Organometallics **2007,** *26,* 2492−2494

Selective Dehydrocoupling of Phosphines by Triamidoamine Zirconium Catalysts

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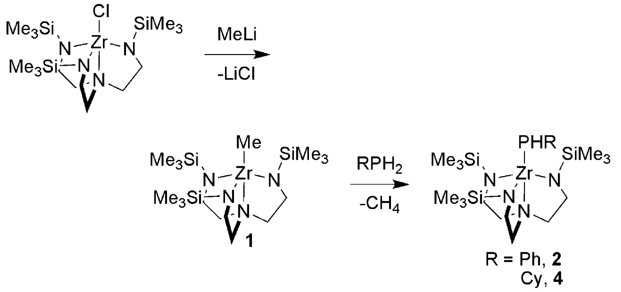
Received February 28, 2007

Summary: New zirconium triamidoamine complexes (N$_3$N)ZrR (N$_3$N = N(CH$_2$CH$_2$NSiMe$_3$)$_3$$^{3-}$; R = Me, ***1****; PHPh,* ***2****; PHCy,* ***4****) are effective catalysts for the dehydrocoupling of primary and secondary phosphines and select for the diphosphine product. Mechanistic analysis revealed that metal-catalyzed P−P bond formation occurs via σ-bond metathesis steps.*

Metal-catalyzed dehydrocoupling is rapidly becoming a mainstay reaction in the formation of element−element bonds.[1] In particular, dehydrocoupling of phosphines has been of heightened interest. Two families of rhodium catalysts have been reported, and in dehydrocoupling reactions of primary phosphines, the diphosphine products are produced.[2,3] Early transition-metal catalysts, particularly those of the group 4 metals, are tremendously promising in phosphine dehydrocoupling due to their high reactivity and low cost.[4−6] However, the observed selectivity has been poor. Reported catalysts form only mixtures of (RPH)$_2$ and (PR)$_n$ (n = 4, 5, or 6) unless the substrate is a bulky 2,4,6-substituted arylphosphine.[4e] To make this catalysis viable for synthetic applications, new metal complexes that improve on the current selectivity are required. Additionally, developing a greater understanding of the P−P bond forming event will aid in improving selectivity.

Triamidoamine complexes of the early transition metals are well known.[7] Limited attention, however, has been seen with triamidoamine-supported zirconium.[8] Such complexes present two orthogonal π-symmetric frontier orbitals,[7] which would allow for some degree of π-donation from a phosphido ligand and also provide a potentially vacant orbital adjacent to the phosphorus center. Given that terminal phosphido ligands display π-bonding with group 4 metallocene complexes,[9] it was anticipated that the electronic structure of triamidoamine-supported zirconium would present unique and favorable properties for phosphine dehydrocoupling catalysis. This communication describes the preparation of new triamidoamine zirconium complexes that exhibit high reactivity in the dehydrocoupling catalysis of primary and secondary phosphines and selectivity to form the diphosphine product in dehydrocoupling reactions of primary phosphines.

Reaction of (N$_3$N)ZrCl (N$_3$N = N(CH$_2$CH$_2$NSiMe$_3$)$_3$$^{3-}$) with MeLi in Et$_2$O afforded analytically pure, colorless crystals of (N$_3$N)ZrMe (**1**) in 82% yield.[10] Complex **1** displayed pseudo-C_3-symmetry with resonances at δ 0.37 and 36.4 for the methyl ligand in the ^{1}H and ^{13}C NMR spectra, respectively. Heating benzene solutions of **1** with excess phenylphosphine results in liberation of methane, as observed by ^{1}H NMR spectroscopy, and formation of the primary phosphido complex (N$_3$N)Zr(PHPh) (**2**) as analytically pure, yellow crystals in 91% yield (eq 1). The phosphido ligand of complex **2** was observed at δ −48.2 in the ^{31}P NMR spectrum with J_{PH} = 203 Hz. The phosphido proton of **2** displayed a resonance at δ 3.97 in the ^{1}H NMR and ν_{PH} = 2273 in the infrared. The spectroscopic data of **2** differ little from the range of values seen for other monomeric zirconium phosphido complexes.[4,11,12]



(1)

Complex **1** is an effective catalyst precursor for the dehydrocoupling of primary and secondary phosphines, and the results of catalytic runs are summarized in Table 1. Primary alkyl (Cy, ^{t}Bu), primary aryl (Ph; p-Tol, Tol = tolyl; 2-EtC$_6$H$_4$), and diphenyl phosphines are tolerated in this catalysis. Mesityl phosphine (MesPH$_2$) was very slow to react with complex **1**, and a limited quantity of (MesPH)$_2$ formed only upon extended heating. The lack of reactivity associated with MesPH$_2$ appears not to be an electronic effect, as p-TolPH$_2$ was readily dehydrocoupled by **1** to give (p-TolPH)$_2$. Reaction of **1** with 2-EtC$_6$H$_4$PH$_2$ is initially rapid, but formation of diphosphine (2-EtC$_6$H$_4$PH)$_2$ requires prolonged heating. This steric effect is pronounced as Ph$_2$PH was efficiently converted to (Ph$_2$P)$_2$ but only after long reaction times.

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10.1021/om070189o CCC: $37.00

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

phosphine	product[b]	time[c]	yield[d]
$PhPH_2$[e]	$(PhPH)_2$, $(PhP)_x$[f]	<1.5	>95
$PhPH_2$	$(PhPH)_2$	7	92
$MesPH_2$[g]	$(MesPH)_2$	>21	<5
p-$TolPH_2$[h]	(*p*-$TolPH)_2$	7	90
2-$EtC_6H_4PH_2$	(2-$EtC_6H_4PH)_2$	10	86
$CyPH_2$[i]	$(CyPH)_2$, $(CyP)_4$[j]	2	>98
$^tBuPH_2$[i]	$(^tBuPH)_2$	3	>98
Ph_2PH	$(Ph_2P)_2$	12	90
$PhPH_2/CyPH_2$	PhHP−PHCy[k]	8	55

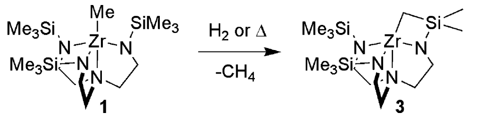
[a] Catalysis was performed in a sealed vessel in degassed benzene or benzene-d_6 solution at 90 °C with 5 mol % catalyst loading. [b] Characterization data for new compounds can be found in the Supporting Information. [c] Reaction time in days. [d] Percent formation of product(s) measured by integration vs internal standard (^{31}P NMR). [e] Run at 120 °C, 1 mol % catalyst. [f] Mixture of $x = 4$, 5, and 6. [g] Mes = mesityl. [h] Tol = tolyl. [i] Run at 70 °C. [j] $(CyPH)_2$ to $(CyP)_4$ ratio was highly variable, ranging from 4:1 to 1:2. [k] 40% of $PhPH_2$ was consumed to competitively form $(PhPH)_2$.

At 1 mol %, complex **1** completely consumed $PhPH_2$ in benzene-d_6 solution in less than 36 h at 120 °C as observed by ^{31}P NMR spectroscopy. This qualitative measure implies that **1** is a faster catalyst than anionic zirconocene catalysts under these conditions.[4a] The products of this dehydrocoupling were identified by ^{31}P NMR spectroscopy as a mixture of $(PHPh)_2$, $(PPh)_4$, $(PPh)_5$, and $(PPh)_6$. It has been suggested that the formation of $(PPh)_5$ results from the high reaction temperature, as titanocene-catalyzed dehydrocoupling of $PhPH_2$ forms a mixture of only $(PHPh)_2$, $(PPh)_4$, and $(PPh)_6$ at ambient temperature.[5]

Repeating the catalysis with **1** at 90 °C affords $(PHPh)_2$ as the exclusive dehydrocoupling product in a nearly 1 to 1 ratio of the *rac* and *meso* isomers. Despite this high selectivity for the diphosphine, the reaction is markedly slower at this temperature, proceeding to completion after 7 days.

Phosphido complex **2** was identified by ^{1}H and ^{31}P NMR spectroscopy as the resting state of the catalyst during dehydrocoupling. Additionally, complex **2** was found to be catalytically competent for dehydrocoupling of $PhPH_2$. Under catalytic conditions, the disappearance of $PhPH_2$ obeyed second-order kinetics in $[PhPH_2]$ over at least 3 half-lives as monitored by ^{1}H and ^{31}P NMR spectroscopy in benezene-d_6. At times greater than 4 half-lives, some decomposition of catalyst is observed. A first-order dependence on zirconium (added as **2**) was established by a plot of [**2**] versus k_{obs}, which was linear for 0.5−8 mol % of complex **2**. An overall rate law of rate = k_{obs}[**2**]$[PhPH_2]^2$ can be proposed where $k_{obs} = 2.46(4) \times 10^{-5}$ M^{-2} s^{-1} at 90 °C. Activation parameters $\Delta H^{\ddagger} = 13.4(2)$ kcal/mol and $\Delta S^{\ddagger} = -35.7(2)$ eu ($T = 67.5-119.8$ °C) were obtained from an Eyring analysis. A kinetic isotope effect (KIE) $k_H/k_D = 3.1(5)$ was obtained by measuring the ratio of PhHP−PDPh to $(PhPH)_2$ for the first equivalent of diphosphine product formed in the reaction of **2** with 30 equiv of PhPHD.[13] These data are consistent with an ordered transition state and support the working hypothesis that the P−P bond forming step proceeds via σ-bond metathesis.[14] It was further observed that performing the catalysis under an atmosphere of hydrogen led to a reduced rate of diphosphine formation.

A σ-bond metathesis reaction between phenylphosphine and **2** to afford $(PhPH)_2$ would presumably generate a zirconium hydride product, $(N_3N)ZrH$. Such a complex was sought synthetically. Exposure of benzene-d_6 solutions of **1** to 1 atm of hydrogen cleanly formed methane and a new zirconium complex where the C_3-symmetry of the triamidoamine ligand had been lifted. Analysis of the ^{1}H and ^{13}C NMR spectra and an HMQC experiment revealed that the product of hydrogenation is the metalated complex $[\eta^5\text{-}(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (**3**, eq 2). It was found that thermolysis of benzene solutions of **1** in the absence of H_2 gave analytically pure, colorless crystals of **3** in 47% yield. The limited isolated yield of **3** is the result of the high solubility of **3** in hydrocarbon solvents. Monitoring the reaction in benzene-d_6 by ^{1}H NMR spectroscopy showed complete conversion of **1** to complex **3** under the thermolysis conditions. Complex **3** is highly related to the dimethyl-*tert*-butylsilyl derivative, $[\eta^5\text{-}(Me_2{}^tBuSiNCH_2CH_2)_2NCH_2CH_2NSi^tBuMeCH_2]Zr$, reported by Scott and coworkers.[8b] The presence of *tert*-butyl substituents in the latter complex gave well-resolved ^{1}H NMR data, whereas significant overlap of chemically inequivalent methylene resonances of the ethyl groups as well as overlap of the metalated methyl group and the trimethylsilyl substituents was observed in the ^{1}H NMR spectrum of complex **3**.



(2)

Complex **3** reacted cleanly with $PhPH_2$ in benzene-d_6 at ambient temperature to quantitatively form phosphido **2**.

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(10) See Supporting Information for complete experimental and characterization details. Selected spectral data for new zirconium compounds: $(N_3N)ZrCl$: ^{1}H (C_6D_6, 500.1 MHz) δ 3.230 (t, CH_2, 2 H), 2.243 (t, CH_2, 2 H), 0.315 (s, CH_3, 27 H). $(N_3N)ZrMe$ (**1**): ^{1}H (C_6D_6, 500.1 MHz) δ 3.228 (t, CH_2, 2 H), 2.171 (t, CH_2, 2 H), 0.370 (s, CH_3, 3 H), 0.264 (s, CH_3, 27 H); $^{13}C\{^1H\}$ (C_6D_6, 125.8 MHz) δ 62.19 (s, CH_2), 47.47 (s, CH_2), 36.41 (s, $ZrCH_3$), 1.23 (s, CH_3). $(N_3N)Zr(PHPh)$ (**2**): ^{1}H (C_6D_6, 500.1 MHz) δ 7.622 (t, C_6H_5, 2 H), 7.110 (m, C_6H_5, 1 H), 6.914 (t, C_6H_5, 2 H), 3.974 (d, P*H*, $J_{PH} = 203$ Hz, 1 H), 3.212 (t, CH_2, 6 H), 2.160 (t, CH_2, 6 H), 0.275 (s, CH_3, 27 H); $^{31}P\{^1H\}$ (C_6D_6, 202.4 MHz) −48.16 (s). $[\eta^5\text{-}(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (**3**): ^{1}H (C_6D_6, 500.1 MHz) δ 3.605 (t, CH_2, 2 H), 3.126^a (m, CH_2, 4 H), 2.400^b (m, CH_2, 6 H), 0.416 (s, CH_3, 6 H), 0.276 (s, CH_3 and $ZrCH_2$, 20 H); $^{13}C\{^1H\}$ (C_6D_6, 125.8 MHz) δ 56.64 (s, CH_2), 56.08 (s, CH_2), 49.96 (s, CH_2), 46.80 (s, CH_2), 32.96 (s, $ZrCH_2$), 2.65 (s, CH_3), 0.48 (s, CH_3). $(N_3N)Zr(PHCy)$ (**4**): ^{1}H (C_6D_6, 500.1 MHz) δ 3.246 (t, CH_2, 6 H), 2.824 (dd, P*H*, $J_{PH} = 212$ Hz, $J_{HH} = 4.3$ Hz, 1 H), 2.626 (m, C_6H_{11}, 1 H), 2.232 (m, C_6H_{11}, 2 H), 2.160 (t, CH_2, 6 H), 1.803 (m, C_6H_{11}, 2 H), 1.612 (m, C_6H_{11}, 3 H), 1.435 (m, C_6H_{11}, 2 H), 1.234 (m, C_6H_{11}, 1 H), 0.355 (s, CH_3, 27 H); $^{31}P\{^1H\}$ (C_6D_6, 202.4 MHz) −26.19 (s).

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(13) Interestingly, a solution of equimolar $PhPH_2$ and $PhPD_2$ underwent conproportionation in the presence of catalytic **2** to give a mixture of $PhPH_2$ (δ −123.0), $PhPD_2$ (δ −125.4), and PhPHD (δ −124.2) in a 1:2:1 ratio. Pure PhPHD was prepared by careful treatment of PhPHLi with 1 equiv of D_2O followed by distillation. A description of this competition experiment can be found in the Supporting Information.

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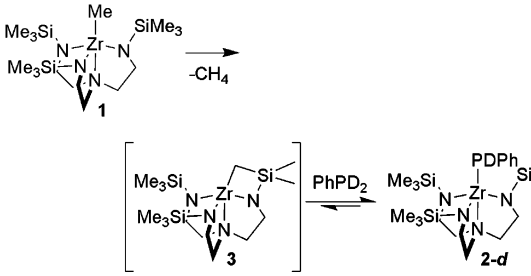
Complex **3** is catalytically competent in the dehydrocoupling of $PhPH_2$, and the rate of dehydrocoupling by **3** was identical to that of **2** within experimental error. Treatment of complex **1** with $PhPD_2$ gave only methane and no methane-d_1 as observed by ^1H and ^2H NMR spectroscopy, suggesting that complex **1** initially decomposes to complex **3** before reaction with phenylphosphine (eq 3). This hypothesis is supported by the observation of deuterium incorporation into the trimethylsilyl substituents in the ^2H NMR spectrum of the product $(N_3N)ZrPDPh$ (**2-*d***).



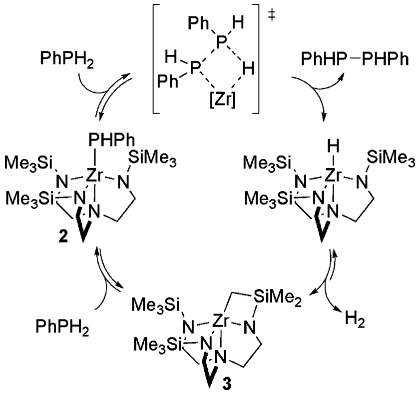
(3)

Current evidence suggests that complex **3** is involved in the dehydrocoupling catalysis. Benzene-d_6 solutions of the deuterated phosphido complex **2-*d*** gradually exchanged the deuterium of phosphido ligand for hydrogen from the trimethylsilyl substituents at ambient temperature, demonstrating that eq 3 is reversible, though it lies heavily to the right. In the catalytic dehydrocoupling of $PhPD_2$ (98% $PhPD_2$, 2% PhPHD) by **3** in benezene-d_6, $(PhPD)_2$, PhDP−PHPh, and $(PhPH)_2$ are formed, and the proteo products are observed in much greater proportions than expected from the $PhPD_2$ starting material. A steady-state concentration of $PhPH_2$ is formed during the course of the catalysis, and the methyl resonances from the trimethylsilyl substituents of **2** decreased in intensity over time, as seen by ^1H NMR spectroscopy. In ^2H NMR spectra of the reaction mixture, a signal corresponding to deuterated trimethylsilyl groups increased in intensity during the course of the catalysis.

A mechanism for the catalysis that incorporates the kinetic data and these observations is shown in Scheme 1. First, this dehydrocoupling requires that 2 equiv of phenylphosphine be consumed per catalytic cycle by mass balance, which is borne out in the kinetic data (vida supra). Additionally, the inhibition by hydrogen suggests a reversible formation of complex **2**. However, the equilibrium between metalated derivative **3** and phosphido **2**, the facile formation of **3** under catalysis conditions, and the inability to observe a hydride complex—even under an atmosphere of hydrogen—suggest that complex **3** is present in the catalytic cycle.

The catalytic dehydrocoupling of $CyPH_2$ by **1** in benzene-d_6 proceeded to $(CyPH)_2$ at 70 °C, but that product began to convert to $(CyP)_4$ upon extended reaction times or at higher temperatures.[15] It is known that many diphosphines $(PHR)_2$ thermally decompose to RPH_2 and $(PR)_n$ ($n = 4, 5$), a facile reaction for $(CyPH)_2$.[15b] The current evidence suggests that $(CyP)_4$ is forming thermally, but a metal-catalyzed process cannot yet be fully discounted. The catalyst resting state was observed to be $(N_3N)Zr(PHCy)$ (**4**) by ^1H and ^{31}P NMR spectroscopy, and the identity of complex **4** was confirmed through an independent synthesis (eq 1). Complex **4** is spectroscopically analogous to phenylphosphido derivative **2** and exhibited resonances at δ 2.82 and −26.2 ($J_{PH} = 212$ Hz) for the phosphido ligand in the ^1H and ^{31}P NMR spectra, respectively.

Scheme 1. Catalytic Cycle for the Dehydrocoupling of Phenylphosphine.



Reaction of **1** with an excess of equimolar quantities of $PhPH_2$ and $CyPH_2$ (20 equiv each) in benzene-d_6 gave exclusively **2** as the sole zirconium-containing product. Upon extended heating at 90 °C, the reaction produced a new diphosphine product, PhHP−PHCy, as identified by ^{31}P and ^1H NMR spectroscopy. Approximately 40% of the phenylphosphine was converted to $(PhPH)_2$ during the course of the reaction. For the first three turnovers of PhHP−PHCy, $(PhPH)_2$ was not observed, and no $(CyPH)_2$ was observed until all phenylphosphine was consumed. If an excess of $PhPH_2$ was present in the reaction, then it was consumed to form $(PhPH)_2$ until the ratio of phosphines was equal, at which time formation of PhHP−PHCy commenced. Efficient separation of these products has not yet been achieved, and efforts to improve this selectivity are underway. To the best of our knowledge, this reaction is unique, as catalytic heterodehydrocoupling of two different phosphines has not been previously reported.

In summary, new triamidoamine zirconium complexes have been prepared that effectively dehydrocouple primary and secondary phosphines. These catalysts select cleanly for the diphosphine product, a feature that may be attributable to the constraints imparted by the triamidoamine ligand, as other early transition-metal catalysts readily form $L_nM(P_xR_x)$ complexes (M = Ti, Zr; $x = 2, 3$) not observed with the triamidoamine ligand used here.[4e,5] Kinetic data and activation parameters indicate a σ-bond metathesis mechanism for P−P bond formation in the dehydrocoupling of phenylphosphine. The metalated complex **3** is important in this catalysis, and it appears to be an appropriate starting point to prepare $(N_3N)Zr-ER_n$ complexes (E = main group element). Further exploration of these reactive zirconium species and related catalytic processes are underway.

Acknowledgment. This work was supported by the University of Vermont. Dr. Bruce Deker is acknowledged for assistance with NMR experiments.

Supporting Information Available: Complete experimental procedures and characterization data, catalysis details, and representative kinetic plots. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070189O

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