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Dimethyl(diorganophosphinodithioformato-*S*,*S*′)-thallium(III) compounds. X-Ray structure of $[Tl(CH_3)_2\{S_2CP(C_6H_5)_2\}(THF)]$

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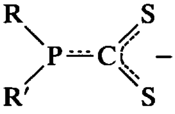
Abstract

Dimethylthallium derivatives $[TlMe_2(S_2CPR_2)]$ (R = Cy or Ph) were prepared. When the phenyl derivative was slowly crystallized from the reaction medium (ethanol/tetrahydrofuran), the complex $[TlMe_2(S_2CPPh_2)(THF)]$ (THF = tetrahydrofuran) formed, the structure of which was solved by X-ray diffraction. In this compound the thallium atom is coordinated to the phosphinodithioformate ligand *via* its two S atoms, to the two methyl groups, and very weakly to the THF molecule. A weak intermolecular $Tl \cdots S$ interaction is also observed. The structure of the compounds $[TlMe_2(S_2CPR_2)]$ is discussed on the basis of their IR and ^1H, ^{13}C, ^{31}P and ^{205}Tl NMR spectra.

Introduction

Diorganophosphinodithioformates (I) are, at first sight, very similar to diorganodithiocarbamates (II), and might be expected to show similar coordination behaviour. However, although information on the complexes of I is at present scarce, the available data [1–3] show a striking difference: $S_2CPR_2^-$ seems often to give *P*,*S*-bonded chelates instead of the *S*,*S*-bonded chelates afforded by $S_2CNR_2^-$, though *S*,*S* coordination has been hypothesized for $[Mn(S_2CPPh_2)_2] \cdot EtOH$ [4] and confirmed by X-ray diffraction for $[Zr(\eta\text{-}C_5H_5)Cl\{S_2CP(SiMe_3)_2\}]$ [5].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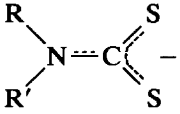
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We report here that the reaction of $TlMe_2NO_3$ with the potassium salt of dicyclohexyl- and diphenyl-phosphinodithioformate in an ethanol/tetrahydrofuran (THF) mixture affords the corresponding compounds $[TlMe_2(S_2CPR_2)]$ or, if the diphenyl derivative is slowly crystallized, $[TlMe_2(S_2CPPh_2)(THF)]$. The latter was shown by X-ray diffraction to be *S,S'*-chelate, and spectroscopic evidence suggests that the other two are too.

Experimental

Dicyclohexylphosphine (Strem), diphenylphosphine (Aldrich) and carbon disulphide (Merck) were used as received. Potassium dicyclohexylphosphinodithioformate and diphenylphosphinodithioformate were synthesized by a published method [2]. Dimethylthallium(III) nitrate was obtained by reaction with nitric acid [7] of a solution of dimethylthallium(III) hydroxide (prepared by treating $TlMe_2I$ with silver oxide [6]).

Dimethylthallium derivatives were synthesized as follows.

Dimethyl(dicyclohexylphosphinodithioformato-S,S')thallium(III), $[TlMe_2(S_2CPCy_2)]$

KS_2CPCy_2 (0.25 g, 0.86 mmol) in tetrahydrofuran (THF) (approx. 10 ml) was slowly added, with stirring, to $TlMe_2NO_3$ (0.25 g, 0.84 mmol) dissolved in ethanol (approx. 10 ml). The mixture was stirred for 3 h and stored at 0°C for 12 h, and the white precipitate formed (probably KNO_3 according to the IR spectrum) was discarded. The filtered solution was concentrated and kept at 0°C for 12 h more, after which the yellow precipitate formed was filtered off, washed with cold ethanol and vacuum dried over $CaCl_2$-KOH. Anal. Found: C, 35.3; H, 5.7; P, 6.0. $C_{15}H_{28}PS_2Tl$ calcd.: C, 36.5, H, 5.6; P, 6.1%. M.p.: 261°C.

Dimethyl(diphenylphosphinodithioformato-S,S')thallium(III), $[TlMe_2(S_2CPPh_2)]$

A solution of KS_2CPPh_2 (0.25 g, 0.84 mmol) in THF (approx. 10 ml) was slowly added, with stirring, to $TlMe_2NO_3$ (0.25 g, 0.84 mmol) dissolved in ethanol (approx. 10 ml). The mixture was stirred for 3 h and the white precipitate formed was discarded. Storage of the filtrate at 0°C yielded orange crystals. The ^1H and ^{13}C NMR spectra of the fresh product in chloroform showed signals for THF, and elemental analysis confirmed the formula $[TlMe_2(S_2CPPh_2)(THF)]$ (Anal. Found: C, 40.0; H, 3.6. $C_{19}H_{24}OPS_2Tl$ calcd.: C, 40.2; H, 4.3%), but after a few days' storage out of the mother liquor the crystals changed to an orange powder whose NMR spectra showed no THF signals. The loss of the THF molecule and the formation of $[TlMe_2(S_2CPPh_2)]$ were confirmed by elemental analysis (Anal. Found: C, 37.0, H, 3.8; P, 6.4. $C_{15}H_{16}PS_2Tl$ calcd.: C, 36.3; H, 3.3; P, 6.3%). M.p: 95°C (decomposition).

Elemental analysis was performed with a Carlo Erba 1108 microanalyser or by Galbraith Lab. Inc. (Knoxville, TN, USA). Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI conditions (70 eV). All the ions included in Table 1 were identified using DS90 software. Infrared spectra were recorded in Nujol or KBr pellets on a Perkin Elmer 1330 spectrometer. ^1H (250.13 MHz), proton-decoupled ^{13}C (62.83 MHz) and ^{31}P (101.26 MHz) NMR spectra were recorded in $CDCl_3$ (in 5 mm o.d. tubes at 25°C) on a Bruker WM-250 spectrometer, and were referred to the solvent

Table 1

Mass spectra (EI) of dimethylthallium compounds (*m*/*e*, (%)) [a]

Species	R = Cy	R = Ph
$[TlMeS_2CPR_2]$	493(23.1)	–
$[TlMeS_2PR_2]$	481(13.9)	469(26.0)
$[TlS_2PR_2 + H]$	–	384(17.6)
$[TlMe_2]$	235(66.2)	235(48.3)
[Tl]	205(100)	205(100)

[a] Nominal values calculated for H = 1,.C = 12, P = 31, S = 32 and Tl = 205.

signal (^1H, 7.27; ^{13}C, 77.00 ppm) and 85% H_3PO_4. Proton-decoupled ^{205}Tl NMR spectra were obtained in $CHCl_3$ (in 10 mm o.d. tubes) on a Bruker AM400 spectrometer at 230.81 MHz and at a probe temperature of $25 \pm 0.5°C$, and were referred to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution. Chemical shifts are given in ppm towards higher frequency.

Crystal structure determination of [TlMe$_2$(S$_2$CPPh$_2$)(THF)]

An orange prismatic crystal of approximately $0.15 \times 0.08 \times 0.05$ mm was used. Crystal data: $C_{19}H_{24}POS_2Tl$, $M = 563.84$, monoclinic, space group $P2_1/c$, $a = 11.719(2)$, $b = 10.289(1)$, $c = 18.653(5)$ Å, $\beta = 105.36(2)°$, $U = 2169(1)$ Å^3, $Z = 4$, $D_{calc} = 1.727$ g cm^{-3}. $F(000) = 1080$, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å and $\mu = 77.85$ cm^{-1}.

X-ray data collection and structure refinement: All X-ray crystallographic measurements were carried out using a CAD-4 Enraf Nonius diffractometer with graphite monochromated Mo-K_α radiation. The $\omega/2\theta$ scan technique was used. 2270 reflections were collected in the range 0–22°; of these, 1129 symmetry-independent reflections with $I > 3\sigma(I)$ were used for refinement. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

The structure was solved using the Patterson heavy atom method and subsequent Fourier difference maps. All atoms were treated anisotropically except those of the phenyl groups and the solvent molecule. The phenyl rings, with their hydrogen atoms included on stereochemical grounds, were refined as rigid groups [C–C distance = 1.40(1), C–H distance = 1.08(1) Å]. R and R_W were 0.057. The atomic scattering factors were taken from references [8–10]. Most calculations were performed on a VAX 6420 computer with the programs SHELX76 [11], VAXSDP [12] and ORTEP [13].

Results and discussion

Synthesis of compounds

Two methods have been used for preparing metallic complexes derived from phosphinodithioformates [1].

i) Insertion of CS_2 in the M–PR_2 bond.

$$[M(PR_2)L_n] + CS_2 \rightarrow [M(S_2CPR_2)L_n]$$

ii) Displacement reactions using phosphinodithioformate prepared *in situ*,

$$MX_n + nCS_2 + nR_2PH + nNR_3 \rightarrow [M(S_2CPR_2)_n] + nNR_3 \cdot HX$$

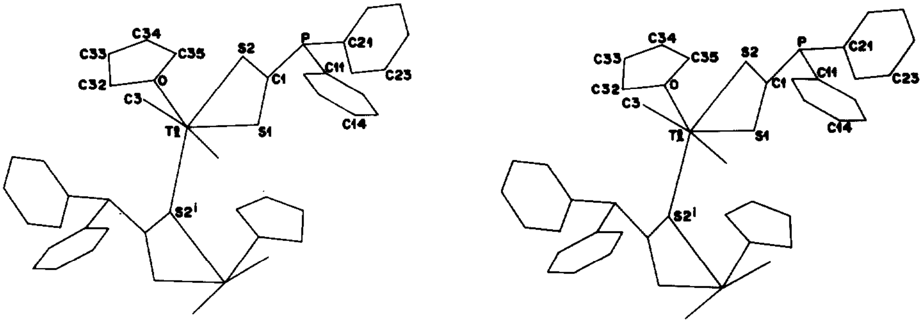

Fig. 1. Stereoscopic view of [$TlMe_2(S_2CPPh_2)(THF)$], with numbering scheme.

or its pre-formed alkali metal salt.

$$[M(A)L_n] + M^{Ia}(S_2CPR_2) \rightarrow [M(S_2CPR_2)L_n] + M^{Ia}A$$

In this work we used the latter method, with dimethylthallium(III) nitrate and the potassium salts as reagents.

Crystal structure of [$TlMe_2(S_2CPPh_2)(THF)$]

Figure 1 shows a stereoscopic view of the asymmetric unit of the [$TlMe_2(S_2CPPh_2)(THF)$] structure, with the numbering scheme. Table 2 lists the frac-

Table 2

Fractional atomic coordinates and isotropic temperature factors (Å^2) for [$TlMe_2(S_2CPPh_2)(THF)$]

Atom	x	y	z	B_{iso}
Tl	0.4505(1)	0.0842(2)	0.1962(1)	5.31(5)
S(1)	0.638(1)	0.091(1)	0.3439(5)	9.1(5)
S(2)	0.6106(7)	0.312(1)	0.2390(4)	5.9(4)
P	0.7670(7)	0.352(1)	0.3884(5)	5.3(3)
C(1)	0.671(2)	0.244(4)	0.322(2)	5(1)
C(2)	0.559(3)	−0.016(3)	0.137(2)	6.0(8)
C(3)	0.311(3)	0.170(4)	0.238(2)	7.1(9)
C(11)	0.821(2)	0.258(2)	0.475(1)	6.3(8)
C(12)	0.746(2)	0.257(2)	0.522(1)	7.8(9)
C(13)	0.779(2)	0.191(2)	0.589(1)	7.7(9)
C(14)	0.887(2)	0.125(2)	0.610(1)	7.4(9)
C(15)	0.962(2)	0.126(2)	0.563(1)	9(1)
C(16)	0.929(2)	0.193(2)	0.496(1)	7.4(9)
C(21)	0.896(1)	0.360(2)	0.353(1)	4.1(6)
C(22)	0.928(1)	0.260(2)	0.312(1)	5.6(7)
C(23)	1.030(1)	0.272(2)	0.287(1)	6.3(8)
C(24)	1.100(1)	0.384(2)	0.303(1)	7.3(9)
C(25)	1.067(1)	0.484(2)	0.345(1)	9(1)
C(26)	0.965(1)	0.472(2)	0.369(1)	6.1(8)
O	0.373(3)	0.233(4)	0.067(2)	13(1)
C(32)	0.251(5)	0.218(6)	0.018(3)	13(1)
C(33)	0.257(5)	0.317(6)	−0.040(3)	15(1)
C(34)	0.366(5)	0.362(5)	−0.031(3)	13(1)
C(35)	0.444(4)	0.319(5)	0.040(3)	11(1)

Table 3

Bond distances (Å) and angles (°), with e.s.d.s. in parentheses for [TlMe$_2$(S$_2$CPPh$_2$)(THF)]

Tl-S(1)	3.04(1)	P-C(1)	1.82(3)
Tl-S(2)	2.98(1)	P-C(11)	1.84(2)
Tl-C(2)	2.15(3)	P-C(21)	1.80(2)
Tl-C(3)	2.18(4)	O-C(32)	1.49(7)
Tl-O	2.80(3)	O-C(35)	1.40(6)
Tl-S(2)^{i}	3.21(1)	C(32)-C(33)	1.50(8)
Tl-P^{i}	3.545(9)	C(33)-C(34)	1.33(9)
S(1)-C(1)	1.70(4)	C(34)-C(35)	1.46(8)
S(2)-C(1)	1.68(3)		
S(1)-Tl-S(2)	59.0(3)	Tl-O-C(32)	121(1)
C(2)-Tl-C(3)	168(1)	Tl-O-C(35)	125(1)
S(1)-Tl-C(2)	95.3(9)	C(1)-S(2)-Tl	96(1)
S(1)-Tl-C(3)	96(1)	C(1)-P-C(11)	106(1)
S(1)-Tl-O	139.6(8)	C(1)-P-C(21)	102(1)
S(1)-Tl-S(2)^{i}	81.8(3)	C(11)-P-C(21)	103(1)
S(2)-Tl-C(2)	95.7(9)	S(1)-C(1)-S(2)	123(1)
S(2)-Tl-C(3)	93.7(9)	S(1)-C(1)-P	123(1)
S(2)-Tl-O	80.7(8)	S(2)-C(1)-P	114(1)
S(2)-Tl—S(2)^{i}	140.8(2)	P-C(11)-C(12)	115(1)
C(2)-Tl-O	85(1)	P-C(11)-C(16)	125(1)
C(2)-Tl—S(2)^{i}	89.8(9)	P-C(21)-C(22)	123(1)
C(3)-Tl-O	89(1)	P-C(21)-C(26)	117(1)
C(3)-Tl-S(2)^{i}	87.4(9)	C(32)-O-C(35)	114(1)
O-Tl-S(2)^{i}	138.5(8)	O-C(32)-C(33)	99(1)
Tl-S(1)-C(1)	88(1)	C(32)-C(33)-C(34)	112(1)
Tl-S(2)-C(1)	90(1)	C(33)-C(34)-C(35)	111(1)
Tl-S(2)-Tl^{i}	127.0(3)	O-C(35)-C(34)	103(1)

^{i} Symmetry operation: $1-x$, $-1/2+y$, $1/2-z$.

tional atomic coordinates, and Table 3 shows the most significant bond lengths and angles.

The thallium atom is bound to two methyl groups, two sulphur atoms belonging to a single phosphinodithioformate ligand, and the oxygen atom of the THF molecule. There is also a weak intermolecular interaction with S(2)^{i} ($i = 1-x$, $-1/2+y$, $1/2-z$) at a distance shorter than the sum of the van der Waals radii (3.76 Å [14]). An additional even weaker interaction with the P^{i} atom may also exist, because the Tl–P^{i} distance is shorter than (though close to) the sum of van der Waals radii of these atoms (3.76 Å [14]), although this is not indicated in Fig. 1.

The thallium–carbon distances are normal, and as usual in dimethylthallium(III) compounds [15] the C(2)–Tl–C(3) angle deviates only slightly from linearity. The Tl–S(1) and Tl–S(2) distances are close to that found in dimethyl(methylxanthato)-thallium(III) [16] but are longer than those observed in diphenyl (*N*,*N*-diethyldithiocarbamato)thallium(III) [15b] and dimethyl (*N*,*N*-dipropyldithiocarbamato)-thallium(III) [17], and are also rather longer than the thallium–sulphur distances in tris(*N*,*N*-dimethyldithiocarbamato)thallium(III) [18]. If only the strong bonds are considered, the thallium has a very distorted tetrahedral coordination geometry; if the weak interactions are included, a very deformed octahedral environment with the two methyl groups apical can be envisaged.

The changes in the S_2CP fragment relative to *S,P*-bonded phosphinodithioformato complexes [2,3] are difficult to assess due to the large e.s.d.s. associated with the structural parameters of this group in the thallium complex. Nevertheless, if the influence of the R radical is ignored, two differences appear to emerge. First, as expected, the two C–S distances tend to become equal in the *S,S*-coordinated compounds (see Table 3 and ref. 5), both being between the values for single and double bonds (1.81 and 1.61 Å [3]); the C(1)–P bond length is shorter than a single bond [3], suggesting delocalization of charge similar to that observed in *S,P*-bonded compounds. Secondly, the S(1)–C–S(2) angle narrows and the S(2)–C–P angle widens in the thallium compound, presumably because of the change from *S,P*- to *S,S*-coordination.

Full lists of structure factors, atomic coordinates, and other parameters are available from the authors.

Mass spectra

The most significant mass spectrum peaks corresponding to metallated species are listed in Table 1. No signals for the molecular ions were detected, although the observation of the demethylated species $[TlMeS_2CPCy_2]^+$ is in keeping with what seems to be the usual ionization pathway for methylthallium derivatives [19]. The signals for $[TlMeS_2PR_2]^+$ ions are rather interesting, suggesting an ionization mechanism leading to the dithiophosphinate ligand, probably through extrusion of a carbon atom. As in other dimethylthallium compounds, the ions $[TlMe_2]^+$ and $[Tl]^+$ account for a large proportion of the ion current.

IR spectra

Table 4 shows the significant bands of the potassium salts of the ligands and of the complexes prepared. In KS_2CPPh_2 $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ are close to the positions previously reported [1d,f], and as in other *S,S*-coordinated complexes [1f] they do not shift appreciably upon coordination to the thallium atom in the Nujol spectrum of $[TlMe_2(S_2CPPh_2)(THF)]$. This contrasts with *P,S*-chelates, in which the 1000 cm^{-1} band shifts to form an essentially $\nu(C{=}S)$ band at about 1100 cm^{-1} [1f,h].

For $[TlMe_2(S_2CPPh_2)]$, the 1000 cm^{-1} band shifts to very slightly higher wavenumbers compared to $[TlMe_2(S_2CPPh_2)(THF)]$, new medium bands appear at 1050 and 1130 cm^{-1} and $\nu_{as}(C{-}Tl{-}C)$ is split. These effects were also partially

Table 4

Infrared data

Compound	$\nu_{as}(CS_2)$	$\nu_s(CS_2)$	$\rho(CH_3)$	$\nu_{as}(C{-}Tl{-}C)$
KS_2CPCy_2	980vs	865m		
$[TlMe_2(S_2CPCy_2)]$	1000vs 995vs	885m	785m, br	520m
KS_2CPPh_2	1005vs, br 995s	870m		
$[TlMe_2(S_2CPPh_2)(THF)]$	1000s 990s	890m	800m, br	530m

[a] br = broad, s = strong, vs = very strong, m = medium.

Table 5

Significant NMR parameters for phosphinodithioformate compounds [a,b,c]

Compound	^1H		^{13}C		^{31}P		
	$\delta(CH_3{-}Tl)$	$^2J(^1H{-}^{205}Tl)$	$\delta(CH_3{-}Tl)$	$^1J(^{13}C{-}^{205}Tl)$	$\delta(^{31}P)$	$\Delta\delta$	$\delta(^{205}Tl)$
KS_2CPCy_2					60.8s [d]		
$TlMe_2(S_2CPCy_2)$	1.34d	351.2	22.89	2375	71.1s	10.3	4015.9s
					69.3s [d]	8.5	
KS_2CPPh_2					41.5s [d]		
$[TlMe_2(S_2CPPh_2)$-$(THF)]$ [e]	1.36d	35.0	23.19	2347	53.9s	8.8	3962.5
					55.8s [d]	10.7	

[a] δ in ppm and J in Hz. [b] s = singlet, d = doublet. [c] $\Delta\delta = \delta(^{31}P)$complex $- \delta(^{31}P)$ligand. [d] THF as solvent. [e] THF signals: 1.86, 3.75 (^1H spectrum); 25.55, 67.94 (^{13}C spectrum).

observed when the IR of $[TlMe_2(S_2CPPh_2)(THF)]$ was recorded in KBr pellets, and may be indicative of some reinforcement of the weak Tl–P interaction upon the loss of THF and disappearance of the Tl–O bond.

For $[TlMe_2(S_2CPCy_2)]$ the positions of $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ are again typical of *S,S*-coordination.

In both the phenyl and cyclohexyl derivatives the $\rho(CH_3)$ and $\nu_{as}(C{-}Tl{-}C)$ bands of the organometallic fragment are close to positions reported for similar *S,S*-bonded compounds [16].

Solution studies

The solubility of the compounds in organic solvents of low dielectric constant suggests a covalent nature. Their molar conductivities in acetonitrile (2 and 5 ohm^{-1} cm^2 mol^{-1} for 10^{-3} M solutions of $[TlMe_2(S_2CPPh_2)(THF)]$ and $[TlMe_2(S_2CPCy_2)]$ respectively) confirm their non-ionic nature [20].

Table 5 lists the chief ^1H, ^{13}C, ^{31}P and ^{205}Tl NMR data measured in chloroform. Although the complexes exhibit considerable solubility in this medium, the signal of the carbon atom belonging to the dithioformate group was not observed. ^{31}P NMR data for the complexes and the potassium salts of the ligands in THF are included for comparative purposes.

The ^{31}P NMR spectra of $[TlMe_2(S_2CPR_2)]$ contain only one signal. In the dimethylthallium compounds this nuclide is deshielded by *ca.* 10 ppm with respect to the alkali salt. This may be due to the inductive effect that coordination to the metal has on the PCS_2 group, and is just the opposite of what is observed in *P,S*-chelate complexes [1h], suggesting that ^{31}P NMR spectroscopy may be an adequate tool for distinguishing between the two coordination modes of these ligands.

Probably due to the poor solubility of dimethylthallium(III) compounds in low permittivity media, only a few have been studied in chloroform. Most of the available data are for $^2J(^1H{-}^{205}Tl)$, reported values for which have generally fallen within the range established by Matthews *et al.* [21] for complexes dissolved in non-polar solvents, 340–380 Hz (the exception is $TlMe_2$ (O_4C_2), for which $^2J(^1H{-}^{205}Tl) = 391$ Hz [22]). In the two neutral compounds with donor sulphur atoms that have been described in the literature, $[TlMe_2(S_2CNMe_2)]$ [22] and $TlMe_2L \cdot HL$

(HL = cyclopentanone thiosemicarbazone) [23], $^2J(^1H-^{205}Tl)$ is below 360 Hz, as in our complexes (Table 5). *N*- or *O*-bound compounds seem to have coupling constants above 360 Hz in $CDCl_3$ [22,24], although the paucity of data prevents a definite conclusion from being drawn.

The values of $^1J(^{13}C-^{205}Tl)$ (Table 5) are clearly below the range observed for $[TlMe_2(OC_6H_5)]$ in dichloromethane and toluene [21], and the thallium nuclide is more shielded in the phosphinodithioformate complexes than in the phenoxy derivative [21]. Although $\delta(^{205}Tl)$ for $[TlMe_2(S_2CNEt_2)]$ has been measured as 3728 ppm [25] at −50°C in $CDCl_3$ solution, the great influence of temperature on the ^{205}Tl chemical shift for dimethylthallium compounds [26] prevents direct comparison with the data of Table 5.

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References

1 (a) H. Schumann, P. Jutzi and M. Schmidt, Angew. Chem., Int. Ed. Engl., 4 (1965) 787; (b) J.G. Noltes, Recl. Trav. Chim. Pays Bas, 84 (1965) 782; (c) H. Schumann and P. Jutzi, Chem. Ber., 101 (1968) 24; (d) R. Kramolowsky, Angew. Chem., Int. Ed. Engl., 8 (1969) 202; (e) O. Dahl, N.C. Gelting and O. Larsen, Acta Chem. Scand., 23 (1969) 3369; (f) A.W. Gal, J.W. Gosselink and F.A. Vollenbroek, J. Organomet. Chem., 142 (1977) 357; (g) F.G. Moers, D.H.M.W. Thewissen and J.J. Steggerda, J. Inorg. Nucl. Chem., 39 (1977) 1321; (h) K.G. Steinhäuser, W. Klein and R. Kramolowsky, J. Organomet. Chem., 209 (1981) 355; (i) U. Kunze, A. Antoniadis and M. Moll, J. Organomet. Chem., 215 (1981) 187; (j) A. Gutiérrez-Alonso, L. Ballester-Reventós, V. Pérez-García and C. Ruiz-Valero, Polyhedron, 9 (1990) 2163; (k) A.E. Sánchez-Peláez, M.F. Perpiñán, E. Gutierrez-Puebla, A. Monge and C. Ruiz-Valero, J. Organomet. Chem., 384 (1990) 79.

2 J. Kopf, R. Lenck, S.N. Olafsson and R. Kramolowsky, Angew. Chem., Int. Ed. Engl., 15 (1976) 768.

3 D. Dakternieks, B.F. Hoskins and E.R.T. Tiekink, Aust. J. Chem., 37 (1984) 197.

4 P. August, Thesis, Hamburg, 1973 (cited in ref. 1f).

5 J. Hey, M.F. Lappert, J.L. Atwood and S.G. Bott, J. Chem. Soc., Chem. Commun., (1987) 421.

6 H. Gilman and R.G. Jones, J. Am. Chem. Soc., 68 (1964) 517.

7 G.D. Shier and R.S. Drago, J. Organomet. Chem., 5 (1966) 330.

8 D.T. Cromer and J.B. Mann, Acta Crystallogr., Sect. A, 24 (1968) 321.

9 D.T. Cromer and D.J. Liberman, Chem. Phys., 533 (1970) 1891.

10 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.

11 G.M. Sheldrick, SHELX76. Program for crystal structure determination. Univ. of Cambridge, 1976.

12 B.A. Frenz, The Enraf–Nonius CAD4 SDP, in Computing Crystallography, Delft University Press, Delft, 1985, p. 64–71.

13 C.K. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

14 A. Bondi, J. Phys. Chem., 68 (1964) 441.

15 a) M.S. Garcia-Tasende, M.I. Suárez, A. Sánchez, J.S. Casas, J. Sordo, E.E. Castellano and Y.P. Mascarenhas, Inorg. Chem., 26 (1987) 3818 and references therein; (b) R.T. Griffin, K. Henrich, R.W. Matthews and M. McPartlin, J. Chem. Soc., Dalton Trans., (1980) 1550.

16 W. Schwarz, G. Mann and J. Weidlein, J. Organomet. Chem., 122 (1976) 303.

17 M.V. Castaño, C. Freire, A. Sánchez, J.S. Casas, J. Sordo, E.E. Castellano and J. Zukerman-Schpector, unpublished work.

18 H. Abrahamson, J.R. Heiman and L.H. Pignolet, Inorg. Chem., 14 (1975) 2070.

19 M.V. Castaño, A. Macias, A. Castiñeiras, A. Sánchez-González, E. García-Martínez, J.S. Casas, J. Sordo, W. Hiller and E.E. Castellano, J. Chem. Soc., Dalton Trans., (1990) 1001.

20 W.L. Geary, Coord. Chem. Rev., 7 (1971) 81.

21 P.J. Burke, R.W. Matthews and D.G. Gillies, J. Organomet. Chem., 118 (1976) 129.

22 H. Kurosawa, K. Yasuda and R. Okawara, Inorg. Nucl. Chem. Lett., 1 (1965) 131.

23 A. Macias, M.C. Rodríquez-Argüelles, M.I. Suárez, A. Sánchez, J.S. Casas, J. Sordo and U. Englert, J. Chem. Soc., Dalton Trans., (1989) 1787.

24 H.U. Schwering and J. Weidlein, J. Organomet. Chem., 99 (1975) 223; A.J. Canty, K. Mills, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1986) 939.

25 G.M. Sheldrick and J.P. Yesinowski, J. Chem. Soc., Dalton Trans., (1975) 870.

26 B.J. Burke, R.W. Matthews, I.D. Cresshull and D.G. Gillies, J. Chem. Soc., Dalton Trans., (1981) 132.