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COMMUNICATION

Differences in the stability of zirconium(IV) complexes related to catalytic phosphine dehydrocoupling reactions[†]

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Relating to the catalytic dehydrocoupling of secondary phosphine substrates, zirconium phosphide complexes supported by triamidoamine and pentamethylcyclopentadienyl ligands exhibit different stability that is attributed to β -hydride elimination.

Dehydrogenative bond forming catalysis has become an increasingly general and important synthetic method for maingroup systems (Scheme 1).¹⁻² Recent important advances utilizing dehydrocoupling catalysis include the preparation of materials and chemicals for hydrogen storage.³⁻⁶ Complexes of d⁰ metals have stood at the forefront of this chemistry for some time. One example of this phenomenon is the high reactivity and selectivity of d⁰ metal complex catalysts in the dehydrocoupling of phosphines.⁷ This reactivity follows from well developed catalytic dehydrocoupling chemistry of silanes by group 4 metal complexes.⁸⁻¹¹

2
$$R_n E - H \xrightarrow{L_n M} R_n E - ER_n + H_2$$

Scheme 1 Dehydrocoupling catalysis.

Despite the substantial contributions to phosphine dehydrocoupling catalysis from rhodium and recently tin catalysts,¹²⁻¹⁴ the dominant catalyst type in this transformation has been those of d⁰ group 4 metals, zirconium in particular.⁷ The premier catalyst in the field remains $[Cp*_2Zr(H)_3]^-$ as well as related phosphinimide derivatives discovered by Stephan and coworkers.¹⁵⁻¹⁷ We have reported on the utility of triamidoamine-supported zirconium complexes in this transformation.¹⁸⁻²⁰ Herein, we report initial work in a comparative study of metallocene and triamidoaminesupported zirconium(IV) complexes that reveals the importance of β -hydrogen elimination for phosphine substrates in dehydrocoupling catalysis.

Reaction of (±)-methylphenylphosphine with 5 mol% of $[\kappa^5-N,N,N,N,C-(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (1) in benzene- d_6 solution resulted in evolution of hydrogen gas and consumption of phosphine as observed by NMR spectroscopy (Scheme 2). Persistent heating at 90 °C with venting of hydrogen



Scheme 2 Dehydrocoupling of (\pm) -methylphenylphosphine by zirconium pre-catalysts supported by triamidoamine and pentamethylcyclopentadienyl ligands.

gas afforded (PPhMe)₂²¹ in conversions exceeding 95% as a mixture of diastereomers as observed by ³¹P NMR spectroscopy. The final diphosphine product can be isolated from the reaction in 42% yield as a 55:45 ratio of diastereomers. Han and Tilley reported a slight but consistent diastereoselectivity in the formation of *meso*-diphosphines with (dippe)Rh(η^3 -CH₂Ph) (dippe = 1,2-bis(diisopropylphosphino)ethane) as a dehydrocoupling catalyst.¹³ Interestingly, the reductive coupling of MePhPfragments gives a similar ratio of diastereomers.²²

During the catalysis, a complex tentatively assigned to the zirconium phosphido derivative was observed with a ³¹P NMR resonance at δ 35.3. The identity of this complex was confirmed in an independent synthesis of (N₃N)ZrPMePh (**2**, N₃N = N(CH₂CH₂NSiMe₃)₃⁻³)[‡] by reaction of complex **1** with one equiv. of MePhPH in benzene solution (eqn (1)). Analytical and spectroscopic data for **2** are consistent with the formulation given as well as the family of terminal phosphido complexes of the (N₃N)Zr fragment that are known.^{18,20,23} Complex **2** is also competent for the dehydrocoupling of (±)-methylphenylphosphine in both benzene and THF solvent and appears to be the resting state of the catalyst during the catalytic reaction.



Reaction of (±)-cyclohexylmethylphosphine with 5 mol% of complex 1 in benzene- d_6 did not give (PCyMe)₂ (Cy = cyclohexyl) upon extended heating. A new resonance was observed at δ –38.2 in the ³¹P NMR spectra of the reaction mixture. However, attempts to prepare (N₃N)ZrPCyMe (**3**), the putative phosphido complex

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that the resonance is tentatively assigned to, were not successful. It is hypothesized that P–H activation at complex **1** is disfavored because this phosphine is too sterically encumbered and that the observation of **3** is only a function of high concentrations of CyMePH, a phenomenon that has been seen for reaction of **1** with bulky primary phosphines.^{20,23} Moreover, the importance of the equilibrium between the metallacyclic complex **1** and E–H (E = C, P) bonds has been described in the context of hydrophosphination catalysis.²⁴ Therefore, alternative catalysts with broader substrate scope that might also give diastereoselectivity were sought, and metallocene derivatives were approached as potential candidates.

Reaction of MePhPH with 5 mol% of $[Li][Cp*_2Zr(H)_3]$ (4) in THF solution gave (PPhMe)₂ in conversions greater than 80% with a ratio of diastereomers of approximately 55:45 as observed by ³¹P NMR spectroscopy (Scheme 2). Immediately upon addition of the reagents, formation of LiPMePh was observed. In contrast, complex 4 was found *not* to catalyze the dehydrocoupling of CyMePH to any detectable extent under similar conditions. Steric factors seem less likely in thwarting this reactivity given that Cp*_2ZrH(PCy_2)_2⁻ is known.¹⁶ Anionic zirconocene hydride complexes were found by Stephan and coworkers to effectively dehydrocouple Ph₂PH in high yield. However, the dehydrocoupling of Et₂PH with the same family of catalysts gave a poor yield (10%).¹⁷

Treatment of Cp*₂ZrCl₂ with LiPMePh resulted in a green solution. Attempts to isolate a crystalline product from the reaction routinely failed due to decomposition (eqn (2)). Crude reaction mixtures contained a predominate product with a new ³¹P NMR resonance at δ 95.6 that is potentially the bis(phosphide) Cp*₂Zr(PMePh)₂. Decomposition products included small quantities of MePhPH and (PPhMe)₂. Similar reactivity was observed with LiPCyMe, but these reactions were not explored in detail.



Reductive elimination of a diphosphine from a bis(phosphido) metallocene complex has been reported.25 The limited quantity of (PMePh)₂ that was produced in the decomposition of the putative $Cp*_{2}Zr(PMePh)_{2}$ suggested that decomposition occurs here by an alternative mechanism. Our working hypothesis is that unstable phosphorus-containing compounds are generated *via* β-hydride elimination. This hypothesis is supported by the observation of trace quantities of Cp*₂Zr(H)₂²⁶ in attempted preparation of $Cp*_2Zr(PPhMe)_2$ by salt metathesis and by the observation of a broad resonance at δ 167.6 by ³¹P NMR spectroscopy, which is the majority of the phosphorus-containing product and consistent with the decomposition of PhP=CH₂ reported by other groups.²⁷⁻²⁸ Attempted preparation of Cp*₂Zr(PPhMe)₂ by reaction of Cp*2Zr(H)2 with MePhPH behaved similarly. However, addition of one equiv of LiPMePh to solutions that contain $Cp*_2Zr(PPhMe)_2$ provide an active catalyst for the dehydrocoupling of MePhPH. The relative stability of the zirconium complex in the catalytic reaction suggests that coordination of a third ligand to zirconium may thwart β -hydride elimination (or other processes), allowing dehydrocoupling to occur.

In contrast, it has been observed that $(N_3N)Zr$ complexes are stable with respect to β -hydride elimination. For example, $(N_3N)ZrPH(CH_2)_2PH_2$ is isolable, and heating this complex prompts loss of phosphine and formation of complex 1 followed by dehydrocoupling rather than decomposition.¹⁸

Based on prior study, there are significant mechanistic differences between these two catalysts. Reported data support a σ-bond metathesis mechanism for P-P bond formation by triamidoamine-zirconium complexes regardless of primary or secondary phosphine substrate.20 From work by Stephan, the dehydrocoupling of primary phosphines by group 4 metallocene complexes proceeds with two key features: (1) formation of diand tri-phosphinato intermediates and (2) formation of terminal phosphinidene ligands.¹⁶⁻¹⁷ The dehydrocoupling of secondary phosphines by 4 has been described, but it is less well understood. The nature of the substrate can substantially affect the mechanism. For example, a difference in dehydrocoupling mechanism between primary and secondary arsines has been reported for the triamidoamine-zirconium complex 1.29 Therefore, it is possible that both catalysts may be operating with a σ bond metathesis mechanism for the dehydrocoupling of secondary phosphine substrates, but the differences in stability of the phosphido complexes may be the result of β -hydrogen elimination at the zirconocene catalyst. These observations suggest that such reactivity considerations are important in catalyst selection for dehydrocoupling applications, and further investigation of these two different catalysts is underway.

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Notes and references

 (N_3N) ZrPMePh (2) 60% isolated yield. Anal. Calcd for C₂₂H₄₇N₄PSi₃Zr: C, 46.03; H, 8.25; N, 9.76. Found: C, 46.16; H, 8.25; N, 9.76. ¹H NMR (500.1 MHz): δ 7.56 (t, C₆H₅, 2 H), 7.22 (t, C₆H₅, 2 H), 6.95 (vt, C₆H₅, 1 H), 3.26 (t, CH₂, 6 H), 2.22 (t, CH₂, 6 H), 2.11 (d, J_{PH} = 25 Hz, CH₃, 3 H), 0.26 (s, CH₃, 27 H). ³¹P{¹H} NMR (202.5 MHz): δ 35.3 (s, PCH₃). For complete experimental and spectroscopic details, see ESI.[†]

- 1 T. J. Clark, K. Lee and I. Manners, Chem.-Eur. J., 2006, 12, 8634-8648.
- 2 J. F. Harrod, Y. Mu and E. Samuel, Polyhedron, 1991, 10, 1239-1245.
- 3 A. Staubitz, A. P. M. Robertson, M. E. Sloan and I. Manners, *Chem. Rev.*, 2010, **110**, 4023–4078.
- 4 F. H. Stephens, V. Pons and R. T. Baker, *Dalton Trans.*, 2007, 2613–2626.
- 5 N. Matsumi and H. Ohno, Main Group Chem., 2006, 5, 297-307.
- 6 G. R. Whittell and I. Manners, Prepr. Symp. Am. Chem. Soc., Div. Fuel Chem., 2009, 54, 1037–1038.
- 7 R. Waterman, Curr. Org. Chem., 2008, 12, 1322-1339.
- 8 T. D. Tilley, Acc. Chem. Res., 1993, 26, 22-29.
- 9 J. Y. Corey, Adv. Organomet. Chem., 2004, 51, 1-52.
- 10 F. Gauvin, J. F. Harrod and H. G. Woo, Adv. Organomet. Chem., 1998, 42, 363–405.
- 11 T. D. Tilley, Comments Inorg. Chem., 1990, 10, 37-51.
- 12 V. P. W. Böhm and M. Brookhart, Angew. Chem., Int. Ed., 2001, 40, 4694–4696.
- 13 L.-B. Han and T. D. Tilley, J. Am. Chem. Soc., 2006, 128, 13698-13699.
- 14 V. Naseri, R. J. Less, R. E. Mulvey, M. McPartlin and D. S. Wright, *Chem. Commun.*, 2010, 46, 5000–5002.
- 15 N. Etkin, M. C. Fermin and D. W. Stephan, J. Am. Chem. Soc., 1997, 119, 2954–2955.
- 16 M. C. Fermin and D. W. Stephan, J. Am. Chem. Soc., 1995, 117, 12645– 12646.

- 17 J. D. Masuda, A. J. Hoskin, T. W. Graham, C. Beddie, M. C. Fermin, N. Etkin and D. W. Stephan, *Chem.-Eur. J.*, 2006, **12**, 8696–8707.
- 18 M. B. Ghebreab, T. Shalumova, J. M. Tanski and R. Waterman, *Polyhedron*, 2010, 29, 42–45.
- 19 A. J. Roering, S. N. MacMillan, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2007, 46, 6855–6857.
- 20 R. Waterman, Organometallics, 2007, 26, 2492-2494.
- 21 J. W. B. Reesor and G. F. Wright, J. Org. Chem., 1957, 22, 385-387.
- 22 H. C. E. McFarlane and W. McFarlane, J. Chem. Soc. D, 1971, 1589– 1590.
- 23 A. J. Roering, A. F. Maddox, L. T. Elrod, S. M. Chan, M. B. Ghebreab, K. L. Donovan, J. J. Davidson, R. P. Hughes, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2009, 28, 573–581.
- 24 A. J. Roering, S. E. Leshinski, S. M. Chan, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2010, 29, 2557– 2565.
- 25 R. T. Baker, J. F. Whitney and S. S. Wreford, *Organometallics*, 1983, 2, 1049–1051.
- 26 J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw, J. Am. Chem. Soc., 1978, 100, 2716–2724.
- 27 L. D. Quin, A. N. Hughes and B. Pete, *Tetrahedron Lett.*, 1987, 28, 5783–5786.
- 28 T. A. Van der Knaap, T. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam and M. Konijn, *Tetrahedron*, 1984, 40, 765– 776.
- 29 A. J. Roering, J. J. Davidson, S. N. MacMillan, J. M. Tanski and R. Waterman, *Dalton Trans.*, 2008, 4488–4498.