Supporting Information for

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

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General considerations

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Benzene-d_6 was purchased from Cambridge Isotope Laboratory then degassed and dried over NaK alloy. Celite-454 was heated to a temperature greater than 180 °C under dynamic vacuum for at least 8 h. Elemental analysis was performed on an Elementar varioMICRO cube. A Bruker AXR or Varian 500 MHz spectrometer was used to collect NMR spectra in benzene-d_6 solution and are reported with reference to residual solvent resonances (δ 7.16 and δ 128.0). For benzene-d_6 in tetrahydrofuran, a reference value of δ 7.31 was used.[1] External 85% H_3PO_4 (δ 0.0) was used as reference for ^{31}P NMR spectra. Infrared spectra were collected on an Alpha FT-IR spectrometer (Bruker Optics) with an attached ATR-unit. Starting metal complexes ([κ^5-*N,N,N,N,C*-$(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2$]Zr (**1**),[2] $Cp^*_2ZrCl_2$,[3] and $Cp^*_2Zr(H)_2$,[4] and [Li][$Cp^*_2Zr(H)_3$] (**4**)[5] were prepared according to literature procedures.[1] (±)-Methylphenylphosphine and (±)-cyclohexylmethylphosphine were prepared via deprotonation of (RPH_2, R= Ph or Cy) using BuLi and quenched with MeI. After purification by distillation, the products were identified by comparison of spectral data with literature values.[6-7] All other chemicals were obtained from commercial suppliers and dried by conventional means.

(N_3N)$ZrPCH_3$(Ph) (2). A scintillation vial was charged with **1** (200 mg, 0.444 mmol) and 3 mL of benzene. To the solution of **1**, (±)-methylphenylphosphine (55.2 mg, 0.443 mmol) was added, and the resultant red solution was stirred at ambient temperature for 30 min then frozen and lyophilized. The red powder was dissolved in Et_2O, and the solution was filtered through a bed of Celite and concentrated until incipient crystallization. Gentle warming redissolved the solids, and red crystals of **2** formed upon cooling to –30 °C overnight (154 mg, 0.269 mmol, 60%). ^{1}H (500.1 MHz): δ 7.56 (t, C_6H_5, 2 H), 7.22 (t, C_6H_5, 2 H), 6.95 (vt, C_6H_5, 1 H), 3.26 (t, CH_2, 6 H), 2.22 (t, CH_2, 6 H), 2.11 (d, J_{PH} = 25 Hz, CH_3, 3 H), 0.26 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 146.8 (d, J_{PH} = 12 Hz, *Ph*), 130.5 (s, *Ph*), 128.7 (s, *Ph*), 123.5 (s, *Ph*), 64.1 (s, CH_2), 47.5 (s, CH_2), 8.9 (d, CH_3), 1.6 (s, CH_3). ^{31}P{^{1}H} (202.5 MHz): δ 35.3 (s, *P*CH_3). IR (KBr, Nujol): 3067 w, 3050 w, 2941 s, 2905 s, 2888 s, 2827 s, 1577 w, 1477 w, 1431 w, 1334 w, 1263 m, 1243 s, 1143 w, 1090 w, 1046 s,1018 m, 926 s, 892 m, 824 s, 770 s, 732 s, 684 s, 562 s, 450 s cm^{-1}. Anal. Calcd for $C_{22}H_{47}N_4PSi_3Zr$: C, 46.03; H, 8.25; N, 9.76. Found: C, 46.16; H, 8.25; N, 9.76.

Attempted preparation of $Cp^*_2Zr(PMePh)_2$. A solution of $Cp^*_2ZrCl_2$ (43 mg, 0.10 mmol) in 5 mL of diethyl ether was cooled to –30 °C, and a solution of LiPMePh (23 mg, 0.20 mmol) in diethyl ether (5 mL) was added slowly with stirring. As the reaction mixture warmed to ambient temperature, it took on a dark green color. After 1 h, the mixture was dried under reduced pressure, the residue was extracted with pentane, filtered, and dried again to give the crude product as a glassy green solid (40 mg, 0.066 mmol). Analysis by NMR (^{1}H and ^{31}P) gave a mixture of products, including those noted below. Attempts to produce single crystals for X-ray analysis by cooling saturated pentane solutions of the crude product to –30 °C were unsuccessful. Data attributed to $Cp*_2Zr(PMePh)_2$: ^{1}H (500.1 MHz): δ 2.01 (d, J = 5.0 Hz, PCH_3, 3 H), 1.80 (s, CH_3, 30 H). Positive assignment of the phenyl resonances could not be made. $^{31}P\{^1H\}$ (202.5 MHz): δ 95.6 (s, PCH_3).

Monitoring reaction of LiPMePh with $Cp*_2ZrCl_2$. The addition of two equivalents of LiPMePh to $Cp*_2ZrCl_2$ in benzene-d_6 immediately gave a deep green mixture with ^{31}P NMR resonances at δ 95.6 and –8.4. In the ^{1}H NMR spectrum, there were resonance at δ 2.01 (d, J = 5.0 Hz, PCH_3, 3 H) and 1.80 (s, CH_3, 30 H). Upon allowing the solution to stand at ambient temperature, a broad new resonance was observed at δ 167.6, assigned to the polymerization product of $PhP{=}CH_2$,[8-9] with minor peaks corresponding to MePhPH at δ –68.4 and the dehydrocoupled products at δ –36.3 and –39.7. This process can be accelerated by heating the solution to 60 °C.

Reaction of MePhPH with $Cp*_2Zr(H)_2$. The addition of two equivalents of MePhPH to $Cp*_2ZrH_2$ in benzene-d_6 gave a pale green solution with a new ^{31}P NMR resonance at δ 58.4 (d, J_{HP} = 233 Hz), which corresponds to a new peak in the ^{1}H NMR spectrum at δ 4.87 (d, J_{HP} = 233 Hz) as well as resonances for $Cp*_2Zr(PMePh)_2$ (see above). Upon heating for 1 h at 60 °C, a resonance at δ 167.6 ($PhP{=}CH_2$) was the dominant phosphorus-containing product with a minor peak in the ^{31}P spectrum at δ 1.5 and only a trace amount of dehydrocoupled product at δ –36.0 and –39.6 as opposed to the rapid dehydrocoupling observed for reactions with $Cp*_2Zr(H)_3^-$. Repeating the reaction with 1 equiv. of LiPMePh per $Cp*_2Zr(H)_2$ was sufficient to effect dehydrocoupling rather than decomposition.

Catalytic dehydrocoupling of phosphines

Dehydrocoupling of PhMePH using $(N_3N)Zr$-complexes. An NMR tube fitted with PTFE stopcock was charged with 5 mol % of **1** (7.0 mg, 0.0155 mmol) or **2** (8.9 mg, 0.0155 mmol), and (±)-methylphenylphosphine (34.0 mg, 0.274 mmol) with sufficient benzene-d_6 to bring the volume to at least 0.5 mL. The solution was then heated at 80 °C in an oil bath, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. The initial color of the solution changed from light red and to a gradually darker red upon heating. During the reaction, the head space of the NMR tube was evacuated of any H_2 gas at daily intervals by a freeze-pump-thaw cycle. Observation of the reaction via ^{31}P NMR spectroscopy revealed formation (or retention) of phosphido complex **2** and gradual formation of dehydrocoupled product $(PhMeP)_2$. Complete conversion to $(PhMeP)_2$ occurred after approximately two weeks according to ^{31}P NMR spectroscopy. Diphosphine product was isolated by filtration of the reaction mixture followed by removal of volatile materials under reduced pressure. This residue was washed with cold pentane to give a colorless solid (14 mg, 42%), which was identified by comparison to the authentic compound prepared by the literature route.[2,4] This reaction can also be run in THF in an analogous method as to that described below, which gives the same products with little change in qualitative rate.

Dehydrocoupling of secondary phosphines using [Li][Cp*Zr(H)$_3$]. Reaction mixtures containing the appropriate secondary phosphine (0.538 mmol) and [Li][Cp*Zr(H)$_3$] (10.0 mg, 0.273 mmol, 5 mol % catalyst loading) in THF (0.5 mL) with a drop of benzene-*d*$_6$ for NMR lock were placed in NMR tube fitted with PTFE stopcock, and the solution was degassed via two freeze-pump-thaw cycles. The tubes were then placed in a 60 °C oil bath. After 80, 160, and 1080 minutes, the samples were degassed and the conversion to dehydrocoupled product was measured by integration of the ^{31}P NMR spectrum (Table S1).

Table S1. Results of catalytic dehydrocoupling.[a]

	80 min.	160 min.	1080 min.
MPMePh	67 %	81 %	83 %
HPMeCy	0 %	0 %	0 %

[a] Conditions: $Cp^*_2Zr(H)_3^-Li^+$ (10.0 mg, 0.273 mmol, 5 % catalyst loading) in THF (0.5 mL with a drop of C_6D_6 for NMR lock); 60 °C; degassed after each measurement.

References

1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
2. 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, **29**, 573–581.
3. J. M. Manriquez, D. R. McAlister, A. M. Rosenberg, A. M. Shiller, K. L. Williamson, S. I. Chan and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 3078-3083.
4. J. A. Pool, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 2241-2251.
5. N. Etkin, A. J. Hoskin and D. W. Stephan, *J. Am. Chem. Soc.*, 1997, **119**, 11420-11424.
6. H. C. E. McFarlane and W. McFarlane, *J. Chem. Soc. D.*, 1971, 1589-1590.
7. K. Issleib and G. Doll, *Chem. Ber.*, 1961, **94**, 2664-2668.
8. L. D. Quin, A. N. Hughes and B. Pete, *Tetrahedron Lett.*, 1987, **28**, 5783-5786.
9. 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.