Organolanthanide-Catalyzed Intramolecular Hydrophosphination/Cyclization of Phosphinoalkenes and Phosphinoalkynes

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Although the catalytic addition of P−H bonds to C−C multiple bonds is a highly desirable transformation, it is generally difficult to accomplish with transition metal complexes.[1] In contrast, organolanthanide-mediated intramolecular hydroamination/cyclization of aminoalkenes,[2] aminoalkynes,[3] and aminoallenes[4] has been shown to have significant selectivity and generality, raising the intriguing question of whether the corresponding hydrophosphination processes might also be feasible. Thermodynamic considerations for a prospective organolanthanide-catalyzed hydrophosphination process (Figure 1) predict insertion (step *i*) to be exothermic (∼−33 kcal/mol for alkynes) or approximately thermoneutral (alkenes, ∼+2 kcal/mol) and subsequent Ln-C protonolysis (step *ii*) to be exothermic (∼−7 kcal/mol for alkynes; −17 kcal/mol for alkenes).[5,6] The resulting phosphorus heterocycles belong to a class of interest as alkaloid mimics[7] and as ligand building blocks in asymmetric catalysis.[8] Herein we report the catalytic intramolecular hydrophosphination/cyclization of phosphinoalkenes and phosphinoalkynes using organolanthanide precatalysts of the type $Cp'_2LnCH(TMS)_2$ ($Cp' = \eta^5$-C_5Me_5; Ln = La, Sm, Y; TMS = $SiMe_3$) and $Me_2Si(Me_4C_5)(^tBuN)$-$SmNTMS_2$, and observations on factors affecting the scope, diastereoselectivity, and kinetics of these transformations vis-à-vis the nitrogen analogues.[9,10]

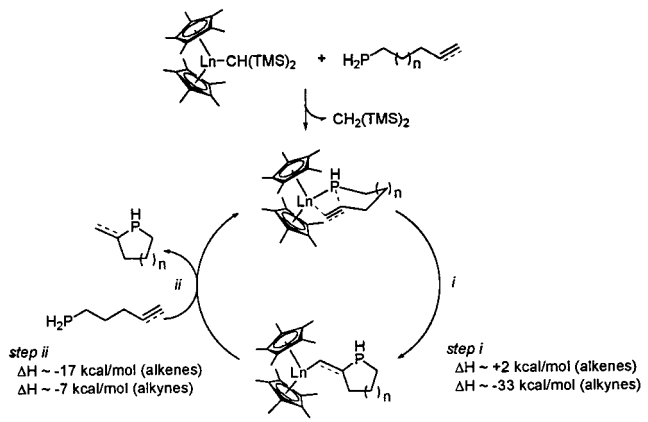
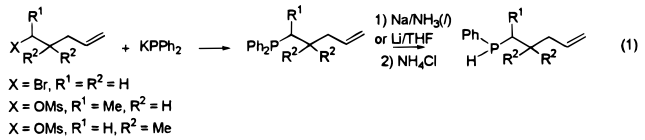
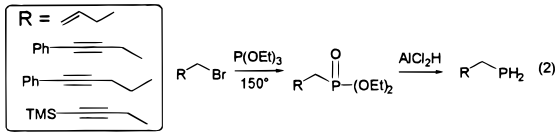


Figure 1. Proposed catalytic cycle for organolanthanide-mediated hydrophosphination/cyclization of phosphinoalkenes and phosphinoalkynes.

Although the synthesis of primary and secondary phosphines has been explored, few general routes are available.[11] The synthesis of secondary phenyl alkenyl phosphines (eq 1) can be



accomplished by reaction of $KPPh_2$ with the desired alkenyl fragment bearing an appropriate leaving group, followed by Na/$NH_3(l)$ or Li/THF[12] cleavage of a single phenyl substituent. Protolytic workup yields the desired secondary phosphine.[13] Primary phosphines were synthesized via dicholoroalane reduction of phosphonate precursors (eq 2),[14] in turn prepared via Arbuzov reaction of $P(OEt)_3$ with the corresponding alkenyl or alkynyl halide.[13,15]



Anaerobic cyclization of primary and secondary alkynyl and alkenyl phosphines mediated by $Cp'_2LnCH(TMS)_2$ precatalysts ($Cp' = \eta^5$-Me_5C_5; Ln = La, Sm, Y; TMS = Me_3Si) is general in scope (Table 1).[13] Secondary phosphinoalkenes undergo cyclization to yield reasonably stable tertiary phospholanes (entries 2−4), albeit somewhat sluggishly, presumably due to the phenyl group bulk. A notable competing side reaction is *noncatalytic* intramo-

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(6) AM-1 level calculations indicate that addition of methyl phosphine to ethylene is exothermic by ∼−15 kcal/mol, while addition to acetylene is exothermic by ∼−38 kcal/mol. We thank Dr. Albert Israel for these calculations.

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(14) Ashby, E. C.; Prather, J. *J. Am. Chem. Soc.* **1966**, *88*, 729−733. (b) Reference 11a.

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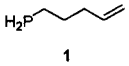
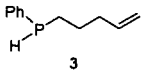
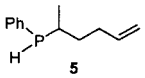
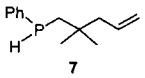
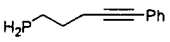
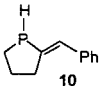
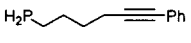
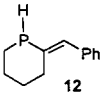
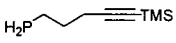
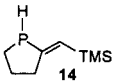
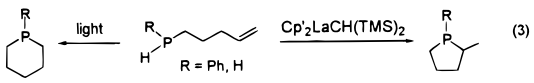
Table 1. Results for the Organolanthanide-Catalyzed Hydrophosphination/Cyclization of Phosphinoalkenes and Phosphinoalkynes[a]

entry	substrate	product	N_t, h^{-1} (°C)
1.	 **1**	 **2**	2.3 (22)[c]
2.	 **3**	 **4**	0.25 (40)[b]
3.	 **5**	 **6**	~ 0.05 (60)[b]
4.	 **7**	 **8**	0.31 (40)[b]
5.	 **9**	 **10**	12.4 (22)[b] 2.0 (40)[c] 0.08 (40)[d] 12.9 (22)[e]
6.	 **11**	 **12**	3.6 (22)[b]
7.	 **13**	 **14**	0.11 (40)[b]

[a] Turnover frequencies measured in C_6D_6 with 2−3 mg, precatalyst. Conversion is >95% by ^{1}H and ^{31}P NMR spectroscopy. [b] $Cp'_2LaCH(TMS)_2$ as precatalyst. [c] $Cp'_2SmCH(TMS)_2$ as precatalyst. [d] $Cp'_2YCH(TMS)_2$ as precatalyst. [e] $Me_2Si(Me_4C_5)(^tBuN)SmNTMS_2$ as precatalyst.

lecular 1,2 P−H addition[16] to afford a six-membered phosphorinane (eq 3). Control experiments reveal that this pathway can



(3)

be significantly suppressed by carrying out cyclizations at relatively low temperatures with exclusion of light. Final product mixtures for entries 1−4 contain exclusively the desired phospholane, contaminated with ~5−20% of the phosphorinane.[17] Primary phosphinoalkenes undergo more rapid cyclization (entry 1), as do phosphinoalkynes (entries 5−7). Although products **2**−**8** are stable and can be isolated, secondary phospholanes resulting from alkynyl phosphine cyclization (products **10**−**14**) are somewhat unstable and could only be characterized in situ by NMR. The ultimate products exhibit molecular weights (GC/MS) corresponding roughly to dimers; however, NMR data indicate several products that could not be completely characterized. Phosphine **14** is inferred but never observed by NMR; products with molecular weights of dimers are observed, and thus presumably the unstable secondary phospholane formed undergoes rapid conversion to a dimer.

In principle, four stereoisomers can result from alkenyl phosphine cyclizations, because inversion at phosphorus is slow.[18] For **1** → **2**, the ^{31}P NMR exhibits two product resonances in a ~2:1 ratio, while for **3** → **4**, the product exhibits two resonances in varying ratios depending on the catalyst. Transformations **5** → **6**[19] and **7** → **8** exhibit two product ^{31}P signals of equal magnitude regardless of the catalyst. Complex ^{1}H spectra for **6** are consistent with mixtures of *cis*-(*R*,*S*) and *trans*-(*R*,*R* or *S*,*S*) methyl dispositions.

Kinetic studies of the hydrophosphination/cyclization by ^{1}H NMR (integration of olefinic or P−H resonances vs that of CH_2TMS_2 formed in catalyst initiation; 30−150:1 substrate:catalyst) reveal linear dependence of [substrate] on reaction time, consistent with zero-order rate dependence on [substrate]. The data thus implicate the same turnover-limiting catalytic step observed for organolanthanide-mediated hydroamination,[2−4] that is, insertion of the carbon−carbon unsaturation into the Ln−heteroatom bond. However, for analogous substrates and catalysts, hydrophosphination is ~5−10 times slower than the corresponding hydroamination process.[2,3] Another deviation from the hydroamination pathway is the protolytic initiating step of the catalytic cycle. As judged by NMR, cleavage of the Ln−$CH(TMS)_2$ bond by phosphine is not immediate upon mixing precatalyst and substrate. The corresponding organolanthanide hydrides,[20] however, effect immediate catalytic initiation (presumably evolving H_2),[5] with appropriate color changes. Transformation **9** → **10** exhibits the highest turnover frequencies, with declining N_t values on proceeding from the largest eight-coordinate lanthanide ionic radius La^{3+} (1.160 Å) to smaller Sm^{3+} (1.079 Å) and Y^{3+} (1.019 Å),[21] analogous to the trend for aminoalkenes,[2] and opposite of that for aminoalkynes.[3] Opening the lanthanide coordination sphere (with constant metal) using the $Me_2Si(Me_4C_5)(^tBuN)$ ancillary ligand[22] leads to enhanced rates, from 2 h^{-1} at 40 °C to 13 h^{-1} at 22 °C (entry 4).

These results demonstrate that lanthanocenes are competent catalysts for the hydrophosphination/cyclization of primary and secondary alkenyl and alkynyl phosphines and that both parallels and distinct differences are observed versus the corresponding hydroamination processes. Further explorations of the scope, selectivity, and mechanism of catalytic hydrophosphination are in progress.

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Supporting Information Available: Detailed synthetic procedures and analytical data for compounds **1**−**14** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Substrates undergo ~10−15% conversion to the corresponding phosphorinanes during drying procedures, i.e., before the catalytic reaction is initiated; the percentage of the final product mixture can be as high as ~10−30% phosphorinane. Phospholanes and phosphorinanes are reported to be separable by fractional distillation.[16a] Although it seems unlikely that endocyclic rings are catalytic products,[2−4] this possibility cannot be rigorously excluded at present.

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