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Triamidoamine-supported zirconium complexes in the catalytic dehydrocoupling of 1,2-bisphosphinobenzene and -ethane

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This work is dedicated to Prof. William Geiger – an innovative chemist, valued colleague, and wonderful person – on the occasion of his 65th birthday.

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ABSTRACT

The readily prepared zirconium complex, [κ^5-$(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2$]Zr (**1**), is an effective precatalyst in the dehydrocoupling of *o*-bisphosphinobenzene and 1,2-bisphosphinoethane to the known intercalated products. The phosphanido complex $(N_3N)Zr[\kappa^2$-1,2-$PH(PH_2)C_6H_4]$ ($N_3N=N(CH_2CH_2NSiMe_3)_3^{3-}$), **2** was prepared independently by reaction of **1** with *o*-bisphosphinobenzene. Complex **2** was identified as an intermediate zirconium complex in the catalytic dehydrocoupling of *o*-bisphosphinobenzene. Likewise, previously reported $(N_3N)Zr(PHCH_2CH_2PH_2)$ (**3**) was identified in the catalytic dehydrocoupling of 1,2-bisphosphinoethane. Investigation of the thermal decomposition of **2** and the reactivity of **2** with stoichiometric *o*-bisphosphinobenzene suggest that the catalysis proceeds via sequential P—P bond forming steps. The solid state structure of **2**, which features a six-coordinate $(N_3N)Zr$-complex, is reported.

1. Introduction

Catalytic dehydrocoupling of phosphines has witnessed expanded interest over the last several years [1], and this reaction is assuming a more prominent role among metal-catalyzed transformations that feature P—H bond activation [2–9]. However, a limited understanding of the mechanism of dehydrocoupling and a short list of catalysts suggest there is unrealized potential for this transformation [1].

A readily prepared, triamidoamine-supported zirconium complex [κ^5-$(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2$]Zr (**1**) [10] and related $(N_3N)ZrX$ ($N_3N=N(CH_2CH_2NSiMe_3)_3^{3-}$, X = Me, PHR, PR_2) derivatives have been shown to be effective catalysts in the dehydrocoupling of primary and secondary phosphines to the respective diphosphine products [11]. This family of complexes also affects the heterodehydrocoupling of phosphines with silanes and germanes and the dehydrocoupling of arsines [12,13].

The differences between complex **1** and $Cp^*_2Zr(H)_3^-$, the first phosphine dehydrocoupling catalyst discovered by Stephan and co-workers [14], are substantial despite both being zirconium based [15]. The latter may undergo P—H bond activation across a phosphinidene (Zr=PR) moiety, and di- and triphosphinato ($P_2R_2^{2-}$ and $P_3R_3^{2-}$) ligated zirconium appear to be important intermediates [16,17]. Furthermore, this dehydrocoupling catalysis bears a striking similarity to main-group-mediated processes reported by Wright and co-workers [15]. On the other hand, current evidence supports σ-bond metathesis reactivity at a single active site for complex **1** [11]. The differences between the triamidoamine-supported zirconium complexes and cyclopentadienyl-supported species led to an investigation of similar dehydrocoupling substrates, namely *o*-bisphosphinobenzene and 1,2-bisphosphinoethane. It has already been shown that these complexes can be dehydrocoupled by $Cp^*_2Zr(H)_3^-$ [17,18]. Our goal in this study was to test the capacity of complex **1** to engage in the similar reactivity while a Zr=P moiety is unlikely to be at play and to see what mechanistic understanding could be garnered about the dehydrocoupling process.

2. Experimental

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 500 MHz was used to collect 1D data, and a Varian 500 spectrometer was used to record HMQC and HMBC spectra using standard Varian pulse sequences with modified P-90 values and relaxation

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times. Spectra were collected in benzene-d_6 solution and are reported with reference to residual solvent resonances (δ 7.16 and δ 128.0) or external 85% H_3PO_4 (δ 0.0). Infrared spectra were collected on a Perkin–Elmer System 2000 FT-IR spectrometer at a resolution of 1 cm^{-1}. Mass spectra were collected on an Applied Biosystems 4000QTrap Pro. Complex **1** was prepared according to literature procedures [10]. Phosphanes were purchased from Strem Chemicals and used without further purification.

2.1. Preparation of (N_3N)Zr[κ^2-1,2-PH(PH_2)C_6H_4] (**2**)

A scintillation vial was charged with **1** (100 mg, 0.22 mmol) and 3 mL of benzene. To the solution of **1**, *o*-bisphosphinobenzene (31 mg, 0.22 mmol) was added, and the resulting pale yellow solution was stirred at ambient temperature for 30 min then frozen and lyophilized. The resultant powder was dissolved in Et_2O, and the solution was filtered through a bed of Celite and concentrated until incipient crystallization. Yellow crystals of **2** formed upon cooling to −30 °C overnight (83 mg, 0.14 mmol, 64%). ^{1}H (500.1 MHz): δ 7.44 (t, C_6H_5, 1 H), 7.17 (obscured by solvent, C_6H_4, ~1 H), 6.88 (t, C_6H_4, 1 H), 6.68 (t, C_6H_4, 1 H), 4.67 (dd, J_{PH} = 221.5 Hz, J_{PH} = 31.6 Hz, P*H*, 1 H), 4.61 (dd, J_{PH} = 270 Hz, J = 5.3 Hz, PH_2, 2 H), 3.20 (t, CH_2, 6 H), 2.28 (t, CH_2, 6 H), 0.27 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 147.2 (m, C_6H_4), 143.3 (m, C_6H_4), 136.3 (m, C_6H_4), 132.2 (m, C_6H_4), 130.2 (s, C_6H_4), 122.7 (s, C_6H_4), 63.2 (s, CH_2), 47.6 (s, CH_2), 2.2 (s, CH_3). ^{31}P (202.46 MHz): δ −24.1 (dd, J_{PP} = 95 Hz, J_{PH} = 221.5 Hz, P*H*), −92.1 (ddt, J_{PP} = 95 Hz, J_{PH} = 270 Hz, J_{PH} = 32 Hz, PH_2). IR (KBr, Nujol): 2918 s, 2849 s, 2722 w (ν_{PH}), 2673 w (ν_{PH}), 1461 s, 1377 s, 1299 w, 1260 w, 1153 w, 1094 w, 1022 w, 928 w, 803 w, 720 w cm^{-1}. *Anal.* Calc. for $C_{21}H_{46}N_4P_2Si_3Zr$: C, 42.60; H, 7.83; N, 9.46. Found: C, 42.78; H, 7.94; N, 9.46%.

2.2. Data for phosphine intermediates

2.2.1. [(C_6H_4)PH_2(μ-PH)]$_2$ (**4a**)

^{1}H (500.1 MHz): δ 6.84–7.35 (m, C_6H_4, 8 H), 3.99 (dd, J_{PH} = 201.5 Hz, J_{PH} = 15 Hz, PH_2, 4 H), 3.43 (dd, J_{PH} = 201 Hz, J_{PH} = 16 Hz, P*H*, 2 H). ^{31}P{^{1}H} (202.46 MHz): δ, −120.5 (d, J_{PP} = 73.5 Hz, J_{PH} = 201.5 Hz, J_{PH} = 15 Hz, PH_2), −123.7 (d, J_{PP} = 73.3 Hz, J_{PH} = 201 Hz, J_{PH} = 16 Hz, P*H*). MS (*m*/*z*): 282.0.

2.2.2. $C_6H_4(PH)_2$ (**4b**)

^{1}H (benzene-d_6, 500.1 MHz): δ 7.11 (obscured, C_6H_4, ~2 H), 6.63 (m, C_6H_4, 2 H), 4.34 (d, J_{PH} = 352 Hz, P*H*, 2 H). ^{31}P{^{1}H} (202.46 MHz): δ −33.5 (s, *P* H). MS (*m*/*z*): 140.0.

2.3. General conditions for catalytic dehydrocoupling of primary phosphines

An NMR tube fitted with PTFE stopcock was charged with 10 mol% of **1** (20 mg, 0.022 mmol), the appropriate bisphosphino reagent (0.22 mmol), and sufficient benzene-d_6 to bring the volume to greater than 0.5 mL. The solution was then heated for 4–6 weeks at 100 °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 yellow and to a gradually darker yellow upon heating. During the reaction, the head space of the NMR tube was evacuated of any H_2 gas generated at daily intervals. The products were identified by comparison to the chemical shifts in the literature data [18].

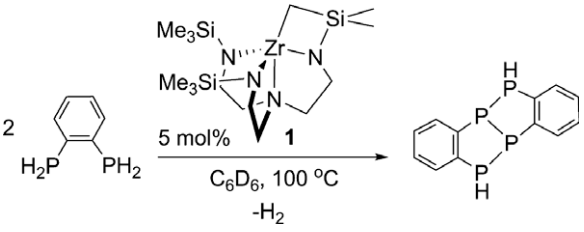
2.4. X-ray structure of complex **2**

X-Ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα, λ = 0.71073 Å) at 125 K. A suitable crystal of complex **2** was mounted in a nylon loop with Paratone-*N* cryoprotectant oil. The structure was solved using direct methods and standard difference map techniques and refined by full-matrix least squares procedures on F^2 with SHELXTL (version 6.14) [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. The hydrogen atoms on the phosphorus atoms of **2**, H(1), H(2), and H(3), were located in the Fourier difference map and refined freely. Crystal data and refinement details are presented in Table 1.

3. Results and discussion

3.1. Catalysis

Heating benzene-d_6 solutions of *o*-bisphosphinobenzene with 5 mol% of complex **1** resulted in the liberation of hydrogen and formation of several new products and consumption of **1**. Over time, a new phosphorus-containing product emerges, [(C_6H_4)PPH]$_2$, and forms in 97% yield based on ^{31}P NMR spectroscopy (Eq (1)). The product is known and was previously prepared by the catalytic dehydrocoupling of *o*-bisphosphinobenzene by $Cp^*_2Zr(H)_3^-$ [17,18]. It is known that in the dehydrocoupling of *o*-bisphosphinobenzene reported by Stephan, a high molecular weight product, [(C_6H_4)P_2]$_8$, is formed [18]. However, extended heating of reaction mixtures of **1** with the phosphine substrate or of the completed catalytic reaction gave no evidence for the formation of this macrocycle.



(1)

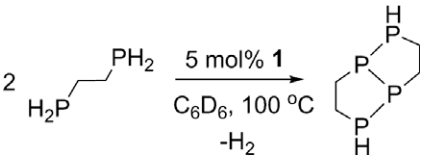
Likewise, 5 mol% of complex **1** dehydrocoupled 1,2-bisphosphinoethane to the highly related, known phosphine, [(C_2H_4)PPH]$_2$, in 95% yield, with liberation of hydrogen gas (Eq (2)) [18]. In both

Table 1
Crystal and refinement parameters for complex **2**.

	2
Formula	$C_{21}H_{46}N_4P_2Si_3Zr$
Molecular weight	592.05
Crystal system	monoclinic
Color	yellow
a (Å)	15.958(2)
b (Å)	9.212(1)
c (Å)	21.320(2)
α (°)	90
β (°)	100.767(2)
γ (°)	90
Unit cell volume (Å^3)	3078.9(6)
Space group	$P2_1/c$
Z	4
θ Range (°)	1.94–28.28
μ (mm^{-1})	0.594
N	33 171
N_{ind}	7646
R_{int}	0.0351
R_1[a] ($I > 2\sigma(I)$)	0.0271
wR_2[b] ($I > 2\sigma(I)$)	0.0613
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^3)	0.431; −0.252
GoF on R_1	1.036

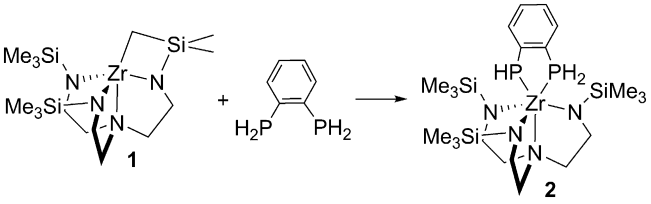
[a] $R_1 = ||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

cases, hydrogen gas inhibited phosphorus product formation, and unless the H_2 byproduct, which was observed by ^{1}H NMR spectroscopy, was vented from the reaction, the catalysis was stunted.



(2)

In each catalytic reaction, a single new zirconium complex was observed to be formed that persisted throughout the catalysis. For the dehydrocoupling of *o*-bisphosphinobenzene, this complex was unknown. However, reaction complex **1** with 1 equiv of *o*-bisphosphinobenzene resulted in quantitative formation of a new, pseudo-C_3-symmetric zirconium product that was identical to the complex observed in the catalytic reaction as measured by ^{1}H and ^{31}P NMR spectroscopy in benzene-d_6. The product is $(N_3N)Zr[\kappa^2$-1,2-$PH(PH_2)C_6H_4]$ (**2**), which was readily isolated as analytically pure, yellow crystals in 64% yield upon crystallization from Et_2O (Eq (3)). Routine characterization by NMR and IR spectroscopy confirmed the basic formulation of the complex. A ^{1}H-coupled ^{31}P NMR experiment allowed assignment of the phosphanido and phosphine ^{31}P nuclei at δ −24.1 and −92.1, respectively. Interestingly, no evidence of proton exchange was observed by NMR spectroscopy in benzene-d_6. This observation may be the result of a limited sample of temperatures available in this solvent, slow proton exchange, or very rapid proton exchange on the NMR timescale.



(3)

In the latter catalytic reaction, all of the observable zirconium was rapidly converted to $(N_3N)Zr(PHCH_2CH_2PH_2)$ (**3**), which was the only zirconium complex observed by NMR spectroscopy throughout the course of the reaction. An independent preparation of complex **3** was recently reported via reaction of **1** with 1,2-bisphosphinoethane [10].

3.2. Molecular structure of *2*

Single crystals of complex **2** were grown from concentrated Et_2O solution cooled to −30 °C. The molecular structure of complex **2** features a κ^2-phosphanido/phosphine ligand that results in a six-coordinate complex (Fig. 1). Isolated six-coordinate $(N_3N)Zr$ species are rare. However, such complexes are important in the formation of element–element bonds via σ-bond metathesis, as have been proposed for the dehydrocoupling of phosphines by these $(N_3N)Zr$-complexes [11].

In the solid state, these two Zr—P bonds are different. The bond between the phosphanido phosphorus, P(2), and zirconium is markedly shorter than that for the phosphine phosphorus, P(1), and zirconium (ca. 0.17 Å, Table 2). With the located hydrogen atom, P(2) is pyramidal, and the short bond length of 2.7375(5) Å may be due to electrostatic attraction rather than any π-bonding component. Indeed, this is consistent with the highly ionic bonding model for triamidoamine–zirconium complexes developed in recent theoretical investigations [10].

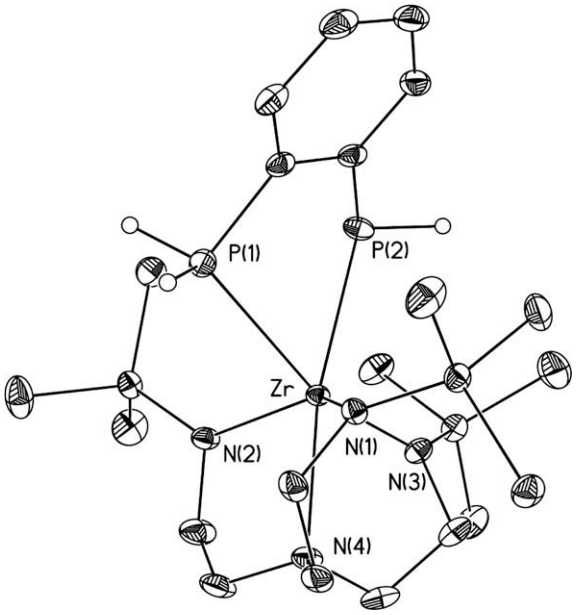


Fig. 1. Perspective view of complex **2** with thermal ellipsoids drawn at the 35% probability level and hydrogen atoms, except those located on the two phosphorus atoms, omitted for clarity.

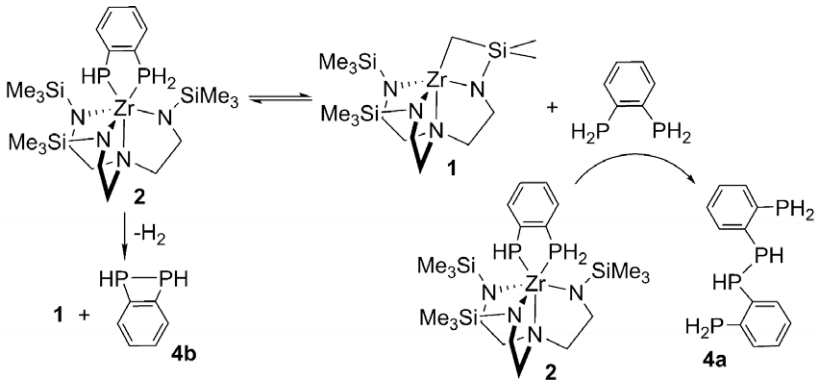
Table 2
Selected bond lengths (Å) and angles (°) for $(N_3N)Zr[\kappa^2$-1,2-$PH(PH_2)C_6H_4]$ (**2**).

Zr–P(1)	2.9089(6)	Zr–N(1)	2.085(1)
Zr–P(2)	2.7375(5)	Zr–N(2)	2.112(1)
P(1)–C(16)	1.821(2)	Zr–N(3)	2.088(2)
P(2)–C(21)	1.828(2)	Zr–N(4)	2.469(2)
C(16)–P(1)–Zr	104.19(6)	C(21)–P(2)–Zr	105.19(6)
Zr–P(1)–H(1)	129.6(9)	Zr–P(2)–H(3)	106.6(9)
Zr–P(1)–H(2)	117.6(9)	P(2)–Zr-P(1)	68.81(2)
H(1)–P(1)–H(2)	96.2(13)		

The interaction of the phosphine group with zirconium is the likely result of the proximity that the rigid phenylene backbone places this substituent to the metal. This arrangement stands in contrast with complex **3**, in which the phosphine donor is nearly as far from the zirconium as possible being separated by the extended ethylene backbone [10]. If the six-coordinate complex were more stable, presumably complex **3** would have adopted a similar configuration in the solid state.

3.3. Mechanistic study

To gain some additional insight into these reactions, studies on the decomposition of **2** were undertaken. Heating benzene-d_6 solutions of **2** at 70 °C resulted in several changes. In all experiments, $[(C_6H_4)PPH]_2$ product was formed as identified by ^{31}P NMR spectroscopy. The amount of product varied by run and never appeared in more than 10% yield based on complex **2**. Two intermediate complexes were formed rapidly in the reaction, which dominated the phosphorus-containing species. The first complex appeared to be $[(C_6H_4)PH_2(\mu\text{-}PH)]_2$ (**4a**) based on ^{31}P and ^{1}H NMR spectroscopy, ^{31}P–^{1}H HMBC and HMQC experiments, and mass spectrometry. The spectroscopic data shows a single product rather than a mixture of rac and meso forms. From our data, it is not clear if these two forms coincidentally exhibit the same chemical shifts or if there is some selectivity. Formation of **4a** would be the product of reacting complex **2** with 1 equiv of *o*-bisphosphinobenzene. The free phosphine would likely be generated through the



Scheme 1. Thermal reaction pathways of complex **2**.

equilibrium of **2** with **1** and *o*-bisphosphinobenzene (Scheme 1). Kinetic accessibility of **1** and phosphine from (N_3N)Zr-phosphanido complexes is a common feature of this system [10,11]. Compound **4a** is observed in low concentration during the catalytic reactions.

The other major phosphorus-containing product is tentatively assigned to be $C_6H_4(PH)_2$ (**4b**) based on similar experiments. Formation of **4b** would likely be the result of an intramolecular phosphine dehydrocoupling to give a putative zirconium–hydride complex, which would rapidly eliminate hydrogen to form complex **1** (Scheme 1). Observation of hydrogen by ^{1}H NMR spectroscopy lends indirect support to this reaction path. If this hypothesis is correct, it suggests that this intramolecular dehydrocoupling is competitive with the intermolecular dehydrocoupling that forms **4a** at 70 °C. Phosphines **4a** and **4b** form in similar concentrations, which further suggests that the sequence of reactions to form **4a** is relatively rapid or the intramolecular dehydrocoupling to afford **4b** is relatively slow. Current data do not allow a distinction between these possibilities to be made.

Several other phosphorus-containing intermediates were observed, but the concentration of these species could not be sufficiently enhanced to provide definitive assignment. Prolonged heating of complex **2** at 70 °C or heating to temperatures >100 °C ultimately resulted in decomposition to a myriad of minor products and insoluble materials.

Heating benzene-d_6 solutions of complex **2** with an equimolar quantity of *o*-bisphosphinobenzene resulted in predominate formation of **4a** with very little of **4b** observed. This observation suggests that the formation of these two compounds is based on competitive reactivity in the decomposition of complex **2**, and that the added phosphine established favorable conditions for the formation of **4a**. Further heating of this reaction mixture yielded considerably more of the final dehydrocoupling product $[(C_6H_4)PPH]_2$.

4. Conclusion

Triamidoamine-supported zirconium complexes readily dehydrocouple *o*-$(PH_2)_2C_6H_4$ and 1,2-$(PH_2)_2C_2H_4$ to known diphosphine products. The identity of an intermediate complex (N_3N)Zr[κ^2-1,2-$PH(PH_2)C_6H_4$] (**2**) was confirmed by independent preparation and an X-ray diffraction study. The initial step in the catalysis appears to be a P—P bond forming event to give complex **4a** as identified in the decomposition of **2** and the reaction of **2** with one equiv of phosphine. These observations suggest that **4a** reacts with complex **1** to form final product.

Supplementary data

CCDC 729412 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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References

[1] R. Waterman, Curr. Org. Chem. 12 (2008) 1322.
[2] F. Gauvin, J.F. Harrod, H.G. Woo, Adv. Organomet. Chem. 42 (1998) 363.
[3] S. Greenberg, D.W. Stephan, Chem. Soc. Rev. 37 (2008) 1482.
[4] T.J. Clark, K. Lee, I. Manners, Chem. Eur. J. 12 (2006) 8634.
[5] D.S. Glueck, Synlett (2007) 2627.
[6] M.L. Clarke, Polyhedron 20 (2001) 151.
[7] L. Coudray, J.-L. Montchamp, Eur. J. Org. Chem. (2008) 3601.
[8] H. Yorimitsu, K. Oshima, Pure Appl. Chem. 78 (2006) 441.
[9] O. Delacroix, A.C. Gaumont, Curr. Org. Chem. 9 (2005) 1851.
[10] 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, R. Waterman, Organometallics 28 (2009) 573.
[11] R. Waterman, Organometallics 26 (2007) 2492.
[12] A.J. Roering, J.J. Davidson, S.N. MacMillan, J.M. Tanski, R. Waterman, Dalton Trans. (2008) 4488.
[13] A.J. Roering, S.N. MacMillan, J.M. Tanski, R. Waterman, Inorg. Chem. 46 (2007) 6855.
[14] M.C. Fermin, D.W. Stephan, J. Am. Chem. Soc. 117 (1995) 12645.
[15] R.J. Less, R.L. Melen, V. Naseri, D.S. Wright, Chem. Soc. Rev., in press.
[16] D.W. Stephan, Angew. Chem., Int. Ed. 39 (2000) 315.
[17] J.D. Masuda, A.J. Hoskin, T.W. Graham, C. Beddie, M.C. Fermin, N. Etkin, D.W. Stephan, Chem. Eur. J. 12 (2006) 8696.
[18] N. Etkin, M.C. Fermin, D.W. Stephan, J. Am. Chem. Soc. 119 (1997) 2954.
[19] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.