Calcium-centred phosphine oxide reactivity: P–C metathesis, reduction and P–P coupling[†]

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Reactions of triphenylphosphine oxide and diphenylphosphine oxide with calcium alkyls and amides in the presence of $PhSiH_3$ occur to give P–C bond cleavage, P(v) to P(m) reduction and P–P coupling.

Despite recent interest in both metal-catalysed homo- and heterodehydrocoupling of, for example,¹ silanes,² phosphines,³ and amine boranes,⁴ catalytic reactivity derived from inorganic substrates (*i.e.* non-carbon-centric reactivity) is very much less developed. Over the last five years, the catalysis of a growing number of organic transformations by M²⁺ complexes of the heavier alkaline earth elements has been demonstrated.⁵ Spielmann and Harder, for example, have reported that the hydrosilylation of ketones may be catalysed by the presumed intermediacy of calcium hydrido species.⁶ In this submission we report our initial observations of reactions which target the calcium-catalysed reduction of organophosphine oxides to organophosphines in the presence of organosilanes (eqn (1)).^{7,8}

$$\mathbf{R}_{3}\mathbf{P} = \mathbf{O} + 2\mathbf{H} - \mathbf{SiR}_{3} \xrightarrow{\operatorname{cat}} \mathbf{R}_{3}\mathbf{P} + (\mathbf{R}_{3}\mathbf{Si})_{2}\mathbf{O} + \mathbf{H}_{2} \quad (1)$$

We have previously reported that addition of two equivalents of Ph₃PO to the homoleptic amide [Ca{N(SiMe₃)₂}₂]₂ results in the formation of a four-coordinate bis(phosphine oxide) adduct, 1.⁹ The ${}^{31}P{}^{1}H$ NMR spectrum of an analogous reaction employing the dialkyl, [Ca{CH(SiMe₃)₂}₂(THF)₂],¹⁰ displayed a broad signal at 34.5 ppm which was similar to that observed for compound 1 (33.8 ppm) and provided a ¹H NMR spectrum consistent with the expected ligand exchange. X-Ray diffraction analysis of a crystal of the product confirmed the identity of 2 as a *pseudo*-tetrahedral bis(phosphine oxide) adduct, [Ca{CH(SiMe₃)₂}₂(OPPh₃)₂] (Fig. 1).[‡] In a similar manner, addition of Ph₃PO to [(BDI)CaN(SiMe₃)₂(THF)], where BDI refers to the bidentate anionic ligand formed by deprotonation of 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]-pent-2-ene, resulted in displacement of THF and formation of the expected phosphine oxide adduct, compound 3 (eqn (2)).

 $\begin{array}{c} & & & & \\ & & & \\ Ar & & & \\ (Me_{3}Si)_{2}N & THF & & \\ & & & \\ Ar & & & \\ & & \\ & & \\ Ar = 2,6-di-iso-propylphenyl \end{array}$

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Fig. 1 ORTEP representation (thermal ellipsoids 50%) of **2**. Hydrogens, with the exception of those attached to C1, and lattice solvent have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): P1–O1 1.5010(15), Ca1–C1 2.540(2), Ca1–O1 2.2618(14), C1–Ca1–C1' 111.73(10), O(1)–Ca(1)–C(1) 112.34(6). Symmetry transformation used to generate equivalent atoms -x, y, $\frac{1}{2} - z$.

Treatment of an NMR scale sample of either 1 or 2 in d₈-toluene with two equivalents of phenylsilane provided immediate and complete consumption of the Ca-bonded silylamido or alkyl ligands (Fig. S1 and S2 of the ESI⁺). In line with the precedent provided by Harder's calcium hydride synthesis and our own studies of related magnesium chemistry,^{11,12} the formation of these products implies that a calcium hydride is also produced and may be envisaged as a key intermediate in subsequent reactivity. Monitoring of both ${}^{31}P{}^{1}H$ NMR spectra revealed the appearance of broad intense signals at 87 ppm, significantly shifted downfield from that of either free (24.4 pm) or calcium-coordinated Ph₃PO (ca. 34 ppm). The chemical shift of these signals also did not correspond to that of the expected P(III) reduction product, Ph_3P (-5.2 ppm). Similar observations, albeit with sharper ${}^{31}P{}^{1}H{}$ NMR signals, also resulted from the addition of PhSiH₃ to compound 3 (Fig. S2, ESI⁺). In all cases a simultaneous observation of benzene formation in the ¹H NMR spectra suggested the occurrence of a chemoselective P-C bond activation within the Ph₃PO and an assignment of the ${}^{31}P{}^{1}H$ NMR resonance observed at 87 ppm as resulting from formation of the [Ph₂PO]⁻ anion. Although, to the best of our knowledge, this reactivity is unprecedented, it is notable that Castillo and Tilley have previously reported P-N bond cleavage and formation of a [(Me₂N)₂PO]⁻ anion in a reaction between HMPA and the samarium silyl [Cp*2SmSiH3]3.¹³ In contrast, reaction of this Sm compound with Ph₃PO yielded a more stable adduct, which, on heating, was prone to ortho-CH activation and cyclometalation by elimination of SiH₄.

Although attempts to confirm the formation of $[Ph_2PO]^-$ through reactions of diphenylphosphine oxide and either

 $[Ca{CH(SiMe_3)_2}_2(THF)_2]$ or $[Ca{N(SiMe_3)_2}_2]_2$ resulted in immediate protonation of the alkyl and amide ligands, analysis was frustrated by precipitation of the proposed homoleptic species, $[Ca{(O)PPh_2}_2]$. In contrast, a reaction of equimolar quantities of the β -diketiminato calcium amide, [(BDI)CaN(SiMe₃)₂(THF)], and Ph₂P(O)H in toluene provided smooth access to the desired heteroleptic [Ph2PO]⁻ derivative, 4 [(BDI)CaN(OPPh₂)]₂, which was crystallised direct from the reaction mixture. The result of a single crystal X-ray analysis is illustrated in Fig. 2.‡ This revealed a dimeric structure in which the calcium centres exhibit a *nseudo*-tetrahedral N_2O_2 coordination geometry augmented by additional long range interactions (2.9772(10) Å) with the phosphorus centres through a canting of each phosphorus-oxygen bond towards calcium. Significantly, analysis by ${}^{31}P{}^{1}H{}$ NMR spectroscopy revealed a single sharp resonance at 89.6 ppm for the [Ph₂PO]⁻ anion, confirming an almost identical phosphorus environment to that produced during the reactions of 1-3 with PhSiH₃.

Although attempts to synthesise homoleptic calcium derivatives were unsuccessful, analogous reactions of two equivalents of Ph₂P(O)H with [Ca{CH(SiMe₃)₂}₂(THF)₂] in the presence of PhSiH₃ were observed to remain homogeneous and to be accompanied by the evolution of a steady stream of bubbles. Monitoring by ³¹P{¹H} NMR spectroscopy over three days at room temperature provided evidence of some complex but notable reactivity, which is summarised in the stack plot illustrated in Fig. 3. A broadened resonance attributable to diphenvlphosphine oxide was observed throughout the course of reaction and the deprotonation of this substrate is evidently perturbed in the presence of PhSiH₃. Broad signals in the region 82-87 ppm, however, indicated that some formation of [Ph₂PO]⁻ had occurred. Continued monitoring revealed complete consumption of this species over the subsequent three days with concomitant formation of diphenylphosphine, evidenced by a sharp singlet at -39 ppm,



Fig. 2 ORTEP representation (thermal ellipsoids 50%) of the Ca(1)-containing molecule of compound **4**. All hydrogens and isopropyl carbons from the supporting ligand have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ca1–O1 2.384(2), Ca1–O1' 2.270(2), Ca1–N1 2.354(2), Ca1–N2 2.383(2), Ca1–P1 2.9772(10), P1–O1 1.5962(2), O1–Ca1–N1 113.14(8), O1–Ca1–N2 147.56(8), O1'–Ca1–N1 122.97(8), O1'–Ca1–N2 116.13(8), N1–Ca1–N2 82.32(8), O1–Ca1–O1' 80.39(7), P1–O1–Ca1 94.76(9), P1–O1–Ca1' 142.53(11). Atoms with primed labels are related to those in the asymmetric unit by the -x + 2, -y + 1, -z symmetry transformation.



Fig. 3 Stack plot displaying selected ${}^{31}P{}^{1}H$ NMR spectra for the reaction between PhSiH₃, Ph₂P(O)H and [Ca{CH(SiMe_3)_2}_2(THF)_2] recorded after (a) 30 minutes; (b) 20 hours; (c) 3 days, at room temperature.

and indicative of reduction of the P(v) centre of $Ph_2P(O)H$ to P(III). An additional AX spin system ($\delta = 36.7, -21.7$ ppm; ${}^{1}J_{\rm PP} = 220$ Hz) was also observed and deduced to be the known P(v)-P(III) mixed valence species Ph₂(O)P-PPh₂ by comparison to literature data.¹⁴ This latter species is especially notable as it may be considered as resulting from the overall dehydrocoupling of Ph₂P(O)H and the diphenylphosphine produced. A longer reaction time also evidenced the formation of the fully reduced P-P coupled product, tetraphenyldiphosphine. Although it is possible that this diphosphine was produced by dehydrocoupling of Ph2PH, we have observed no evidence for this reactivity in our previous studies of calcium diphenylphosphide chemistry.¹⁵ It appears more likely, therefore, that P₂Ph₄ is produced by the reduction of Ph₂(O)P-PPh₂. This contention was supported by subsequent heating of the sample at 60 °C, which, after 24 hours, was shown by ³¹P NMR analysis to contain Ph₂PH and P₂Ph₄ as the only phosphorus-containing products. It is notable that similar heating of the initial reaction between PhSiH₃ and the triphenylphosphine oxide adducts 1-3 also resulted in the production of P₂Ph₄ albeit without the observation of either Ph₂PH or Ph₂(O)P–PPh₂.

These observations, therefore, infer that the synthesis of a tetraaryldiphosphine from a triarylphosphine oxide may be achieved under remarkably mild conditions *via* a sequence of discrete P–C cleavage, reduction and dehydrocoupling steps. Although numerous mechanistic scenarios may be envisaged, it appears likely that these processes are mediated by the intermediacy of a highly reactive calcium hydride species. We are continuing to study this hypothesis and to explore extensions to this unusual reactivity.

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Notes and references

‡ Crystallographic data for **2**: (C₆₂H₈₀CaO₂P₂Si₄, $M_r = 1071.64$) crystal dimensions 0.20 × 0.20 × 0.20 mm: monoclinic, space group C2/c, a = 26.5254(5), b = 11.7454(2), c = 23.6923(5) Å, $\beta = 122.870(1)^\circ$, V = 6199.6(2) Å³, Z = 4, $\rho_{calcd} = 1.148$ g cm⁻³, $\mu = 0.270$ mm⁻¹. Of 31751 reflections measured (3.62 < $\theta < 25.03^\circ$), 5430 were independent

 $\begin{array}{ll} (R_{\rm int}=0.1448), R_1=0.0466, wR_2=0.1092 \ [for 4255 \ reflections with I>2\sigma(I)], R_1=0.0677, wR_2=0.1219 \ (all \ data), \ {\rm GOF}=1.050. \\ {\rm Crystallographic \ data \ for \ 4: (C_{89}H_{110}{\rm Ca_2N_4O_2P_2}, M_{\rm r}=1409.91) \ {\rm crystall \ dimensions}\ 0.30\ \times\ 0.25\ \times\ 0.08 \ {\rm mm: \ triclinic, \ space \ group \ P\overline{1}, \ a=13.4254(2), \ b=15.0443(3), \ c=19.9224(4) \ {\rm \AA}, \ \alpha=86.844(1)^\circ, \\ \beta=82.166(1)^\circ, \ \gamma=85.912(1)^\circ, \ V=3971.96(13) \ {\rm \AA}^3, \ Z=2, \ \rho_{\rm calcd}=1.179 \ {\rm g\, cm^{-3}}, \ \mu=0.233 \ {\rm mm^{-1}}. \ 0.6872 \ {\rm reflections \ measured}\ (4.13< < \theta<26.40^\circ), \ 16.164 \ {\rm were \ independent}\ (R_{\rm int}=0.0898), \ R_1=0.0627, \\ wR_2=0.1555 \ [for \ 10.610 \ {\rm reflections \ with \ I>2\sigma(I)], \ R_1=0.1054, \ wR_2=0.1744 \ (all \ data), \ {\rm GOF}=1.053. \end{array}$

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