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# Infrared Spectra and Stereochemistry of Bis-pyridine Complexes of Tin(IV)

Toshio TANAKA, Yoshio MATSUMURA and Rokuro OKAWARA
*Department of Applied Chemistry, Osaka University, Suita, Osaka*

and Yoshihiko MUSYA and Susumu KINUMAKI
*Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira-cho, Sendai*

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Assignments are given for the infrared spectra of bis-pyridine complexes of $SnX_4$, $(CH_3)_2SnX_2$ (X=Cl, Br and I), and $(C_2H_5)_2SnCl_2$ in the 80—1610 cm$^{-1}$ region. These complexes show the Sn–N stretching band near 200 cm$^{-1}$. Most pyridine vibrations shift to a higher or a lower frequency upon complex formation. Among these, the $\nu_{10}$, in-plane ring deformation vibration is the most sensitive to the substituents on the tin atom as well as to the complex formation. Thus, the frequency may be a qualitative measure of the tin-pyridine coordination bond strength. The infrared spectra suggest a *cis*-configuration for the tin tetrahalide complexes and a distorted octahedral configuration for the dimethyltin diiodide complex. The remaining complexes may be assumed to have *trans*-alkyl and *cis*-halogen configurations.

It is well known that pyridine (Py) is a Lewis base which can coordinate to metal atoms or ions. For instance, it forms stable 2 : 1 adducts with $SnX_4$[1,2] and $(CH_3)_2SnX_2$[3] (X=Cl, Br and I), and a 1 : 1 adduct with $(CH_3)_3SnCl$.[4] Of these adducts, only $(CH_3)_3SnCl\cdot Py$ has been studied by X-ray crystallographic analysis; this analysis indicated that the adduct has a triangular bipyramidal structure, in which the pyridine molecule and the chlorine atom are located in the axial positions.[4] The infrared spectra of the tin(IV)-pyridine complexes have been described only for the CsBr region, in which tin-halogen and tin-carbon stretching vibrations are expected to be observed. For the $SnCl_4\cdot 2Py$ complex a *trans*-configuration has initially been assumed on the basis of the infrared study.[2] However, X-ray powder photographs showed that the complex is a crystal structure closely similar to that of $SnBr_4\cdot 2Py$, whose infrared spectrum, with three well-resolved Sn–Br stretching bands, indicates a *cis*-configuration.[3] On the other hand, the infrared spectra of $(CH_3)_2SnX_2\cdot 2Py$ (X=Cl, Br and I) have suggested *trans*-methyl and *cis*-halogen configurations.[3]

This paper will report on the assignments for the infrared spectra in the 80—1610 cm$^{-1}$ region and the stereochemistry of bis-pyridine complexes of $SnX_4$, $(CH_3)_2SnX_2$ (X=Cl, Br and I) and $(C_2H_5)_2SnCl_2$; for the $(CH_3)_2SnI_2\cdot 2Py$ complex a distorted octahedral configuration is proposed; this is unlike that previously reported.[3]

## Experimental

**Preparation of Complexes.** Bis-pyridine complexes of tin(IV) were prepared by reactions of the corresponding tin(IV) compounds with pyridine (mole ratio of about 1 : 2) in benzene, except for the case of the dimethyltin dibromide and diiodide complexes, which were synthesized in petroleum ether. Since the tin tetrahalide complexes are insoluble in common organic solvents, the precipitates resulting from the reactions were washed by petroleum ether until the pyridine smells had vanished. The dimethyltin dichloride complex was purified by sublimation under a reduced pressure, and the other three, by recrystallization from dichloromethane. The melting points and the analytical data are shown in Table 1.

**Infrared Spectra.** The spectra were recorded in Nujol and hexachlorobutadiene mulls using Hitachi EPI-2G (400—5000 cm$^{-1}$) and EPI-L (200—700 cm$^{-1}$) spectrophotometers, and in solid paraffin of a low melting point on a Hitachi FIS-1 vacuum spectrophotometer (80—500 cm$^{-1}$), all equipped with gratings. These spectrophotometers were calibrated with polystyrene film, $CO_2$ gas, and $H_2O$ vapor.

## Results and Discussion

**Pyridine Vibrations.** Assignments of the infrared spectra and a normal-coordinates analysis of pyridine and deuterated pyridines have been made by Long *et al.*[5,6] Using their results, the

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[1] I. R. Beattie, *Quart. Revs.*, **1963**, 382.
[2] I. R. Beattie, G. P. McQuillan, L. Rule and M. Webster, *J. Chem. Soc.*, **1963**, 1514.
[3] J. P. Clark and C. J. Wilkins, *ibid.*, **1966**, 871.
[4] R. Hulme, *ibid.*, **1963**, 1524.
[5] D. A. Long, F. S. Murfin and E. L. Thomas, *Trans. Faraday Soc.*, **59**, 12 (1963).
[6] D. A. Long and E. L. Thomas, *ibid.*, **59**, 783 (1963).

Table 1. Melting points and analytical data of bis-pyridine complexes of tin(IV)

| Complex | Mp, °C | C% Anal. (Calcd) | H% Anal. (Calcd) | Sn% Anal. (Calcd) |
|---|---|---|---|---|
| $SnCl_4\cdot 2Py$ | 300, decomp. | 29.56<br>(28.66) | 2.67<br>(2.38) | 28.29<br>(28.34) |
| $SnBr_4\cdot 2Py$ | 290, decomp. | 20.36<br>(20.12) | 1.85<br>(1.68) | 19.70<br>(19.87) |
| $SnI_4\cdot 2Py$ | 270, decomp. | 15.72<br>(15.30) | 1.77<br>(1.28) | 14.64<br>(15.13) |
| $(CH_3)_2SnCl_2\cdot 2Py$ | 162—163 | 38.40<br>(38.12) | 4.22<br>(4.23) | |
| $(CH_3)_2SnBr_2\cdot 2Py$ | 167.5—168 | 30.31<br>(30.88) | 3.44<br>(3.46) | |
| $(CH_3)_2SnI_2\cdot 2Py$ | 128, decomp. | 25.90<br>(25.70) | 2.99<br>(2.88) | |
| $(C_2H_5)_2SnCl_2\cdot 2Py$ | 128—131 | 41.18<br>(41.40) | 4.91<br>(4.92) | |

infrared absorption bands related to the pyridine vibrations of bis-pyridine complexes of tin(IV) can easily be assigned, except for the $\nu_{17}$, $\nu_{18}$, and $\nu_{23}$ vibrations,[*1] which are sometimes difficult to observe because of their weak intensities in the complexes. The observed frequencies of the pyridine vibrations and their probable assignments are given in Table 2.

As may be seen in Table 2, most pyridine vibrations shift to a higher or a lower frequency upon complex formation. It has already been indicated for the transition-metal complexes that the $\nu_{10}$ and $\nu_{27}$ vibrations undergo shifts to significantly higher frequencies upon the coordination of pyridine to metal,7) and that the magnitude of these shifts depends on the stereochemistry of the complexes and on the metal atoms.8) In the bis-pyridine complexes of tin(IV), the frequencies of $\nu_4$, $\nu_9$, $\nu_{10}$, $\nu_{24}$, and $\nu_{27}$ vibrations are sensitive to the substituents on the tin atom as well as to the complex formation; the most remarkable one is the $\nu_{10}$ vibration.

It has previously been described by the present authors, in reporting on the infrared spectra of YZSn(acac)$_2$[*2] and $Y_2Z_2Sn\cdot 2DMSO$[*2] (Y, Z= Cl, Br, I, alkyl and aryl), that the inductive effect of the substituents on the tin atom affects mainly the Sn–O coordination bond strength; the Sn–O stretching band shifts to a higher frequency with an increase in the electronegativity of the substituents on the tin atom.9,10) This trend is not always clear in the Sn–N stretching frequency of the bis-pyridine complexes of tin(IV), probably because of its mixing with tin-halogen stretching vibrations, as will be described below. However, the $\nu_{10}$ vibration showed quite a similar tendency to the Sn–O vibrations of YZSn(acac)$_2$ and $Y_2Z_2Sn\cdot 2DMSO$, suggesting that the $\nu_{10}$ vibrational frequency may be used qualitatively as a measure of the bond strength of the tin-pyridine coordination bond. The $\nu_{27}$ vibration also shifted to a higher frequency with an increase in the electronegativity of the substituents on the tin atom, except for the diethyltin dichloride complex, which showed the band at an unexpected high frequency.

**Skeletal Vibrations.** Since the first-row transition metal-pyridine stretching vibration has been placed near 220 cm$^{-1}$,8) the tin-pyridine vibration might be expected to occur in a rather lower frequency region in view of mass considerations. Figures 1 and 2 show the far infrared

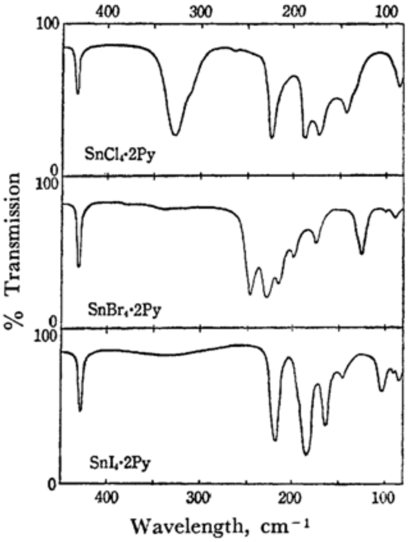

Fig. 1. Far infrared spectra of $SnX_4\cdot 2Py$ (X= Cl, Br and I).

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[*1] The numbering of the vibrations follows that of Ref. 6.

7) N. S. Gill, R. H. Nuttall, D. E. Scaife and D. W. A. Sharp, *J. Inorg. and Nucl. Chem.*, **18**, 79 (1961).

8) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

9) Y. Kawasaki, T. Tanaka and R. Okawara, *Spectrochim. Acta*, **22**, 1571 (1966).

10) T. Tanaka, *Inorg. Chim. Acta*, **1**, 217 (1967).

[*2] acac: Acetylacetonate; DMSO: Dimethylsulfoxide.

TABLE 2. OBSERVED FREQUENCIES AND ASSIGNMENTS FOR THE PYRIDINE VIBRATIONS OF BIS-PYRIDINE COMPLEXES OF TIN(IV), cm$^{-1}$ [a]

| Assignments[b] | | Py[c] | $SnCl_4 \cdot 2Py$ | $SnBr_4 \cdot 2Py$ | $SnI_4 \cdot 2Py$ | $(CH_3)_2SnCl_2 \cdot 2Py$ | $(CH_3)_2SnBr_2 \cdot 2Py$ | $(CH_3)_2SnI_2 \cdot 2Py$ | $(C_2H_5)_2SnCl_2 \cdot 2Py$ |
|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | $\nu_4$ | 1583 vs | 1608 s | 1605 s | 1600 s | 1602 s | 1603 s | 1603 s | 1602 s |
| | $\nu_5$ | 1482 s | 1482m | 1482m | 1481m | 1482m | 1484m | 1484m | 1481m |
| | $\nu_6$ | 1218 s | 1208 s | 1208 s | 1208 s | 1209 s | 1210 s | 1209 s | 1209 s |
| | $\nu_7$ | 1068 s | 1062 s | 1062 s | 1061 s | 1062 s | 1062 s | 1064 s | 1063 s |
| | $\nu_8$ | 1030 s | 1042m | 1038m | 1034m | 1036 s | 1036 s | 1037 s | 1036 s |
| | $\nu_9$ | 992 s | 1018 s | 1016 s | 1011 s | 1010 s | 1010 s | 1009 s | 1006 s |
| | $\nu_{10}$ | 605 s | 644 s | 641 s | 634 s | 627 vs | 627 vs | 626 vs | 625 vs |
| $B_1$ | $\nu_{13}$ | 1572m | 1571 w | 1570w | 1570w | 1572w | 1572 w | 1573 w | 1570 w |
| | $\nu_{14}$ | 1439 vs | 1449 vs | 1447 vs | 1444 vs | 1448 vs | 1446 s | 1444 vs | 1443 vs |
| | $\nu_{15}$ | 1375w | 1351 vw | 1351 vw | 1351 vw | 1355 vw | 1355 vw | 1353 vw | ? |
| | $\nu_{16}$ | 1218 s | 1208 s | 1208 s | 1208 s | 1209 s | 1210 s | 1209 s | 1209 s |
| | $\nu_{17}$ | 1148 s | 1155 vw (?) | 1155 vw (?) | 1153 w | 1154 vw (?) | 1151 w | 1152m | 1146m |
| | $\nu_{18}$ | 1085 vw | 1090 vw | 1090 vw | 1089 vw | ? | 1090 vw | 1088 vw | ? |
| | $\nu_{19}$ | 652 w | 649 vw | 648 vw | ? | 649 vw | 648 vw | 649 vw | 649 vw |
| $B_2$ | $\nu_{23}$ | 942 vw | 945 w | 942 w | 937 w | ? | 946 w (?) | 939 w | ? |
| | $\nu_{24}$ | 886 vw | 863 w | 858 w | 858 w | 826 vw | 875 w (?) | ? | 886 w (?) |
| | $\nu_{25}$ | 749 vs | 755 vs | 753 vs | 750 vs | 756 vs<br>745 s | 751 vs | 751 vs | 766 vs |
| | $\nu_{26}$ | 700 vs | 682 vs | 682 vs | 682 vs | 698 vs<br>687 vs | 692 vs | 692 vs | 707 vs<br>688 vs |
| | $\nu_{27}$ | 405 s | 432 s | 431 s | 428 s | 423 s | 423m | 423m | 427 s |

a) vs: Very strong, s: Strong, m: Medium, w: Weak, vw: Very weak.

b) The $\nu_1$, $\nu_2$, $\nu_3$, $\nu_{11}$, and $\nu_{12}$ are C-H stretching modes and the $\nu_{20}$—$\nu_{22}$ $A_2$ modes.

c) Ref. 6.

TABLE 3. OBSERVED FREQUENCIES FOR THE SKELETAL VIBRATIONS OF BIS-PYRIDINE COMPLEXES OF TIN(IV), cm$^{-1}$ a)

| $SnCl_4 \cdot 2Py$ | $SnBr_4 \cdot 2Py$ | $SnI_4 \cdot 2Py$ | $(CH_3)_2SnCl_2 \cdot 2Py$ | $(CH_3)_2SnBr_2 \cdot 2Py$ | $(CH_3)_2SnI_2 \cdot 2Py$ | $(C_2H_5)_2SnCl_2 \cdot 2Py$ | Approximate descriptions |
|---|---|---|---|---|---|---|---|
| — | — | — | 563m | 560m | 550m | 531m | ν(Sn–C) |
| — | — | — | — | — | 514 vw | 480 w | |
| 324 vs | 248 s | 218m | 245 s | | | 218 s | ν(Sn–X)b) and ν(Sn–N) |
| 305 sh | 230 s | 196 sh(?) | 197m | 193m | 191m | 206 s | |
| 225 s | 216m | 183 s | 173 s | 160 s | 147 s | 180sh | |
| 186 s | 200m | 163m | | | | | |
| 168 s | 174m | 145 w | | | | | |
| 144m | 123m | 104m | 146 s | 135 s | 133 s | 131 sh | δ(skeletal) |
| 136 sh | 93 w | 82 w | 136 s | 115 s | 94m | 126 s | |
| 84m | | | 98 w | 95 w | | | |

a) vs: Very strong, s: Strong, m: Medium, w: Weak, vw: Very weak, sh: Shoulder.
b) X: Halogen atoms.

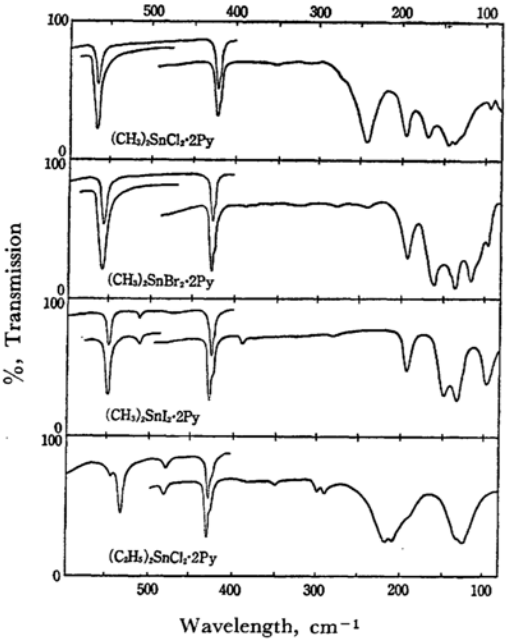

Fig. 2. Far infrared spectra of $(CH_3)_2SnX_2 \cdot 2Py$ (X=Cl, Br and I) and $(C_2H_5)_2SnCl_2 \cdot 2Py$.

spectra of bis-pyridine complexes of tin(IV). These complexes are considered to be non-ionic in the solid state.*3 Therefore except for the $\nu_{27}$ vibration of pyridine, the infrared spectra below 600 cm$^{-1}$ may tentatively be assigned to skeletal vibrations around the hexa-coordinated tin atom, as is shown in Table 3. Among these, the bands of the dimethyltin and the diethyltin dihalide complexes in the 480—570 cm$^{-1}$ range can undoubtedly be assigned to Sn–C stretching modes.

The three dimethyltin dihalide complexes showed a medium-intense band at 190—200 cm$^{-1}$. These frequencies decrease with a decrease in the electronegativity of the substituents on the tin atom, which is a similar trend to that of the Sn–O stretching frequencies of $YZSn(acac)_2$[9] and $Y_2Z_2Sn \cdot 2DMSO$.[10] The bands in this region may, therefore, be associated with the Sn-pyridine stretching mode. For the $(C_2H_5)_2SnCl_2 \cdot 2Py$ and $SnX_4 \cdot 2Py$ (X=Cl, Br and I) complexes, the assignment of the Sn–N vibration is not unambiguous, because these complexes give Sn-halogen stretching bands near 200 cm$^{-1}$, which could be mixed with the Sn–N stretching. This may spread the Sn–N stretching vibration over two or more frequencies.

It has previously been mentioned by one of the present authors that the Sn-halogen stretching bands of dimethyltin dichloride and dibromide shift to considerably lower frequencies upon the coordination of some donor molecules, such as DMSO[10] and dimethylselenoxide.[11] A similar shift of the Sn-halogen stretching bands might also be expected upon the coordination of pyridine. Thus, each strong band of the dimethyltin dihalide complexes at 245, 160, and 147 cm$^{-1}$ may be associated with Sn-halogen stretching vibrations. The latter two frequencies may be contributed by the deformation vibrations around the tin atom, some of which may appear near these frequencies. The diethyltin dichloride complex showed split broad bands near 210 cm$^{-1}$. These are also assigned to Sn–Cl stretching vibrations, although they are probably mixed with Sn–N vibrations.

The far infrared spectrum of the tin tetrachloride complex (Fig. 1a) showed a fairly strong band due to the Sn–Cl stretching mode at 324 cm$^{-1}$, with a

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*3 Although the electric conductance has not been measured for these complexes in solution, 2,2′-bipyridyl complexes of dimethyltin dichloride and dibromide gave non-conducting solutions in acetonitrile; T. Tanaka *et al.*, to be published.

11) T. Tanaka and T. Kamitani, *Inorg. Chim. Acta*, in press.

shoulder at 304 cm$^{-1}$; this finding is in agreement with that of the previous workers,3) who also reported another weak shoulder at 327 cm$^{-1}$.[*4] Another strong band, at 225 cm$^{-1}$, is more likely to be due to the $\nu$(Sn–Cl) fundamental, in which there might be some contribution by the Sn–N stretching vibration.

The tin tetrabromide complex showed several absorption bands in the skeletal stretching region (Fig. 1b). The two highest frequencies are assigned to Sn–Br stretching modes because of their strong intensities. The remaining three may be associated with the Sn–Br and the Sn–N stretching vibrations, which are presumably coupled with each other. The four infrared bands of the tin tetraiodide complex, 218, 183, 163, and 145 cm$^{-1}$ (Fig. 1c), are comparable with those of the corresponding bis(pyridine-*N*-oxide) complex, 210, 184, 157, and 140 cm$^{-1}$.12) Therefore, these four bands of the $SnI_4$·2Py are likely to be associated with Sn–I stretching modes, although the Sn–N stretching may also contribute to these frequencies.

**Stereochemistry.** We shall assume the presence of discrete hexa-coordinated species for the solid bis-pyridine complexes of tin(IV). There is some disagreement on the stereochemistry of the $SnCl_4$·2Py complex. Beattie *et al.* initially considered, on the basis of the infrared spectrum, that the complex was more likely to be the *trans* than the *cis*-configuration.2) On the contrary, Clark and Wilkins concluded it to have the *cis*-configuration after comparing an X-ray powder photograph with one of $SnBr_4$·2Py and after considering the infrared spectrum.3) In the present infrared study, at least two strong bands (324 and 225 cm$^{-1}$) have been assigned to $\nu$(Sn-Cl) fundamentals; therefore, it is reasonable to assume the *cis*-configuration for the $SnCl_4$·2Py complex. The tin tetrabromide and tetraiodide complexes showed several infrared bands associated with tin-halogen stretching modes, indicating the *cis*-configuration for these complexes also.

The dimethyltin dichloride and dibromide complexes showed only the asymmetric Sn–C stretching band in their infrared spectra, no symmetric ones (Fig. 2a and 2b), suggesting a linear geometry of the $(CH_3)_2Sn$ moieties.10) The Sn–Cl stretching frequency of the former complex is close to those of $(CH_3)_2SnCl_2$·2DMSO and $(CH_3)_2SnCl_2$·bipyridyl, whose chlorine atoms are in *cis*-positions.10) On the other hand, this frequency is quite a bit lower than that of $Cl_2Sn(acac)_2$ (345 cm$^{-1}$),9) which has a *trans*-configuration,13) as well as dimethyltin dichloride (361 and 356 cm$^{-1}$).[*5] The Sn–Br stretching frequency of the $(CH_3)_2SnBr_2$·2Py complex is also markedly lower than those of dimethyltin dibromide (252 and 241 cm$^{-1}$).[*5] These results would indicate the *trans*-methyl and *cis*-halogen configuration for the $(CH_3)_2SnCl_2$·2Py and $(CH_3)_2SnBr_2$·2Py complexes, which is in agreement with the findings of previous workers.3)

On the other hand, the dimethyltin diiodide complex gave the symmetric Sn–C stretching band with less intensity as well as the asymmetric one (Fig. 2c), although the former had not been observed by the previous workers.3) This is suggestive of a non-linear geometry of the C–Sn–C linkage. Thus, it is reasonable to assume a distorted octahedral configuration for the $(CH_3)_2SnI_2$·2Py complex, as is shown in Fig. 3. This configuration is comparable with those of dimethyltin diacetate14) and dimethyltin bis(kojate).15)

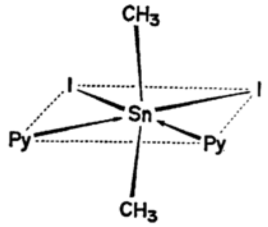

Fig. 3. Distorted octahedral configuration of $(CH_3)_2SnI_2$· 2Py.

The diethyltin dichloride complex also showed two Sn–C stretching bands. The considerable intensity of the symmetric one may be due to coupling with the inner vibrations of ethyl groups, as has been mentioned in the cases of bis-DMSO10) and bis-dimethylselenoxide11) complexes of diethyltin dichloride. The $(C_2H_5)_2SnCl_2$·2Py complex is, therefore, assumed to have a similar around the tin atom geometry to that of the dimethyltin dichloride complex, although a more or less distorted configuration can not be ruled out.

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[*4] This shoulder is not unambiguous in the present study.

12) Y. Kawasaki, M. Hori and K. Uenaka, This Bulletin, **40**, 2463 (1967).

13) Y. Kawasaki and T. Tanaka, *Inorg. and Nucl. Chem. Letters*, **3**, 15 (1967).

[*5] The wave numbers in cyclohexane solution; F. K. Butcher *et al.*, *J. Organometal. Chem.*, **1**, 431 (1964).

14) Y. Maeda and R. Okawara, *J. Organometal. Chem.*, **10**, 247 (1967).

15) J. Otera, Y. Kawasaki and T. Tanaka, *Inorg. Chim. Acta*, **1**, 294 (1967).