Calcium-Catalyzed Intermolecular Hydrophosphination

Mark R. Crimmin,[†] Anthony G. M. Barrett,*[,†] Michael S. Hill,*[,†] Peter B. Hitchcock,[‡] and Panayiotis A. Procopiou[§]

Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, U.K., The Chemistry Laboratory, University of Sussex, Falmer, Brighton, East Sussex BN1 9QJ, U.K., and GlaxoSmithKline Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2NY, U.K.

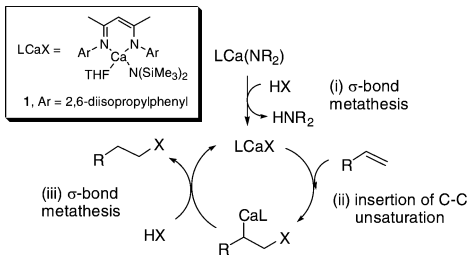
Received March 5, 2007

Summary: The β-diketiminato complex [{HC(C(Me)$_2$N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}Ca{N(SiMe$_3$)$_2$}(THF)] effects intermolecular hydrophosphination of a range of alkenes and alkynes. In behavior reminiscent of lanthanocene(III) catalysis, a more electrophilic alkene is polymerized to phosphine-terminated macromolecules.

Organophosphines, R_3P, are an important class of compound widely employed in transition metal catalysis and organic synthesis. Hydrophosphination, the addition of the P−H bond of a primary or secondary phosphine to an unsaturated C−C bond, is a potentially powerful and, importantly, atom-efficient route to such compounds.[1] The transformation can be achieved under radical conditions or, alternatively, may be promoted by group 1,[2] late transition metal,[3] or lanthanide based catalysts.[4]

On the basis of a proposed analogy between catalytic lanthanide and heavier group 2 metal centers, we have previously reported the β-diketiminato-stabilized calcium amide **1** as an effective catalyst for the intramolecular hydroamination of aminoalkenes and aminoalkynes.[5] The reaction was postulated to occur by the generalized catalytic cycle outlined in Scheme 1, via (i) initiation of the precatalyst by a σ-bond metathesis (or protonolysis) of **1** with a primary amine to form a calcium primary amide, (ii) an intramolecular insertion of the alkene into the Ca−N bond, and (iii) the σ-bond metathesis of the resultant calcium alkyl with a further equivalent of amine to liberate the product and regenerate the active catalyst. On the basis of the numerous applications of lanthanide-based catalysts to the heterofunctionalization of unsaturated carbon−carbon bonds, we speculated that the observed reactivity was not confined to the intramolecular hydroamination of alkenes and alkynes. Indeed, Harder has very recently shown that homoleptic benzyl alkaline earth complexes may act as precatalysts for the hydrosilylation of alkenes.[6]

Scheme 1. Calcium-Mediated Heterofunctionalization of Alkenes



Lanthanocene catalysts of the form Cp*$_2$LnX (X = H, CH(SiMe$_3$)$_2$, Ln = La, Sm, Y, Lu) have been applied to the intramolecular hydrophosphination/cyclization of a variety of phosphinoalkenes.[7] In this case, the reaction mechanism has been studied in depth and occurs via a pathway analogous to that depicted in Scheme 1. Both experimental and theoretical studies suggest that the σ-bond metathesis of the Ln−C bond of the intermediate is the rate-determining step (cf. Scheme 1, step iii). Furthermore, the intermolecular hydrophosphination of alkenes with such catalysts has not been achieved; rather, a lanthanocene phosphide mediated polymerization of ethylene has been reported.[8] Although divalent ytterbium catalysts have been applied to the intermolecular variant of this reaction,[4] the reaction mechanism in these cases is potentially complicated by reductive initiation.

We now present a preliminary account of the application of **1** to the *intermolecular* hydrophosphination of unsaturated C−C bonds. In this regard it is noteworthy that limited evidence exists for both σ-bond metathesis and insertion steps requisite for the proposed catalytic cycle. Thus, the homoleptic calcium phosphide complex [Ca{P(SiMe$_3$)$_2$}$_2$(TMTA)$_2$] (TMTA = 1,3,5-trimethylhexahydro-1,3,5-triazine) has been synthesized by the addition of HP(SiMe$_3$)$_2$ to [Ca{N(SiMe$_3$)$_2$}(THF)$_2$],[9] and Westerhausen has isolated and characterized a novel homoleptic

* To whom correspondence should be addressed. E-mail: mike.hill@imperial.ac.uk (M.S.H.).
† Imperial College London.
‡ University of Sussex.
§ GlaxoSmithKline Medicines Research Centre.

(1) For general reviews on hydrophosphination, see: (a) Togni, G.; Grützmacher, H. *Catalytic Heterofunctionalization*; VCH: Weinheim, Germany, 2001. (b) Delacroix, O.; Gaumout, A. C. *Curr. Org. Chem.* **2005**, *9*, 1851.

(2) (a) Bunlaksananusorn, T.; Knochel, P. *Tetrahedron Lett.* **2002**, *43*, 5817. (b) Bunlaksananusorn, T.; Knochel, P. *J. Org. Chem.* **2004**, *69*, 4595. (c) Bookham, J. L.; Smithies, D. M.; Wright, A.; Thornton-Pett, M.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1998**, 811.

(3) (a) Kazankova, M. A.; Efimova, I. V.; Kochetkov, A. N.; Afanes'ev, V. V.; Beletskaya, I. P.; Dixneuf, P. H. *Synlett* **2001**, 497. (b) Shulyupin, M. O.; Kazankova, M. A.; Beletskaya, I. P. *Org. Lett.* **2002**, *4*, 761.

(4) (a) Takaki, K.; Komeyama, K.; Takehira, K. *Tetrahedron* **2003**, *59*, 10381. (b) Takaki, K.; Takeda, M.; Koshoji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, 6357. (c) Takaki, K.; Koshoji, G.; Komeyama, K.; Takeda, M.; Shishido, T.; Kitani, A.; Takehira, K. *J. Org. Chem.* **2003**, *68*, 6554.

(5) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042.

(6) Buch, F.; Brettar, J.; Harder, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2741.

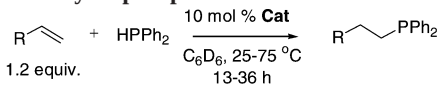
(7) (a) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824. (b) Douglass, M. R.; Stern. C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221. (c) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630. (d) Motta, A.; Fragalà, I. L.; Marks, T. J. *Organometallics* **2005**, *24*, 4995.

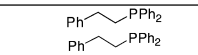
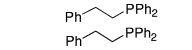
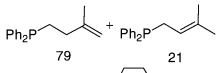
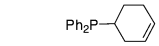
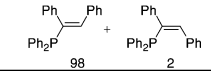
(8) (a) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 12764. (b) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 6311.

(9) Westerhausen, M.; Schwarz, W. *J. Organomet. Chem.* **1993**, *463*, 51.

10.1021/om070200k CCC: $37.00
Publication on Web 05/03/2007

Table 1. Calcium-Mediated Intermolecular Hydrophosphination of Alkenes



Sub.[a]	Product	Cat	T / °C	t / h	Conv. / %[b]
A		**1**	75	20	95
A		**2**	75	36	92
A		**3**	60	24	89
B	 79 21	**1**	25	24	95
C		**1**	75	24	78
D	 98 2	**1**[c]	75	13	94

[a] Legend: **A**, styrene; **B**, isoprene; **C**, 1,3-cyclohexadiene; **D**, diphenylacetylene. [b] Based on the consumption of phosphine from integration of signals in the ^{1}H and ^{31}P NMR. [c] 20 mol % catalyst used.

phosphacyclopentadienide calcium complex derived from the insertion of 1,4-diphenylbutadiyne into a Ca−P bond.[10]

Encouraged by this literature precedent, an initial NMR-scale reaction, in C_6D_6, was conducted between styrene and diphenylphosphine in the presence of 10 mol % of **1**. After 20 h at 75 °C diphenylphosphine, observed at −40.6 ppm in the ^{31}P NMR spectrum, was almost completely consumed with concurrent production of $PhCH_2CH_2PPh_2$ (95% conversion). The identity of the product was confirmed by a characteristic peak at −15.9 ppm in the ^{31}P NMR and by GC-MS analysis following aqueous workup. On the basis of this finding, **1** was applied to the intermolecular hydrophosphination of a series of moderately activated alkenes, dienes, and alkynes with diphenylphosphine. The reactions were conducted first on an NMR scale and subsequently on a preparative scale, using 10 mol % of the catalyst **1**.[11]

The results of this study are presented in Table 1. The hydrophosphination of a series of unhindered activated substrates with diphenylphosphine was achieved. The structures of the isolated products are consistent with an anti-Markovnikov syn addition of the P−H bond across the least hindered, unsaturated C−C bond of the substrate. The reaction proved to be highly dependent upon the steric demands of the alkene, and more hindered substrates such as α-methylstyrene, 1,2-diphenylethene, and *trans*-stilbene did not readily undergo hydrophosphination under these reaction conditions. Similar observations have been made in the hydrosilylation of styrenes with calcium benzyl complexes, with α-methylstyrene being less reactive toward hydrosilylation than styrene itself.[6] Following hydrophosphination, the products were purified by flash column chromatography and isolated as the organophosphine oxides. The isolated yields, 51−93%, reflected those observed on an NMR scale.

Although the reaction times are long (13−24 h) and in many cases elevated temperatures (25−75 °C) are required to effect hydrophosphination, the observed activities compare well with those reported in the literature for the later transition metals.[3] Only recently have $[Ni\{P(OEt)_3\}_4]$ and $[Pd(MeCN)_2Cl_2]$ been applied as catalysts to the intermolecular hydrophosphination of substituted styrenes with diphenylphosphine, with reaction times ranging from 20 to 40 h at temperatures of 90−130 °C.[3b] The observation of regio- and stereoselectivity in the calcium-mediated reaction is consistent with not only the mechanism outlined in Scheme 1 but also precedent set by lanthanide(III) intermolecular hydroamination catalyses. The preferential anti-Markovnikov or 2,1-addition of diphenylphosphine to styrene can be attributed to the organization of the transition state to P−C bond formation. As with the organolanthanides, the bonding in heavier group 2 organometallic compounds is largely ionic and any transition state toward bond formation is also likely to have a large ionic contribution. Factors that stabilize the developing anionic charge upon the atom adjacent to the metal center in the transition state to P−C bond formation will, therefore, be expected to lower the activation energy of the insertion step. In the case of the 2,1-insertion of styrene into the Ca−P bond, the phenyl group may stabilize the adjacent anionic center. In the case of a 1,2-insertion, no such stabilization exists. Furthermore, the almost exclusive syn addition of diphenylphosphine to diphenylacetylene can be attributed to a concerted insertion of the alkyne into the Ca−P bond.

Attempts to catalyze the hydrophosphination of alkenes with $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (**2**) met with limited success. Although the hydrophosphination of styrene with diphenylphosphine could be achieved in the presence of 10 mol % of **2**, the reaction was slow and took 36 h at 75 °C to near completion. The reaction was accompanied by the precipitation of a small amount of a yellow insoluble solid, assumed to be a homoleptic calcium phosphide of the form $[Ca(PPh_2)_2(S)_x]_y$ (S = THF, $HPPh_2$). We have recently isolated and characterized $[Ca(PPh_2)_2(THF)_4]$, from the reaction of $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ with two equivalents of $HPPh_2$ in THF, and this compound demonstrates very limited solubility in benzene.[12] These results suggest that the presence of the β-diketiminate spectator ligand is necessary to increase the solubility of the calcium phosphide intermediate and, hence, maintain a high concentration of the catalyst in solution. We have made similar observations when attempting the intramolecular hydroamination of aminoalkenes with $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$. The homoleptic amide is inactive for this latter reaction, due to the insolubility of the intermediate calcium primary amide in noncoordinating hydrocarbon solvents.[5]

A number of common features were apparent in each of the NMR-scale reactions. After several hours at room temperature the protonolysis of $HN(SiMe_3)_2$ from **1** was observed by production of a singlet at 0.09 ppm in the proton NMR. Over the same time period the NMR solutions gradually became yellow-orange, characteristic of the formation of a group 2 phosphide complex.[10,12] In order to investigate the reaction further, the stoichiometric reaction between **1** and diphenylphosphine was conducted on an NMR scale (Scheme 1, step i). Monitoring of the ^{1}H NMR spectrum revealed the consumption of diphenylphosphine with concurrent production of $HN(SiMe_3)_2$ and a single new product peak at −21.3 ppm, in the ^{31}P NMR. In line with the expectation provided by the precedent in organolanthanide catalysis,[7] the stoichiometric reaction was very slow.

Indeed, plotting the normalized associated $-N(SiMe_3)_2$ as a function of time for the reaction of **1** with 15 equiv of $HPPh_2$ showed that the half-life of this reaction is approximately 200 min at room temperature (Figure 1). Furthermore, the reaction appears to be highly dependent upon the concentration

(10) Westerhausen, M.; Digeser, M. H.; Nöth, H.; Poinkwar, W.; Seifert, T.; Polborn, K. *Inorg. Chem.* **1999**, *38*, 3207.

(11) NMR-scale experiments: in a glovebox, diphenylphosphine (20 μL, 0.115 mmol) was added to a solution of the catalyst (0.01 mmol, 10 mol %) in C_6D_6 and the alkene/alkyne (0.137 mmol) was added as either a solid or a solution in the same solvent. The solution was then loaded into a Youngs tap NMR tube and the reaction monitored by ^{1}H and ^{31}P NMR spectroscopy.

(12) Barrett, A. G. B.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. Manuscript in preparation.

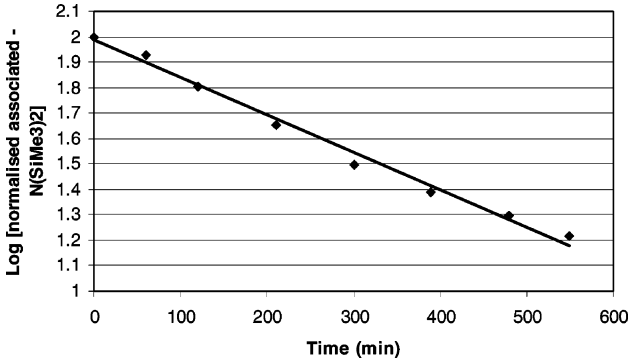


Figure 1. Plot of the log of the normalized associated $-N(SiMe_3)_2$ as a function of time for the reaction of **1** with 15 equiv of $HPPh_2$, on the basis of an initial [**1**] of 0.146 M, measured by ^1H NMR against $(Me_3Si)_4Si$ as an internal standard.

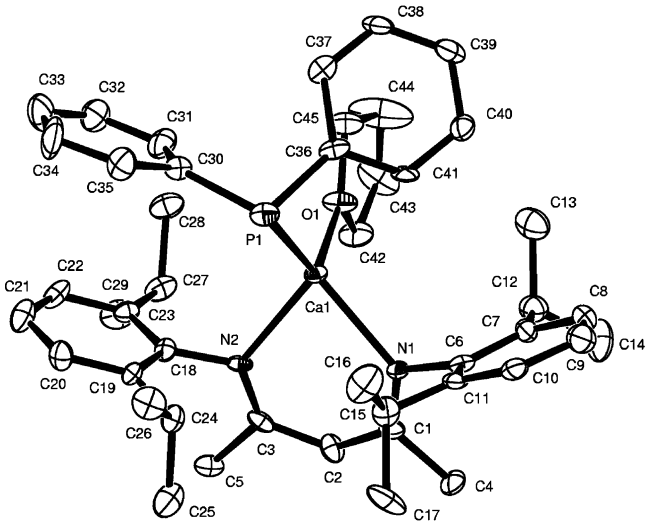
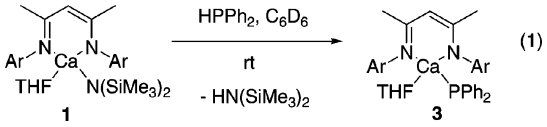


Figure 2. Ortep representation of **3**, with thermal ellipsoids at 20% probability. Selected bond lengths (Å) and bond angles (deg): Ca(1)−O(1) = 2.313(8), Ca(1)−N(1) = 2.319(8), Ca(1)−N(2) = 2.332(8), Ca(1)−P(1) = 2.872(4); N(1)−Ca(1)−N(2) = 81.9(3), O(1)−Ca(1)−N(1) = 104.1(3), O(1)−Ca(1)−N(2) = 103.1(3), O(1)−Ca(1)−P(1) = 123.8(2), N(1)−Ca(1)−P(1) = 122.7(3), N(2)−Ca(1)−P(1) = 112.1(2).

of the phosphine, as the stoichiometric reaction of **1** with $HPPh_2$ is much slower and requires several days to near completion.

To eliminate the possibility that the slow σ-bond metathesis step was due to steric factors, the reaction of **1** with the isosteric diphenylamine was conducted. Monitoring by ^1H NMR spectroscopy revealed the reaction to be quantitative within the first point of analysis (30 min at room temperature). The resulting β-diketiminato-stabilized diphenylamide was isolated and characterized and will be reported in a subsequent publication. The contrasting rates of the reactions of **1** with diphenylphosphine and diphenylamine can be attributed to the fact that a coordination of the substrate to the metal is required for the σ-bond metathesis step to occur and that the soft phosphine is a poorer ligand than the amine for the hard calcium center. Consistent with the hypothesis that the slow rate of this reaction is due to a coordination effect, the reaction of **1** with $HPPh_2$ could be inhibited by the addition of a large excess of $HN(SiMe_3)_2$. Furthermore, a competition experiment between **1** and a 1:1 mixture of $HNPh_2$ and $HPPh_2$ showed, after 30 min at room temperature, exclusive formation of the calcium diphenylamide in preference to **3**, despite the fact that the pK_a of diphenylphosphine is calculated to be several orders of magnitude smaller than that of diphenylamine.[13]

A preparative-scale experiment in hexane allowed the isolation of the THF-solvated, heteroleptic calcium phosphide **3** as an orange crystalline solid (eq 1).[14] Compound **3** has been



characterized in both solution and the solid state. X-ray diffraction analysis of a single crystal of **3** revealed there to be four unique conformers present within the unit cell, the gross features of which were nearly identical. Presented in Figure 2 is a representation of a single conformer; important bond distances and bond lengths are given in the figure caption, while full details are given in the Supporting Information. The compound is monomeric in the solid state. The calcium center is four-coordinate with the coordination sphere being provided by the chelating β-diketiminate ligand, the σ-bonded diphenylphosphine, and a single molecule of THF. Both the Ca−N bond lengths of 2.313(8) and 2.319(8) Å and the N−C−N bite angle of 81.9(3)° are consistent with our previously structurally characterized β-diketiminate stabilized calcium amides, acetylides, and cyclopentadienyls.[15] The Ca−P bond of 2.872(4) Å is considerably shorter than those reported for $[Ca\{P(SiMe_3)_2\}_2(TMTA)_2]$[9] and $[Ca(PPh_2)_2(THF)_4]$,[12] 2.992(2) and 2.9882(4) Å, respectively, a fact that may be attributed to the lower coordination number at calcium in **3**. A number of heteroleptic calcium phosphides have been reported, including mixed phosphide−amides of the form $[Ca(PHSi^tBu_3)\{N(SiMe_3)_2\}]$,- which, in contrast, are dimeric in solution.[16]

The calcium phosphide **3** proved unstable in solution, and heating samples of **3** in benzene or toluene for extended periods at 60 °C resulted in a Schlenk-like redistribution to the previously reported homoleptic compound [{(Ar)NC(Me)CHC(Me)N(Ar)}$_2$Ca], (Ar = 2,6-diisopropylphenyl)[17] and, presumably, $[Ca(PPh_2)_2(THF)_2]$. Likewise, hydrophosphination reactions conducted with **1** at elevated temperatures and our previously reported intramolecular hydroamination of aminoalkenes and aminoalkynes were accompanied by this solution redistribution of the catalyst.[5]

(13) Li, J.-N.; Liu, L.; Fu, F.; Guo, Q.-X. *Tetrahedron* **2006**, *62*, 4453.

(14) Synthesis of [{ArNC(Me)CHC(Me)NAr}Ca(PPh$_2$)(THF)] (**3**): A solution of diphenylphosphine (0.207 g, 1.1 mmol) in hexane (5 mL) was added to a solution of **1** (0.75 g, 1.1 mmol) in the same solvent (30 mL). The reaction mixture was filtered and then stored at 5 °C. The solution gradually changed to a deep orange color and after 4 days yielded bright orange crystals of compound **3**, collected as two crops (0.401 g, 0.56 mmol, 51%). Mp (hexane): 180−184 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 1.05 (m, 4H, β-THF), 1.18 (d, 12H, 6.8 Hz, −CHMe_2), 1.19 (apparent d, 12H, −CHMe_2), 1.62 (s, 6H, HC(C(Me)=NAr)$_2$), 3.15 (hept, 4H, J = 6.8, CHMe$_2$), 3.27 (m, 4H, α-THF), 4.74 (s, 1H, HC(C=NAr)$_2$), 6.68 (apparent dd, 2H, J = 7.2, p-(C$_6H_5$)$_2$P), 6.79 (apparent dd, 4H, J = 7.4, o-(C$_6H_5$)$_2$P), 7.11−7.15 (m, 10H, Ar H). ^{13}C NMR (100.7 MHz, C_6D_6): δ 24.4 (β-THF), 24.5 (−CHMe_2), 25.1 (−CHMe_2), 25.2 (HC(C(Me)=NAr)$_2$), 28.7 (−CHMe$_2$), 69.4 (α-THF), 94.0 (HC(C=NAr)$_2$), 121.9 (−PPh$_2$ C_{para}), 124.4 (C_{meta}), 125.2 (C_{para}), 129.1 (d, $J^{31}P-^{13}C$ = 5.1 Hz, −PPh$_2$ C_{meta}), 129.9 (d, $J^{31}P-^{13}C$ = 17.2 Hz, −PPh$_2$ C_{ortho}), 134.3 (d, $J^{31}P-^{13}C$ = 16.9 Hz, −PPh$_2$ C_{ortho}), 141.9 (C_{ortho}), 145.7 (C_{ipso}), 150.5 (d, $J^{31}P-^{13}C$ = 43.7 Hz, −PPh$_2$ C_{ipso}), 166.3 (HC(C(Me)=NAr)$_2$). ^{31}P NMR (C_6D_6): −21.3. Anal. Calcd for $C_{45}H_{39}CaN_2OP$: C, 75.59; H, 8.32; N, 3.92. Found: C, 75.48; H, 8.26; N, 3.93.

(15) (a) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2005**, 278. (b) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Organometallics* **2005**, *24*, 1184. (c) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *J. Organomet. Chem.* **2006**, *691*, 1242.

(16) Westerhausen, M.; Birg, C.; Krofta, M.; Mayer, P.; Seifert, T.; Nöth, H.; Pfitzner, A.; Nilges, T.; Deiseroth, H.-J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1073.

(17) Harder, S. *Organometallics* **2002**, *21*, 3782.

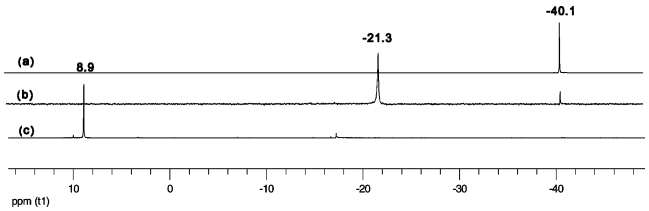


Figure 3. ^{31}P NMR stack plot of (a) diphenylphosphine, (b) the reaction mixture of diphenylphosphine with **1** to give **3**, and (c) the reaction mixture of **3** with an excess of diphenylacetylene and 1 equiv of $HN(SiMe_3)_2$ at 75 °C for 45 min to give (*E*)-PhC(H)═C(PPh_2)Ph.

Support for the mechanism, outlined in Scheme 1, was provided by the reactivity of **3**. The reaction of diphenylphosphine with styrene could be catalyzed by 10 mol % of **3** (Table 1), demonstrating that the latter is kinetically active in the proposed catalytic cycle. More importantly, the reaction of **3** with an excess of diphenylacetylene and 1 equiv of $HN(SiMe_3)_2$ in C_6D_6 at 75 °C for 45 min gave a 1:1 mixture of (*E*)-PhC(H)═C(PPh_2)Ph and **1** in near-quantitative yield. This latter experiment provided unambiguous evidence for the proposed mechanism and can be explained by the concerted insertion of the alkyne into the Ca−P bond of **3** to generate an unstable calcium alkyl intermediate, which then undergoes a subsequent σ-bond metathesis with hexamethyldisilazane to liberate the hydrophosphinated product and regenerate **1** (Figure 3).

The attempted calcium-catalyzed hydrophosphination of a more electrophilic alkene took a different course. The reaction of 2-vinylpyridine with diphenylphosphine in C_6D_6, catalyzed by 10 mol % of **1**, showed complete consumption of the alkene within 1 h at room temperature. Diphenylphosphine, however, was not consumed at the same rate, only depleted. A number of broad peaks were apparent in the proton NMR, characteristic of poly(2-vinylpyridine), along with a number of ^{31}P resonances consistent with an alkyldiphenylphosphine moiety. The calcium phosphide **3** was, therefore, applied to the polymerization of 2-vinylpyridine in benzene on a preparative scale, allowing the isolation of a phosphine-terminated poly(2-vinylpyridine).[18]

Although at this stage an anionic polymerization mechanism cannot be discounted, the stark difference in reactivity with **3** between 2-vinylpyridine and styrene suggests that when more activated alkenes are used as substrates, the rate of insertion of the alkene into the Ca−C bond of the intermediate calcium complex becomes competitive with the rate of σ-bond metathesis of the Ca−C bond with a further equivalent of diphenylphosphine (Scheme 1, step iii). Under these conditions the slow σ-bond metathesis step means that a polymerization of the alkene occurs rather than a hydrophosphination. This reactivity is analogous to that observed for lanthanocene phosphides, which readily polymerize ethylene at room temperature and atmospheric pressure.[8] We are continuing to study the mechanism and scope of these apparently divergent reaction pathways.

Acknowledgment. We thank GlaxoSmithKline for a generous endowment (to A.G.M.B.), the Royal Society for a University Research Fellowship (M.S.H.) and Royal Society Research Merit Award (A.G.M.B.), and the Engineering and Physical Sciences Research Council for generous support of our studies.

Supporting Information Available: Text and a figure giving full experimental details and a CIF file giving crystallographic data for **3**. This material is available free of charge at http://pubs.acs.org.

OM070200K

(18) For an application of alkaline earth organometallics to the polymerization of 2-vinylpyridine, see: Lindsell, W. E.; Robertson, F. C.; Souter, I. *Eur. Polym. J.* **1983**, *19*, 115.