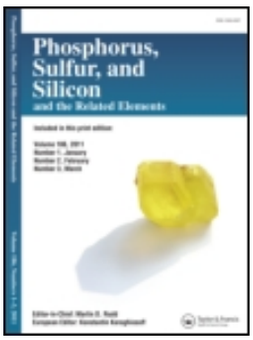

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Selectivity effects in zirconium-catalyzed heterodehydrocoupling reactions of phosphines

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ABSTRACT

Zirconium compounds are known to dehydrocouple phosphines catalytically. An exploration of the factors that may promote selective heterodehydrocoupling was performed, revealing that steric factors are important but do not provide substantial selectivity. It was observed that κ^5-$(Me_3SiNCH_2CH_2)_2N(CH_2CH_2NSiMe_2CH_2)Zr$ (1) may be sufficiently Lewis acidic to perform Lewis acid or frustrated Lewis pair catalysis.

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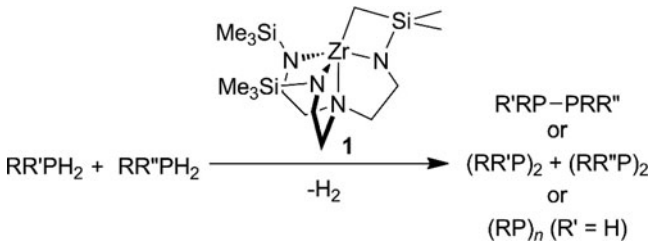
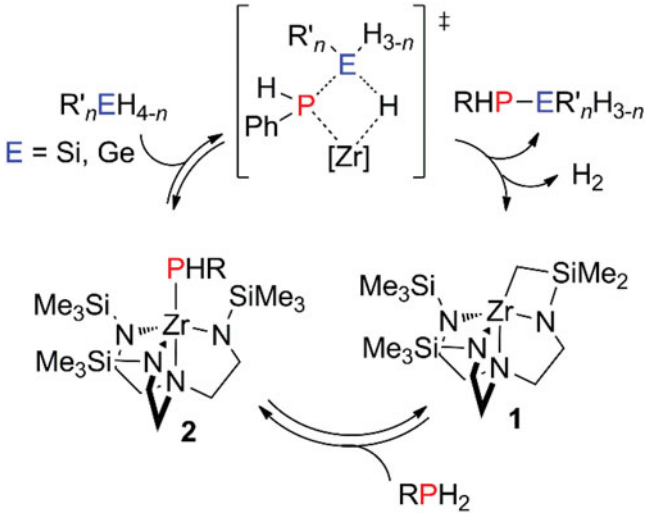
GRAPHICAL ABSTRACT



Introduction

Despite a steady effort in metal-catalyzed dehydrocoupling reactions involving phosphines, a variety of challenges remain.[1,2] In particular, selectivity in dehydrocoupling catalysis is tantalizing. There are examples of selective heterodehydrocoupling reactions between silanes or germanes and phosphines using group 4 metal catalysts.[3,4] In those reactions, where catalysis is likely to involve σ-bond metathesis steps, [5–7] selectivity appears to arise from preferential formation of phosphido compound intermediates and is amplified by the relative stability of a heavier main group element in the β-position of the σ-bond metathesis transition state (Scheme 1).[8]

We have observed unusual selectivity in the heterodehydrocoupling of primary phosphines using zirconium compounds such as κ^5-$(Me_3SiNCH_2CH_2)_2N(CH_2CH_2NSiMe_2CH_2)Zr$ (**1**) or $(N_3N)ZrMe$ $(N_3N) = N(CH_2CH_2NSiMe_2CH_2)_3^{3-}$).[6] In particular, it was found that reaction of $PhPH_2$ and $CyPH_2$ ($Cy = C_6H_{11}$) gave a nonstatistical excess of PhHP–PHCy.[5] What is even more remarkable about this reaction is that the homocoupling of the $CyPH_2$ substrate appears to be completely inhibited by the $PhPH_2$ as supported by the observation of $(CyPH)_2$ formation only after $PhPH_2$ is completely consumed.[5] During the catalysis, only $(N_3N)ZrPHPh$ (**2**) was detected by NMR spectroscopy, leading to the tentative hypothesis that this compound is more stable than $(N_3N)ZrPHCy$ (**3**, Scheme 2). However,



Scheme 1. Heterodehydrocoupling of silanes and germanes with phosphines catalyzed by **1**.

structural and computational data provide no support for that notion and no explanation for the observation, where computational data, for example, predicted virtually identical Zr–P bond dissociation energies for these two compounds.[3,9]

The possibility that selectivity in heterodehydrocoupling reactions may be governed by tunable factors at the phosphine

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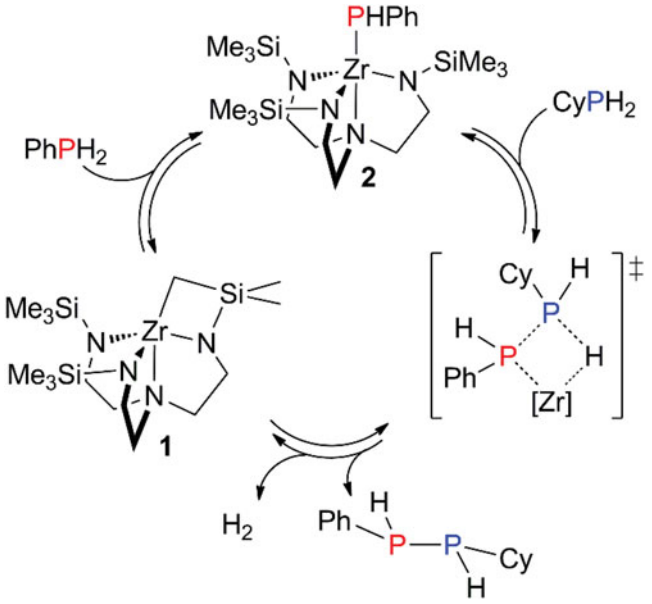


Scheme 2. Heterodehydrocoupling of $PhPH_2$ and $CyPH_2$ catalyzed by **1** that illustrates the proposed origin of selectivity.

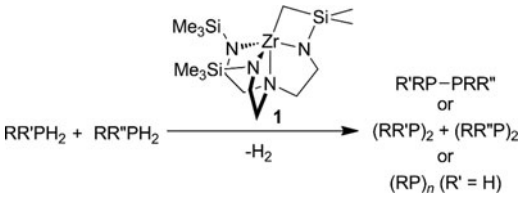
substrates was intriguing, and a rational analysis of the effects were undertaken. If this system is consistent with others that engage in σ-bond metathesis, then electronic effects should not be important.[8] However, an electronic effect may indicate a mechanism other than σ-bond metathesis or afford new insight into that process.

Results and discussion

The observation of exclusively compound **2** in the catalytic heterodehydrocoupling of $PhPH_2$ and $CyPH_2$ was perplexing. Indeed, treatment of one-half equivalent of **1** with a 1:1 mixture of $PhPH_2$ and $CyPH_2$ resulted in the sole formation of **2** in benzene-d_6 solution as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The selectivity is not kinetic. Reaction of isolated samples of compound **3** with $PhPH_2$ in benzene-d_6 solution afford compound **2**. Indeed, compound **3** can be completely converted to **2** by one equivalent of $PhPH_2$. Compound **3** remains, however, kinetically accessible. If isolated samples of **2** are treated with $CyPD_2$, then the deuterium is gradually exchanged from phosphorus. It is known that compound **2** engages in degenerative ligand and H/D exchange rapidly at ambient temperature.[5] However, much of the deuterium is found on the trimethylsilyl substituents of the N_3N ligand. This observation suggests equilibrium formation of **1** followed by reversible formation of **3**-d_2. Equilibrium access to less stable $(N_3N)ZrX$ compounds from more stable derivatives via cyclometalation and formation of **1** has been demonstrated.[10]

Despite the lack of insight these experiments as well as prior structure and computational study seem to provide, the apparent selectivity for the cyclohexyl-substituted substrate in the β-position of the transition state (Scheme 2) provided a good lead for further study. It was hypothesized that secondary phosphines would amplify steric factors and potentially afford greater selectivity. Methyl substitution (e.g., $PhPH_2$ to PhMePH, etc.) is appropriate in this system because β-hydrogen elimination from $(N_3N)ZrX$ compounds is not favorable.[11]

The heterodehydrocoupling of phosphines using **1** as the catalyst was tested with one-to-one mixtures of phosphines (RR'PH) (R = Cy or Ph; R' = H, Me, Cy, Ph), in an attempt to selectively form heterodehydrocoupled products (Equation (1), Table 1). An equimolar mixture of CyMePH and PhMePH was reacted with catalytic **1**, and the homocoupled product $(PhMeP)_2$ was obtained while the heterodehydrocoupling product PhMeP–PMeCy was not observed (entry 1). The attempted heterodehydrocoupling reaction of PhMePH and Ph_2PH resulted first in the formation of $(PhMeP)_2$ followed by dehydrocoupling of Ph_2PH to diphosphine, $(Ph_2P)_2$, only after PhMePH is consumed (entry 2). The anticipated heterodehydrocoupling product was not observed.



(1)

The pattern observed from the attempted heterodehydrocoupling reactions of primary and secondary phosphine mixtures was that reactions of PhMePH with $PhPH_2$ or $CyPH_2$ were more facile than those of CyMePH with $PhPH_2$ or $CyPH_2$ (entries 4–7). In both sets of reactions, it was found that the homocoupling products of the least sterically hindered substrate prevailed. The most facile heterodehydrocoupling reaction, PhMePH and $PhPH_2$–, gave PhMeP–PHPh, based on a distinctive AB splitting pattern in the ^{31}P NMR spectrum at $\delta = -49.8$ (d, $J_{PP} = 215$ Hz),

Table 1. Summary of attempted dehydrocoupling catalysis.[a]

Entry	Substrates		Major product	Minor products	Unobserved[b]
1	PhMePH	CyMePH	$(PhMeP)_2$	PhMeP–PMeCy	$(CyMeP)_2$
2	PhMePH	Ph_2PH	$(PhMeP)_2$	$(Ph_2P)_2$	PhMeP–PPh_2
3	CyMePH		none		$(CyMeP)_2$
4	$CyPH_2$	PhMePH	$(PhMeP)_2$	$(CyP)_4$, CyHP–PMePh	
5	$CyPH_2$	CyMePH	$(CyP)_4$	CyHP–PMeCy	
6	$PhPH_2$	PhMePH	$(PhP)_5$	PhHP–PMeCy	
7	$PhPH_2$	CyMePH	$(PhP)_5$	PhHP–PMePh, $(CyMeP)_2$	
8	$PhPH_2$	$CyPH_2$	PhHP–PHCy[c]		$(CyP)_4$[d]

[a] All reactions were run with equal amounts of phosphine substrates and 5 mol % of **1** in benzene-d_6 solutions. Reactions were monitored by $^{31}P\{^1H\}$NMR spectroscopy, and the relative distributions were unchanged until complete conversion unless noted. Cy = C_6H_{11}.
[b] Compounds identified here are potentially anticipated dehydrocoupling products, but no evidence was detected by ^1H or ^{31}P NMR spectroscopy for their formation.
[c] From Ref. 4.
[d] Observed after complete consumption of $PhPH_2$. See Ref. 4 for details.

and $\delta = -54.0$ (d, $J_{PH} = 215$ Hz) as well as the $(PhMeP)_2$, which is a known dehydrocoupling product with **1** and PhMePh (entry 6).[11] However, the cyclophosphine $(PhP)_5$, associated with dehydrocoupling of $PhPH_2$ by **1**, was the primary product of the reaction (entry 6). The heterodehydrocoupling reaction involving bulkier phosphines, $CyPH_2$ and CyMePH, resulted in predominate formation of $(CyP)_4$ as the major dehydrocoupling product. It is known that some diphosphines $(PHR)_2$ thermally decompose to stable $(RP)_n$ rings.[12,13] Our current evidence suggests that $(CyP)_4$ and $(PPh)_5$ are forming directly because the diphosphines are not observed. Thereafter, the secondary phosphines forms (CyMeP–PHCy) at $\delta = -46.48$ (d, $J_{PP} = 206$ Hz) and $\delta = -53.76$ (d, $J_{PH} = 206$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Interestingly, formation of $(CyP(H)[CyP]_nP(H)Cy)$ in the dehydrocoupling of $CyPH_2$ by Sn(IV) complexes was reported as minor product by Wright and coworkers,[14,15] but that was not observed in this reaction.

Thus, reactions with primary phosphines and sterically encumbered secondary phosphines yield rings. This observation is in contrast to the dehydrocoupling of primary phosphines with **1** under the same conditions, which yield diphosphine products.[5,16] Compound **1** can produce rings, but only under more forcing conditions.[5] These observations are, however, consistent with frustrated Lewis acid catalyzed dehydrcoupling of phosphines. In a recent report by Stephan and coworkers, it was found that $PhPH_2$ was dehydrocoupled by 10 mol% $B(C_6F_4H)_3$ to P_5Ph_5 exclusively.[17] We have accrued evidence to support Lewis acidic reactivity at **1**.[18] The possibility of FLP-like reactivity involving **1** is intriguing, though there is not enough data to fully support such a conclusion at present.

In all reactions, resonances attributed to known $(N_3N)ZrPRR'$ derivatives were identified in NMR spectra.[4,6,8] The selective formation of phosphido complexes suggests that there may be some preferences for steric and electronic properties of the primary and secondary phosphines. However, most selectivity appeared to be steric where, for example, $(N_3N)ZrPPhMe$ was formed over $(N_3N)ZrPCyMe$ (**4**). Attempts to independently prepare and isolate **4** were not successful. Though in the attempted catalytic dehydrocoupling of CyMePH with **1** (entry 2), a new resonance at $\delta = 38.2$ was observed in the ^{31}P NMR spectrum. It is hypothesized that P–H activation of CyMePH by compound **1** is disfavored because this phosphine is too sterically encumbered and that the possible observation of **4** in equilibrium is only a function of high concentrations of CyMePH, a phenomenon that has been seen for reaction of **1** with bulky primary phosphines.[4,6]

Concluding remarks

The steric and electronic factors that may promote more selective phosphine heterodehydrocoupling by $(N_3N)Zr$-catalyst were probed. Substrates that were more significantly sterically encumbered did not promote additional selectivity because they would fail to have sufficient reactivity. Therefore, greater selectivity than the original system was not obtained. However, these observations do imply that compound **1** may be able to act as the Lewis acid partner in FLP chemistry based in the unusual product formation in the dehydrocoupling of $PhPH_2$ in the presence of secondary phosphines.

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