Organic Magnetic Resonance, 1970, Vol. 2, pp. 165 to 172. Heyden & Son Limited. Printed in Northern Ireland

NMR SPECTRA OF SOME ALKYL(OXINATO)TIN(IV) COMPLEXES

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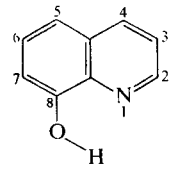
(*Received* 5 *December* 1969; *accepted* 6 *January* 1970)

Abstract—Proton magnetic resonance spectra of a series of alkyl(oxinato)tin(IV) complexes, alkyl-(oxinato)thallium(III), dimethylbis(oxinato)lead(IV), 8-methoxyquinoline, 2-methyl-8-hydroxyquinoline and 8-hydroxyquinoline were studied. The indirect spin-spin coupling constants J_{23}, J_{34} and J_{24} of the oxinato ligand in the alkyl(oxinato)tin(IV) complexes and of 8-methoxyquinoline were found to be $4{\cdot}4 \pm 0{\cdot}2$, $8{\cdot}3 \pm 0{\cdot}2$ and $1{\cdot}7 \pm 0{\cdot}2$ Hz, respectively. When the interaction between tin and nitrogen in the oxinato ligand is not strong as in trialkyl(oxinato)tin(IV), the resonance of the 2-proton of the ligand shifts to high magnetic field relative to that of 8-methoxyquinoline, but in the case of the strong interaction, as in dimethyl(oxinato)halogenotin(IV), the resonance is shifted to low magnetic field. The 4-proton signals, however, shift monotonously to low magnetic field with increasing interaction. The behaviour of the 2-proton signals was explained by a paramagnetic anisotropic effect of a nitrogen lone pair of the oxinato ligand and an intramolecular electric field effect and that of the 4-proton by the latter effect. By comparing the change of the δ-values of the 2-, 3- and 4-protons of the alkyl(oxinato)tin(IV) complexes and those of 8-hydroxyquinoline by altering the solvents, from methylene chloride to benzene, it was found that the electron density around the 2-carbon is reduced in the complexes compared with that of 8-hydroxyquinoline.

INTRODUCTION

8-HYDROXYQUINOLINE [Hox: (**1**)] is a well known bidentate ligand. It forms very stable complexes with metal ions and is frequently used as an analytical reagent.



(**1**)

Usual chelated complexes show an absorption maximum at about 360 to 430 nm in the UV spectra.[1,2] The position of this absorption maximum is closely related to the stability constants of these complexes.[2] Many organo(oxinato)tin(IV)[3 to 10] and organo(oxinato)antimony(V)[11,12,13] complexes have been prepared and the chelated configuration has been established for most of the complexes by X-ray crystallographic analysis[14] and the UV spectra.[3 to 13,15,16] In some cases, however, it has been reported that the oxinato ligand acts as a monodentate ligand in solution.[4,12,15,16] Proton magnetic resonance studies on these organo(oxinato)metal complexes are rather limited.[10,12,13]

For a better understanding of the chelate configuration and the metal-nitrogen interaction, we have studied the proton magnetic resonance spectra of a series of alkyl(oxinato)tin(IV), alkyl(oxinato)thallium(III), dimethylbis(oxinato)lead(IV),

8-methoxyquinoline, 2-methyl-8-hydroxyquinoline and 8-hydroxyquinoline in methylene chloride, deuterochloroform and methanol. The spectra were also measured in benzene in order to examine the interaction of the complexes with this solvent and the change of the electron density in the complexes from that of 8-hydroxyquinoline.

EXPERIMENTAL

8-Hydroxyquinoline and 2-methyl-8-hydroxyquinoline were obtained from commercial sources and were used without further purification. 8-methoxyquinoline was obtained from the reaction of 8-hydroxyquinoline and dimethyl sulfate in 95% ethanol[17] and was purified by distillation at reduced pressure. Alkyl(oxinato)tin(IV) complexes[8] and $Me_2Pb(ox)_2$[18] were obtained by using the reported methods. The proton magnetic resonance measurements were made with a Japan Electron Optics model JNM-3H-60 spectrometer operating at 60 MHz and a Varian HA-100 spectrometer. The chemical shifts were measured relative to tetramethylsilane as internal standard. The concentration was 7 to 10% w/w.

RESULTS AND DISCUSSION

The proton magnetic resonance spectra of most of alkyl(oxinato)metal complexes* in organic solvents show two sharp quartets and a multiplet in a range $\delta 7$ to 9.† The quartet, at low magnetic field, was assigned to the 2-proton of the oxinato ligand§ and that at high magnetic field to the 4-proton by comparison with the result of 8-hydroxyquinoline.[23] The indirect spin-spin coupling constants J_{23}, J_{34} and J_{24} for the oxinato ligand protons, obtained from these two quartets, were found to be $4{\cdot}4 \pm 0{\cdot}2$, $8{\cdot}3 \pm 0{\cdot}2$ and $1{\cdot}7 \pm 0{\cdot}2$ Hz, respectively and are the same for all complexes within experimental error. These values agree with those of 8-hydroxyquinoline[23] and 8-methoxyquinoline.

The assignment of these spectra was confirmed by the results of 2-methyl-8-hydroxyquinoline, which gives a singlet, a multiplet and a doublet at $\delta 2{\cdot}69$, $7{\cdot}32$ and $7{\cdot}97$, respectively. The singlet and the doublet were assigned to the 2-methyl and the 4-protons, respectively. The value J_{34} was found to be $8{\cdot}4 \pm 0{\cdot}2$ Hz, from the separation of the doublet, and is very close to the corresponding value in 8-hydroxyquinoline.

The signals of the 3-proton in alkyl(oxinato)metal complexes and 8-methoxyquinoline overlap with those of the 5-, 6- and 7-proton as in 8-hydroxyquinoline.[23] The δ values of the 3-proton can, however, be obtained by inspection of the multiplet using the values of J_{23} and J_{34}. The δ values of the 2-, 3- and 4- protons for several alkyl(oxinato)metal complexes, 8-methoxyquinoline, 2-methyl-8-hydroxyquinoline and 8-hydroxyquinoline in organic solvents are shown in Table 1. The results for some alkyl(oxinato)antimony(V) complexes[12,13] are also included in this Table.

The chemical shifts of the oxinato ligand for an equimolar mixture of R_2SnX_2 (X = Cl, Br, I, NCS and $C_6H_5CO_2$) and $R_2Sn(ox)_2$ are almost the same as those

* The signals due to alkyl groups are omitted in the present study.

† In the case of aryl(oxinato)metal complexes, we could not obtain well resolved spectra for the oxinato protons. The anisotropic effect of the aryl groups bonded to metal seems to effect these proton signals.

§ For the proton chemical shifts of nitrogen heterocyclic aromatic molecules, the effects of (i) ring current, (ii) paramagnetic anisotropy of nitrogen lone pairs and (iii) charges on the other atoms in the molecule are very important.[19 to 22] For anomolous down-field shifts of the protons bonded to carbon atoms adjacent to nitrogen atoms the latter two effects are very important. The magnitude of these two effects is of the same order for these protons.[19 to 22]

TABLE 1. PROTON CHEMICAL SHIFTS (δ) OF SOME ALKYL(OXINATO)METAL COMPLEXES AND RELATED COMPOUNDS

Compound	Solvent	2-H	3-H	4-H	Reference
8-methoxyquinoline	CH_2Cl_2	8·77	7·31	8·01	*
	CH_3OH	8·69	7·41	8·17	*
8-methoxyquinoline + $(CH_3)_2SnCl_2$	CH_2Cl_2	9·13	7·63	8·43	*
8-hydroxyquinoline	CH_2Cl_2	8·69	7·37	8·11	*
	CH_3OH	8·64	7·33	8·13	*
2-methyl-8-hydroxyquinoline	CH_2Cl_2		7·21	7·97	*
$Me_3Sn(ox)$	CH_2Cl_2	8·53	7·34	8·17	*
$Et_3Sn(ox)$	CH_2Cl_2	8·57	7·31	8·18	*
$^nPr_3Sn(ox)$	CH_2Cl_2	8·58	7·32	8·17	*
$^nBu_3Sn(ox)$	CH_2Cl_2	8·59	7·32	8·18	*
	CH_3OH	8·55	7·33	8·12	*
$Me_2Sn(ox)_2$	CH_2Cl_2	8·45	7·08	8·10	*
$Et_2Sn(ox)_2$	CH_2Cl_2	8·44	7·07	8·06	*
$^nPr_2Sn(ox)_2$	CH_2Cl_2	8·42	7·07	8·05	*
$^nBu_2Sn(ox)_2$	CH_2Cl_2	8·44	7·06	8·06	*
$Me_2SnCl(ox)$	CH_2Cl_2	8·67	7·54	8·42	*
$Me_2SnBr(ox)$†	CH_2Cl_2	8·71	7·55	8·45	*
$Me_2SnI(ox)$†	CH_2Cl_2	8·67§		8·42§	*
$Me_2SnNCS(ox)$	CH_2Cl_2	8·67	7·59	8·50	*
$Me_2Sn(benz)(ox)$†‖	CH_2Cl_2	8·63		8·34	*
$Et_2SnCl(ox)$†	CH_2Cl_2	8·75	7·53	8·44	*
$Et_2SnBr(ox)$†	CH_2Cl_2	8·75	7·55	8·46	*
$Et_2SnNCS(ox)$†	CH_2Cl_2	8·69	7·58	8·50	*
$^nPr_2SnCl(ox)$†	CH_2Cl_2	8·74	7·54	8·44	*
$^nPr_2SnNCS(ox)$	CH_2Cl_2	8·66	7·58	8·49	*
$^nBu_2SnCl(ox)$†	CH_2Cl_2	8·74	7·54	8·44	*
$^nBu_2SnNCS(ox)$†	CH_2Cl_2	8·66	7·59	8·50	*
$MeSnCl(ox)_2$	CH_2Cl_2	8·62¶		8·24§	*
$^nBuSnCl(ox)_2$	CH_2Cl_2	8·62¶		8·24§	*
$^nBuSnBr(ox)_2$	CH_2Cl_2	8·56¶		8·24§	*
$^nBuSn(ox)_3$	CH_2Cl_2	9·01	7·28	8·03	10
$Me_4Sb(ox)$	$CDCl_3$	8·50		8·14	12
$Et_4Sb(ox)$	$CDCl_3$	8·39		7·98	12
$Me_3SbCl(ox)$	$CDCl_3$	8·76		8·24	12
$Me_3SbBr(ox)$	CH_2Cl_2	8·69	7·37	8·17	13
$Et_3SbCl(ox)$	$CDCl_3$	8·70		8·20	12
$Me_2SbCl_2(ox)$	$CDCl_3$	9·36		8·58	12
$Et_2SbCl_2(ox)$	$CDCl_3$	9·31		8·64	12
$MeSbCl_3(ox)$	$CDCl_3$	9·58		8·64	12
$Me_2Pb(ox)_2$	CH_2Cl_2	9·11	7·41	8·24	*
$MeEtTl(ox)$	$CDCl_3$	8·37	7·27	8·06	*
$Et_2Tl(ox)$	$CDCl_3$	8·36	7·25	8·04	*
$MeTl(ox)_2$	$CDCl_3$	8·83¶	7·41	8·11	*
	CD_3OD	8·77¶	7·42	8·19	*
$EtTl(ox)_2$	$CDCl_3$	8·79	7·35	8·10	*

* Present work.

† Mixture of equimolar amount of $R_2Sn(ox)_2$ and R_2SnX_2.

§ Broad.

‖ $C_6H_5COO^-$.

¶ Very broad.

in $(CH_3)_2SnCl(ox)$.* The proton signals in this type of complex are a little broad compared with those in $R_3Sn(ox)$ and $R_2Sn(ox)_2$. The equilibrium (1) is almost at right in the solution, except for X = I, in which the

$$R_2SnX_2 + R_2Sn(ox)_2 \rightleftharpoons 2R_2SnX(ox) \quad (1)$$

signals of the oxinato ligand and also the methyl protons, attached to tin, are rather broad. The result indicates that in this system the equilibrium (1) is not completely shifted to the right side. The very broad signals in the oxinato protons in $RSnX(ox)_2$ are probably due to a configurational exchange as in $RSnX(acac)_2$.[24]

The proton signals of the oxinato ligand in RR'Tl(ox) give sharp quartets for the 2- and 4- protons, but those in $RTl(ox)_2$ are a little broad. The result implies that there is no appreciable indirect spin-spin coupling between thallium and the 2- and 4- protons in RR'Tl(ox) and, therefore, the Tl—N bond is rather weak or ionic, although the UV spectral data have suggested the existence of a chelate configuration.† The particularly broad signal for the 2-proton in $CH_3Tl(ox)_2$, however, may be due to indirect spin-spin coupling with the thallium.

As can be seen from Table 1, the δ value of the 3-proton is almost the same in all types of complexes except for $R_2Sn(ox)_2$ and $R_2SnX(ox)$. The δ values of the 2- and 4- protons, however, change by altering the type of complex. The values are little affected by changing the alkyl groups or halogen in the same type of complexes. The relationship of the δ values of the 2- and 4- protons with the absorption maximum of a ^1L_a band in the UV spectra for 8-hydroxyquinoline,§ 8-methoxyquinoline,[13] a series of alkyl(oxinato)tin(IV) complexes[8,10] and some alkyl(oxinato)antimony(V) complexes[12,13] is shown in Fig. 1. Although there are some discrepancies, the δ values of the 4-proton increases monotonously with increasing wavelength of the ^1L_a band. The δ value of the 4-proton of 8-methoxyquinoline, in which the lone pair on the nitrogen atom is free from interaction with the proton or metal as in 8-hydroxyquinoline and chelated alkyl(oxinato)metal complexes, is the smallest and the position of the ^1L_a band[13] appears at the shortest wave length among the compounds studied in this work. The values for $(CH_3)_2SnCl(ox)$ are at the opposite extremes. On the other hand the δ values of the 2-proton at first decrease with increasing wavelength of the ^1L_a band but at the longer wavelength the values increase. The upfield shifts of the 2-proton for $R_3Sn(ox)$, $R_3SbX(ox)$[12,13] and $R_4Sb(ox)$[12] relative to the value for 8-methoxyquinoline may be due to a reduction of

* From the UV spectral result for $(CH_3)_2SnCl(ox)$ in cyclohexane the position of the absorption maximum at the longest wave length does not change even by an addition of excess $(CH_3)_2SnCl_2$, the equilibrium (1) is shifted almost completely to the right side in $(CH_3)_2SnCl(ox)$.

† H. Kurosawa, private communication.

§ In the UV spectrum of 8-hydroxyquinoline two kinds of absorption bands overlap at 320 nm.‖ The ^1L_a band shows a remarkable red shift on protonation of the nitrogen atom; the ^1L_b band is unaffected. This behaviour of the absorption bands may also be true in the case of metal oxinato complexes, because, in addition to the band (^1L_a) at 360 to 400 nm, a band with fine structures (^1L_b) has been observed at 320 to 330 nm in the several alkyl(oxinato)tin(IV) complexes.[8]

‖ K. Nishimoto, private communication.

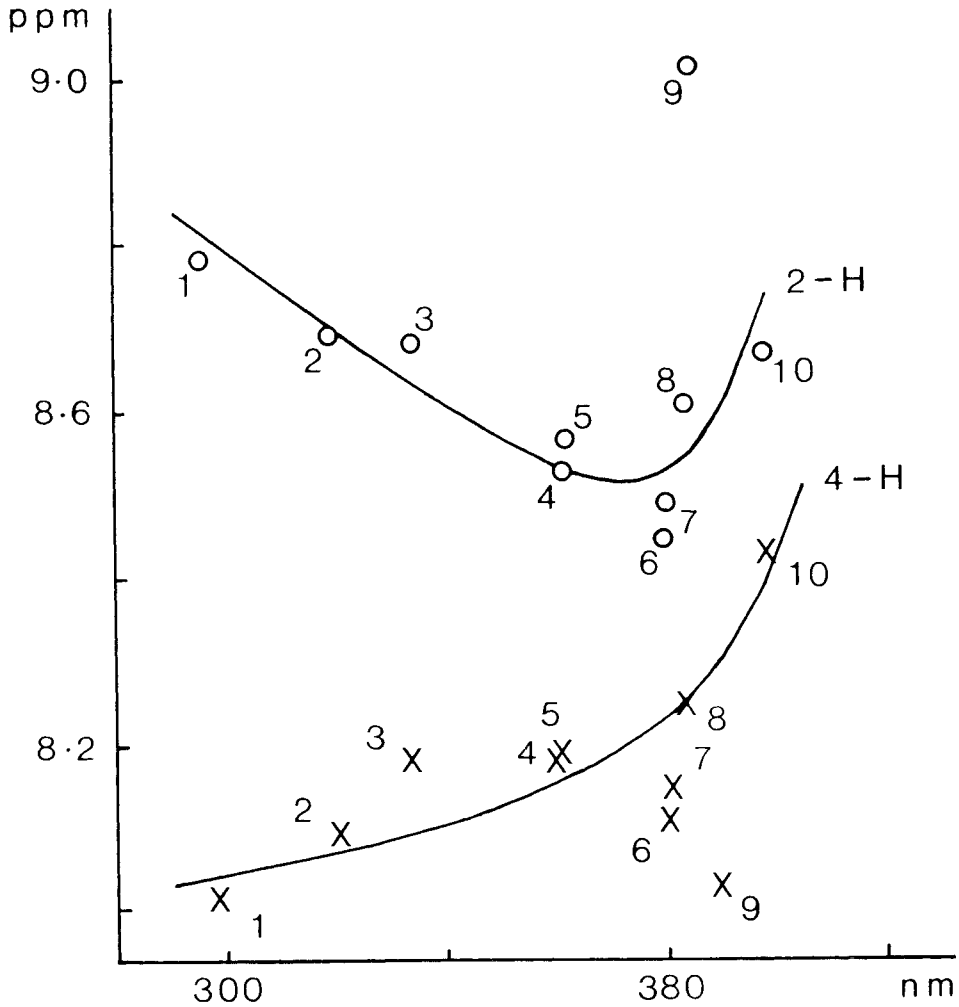


FIG. 1. A relationship between the δ values of the 2- and 4- protons and the wavelength of the ^1L_a band.
1: 8-methoxyquinoline. 2: 8-hydroxyquinoline. 3: $Me_3SbBr(ox)$. 4: $Me_3Sn(ox)$. 5: $^nBu_3Sn(ox)$. 6: $Me_2Sn(ox)_2$. 7: $Me_4Sb(ox)$. 8: $MeSnCl(ox)_2$. 9: $^nBuSn(ox)_3$. 10: $Me_2SnCl(ox)$.

the paramagnetic anisotropic effect of the nitrogen lone pair* by weak interactions with metals.† In this case the intramolecular electric field effect[25,26] is probably not so different from that in 8-methoxyquinoline. While in the case of strong interactions, as in $R_2SnX(ox)$, the electron densities on the nitrogen atom and on other atoms of the oxinato ligand might be diminished by partial drift of electrons to the metal.

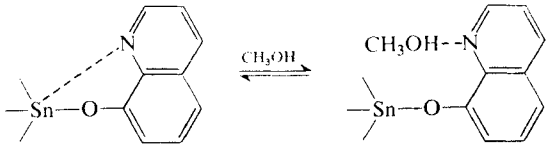
* Gil and Murrell,[19] Gawer and Dailey[20] and Emsley[22] calculated that in pyridine the paramagnetic anisotropic effect of the nitrogen lone pair become very small by the interaction with the proton. The reduction of this effect may also be occurring in the chelated alkyl(oxinato)metal complexes.

† From the study of the UV and IR spectra of several types of alkyl(oxinato)tin(IV) complexes, Kawakami *et al.*[8] have shown that the interactions of the oxinato ligand with tin increases in the order: $R_3Sn(ox) < R_2Sn(ox)_2 \approx RSnX(ox)_2 < R_2SnX(ox)$.

These effects cause the 2-proton signals to shift down-field. The magnitude of these effects may overcome that of the upfield shift due to the reduction of the paramagnetic anisotropic effect of the nitrogen lone pair in the case of the strong interaction. The intramolecular electric field effect produced by polar metal-halogen bonds is probably rather large in $R_2SbCl(ox)$ and $CH_3SbCl(ox)$. The chemical shift of the 4-proton may be mainly due to changes of charge density on the oxinato ligand and to the intramolecular electric field by the metal-halogen bonds, because the paramagnetic anisotropic effect decreases very rapidly with increasing interatomic distance.[19,22]

The δ values of the 2-protons in n-$C_4H_9Sn(ox)_3$ and $(CH_3)_2Pb(ox)_2$ are rather larger while the other proton signals are normal. One possible reason for this, in the former compound, arises from the interactions of the 2-protons with other oxinato ligands. While in the latter compound the paramagnetic effect of lead[27] may be effective in shifting the 2-proton to low field. This effect also seems to be apparent in the chemical shift of the methyl protons bonded directly to lead.*

Although the magnitude of the change is rather small, the δ value of the 2-proton decreases and that of the 4 proton increases in 8-methoxyquinoline, when the solvent was changed from methylene chloride to methanol. This tendency of the chemical shifts can also be explained by the weak interaction of the hydroxy proton of methanol with the nitrogen lone pair. The δ values of the oxinato protons of $(n\text{-}C_4H_9)_3Sn(ox)$ in methanol are almost the same as those in methylene chloride but are different from those for 8-hydroxyquinoline and 8-methoxyquinoline in methanol. The results imply that in $(n\text{-}C_4H_9)_3Sn(ox)$ the chelate configuration of the oxinato ligand also exists in methanol. While, from the UV spectral study for $(C_6H_5)_3Sn(ox)$, in 95% ethanol[4] and methanol[15] the oxinato ligand is monodentate although in cyclohexane[6] and benzene[15] it acts as a bidentate ligand. The main difference between UV and NMR spectral studies is that the concentration of the



(2)

complex in the former is very small (3×10^{-4} Mol/l) but in the latter it is about 10% w/w. The equilibrium (2) shifts to right side at the low concentration of complexes in alcohol.[4,15]

The differences of the chemical shifts ($\Delta_{C_6H_6}^{CH_2Cl_2}$)† of the 2-, 3- and 4- proton of the oxinato ligand in some alkyl(oxinato)tin(IV) complexes and that of 8-hydroxyquinoline on changing the solvent from methylene chloride to benzene are shown in Table 2. Similar values for quinolines[30] are included in this Table for comparison. One remarkable result is that in quinolines the values $\Delta_{C_6H_6}^{CH_2Cl_2}$ of the 2-proton are about one half of those of the 3- and 4- protons, for which the values are almost the same. In alkyl(oxinato)tin(IV) complexes, however, these three values are similar for all

* The δ values of the methyl protons in $(CH_3)_2Pb(ox)_2$ and $(CH_3)_2Pb(acac)_2$ are 2·14 and 2·05, respectively[18] and the values in the corresponding tin complexes are 0·44 and 0·88, respectively.[28] The difference of these chemical shifts could not be explained in terms of the difference of electronegativity of lead and tin alone.[29]

† $\Delta_{C_6H_6}^{CH_2Cl_2} = \delta(CH_2Cl_2) - \delta(C_6H_6)$.

TABLE 2. THE VALUES $\Delta_{C_6H_6}^{CH_2Cl_2}$ FOR METHYL(OXINATO)TIN(IV) COMPLEXES AND SOME QUINOLINES (IN PPM)

Compound	2-H	3-H	4-H	Reference
$Me_3Sn(ox)$	0·53	0·62	0·56	*
$Me_2SnNCS(ox)$	0·68	0·88	0·88	*
8-hydroxyquinoline	0·25	0·69	0·66	*
quinoline†	0·44	0·77	0·80	30
5,7-dimethylquinoline†	0·29	0·58	0·62	30

* This work.
† Values of $\Delta_{C_6H_6}^{C_6H_{14}}$.

protons. It is well established experimentally[31,32,33] that specific interaction of benzene with solute molecules occurs at the positive sites of the solute and as a result diamagnetic shifts are observed for the protons near to these sites. If this experimental rule is applied to the alkyl(oxinato)tin(IV) complexes and the quinolines, the electron density on the 2-carbon and the nitrogen atoms should be smaller in the former than in the latter compounds. It is interesting that even in $(CH_3)_3Sn(ox)$, in which the interaction of the oxinato ligand as the bidentate with tin is found to be weak from the UV and NMR spectral studies, this effect is clearly seen.

Acknowledgment—Thanks are due to Dr H. Kurosawa of Osaka University for supplying alkyl(oxinato)-thallium complexes and to Prof R. Okawara for his continuous encouragement.

REFERENCES

1. T. Moeller and A. J. Cohen, *J. Am. Chem. Soc.* **72,** 3546 (1950); T. Moeller and F. L. Pundsack, *J. Am. Chem. Soc.* **76,** 617 (1954).
2. K. Sone and K. Yamasaki, *Nature* **166,** 998 (1950); K. Sone, *J. Am. Chem. Soc.* **75,** 5207 (1953).
3. D. Blake, C. E. Coates and J. M. Tate, *J. Chem. Soc.* 756 (1961).
4. L. Roncucci, G. Faraglia and R. Barbieri, *J. Organometal. Chem.* **1,** 427 (1964).
5. T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, *J. Organometal. Chem.* **1,** 484 (1964).
6. M. Wada, K. Kawakami and R. Okawara, *J. Organometal. Chem.* **4,** 159 (1965).
7. F. Huber and R. Kaiser, *J. Organometal. Chem.* **6,** 126 (1966).
8. K. Kawakami and R. Okawara, *J. Organometal. Chem.* **6,** 249 (1966).
9. M. Komura and R. Okawara, *Inorg. Nucl. Chem. Letters* **2,** 93 (1966).
10. K. Kawakami, Y. Kawasaki and R. Okawara, *Bull. Chem. Soc. Japan* **40,** 2693 (1967).
11. Y. Matsumura and R. Okawara, *Inorg. Nucl. Chem. Letters* **4,** 521 (1968).
12. H. A. Meinema, E. Rivarola and J. G. Noltes, *J. Organometal. Chem.* **17,** 71 (1969).
13. Y. Kawasaki, *Inorg. Nucl. Chem. Letters* in press. **5,** 805 (1969).
14. E. O. Schlemper, *Inorg. Chem.* **6,** 2012 (1967).
15. L. Roncucci, G. Faraglia and R. Barbieri, *J. Organometal. Chem.* **6,** 278 (1966).
16. M. Wada and R. Okawara, *Inorg. Nucl. Chem. Letters* **5,** 355 (1969).
17. L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, John Wiley & Son, New York, 1967.
18. Y. Kawasaki, *J. Organometal. Chem.* **9,** 549 (1967).
19. V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.* **60,** 248 (1964).
20. A. H. Gawer and B. P. Dailey, *J. Chem. Phys.* **42,** 2658 (1965).
21. P. J. Black, R. D. Brown and M. L. Hefferman, *Australian J. Chem.* **20,** 1305 (1967).
22. J. W. Emsley, *J. Chem. Soc. (A)* 1387 (1968).
23. L. W. Reeves and K. O. Strømme, *Can. J. Chem.* **39,** 2318 (1961).
24. Y. Kawasaki, T. Tanaka and R. Okawara, *Inorg. Nucl. Chem. Letters* **2,** 9 (1966).

25. A. D. Buckingham, *Can. J. Chem.* **38,** 300 (1960).
26. J. I. Musher, *J. Chem. Phys.* **37,** 2731 (1962).
27. J. J. Burke and P. C. Lautebur, *J. Am. Chem. Soc.* **83,** 326 (1961).
28. M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.* **87,** 1909 (1965).
29. H. Spieseck and W. G. Schneider, *J. Chem. Phys.* **35,** 722 (1961).
30. T. Schaefer, *Can. J. Chem.* **39,** 1864 (1961).
31. T. Ledeal, *Tetrahedron Letters* 1683 (1968) and references quoted therein.
32. Y. Kawasaki, *Mol. Phys.* **12,** 287 (1967).
33. M. Honda, Y. Kawasaki and R. Okawara, *Tetrahedron Letters*, 3313 (1967); M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.* **30,** 3231 (1968).