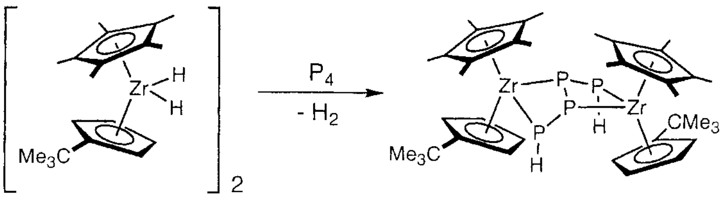
Functionalization of Elemental Phosphorus with $[Zr(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4t\text{Bu})H_2]_2$**

Paul J. Chirik,* Jaime A. Pool, and Emil Lobkovsky

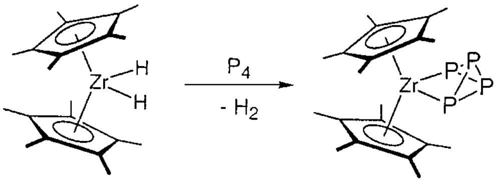
Organophosphorus compounds are indispensable in synthetic chemistry because of their utility as reagents[1] and as ligands for innumerable catalytic processes.[2] Despite these applications, construction of P–H and P–C bonds directly from allotropes of elemental phosphorus remains a significant challenge.[3] Although dinitrogen is converted to ammonia on a several billion ton scale annually by the Haber–Bosch reaction,[4] no comparable process for elemental phosphorus functionalization has been developed.[5] Instead, organophosphorus compounds are prepared by using a multistep procedure involving the chlorination of white phosphorus (P_4) to PCl_3, followed by alkylation with Grignard reagents or reduction with $LiAlH_4$ to assemble the P–C or P–H linkage, respectively.[6]

Insertion of P_4 into a metal–carbon or metal–hydrogen bond offers a direct, efficient, and potentially catalytic methodology for the synthesis of phosphanes. However, reports describing the reaction of P_4 with transition metal hydrides have been limited to only a few cases. Green et al.[7] have described the synthesis of $[Cp_2Mo(\eta^2\text{-}P_2H_2)]$ by reaction of P_4 with $[Cp_2MoH_2]$ at 90 °C, whereas Stephan et al.[8] have used a similar protocol for the preparation of $[Cp_2TaH(\eta^2\text{-}P_2H_2)]$ from $[Cp_2TaH_3]$ and P_4 at 85 °C. More recent reports by Peruzzini and co-workers[9] have described the stoichiometric hydrogenation of P_4 at elevated temperatures with trihydridorhodium and -iridium complexes. Early transition metal hydrides, by virtue of their polarized metal–hydrogen bond, have been shown to be effective in delivering hydride ($H^{\delta-}$) to numerous organic[10] and inorganic[11] substrates and are excellent candidates for functionalizing P_4 under mild conditions. Herein, we report the hydrogenation of P_4 to the unusual $[P_4H_2]^{4-}$ moiety promoted by $[Zr(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4t\text{Bu})H_2]_2$. Preliminary data suggests that the reaction proceeds through a cooperative reductive elimination/insertion sequence involving two zirconium centers.



3 **4** (2)

Attempts to hydrozirconate elemental phosphorus by addition of P_4 to $[Cp^*_2Zr(H)Cl]$[12] ($Cp^* = \eta^5\text{-}C_5Me_5$), produced no reaction over the course of several days at 25 °C. Replacing $[Cp^*_2Zr(H)Cl]$ with the more reactive $[Cp^*_2ZrH_2]$ (**1**),[13] resulted in a facile reaction with P_4 at −35 °C, affording a deep red solid. Analysis of the product by ^1H and ^{31}P NMR spectroscopy revealed that P_4 did not undergo the desired insertion into the Zr–H bond but rather induced reductive elimination of H_2 to afford $[Cp^*_2Zr(\eta^2\text{-}P_4)]$ (**2**), as previously described by Scherer et al. [Eq. (1)].[14] Addition of σ-donating ligands that are also effective in stabilizing low-valent zirconium have been shown to induce reductive elimination of alkane from $[Cp_2Zr(R)H]$ complexes.[15] In the present case, P_4 appears to fall into this ligand class since reductive elimination rather than insertion is observed from the putative $[Cp^*_2ZrH_2(P_4)]$ intermediate.



1 **2** (1)

Based on these results, we postulated that addition of one equivalent of P_4 to two equivalents of **1** may afford one equivalent of a zirconium–phosphorus complex that may be susceptible to hydrogenation by the remaining equivalent of dihydride. Although employing this strategy with **1** led to a mixture of products, including **2**, addition of one equivalent of P_4 (0.5 per Zr center) to a solution of $[\{Cp^*(\eta^5\text{-}C_5H_4t\text{Bu})ZrH_2\}_2]$ (**3**) in toluene at −35 °C resulted in immediate effervescence and formation of a red solution. Removing the toluene in vacuo and recrystallization of the resulting red solid from diethyl ether afforded $[\{Cp^*(\eta^5\text{-}C_5H_4t\text{Bu})\}_2Zr(\mu_2,\eta^2,\eta^2\text{-}P_4H_2)]$ (**4**) in 90 % yield [Eq. (2)]. Interestingly, addition of P_4 to $[Cp^*(\eta^5\text{-}C_5H_4t\text{Bu})Zr(CH_2CHMe_2)(H)]$ produced **4**, along with one equivalent of isobutane, arising from reductive elimination, and one equivalent of isobutene, generated from β-hydrogen elimination.

Brick red **4** is readily soluble in aromatic hydrocarbon and ethereal solvents but insoluble in aliphatic hydrocarbons such as pentane and hexane. Although extremely air- and moisture-sensitive, solutions of **4** in $[D_6]$benzene may be heated to 100 °C for several hours in an inert atmosphere without noticeable decomposition. Compound **4** was characterized through a combination of multinuclear NMR and IR spectroscopies, elemental analysis, and X-ray diffraction. In $[D_6]$benzene, the ^1H NMR spectrum of **4** displays the expected ancillary ligand resonance signals as well as a complex multiplet centered at $\delta = 3.31$ ppm consistent with an AA′BB′XX′ spin system attributable to the P-H resonance signals. Diagnostic symmetric and asymmetric P–H stretches of medium intensity are observed at 2360 and 2342 cm^{-1} in the diethyl ether solution IR spectrum of **4**. The ^{31}P NMR spectrum of **4** in $[D_6]$benzene displays two resonance signals

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centered at $\delta = 11.61$ ppm and -46.25 ppm with an AA′BB′ splitting pattern[16] consistent with observed spectral data for P_4H_6.[17] The resonance signal at $\delta = 11.61$ ppm was assigned to the terminal, hydrogenated phosphorus based on the observation of additional splitting in the proton-coupled ^{31}P NMR spectrum. The peak centered at $\delta = -46.25$ ppm does not change upon proton coupling.

X-ray structural analysis on a single crystal of **4**[18] (Figure 1) reveals a dinuclear zirconium complex with a puckered, bicyclic Zr_2P_4 core. Somewhat surprisingly, the sterically demanding Cp* ligands are arranged in a *cis*-like fashion, although the pyramidalization of the P_4H_2 unit serves to minimize unfavorable steric interactions between the Cp* rings. The X-ray data was of sufficient quality to locate and refine both of the hydrogen atoms attached to phosphorus. No excess electron density around the internal phosphorus atoms was observed in the difference maps, consistent with the spectroscopic data. Each of the P–P distances and angles (Table 1) are in accord with the values typically observed in hydrogenated polyphosphorus chains.[19]

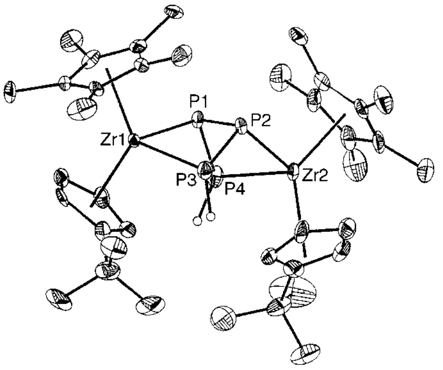

Figure 1. Molecular structure of **4** (thermal ellipsoids at 50% probability level, hydrogen atoms of the cyclopentadienyl ligands omitted for clarity).

In light of the spectroscopic and structural data obtained for **4**, the phosphorus core is best viewed as a $[P_4H_2]^{4-}$ fragment resulting in two formally 16-electron Zr^{IV} centers, and may be considered as a hydrogenated analogue of the P_4^{4-} ligand in $[\{Cp^*Co(CO)\}_2(\mu_2,\eta^2,\eta^2\text{-}P_4)]$ reported by Scherer and coworkers.[20] Isolation of the $[P_4H_2]^{4-}$ moiety is noteworthy since the corresponding neutral tetraphosphorus dihydride P_4H_2 has only been observed by mass spectrometry, and the parent phosphane P_4H_6 exists as a mixture of constitutional isomers.[21] In summary, we have demonstrated the facile reactivity of white phosphorus with zirconium dihydride complexes and used a combination of reductive elimination and insertion processes to prepare the first example of the polyphosphane ion $[P_4H_2]^{4-}$ directly from white phosphorus.

Table 1. Selected bond lengths and angles for **4**.

Bond lengths [Å]	Bond angles [°]
P1-P2 2.2587(18)	Zr1-P1-P4 119.17(7)
P1-P4 2.221(2)	P2-P1-Zr1 73.24(5)
P2-P3 2.2091(19)	P2-P1-P4 113.74(4)
P1-P3 3.7470(19)[a]	P1-P2-P3 114.00(7)
P2-P4 3.751(2)[a]	P1-P2-Zr2 73.69(5)
Zr1-P1 2.6646(14)	Zr2-P2-P3 118.79(7)
Zr1-P3 2.6044(14)	P2-P3-Zr1 75.23(5)
Zr2-P2 2.6602(15)	P2-P3-H(P3) 105(2)
Zr2-P4 2.6146(14)	Zr1-P3-H(P3) 102(2)
P3-H(P3) 1.32(5)	P1-P4-Zr2 75.20(5)
P4-H(P4) 1.32(6)	P1-P4-H(P4) 117(3)
	Zr2-P4-H(P4) 106(2)
	P1-Zr1-P3 90.65(4)
	P4-Zr2-P2 90.04(3)

[a] Non-bonded distances.

Experimental Section

4: A 100-mL flask was charged with **3** (0.400 g, 1.14 mmol) and toluene (ca. 50 mL) and chilled in the dry box freezer to −35 °C. To the clear yellow solution, solid P_4 (73 mg, 0.568 mmol) was added in three portions. Upon addition, a red reaction mixture was immediately formed. The resulting solution was stirred for 5 min and the toluene was removed in vacuo leaving a red solid. Recrystallization from diethyl ether afforded **4** (0.518 g, 0.511 mmol, 90%) as analytically pure red crystals. ^1H NMR (22 °C, 400 MHz, $[D_6]$benzene): $\delta = 1.84$ (s, 30H; C_5Me_5), 1.33 (s, 18H; *t*Bu), 3.31 (m, 2H; P-H), 5.19 (m, 2H; Cp), 5.31 (m, 2H; Cp), 5.39 (m, 2H; Cp), 6.97 ppm (m, 2H; Cp); ^{13}C NMR (22 °C, 100.5 MHz $[D_6]$benzene): $\delta =$ 13.17 ($C_5\mathit{Me}_5$), 33.54 ($C\mathit{Me}_3$), 117.61 (C_5Me_5), 92.68, 94.55, 104.81, 108.03 (Cp) 121.67 ppm ($\mathit{C}Me_3$); ^{31}P NMR ($[D_6]$benzene): $\delta = 11.61$ (PH), −46.35 ppm (P); elemental analysis (%) calcd for $C_{38}H_{58}P_4Zr_2$: C 55.58 H 7.12; found: C 55.21 H 6.89.

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[1] H.-J. Cristau, *Chem. Rev.* **1994**, *94*, 1299.
[2] G. O. Spessard, G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, **1996**, p. 131.
[3] M. Peruzzini, I. de los Rios, A. Romerosa, F. Vizza, *Eur. J. Inorg. Chem.* **2001**, 593.
[4] H. Bielawa, O. Hinrichsen, A. Birkner, M. Muhler, *Angew. Chem.* **2001**, *113*, 1093; *Angew. Chem. Int. Ed.* **2001**, *40*, 1061.
[5] For a discussion on the possibility of hydrogenating elemental phosphorus at high temperature and pressures see: A. Delique, *Bull. Soc. Chim. Fr.* **1933**, *53*, 603.
[6] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth Heineman, Oxford, **1998**, p. 495.
[7] J. C. Green, M. L. H. Green, G. E. Morris, *J. Chem. Soc. Chem. Commun.* **1974**, 212.
[8] N. Etkin, M. T. Benson, S. S. Courtney, M. J. McGlinchey, A. D. Bain, D. W. Stephan, *Organometallics* **1997**, *16*, 3504.
[9] M. Peruzzini, J. A. Ramirez, F. Vizza, *Angew. Chem.* **1998**, *110*, 2376; *Angew. Chem. Int. Ed.* **1998**, *37*, 2255.
[10] a) N. M. Doherty, J. E. Bercaw, *J. Am. Chem. Soc.* **1985**, *107*, 2670; b) P. T. Wolczanski, J. E. Bercaw, *Acc. Chem. Res.* **1980**, *13*, 121.
[11] G. Tainturier, M. Fahim, B. Gautheron, *J. Organomet. Chem.* **1989**, *373*, 193.
[12] H.-G. Woo, W. P. Freeman, T. D. Tilley, *Organometallics* **1992**, *11*, 2198.
[13] J. Manriquez, D. R. McAlister, R. D. Sanner, J. E. Bercaw, *J. Am. Chem Soc.* **1978**, *100*, 2716.
[14] O. J. Scherer, M. Swarowsky, H. Swarowsky, G. Wolmershäuser, *Angew. Chem.* **1988**, *100*, 738; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 694.
[15] K. I. Gell, J. Schwartz, *J. Am. Chem. Soc.* **1981**, *103*, 2687.
[16] Coupling constants: $^1J(P_1,P_4) = {}^1J(P_2,P_3) = 280.95$ Hz, $^1J(P_1,P_2) = 284.04$, $^2J(P_1,P_3) = {}^2J(P_2,P_4) = 74.4$ Hz.
[17] M. Baudler, *Z. Anorg. Allg. Chem.* **1986**, *543*, 45.
[18] Red blocks of $4\cdot Et_2O$ with dimensions of $0.50 \times 0.20 \times 0.15$ mm^3 were obtained from concentrated Et_2O solutions at −35 °C and crystallized in the monoclinic space group *Cc*. Cell, data collection, and refinement parameters: $a = 8.5384(2)$, $b = 25.2891(10)$, $c = 20.7354(8)$ Å, $\beta = 96.915(2)°$, $V = 4444.8(3)$ Å^3, $Z = 8$, with a total of 16106 reflections, and 7212 unique reflections at 173(2) K, ($\lambda = 0.71073$ Å, $1.89° < \theta < 26.37°$), $R = 0.0581$, $R_w = 0.0990$, GOF on $F^2 = 1.096$. Absorption correction with SADABS with min./max. transmission 0.9098 and

0.6305. CCDC-185204 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[19] M. Baudler, *Angew. Chem.* **1987**, *99*, 429; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 419.

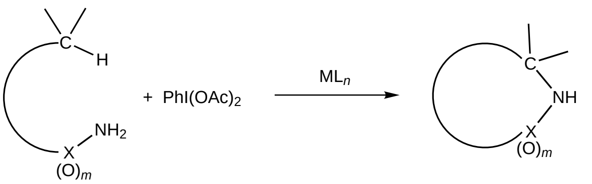
[20] O. J. Scherer, M. Swarowsky, G. Wolmerhäuser *Organometallics* **1989**, *8*, 841.

[21] a) M. Baudler, K. Glinka, *Chem. Rev.* **1994**, *94*, 1277; b) M. Baudler, *Angew. Chem.* **1982**, *94*, 520; *Angew. Chem. Int. Ed. Engl* **1982**, *21*, 492.

Highly Diastereo- and Enantioselective Intramolecular Amidation of Saturated C–H Bonds Catalyzed by Ruthenium Porphyrins**

Jiang-Lin Liang, Shi-Xue Yuan, Jie-Sheng Huang, Wing-Yiu Yu, and Chi-Ming Che*

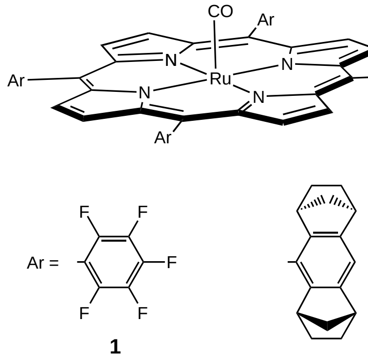
Metal-complex-catalyzed amidation of saturated C–H bonds[1–7] is increasingly attractive as a C–N bond-formation methodology. The nitrogen sources in most of these amidation reactions are iminoiodanes PhI=NR, which are prepared from $PhI(OAc)_2$ and RNH_2 and are currently accessible for rather limited types of R groups (usually $R = ArSO_2$). In very few cases can the PhI=NR amidation procedure be applied to intramolecular amidation.[1b,3c,5] About two years ago,[4d] we found that $PhI(OAc)_2$ and RNH_2 ($R = p\text{-}MeC_6H_4SO_2$, $p\text{-}NO_2C_6H_4SO_2$) could be used directly as the nitrogen source in intermolecular amidation processes. More interestingly, the "$PhI(OAc)_2+RNH_2$" amidation protocol is extendable to "$PhI(OAc)_2+MeSO_2NH_2$"[4d,e,g] and "$PhI(OAc)_2+CF_3CONH_2$[4d] or $PhCONH_2$[4e]", in which cases the respective iminoiodanes are explosive or unknown. We envisioned that such a "$PhI(OAc)_2+RNH_2$" amidation procedure might be applicable to a wide variety of RNH_2 compounds and could be more readily extended to intramolecular amidation, as shown in Equation (1).



(1)

Recent work by Du Bois and co-workers[7] excellently demonstrated that reactions of a series of carbamates ($\text{-}OCONH_2$)[7a] and sulfamate esters ($\text{-}OSO_2NH_2$)[7b] with $PhI(OAc)_2$, catalyzed by dirhodium complexes, afford oxazolidinones and cyclic sulfamidates, respectively, with high regioselectivity and good to excellent diastereoselectivity. These reactions occur by the direct intramolecular amidation of saturated C–H bonds. Du Bois and co-workers found that these intramolecular amidation reactions are stereospecific, allowing synthesis of enantiomerically pure amidation products from enantiomerically pure carbamates or sulfamate esters.[7] However, it remains a challenge to realize asymmetric intramolecular amidation of saturated C–H bonds from prochiral RNH_2 substrates.

Herein, we report the first metalloporphyrin-catalyzed intramolecular amidation reactions of saturated C–H bonds that employ a "$PhI(OAc)_2+RNH_2$" procedure. The catalysts used are mainly the electron-deficient ruthenium porphyrin [Ru(tpfpp)(CO)][8] (**1**, H_2tpfpp = *meso*-tetra(pentafluorophenyl)porphyrin) and the chiral ruthenium porphyrin [Ru(por*)(CO)][9] (**2**, H_2por* = 5,10,15,20-tetrakis{(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl}-porphyrin[10]). In the presence of these catalysts, reactions of sulfamate esters with $PhI(OAc)_2$ afforded cyclic sulfamidates with high regioselectivity and virtually complete diastereoselectivity [Equation (2)]. Remarkably, the intramolecular amidation of prochiral sulfamate esters catalyzed by **2** produced optically active cyclic sulfamidates in up to 87% *ee*.[11] This value contrasts with the highest *ee* value of



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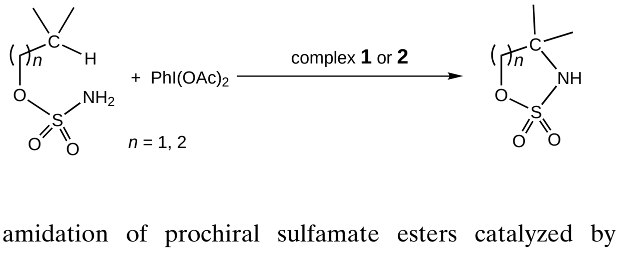

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