Main Group Element Phosphine Complexes. 5.† Tri- and Tetracoordinated, Monomeric Tin(II) Phosphine Complexes and X-ray Structure of $Sn[C(PMe_2)_3]_2$

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$SnCl_2$ reacts with $Li[C(PMe_2)_2X]$ to give yellow, neutral complexes $Sn[C(PMe_2)_2X]_2$ (X = PMe_2, **4**; X = $SiMe_3$, **7**) under exclusive formation of Sn–P bonds. The X-ray structure determination of **4** (space group $P2_1$; $a = 6.540$ (2) Å, $b = 16.338$ (6) Å, $c = 11.720$ (4) Å; $\beta = 98.15$ (3)°; $V = 1239.64$ Å^3; $d_{calcd} = 1.363$ g/cm^3 for $Z = 2$; $R_w = 0.043$ for 189 refined parameters and 4165 reflections with $F_o \geq 4.0\sigma(F_o)$) reveals a distorted Ψ-tbp ground-state geometry with two phosphorus donor atoms in axial (d(SnP) = 2.790 (2), 2.839 (2) Å) and two in equatorial positions (d(SnP) = 2.602 (2), 2.598 (2) Å) at the Sn(II) spiro center. Both **4** and **7** are fluxional in solution at −90 °C, due to a pseudorotation process which equilibrates axial and equatorial positions. At elevated temperatures all six phosphorus atoms in **4** are equilibrated. In contrast to **4** and **7**, $Sn[HC(PPh_2)_2]_2$ (**9**), which is obtained from $SnCl_2$ and $Li[HC(PPh_2)_2]$, exhibits a threefold Sn coordination at low temperature in solution, arising from one chelating $(\overset{\frown}{P\;P})$ and one monodentate (C) diphosphinomethanide ligand. The different PPh_2 groups of the monodentate ligand are quilibrated at 20 °C, whereas at 70 °C, both diphosphinomethanide ligands equilibrate via a twofold coordinated Sn(II) transition state. From $Li[C(PPh_2)_3]$ and $SnCl_2$, two thermally unstable complexes are obtained, $ClSn[C(PPh_2)_3]$ (**13**) and $Sn[C(PPh_2)_3]_2$ (**14**). In solution, **13** is monomeric with a threefold coordination at Sn and **14** resembles **4** and **7** in exhibiting tetracoordination. The results are explained by an inter-/intraligand repulsion model, with additional electronic effects also operating, and are based on NMR (^{1}H, ^{13}C, ^{31}P, ^{119}Sn) measurements.

Introduction

Monomeric coordination compounds of tin(II) are still rare.[1,2] With phosphine ligands, isolated and structurally characterized examples are still unknown.[3-5] On the other hand, SnR_2 compounds have attracted considerable and still growing attention as carbene analogues, but stable and fully characterized examples are restricted to the silylmethanide and silylamino compounds.[6] Phosphinomethanides I are comparable to silylmethanides II and thus should also form stable, monomeric tin(II) compounds, but due to their additional phosphine functionality, new coordination modes at Sn(II) may be envisaged.

$$[H_{(3-x)}C(PMe_2)_x]^- \qquad [H_{(3-x)}C(SiMe_3)_x]^-$$

I II

(x = 1 - 3)

Moreover, phosphinomethanides have been shown to be suitable ligands for the preparation of main group element phosphine complexes, as, e.g., in the case of Li^+.[7,8] The delicate balance between C and P nucleophilicity of the ambidentate phosphinomethanides I[9-12] is shifted in favor of the latter on going from $x = 1$ to $x = 3$ for statistical, electronical, and sterical reasons. Therefore, exclusive P-coordination to a main group element center is expected particularly for triphosphinomethanide derivatives. An extension of these findings to the heavier main group metal Sn(II) was expected to broaden the scope and the applicability of the unique phosphinomethanide ligands I considerably. Preliminary results have been reported previously.[13]

Experimental Section

A. Preparation and Characterization of Compounds. General procedures and instrumentation followed closely those described previously.[8] All compounds were prepared and handled in a dry argon atmosphere using conventional vacuum line or Schlenk tube techniques. Sodium/potassium alloy (ethereal solvents) or $LiAlH_4$ (hydrocarbon solvents) were employed for drying, storage, and redestillation immediately prior to their use. $SnCl_2$ was sublimed in vacuo (260 °C, 10^{-3} torr), $Li[H_{3-x}C(PMe_2)_x]$ (**1**) was prepared according to ref 14 and 15, and $Li[CH(PPh_2)_2]$ (**8**) and $Li[C(PPh_2)_3]$ (**12**) were prepared according to ref 16 and 17. IR spectra were run as Nujol mulls between CsI windows. Toluene-d_8 was used as solvent for the NMR measurements

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throughout. Melting points were determined in sealed capillaries by using a Büchi capillary melting point apparatus and are uncorrected.

Attempted Preparation of $\mathrm{Sn[CH_{3-x}(PMe_2)_x]_2}$ (2, $x = 1$; 3, $x = 2$). To a mixture of 2 mmol of $\mathrm{SnCl_2}$ and 4 mmol of 1 was added 30 mL of THF at −78 °C under stirring. The reaction mixture was stirred for 30 min. A color change from yellow via orange to dark red was observed in all cases. After the solution was warmed to room temperature, the solvent was removed in vacuo. Only in the case of 2, the residue was soluble in pentane. After filtration and evaporation of the solvent, the colorless liquid was identified as $\mathrm{Sn(CH_2PMe_2)_4}$ (NMR).[18] In all other cases, no tin-containing reaction products could be extracted from the residue with hydrocarbon or ethereal solvents.

$\mathrm{ClSn[C(PPh_2)_3]}$ (13). A mixture of 194 mg (1.03 mmol) of $\mathrm{SnCl_2}$ and 589 mg (1.03 mmol) of $\mathrm{Li[C(PPh_2)_3]}$ (**12**) was dissolved at −78 °C in 30 mL of THF. Under stirring, the reaction mixture was allowed to warm to 0 °C and the solvent was removed in vacuo. The residue obtained was extracted twice with 50 mL of $\mathrm{C_6H_6}$ and the clear solution evaporated at 0 °C. A light yellow solid remained, which contained besides **13** a varying amount of $\mathrm{HC(PPh_2)_3}$ (NMR) and an intractable tin, chlorine, and phenylphosphorus containing material.

$\mathrm{Sn[C(PPh_2)_3]_2}$ (4). $\mathrm{Li[C(PMe_2)_3]}$ (**1**) (710 mg, 3.51 mmol) and 332 mg (1.76 mmol) of $\mathrm{SnCl_2}$ were dissolved at −78 °C in 50 mL of diethyl ether. On being stirred and warmed to room temperature, the suspension turned yellow. The solvent was removed by evaporation. The resulting yellow solid was extracted with 30 mL of pentane and washed three times with 20 mL of pentane. The clear solution was cooled to −78 °C. The yellow crystals obtained were washed twice with 10 mL of cold pentane and dried in vacuo: 726 mg (1.43 mmol, 81%) of yellow crystals were obtained in this way: mp 79–80 °C dec; MS, *m/e* (relative intensity) 506, 508, 510, 514 (0.9, $\mathrm{M^+}$); 311, 313, 315, 319 (3.7, $\mathrm{M^+ - C(PMe_2)_3}$); ^{1}H NMR (+30 °C) $\delta(\mathrm{PCH_3})$ 1.87 (s, br); ^{13}C NMR (+30 °C) $\delta(\mathrm{PCH_3})$ 20.64 (s, br), δ(PCP) 31.25 (q, ^1J(PC) = 3.7 Hz); ^{13}C NMR (−70 °C) $\delta(\mathrm{P_{A/B}CH_3})$ 20.75 (superposition with $\mathrm{C_6D_5CD_3}$), $\delta(\mathrm{P_xCH_3})$ 19.18 (d, ^1J(PC) = 14.3 Hz); δ(PCP) 29.30 (dt, ^1J(PC) = 42.7, 17.8 Hz); IR (cm^{-1}) 1000 s, 963 s, 932 s, 709 m, 690 m, 670 m, 418 w. Anal. Calcd for $\mathrm{C_{14}H_{36}P_6Sn}$ (508.98): C, 33.04; H, 7.13. Found: C, 33.10; H, 7.19.

$\mathrm{Sn[C(PMe_2)_2SiMe_3]_2}$ (7). To a solution of 260 mg (1.38 mmol) of $\mathrm{SnCl_2}$ in 40 mL of THF was added a solution of 589 mg (2.75 mmol) of $\mathrm{Li[C(PMe_2)_2SiMe_3]}$ (**6**)[19] in 20 mL of THF at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for another 30 min. After removal of the solvent in vacuo, the remaining residue was extracted with 30 mL of pentane, filtered, and washed twice with 20 mL of pentane. The combined pentane solutions were reduced to small volume and again cooled to −78 °C: yellow crystals separated from the solution. These were washed twice with 5 mL of pentane at −78 °C and then dried in vacuo: 640 mg (1.20 mmol, 87%); mp 93 °C; ^{1}H NMR (+30 °C): $\delta(\mathrm{PCH_3})$ 1.74 (s, br), $\delta(\mathrm{SiCH_3})$ 0.54 (s); ^{13}C NMR (+30 °C) $\delta(\mathrm{PCH_3})$ 22.15 (s, br), $\delta(\mathrm{SiCH_3})$ 5.21 (s), δ(PCP) 27.16 (br); ^{13}C NMR (−80 °C) $\delta(\mathrm{PCH_3})$ 21.60 ("t", *N* = 5.9 Hz, AA′X), $\delta(\mathrm{SiCH_3})$ 5.05 (s), δ(PCP) 24.85 (t, ^1J(PC) = 16.0 Hz); IR (cm^{-1}) 825–50 vs, 749 s, 629 m, 440 w, 400m, 350 w. Anal. Calcd for $\mathrm{C_{16}H_{42}P_4Si_2Sn}$ (533.28): C, 36.04; H, 7.94. Found: C, 35.57; H, 7.82.

$\mathrm{Sn[CH(PPh_2)_2]_2}$ (9). $\mathrm{Li[CH(PPh_2)_2]}$ (**8**) (860 mg, 2.21 mmol) and 208 mg (1.10 mmol) of $\mathrm{SnCl_2}$ were dissolved in 40 mL of THF at −78 °C. The mixture was allowed to warm to room temperature under stirring. Subsequently the solvent was removed in vacuo, and the remaining deep yellow residue was dissolved in 40 mL of $\mathrm{C_6H_6}$. After filtration the solution was evaporated. A 752-mg (0.85 mmol, 77%) sample of a deep yellow solid was obtained: mp 101–102 °C dec; ^{1}H NMR (+30 °C) $\delta(\mathrm{C_6H_5})$ 6.98–7.96 (m, br), δ(SnCH) 3.63 (s, br); ^{13}C NMR (+5 °C) δ(PCP) 24.15 (t, ^1J(PC) = 57.4 Hz), δ(SnC) 17.87 (t, ^1J(PC) = 62.3 Hz); IR (cm^{-1}) 750 s, 742 vs, 699 vs, sh, 371 w. Anal. Calcd for $\mathrm{C_{50}H_{42}P_4Sn}$ (885.47): C, 67.82; H, 4.78. Found: C, 67.50; H, 4.78.

$\mathrm{Sn[C(PPh_2)_3]_2}$ (14). $\mathrm{SnCl_2}$ (400 mg, 2.15 mmol) and 2430 mg (4.25 mmol) of $\mathrm{Li[C(PPh_2)_3]}$ (**12**) were dissolved in 50 mL of THF at −78 °C. Under stirring the mixture was allowed to warm to 0 °C. The solvent was removed in vacuo and the yellow residue extracted with 40 mL of toluene at 0 °C. The solvent was evaporated: the yellow solid obtained contained varying amounts of $\mathrm{HC(PPh_2)_3}$, an untractable solid, and **14** with about 85% purity (NMR). Further attempts for purification were unsuccessful, due to the rapid decomposition in solution.

Table I. Crystal Structure Data of 4

cryst size, mm	0.1 × 0.3 × 0.4
formula	$\mathrm{C_{14}H_{36}P_6Sn}$
M_r	508.98
space group	$P2_1$
a, Å	6.540 (2)
b, Å	16.338 (6)
c, Å	11.720 (4)
β, deg	98.15 (3)
V, Å^3	1239.64
Z	2
d_{calcd}, g/cm^2	1.363
$\mu(\mathrm{Mo\ K\alpha})_{\mathrm{calcd}}$, cm^{-1}	14.11
F(000)	520
T, °C	−35
radiatn	Mo Kα
λ, Å	0.710 69
scan mode	ω
$\Delta\omega$, deg	1.0
scan rate, deg/min	0.9–29.3
$((\sin\theta)/\lambda)_{\max}$	0.593
hkl range	+7, +19, ±13 (+ Friedel opposites)
reflctns measd	5039
reflctns unique	4327
R_{int}	0.045
reflctns obsd	4165
absorptn correctn	empirical
rel transmissn ($T_{\max}/T_{\min}$)	1.00/0.62
param ref	189
(shift/error)$_{\max}$	0.1
R	0.038
R_w	0.043
$\Delta\rho_{\mathrm{fin}}$ (max/min), e/Å^3	+1.69/−2.09

X-ray Structure Determination of $\mathrm{Sn[C(PMe_2)_3]_2}$ (4)

A single crystal (from pentane) was sealed under an atmosphere of argon at dry ice temperature into a glass capillary. Diffractometer measurements (Syntex P2$_1$) indicated a monoclinic unit cell which was confirmed by reduced cell calculations (TRACER) and axial photographs. The systematic extinctions pointed to $P2_1$ or $P2_1/m$ as possible space groups of which the former was confirmed by successful refinement (the molecule has no mirror symmetry or inversion center as implied by $Z = 2$ for $P2_1/m$). The exact cell dimensions were obtained by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 centered high-order reflections from various parts of reciprocal space. Pertinent crystal data as well as a summary of intensity data collection and refinement are given in Table I. Data collection and refinement procedures followed closely those described in ref 8.

The integrated intensities of two forms of data ($+h,+k,\pm l$ and Friedel opposites) were measured on a four-circle diffractometer equipped with a graphite monochromator. One standard reflection (111), repeated every 50 reflections, showed only a random intensity fluctuation. The data were corrected for *Lp* effects and for those of absorption. For the latter an empirical correction based on scans around the scattering vectors of six selected reflections near $\chi = 90°$ was used (Syntex XTL). After equivalent data were merged, structure factors with $F_o \leq 4.0\ \sigma\ (F_o)$ were deemed "unobserved" and not used in all further calculations. The structure was solved by Patterson methods and completed by Fourier techniques. Of the 36 hydrogen atoms, 16 could be located in difference syntheses and the remainder were calculated at idealized geometrical positions. Thereby the found H atoms served to determine the conformation of all methyl groups. Refinement with anisotropic temperature factors (H atoms fixed with $U_{\mathrm{iso}} = 0.05$ Å^2) converged at $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.038$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^{\,2}]^{1/2} = 0.043$, and $w = 1/\sigma^2(F_o)$. The

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 4[a]

atom	x/a	y/b	z/c	U(eq), Å^2
Sn	0.4608 (1)	0.5000 (0)	0.2884 (1)	0.025
P1	0.7724 (3)	0.5350 (1)	0.4445 (1)	0.024
P2	0.7300 (3)	0.3725 (1)	0.3643 (1)	0.026
P3	1.0013 (3)	0.3885 (1)	0.5979 (1)	0.032
P4	0.5942 (3)	0.5172 (1)	0.0912 (1)	0.028
P5	0.4488 (3)	0.6599 (1)	0.1927 (1)	0.028
P6	0.4908 (3)	0.6798 (1)	−0.0627 (1)	0.037
C1	0.8366 (11)	0.4344 (4)	0.4799 (5)	0.026
C2	0.5154 (11)	0.6176 (4)	0.0643 (5)	0.029
C11	0.6891 (12)	0.5932 (4)	0.5619 (6)	0.041
C12	0.9828 (10)	0.5999 (4)	0.4118 (6)	0.036
C21	0.9372 (12)	0.3193 (4)	0.3041 (6)	0.043
C22	0.5977 (11)	0.2862 (4)	0.4228 (6)	0.036
C31	0.9050 (12)	0.4258 (5)	0.7280 (5)	0.044
C32	1.2434 (11)	0.4475 (4)	0.6122 (6)	0.042
C41	0.8621 (11)	0.4949 (6)	0.0753 (5)	0.047
C42	0.4629 (15)	0.4422 (4)	−0.0071 (6)	0.045
C51	0.6035 (12)	0.7514 (4)	0.2326 (6)	0.041
C52	0.1937 (11)	0.7086 (4)	0.1616 (6)	0.042
C61	0.3386 (13)	0.6165 (5)	−0.1731 (6)	0.047
C62	0.7429 (15)	0.6748 (8)	−0.1157 (8)	0.068

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$, where U_1, U_2, and U_3 are the eigenvalues of the $\mathbf{U}_{ij}$ matrix. Esd's are in parentheses.

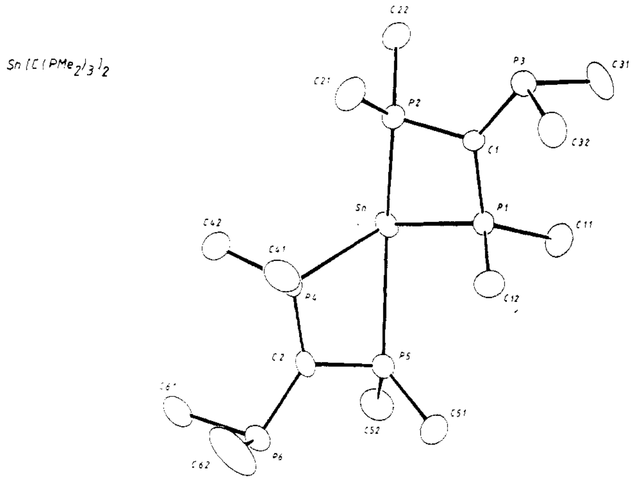


Figure 1. Molecular structure of 4 (ORTEP, thermal ellipsoides at the 50% probability level, H atoms omitted for clarity).

function minimized was $\Sigma w(|F_o| - |F_c|)^2$ (SHELX 76). The residual electron density had all maxima greater than 1.0 e/Å^3 near the Sn atom. Refinement of the inverse coordinate set ($\bar{x}$, $\bar{y}$, $\bar{z}$) did not give significantly different R values nor were bond distances and angles different. Reference 8 also contains the sources of the scattering factors and references to the programs used. Table II contains the atomic coordinates of the non-hydrogen atoms; Table III summarizes important distances and angles. Figure 1 shows the molecular structure.

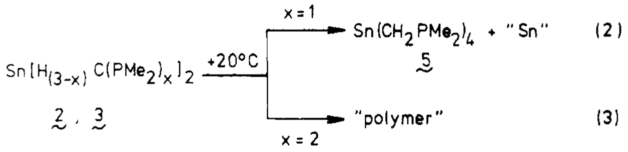
Results and Discussion

A. *P*-Methyl-Substituted Phosphinomethanide Ligands. In the reaction of tin(II) chloride with phosphinomethanides of type I, only for $x = 3$ a stable tin(II) compound could be obtained (eq 1). In all three cases,

$$\mathrm{SnCl_2} + 2\,\mathrm{Li[H_{(3-x)}C(PMe_2)_x]} \xrightarrow[-78\,^\circ\mathrm{C}]{\mathrm{Et_2O}} \mathrm{Sn[H_{(3-x)}C(PMe_2)_x]_2} \qquad (1)$$

$$\underset{\sim}{1}^{9} \qquad x = 1:\ \underset{\sim}{2} \quad x = 2:\ \underset{\sim}{3} \quad x = 3:\ \underset{\sim}{4}$$

light yellow solutions were obtained at −78 °C in diethyl ether, but for $x = 1$ and 2, the color of the solutions darkens on warming via red to brown-black. For $x = 2$ only an insoluble, probably polymeric, material is isolated, whereas for $x = 1$ a disproportionation of the intermediate tin(II) compound 2 to the Sn(IV) species 5 and Sn(0) is observed (eq 2 and 3). The potentially tetradentate



$$\underset{\underset{\sim}{2},\ \underset{\sim}{3}}{\mathrm{Sn[H_{(3-x)}C(PMe_2)_x]_2}} \xrightarrow[x=1]{+20\,^\circ\mathrm{C}} \underset{\underset{\sim}{5}}{\mathrm{Sn(CH_2PMe_2)_4}} + \text{"Sn"} \qquad (2)$$

$$\mathrm{Sn[H_{(3-x)}C(PMe_2)_x]_2} \xrightarrow[x=2]{+20\,^\circ\mathrm{C}} \text{"polymer"} \qquad (3)$$

phosphine 5 is isolated in nearly quantitative yield, and therefore this reaction (eq 2) may be regarded as good alternative to the previously reported preparation of 5.[18] In contrast to the rapid decomposition of 2 and 3, the yellow color of solutions of 4 persists on warming to room temperature, and yellow, low melting crystals may be isolated from pentane solutions, which proved suitable for X-ray diffraction.

Table III. Bond Distances (Å) and Angles (deg) for 4[a]

Bond Distances			
Sn–P1	2.602 (2)	Sn–P4	2.598 (2)
Sn–P2	2.790 (2)	Sn–P5	2.839 (2)
C1–P1	1.733 (6)	C2–P4	1.735 (6)
C1–P2	1.754 (6)	C2–P5	1.765 (6)
C1–P3	1.792 (6)	C2–P6	1.791 (6)
P1–C11	1.818 (7)	P4–C41	1.825 (7)
P1–C12	1.820 (7)	P4–C42	1.812 (7)
P2–C21	1.834 (7)	P5–C51	1.829 (7)
P2–C22	1.837 (7)	P5–C52	1.838 (7)
P3–C31	1.835 (7)	P6–C61	1.835 (8)
P3–C32	1.841 (7)	P6–C62	1.845 (11)
Bond Angles			
P1–Sn–P2	62.9 (1)	P4–Sn–P5	62.8 (1)
P2–Sn–P5	142.5 (1)	P1–Sn–P4	105.9 (1)
P1–Sn–P5	92.9 (1)	P2–Sn–P4	95.1 (1)
C1–P1–Sn	95.7 (2)	C2–P4–Sn	97.8 (2)
C1–P2–Sn	88.8 (2)	C2–P5–Sn	88.8 (2)
P1–C1–P2	107.8 (3)	P4–C2–P5	108.6 (3)
P1–C1–P3	132.9 (4)	P4–C2–P6	132.6 (4)
P2–C1–P3	119.0 (3)	P5–C2–P6	118.8 (3)

[a] Esd's in units of the last significant figure are in parentheses.

Description of the Structure of 4. In the crystal both triphosphinomethanide ligands are coordinated exclusively via two of their phosphorus atoms to Sn(II). The latter acts as spiro center for the two four-membered rings thus formed. The four coordinated P atoms form a distorted coordination geometry around Sn which clearly resembles a pseudo trigonal bipyramid (Ψ-tbp) with one vacant side (Figure 1). Most noteworthy are the drastically different axial and equatorial Sn–P bond lengths (Table III). Sn–P2/P5 (2.790 (2), 2.839 (2) Å) and Sn–P1/P4 (2.602 (2), 2.598 (2) Å) differ by up to 0.24 Å! Distortions from an ideal tbp arrangement arise mainly from the bond angles at Sn. By virtue of the small bite angle of the ligands the intraligand angles P1–Sn–P2 and P4–Sn–P5 are only 62.9 (1)° and 62.8 (1)°. The rather large discrepancy from the ideal 90° of four-membered rings certainly arises from the large angles at C1/C2, which themselves are compressed to 107.8 (3)/108.6 (3)° from the sp^2 standard, and the long Sn–P bonds. On the other hand, the ring angles at P1/P2 and P4/P5 are much closer to 90°.

The remaining two angles at Sn (P1–Sn–P5 = 92.9 (1)°, P2–Sn–P4 = 95.1 (1)°) are less affected and come close to their ideal tbp values. The third equatorial coordination site of the tbp is empty, and it is reasonable to assume the free electron pair of Sn(II) to be oriented in this direction. Its stereochemical activity is clearly seen in the compressed axial and equatorial angles at Sn. This effect, together with the ring strain, contributes mainly to the overall distortions observed. Certainly, the influence of the additional lone pairs at the carbanionoid centers C1 and C2 and those at the uncoordinated phosphorus atoms P3 and P6 is less effective in determining the overall shape of the molecule. (All together, in 4 the mutual interaction of not less than five "free" electron pairs has to be minimized effectively!). Yet, the methyl groups at P3/P6 are oriented in such a way that the phosphorus lone pairs are in approximate orthogonal positions with those at C1/C2. Moreover, though highly strained, the four-membered chelate rings are not planar, but C1/C2 are displaced by 0.41/0.27 Å from the respective SnP_2 planes away from the free equatorial site at Sn (lone pair), thus minimizing the mutual interaction of the carbanionic lone pairs at C1 and C2 with the Sn lone pair. In the related compound $Al[C(PMe_2)_2SiMe_3]_3$, where no such interaction has to be considered, the four-membered chelate rings are exactly planar.[20]

As the sums of their valence angles (359.7, 360.0°) imply, C1 and C2 are exactly planar, thus resembling ylidic carbanionic centers, as, e.g., in $[(Me_3P)_3C]I_2$.[21] This is at variance, however, with the Li complex of I ($x = 3$): $\{Li[C(PMe_2)_3]\cdot THF\}_2$ whose central C atom is slightly pyramidalized as a consequence of its involvement in the heteroallylic coordination of the ligand to the second Li^+ in the dimeric molecule.[7,11] In 4 metal–carbon interactions are observed neither in an intramolecular nor in an intermolecular fashion. Although the SnPCP four-membered rings are envelope-shaped (vide supra), with dihedral angles SnP_2/P_2C of 159.7° and 164.6°, the Sn–C1/C2 distances (3.265 (5)/3.313 (5) Å) are certainly too long to be considered bonding.

Finally, the bond lengths deserve a comment. The already mentioned Sn(II)–P distances have no precedent in the literature. Among the few available Sn(IV)–P distances those in *trans*-$SnCl_4(PEt_3)_2$[22] (2.615 (5) Å) are of comparable length to the equatorial ones in 4, whereas the axial ones are considerably longer. The short C1/C2–P bonds reflect a high degree of polarity, as, e.g., in phosphorus ylides. Most noteworthy, the bonds to the coordinated P atoms P1/P2 and P4/P5 are shorter than those to the trivalent P3/P6. Among the former, those to the equatorial P atoms are consistently shorter than those to the axial ones, which is in accord with higher P_{eq}–C bond polarity as a result of more electron donation to Sn(II) via the shorter equatorial Sn–P bonds.

Dynamic Behavior of 4. The NMR spectra of 4 at −80 °C are in accord with the observed Ψ-tbp structure in the solid state (4/I), if a rapid pseudorotation is assumed to equilibrate the axial and equatorial positions P_A/P_B at Sn. Thus in the ^{31}P NMR a degenerate $A_2A_2'XX'$ spectrum (apparently A_4X_2) is observed: $\delta(P_A)$ −17.2 (t, $J = 13.7$ Hz); $\delta(P_X)$ −41.5 (quin, $J = 13.7$ Hz). The P_A signal shows $^{117/119}Sn$ satellites $J = 742, 776$ Hz). On warming to +20 °C, the spectrum collapses to a single line. Apparently all six phosphorus atoms now become equivalent on the NMR time scale by a rapid P_A/P_X exchange process ($\Delta G_{+20\ °C} = 12.7$ kcal/mol). Most noticeable, this ^{31}P singlet likewise shows $^{117/119}Sn$ satelites ($J = 522, 552$ Hz). This may be explained in terms of a three-coordinate intermediate 4/II, where both $P_{A'}$ and P_X may occupy the fourth coordination site (rotation around the Sn–P and/or PC axis. Alternatively, one may assume participation of the carbanion in the Sn-coordination (4/III).

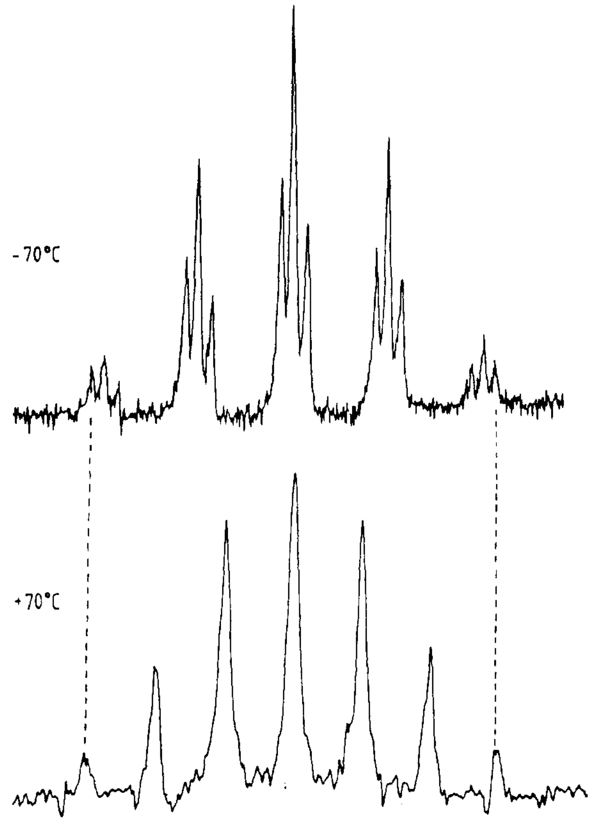
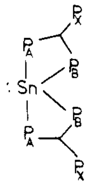
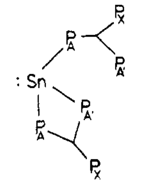


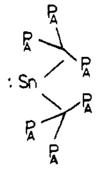
Figure 2. ^{119}Sn NMR spectra of 4 at −70 and +70 °C (74.60 MHz, toluene-d_8).



4/I



4/II



4/III

Further clarification is obtained from the ^{119}Sn NMR spectra. In line with the ^{31}P observations, at −78 °C (δ −258.0 (quin t)) a one-bond coupling to a donor set of four equivalent phosphorus nuclei ($^1J(SnP) = 776$ Hz) and a three-bond coupling ($^3J(SnP) = 102$ Hz) is observed. On warming to +70 °C, the signal (δ −247.7 (sept)) indicates all phosphorus atoms now to be equivalent with an apparent coupling constant of 551 Hz, the "weighted average" of the low-temperature values (Figure 2). The rather small differences of these values (δ, J) at both temperatures indicate that the structure in solution should not change drastically with temperature; hence 4/III appears less likely. On the other hand, the constancy of the average coupling constants gives rise to the assumption that the three-coordinate intermediate 4/II has only a very short lifetime.

In order to definitely rule out structure 4/III and to clarify the role of P_X in this process, the P_XMe_2 group was replaced by the $SiMe_3$ substituent (eq 4). 7 is prepared

$$\underset{6^{19}}{\underbrace{}}SnCl_2 + 2\ \underset{6^{19}}{Li[C(PMe_2)_2SiMe_3]} \longrightarrow \underset{7}{Sn[C(PMe_2)_2SiMe_3]_2} \quad (4)$$

and isolated similar to 4 as yellow crystals. Both in the ^{31}P NMR ($\delta(P)$ −23.0 (s, $^{117/119}Sn$ satellites, $J = 705, 737$ Hz)) and in the ^{119}Sn NMR spectrum ($\delta(Sn)$ −175.4 (quin,

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(20) Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics*, in press.

(21) Zimmer-Grasser, B.; Neugebauer, D.; Schubert, U.; Karsch, H. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1267.

(22) Mather, G. G.; McLaughlin, G. M.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1973**, 1823.

$^1J(PSn)$ = 737 Hz)) no noticeable temperature effect is observed in the range −90 to +70 °C.

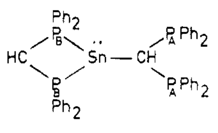
Besides a rapid pseudorotation in solution, which obviously is operating also in this case, no fluxionality of **7** is apparent, which confirms the results and conclusions for **4**.

B. *P*-Phenyl-Substituted Phosphinomethanide Ligands. Whereas with $[(Me_2P)_2CH]^-$ as the ligand no stable Sn(II) compound could be isolated (vide supra), the phenyl analogue $[(Ph_2P)_2CH]^-$ forms an isolable, yellow solid **9** according to eq 5. **9** has only a very low solubility

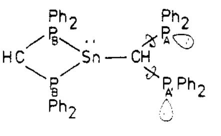
$$SnCl_2 + 2\,Li[CH(PPh_2)_2] \longrightarrow Sn[CH(PPh_2)_2]_2 \qquad (5)$$

8 **9**

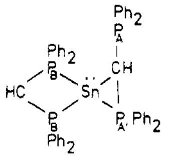
in pentane but readily dissolves in aromatic solvents. Quite remarkably, the NMR spectra indicate a threefold Sn coordination. In the ^{31}P spectra at −15 °C, an A_2B_2 system shows up ($\delta(P_A)$ −12.5 (t), $\delta(P_B)$ −17.9 (t) ($J(P_AP_B)$ = 24 Hz)).[23]



9/I

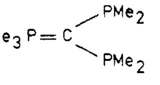


9/II



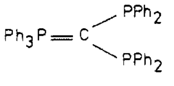
9/III

The ^{119}Sn NMR signal ($\delta(^{119}Sn)$ +175.6 (tt, J = 1172, 163 Hz)) appears at very low field compared to **4** and **7**, in line with the expectation for a lower coordination number. The inequivalence of the two carbanionic C nuclei is evident from the ^{13}C NMR: $\delta(^{13}C_A)$ 17.8 (t, J = 62.3 Hz); $\delta(^{13}C_B)$ 24.2 (t, J = 57.4 Hz) (C_A/C_B, arbitrary assignment). The NMR spectra of **9** are temperature dependent. On cooling, the P_A signal broadens and finally, at −90 °C, splits into two 1:1 signals ($\delta(P_A)$ −9.5 (t, br, J = 33 Hz)), $\delta(P_{A'})$ −16.1, partial superposition with P_B), whereas the P_B signal is little affected ($\delta(P_B)$ −15.7, partial superposition with $P_{A'}$).[23] The ^{119}Sn NMR signal at −90 °C is only shifted a little to high field ($\delta(^{119}Sn)$ 158.4 (tdd, J = 1136, 193, 122 Hz)) and confirms the inequivalence of the P_A and $P_{A'}$ nuclei (the assignment of P_A and $P_{A'}$ is arbitrary) (Figure 3). Therefore a hindered rotation around the P–C bond ($\Delta G_{-70°C}$ = 9.2 kcal/mol) is assumed to occur (**9/II**). A tetrahedral Sn coordination **9/III** seems unlikely, since this would afford a more pronounced high-field ^{119}Sn shift and a large $J(P_{A'}Sn)$ coupling constant. The hindered rotation resembles very much the behavior of the phosphino substituents in *C*-phosphino-substituted phosphorus ylides, e.g., **10**[24] and **11**.[25] The barrier of rotation in the phenyl-substitued ylide **11** is much higher (ΔG = 11.7 kcal/mol)[25] compared to **10** (ΔG = 7.9 kcal/mol)[26] and demonstrates that steric effects may play an important role in related structures, as, e.g., in **9**.[27] An additional effect on the NMR spectra of **9** is observed on warming the solutions. The ^{31}P spectrum observed at 20 °C (A_2B_2) disappears at +50 °C, and at +70 °C a new single, yet broad, signal ($\delta(P)$ −14.5)[23] shows up ($\Delta G_{+50°C}$ = 15.0 kcal/mol). Further warming causes decomposition of the sample. The chemical shift is similar to the former P_A signal. Apparently now all four phosphorus nuclei become equivalent; their average bonding situation should approach the C-bonded diphosphinomethanide coordination mode. Therefore, formula **9/IV** with coordination number two for tin(II) seems to be an adequate description for the transition state of **9** at this temperature, which is related to the structure of $Sn[CH(SiMe_3)_2]_2$ in solution.[6]



$$Me_3P{=}C(PMe_2)_2$$

10



$$Ph_3P{=}C(PPh_2)_2$$

11

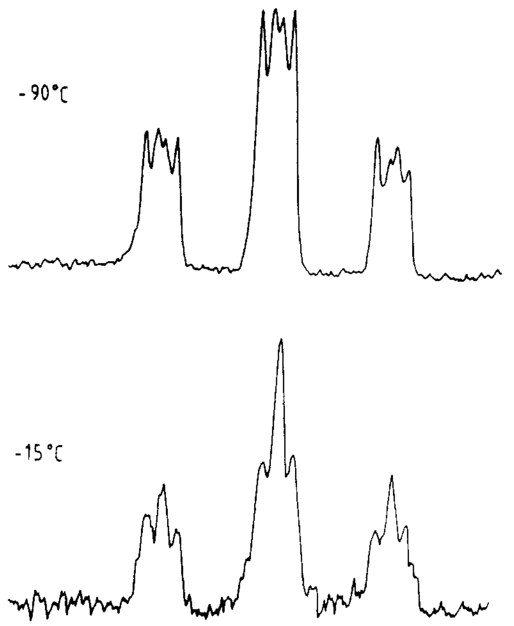
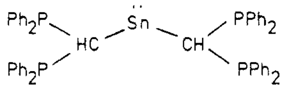
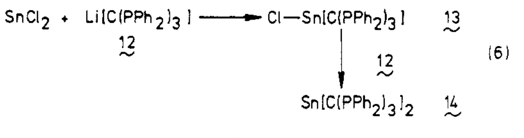


Figure 3. ^{119}Sn NMR spectra of **9** at −90 and −15 °C (74.60 MHz, toluene-d_8).



9/IV

This indicates that phosphinomethanides indeed may behave similarly silylmethanides with respect to metal coordination. Further increase in the steric congestion in these compounds has been probed by using the hexaphenyltriphosphinomethanide ligand. This increase now also allows for the isolation of an intermediate in the reaction of $SnCl_2$ with phosphinomethanides (eq 6).[28]



$$SnCl_2 + Li[C(PPh_2)_3] \longrightarrow Cl{-}Sn[C(PPh_2)_3] \xrightarrow{\textbf{12}} Sn[C(PPh_2)_3]_2 \qquad (6)$$

Both **13** and **14** are very air-sensitive, yellow solids, which decompose on storage at room temperature. Their solutions in toluene decompose within 3 h at this temperature (NMR). **13** is exceptional, since its additional Cl functionality allows for various substitution reactions.[29] From the NMR spectra, a threefold tin coordination **13/I** is evident. The ^{119}Sn NMR signal (δ +56.2 (dt, J = 152, 1144 Hz)) again is shifted to low field. ^{31}P NMR signals at δ +12.9 (t) and at −5.8 (d) (J = 34 Hz) are remarkable, since

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(23) $\delta(P)$ values for **9** were determined with $Ph_2PCH_2PPh_2$ as internal standard: $\delta(PH_2PCH_2PPh_2)$ −22.1 (+70 °C), −23.1 (+25 °C), −23.6 (−15 °C), −25.7 (−90 °C) rel to H_3PO_4 (external).

(24) Karsch, H. H. *Chem. Ber.* **1982**, *115*, 1956.

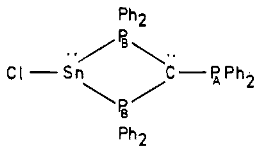
(25) Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B. *Chem. Ber.* **1983**, *116*, 1393.

(26) Karsch, H. H., unpublished results.

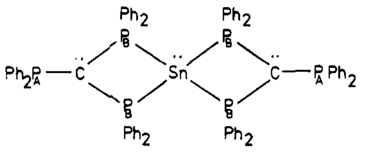
(27) The rotation barrier in **11** is higher than in **9** probably due to the sp^2 C atom with shorter P–C bond lengths.

(28) No such intermediates could be isolated in the systems $SnCl_2/Li[CH(PPh_2)_2]$, $SnCl_2/Li[C(PMe_2)_3]$, and $SnCl_2/Li[C(PMe_2)_2SiMe_3]$.

(29) Karsch, H. H.; Appelt, A., work in progress.

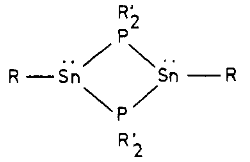


13/I



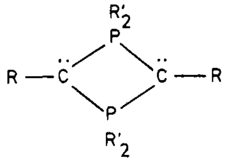
14/I

the coordinated phosphorus nuclei P_B obviously are more shielded than the noncoordinated P_A nucleus. We attribute this effect to the Sn lone pair in a pseudotetrahedral coordination. In the likewise threefold coordinated **9**, the situation is quite similar: the nonbonded phosphorus nuclei P_A appear at lower field than the coordinated ones (P_B). A similar observation has been made in the likewise threefold coordinated Sn(II) compound **15**.[5] It is an attractive view to consider the four-membered ring system in **13** (and as well in **9**) as an intermediate case between **15** and **16**.[30] Yet, one should keep in mind that the carbanionic centers are planar, whereas the Sn atoms probably are pyramidal.



(R = P ^{t}Bu$_2$, R' = ^{t}Bu)

15

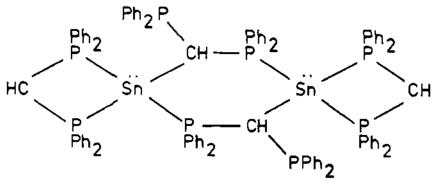


(R = H , R' = NMe$_2$)

16

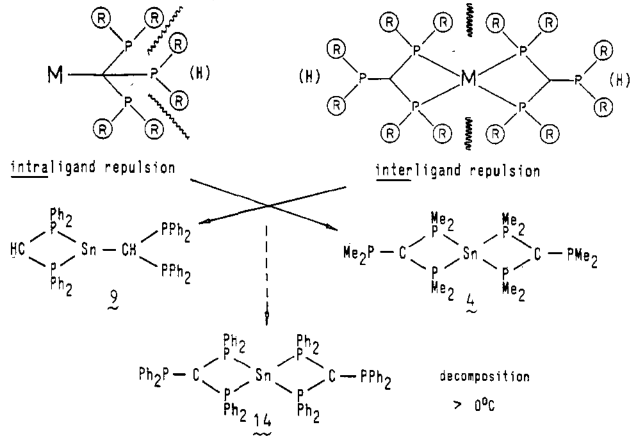
In contrast to this, **14** again is tetracoordinated and thus is similar to **4** and **7**. This is derived mainly from the high-field shift of the ^{119}Sn resonance (δ(^{119}Sn) −345.8 (quin t; J = 1055, 161 Hz)). The ^{31}P NMR data are in accord with this assignment. The δ(^{31}P) values in this case are "normal": $\delta(P_A)$ 1.9 (quin), $\delta(P_B)$ 17.7 (t, J = 9 Hz). Again, a degenerate spin system (apparently A_4X_2) is observed. Even in the case of this highly congested molecule, cooling causes no additional splitting of the signals, which might be expected for a rigid Ψ-tbp structure. However, we were not able to decide whether an additional dynamic process as in **4** also is operating in the case of **14** since warming above 0 °C causes rapid decomposition of the sample.

C. Steric Considerations. Looking back to what we have found, a puzzling situation has to be recalled. In **9**, two diphosphinomethanide ligands realize a threefold tin(II) coordination, whereas two of the much bulkier triphosphinomethanide ligands lead to tetracoordination. Certainly, the nucleophilicity of the carbanion $[HC(PPh_2)_2]^-$ is higher than that of $[C(PPh_2)_3]^-$ and should promote a coordination via the carbanion, as is observed in **9** for one of the ligands. But, as is obvious from the P,P-coordination of the second phosphinomethanide ligand, this point cannot be decisive to prevent a twofold P,P-coordination as in **4**, **7**, or **14**. Moreover, a tetracoordination might also be achieved by a C,P-coordination as in **9**/III or by dimerization (**9**/V).



9/ V

Scheme I. Steric Interactions in Tin(II) Phosphinomethanides



A simple intra-/interligand repulsion model (Scheme I) may be envoked which readily accounts for the apparent discrepancies. In this model, the actual coordination mode is a "balanced" consequence of the two steric interactions. The *intraligand* repulsion is most severe in the case of a carbanion coordination of *triphosphinomethanides*, whereas the *interligand* repulsion mostly depends on the steric requirements of the P substituents (phenyl or methyl). Thus, in the *diphosphinomethanide* derivative **9** (R = Ph) the *interligand* repulsion in a tetracoordinated environment is unfavorable and leads to tricoordinated species. The *triphosphinomethanide* compound **4** (R = Me) adopts a tetracoordinated arrangement of the ligands because of the unfavorable *intraligand* repulsion, whereas the *interligand* interaction is much less severe with the *P*-methyl substituents. The coordination of **14** demonstrates that the intraligand repulsion is somewhat more important than the interligand repulsion, but nevertheless, the overall situation is not very favorable: **14** is the least stable of the three compounds (decomposition > 0 °C). This model thus provides a useful tool for the understanding of steric effects in phosphinomethyl tin(II) compounds. It may be easily adapted to many other metal complexes of phosphinomethanides[31] and potentially to other ambidentate ligands as well.

Conclusions

Ambidentate phosphinomethyl ligands are suitable for the preparation of Sn(II) coordination compounds which show several new remarkable features. They (a) form stable, monomeric, and neutral complexes, which (b) are highly soluble in hydrocarbon solvents and (c) exhibit dynamic behavior in solution, and (d) lead to tri- and tetracoordination at Sn(II) as well as to (e) homoleptic Sn(II) species.

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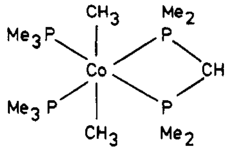
[30] Svara, J.; Fluck, E.; Riffel, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 1258.

[31] The interligand repulsion argument has previously been used to account for the different coordination modes (P, P vs. C, P) of diphosphinomethanide ligands in transition-metal complexes, as, e.g., in **17** and **18**.[32]



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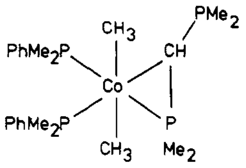

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[32] Karsch, H. H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 921. Karsch, H. H. *Chem. Ber.* **1983**, *116*, 1656.

The ligand capacities span the range from bulky carbanionic substituents (comparable to silylmethanides) to chelating phosphine donors and may be controlled primarily by adjusting their steric demand. Thus, not only is a new fruitful field of Sn(II) chemistry opened, but also a general application to other main group element coordination compounds clearly lies at hand.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Mr. J. Riede for the data collection and Dr. F. R. Kreissl for the mass spectroscopic measurements of 4.

Registry No. 1, 70377-69-4; 4, 102505-21-5; 6, 102493-28-7; 7, 102505-22-6; 8, 28926-61-6; 9, 102505-23-7; 12, 102493-27-6; 13, 102505-20-4; 14, 102505-24-8; $SnCl_2$, 7772-99-8.

Supplementary Material Available: Tables of additional crystal structure data, thermal parameters, H atom coordinates, and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

Reactions of Ethyl Cyanoformate with $(np_3)Ni$, $(np_3)CoH$ [np_3 = $N(CH_2CH_2PPh_2)_3$], and (triphos)Ni [triphos = $MeC(CH_2PPh_2)_3$]. Crystal Structures of the Ethoxycarbonyl Complexes $[(np_3)Ni(CO_2Et)]BPh_4$ and (triphos)Ni(CN)(CO_2Et)

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Ethyl cyanoformate, $NCCO_2Et$, is used as starting material to introduce ethoxycarbonyl and/or cyanide groups into complex frameworks. Thus, $NCOO_2Et$ reacts with the Ni(0) complex $(np_3)Ni$ (1) [np_3 = $N(CH_2CH_2PPh_2)_3$] or with the Ni(0) fragment (triphos)Ni [triphos = $MeC(CH_2PPh_2)_3$] to give $[(np_3)Ni(CO_2Et)]^+$ (3) and (triphos)Ni(CN)(CO_2Et) (4), respectively. The crystal structures of 3·BPh_4 and 4 have been determined by standard X-ray methods. Compound 3·BPh_4 crystallizes in the monoclinic space group *C2/c* with $a = 33.429$ (10) Å, $b = 8.929$ (2) Å, $c = 38.773$ (11) Å, $\beta = 100.25$ (2)°, and $Z = 8$. The structure was refined to an *R* factor of 0.068 ($R_w = 0.068$) by using 2908 reflections with $I > 3\sigma(I)$. The coordination polyhedron of the nickel(II) atom can be described as a trigonal bipyramid whose equatorial plane is defined by the three phosphorus atoms of np_3. Compound 4 crystallizes in the orthorhombic space group $Pn2_1a$ with $a = 26.957$ (8) Å, $b = 13.480$ (4) Å, $c = 10.690$ (3) Å, and $Z = 4$. The structure was refined to an *R* factor of 0.055 ($R_w = 0.056$) by using 1897 reflections with $I > 3\sigma(I)$. The compound exhibits quite regular square-pyramidal environment of the nickel(II) atom. Reaction of $NCCO_2Et$ with the Co(I) hydride $(np_3)CoH$ (5) yields $(np_3)Co(CN)$ and HCO_2Et.

Introduction

Alkoxycarbonyl metal complexes constitute a ubiquitous class of compounds whose chemistry is presently the object of intense speculation. In fact, these organometallic compounds can participate as starting,[1] final,[1a,2] or intermediate[1a,e,3] products in several important reactions involving carbon oxides and other carbonyl-derived functional groups.

At least six different synthetic routes to alkoxycarbonyl complexes are available. These include alkoxide ion attack on carbonylmetal cations,[1a,d,e] nucleophilic attack on chloroformates by anionic metal complexes,[1a] oxidative addition of chloroformates to coordinatively unsaturated metal fragments,[1a] alkylation of η^1-CO_2 complexes,[2] carbonylation of alkoxo complexes,[3b] and, finally, reaction of alkoxide ions with neutral metal carbonyls or halometal carbonyls.[3c]

In this paper we report on the potential applications of ethyl cyanoformate, $NCCO_2Et$, to synthesize ethoxycarbonyl derivatives. Ethyl cyanoformate reacts with the Ni(0) complex $(np_3)Ni$[4] (1) [np_3 = $N(CH_2CH_2PPh_2)_3$] or with the Ni(0) metal fragment (triphos)Ni (2) [triphos = $MeC(CH_2PPh_2)_3$] to give the stable Ni(II) ethoxycarbonyls $[(np_3)Ni(CO_2Et)]^+$ (3) and (triphos)Ni(CN)(CO_2Et) (4), respectively. The structures of 3·BPh_4 and 4 have been established by X-ray methods. The reaction between the Co(I) hydride $(np_3)CoH$[4] (5) and $NCCO_2Et$ is also presented.

Results and Discussion

Reaction of 1 with $NCCO_2Et$. Reaction of the Ni(0) complex 1 in THF with a slight excess of $NCCO_2Et$, fol-

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