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Zirconium-Catalyzed Heterodehydrocoupling of Primary Phosphines with Silanes and Germanes

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Triamidoamine-supported zirconium complexes catalyze the heterodehydrocoupling of primary phosphines with silane and germanes. In this catalysis, P–Si or P–Ge products are observed exclusively with no competitive P–P bond formation. Phosphido complexes $(N_3N)ZrPHR$ ($N_3N = N(CH_2CH_2NSiMe_3)_3{}^{3-}$, R = Ph, **2**; Cy, **3**) were observed to be the catalyst resting state, and complex **2** was structurally characterized.

Catalytic dehydrocoupling is a powerful and atom-economical strategy for the formation of element−element bonds.[1] This kind of catalysis has become a useful surrogate for the Würst-type reductions of halogen-substituted group 14 and 15 elements, including phosphorus, and several families of catalysts that effect dehydrocoupling of phosphines have been developed.[2] However, catalysts that engage in heterodehydrocoupling reactions involving phosphines are far less common, though an increased demand for catalytic reactions that produce phosphorus−element bonds is emerging.[3,4] We wish to report that complexes of the type $(N_3N)ZrR$ ($N_3N = N(CH_2CH_2NSiMe_3)_3{}^{3-}$, R = Me, **1**; PHPh, **2**; PHCy, **3**) are catalysts for the dehydrocoupling of primary phosphines with silanes and germanes to form P−Si and P−Ge bonds. This catalysis is, to the best of our knowledge, the first instance of high-yielding heterodehydrocoupling involving primary phosphines, though dimethyltitanocene has been shown to heterodehydrocouple secondary phosphines with primary or secondary silanes.[5] The use of primary phosphines herein is advantageous, avoiding transmetalation or additional reduction steps to form P−H and Si−H/Ge−H bonds in conventional stoichiometric syntheses of silyl- or germylphosphines.[6]

Two other instances of phosphine heterodehydrocoupling are known. A variety of simple metal derivatives, including Rh(I), form P−B bonds via dehydrocoupling of phosphine-boranes.[7] Catalytic P−S bond formation has been observed with a rhodium bisphosphine catalyst.[4]

Recently, triamidoamine-supported zirconium complexes have been shown to catalytically dehydrocouple primary and secondary phosphines.[8] It was observed that in the reaction of **1** with an equimolar mixture of excess $CyPH_2$ (Cy = cyclohexyl) and $PhPH_2$, the phenylphosphido derivative, **2**, was formed exclusively. Interestingly, a modest selectivity for the heterodehydrocoupling product, CyHP−PHPh, was observed over $(RPH)_2$ (R = Ph, Cy) under catalytic conditions.[8] Seeking to exploit this selectivity, heterodehydrocoupling reactions of primary phosphines with silanes and germanes have been explored.

Reaction of $PhPH_2$ with $PhSiH_3$, $TolSiH_3$ (Tol = *p*-tolyl), and $PhMeSiH_2$ proceeded smoothly in the presence of 5 mol % of complex **1** or **2** at 90 °C to give the secondary silylphosphine product with liberation of hydrogen (Table 1). Only minor byproducts were observed ($<5\%$), and the

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Table 1. Results of Dehydrocoupling Reactions with Catalytic $(N_3N)ZrMe$ (**1**)[a]

phosphine	substrate	product(s)[b]	time[c]	yield[d]
$PhPH_2$	$PhSiH_3$	$PhH_2Si{-}PHPh$	3	94(72)
$PhPH_2$	$TolSiH_3$	$TolH_2Si{-}PHPh$	3	92(62)
$PhPH_2$	$PhMeSiH_2$	$PhMeHSi{-}PHPh$	6	96(67)
$CyPH_2$	$TolSiH_3$	$TolH_2Si{-}PHCy$	2	58
		$TolHSi(PHCy)_2$		37
$CyPH_2$	$PhMeSiH_2$	$PhMeHSi{-}PHCy$	5	93(58)
$PhPH_2$	$^{t}BuGeH_3$	$^{t}BuH_2Ge{-}PHPh$	4	92(86)
$PhPH_2$	Ph_2GeH_2	$Ph_2HGe{-}PHPh$	10	94(77)
$CyPH_2$	$^{t}BuGeH_3$	complex mixture	5	61
		with $^{t}BuH_2Ge{-}PHCy$		33
$CyPH_2$	Ph_2GeH_2	$Ph_2HGe{-}PHCy$	1.5	50
		$Ph_2Ge(PHCy)_2$		44

[a] Catalysis was performed in a sealed vessel in degassed benzene or benzene-d_6 solution at 90 °C with 5 mol % **1**. [b] Characterization data for new compounds can be found in the Supporting Information. [c] Reaction time (days) is the length of time required to consume >95% of the phosphine as monitored by ^{31}P NMR spectroscopy. [d] Estimated yield of product(s) measured by integration against an internal standard by ^{31}P NMR spectroscopy (isolated yield).

product silylphosphine was isolated by short-path distillation. Likewise, $CyPH_2$ readily underwent heterodehydrocoupling with the $TolSiH_3$ and $PhMeSiH_2$ using complex **1** or **3** as a catalyst.

Reaction of $PhPH_2$ with $^{t}BuGeH_3$ or Ph_2GeH_2 using 5 mol % of complex **1** or **2** as a catalyst provided the secondary germylphosphine with liberation of hydrogen (Table 1). Reaction of $CyPH_2$ with $^{t}BuGeH_3$ or Ph_2GeH_2 under analogous conditions also resulted in catalytic heterodehydrocoupling. The formation of the germylphosphines is very clean with respect to any byproducts and appears to be more facile than the heterodehydrocoupling reactions with silanes. In a direct comparison between Si and Ge, the catalytic heterodehydrocoupling of $PhPH_2$ and Ph_2SiH_2 proceeds but was too sluggish to elaborate on here. In contrast, Ph_2GeH_2 reacted with $PhPH_2$ under catalytic conditions, and while this reaction was slow, $Ph_2HGe{-}PHPh$ was formed cleanly. This difference in reactivity is significant. It may reflect both the ca. 10% difference in E−H bond dissociation energies for silicon and germanium, as well as the increased size of germanium,[9] which might allow for kinetic access to the Ge−H bond. Such an analysis is based on the assumption that the turnover-limiting step is P−E bond formation, and studies are underway to test this working hypothesis.

Catalytic P−Ge bond formation via heterodehydrocoupling appears not to have been previously reported. Additionally, this appears to be the first instance of high-yielding, catalytic heterodehydrocoupling involving primary phosphines and silanes.[5] Titanocene catalysts reported by Harrod and coworkers efficiently heterodehydrocouple secondary phosphines and silanes, but at best, limited quantities of heterodehydrocoupling products between $CyPH_2$ and $TolSiH_3$ were observed.[5] It was suggested that primary phosphines coordinate too strongly to the titanium center and thus prohibit heterodehydrocoupling. The sterically demanding trimethylsilyl-substituted triamidoamine ligand employed here may prevent such coordination.

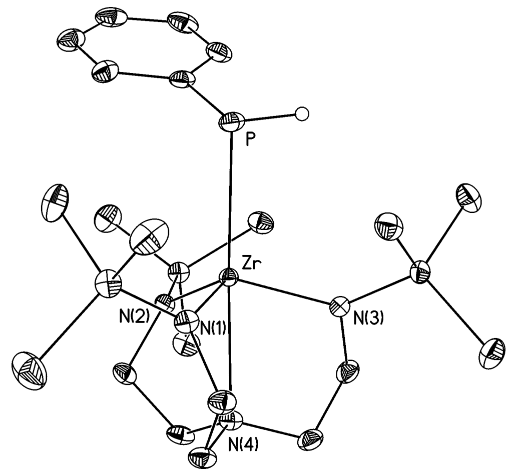
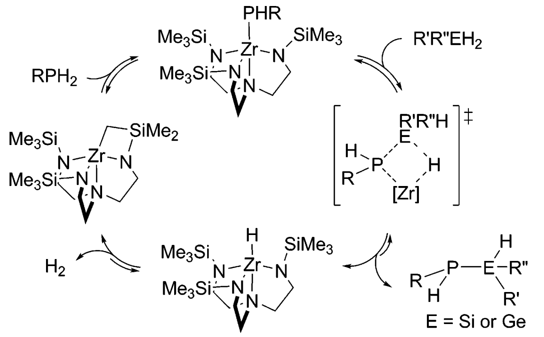


Figure 1. Molecular structure of **2** with thermal ellipsoids drawn at the 35% probability level. Methyl groups and hydrogen atoms, except H(1), omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−P = 2.7254(6), P−C(21) = 1.830(2), P−H(1) = 1.33(2), Zr−N(3) = 2.049(2), Zr−N(1) = 2.057(2), Zr−N(2) = 2.072(2), Zr−N(4) = 2.526(2); C(21)−P−Zr = 111.50(7), C(21)−P−H(1) = 98.1(11), Zr−P−H(1) = 96.1(11).

Scheme 1. Proposed Catalytic Cycle for Heterodehydrocoupling of Primary Phosphines with Silanes or Germanes



A catalytic cycle for this heterodehydrocoupling, based partly on the known chemistry of $(N_3N)ZrPHPh$,[8] can be proposed to explain the observed reactivity (Scheme 1). In these reactions, the respective phosphido complex, **2** or **3**, was the catalyst resting state, as observed by ^{1}H and ^{31}P NMR spectroscopy (benzene-d_6). Selective formation of a phosphido complex over silyl or germyl derivatives is not unexpected given the potential stability of ligand-to-metal π-bonding from a phosphido ligand.[10] In the solid-state structure of **2**, (Figure 1) determined by a single-crystal X-ray diffraction study, the phosphorus center is not planar ($\sum\angle(P) = 305.7(1)°$). Planarity at phosphorus is a feature attributed to π-bonding despite theoretical studies on zirconocene complexes that have shown a pyramidal phosphorus is energetically favored.[11] Though the Zr−P bond length of **2** (2.7254(6) Å) is long compared to the range of zirconocene complexes with terminal phosphido ligands (2.488(1)−2.726(2) Å),[10−12] the degree to which complex **2** engages in ligand-to-metal π-bonding is not clear. However, it is well known that other metals supported by triamidoamine ligands engage

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in multiple bonding.[13] Thus, selective formation of phosphido over silyl or germyl complexes may be due to factors other than π-bonding.

In reactions with $CyPH_2$, the products were susceptible to heterodehydrocoupling with additional $CyPH_2$. For instance, reaction of $TolSiH_3$ with $CyPH_2$ gave predominately $TolH_2Si-PHCy$, but a second product, $TolHSi(PHCy)_2$, was also formed.[5] Similarly, a second dehydrocoupling event to form $Ph_2Ge(PHCy)_2$ was observed, and multiple heterodehydrocoupling reactions of $CyPH_2$ with $^tBuGeH_3$ occurred. Efficient separation of these products has yet to be uncovered, and conditions that select exclusively for a single heterodehydrocoupling $CyPH_2$ remain elusive. Reactions with $CyPH_2$ were qualitatively faster than those with $PhPH_2$, and only in reactions with $CyPH_2$ were multiple heterodehydrocoupling events observed.

Another intriguing feature of the catalysis is the selectivity for the zirconium phosphido complexes **2** or **3** to react exclusively with Si$-$H or Ge$-$H bonds without competitive formation of $(RPH)_2$ (R $=$ Ph, Cy). For instance, the catalytic heterodehydrocoupling of $PhGeH_2$ and $PhPH_2$ by **2** requires 10 days to proceed to completion. However, the catalytic dehydrocoupling of $PhPH_2$ to $(PhPH)_2$ under similar conditions by **2** requires only 7 days.[8] This observation implies that the mechanism may be more complex than this working hypothesis, possibly involving some degree of association between Ph_2GeH_2 and **2** to prohibit competitive formation of $(PhPH)_2$.

In summary, triamidoamine zirconium complexes are effective catalysts for the heterodehydrocoupling of primary phosphines with silanes and germanes. This catalysis provides hydrogen-rich silyl- and germylphosphines otherwise accessible only by multistep stoichiometric syntheses.[6] Efforts to uncover the root of the observed selectivity in this catalysis and establish other novel bond-forming reactions are underway.

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Supporting Information Available: Experimental details, characterization data, and crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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