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Structural chemistry of organotin carboxylates

XIV *. Diorganotin(IV) complexes of monochloroacetyl-L-phenylalanine. Crystal structure of $[^nBu_2Sn(O_2C(CH_2Ph)C(H)N(H)C(O)CH_2Cl)_2]$

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Abstract

New diorganotin(IV) complexes of the general formulae $[R_2Sn(A)_2]$ and $\{[R_2Sn(A)]_2O\}$ (A = the anion of monochloroacetyl-L-phenylalanine and R = Me, ^{n}Pr, ^{n}Bu and ^{n}Oct) have been prepared and characterized by IR and ^{1}H NMR spectroscopy and, in the case of the $[^nBu_2Sn(A)_2]$ compound, by X-ray crystallographic methods. The 1:2 (Sn:ligand) compounds are monomeric, and the Sn atom has a skew trapezoidal planar geometry, whereas the 1:1 compounds are dimeric with Sn–O–Sn bridges and possess trigonal bipyramidal Sn atom geometries.

Introduction

Although several diorganotin(IV) derivatives of *N*-acetylamino acids have been reported recently [2], no derivatives of monochloroacetyl amino acids have been described. In this paper, the synthesis of a series of diorganotin(IV) derivatives of monochloroacetyl-L-phenylalanine (AH) is reported. The crystal structure determination of one complex, $[^nBu_2Sn(A)_2]$, has been determined. This paper represents part of a continuing study of diorganotin(IV) compounds of amino acids and peptides [3–5].

Results and discussion

Diorganotin(IV) complexes of monochloroacetyl-L-phenylalanine (AH) have been prepared in 1:2 and 1:1 (Sn:AH) stoichiometries and characterized by elemental

* For Part XIII see ref. 1

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Table 1

Physical and analytical data for diorganotin(IV) complexes of monochloroacetyl-L-phenylalanine

Complex [a,b]	m.p. (°C)	Yield (%)	Solvent [c]	Analysis Found (calc.) (%)			
				C	H	N	Sn
$[Me_2Sn(A)_2]$	195	78	I	44.63 (45.70)	4.38 (4.44)	3.49 (3.44)	23.23 (23.28)
$[^nPr_2Sn(A)_2]$	166	71	II	49.67 (49.00)	5.68 (5.25)	3.52 (4.08)	17.29 (17.31)
$[^nBu_2Sn(A)_2]$	174	81	I	50.95 (50.40)	5.77 (5.60)	3.74 (3.92)	16.66 (16.63)
$[^nOct_2Sn(A)_2]$	136	86	I	54.91 (55.22)	7.16 (6.78)	3.34 (3.39)	14.37 (14.32)
$\{[Me_2Sn(A)_2]_2O\}$	177	73	III	38.98 (39.29)	4.09 (4.28)	3.20 (3.52)	29.73 (29.89)
$\{[^nPr_2Sn(A)_2]_2O\}$	158	69	I	49.00 (49.44)	5.64 (5.50)	4.12 (3.08)	26.29 (26.48)
$\{[^nBu_2Sn(A)_2]_2O\}$	120–122	80	I	46.95 (47.87)	6.45 (5.03)	2.90 (2.93)	24.67 (24.88)
$\{[^nOct_2Sn(A)_2]_2O\}$	86	83	III	54.46 (55.00)	8.11 (6.80)	2.82 (2.38)	19.98 (20.18)

[a] Where AH = monochloroacetyl-L-phenylalanine. [b] All complexes were white. [c] Solvents of recrystallization: I, absolute alcohol; II, benzene; III, benzene/absolute acohol.

Table 2

Infrared spectral data (cm^{-1}) for diorganotin(IV) complexes of monochloroacetyl-L-phenylalanine [a]

Complex [b]	ν(NH) amide	ν(CO) amide I	ν(CO) amide II [c]	ν(COO) asym	ν(COO) sym	Δν	ν(Sn–C)	ν(Sn–O)	ν(Sn–O–Sn)
AH	3320s	1630s	1545s	1705s	1250s	455	–	–	–
NaA	3200s, b	1640s	1540s	1600s	1400s	200	–	–	–
EtA [d]	3315s	1640s	1525s	1730s	1375s	355	–	–	–
$[Me_2Sn(A)_2]$	3295s	1670s	1590s	1655s	1400s	255	580m 525w	425s	–
$[^nPr_2Sn(A)_2]$	3340s 3280s	1640m	1580s	1610s	1400s	210	585w	490s 420s	–
$[^nBu_2Sn(A)_2]$	3290s	1655sh	1550s	1680s	1390s	290	525s	490m 420m	–
$[^nOct_2Sn(A)_2]$	3340s	1655s	1520m	1600s	1390s	210	585m	460m 420s	–
$\{[Me_2Sn(A)_2]_2O\}$	3300s	1645s	1510s	1725m 1600m	1410s	190	570m 530m	490m 450m	620s
$\{[^nPr_2Sn(A)_2]_2O\}$	3340s	1660s	1520s	1725m 1600s	1410s	190	560m	490m 445m	615s
$\{[^nBu_2Sn(A)_2]_2O\}$	3280s	1630s	1540s	1725m 1585s	1395s	190	550s	415m	615s
$\{[^nOct_2Sn(A)_2]_2O\}$	3400m 3280s	1655s	1530m	1735m 1625s	1395s	220	600sh 560m	520m 480m	615s

[a] Spectra were recorded as KBr discs, the symbols s, m, b, w and sh have their usual meanings. [b] Where AH is monochloroacetyl-L-phenylalanine. [c] Amide II band is [ν(CN) + δ(NH)]. [d] Ethyl ester of monochloroacetyl-L-phenylalanine.

Table 3

^{1}H NMR data (δ; ppm) for diorganotin(IV) complexes of monochloroacetyl-L-phenylalanine [a]

Complex [b]	C_6H_5 + NH [c]	CH	CH_2	CH_2Cl	Sn–R	
					CH_2	CH_3
AH	8.39–7.60 (bm, 6H)	5.91–5.51 (bm, H)	4.25–4.00 (d, 2H)	4.95 (s, 2H)	–	–
$[Me_2Sn(A)_2]$	7.55–7.15 (bm, 12H)	4.95–4.70 (bm, 2H)	3.50–3.10 (m, 4H)	4.15 (s, 4H)	–	1.00, 0.77 2× (s, 3H)
$[^nPr_2Sn(A)_2]$	7.45–6.85 (bm, 12H)	4.95–4.45 (bm, 2H)	3.32–3.05 (m, 4H)	4.10–3.95 (m, 4H)	1.88–1.32 (m, 8H)	1.20–0.88 (t, 6H)
$[^nBu_2Sn(A)_2]$	7.42–6.85 (m, 12H)	5.12–4.75 (bm, 2H)	3.40–3.10 (m, 4H)	4.05 (s, 4H)	1.90–1.30 (m, 12H)	1.10–0.65 (m, 6H)
$[^nOct_2Sn(A)_2]$	7.45–7.15 (m, 12H)	5.10–4.85 (bm, 2H)	3.45–3.20 (m, 4H)	4.10 (s, 4H)	1.48–1.20 (m, 28H)	1.15–0.90 (m, 6H)
$\{[Me_2Sn(A)_2]_2O\}$	7.50–7.15 (bm, 12H)	4.90–4.75 (bm, 2H)	3.45–3.15 (m, 4H)	4.15 (s, 4H)	–	1.08–0.80 (d, 12H)
$\{[^nPr_2Sn(A)_2]_2O\}$	7.40–6.70 (m, 12H)	4.95–4.45 (bm, 2H)	3.30–3.00 (d, 4H)	4.05 (s, 4H)	1.90–1.30 (m, 16H)	1.19–0.80 (t, 12H)
$\{[^nBu_2Sn(A)_2]_2O\}$	7.50–6.90 (m, 12H)	5.05–4.62 (bm, 2H)	3.41–3.05 (m, 4H)	4.10 (s, 4H)	1.88–1.28 (m, 24H)	1.19–0.72 (m, 12H)
$\{[^nOct_2Sn(A)_2]_2O\}$	7.35–6.90 (m, 12H)	4.85–4.55 (bm, 2H)	3.31–3.01 (bm, 4H)	4.00 (s, 4H)	1.70–1.15 (m, 56H)	1.05–0.60 (m, 12H)

[a] Spectra were recorded in $CDCl_3$ solution; the symbols b, m, s, and t have their usual meanings. [b] Where AH is monochloroacetyl-L-phenylalanine. [c] NH protons overlap phenyl protons.

analysis (Table 1) and infrared (Table 2) and ^{1}H NMR (Table 3) spectroscopy. All the complexes are white, and are soluble in common organic solvents such as benzene, ethanol, methanol, and chloroform.

Infrared data for the ligands and complexes have been recorded as KBr discs in the region 4000–200 cm^{-1}; the stretching frequencies for the NH, amide C=O, acid COO, Sn–C, Sn–O and Sn–O–Sn bands are listed in Table 2. The deprotonation of the carboxylic acid group in the complexes is evident from the absence of the broad band due to COOH in the 3000–2800 cm^{-1} region. The N–H stretching frequencies in the complexes are higher than those for the sodium salt of the ligand, suggesting that the amido N atom is not coordinated to the Sn atom [2]. The C=O stretching frequencies for the amido groups are slightly greater for the complexes than for the free ligands. The $\Delta\nu$ values (where $\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO)$) are lower in the spectra of all complexes than in the spectra of the free ligand ($\Delta\nu = 450$ cm^{-1}) and are comparable to the $\Delta\nu$ value of 200 cm^{-1} for the sodium salt of the ligand. These observations clearly indicate the presence of asymmetrically coordinating carboxylate ligands [2]. The observation of two Sn–C absorption bands in the 600–500 cm^{-1} region reveals a non-linear configuration of the R_2Sn moiety [5]. A band in the 500–400 cm^{-1} region is assigned to an stretching frequency associated with the Sn–O bond. A strong band in the 620–615 cm^{-1} region for the $\{[R_2Sn(A)_2]_2O\}$ complexes is assigned to ν(Sn–O–Sn), indicating a Sn–O–Sn bridged structure.

The ^{1}H NMR spectra of the ligands and the complexes have been recorded in $CDCl_3$ solution and these data are listed in Table 3. In the spectra of the free ligand there is single resonance at 7.95 ppm which is absent in the spectra of the complexes, indicating replacement of the carboxylic acid proton by a diorganotin(IV)

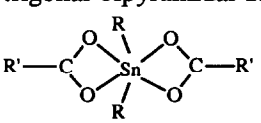
Table 4

Selected bond lengths (Å) and angles (°) in [^{n}Bu$_2$Sn(O$_2$C(CH$_2$Ph)C(H)N(H)C(O)CH$_2$Cl)$_2$]

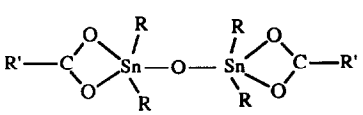
Sn–O(41)	2.140(4)	Sn–O(42)	2.506(5)
Sn–C(6)	2.136(6)	C(4)–O(41)	1.30(1)
C(4)–O(42)	1.24(1)	C(4)–C(1)	1.52(1)
C(1)–N(1)	1.45(1)	N(1)–C(2)	1.358(8)
C(2)–O(2)	1.24(1)	C(2)–C(3)	1.48(1)
C(3)–Cl	1.781(8)	C(1)–C(5)	1.544(8)
C(5)–C(51)	1.504(9)	C(6)–C(7)	1.52(1)
C(7)–C(8)	1.529(9)	C(8)–C(9)	1.51(1)
O(41)–Sn–O(42)	55.6(2)	O(41)–Sn–C(6)	106.5(2)
O(41)–Sn–O(41)′ [a]	81.8(2)	O(41)–Sn–O(42)′	137.3(2)
O(41)–Sn–C(6)′	104.7(2)	O(42)–Sn–C(6)	87.2(2)
O(42)–Sn–O(42)′	167.1(2)	O(42)–Sn–C(6)′	88.2(2)
C(6)–Sn–C(6)′	138.3(2)	Sn–O(41)–C(4)	100.4(5)
Sn–O(42)–C(4)	84.8(5)	O(41)–C(4)–O(42)	100.3(6)
O(41)–C(4)–C(1)	118.6(7)	O(42)–C(4)–C(1)	122.2(7)
C(4)–C(1)–N(1)	111.7(5)	C(4)–C(1)–C(5)	109.3(5)
N(1)–C(1)–C(5)	109.4(6)	C(1)–N(1)–C(2)	120.4(8)
N(1)–C(2)–O(2)	123.1(8)	N(1)–C(2)–C(3)	113.2(9)
O(2)–C(2)–C(3)	123.6(7)	C(2)–C(3)–Cl	112.4(6)
C(1)–C(5)–C(51)	114.2(5)		

[a] Primed atoms related by 2-fold axis.

moiety on complex formation. In the dimethyltin(IV) complexes, two resonances are observed, indicating inequivalence of the methyl groups. By contrast, for the di-n-propyltin complexes there is a triplet in the 1.20–0.80 ppm region, indicating that all the methyl protons are equivalent. In the spectra of the remaining complexes, only complex multiplets were observed in the 1.19–0.60 ppm region due to the tin bound alkyl protons. In all the spectra there is a multiplet in the region 7.50–6.85 ppm, indicating the overlap of phenyl and NH protons. The number of protons calculated from the integrated spectrum is equivalent to the number of protons expected from the proposed structures I for the 1 : 2 complexes and II for the 1 : 1 complexes. I contains six-coordinate Sn centres which exist in skew-trapezoidal planar geometries and II features Sn–O–Sn bridges and five-coordinate, trigonal bipyramidal Sn centres.



(I)



(II)

Crystallographic information has been obtained for I, but in the case of II no crystals suitable for X-ray structure determination could be obtained to support the formulation. Selected interatomic parameters for [^{n}Bu$_2$Sn(A$_2$)] are listed in Table 4 and the numbering scheme employed is shown in Fig. 1. The Sn atom is located on a crystallographic 2-fold axis such that only half the molecule defines the asymmetric unit. The Sn atom is chelated by two symmetry-related, asymmetrically coordinating carboxylate ligands with Sn–O(41) 2.140(4) Å and Sn–O(42) 2.506(5) Å; this asymmetry is reflected in the disparate C(4)–O(41) and C(4)–O(42) bond distances,

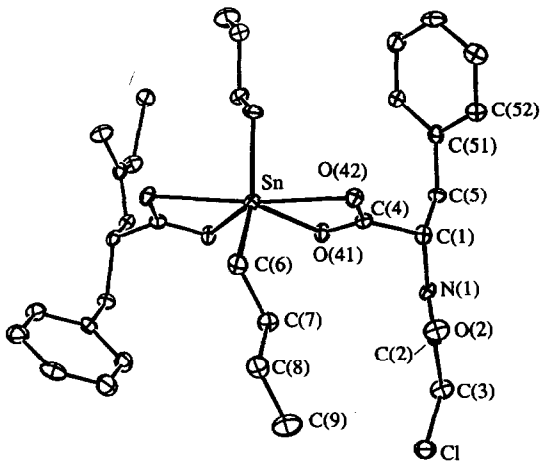


Fig. 1. Molecular structure and crystallographic numbering scheme employed for [^{n}Bu$_2$Sn(O$_2$C(CH$_2$-Ph)C(H)N(H)C(O)CH$_2$Cl)$_2$].

with the longer C–O bond being associated with the O atom involved in shorter Sn–O bond. The remaining sites about the six coordinate Sn atom are occupied by two n-butyl groups, which lie over the weaker Sn–O(42) bonds and define a C–Sn–C angle of 138.3(2)°. The Sn atom geometry is thus best described as based on a skew-trapezoidal planar geometry.

There is one basic structural type for compounds of the formula [R$_2$Sn(O$_2$CR′)$_2$] and the structure found for [^{n}Bu$_2$Sn(A)$_2$] conforms closely to this [6]. More recently [7–9], several [R$_2$Sn(O$_2$CR′)$_2$] structures have been reported in which there are

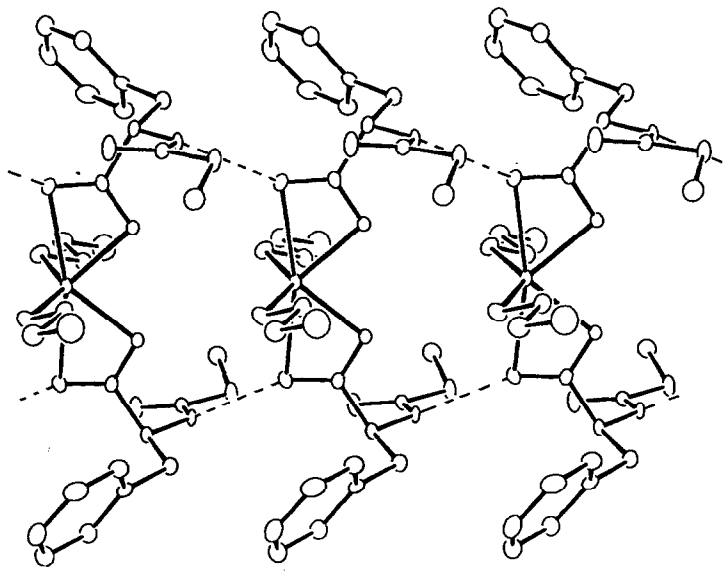


Fig. 2. Chains of [^{n}Bu$_2$Sn(O$_2$C(CH$_2$Ph)C(H)N(H)C(O)CH$_2$Cl)$_2$] linked by NH · · · O(42) interactions between molecules related by a unit translation along the *b*-axis.

close Sn · · · O′ interactions in the crystal lattice. However, in the case of [^{n}Bu$_2$Sn(A)$_2$] there are no such interactions; the intermolecular interactions in this are confined to those involving the ligand atoms only.

The most significant interaction in the crystal lattice of [^{n}Bu$_2$Sn(A)$_2$] is that between the amide H atom and the O(42) atom of a neighbouring molecule related by a translation along the crystallographic *b*-axis. The amide-bound H atom was not located in the crystallographic refinement and therefore only the N(1) · · · O(42) separation of 2.83 Å may be quoted. Owing to the 2-fold axis of symmetry, each molecule is involved in four such contacts, i.e. two contacts with each of two different molecules. Thus the lattice is comprised of chains of [^{n}Bu$_2$Sn(A)$_2$]$_n$, connected via the NH · · · O(42) contacts (see Fig. 2, where the N · · · O(42) interactions are indicated by the dashed lines). Perpendicular to these ribbons are significantly weaker amide-H · · · O(2)′ contacts, the N(1) · · · O(2)′ (symmetry operation: $-x$, y, $1-x$) separation being 3.68 Å.

Experimental

Synthesis

Dimethyl-, di-n-propyl-, di-n-butyl- and di-n-octyl-tin oxides were purchased from Alfa. Monochloroacetyl-L-phenylalanine was prepared as previously reported [10].

To a solution of monochloroacetyl-L-phenylalanine (2 mmol) in a mixture of anhydrous benzene (30 cm^3) and absolute ethanol (10 cm^3) was added the dialkyltin oxide (1 or 2 mmol). The mixture was then refluxed on a water bath with azeotropic removal of water. Within 10–15 min. the dialkyltin oxide had dissolved to yield a clear solution. This solution was refluxed for a further 3–4 h, and then cooled. The solvent was removed under reduced pressure and the residual white solid was collected and recrystallized from the solvent as indicated in Table 1.

Melting points were determined in open capillaries and are uncorrected. Elemental analysis for C, H and N were carried out by the Microanalytical Service R.S.I.C., Panjab University, Chandigarb. Tin was determined as SnO_2. Infrared spectra were recorded on a Pye-Unicam SP300 spectrometer as KBr discs. The ^{1}H NMR spectra were recorded on a Tesla BS487C (80MHz) using TMS as internal standard.

Crystallography

Intensity data for [^{n}Bu$_2$Sn(A)$_2$] were measured at 220 K on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The ω–2θ scan technique was employed to measure data up to a maximum Bragg angle of 22.5° C. The data set was corrected for Lorentz and polarization effects and for absorption by use of an analytical procedure. Relevant crystal data are given in Table 5.

The Sn atom, constrained to lie on a crystallographic 2-fold axis, was placed at the origin and a subsequent difference map revealed the sites of the remaining atoms. The structure was refined by a full-matrix least-squares procedure based on F [11] with anisotropic thermal parameters for non-H atoms. C-bound H atoms were included in the model at their calculated positions; the amide-bound H atom was not located. After the inclusion of a weighting scheme of the form $w = [\sigma^2(F) + g|F|^2]^{-1}$, the refinement was continued until convergence; final refinement

Table 5

Crystal data and refinement details for [^{n}Bu$_2$Sn(O$_2$C(CH$_2$Ph)C(H)N(H)C(O)CH$_2$Cl)$_2$]

Formula	$C_{30}H_{40}Cl_2N_2O_6Sn$
Mol. wt.	714.2
Crystal system	monoclinic
Space group	$C2$
a, Å	25.41(1)
b, Å	5.383(2)
c, Å	12.043(1)
β, deg	104.33(2)
V, Å^3	1596.0
Z	2
D_c, g cm^{-3}	1.486
$F(000)$	732
μ, cm^{-1}	9.17
T, K	220
Max./min. transmission factors	0.906, 0.832
No. of data collected	1301
No. of unique data	1244
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	1197
R	0.034
g	0.0094
R_w	0.031
Residual ρ_{max}, e Å^{-3}	0.71 (near Sn)

Table 6

Fractional atomic coordinates ($\times 10^4$) for [^{n}Bu$_2$Sn(O$_2$C(CH$_2$Ph)C(H)N(H)C(O)CH$_2$Cl)$_2$]

Atom	x	y	z
Sn	0(−)	0(−)	0(−)
Cl	−1443(1)	−6138(4)	3489(1)
O(2)	−544(3)	−2489(12)	3780(5)
O(41)	170(2)	−3005(9)	1199(3)
O(42)	269(2)	523(11)	2134(4)
N(1)	66(2)	−5183(18)	3321(3)
C(1)	451(3)	−3236(12)	3269(5)
C(2)	−412(2)	−4634(20)	3577(4)
C(3)	−743(3)	−6866(17)	3661(7)
C(4)	286(3)	−1785(16)	2156(6)
C(5)	1018(2)	−4387(12)	3379(5)
C(51)	1459(2)	−2516(14)	3391(5)
C(52)	1611(3)	−845(14)	4296(6)
C(53)	2010(3)	899(16)	4309(6)
C(54)	2271(2)	1000(17)	3419(6)
C(55)	2132(3)	−705(17)	2542(6)
C(56)	1727(2)	−2424(16)	2519(5)
C(6)	−780(2)	1414(17)	47(5)
C(7)	−1104(2)	−359(18)	605(5)
C(8)	−1651(3)	744(16)	658(6)
C(9)	−1987(3)	−971(22)	1191(8)

details are listed in Table 5. The analysis of variance showed no special feature indicating that an appropriate weighting scheme had been applied. Differences i Friedel pairs included in the data set confirm the presence of L-phenylalanine Fractional atomic coordinates are listed in Table 6 and the numbering schem employed is shown in Fig. 1 which was drawn with ORTEP [12] at 25% probabilit ellipsoids. Scattering factors were as incorporated in the SHELX76 program [11] an the refinement was performed on a SUN4/280 computer. Lists of thermal parame ters, H-atom parameters, all bond distances and angles, and observed and calculate structure factors are available from ERTT.

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References

1 S.W. Ng, V.G. Kumar Das and E.R.T. Tiekink, J. Organomet. Chem., 411 (1991) 121.
2 G.K. Sandhu, R. Gupta, S.S. Sandhu and R.V. Parish, Polyhedron, 4 (1985) 81.
3 G.K. Sandhu, R. Gupta, S.S. Sandhu, R.V. Parish and K. Brown, J. Organomet. Chem., 279 (1985 373.
4 G.K. Sandhu, R. Gupta, S.S. Sandhu, L.S. Moore and R.V. Parish, J. Organomet. Chem., 311 (1986 281.
5 G.K. Sandhu, N. Sharma and E.R.T. Tiekink, J. Organomet. Chem., 371 (1989) C1.
6 E.R.T. Tiekink, Appl. Organomet. Chem., 5 (1991) 1.
7 S.W. Ng, V.G. Kumar Das, W.-H. Yip, R.-J. Wang and T.C.W. Mak, J. Organomet. Chem., 39 (1990) 201.
8 E.R.T. Tiekink, J. Organomet. Chem., 408 (1991) 323.
9 C. Vatsa, V.K. Jain, T. Kesavadas and E.R.T. Tiekink, J. Organomet. Chem., 410 (1991) 135.
10 E. Ranwin, J. Org. Chem. 18 (1953) 127.
11 G.M. Sheldrick, SHELX76, Program for crystal structure determination, Cambridge University, U.K. 1976.
12 C.K. Johnson, ORTEP-II Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976