

Reactions of silylated Schiff bases with organotitanium(IV) and organotin(IV) chlorides

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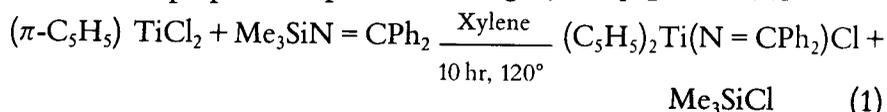
MS received 3 May 1982; revised 18 September 1982

Abstract. The interactions of silylated dibasic quadridentate Schiff bases derived from *o*-hydroxyacetophenone and ethylenediamine and orthophenylenediamine with $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$, $(\pi\text{-C}_5\text{H}_5)(\text{MeO})\text{TiCl}_2$, $(\text{MeO})_2\text{TiCl}_2$, Me_2SnCl_2 and MeSnCl_3 yield a new series of organotitanium(IV) and tin(IV) compounds. The reactivity of $(\pi\text{-C}_5\text{H}_5)\text{Ti}(\text{L}_1)\text{Cl}$ and $\text{MeSn}(\text{L}_1)\text{Cl}$, towards MeSH , $\text{Me}_2\text{NSiMe}_3$, SiMe_3N_3 and $\text{Me}_3\text{SiC}\equiv\text{CPh}$ are also described. The structures for the compounds isolated are proposed on the basis of elemental analyses, molecular weights, IR and ^1H NMR spectroscopic studies.

Keywords. Organometallic reactions; silylated Schiff bases; organotitanium; organotin.

1. Introduction

Although Schiff base complexes of most transition metals and some non-transition metals have been thoroughly studied (Holm *et al* 1966; Dey 1974), there are only a few known organotitanium(IV) Schiff base complexes (Wailes *et al* 1974; Sharma *et al* 1980, 1981). In fact, very few reports are available on the reactions of silylated Schiff bases with organo (group IV) metal halides (Dey *et al* 1981, 1982). However, Dilworth *et al* (1977) reported the reactions of silylated schiff base complexes with $[\text{MoCl}_3\text{O}(\text{thf})_2]$ (thf = tetrahydrofuran) to synthesize $[\text{MoCl}(\text{O})\text{L}]$ (where H_2L = quadridentate Schiff bases derived from salicylaldehyde and ethylenediamine and orthophenylenediamine). Lappert and coworkers have prepared (Collier *et al* 1970, 1973) a range of metal ketimides including organotitanium derivatives $(\pi\text{-C}_5\text{H}_5)\text{Ti}(\text{Cl})\text{N}=\text{CR}_2$ ($\text{R} = \text{CMe}_3$ or Ph), where a chlorosilane elimination has been used to prepare the products in high yield [equation (1)].



This paper records the reactions of silylated Schiff base complexes abbreviated as $\text{L}_1(\text{SiMe}_3)_2$ and $\text{L}_2(\text{SiMe}_3)_2$ with $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$, $(\pi\text{-C}_5\text{H}_5)(\text{MeO})\text{TiCl}_2$, $(\text{MeO})_2\text{TiCl}_2$, Me_2SnCl_2 and MeSnCl_3 . The reactivity of $(\pi\text{-C}_5\text{H}_5)\text{Ti}(\text{L}_1)\text{Cl}$ and $\text{MeSn}(\text{L}_1)\text{Cl}$ synthesized in the present investigation, towards MeSH , $\text{Me}_2\text{NSiMe}_3$, SiMe_3N_3 and $\text{Me}_3\text{SiC}\equiv\text{CPh}$ are also described.

2. Experimental

All solvents were purified and dried according to standard procedures. Manipulations were carried out in an atmosphere of nitrogen.

Titanium tetrachloride, a commercial product, and $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_2$ (Alfa products) were used as such. The compounds $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$, $(\pi\text{-C}_5\text{H}_5)\text{-Ti(OMe)Cl}_2$ and $(\text{MeO})_2\text{TiCl}_2$ were prepared by literature methods (Gorsich 1960; Nesmeyanov *et al* 1968; Gattow and Yildirimyan 1977). The tin compounds Me_2SnCl_2 and MeSnCl_3 were prepared following the methods of Luijten and van der Kerk (1959), while $\text{Me}_3\text{SiC} \equiv \text{CPh}$ was prepared as described by Petrov and Shchukoskaya (1953) and Birkofer and Ritter (1963, 1965). Physical measurements were as described in Dey and Werner (1977, 1979). Schiff bases were prepared by usual methods and the silylation was by methods published earlier (Dey *et al* 1981).

2.1. Preparation of complexes:

(a) Reaction of $\text{L}_1(\text{SiMe}_3)_2$ with $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$

To $\text{L}_1(\text{SiMe}_3)_2$ (0.005 mol) in 25 ml of thf was added $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$ (0.005 mol) in 30 ml of toluene with stirring. The reaction mixture was stirred for about 8 hr at 50-60°C and the solvent was then removed under reduced pressure. Hexane (20 ml) was then added to this crude product and cooled to -20°C to get red-brown crystals of $(\pi\text{-C}_5\text{H}_5)\text{Ti(L}_1\text{)Cl}$ (**1**). It was filtered off, washed with hexane and dried *in vacuo*, yield 70%; m.p. 270-276°C (dec.).

(b) Reactions of $\text{L}_1(\text{SiMe}_3)_2$ with $(\pi\text{-C}_5\text{H}_5)\text{Ti(OMe)Cl}_2$, $(\text{MeO})_2\text{TiCl}_2$, Me_2SnCl_2 and MeSnCl_3 : As in (**1**) above the reactions of $\text{L}_1(\text{SiMe}_3)_2$ with $(\pi\text{-C}_5\text{H}_5)\text{-Ti(OMe)Cl}_2$, $(\text{MeO})_2\text{TiCl}_2$, Me_2SnCl_2 and MeSnCl_3 in equimolar quantities gave the following complexes:

$(\pi\text{-C}_5\text{H}_5)\text{TiL}_1(\text{OMe})$ (**2**), brown, m.p. 202-204°C(dec.), yield, 70%; $(\text{MeO})_2\text{-TiL}_1$ (**3**), orange red, m.p. 190-194°C(dec.), yield 75%; Me_2SnL_1 (**4**), Light brown, m.p. 210-213°C(dec.), yield 73%; $\text{MeSn(L}_1\text{)Cl}$ (**5**), yellow m.p. 198-200°C (dec.,) yield 70%.

Reaction of $\text{L}_2(\text{SiMe}_3)_2$ with $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$: One equivalent of $\text{L}_2(\text{SiMe}_3)_2$ was added to 1 equivalent of $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$ in solution in thf and toluene (50% 50, V/V) and heated under reflux for 4 hr and $(\pi\text{-C}_5\text{H}_5)\text{Ti(L}_2\text{)Cl}$ (**6**) was isolated as brownish-red crystals in 75% yield. The complex was washed with pentane and dried under vacuum, m.p. above 250°C.

(d) Reactions of $\text{L}_2(\text{SiMe}_3)_2$ with $(\pi\text{-C}_5\text{H}_5)\text{Ti(OMe)Cl}_2$ and $(\text{MeO})_2\text{TiCl}_2$: As above, the reaction of $\text{L}_2(\text{SiMe}_3)_2$ with $(\pi\text{-C}_5\text{H}_5)\text{Ti(OMe)Cl}_2$ and $(\text{MeO})_2\text{-$

TiCl₂ gave two compounds in more than 70% yield: (π -C₅H₅)Ti(L₂)(OMe) (**7**), brown powder, m.p. 278-280°C (dec.); (MeO)₂Ti(L₂), (**8**), red-orange, m.p. 248-250°C (dec.).

2.2. Some reactions of (π -C₅H₅)Ti(L₁)Cl, (**1**) and MeSn(L₁)Cl, (**5**):

(i) *Reaction with MeSH.* One equivalent of (**1**) was added to 1 equivalent of MeSH in a mixed solvent (50% 50, V/V) of thf-toluene and stirred at room temperature in the presence of stoichiometric amount of Et₃N for 7d. After removing Et₃N.HCl, the volume of the solution was reduced under vacuum, which yield dark brown crystals of (π -C₅H₅)Ti(L₁)(SMe), (**9**) on cooling to -20°C. It was filtered, washed with hexane and dried *in vacuo*, yield 80%, m.p. 285-290°C(dec.). Similarly when (**5**) was induced to react with MeSH, the complex MeSn(L₁)(SMe), (**14**) was isolated as yellow powder, yield 75%, m.p. above 300°C.

(ii) *Reaction with Me₂NSiMe₃.* As in (**9**) above, (**1**) and (**5**) were treated with Me₂NSiMe₃ in equimolar quantities and (π -C₅H₅)Ti(L₁)(NMe₂), (**10**) and MeSn(L₁)(NMe₂), (**15**) respectively were isolated in more than 60% yield. Both the compounds did not melt within 250°C. One equivalent of the complex (**10**) was mixed with one equivalent of Ph₃SnH in thf and thoroughly stirred at room temperature for 8d to get (π -C₅H₅)Ti(L₁)(SnPh₃), (**11**) as brown powder.

(iii) *Reaction with (SiMe₃)(N₃).* The reaction of (**1**) and (**5**) with (SiMe₃)(N₃) in thf similarly gave (π -C₅H₅)Ti(L₁)(N₃), (**12**), decomposed with mild explosion at 220-224°C and MeSn(L₁)(N₃), (**16**), decomposed with mild explosion at 248-250°C respectively.

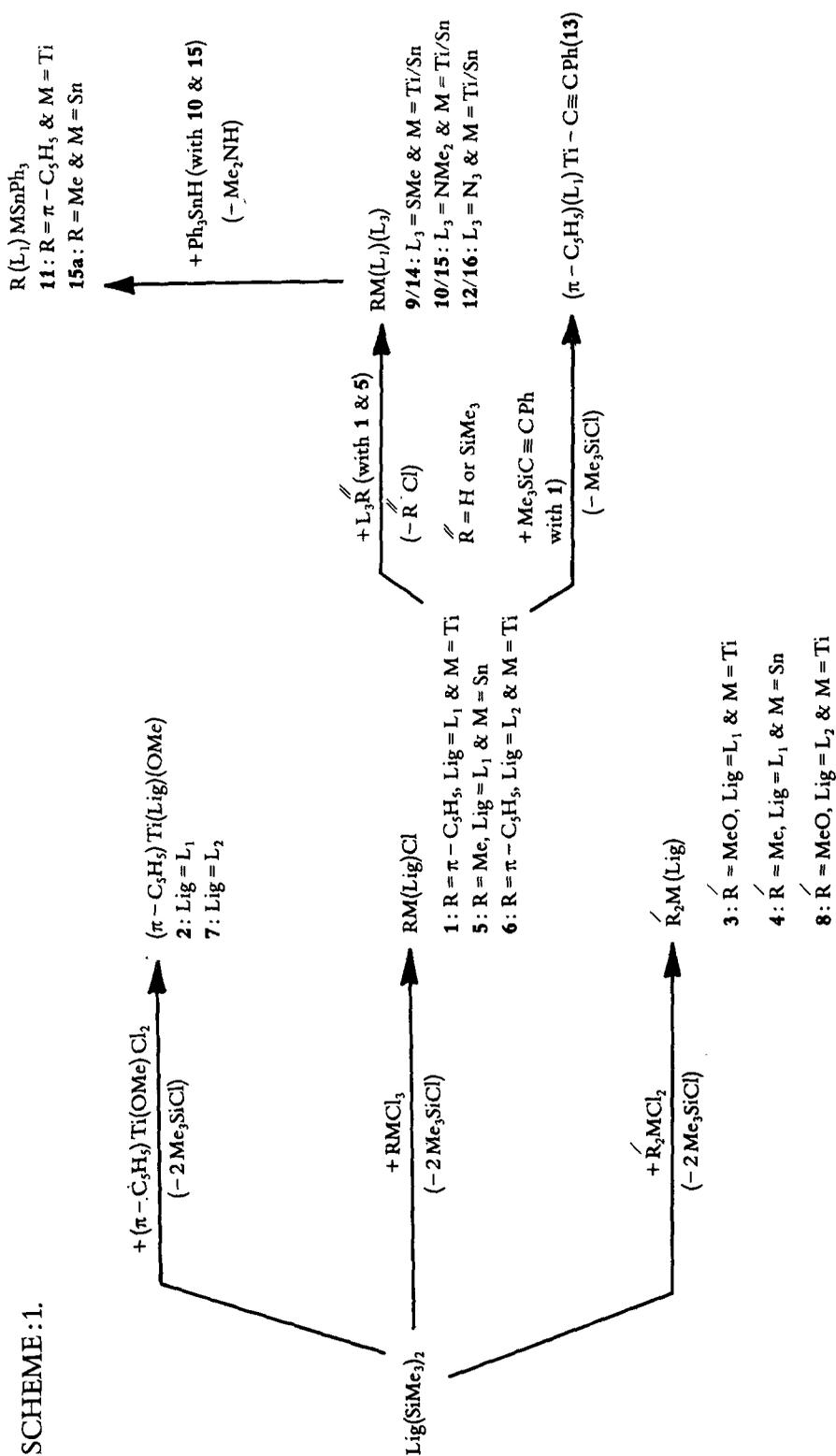
(iv) *Reaction with Me₃SiC \equiv CC₆H₅.* The compound (**1**) was treated with Me₃SiC \equiv CC₆H₅ (1:1 equivalent) in thf yielded a light brown complex, (π -C₅H₅)Ti(L₁) (C \equiv CPh), (**13**) in 55% yield, m.p. 165-167°C (dec.).

3. Results and discussion

3.1. Synthesis

Reaction of organo- and organoxy-titanium(IV) and organotin(IV) chloride, such as (π -C₅H₅)TiCl₃, (π -C₅H₅)Ti(OMe)Cl₂, (MeO)₂TiCl₂, Me₂SnCl₂ and MeSnCl₃, with silylated Schiff bases L₁(SiMe₃)₂ and L₂(SiMe₃)₂ [abbreviated as Lig((SiMe₃)₂)] gave coloured Schiff base complexes of organo- and organoxy-titanium(IV) and organotin(IV) derivatives (**1**) - (**8**).

The complexes (π -C₅H₅)Ti(L₁)Cl, (**1**) and MeSn(L₁)Cl (**5**) smoothly reacted with MeSH, Me₂N SiMe₃ and SiMe₃(N₃) leading to the formation of thiolato-, amino- and azido-complexes of titanium(IV) of the type (π -C₅H₅)-



Ti(L₁)(L₃) [where, L₃ = SMe, **(9)**; L₃ = NMe₂, **(10)**; L₃ = N₃, **(12)**] and tin(IV) of the type MeSn(L₁)(L₃) [where, L₃ = SMe, **(14)**; L₃ = NMe₂, **(15)**, and L₃ = N₃, **(16)**].

Treatment of (π -C₅H₅)Ti(L₁)(NMe₂), **(10)** with Ph₃SnH in thf gave a solution from which a brown powdery complex, (π -C₅H₅)Ti(L₁)(SnPh₃), **(11)** was recovered. The complex **(11)** is not stable in air and decomposed on heating at 210-215°C. It was further observed, in a preliminary reaction, that the complex MeSn(L₁)(NMe₂), **(15)** gave a 'Sn-Sn' bonded complex, MeSn(L₁)SnPh₃, **(15a)** when it was made to react with Ph₃SnH in thf. The azido-complex **(12)** mentioned above was also isolated when the methoxo-complex **(2)** was reacted with SiMe₃(N₃). Syntheses of azido-complexes of titanium(IV) by metathetical reactions between a metal-chlorine and metal-alkoxo bonds and SiMe₃(N₃) have recently been demonstrated (Chonkroun *et al* 1979; Chonkroun and Gervais 1980) and for the synthesis of (π -C₅H₅)-TiCl₂(N₃), (PrⁱO)₂Ti(N₃)₂, (PrⁱO)₂TiCl(N₃) and similar other complexes. However, not much reports are available on the reactions of SiMe₃(N₃) with Sn-Cl/Sn-OMe bonds for the synthesis of tin-azido complexes. It was further observed that Me₃SiC \equiv CPh could be induced to react with **(1)** in thf leading to the formation of (π -C₅H₅)(L₁)Ti.C \equiv CPh, **(13)**. This complex is not stable in air and decomposed on heating at around 165°C. The laboratory atmospheric conditions turned the complex **(13)** to a dark blue semi-solid mass, which could not be identified as yet, and did not show the presence of ν (C \equiv C) in IR spectral measurement.

All the reactions described above for the synthesis of the new complexes are shown in the scheme given below.

3.2. Characterization and spectroscopic data

Elemental analyses of all the newly synthesized compounds agree with the formulations shown in the scheme. The complexes are not sufficiently soluble in benzene and other cryoscopic solvents which prevent reliable molecular weight measurements. However, the complexes are soluble in coordinating solvents.

The IR spectra of the isolated complexes showed that the ν (C=N) appeared about $10 \pm 5 \text{ cm}^{-1}$ lower than those observed in the free Schiff base ligands ($\nu_{\text{C=N}}$ at 1638 cm^{-1} in L₁(SiMe₃)₂ and at 1642 cm^{-1} in L₂(SiMe₃)₂). This demonstrates the coordination of azomethine nitrogen. The phenolic ν (C-O) in the silylated Schiff bases appeared around 1535 cm^{-1} in L₁(SiMe₃)₂ and around 1540 cm^{-1} in L₂(SiMe₃)₂, which shifted to 1542 and 1550 cm^{-1} respectively in the present complexes. The same phenolic C-O stretching vibrations appeared around 1500 cm^{-1} in the Schiff bases L₁H₂ and L₂H₂ before silylation. All these suggest the coordination of phenolic C-O with titanium(IV) and tin(IV) ions in the complexes under discussion (Pasquali *et al* 1978; Bowden and Ferguson 1974; Dey *et al* 1981). Besides, several bands

Table 1. Proton-NMR spectral data (δ ppm)^a of some representative titanium and tin compounds in (CD₃)₂SO with TMS as internal standard^b.

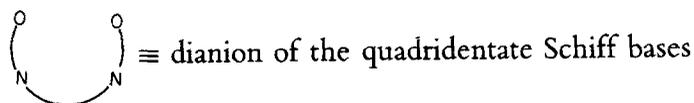
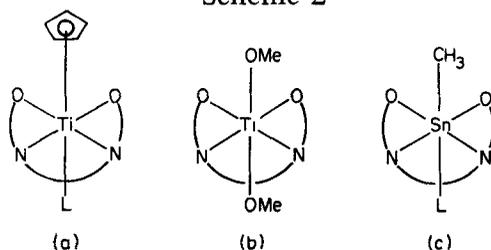
Compound	C ₆ H ₅	C ₃ H ₅	CH ₃ C=N	N-CH ₂	CH ₃ Sn	CH ₃ S	(CH ₃) ₂ N	CH ₃ O
(π -C ₅ H ₅)Ti(L ₁)/Cl	6.6-7.9 (m)	6.65 (s)	0.98 (s)	3.86 (s, br)	-	-	-	-
(π -C ₅ H ₅)Ti(L ₁)(OMe)	6.8-7.6 (m)	6.60 (s)	1.02 (s)	3.82 (s, br)	-	-	-	1.22 (s)
(MeO) ₂ Ti(L ₁)	6.8-7.8 (m)	6.75 (s)	0.98 (s)	3.88 (s, br)	-	-	-	1.20 (s)
Me ₃ Sn (L ₁)	6.5-7.2 (m)	-	1.00 (s)	3.85 (s, br)	0.85 (s)	-	-	-
(π -C ₅ H ₅)Ti(L ₂)(OMe)	6.5-8.0 (m)	6.70 (s)	1.00 (s)	-	-	-	-	1.06 (s)
(π -C ₅ H ₅)Ti(L ₁)(SMe)	7.0-7.5 (m)	6.50 (s)	1.18 (s)	3.88 (s, br)	-	3.28 (s)	-	-
(π -C ₅ H ₅)Ti(L ₁)(NMe ₂)	6.88-7.5 (m)	6.70 (s)	0.98 (s)	3.85 (s, br)	-	-	3.40 (s)	-
(π -C ₅ H ₅)Ti(L ₁)(SnPh ₃)	6.8-7.8 (m)	6.65 (s)	0.95 (s)	3.86 (s, br)	-	-	-	-
(π -C ₅ H ₅)Ti(L ₁)(C \equiv CPh)	6.8-7.6 (m)	6.58 (s)	0.95 (s)	3.38 (s, br)	-	-	-	-
MeSn(L ₁)(SMe)	6.6-7.9 (m)	-	1.28 (s)	3.85 (s, br)	0.95 (s)	3.30 (s)	-	-

(a) Right integrations are obtained; (b) m = multiplet; (s) = singlet; br = broad

appear in the $650\text{-}350\text{ cm}^{-1}$ region in the IR spectra of the complexes. These bands are within the region where $\nu(\text{Ti-O})$, $\nu(\text{Ti-N})$, $\nu(\text{Ti-S})$, $\nu(\text{Ti-Cl})$, $\nu(\text{Sn-O})$, $\nu(\text{Sn-N})$, $\nu(\text{Sn-S})$ and $\nu(\text{Sn-Cl})$ frequencies occur (Sharma *et al* 1981; Aleya 1974; Nakamoto 1970). Metal-carbon stretching and bending vibrations may also appear in this region. In the azido complexes **(12)** and **(16)** the IR bands are observed namely ν_{asym} at about $2200\text{-}2190\text{ cm}^{-1}$ and ν_{sym} at about $1350\text{-}1345\text{ cm}^{-1}$ region. However, these data cannot establish definitely the mode of attachment (terminal or bridged) of the N_3 group, as stressed in a recent paper (Rigby *et al* 1979). Furthermore, the complex, $(\pi\text{-C}_5\text{H}_5)(\text{L}_1)\text{Ti-C}\equiv\text{CPh}$ **(13)** shows a weak band at 2090 cm^{-1} in the IR spectrum assignable to the $\nu(\text{C}\equiv\text{C})$.

^1H NMR spectral data along with their assignments are recorded in table 1. The broad signals for the hydrogen bonded phenolic OH in L_1H_2 and L_2H_2 at about δ 12 and 12.5 ppm respectively disappeared in the silylated Schiff bases $\text{L}_1(\text{SiMe}_3)_2$ and $\text{L}_2(\text{SiMe}_3)_2$ and the silylation is further demonstrated by the appearance of new signals at about δ 0.85 and 0.72 ppm (for Me_3Si group). The chemical shifts of the sharp singlets for $\text{CH}_3\text{C}=\text{N}$ (δ 1 ppm) and $\text{N}-\text{CH}_2$ (δ 3.92 ppm) protons in L_1H_2 and L_2H_2 have been found to remain almost unchanged in $\text{L}_1(\text{SiMe}_3)_2$ and $\text{L}_2(\text{SiMe}_3)_2$. However, in the present titanium(IV) and tin(IV) complexes these signals appeared as sharp singlets at slightly lower fields (table 1). It may, therefore, be inferred that in these complexes both the Schiff base ligands assume planar configuration (Dey *et al* 1982). Besides, the sharp signals for C_5H_5 , CH_3 , CH_3S , $(\text{CH}_3)_2\text{N}$, and CH_3O protons in the complexes suggest *trans* arrangement of these ligands; on the basis of which the present complexes may be represented by the structures (a, b, c) shown in scheme 2

Scheme 2



(a) $\text{L} = \text{Cl}, \text{Me}, \text{MeS}, \text{Me}_2\text{N}, \text{Ph}_3\text{Sn}, \text{C}\equiv\text{CPh}$

(c) $\text{L} = \text{Cl}, \text{MeS}, \text{Me}_2\text{N}, \text{Ph}_3\text{Sn}, \text{Me}$

As no suitable crystals of the compounds are yet isolated, x-ray crystal structure could not be determined.

Acknowledgement

This work was made possible by a grant from the Council of Scientific and Industrial Research, New Delhi. DK and SBR thank CSIR, New Delhi for fellowships. Financial assistance from the University is also gratefully acknowledged. The authors thank Prof. P L Pauson, University of Strathclyde, Glasgow, U. K. and Prof. H Werner, University of Wurzburg, West Germany for elemental analyses and spectroscopic data.

References

- Alyea E C 1974 *J. Coord. Chem.* **4** 55
 Birkofer L and Ritter A 1963 *Chem. Ber.* **96** 3280
 Birkofer L and Ritter A 1965 *Angew Chem. int. ed.* **4** 417
 Bowden F L and Ferguson D 1974 *J. Chem. Soc.* 460
 Chonkroun R, Gervais D and Dilworth J R 1979 *Trans. Metal. Chem.* **4** 249
 Chonkroun R and Gervais D 1980 *J. Chem. Soc. Dalton Trans.* 1800
 Collier M R, Lappert M F and McKeeping J 1970 *Abstr. 13th Int. Conf. Coord. Chem.* 3213
 Collier M R, Lappert M F and Pearce R 1973 *J. Chem. Soc. Dalton Trans.* 445
 Dey K 1974 *J. Sci. Ind. Res.* **33** 76
 Dey K and Werner H 1977 *J. Organometal. Chem.* **137** C 28
 Dey K and Werner H 1979 *Chem. Ber.* **112** 823
 Dey K, Biswas A K and Sinha Ray A K 1981 *Indian J. Chem.* (A)**20** 848
 Dey K, Biswas A K, Koner D and Ray S B 1982 *J. Chem. Soc. Dalton Trans.* 911
 Dilworth J R, McAuliffe C A and Sayle B J 1977 *J. Chem. Soc. Dalton Trans.* 849
 Gorsich R D 1958 *J. Am. Chem. Soc.* **80** 4744
 Gorsich R D 1960 *J. Am. Chem. Soc.* **82** 4211
 Gattow G and Yildirimyan H 1977 *Z. Anorg. allg. Chem.* **431** 175, 179
 Holm R H, Everett Jr. and Chakraborty A 1966 *Prog. Inorg. Chem.* **7** 83
 Luijten J G A and van der Kerk G J M 1959 *Investigation in the field of organotin chemistry* (Tin Research Institute)
 Nakamoto K 1970 *Infrared spectra of inorganic and coordination compounds* 2nd ed (New York: Wiley)
 Nesmeyanov A N, Nogina O V and Dubovitskii V A 1968 *Izv. Akad. Nauk SSSR Ser. Khim.* 527
 Nesmeyanov A N, Nogina O V, Lazareva N A and Dubovitskii V A 1967 *Izv. Akad. Nauk. SSSR Ser. Khim.* 808
 Petrov A D and Shchukoskaya L L 1953 *Chem. Abstr.* **47** 12225
 Pasquali M, Marchitti F, Landi A and Floriani C 1978 *J. Chem. Soc. Dalton Trans.* 545
 Rigby W, Bailey P M, McCleverty J A and Maitlis P M 1979 *J. Chem. Soc. Dalton Trans.* 371
 Sharma R K, Singh R V and Tandon J P 1980 *J. Inorg. Nucl. Chem.* **42** 463, 1382
 Sharma R K, Singh R V and Tandon J P 1981 *J. Inorg. Nucl. Chem.* **43** 410
 Wailes P C, Coutts R S P and Weigold H 1974 *Organometallic chemistry of Ti, Zr and Hf* (New York/London: Academic Press)