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2,5-Di-(*tert*-butyl)phospholyl sandwich complexes containing group 14 elements (Ge, Sn, Pb). Synthesis, molecular structure, and ring transfer chemistry of $[M(PC_4H_2Bu^t_2)_2]$ (M = Sn, Pb)

Kareen Forissier, Louis Ricard, Duncan Carmichael* and François Mathey*

Laboratoire 'Hétéroéléments et Coordination', CNRS UMR 7653, DCPH Ecole Polytechnique, 91128 Palaiseau Cedex, France. E-mail: Duncanc@mars.polytechnique.fr

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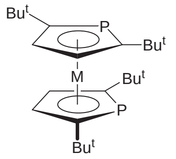
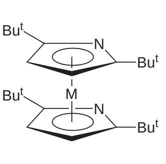
Structurally characterised tin and lead sandwich compounds are shown to contain aromatic phospholyl ligands which can be transferred to rhodium and iridium centres under mild conditions.

The coordination chemistry of phospholyl ligands towards transition metals is an area reaching maturity[1] and a number of recent studies have also highlighted the chemistry of alkali metal phospholides.[2] However, simple π complexes involving monophospholyl ligands and elements of the p block have yet to appear.[3] Lying somewhere between the classical ionic chemistry of the phospholide anions and covalent transition metal phospholyls, these complexes may answer some interesting questions concerning the nature of the metal–phospholyl bond and the potential for η^5–η^1 equilibria. Furthermore, it seems reasonable to assume that they will be useful reagents.[4]

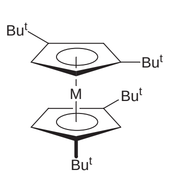
We present here the synthesis of three group 14 sandwich complexes **1**–**3** containing the 2,5-di(*tert*-butyl)phospholyl ligand and the molecular structures of $[Pb(PC_4H_2Bu^t_2)_2]$ **1** and $[Sn(PC_4H_2Bu^t_2)_2]$ **2**. Using the 2,5-di-(*tert*-butyl)phospholyl ligand[5] diminishes the potential for electron-transfer chemistry† at the relatively redox-sensitive tin and lead centres and allows comparisons to be made with the published complexes $[M(NC_4H_2Bu^t_2)_2]$ (M = Sn **4**,[6a] Pb **5**[6b]) and $[M(C_5H_3Bu^t_2)_2]$ (M = Ge **6**, Sn **7**, Pb **8**[7a]).



M = Pb, **1**; Sn, **2**; Ge, **3**

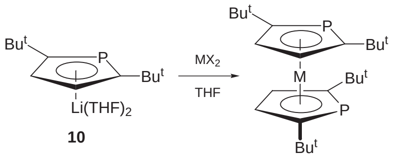


M = Sn, **4**; Pb, **5**



M = Ge, **6**; Sn, **7**; Pb, **8**

Stirring THF solutions containing $[Li(PC_4H_2Bu^t_2)(THF)_2]$ **10**[5] with MCl_2 (M = Sn, Pb) for 30 min at room temp. followed by evaporation to dryness *in vacuo*, extraction of $[M(PC_4H_2Bu^t_2)_2]$ into pentane and crystallisation at −78 °C produced air and moisture-sensitive deep (Pb, **1**) and pale (Sn, **2**) yellow cubes in *ca*. 80% yield. A similar procedure using GeI_2 gave $[Ge(PC_4H_2Bu^t_2)_2]$ **3** (50%) as a pale yellow powder.‡



M = Pb, **1**; Sn, **2**; Ge, **3**

X-Ray diffraction studies upon single crystals of the isostructural lead and tin compounds (Fig. 1 and 2, respectively) show two discrete molecular η^5 complexes within each unit cell.§ In each case, the Bu^t groups almost perfectly eclipse the phosphorus and CH functionalities, thus relieving nonbonding interactions between the rings. The angles at the intersection of the planes defined by the flat phospholyl ligands (Pb: 17.3; Sn: 19.2°) predictably[1] resemble the cyclopentadienyl-derived stannocenes and plumbocenes more than the aza-analogues **4** and **5**. The tilt of 5.7° for the phospholyl ring in the related phospharuthenocene[5] suggests that these angles may simply reflect the preferred geometry of the 2,5-di-(*tert*-butyl)phospholyl ligand rather than any significant electronic drive for a bent metallocene structure. Thus, the small $^1J_{PSn}$ coupling in **2**¶ probably reflects high *s*-electron character in both the P *and* the Sn lone pair orbitals.[7b,8] The equalisation of bond lengths within the phospholyl component indicates extensive delocalisation (Table 1)[9] which is confirmed by the large intracyclic $^1J_{PC}$ coupling constants ([Pb = 51.4, Sn = 48.5 and Ge = 47.0 Hz; *cf.* $(Me_3Sn)PC_4H_2Bu^t_2$ **9**, (27.5 Hz) and the delocalised $[Li(PC_4H_2Bu^t_2)(THF)_2]$ **10** (47.0 Hz), $[Ru(C_5Me_5)(PC_4H_2Bu^t_2)]$ **11** (62.7 Hz), **12** (65.3 Hz)]. These data suggest strongly that the rings are highly aromatic.

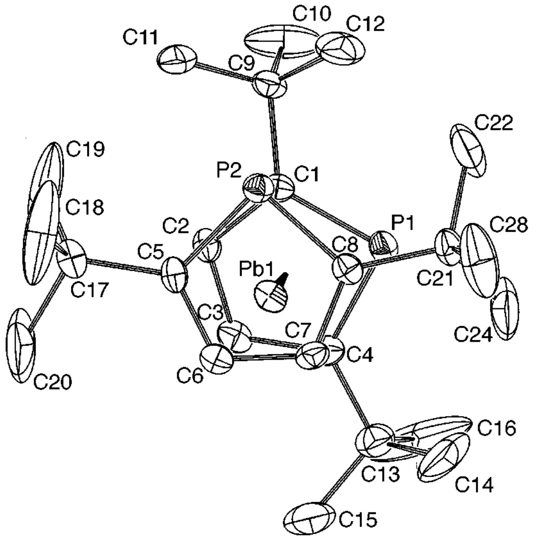


Fig. 1 Molecular structure of one of the essentially identical molecules of $[Pb(PC_4H_2Bu^t_2)_2]$ **1**, found in the unit cell. Selected bond lengths (Å): Pb(1)–P(1) 2.8732(8), Pb(1)–P(2) 2.9012(7), Pb(1)–C(1) 2.763(3), Pb(1)–C(2) 2.796(3), Pb(1)–C(3) 2.863(3), Pb(1)–C(4) 2.872(3), Pb(1)–C(8) 2.820(3), Pb(1)–C(7) 2.860(3), Pb(1)–C(6) 2.905(3), Pb(1)–C(5) 2.895(3), P(1)–C(1) 1.789(3), P(1)–C(4) 1.787(3), P(2)–C(5) 1.787(3), P(2)–C(8) 1.785(3), C(1)–C(2) 1.385(4), C(2)–C(3) 1.530(4), C(3)–C(4) 1.381(4), C(5)–C(6) 1.391(4), C(6)–C(7) 1.415(4), C(7)–C(8) 1.390(4).

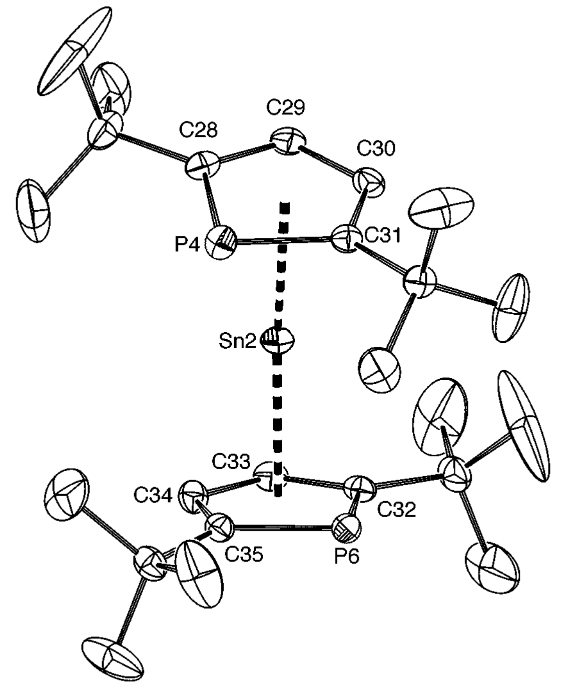
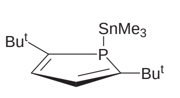


Fig. 2 Molecular structure of one of the essentially identical molecules of $[Sn(PC_4H_2Bu^t{}_2)_2]$ **2**, found in the unit cell. Selected bond lengths (Å): Sn(2)–P(4) 2.8018(7), Sn(2)–P(6) 2.8348(7), Sn(2)–C(28), 2.822(3), Sn(2)–C(29) 2.825(3), Sn(2)–C(30) 2.741(3), Sn(2)–C(31) 2.688(3), Sn(2)–C(32) 2.854(3), Sn(2)–C(33) 2.871(3), Sn(2)–C(34) 2.813(3), Sn(2)–C(35) 2.770(3), P(4)–C(31) 1.788(3), P(4)–C(28) 1.794(3), P(6)–C(32) 1.785(3), P(6)–C(35) 1.790(3), C(28)–C(29) 1.372(4), C(29)–C(30) 1.425(4), C(30)–C(31) 1.385(4), C(32)–C(33) 1.393(4), C(33)–C(34) 1.419(4), C(34)–C(35) 1.384(4).

Table 1 Bond length equalisation in selected phospholyl motifs

Complex	*r*(C=C)/Å	*r*(C–C)/Å	Ref.
$[Mo_2(PC_4H_2Bu^t{}_2)_2(CO)_4]$	1.407	1.425	*a*
$[PC_4Me_4][Li(tmeda)]$	1.396	1.424	*b*
$[Pb(PC_4H_2Bu^t{}_2)_2]$	1.387	1.417	*c*
$[Sn(PC_4H_2Bu^t{}_2)_2]$	1.384	1.422	*c*
PhCH2PC4H4	1.343	1.438	*d*

References: (*a*) D. Carmichael, L, Ricard and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1994, 2489; (*b*) T. A. Douglas, K. H. Theopold, B. S. Haggerty and A. L. Rheingold, *Polyhedron*, 1990, **9**, 209; (*c*) this work; (*d*) P. Coggan and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1973, 1888.



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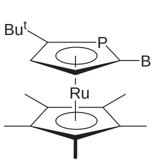

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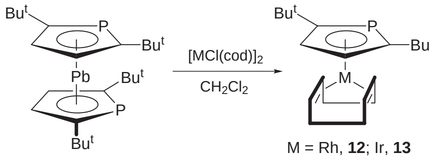
Complexes **1**–**3** are hydrocarbon-soluble and may also be recovered unchanged after several days at room temperature in dichloromethane. Such solution properties suggest a significant covalent contribution to the metal–ring interaction and imply some potential as 'mild' sources of phospholyl ligands. This has been confirmed in studies of the reactivity of $[M(cod)Cl]_2$ towards warm dichoromethane solutions of **1**, which permitted clean and quantitative isolation of the new compounds $[M(cod)(PC_4H_2Bu^t{}_2)]$ (M = Rh, **12**, yellow; M = Ir, **13**, orange) after filtration from $PbCl_2$.

Thus, in addition to their theoretical interest, these main group complexes may be useful precursors for the synthesis of further metal phospholyl compounds.



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Notes and references

† To date, attempts to prepare bis(3,4 dimethylphospholyl)plumbocene by an analogous route have failed.

‡ *Selected spectroscopic data:* (NMR: C_6D_6, Bruker AC200; MS: HP5989B). **1** δ_P 75. δ_C 168.3 ($^1J_{PC}$ 51.4, $^1J_{PbC}$ 50.9), 123.7 ($^2J_{PC}$ 3.4, $^1J_{PbC}$ 73.0). δ_H 6.90 ($^3J_{PH}$ 4.2). **2** δ_P 62 ($^1J_{SnP}$ 74.7). δ_C 166.2 ($^1J_{PC}$ 48.5, $^1J_{SnC}$ 10.6), 125.5 ($^1J_{PC}$ 4.6, $^1J_{SnC}$ 53.4). δ_H 6.90 ($^3J_{PH}$ 4.2, $^3J_{SnH}$ 10.6). **3** δ_P 67. δ_C 161.2 ($^1J_{PC}$ 47.5). MS −ve CI(NH_3) *m/z* (%): 464 (2) [M$^+$], 195 (100) $[PCl_{12}H_{20}]$. δ_P −3.8 ($^1J_{RhP}$ 15.2). δ_C 138.0 ($^1J_{PC}$ 62.7, $^1J_{RhC}$ 13.5), 95.7 ($^2J_{PC}$ 13.7), 65.3 ($^1J_{RhC}$ 13.7), 33.8 ($^2J_{RhC}$ 6.1), δ_H 5.46 ($^3J_{PH}$ 4.4). EI-MS *m/z* (%): 406 (81) [M$^+$], 347 (100) [M$^+$− C_4H_9]. **13** δ_P −28.1. δ_C 128.1 ($^1J_{PC}$ 65.6), 93.2 ($^2J_{PC}$ 4.6), 49.3, 34.4 δ_H 5.46 ($^3J_{PH}$ 4.4). EI-MS *m/z* (%): 496 (31) [M$^+$], 437 (38) [M$^+$ − C_4H_9].

§ *Crystal structure determinations*: for **1**: $C_{24}H_{40}P_2Pb$, $M = 597.69$, yellow plate (0.22 × 0.16 × 0.14 mm) from pentane. Data collected at 150.0(1) K on an Enraf Nonius Kappa CCD diffractometer using Mo-Kα ($\lambda = 0.71073$ Å) radiation and graphite monochromator; solved with the maXus package and refined using SHELXL97; monoclinic, space group $P2_1/n$, $a = 16.0550(2)$, $b = 20.3550(4)$, $c = 16.4910(3)$ Å, $\beta = 101.323(1)°$, $V = 5284.35(16)$ Å^3, $Z = 8$, $D_c = 1.503$ g cm^{-3}, $\mu = 6.513$ cm^{-1}, $F(000) = 2368$, reflections collected = 10807, maximum $\theta = 26.37°$, used = 9859 $[F^2 > 2\sigma(F^2)]$. Final agreement factors: $wR_2 = 0.0635$, $R_1 = 0.0237$, GOF = 1.010, $\Delta\rho$ max./min. = 1.616(0.093)/−0.831(0.093) e Å^{-3}.

For **2**: $C_{24}H_{40}P_2Sn$, $M = 509.19$, pale yellow plate (0.20 × 0.20 × 0.15 mm) from pentane, monoclinic, space group $P2_1/n$, $a = 16.0460(2)$, $b = 20.3280(2)$, $c = 16.3740(2)$ Å, $\beta = 101.089(6)°$, $V = 5241.20(11)$ Å^3, $Z = 8$, $D_c = 1.291$ g cm^{-3}, $\mu = 1.104$ cm^{-1}, $F(000) = 2112$, reflections collected = 10683, maximum $\theta = 26.35°$, used = 9926 $[F^2 > 2\sigma(F^2)]$. Data collected and processed as above. Final agreement factors $wR_2 = 0.0754$, $R_1 = 0.0278$, GOF = 1.034, $\Delta\rho$ max./min. = 1.354(0.069)/−0.921(0.069) e Å^{-3}.

CCDC 182/1270. See http://www.rsc.org/suppdata/cc/1999/1273/ for crystallographic files in .cif format.

¶ No PbP coupling could be observed at room temp. for **1** (C_6D_6, ^{31}P = 81 MHz).

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4 See, for example, F. Nief and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1988, 770.
5 D. Carmichael, L. Ricard and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1994, 1167.
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