electron density is spread over all five atoms: N(1)–N(2) (1.35(1) Å) is intermediate between the single (1.48 Å in hydrazine) and the double (1.24 Å in azomethane) N–N bond; N(1)–C(4) (1.34(1) Å) and N(2)–C(2) (1.32(1) Å) are close to the aromatic N–C length (1.340(1) Å in pyridine [22]); and C(2)–C(3) (1.37(1) Å) and C(3)–C(4) (1.38(1) Å) are only slightly longer than a C=C double bond. The fact that these bond lengths are all very close to those found in the free pyrazole ring [23] shows that the ring structure is not significantly influenced by either the N-substitution or the coordination via oxygen. Bond lengths and angles in the substituent are normal.

The circumstance that the ligand is coordinated to SnMe_2X_2 via O (rather than N, as in pyrazole [1]), seems to be reasonable if one takes in account the steric hindrance of the $-\text{CH}_2\text{OH}$ substituent.

IR and Raman spectra

The strong and broad band in the IR spectrum of the free ligand at 3140 cm^{-1} ($\nu(\text{OH}) + \nu(\text{CH})$ ring) shows that the OH group is involved in hydrogen bonding in the solid [22]. When the ligand coordinates, this IR band disappears, although narrow bands located around 3110 cm^{-1} (IR, Raman) ($\nu(\text{OH}) + \nu(\text{CH})$ ring) remain. Other significant ligand bands, especially the CH_2OH group vibrations [24] at 1440, 1305, 1280 ($\delta(\text{COH}) + \omega(\text{CH}_2)$), 1085 ($\nu(\text{CO}) + \delta(\text{OH})$) and 1055 ($\nu_{\text{as}}(\text{NCO})$) cm^{-1} or the ring stretching vibrations [25] ($1520\text{--}1340\text{ cm}^{-1}$), undergo very slight shifts on coordination.

The positions and intensities of $\nu_{\text{as}}(\text{Sn-C})$ (580 m, IR; 577 w, R), $\nu_s(\text{Sn-C})$ (530 m, IR; 526 s, R) and $\nu(\text{Sn-Cl})$ (335 s, b, IR; 322 m, R; 270 s, IR; 274 m, R) in the dichloride and $\nu_{\text{as}}(\text{Sn-C})$ (570 m, IR; 568 m, R), $\nu_s(\text{Sn-C})$ (520 m, IR; 517 s, R) and $\nu(\text{Sn-Br})$ (230 s, IR; 228 s, R) in the dibromide are consistent [4, 14, 26] with a trigonal bipyramidal geometry for both compounds.

Mass spectra

That neither compound shows a molecular ion signal may be attributed to the fast fragmentation of these species under EI conditions and/or to thermal decomposition. In the chloride compound spectrum

the very intense [L] ion signal and several others due to its fragmentation which are in keeping with the pattern proposed for fragmentation of alcohols [27], and the abundance of SnMe_2Cl_2 fragments, are in accordance with a fragmentation pathway in which the breakdown of the Sn–O bond is the first stage. On the other hand, the absence of the ligand signal and the low abundance of ligand fragments in the spectrum of the bromide derivative, suggest that a different fragmentation path may be followed.

Solution study

The low values of the molar conductivities indicate non-ionogenic behaviour in CH_3CN for both compounds.

The ^1H NMR spectrum of the ligand at a concentration of 0.1 M in CDCl_3 (5.54, (s, $-\text{CH}_2$); 6.31 (t, H(3)); 7.11 (s,b, $-\text{OH}$) and 7.60 (q, H(2), H(4)) is similar to that recorded by Driessen [8] in 1:1 $\text{CCl}_4/\text{CDCl}_3$ mixture, except for the $-\text{OH}$ signal.

When an equimolar amount of SnMe_2Cl_2 was added to the ligand, the $-\text{OH}$ signal was shifted to 6.65 ppm showing that this group interacts with the tin atom; this interaction may modify the hydrogen bonding that occurs in the free ligand via the $-\text{OH}$ group. The ring signals remain unchanged. When the bromide was added instead of the chloride, $\delta(\text{OH})$ was shifted to 6.95 ppm.

The $\delta(\text{CH}_3\text{-Sn})$ and $^2J(^{117/119}\text{Sn-}^1\text{H})$ values for 1:1 $\text{SnMe}_2\text{Cl}_2/\text{PzCH}_2\text{OH}$ and $\text{SnMe}_2\text{Br}_2/\text{PzCH}_2\text{OH}$ mixtures are 1.20 ppm and 67.3/70.4 Hz, and 1.37 ppm and 63.9/66.8 Hz, respectively. The values of 2J , which is very sensitive to tin coordination type [28], are indicative of weak donor–acceptor interaction because they are close to the values of free SnMe_2Cl_2 (65.6/68.5 Hz) and SnMe_2Br_2 (63.2/66.1 Hz) in CDCl_3 (0.1 M). The values obtained with an acceptor–donor mole ratio of 1:4 (70.8/72.8 Hz for the chloride and 65.7/68.5 Hz for the bromide) show that even under these conditions adduct formation is only slightly favoured. In this case, $\delta(\text{OH})$ is found close to 7.5 ppm, showing reinforcement of the hydrogen bond as the ligand concentration increases.

That the acceptor–donor interaction is weak is supported by the ^{119}Sn NMR data. $\delta(^{119}\text{Sn})$ for a 1:2 $\text{SnMe}_2\text{Cl}_2/\text{PzCH}_2\text{OH}$ mixture is 114.5 ppm, whereas for free SnMe_2Cl_2 at the same 0.1 M concentration the value is 141.9 ppm. This shows that although, as in other systems [29], an increase in the coordination number produces an upfield shift of $\delta(^{119}\text{Sn})$, in this case this shift is small even by comparison with those found for complexes of SnMe_2Cl_2 with weak donors [30].

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References

- B. Alberte, A. Sánchez González, E. García, J. S. Casas, J. Sordo and E. E. Castellano, *J. Organomet. Chem.*, **338** (1988) 187.
- A. Sánchez González, B. Alberte, J. S. Casas, J. Sordo, A. Castiñeiras, W. Hiller and J. Strähle, *J. Organomet. Chem.*, **353** (1988) 169.
- E. García Martínez, A. Sánchez González, A. Macías, M. V. Castaño, J. S. Casas and J. Sordo, *J. Organomet. Chem.*, **385** (1990) 329.
- A. Sánchez González, J. S. Casas, J. Sordo, U. Russo, M. I. Lareo and B. J. Regueiro, *J. Inorg. Biochem.*, **39** (1990) 227.
- G. Atassi, *Rev. Si, Ge, Sn, Pb Comp.*, **8** (1985) 219.
- P. C. Bansal, I. H. Pitman, J. N. S. Taon, M. Mertes and J. J. Kaminski, *J. Pharm. Sci.*, **70** (1981) 850.
- H. Bundgaard, E. Falch and E. Jensen, *J. Med. Chem.*, **32** (1989) 2503.
- W. L. Driessen, *Recl. Trav. Chim. Pays-Bas*, **101** (1982) 441.
- A. T. C. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24** (1968) 351.
- G. M. Sheldrick, *SHELX 76*, a program for crystal structure determination, University of Cambridge, U.K., 1976.
- A. Bondi, *J. Phys. Chem.*, **68** (1964) 441.
- M. M. Amini, E. M. Molt and J. J. Zuckerman, *J. Organomet. Chem.*, **327** (1987) 147.
- D. Cunningham, I. Douek, M. J. Frazer, M. McPartlin and J. D. Matthews, *J. Organomet. Chem.*, **90** (1975) C23.
- (a) G. Valle, S. Calogero and U. Russo, *J. Organomet. Chem.*, **228** (1982) C79; (b) S. Calogero, G. Valle and U. Russo, *Organometallics*, **3** (1984) 1205.
- S. W. Ng and A. L. Rheingold, *J. Organomet. Chem.*, **378** (1989) 339.
- G. Valle, R. Ettore, V. Peruzzo and G. Plazzogna, *J. Organomet. Chem.*, **326** (1987) 169.
- G. Valle, G. Plazzogna and R. Ettore, *J. Chem. Soc., Dalton Trans.*, (1985) 1271.
- (a) R. J. F. Jans, G. Van Koten, K. Vrieze, B. Kojiá-Prodiá, A. L. Spek and J. L. de Boer, *Inorg. Chim. Acta*, **105** (1985) 193; (b) R. J. F. Jans, G. Van Koten, R. R. Andreá, K. Vrieze, A. L. Spek, B. Kojiá-Prodiá and J. L. de Boer, *Recl. Trav. Chim. Pays-Bas*, **105** (1986) 317.
- S. W. Ng, Chen Wei, W. G. Kumar Das, J. P. Charland and F. E. Smith, *J. Organomet. Chem.*, **364** (1989) 343.
- M. Webster and P. H. Collins, *Inorg. Chim. Acta*, **9** (1974) 157.
- (a) S. W. Ng, Chen Wei, W. G. Kumar Das and T. C. W. Mak, *J. Organomet. Chem.*, **373** (1989) 21; (b) **379** (1989) 247.
- B. Bak, L. Hansen and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, **2** (1958) 361.
- J. Berthou, J. Elguero and C. Rerat, *Acta Crystallogr., Sect. B*, **16** (1970) 1880.
- J. P. Perchard and M. L. Josien, *J. Chim. Phys.*, **65** (1968) 1856.
- (a) G. Zerbi and C. Alberti, *Spectrochim. Acta*, **18** (1962) 407; (b) A. Zecchina, L. Cerruti, S. Coluccia and E. Borello, *J. Chem. Soc. B*, (1967) 1363.
- B. V. Liengme, R. S. Randall and J. R. Sams, *J. Can. Chem.*, **50** (1972) 3212.
- R. Davis and M. Frearson, *Mass Spectrometry*, Wiley, New York, 1987.
- T. P. Lockhart and W. F. Manders, *Inorg. Chem.*, **25** (1986) 892.
- J. Otera, *J. Organomet. Chem.*, **221** (1981) 57.
- A. Saxena, F. Huber, L. Pellerito, A. Girasolo, G. C. Stocco, *Inorg. Chim. Acta*, **125** (1986) 197.