Lipophilic Metal (Na, Ti^{III}, Zr^{IV}, Rh^{I} and Pd^{II}) Complexes derived from the Hybrid Ligands $^-$OR and HOR (R = Me$_2$PCH$_2$CBu$^t{}_2$); the X-Ray Structures of [TiCl(OCBu$^t{}_2$CH$_2$PMe$_2$)$_2$] and trans-[Rh(CO)Cl(PMe$_2$CH$_2$CBu$^t{}_2$OH)$_2$]†

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From crystalline [Li(μ-OCBu$^t{}_2$CH$_2$PMe$_2$)$_2$]$_2$ [≡ Li(μ-OR)$_2$] the following crystalline pentane-soluble derivatives have been obtained: ROH 1, [TiCl(OR)$_2$] and [Zr(η-C$_5$H$_5$)$_2$Cl(OR)] 4; 1 is a source of the similarly lipophilic crystalline [Na(μ-OR)]$_2$ and trans-[Rh(CO)Cl(ROH)$_2$], and 4 of the heterotrimetallic complexes trans-[M(CO)$_n$Cl$_{2-n}${(RO)Zr(η-C$_5$H$_5$)$_2$Cl}$_2$] (M = Rh and n = 1 or M = Pd and n = 0).

γ-P^{III}-Functionalised alkoxides $^-$OCR'$_2$CH$_2$PR$_2$ are an interesting class of hybrid ligand, as they contain both a hard ($^-$O) and a soft (P) nucleophilic centre. One of their applications is in the construction of heterobimetallic (*e.g.* of Zr^{IV} and Rh^{I}) compounds, which may have a role as catalysts.[1] Another is in the formation of crystalline, lipophilic alkoxides of metals which have a predominantly ionic chem-

istry, as in [{M(OCBu$^t{}_2$CH$_2$PR$_2$)$_n$}$_m$] (M = Li, R = Me or Ph, n = 1, and m = 2;[2] or M = Y or Nd, R = Me, n = 3, and m = 1).[3]

We now report further results on $^-$OCBu$^t{}_2$CH$_2$PMe$_2$ and the parent alcohol **1** which have implications for both aspects. Noteworthy are the following observations. (*i*) Not only the dimeric structure of the crystalline [Na(μ-OCBu$^t{}_2$CH$_2$PMe$_2$)]$_2$ **2**, but also its good pentane-solubility, are without precedent for a sodium alkoxide. (*ii*) The crystalline lipophilic complex

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[$\overline{\text{TiCl(OCBu}^t_2\text{CH}_2\text{PMe}_2)_2}$] **3** is the first X-ray-characterised monomeric phosphinetitanium(III) complex and also Ti^{III} alkoxide. (*iii*) The compound [Zr(η-C$_5$H$_5$)$_2$Cl(OCBu$^t_2$-CH$_2$PMe$_2$)] **4** behaves as a *P*-centred ligand in the hetero-trimetallic complexes *trans*-[M(CO)$_n$Cl$_{2-n}${PMe$_2$CH$_2$CBu$^t_2$-OZr(η-C$_5$H$_5$)$_2$Cl}$_2$] (M = Rh and n = 1 **5**, and M = Pd and n = 0 **6**). (*iv*) Although the alcohol **1** or the phenyl analogue HOCBu$^t_2$CH$_2$PPh$_2$ **7** functions as a tertiary phosphine in

2[Zr(η-C$_5$H$_5$)$_2$Cl(OCBu$^t_2$CH$_2$PMe$_2$)]

4 43%, cream,
m.p. 172–177 °C

trans-[M(CO)$_n$Cl$_{2-n}$((PMe$_2$CH$_2$CBu$^t_2$O)Zr(η-C$_5$H$_5$)$_2$Cl}$_2$]

5 M = Rh and n = 1, 87%, yellow
6 M = Pd and n = 0, 88%, pale yellow

[Li(μ-OCBu$^t_2$CH$_2$PMe$_2$)]$_2$ ──i──→ 2HOCBu$^t_2$CH$_2$PMe$_2$

ref. 2

1, 87%, white,
m.p. 40 °C

2HOCBu$^t_2$CH$_2$PPh$_2$

7 ref. 2

[$\overline{\text{TiCl(OCBu}^t_2\text{CH}_2\text{PMe}_2)}$]$_2$

3 41%, purple

trans-[Rh(CO)Cl(PR$_2$CH$_2$CBu$^t_2$OH)$_2$]

R = Me **8** 86%, yellow
R = Ph **9** 60%, yellow

2 33%, white
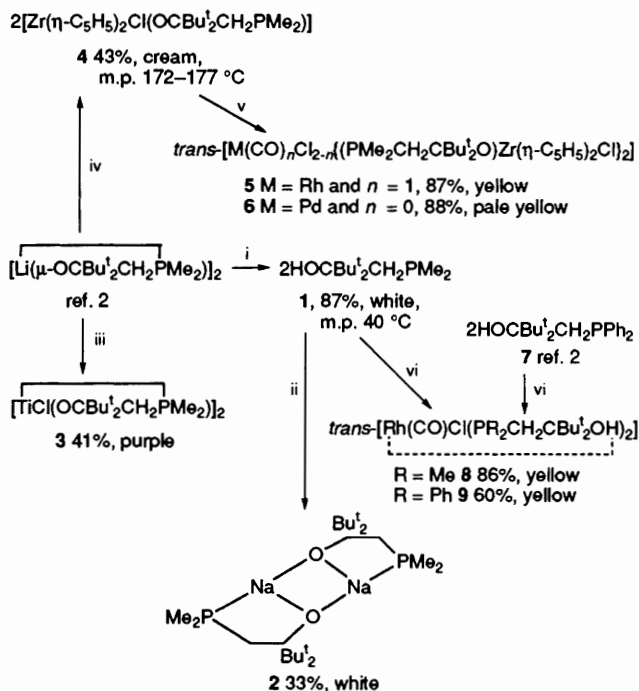
Scheme 1 *Reagents and solvents* (at 25 °C): i, [NHMe$_3$]Cl, OEt$_2$; ii, 2Na[N(SiMe$_3$)$_2$], C$_5$H$_{12}$; iii, TiCl$_3$, tetrahydrofuran (THF); iv, 2 [Zr(η-C$_5$H$_5$)$_2$Cl$_2$], THF; v (for **5**), $\frac{1}{2}$[{Rh(CO)$_2$(μ-Cl)}$_2$], PhMe; v (for **6**), *trans*-[PdCl$_2$(NCPh)$_2$], C$_6$H$_6$; vi, $\frac{1}{2}$[{Rh(CO)$_2$(μ-Cl)}$_2$], PhMe. Yields refer to isolated crystalline material; the low yields reflect the high C$_5$H$_{12}$-solubility of compounds, especially **2–4**.
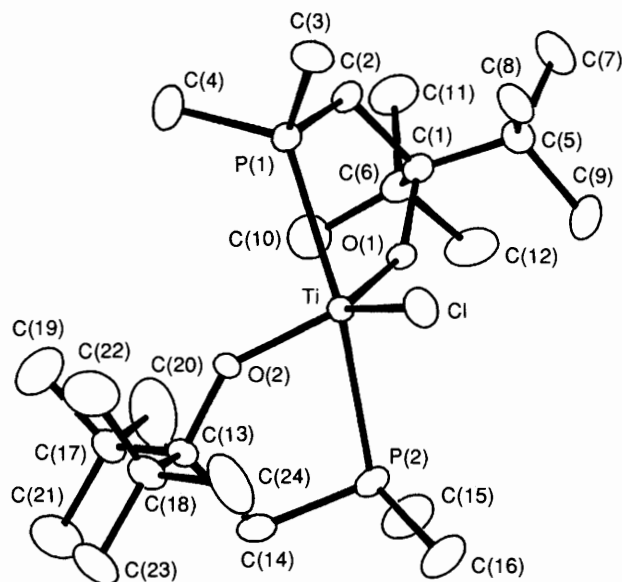

Fig. 1 The molecular structure of [$\overline{\text{TiCl(OCBu}^t_2\text{CH}_2\text{PMe}_2)_2}$] **3** and atom numbering scheme. Selected bond lengths and angles: Ti–Cl 2.366(2), Ti–O(1) 1.841(3), Ti–O(2) 1.843(3), Ti–P(1) 2.600(2), Ti–P(2) 2.591(2) Å; Cl–Ti–O(1) 114.7(1), Cl–Ti–O(2) 113.8(1), Cl–Ti–P(1) 98.49(6), Cl–Ti–P(2) 95.59(6); O(1)–Ti–O(2) 131.5(2), P(1)–Ti–P(2) 165.91(6), O(1)–Ti–P(1) 75.5(1), O(1)–Ti–P(2) 99.1(1), O(2)–Ti–P(1) 98.5(1), O(2)–Ti–P(2) 75.1(1)°.

yielding the crystalline complex *trans*-[Rh(CO)Cl(PMe$_2$-CH$_2$CBu$^t_2$OH)$_2$] **8** (or the phenyl analogue **9**), there is a close Rh···HO contact. (*v*) The ^{1}H NMR solution spectrum in CDCl$_3$ of **6** or **8** shows virtual coupling for both the *P*-bound CH$_3$ groups and the CH$_2$ group, each being a 1 : 2 : 1 triplet.‡ (*vi*) Single crystal X-ray data are reported for **3** (Fig. 1) and **8** (Fig. 2);§ the quality of the data for **2** was adequate to establish its structure as being that shown in Scheme 1 (similar to that found for the lithium analogue^2).‡ (*vii*) The EPR spectrum of **3** in toluene at 298 K revealed a triplet signal, g_{av} 1.964, $a(^{31}\text{P})$ 20 G, comparable to that for [TiCl$_3$(PEt$_3$)$_2$], g_{av} 1.9626, $a(^{31}\text{P})$ 22.82 G.^{4}
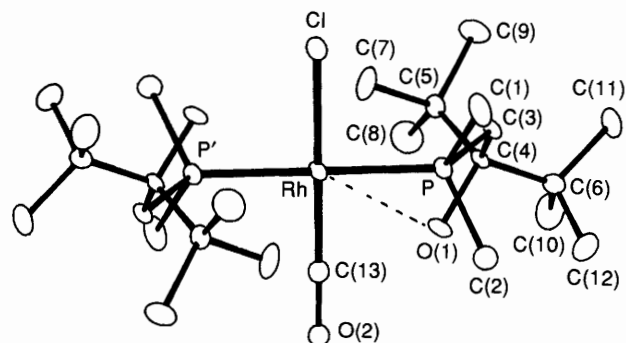

Fig. 2 The molecular structure of *trans*-[Rh(CO)Cl(PMe$_2$CH$_2$C-Bu$^t_2$OH)$_2$] **8** and atom numbering scheme. Selected bond lengths and angles: Rh–Cl ☐ Rh–CO (disordered) 2.366(7), Rh–P 2.327(3), Rh···OH 3.8, Rh···H 2.68, O···Cl 3.29, Cl···H 2.66 Å; Cl–Rh–P ($\equiv$OC–Rh–P) 88.9(2)°.

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‡ *Selected NMR spectroscopic data* [^{31}P at 34.2 MHz (δ rel. to 85% aq. H$_3$PO$_4$), ^{1}H at 80 MHz in C$_6$D$_6$, C$_7$D$_8$, or CDCl$_3$ (**6**, **8**, and **9**) at 305 K]. **1**: ^{31}P{^{1}H} δ −57.0; ^{1}H δ 2.28 [OH, d, $J(^1\text{H}-^{31}\text{P})$ 7.4 Hz]. **2**: ^{31}P{^{1}H} δ −59.1 (br); ^{1}H: δ 1.99 [CH$_2$, d, $^2J(^1\text{H}-^{31}\text{P})$ 6.3 Hz]. **4**: ^{31}P{^{1}H} δ −54.0; ^{1}H δ 2.00 [CH$_2$, d, $^2J(^1\text{H}-^{31}\text{P})$ 6 Hz]; **5**: ^{31}P{^{1}H} showed three A$_2$X patterns (δ −2.7, −4.1 and −5.4) with rel. intensities 3 : 3 : 1 and $^1J(^{31}\text{P}-^{103}\text{Rh})$ ~120 Hz (indicative of three rotamers one of which has non-equivalent P nuclei); ^{1}H δ 1.97 (CH$_2$, t) and 1.62 (CH$_3$, t). **6** (sparingly soluble): ^{31}P{^{1}H} only a single signal, δ −5.0; ^{1}H δ 2.22 (CH$_2$, t) and 1.56 (CH$_3$, t). **7**: ^{31}P {^{1}H} δ −21.5; ^{1}H δ 2.24 [OH, d, $J(^1\text{H}-^{31}\text{P})$ 5.9 Hz]. **8**: ^{31}P{^{1}H} δ −5.0 [d, $^1J(^{31}\text{P}-^{103}\text{Rh})$ 115 Hz]; ^{1}H δ 2.75 (OH), 2.34 (CH$_2$, t, J 4.6 Hz), and 1.60 (CH$_3$, t, J 4.6 Hz). **9**: ^{31}P{^{1}H} 69.8 [d, $^1J(^{31}\text{P}-^{103}\text{Rh})$ 168 Hz]; ^{1}H δ 3.02 [OH, d, $J(^1\text{H}-^{103}\text{Rh})$ 2.7 Hz].

§ *Crystal data* [T 295 K, Enraf-Nonius CAD-4 diffractometer, no absorption corrections, full-matrix least-squares, refinement with non-hydrogen atoms anisotropic, H atoms fixed, $w = 1/\sigma^2(F)$]; direct method for **2** and heavy atom method for **3** and **7**.

2 C$_{24}$H$_{52}$Na$_2$O$_2$P$_2$. M = 480.6, orthorhombic, space group *Pna2$_1$*, a = 15.530(5), b = 8.397(7), c = 22.365(8) Å, U = 2916.5 Å^3, F(000); Z = 4, D_c = 1.09 g cm^{-3}; μ(Mo-Kα) = 1.9 cm^{-1}, specimen 0.6 × 0.6 × 0.4 mm, 1262 unique reflections for 2 < θ < 18°, 709 reflections with $|F^2| > \sigma(F^2)$ used in the refinement where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}$/Lp; R = 0.130, R_w = 0.155.

3 C$_{24}$H$_{52}$ClO$_2$P$_2$Ti, M = 518.0, orthorhombic, space group *P2$_1$2$_1$2$_1$*, a = 10.214(1), b = 13.964(2), c = 21.028(2) Å, U = 2999.1 Å^3, F(000); Z = 4, D_c = 1.15 g cm^{-3}; μ(Mo-Kα) = 4.9 cm^{-1}, specimen 0.3 × 0.3 × 0.25 mm, 3152 unique reflections for 2 < θ < 25°, 1901 reflections with $|F^2| > \sigma(F^2)$ used in the refinement where $\sigma(F^2) = [\sigma(I) + (0.04T)^2]^{\frac{1}{2}}$/Lp; R = 0.039, R_w = 0.040.

8 C$_{25}$H$_{52}$ClO$_3$P$_2$Rh, M = 601.0, monoclinic, space group *P2$_1$/c*, a = 9.819(5), b = 13.313(9), c = 12.350(8) Å, β = 111.00(5)°, U = 1507.0 Å^3, F(000); Z = 2, D_c 1.32 g cm^{-3}; μ(Mo-Kα) 7.7 cm^{-1}; specimen 0.2 × 0.2 × 0.1 mm, 3085 unique reflections for 2 < θ < 25°, 1491 with $|F^2| > \sigma(F^2)$ used in the refinement where $\sigma(F^2) = [\sigma^2(I) = (0.04I)^2]^{\frac{1}{2}}$/Lp; R = 0.071, R_w = 0.081. The molecule lies on an inversion centre with the Cl$^-$ and CO ligands disordered between *trans* sites.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Routes to compounds 1–9 are summarised in Scheme 1. Each compound gave satisfactory microanalytical and NMR spectroscopic (except for the paramagnetic 3) results.† The sodium alkoxide 2 did not show ^{31}P–^{23}Na coupling (its observation would have been unprecedented), in contrast to the $^1J(^{31}P–^7Li)$ observed for the lithium analogue.[2]

Crystalline [$\overline{TiCl(OCBu^t_2CH_2PMe_2})_2$] 3 is monomeric, having a distorted trigonal bipyramidal geometry about the metal, with axial phosphines, P(1)–Ti–P(2) 165.91(6)°. Crystalline trans-[Rh(CO)Cl(PMe$_2$CH$_2$CBu$^t_2$OH)$_2$] 8 has square planar rhodium; the molecule lies on an inversion centre with the Cl$^-$ and CO ligands disordered between trans-sites; the Rh–Cl, Rh–C, and Rh–P bond lengths are unexceptional, but there are unexpected close Rh···HO and OH···Cl contacts. The related complex trans-[Rh(CO)Cl(PPh$_2$CH$_2$CBu$^t_2$OH)$_2$] 9, unlike 8, showed $J(^1H–^{103}Rh)$ of 2.7 Hz for δ(OH) 3.02, indicating that the chelation was maintained in solution.

Work on $^-OCBu^t_2CH_2PR_2$ (R = Me or Ph) dates back to 1986;[2] as well as the derived Li,[2] Y^{III},[3] and Nd^{III} alkoxides, a number of Zr^{IV} analogues[1] have been made. Related ligands $^-OCR'_2CH_2PR_2$ include those with R = Ph and R′ = CF$_3$ (Ni^{II}, Pd^{II}, Pt^{II})[5] or Me (Zr^{IV}),[1] while Ph$_2$PCH$_2$CMe$_2$OH has been employed as a P-centred ligand in Pt^{II} chemistry.[6]

The amphiphilic ligating character of $^-OCBu^t_2CH_2PMe_2$ and of its conjugate base the parent alcohol have much further potential utility in their coordination chemistry; it is interesting that both ligands, even possibly the alcohol [the small value of $J(^{31}P^1H)$‡ in 1 and 7 may alternatively be due to a four-bond coupling], can function in a chelating fashion.

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