Direct Conversion of Carbon Monoxide to a Coordinated Secondary Alcohol Derivative by a Thorium Phosphido Complex

Peter G. Edwards,* Michael B. Hursthouse, K. M. Abdul Malik and Julian S. Parry

School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, PO Box 912, Cardiff, UK CF1 3TB

The homoleptic eight coordinate thorium dialkylphosphide, $Th[P(CH_2CH_2PMe_2)_2]_4$ **1** reacts with carbon monoxide to give the first reported double insertion product where CO is incorporated into a coordinated secondary alcohol derivative by the coupling of two dialkyl phosphide groups at the same carbon atom.

We have recently described[1] the synthesis and characterisation of the first homoleptic thorium dialkylphosphide Th(**PPP**)$_4$ **1** [**PPP** = $-P(CH_2CH_2PMe_2)_2$]. Here we report on the reaction of **1** with CO. In the presence of CO_2, NO_2, CS_2, H_2, MeCN and alkenes, **1** reacts to give unidentified products. However, interaction of red **1** with CO in hydrocarbons generates burgundy coloured solutions from which a new orange crystalline product **2**, of stoichiometry [Th{(**PPP**)$_2$CO}]$_2$, is readily isolated from petroleum solutions in high yield (73%).

NMR spectroscopy highlights substantial differences between the tetraphosphide **1** and the product **2**. The $^{31}P-\{^1H\}$ NMR spectrum† shows resonances in regions commonly attributed to coordinated and uncoordinated tertiary phosphines (resonances attributable to phosphido phosphorus are absent) which numerically account for all the phosphorus centres that were originally present in **1**. Two are readily assigned to uncoordinated pendant tertiary phosphine. The lowest field signal (δ +2.9) is displaced *ca.* 80 ppm upfield from the phosphido signals in **1** implying that CO insertion has occurred into the thorium–phosphide bonds in **1**. Assignments are aided by comparison with the ^{13}C enriched analogue (readily prepared by reaction of **1** with ^{13}CO); two resonances show coupling to ^{13}C, the low-field resonance at δ +2.9 becomes a complex symmetrical multiplet of at least 14 lines and the doublet at δ +22.6 becomes a doublet of doublets (J_{PC} = 68 Hz). Thus the spectrum indicates that **2** contains two pairwise related ligands with two sets of ^{31}P nuclei bonded to CO, two sets of tertiary ^{31}P nuclei coordinated to Th and two sets of uncoordinated ^{31}P nuclei. The $^{13}C-\{^1H\}$ NMR is complex in the aliphatic region, more so than that observed for **1**, resonances attributable to tertiary phosphine methyl carbons and to backbone carbons may be identified, however a new resonance appears as a doublet of overlapping doublets at δ +75.0 (separation of outer lines = 110 Hz, J_{CP} 68 and 42 Hz). It is only this resonance that is enhanced in the spectrum of the ^{13}C enriched analogue confirming its origin as the carbon in CO. This signal is in a position more commonly associated with secondary alcohols than carbonyls, *cf* δ +3.3 in the structurally characterised phosphidoacyl, $[(C_5Me_5)Hf-Cl_2(\eta^2-COPBu^t_2)]$.[2]

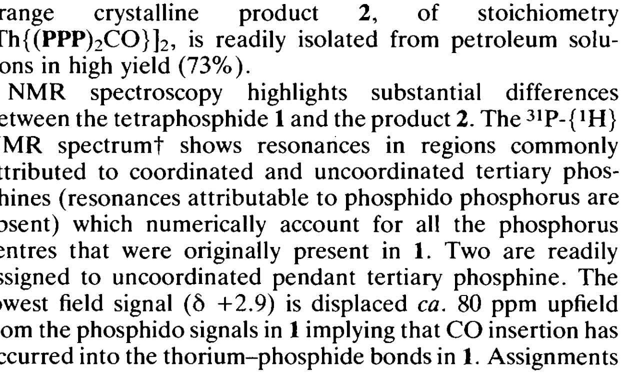

Fig. 1 The molecular structure of $Th\{OC[P(CH_2CH_2PMe_2)_2]_2\}_2$, **2**, showing the atom numbering scheme. The hydrogen atoms and terminal methyl groups of the pendant uncoordinated tertiary phosphines have been omitted for clarity. Selected bond lengths (Å); Th–O(1) 2.210(5), Th–O(2) 2.231(5), Th–C(33) 2.559(8), Th–C(34) 2.607(8), Th–P(6) 3.174(2), Th–P(1) 3.163(2), Th–P(5) 3.071(2), Th–P(7) 3.131(2), Th–P(8) 3.019(2), Th–P(12) 3.067(2), C(33)–O(1) 1.430(8), C(34)–O(2) 1.434(8), P(1)–C(33) 1.796(7), P(1)–C(1) 1.848(8), P(1)–C(3) 1.862(8), P(3)–C(33) 1.798(8), P(3)–C(7) 1.885(9) P(3)–C(11) 1.859(8), P(10)–C(34) 1.788(8), P(10)–C(29) 1.841(9), P(10)–C(25) 1.888(10). Selected bond angles (°): P(1)–C(33)–P(3) 120.1(4), O(1)–C(33)–P(1) 110.0(5), O(1)–C(33)–P(3) 117.3(5), O(2)–C(34)–P(8) 110.3(5), O(2)–C(34)–P(10) 120.4(5), P(10)–C(34)–P(8) 123.1(4).

The ^1H NMR spectrum‡ of **2** is complex and relatively uninformative. In the IR, ν(CO) 1063 cm^{-1} is more consistent with a C–O single bond than a carbonyl. The assignment is confirmed by the expected isotopic shift in the ^{13}C enriched derivative, [$\nu(^{13}co)$ = 1035 cm^{-1}].

The structure of **2** was determined by X-ray crystallography§ (Fig. 1). The molecule contains ten-coordinate thorium bonded to two di-anionic (formally for Th^{IV}) diphospha-secondary alkoxy ligands generated as a result of CO insertion. A number of features of the structure of **2** are noteworthy. Only two CO molecules have inserted, each between two metal–phosphide bonds, thereby coupling two phosphido phosphorus atoms at each CO carbon atom generating two new tertiary phosphines with concomitant formal reduction of the CO bond order from 3 to 1. Each P_2CO unit in the newly generated $[(Me_2PCH_2CH_2)_2P]_2CO^{2-}$ ligands is η^3-bonded to the thorium atom with one of the phosphorus atoms coordinated to thorium; for each phosphorus atom, one pendant dimethylphosphino donor remains coordinated to thorium and one is uncoordinated (Fig. 2). Although the geometry of the ten-coordinate thorium atom cannot be described in terms of any idealised polyhedron, if each η^3-PCO unit is considered to occupy one coordination site then the geometry is distorted *trans*-octahedral. The Th–P distances vary from 3.019(2) to 3.174(2) Å and are comparable to reported values.[3] The Th–C bonds [average: 2.583(8) Å] are longer than the Th–C(amidoacyl) bond (2.418 Å) in $[(C_5Me_5)_2ThCl(\eta^2-CONEt_2)]$.[4] The average C–O bond length [1.432(8) Å] is consistent with a single bond[5] and the Th–O bond [average: 2.220(5) Å] is comparable to other actinide oxygen single bonds.[6] The inserted carbon atoms are pyramidal with similar P–C bond lengths to others in the molecule. The insertion product **2** represents the second structurally characterised example of an insertion reaction into a M–P bond,[7] the first for an *f*-element metal and a new mode of insertion for CO.

Since this observation represents new reactivity for CO, it

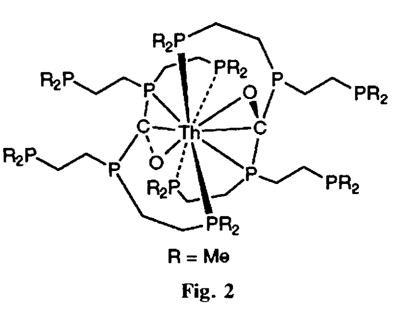

Fig. 2

clearly has important implications for the study of the chemistry of small molecules and of metal phosphides.

Received, 21st February 1994; Com. 4/01036A

Footnotes

† $^{31}P\{^1H\}$ NMR (145 MHz, C_6D_6, relative to H_3PO_4), δ 2.9 (dt, *J* 35 and 14 Hz), −16.4 (virtual q), −22.6 (d, *J* 15 Hz), −23.3 (d, *J* 6 Hz), −23.8 (d, *J*, 6 Nz), −51.0 (d, *J* 15 Hz), −52.1 (d, *J* 15 Hz); relative areas 2:2:2:1:1:2:2.

‡ The P–Me resonances appear as five doublets δ 0.9–1.4 (J_{PH} 2.7–3.6 Hz) with relative areas 1:1:1:1:1 and a multiplet (relative area 3) of coincident Me resonances, δ 0.98; br m, 1.34–1.9, attributed to Me protons.

§ *Crystal data* for $C_{34}H_{80}P_{12}O_2Th$, $M_r = 1124.73$, triclinic, $P\bar{1}$, $a = 10.186(2)$, $b = 13.920(5)$, $c = 20.989(5)$ Å, $\alpha = 107.90(2)$, $\beta = 98.22(2)$, $\gamma = 101.84(2)°$, $U = 2703(1)$ Å^3, $Z = 2$, $D_c = 1.38$ g cm^{-3}, μ(Mo-Kα) = 31.4 cm^{-1}, *F*(000) 1140 e, *T* = 150 K. Intensity data were collected on a FAST area detector diffractometer with Mo-Kα radiation (λ = 0.71069 Å) following previously described procedures.[8] 8623 reflections were measured giving 7356 unique data. The structure was solved by Patterson methods (SHELX-S)[9] and refined by full-matrix least-squares on F_o^2 (SHELXL-93)[10] using all unique data. Final wR_2 (on F_o^2) and *R* (on *F*) were 0.110 and 0.048 for all data [0.100 and 0.040 for 4796 data with $I > 2\sigma(I)$]. One pendant dimethyl phosphino group P(11) and one methyl group on P(9) were disordered. The disorder was satisfactorily modelled assuming two-site occupancies for these atoms indicating rotational disorder in the pendant arms as may be anticipated in compounds of this nature. The P–C bonds for P(11) had to be constrained and P(11) was refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1, 1994.

References

1 P. G. Edwards, M. Harman, M. B. Hursthouse and J. S. Parry, *J. Chem. Soc., Chem. Commun.*, 1992, 1469.
2 D. M. Roddick, B. D. Santarsiero and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 4670.
3 P. G. Edwards, R. A. Andersen and A. Zalkin, *Organometallics*, 1984, **3**, 293.
4 P. J. Fagan, J. M. Manriquez, T. J. Marks, V. W. Day, S. H. Vollmer and C. S. Day, *J. Am. Chem. Soc.*, 1980, **102**, 5369.
5 H. Blau and W. Malisch, *Angew. Chem.*, 1980, **92**, 1065.
6 P. G. Edwards, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1981, **103**, 7792.
7 See reference 2 and W. F. Smith, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1976, 896.
8 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.
9 G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467.
10 G. M. Sheldrick, 1993, SHELXL-93 (beta test version), University of Göttingen, Germany.