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Coordination complexes of dimethyltin dichloride with C-nitroso compounds

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Abstract

Coordination complexes of five nitrosoanilines with dimethyltin dichloride have been prepared and studied by ^{13}C, ^{15}N and ^{119}Sn solid state NMR spectroscopy and by Mössbauer spectroscopy. The ^{13}C resonances of the CH_3–Sn groups, the ^{119}Sn resonances and the Mössbauer quadrupole splitting values permit assignment of the two classes of coordination complexes. The *C*–NO resonances decrease on coordination. The ^{15}N resonances demonstrate that coordination is accompanied by an enhancement of the quinonoid contribution in the ligand itself.

Key words: Dimethyltin; Nuclear magnetic resonance; Mössbauer spectroscopy

1. Introduction

In 1982 Matsubayashi and Nakatsu [1] established that *p*-nitrosodimethylaniline (NODMA) formed a coordination compound with dimethyltin dichloride of composition Me_2SnCl_2 $(NODMA)_2$ in which the C-nitroso compound is σ_0-coordinated to the tin atom. They also demonstrated from the C–C bond lengths in the benzene ring that there is some quinonoid contribution to the structure.

We have discussed the use of IR spectroscopy for determination of the coordination mode of NODMA [2] and summarised the coordination chemistry of C-nitroso compounds in terms of the seven different coordination modes [3] and also demonstrated that the N–O bond lengths and stretching frequencies are interrelated in complexes of aromatic C-nitroso compounds in the same manner as in the free ligands [4].

A variety of spectroscopic techniques has been used to assist understanding of the coordination chemistry of dimethyltin dichloride, namely Mössbauer spectroscopy [5], ^{119}Sn NMR [6], ^{1}H NMR [7] and ^{13}C NMR [8]. It seemed appropriate therefore to bring together a number of NMR spectroscopies and Mössbauer spectroscopy in conjunction with synthetic studies of coordination of a range of substituted nitrosoanilines with dimethyltin dichloride in order to establish correlations of structure with spectroscopy. It was expected that coordination would be σ_0 in character throughout, this being characteristic of non-transition metal complexes of C-nitroso compounds [3].

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2. Experimental details

2.1. Nitrosocompounds

p-Nitroso-*N*,*N*-dimethylaniline (NODMA) and *p*-nitroso-*N*,*N*-diethylaniline (NODEA) were commercially available, *p*-nitrosoaniline (NOA) was donated by Dr. D.A.R. Happer, and 3,5,*N*,*N*-tetramethyl-4-nitrosoaniline (NOTMA) was prepared by nitrosation of commercially available 3,5,*N*,*N*-tetramethylaniline [9]. *N*,*N*-Diphenylpiperazine was prepared by an established procedure [10] and was then nitrosated to give di-(4-nitrosophenyl)-*N*,*N*-piperazine (DNPP) [11]. N^{15} labelling of the nitroso group was achieved by converting, 5% N^{15} enhanced sodium nitrate (Aldrich) to the nitrite by heating with powdered lead [12] and was recrystalled from water. The N^{15}-enhanced sodium nitrite was then used to produce the labelled nitroso compound by nitrosation of the aromatic amine. The hydrochloride hydrate of NODMA was prepared as described by Drangfelt and Rømming [13].

2.2. Coordination compounds

These were prepared by mixing benzene solutions of the ligand and of dimethyltin dichloride in the molar ratio 2.5 : 1 [1]. The complexes separated out at once, and were filtered off and recrystallised from benzene. The analytical data are summarised in Table 1.

Solid state CPMAS NMR spectra (^{13}C, ^{15}N, ^{119}Sn) were recorded by the SERC service at the Industrial Research Laboratories, University of Durham. ^{13}C NMR spectra of solid samples were obtained at 75.431 MHz using cross-polarization (CP), magic angle spinning (MAS), and high power decoupling. Contact times ranged from 1.0 to 2.0 ms. Relaxation delays ranged from 2 to 15 s. MAS rates were 3685–5160 Hz. All cross-polarization spectra were obtained with the Hartman–Hahn match condition fulfilled. The carbon secondary reference standard was adamantane CH_2 signal at 38.4 ppm relative to TMS.

^{15}N NMR spectra were obtained at 30.405 MHz. Contact times ranged from 4.0 to 9.0 ms. Relaxation delays ranged from 1 to 10 s. MAS rates were 2411–5360 Hz. The nitrate signal in a 20% enriched solid sample of ammonium nitrate was used as the primary reference (*i.e.* 0 ppm). The magic angle was set by minimising the nitrate signal linewidth for the ammonium nitrate sample.

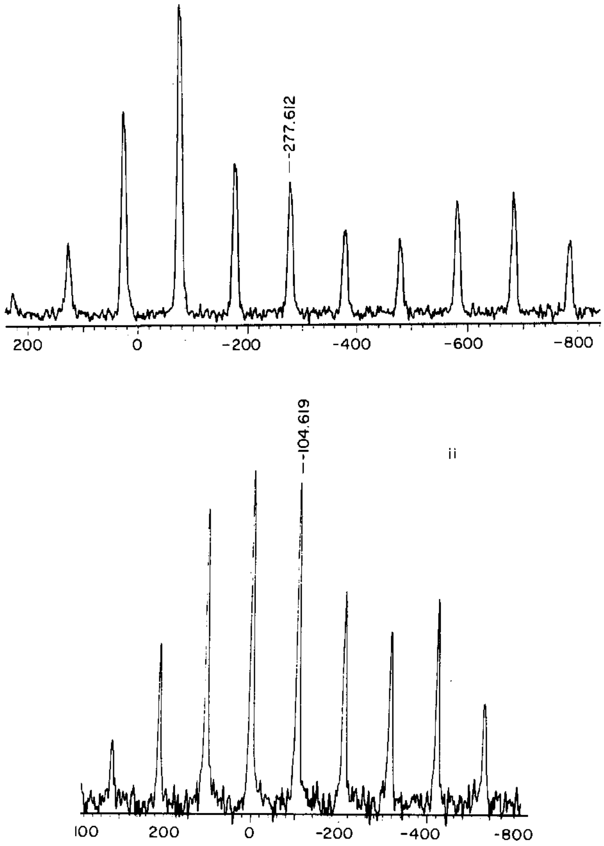


Fig. 1. ^{119}Sn solid state CPMAS NMR spectra of: (i) $(NOTMA)_2$-Me_2SnCl_2; (ii) (NODEA) Me_2SnCl_2.

Sn NMR spectra were obtained at 111.862 MHz using CP MAS and high power decoupling. Contact times ranged from 2.6 to 20.0 ms. Relaxation delays varied from 2.0 to 20.0 s. MAS rates were 5320–13 370 Hz. The secondary reference standard was tetra cyclohexyltin (signal at −97.4 ppm relative to tetramethyltin, the primary standard.).

Figure 1 displays some of the ^{119}Sn NMR spectra.

TABLE 1. M.p. and analytical data for the coordination compounds (A denotes dimethyltin dichloride)

Compound	M.p. (°C)	Found			Formula requires		
		%C	%H	%N	%C	%H	%N
$A \cdot (NODMA)_2$	143–145 dec	41.7	5.1	10.7	41.5	5.0	10.8
A · NODEA	116.8 dec	38.3	5.7	7.3	36.2	5.0	7.0
$A \cdot (NOTMA)_2$	147–148 dec	45.7	5.8	9.7	45.8	5.9	9.7
$A \cdot (NOA)_2$	178–181	36.3	3.9	11.9	36.2	3.9	12.1
A · DNPP	200–205	42.3	4.3	11.3	41.9	4.3	10.9

TABLE 2. ^{13}C, ^{15}N and ^{119}Sn resonances for Me_2SnCl_2 complexes and ^{13}C and ^{15}N resonances for the free ligands (values in ppm)

	C(1) [a]	C(2)	C(3)	C(4)	C(5)	C(6)	$(CH_3)_2Sn$	$N(CH_3)_2$	Other C	NO [b]	NR_2 [b]	Sn
NODMA	165.0	112.0	112.0	156.4	112.0	142.5	–	41.3	–	429.7	−295.3 −299.1	–
NODMA.HCl	162.8	126.0	124.4	151.5	121.8	142.8	–	45.7	–	54.8	−207.3	–
$(NODMA)_2.Me_2SnCl_2$	159.7	121.9	118.0	159.7	118.0	144.1	22.4	43.8	–	238.6 223.2	−251.1	−281.0
NODEA	163.2	109.8	109.8	153.5	109.8	142.3 140.8	–	44.6	11.0 12.6	420.7	−264.0	–
$NODEA.MeSnCl_2$	157.9	121.8	115.5	157.4	114.4	140.9	19.6	48.7 47.7	14.8 16.5	237.8	−228.2	−106.0
NOTMA	162.0	138.7	112.7	153.9	111.3	135.2	–	39.2 38.4	22.8 20.9	6.43	−294.5	–
$(NOTMA)_2Me_2SnCl_2$	157.5	135.4	115.1	154.8	115.1	135.4	18.8	43.9 42.5	25.2 21.8	64.3	−253.3	−277.6
NOA [c]	163.4	125.8	112.2	157.0	112.2	125.8	–	–	–	[d]	[d]	–
$(NOA)_2Me_2SnCl_2$	164.5	125.9	117.7	160.0	117.7	146.7	19.8	–	–	[d]	−255.1	−254.8
DNPP	164.4	122.3	109.1	154.3	109.1	139.7	–	44.7 42.7	–	[d]	−290.3 −309.1	–
$DNPP.Me_2SnCl_2$	163.0 156.0	115.8	111.3	157.6 153.7	111.3	145.5 141.1	14.5	48.4 45.1	–	[d]	−288.4 −236.5	−95.2

[a] Numbering based on I. [b] Values relative to $NH_4^+NO_3^-$ solid. [c] Solution spectra. [d] Not determined.

The data are summarised in Table 2. Mössbauer spectra were obtained with samples cooled to *ca.* 80 K with ($CaSnO_3$) at ambient temperature as the source, in conventional transmission geometry, using a Harwell 6000 spectrometer and proportional detector. The spectra were fitted as Lorentzian doublets. The results are summarised in Table 3.

3. Discussion of results

It is well established that diorganotin dihalides can form both 1:1 and 1:2 adducts with a variety of bases [6]. Several techniques have been employed in the study of the structures of these compounds. It is of obvious advantage to focus upon those used for the study of complexes of dimethyltin dichloride. Lockhart and Manders [8] showed that the ^{13}C-shifts of the Sn–methyl generally increased in the series tetra- < penta- < hexa- < hepta-coordinated methyltin(IV) compounds. From their data for coordination through oxygen to dimethyltin dichloride the shifts for three 1:2 adducts is seen to fall within the range 19.6–28.5 ppm, and for four 1:1 adducts in the range 14.6–19.0 ppm, and our values for the Sn–methyl shifts show that the NODMA, NOTMA and NOA complexes are 1:2 adducts whereas the NODEA and DNPP complexes are 1:1 adducts.

TABLE 3. Mössbauer spectra of dimethyltin dichloride complexes. (isomer shift and quadrupole splitting at 80 K in the compounds listed; all values are in mm s^{-1} with an accuracy of ±0.03 mm s^{-1})

Compound	Isomer shift	Quadrupole splitting	Widths	
$Me_2SnCl_2(NODMA)_2$	1.42	4.03	0.93	1.05
$Me_2SnCl_2.NODEA$	1.45	3.70	0.98	0.95
$Me_2SnCl_2(NOTMA)_2$	1.42	4.04	0.86	0.96
$Me_2SnCl_2(NOA)_2$	1.41	4.30	0.96	0.97
$Me_2SnCl_2.DNPP$	1.30	3.43	1.01	1.08

Lockhart and Manders have also observed an empirical relationship

$$^1J(^{119}Sn, ^{13}C) = 10.7(Me\text{–}Sn\text{–}Me \text{ angle}) - 778$$

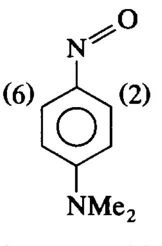
for 28 compounds whose X-ray crystal structures are known. Use of the literature value [1] of 180° for the angle in the NODMA derivative predicts a value for ^1J of 1148 Hz, whereas our experimental value is 423 Hz. It should be noted that Lockhart and Manders clearly demonstrated that predicted Me–Sn–Me angles are suspect for hexacoordinated dimethyltin(IV) compounds that have ^1J values less than about 650 Hz and bear three or four strongly electronegative atoms (O, N, Cl) bonded to tin.

The ^{119}Sn NMR data fall into two distinct groups. The 1:2 complexes give values for δ ^{119}Sn similar to that, of −246 ppm, reported [14] for $Me_2SnCl_2(DMSO)_2$, whereas the pentacoordinated 1:1 complexes have δ ^{119}Sn values intermediate between that for dimethyltin dichloride (coordination number four) (+141.2 ppm in saturated carbon tetrachloride [15]) and those for our hexacoordinated compounds.

A further discrimination between the two groups of coordination compounds is provided by Mössbauer spectroscopy. The quadrupole splitting values of the 1:2 complexes 4.03 (NODMA), 4.04 (NOTMA) and 4.30 (NOA) mm s^{-1} are consistent with a *trans*-octahedral structure in each case and essentially linear C–Sn–C units. The lower quadrupole splitting values for the two other complexes 3.70 (NODEA) and 3.43 (DNPP) mm s^{-1} are consistent with five coordinate Me_2Sn units. A recently studied distorted octahedral complex of dimethyltin dichloride has a quadrupole splitting value of 4.32 mm s^{-1} [16].

This combination of the analytical data, Mössbauer spectroscopy, ^{119}Sn NMR spectroscopy and ^{13}C NMR spectroscopy of the $(CH_3)_2SnCl_2$ give a consistent picture of the structural possibilities at the Me_2Sn unit in the solid complexes. It is, however, of considerable interest to establish the structural consequences for the nitroso-compounds themselves when they engage in σ_0-coordination to tin. Information concerning this is provided by ^{13}C and ^{15}N NMR spectroscopy and we consider these in turn below.

Some years ago one of us pointed out that the very large substituent ^{13}C NMR chemical shift of the *ipso*-C in nitrosobenzene was accompanied by a unique effect of the NO group upon electron acceptor groups situated *para* to NO [17] in that they became electron donating. It was also shown that even strong electron donor groups in the *para* position, such as dialkylamino, had smaller effects upon the chemical shift of the carbon attached to the NO group than would be the case in other *p*-disubstituted benzenes. It was of interest to see whether coordination by the NO group to metals had any marked effect upon the ^{13}C NMR spectra compared to that in the free ligand. A study of some σ_N coordinated nitrosocompounds of platinum was previously undertaken [18] but there have been no previous reports of the effect of σ_0-coordination on the ^{13}C NMR spectra of substituted *p*-nitrosoanilines. After these studies were initiated a solid state ^{13}C NMR spectrum of NODMA was reported [19], and the authors showed that the difference between the chemical shifts of C-2 and C-6 ($\Delta_{2,6}$) in the solid (I) (−30.8 ppm) is comparable with the low temperature solution values for nitrosobenzene [20] (−34.5 ppm) and NODMA [21] (−31.6 ppm). These $\Delta_{2,6}$ values are by far the largest yet discovered for any functional group (compare CHO 6.7, COMe 3.8, OMe 7.9, NHMe 6.4, SMe 4.2 ppm [19]) and arise from the considerable magnetic anisotropy of the NO group. They are found for any nitrosobenzene derivative where the NO group is in a fixed *anti*-configuration either in the solid state or by inhibition of rotation at low temperatures in solution or by bulky substituents in the C-6-position [22]. The same effect seen in the low temperature solution data for NODEA, where the value [23] for $\Delta_{2,6}$ is −30.9 ppm. The solid state of NODEA has two crystallographically distinct forms [24], reflected in a doublet line for C-2 and $\Delta_{2,6}$ of −31.0 and −32.5 ppm.



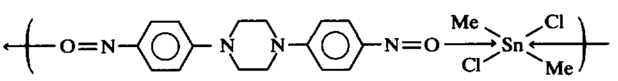
(I)

The effect described in the preceding paragraph has long been known in the proton NMR spectra of a range of *ortho*-substituted aromatic nitroso compounds [25,26], and it has been ascribed to the large magnetic anisotropy of the nitroso group. It is apparent that the N=O group displays a unique property in the ^{13}C NMR spectra of substituted nitrosobenzenes which is quite distinct from that of the isoelectronic -CHO and other non-symmetrical nitrogen functional groups that possess a non-bonded electron pair. The large $\Delta_{2,6}$ effect can perhaps best be interpreted in terms of transoid/cisoid electronic effects in the *anti/syn* dispositions, but, in keeping with the explanation advanced in the literature we provisionally ascribe the effect to magnetic anisotropy.

It was of interest to see whether this effect of the magnetic anisotropy of the NO group persists after σ_0-coordination to tin. It is evident that for coordinated NODMA the value of $\Delta_{2,6}$ has changed to −22.2 and that for coordinated NODEA to −19.1 ppm. In NOA the coordination compound shows a $\Delta_{2,6}$ value of −20.8 ppm. It is evident, therefore, that a considerable measure of magnetic anisotropy persists in these complexes even though the electron distribution at the O atom is modified by σ_0 coordination. In this context the position of the NOTMA ligand shows an interesting variation because of the presence of methyl groups on the 2 and 6 ring carbons. There is a small magnetic anisotropy effect on the 2 and 6 carbons in NOTMA itself, $\Delta_{2,6}$ being only −6.2 ppm, and this is presumably due to the NO being twisted out of the plane of the ring as a result of to the steric effect of the methyl groups. It is noteworthy that Belya'ev [27] used dipole moment data to show that the NO group is twisted by ~ 14° out of the plane of the ring in 3,5-dimethyl-*N*,*N*-diethyl-4-nitrosoaniline. On the other hand, the NO cannot be twisted into orthogonality with the ring in NOTMA, because in such a case the effect on both the 2,6 carbons would be the same. In the NOTMA coordination complex, however, the value $\Delta_{2,6}$ has fallen to zero, and this suggests that the NO is now orthogonal to the ring. The alteration in the value of $\Delta_{2Me,6Me}$ on coordination from −1.9 to −6.4 ppm is presumably due to the fact that in the coordination compound one of the ring methyls lies closer to the Me_2SnCl_2 plane than the other.

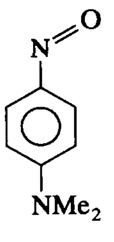
The effects on the other ring carbons on coordination are similar. Thus the C1 resonance falls by 5.3 (NODMA), 4.5 (NOTMA), or 5.3 ppm (NODEA), with corresponding rises for the C3,5 resonances of 6.0 (NODMA), 3.8 (NOTMA), and 5.6 ppm (NODEA), and for the C4 resonance of 3.3 (NODMA), 0.9 (NOTMA), and 3.9 ppm (NODEA). Thus in species involving σ_0 coordination there are generally similar effects at these four ring carbons even though the stoicheiometry of the NODEA complex differs from that of the other two. The fall in the C1 resonance on coordination is in marked contrast to effect for the σ_N complex $PhNO.PtCl_3^-$, for which the C1 resonance rises by 6.2 ppm on coordination [18]. Further studies are required for other σ_0 and σ_N cordination complexes before any generalisations can be made. We have noted previously [2,4] that some proposed correlations of single spectroscopic parameters with coordination mode can be misleading.

The DNPP ligand was chosen for study because it contains two separate nitroso-groups, and we envisaged the possibility of coordinative polymerization in which the repeating units would be

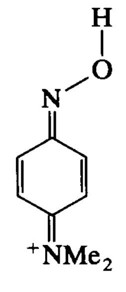


This however does not occur since the coordination at the tin is clearly pentacoordinate, as demonstrated by the three spectroscopic techniques employed. In the ^{13}C NMR spectrum of this 1:1 complex there is an indication of the asymmetry of the ligand arising from the fact that coordination takes place with only one of two NO groups.

It remains to discuss the ^{15}N NMR spectra. We emphasise that the natural abundance spectra give data only for the amino nitrogen, and that it is necessary to use 5% enhanced nitrite in the nitrosation step in order to determine the nitroso nitrogen resonance. The combination of both of these values allows estimation of the quinonoid character of the nitrosocompound in the coordination compound. Some years ago Bonnett noted [28] that the ^{15}N resonance of the NO group in NODMA fell by 386 ppm when the hydrochloride was formed owing to the change in structure from **II** to **III**.



(II)



(III)

Some evidence for quinonoid contribution to the structures of nitrosoanilines coordinated to metals has been provided by the X-ray crystallographically determined bond lengths in NODMA σ_0 coordinated to dimethyltin dichloride [1] or zinc chloride [29] or σ_N coordinated to cobalt chloride [30], although this effect is smaller than that in the hydrochloride of NODMA [13]. In the absence of X-ray crystal structure analysis ^{15}N NMR spectral data for the ligands provides a good indication of the quinonoid contribution (see Table 2). The shift for the nitroso nitrogen is 429.7 ppm in NODMA itself and falls to 54.8 ppm in the hydrochloride, a change similar to that observed by Bonnett for solutions. The intermediate values of 238.6 and 223.2 ppm in $(NODMA)_2\ Me_2SnCl_2$ are close to the average of the above values. A similar situation is revealed for the amino nitrogen, for which the shift rises from NODMA itself (−295.3 ppm), through the coordination complex (−251.6 ppm), to the hydrochloride (−207.3 ppm).

The wide range of NODMA coordination compounds suggests that detailed studies of ^{15}N NMR spectra of these complexes would provide useful evidence for the effect of both σ_N and σ_0 coordination on the structure of the ligand.

There appears to be a similar effect on the ^{15}N resonances for the other nitrosoaniline ligands, and it is noteworthy that the large shifts of the NO resonance that is the coordinating site of the molecule (*ca.* 200 ppm) are accompanied by smaller shifts for the R_2N nitrogen (approx 40 ppm) even though this is remote from the coordination site. We conclude that coordination by the NO generally increases the contribution of the quinonoid form of nitrosoaniline ligands. Confirmation by X-ray crystallographic studies is desirable.

It is clear that the range of shifts of the ^{15}N resonances on coordination does not differ for 1:1 and 2:1 complexes.

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References

1 G.E. Matsubayashi and K. Nakatsu, *Inorg. Chim. Acta, 64* (1982) L163.

2 M. Cameron, B.G. Gowenlock and G. Vasapollo, *J. Organomet. Chem.*, *378* (1989) 493.

3 M. Cameron, B.G. Gowenlock and G. Vasapollo, *Chem. Soc. Rev.*, *19* (1990) 355.

4 M. Cameron, B.G. Gowenlock and G. Vasapollo, *J. Organomet. Chem.*, *40* (1991) 325.

5 M. Cordey-Hayes, R.D. Peacock and M. Vucelic, *J. Inorg. Nucl. Chem.*, *29* (1967) 1177.

6 C.H. Yoder, D. Mokrynka, S.M. Coley, J.C. Otter, R.E. Haines, A. Grushow, L.J. Ansel, J.W. Hovick, J. Mikus, M.A. Shermak and J.N. Spencer, *Organometallics*, *6* (1987) 1679.

7 B. Alberte, A. Sanchez Gonzalez, E. Garcia, J.S. Casas, J. Sordo and E.E. Castellano, *J. Organomet. Chem.*, *338* (1988) 187.

8 T.P. Lockhart and W.F. Manders, *J. Am. Chem. Soc.*, *109* (1987) 7015.

9 G. Matsubayashi, Y. Takaya and T. Tanaka, *Spectrochim. Acta A*, *26* (1970) 1851.

10 D.S. Pratt and C.O. Young, *J. Am. Chem. Soc.*, *40* (1918) 1428.

11 R. Fabré and G. Bertrand, *Rev. gen. caout. plast.*, *42* (1965) 405.

12 V.A. Maimind, B.V. Tokarev, E. Gomes, R.G. Vdovina, K.M. Ermolaev and M.M. Shemyakin, *J. Gen. Chem. USSR*, *26* (1956) 2187; *Chem. Abs.*, *51* (1957) 5001c.

13 O. Drangfelt and C. Rømming, *Acta Chem. Scand., A.*, *28* (1974) 1101.

14 J.D. Kennedy and W. McFarlane, *J. Chem. Soc., Perkin Trans. 2*, (1974) 146.

15 C.R. Lassigne and E.J. Wells, *Can. J. Chem.*, *55* (1977) 927.

16 T.K. Chattopadhyay, A.K. Kumar, A. Roy, A.S. Batsanov, E.B. Shamuratov and Yu.T. Struchkov, *J. Organomet. Chem.*, *419* (1991) 277.

17 B.M. Al-Tahou and B.G. Gowenlock, *Rec. Trav. Chim. Pays Bas*, *105* (1985) 253.

18 A.S.F. Boyd, G.M. Browne, B.G. Gowenlock and P. McKenna, *J. Organomet. Chem.*, 345 (1988) 217.

19 G.H. Penner and R.E. Wasylishen, *Can. J. Chem.*, *67* (1989) 525.

20 L. Lunazzi, D. Macciantelli and G. Placucci, *Tetrahedron Lett.*, *21* (1980) 975.

21 Y.K. Grishin, N.M. Seryeyev, O.A. Subbotin and Y.A. Ustynyuk, *Mol. Phys.*, *25* (1973) 297.

22 M. Cameron, *Ph.D. Thesis*, Heriot-Watt University, 1992.

23 V.V. Negrebetskii, A.I. Bokanov and B.I. Stepanov, *Zhur. Strukt. Khim.*, *22* (1981) 88.

24 H.J. Talberg, *Acta Chem. Scand.*, *A31* (1977) 743.

25 R.J. Sundberg, *Tetrahedron*, *23* (1967) 1583.

26 R. Okazaki and N. Inamoto, *J. Chem. Soc., B*, (1970) 1583.

27 E. Yu Belyaev, G.A. Suboch and A.V. El'tsov, *J. Org. Chem. USSR*, *15* (1979) 1185.

28 R. Bonnett, R. Holleyhead, B.L. Johnson and E.W. Randall, *J. Chem. Soc., Perkin Trans. 1*, (1975) 2261.

29 S. Hu, D.M. Thompson, P.O. Ikekwere, R.J. Barton, K.E. Johnson and B.E. Robertson, *Inorg. Chem.*, *28* (1989) 4552.

30 D.B. Sams and R.J. Doedens, *Inorg. Chem.*, *18* (1979) 153.