Rh-catalyzed P–P bond activation†
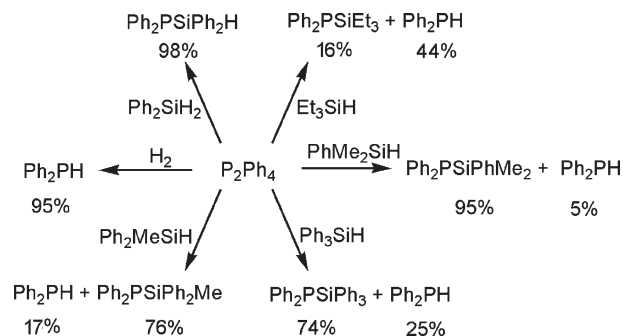
Stephen J. Geier and Douglas W. Stephan*

A Rh-catalyst derived from (NacNac)Rh(COE)(N$_2$) effects the hydrogenation and silylation of P–P bonds to give secondary phosphines and silylphosphines, (Ph$_2$PH) and (Ph$_2$PSiRR′$_2$) respectively; the latter process is shown to also involve the silylation of secondary phosphines.

The impact of organometallic chemistry and catalysis on organic chemistry has been dramatic, as is evidenced by the awarding of Nobel Prizes in 2001 and 2005. A related area, ripe for impact, involves the application of the concepts of organometallic chemistry to main group synthesis and materials chemistry. Such "inorganometallics" has drawn some recent attention.[1] While much of the work to date has involved stoichiometric transformations, some catalytic processes are emerging.[2–5] For example, we previously reported the use of [Cp*$_2$ZrH$_3$]$^{−}$[6–8] and CpTi(NPt-Bu$_3$)(C$_2$H$_4$)$_2$ as precatalysts for the dehydrocoupling of primary and secondary phosphines, affording a variety of P–P bonded oligomers.[9] In a similar fashion, Harrod and co-workers showed that titanocene derivatives can act as catalysts for the heterocoupling of silanes and phosphines.[10,11] A recent report by Waterman and co-workers highlights the catalytic heterocoupling of primary phosphines and silanes by a Zr(IV) triamidoamine complex.[15] Waterman and Tilley have also reported similar use of zirconocene and hafnocene complexes to effect catalytic dehydrocoupling of stibines, affording oligostibines.[12] Brookhart and Bohm have also probed similar dehydrocoupling of secondary phosphines using the Rh precatalyst Cp*Rh(CH$_2$=CHSiMe$_3$)$_2$,[13] although this system gave only high yields for select phosphines under harsh conditions. Most recently, Han and Tilley have reported dehydrocoupling of phosphines using a catalyst based on the Rh(iPr$_2$PCH$_2$CH$_2$PiPr$_2$) fragment.[14] In related chemistry, stoichiometric functionalizations of P–P bonds have been investigated to some extent;[16] metal-mediated reactions involving the activation of P–P bonds has drawn less attention. We have recently examined the stoichiometric reactivity of Ni and Fe β-diketiminates with P–H and P–P bonds.[17] In this paper, we report the discovery of a catalyst for the activation of P–P bonds derived from the β-diketiminate-complex Rh(NacNac)(C$_8$H$_{14}$)N$_2$ **1**.[18]

In initial trials, we attempted to probe the utility of **1** in the dehydrocoupling of Ph$_2$PH. Over a 12 h period at 70 °C compound **1** proved to be a poor catalyst for such dehydrocoupling, giving P$_2$Ph$_4$ in only 30% yield. We hypothesized that the steric demands of the NacNac ancillary ligand

(NacNac = HC(CMeN(iPr$_2$C$_6$H$_2$))$_2$) favor non-productive P–H elimination over dehydrocoupling to give P–P bond formation. This supposition prompted us to probe the catalytic activity of **1** in reactions with diphosphine substrates. Treatment of P$_2$Ph$_4$ under 4 atm of H$_2$ with 10 mol% of **1** at 50 °C resulted in the hydrogenation of the P–P bond to give Ph$_2$PH in 95% yield in 12 h (Scheme 1). In a similar fashion, the product Ph$_2$P(SiPh$_2$H) was also prepared in 98% yield using 10 mol% **1** to catalyze the activation of P$_2$Ph$_4$ in the presence of 5 equivalents of Ph$_2$SiH$_2$ at 100 °C for 48 h (Scheme 1). Analogous use of PhMe$_2$SiH gave the phosphine Ph$_2$P(SiPhMe$_2$) in 95% yield with 5% of the by-product Ph$_2$PH, while bulkier silanes resulted in lower yields of the silylphosphine. For instance, use of Ph$_2$MeSiH or Ph$_3$SiH gave 76% and 74% of the P–Si coupled products Ph$_2$P(SiPh$_2$Me) and Ph$_2$P(SiPh$_3$) together with 17% and 25% yield of Ph$_2$PH, respectively. Alkylsilanes proved to be less reactive. Et$_3$SiH resulted in conversion of P$_2$Ph$_4$ to 16% of Ph$_2$PSiEt$_3$ with 44% Ph$_2$PH, while iPr$_3$SiH afforded no P–Si coupling product and only 29% Ph$_2$PH.

To garner further information regarding these P–P bond activations, the catalyst precursor **1** was reacted stoichiometrically with P$_2$Ph$_4$ in toluene and allowed to stir overnight at 25 °C. Subsequent work-up gave a dark-red residue which was recrystallized from pentane to give dark-red crystals of **2** in 50% yield.‡ It should be noted that this diminished yield is due to loss during crystallization as NMR data for reaction mixtures show near quantitative formation of **2**. This product exhibits a single ^{31}P{^{1}H} resonance at −51.4 ppm with a Rh–P coupling of 140 Hz. The ^{1}H NMR data for **2** was consistent with the presence of a 1 : 1 ratio of NacNac and P$_2$Ph$_4$. An X-ray diffraction study confirmed the formulation of **2** as Rh(NacNac)(P$_2$Ph$_4$) (Scheme 2, Fig. 1). The N$_2$P$_2$ coordination sphere about Rh is a distorted square-plane. The Rh–N distances of 2.054(3) Å and 2.065(3) Å are slightly shorter than those seen in the precursor **1** (2.076(3) Å and 2.074(3) Å) suggesting that the (P$_2$Ph$_4$) fragment has weaker *trans*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4. E-mail: Stephan@uwindsor.ca; Fax: +1 519-973-7098

Scheme 1 Hydrogenation and silylation of P$_2$Ph$_4$ catalyzed by **1**.
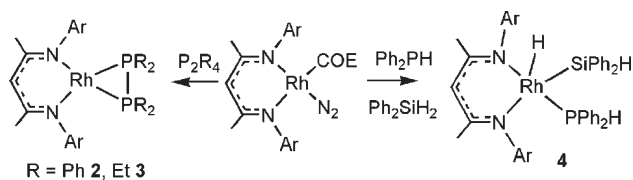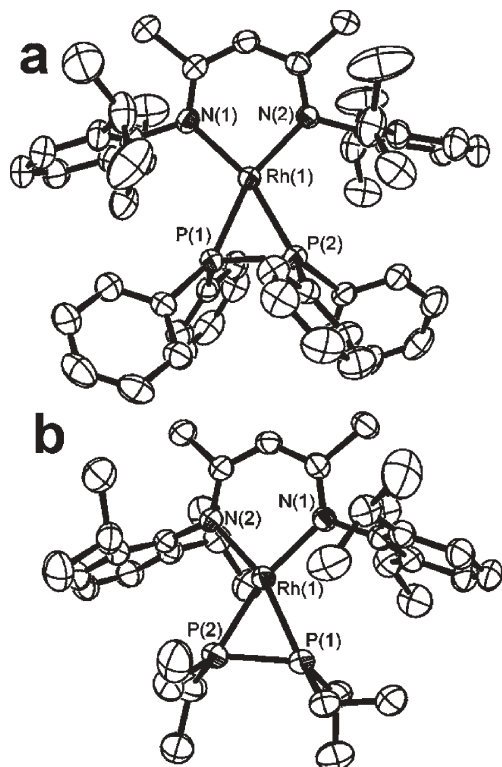
Scheme 2 Synthesis of **2**, **3** and **4**.

Fig. 1 ORTEP depictions of (a) **2**, and (b) **3**.

influence than *cis*-cyclooctene and N_2. The NacNac ligand bite angle in **2** is 90.53(11)°, while Rh–P distances are 2.2301(10) Å and 2.2423(10) Å. The P–P bond in **2** is 2.1389(14) Å and is comparable to the P–P bond in [Ni(NacNac)$_2$(P$_2$Ph$_2$)] (2.125(3) Å).[17] The RhP$_2$ ring gives rise to a P–Rh–P angle of 57.14(4)° and thus the square-planar geometry about Rh is distorted with pseudo-*trans* N–Rh–P angles of 160.02(8)° and 162.37(9)° and pseudo-*cis* N–Rh–P angles of 107.38(9)° and 106.23(8)°. The steric crowding of the Rh coordination sphere is further evidenced from the twisting of the RhP$_2$ plane with respect to the RhN$_2$ plane by 14.8°. The presence of the η^2-P$_2$Ph$_4$ to a single metal center in **2** appears to be unique in that literature precedent demonstrates the propensity of P$_2$Ph$_4$ to bind in a monodentate fashion, or to bridge two metal centers.[19–29] In addition, the related complex Ni(NacNac)(Ph$_2$PH)[17] binds only one phosphine ligand yielding the three coordinate species, presumably a result of the slightly larger atomic radius of Rh as well as the aforementioned geometry distortions which accommodate the η^2-P$_2$Ph$_4$.

Reactions with P$_2$Et$_4$ seem to support partial dissociation of the P$_2$ fragment as a key step in the reaction. While attempts to carry out catalytic P–P activation reactions with P$_2$Et$_4$ proved unsuccessful, the species Rh(NacNac)(P$_2$Et$_4$) **3**, the analog of **2**, was readily formed in a stoichiometric reaction of P$_2$Et$_4$ with **1**

(Scheme 2). The metric parameters in **3** were found to be similar to those in **2**, with Rh–N distances of 2.064(2) Å and 2.067(2) Å and Rh–P bond lengths of 2.2229(11) Å and 2.2466(10) Å, while the P–P distance was determined to be 2.1254(14) Å. These latter observations suggest that the smaller, more basic diphosphine binds to Rh more strongly, precluding the partial dissociation that initiates subsequent P–P cleavage reactions.

Addition of H$_2$ to solutions of **2** resulted in no observable reactions at ambient temperatures, further suggesting that reaction of P$_2$Ph$_4$ requires thermal dissociation of the η^2-P$_2$Ph$_4$ to at least an η^1-P$_2$Ph$_4$ to permit oxidative addition at Rh.

In the case of H$_2$ reactions, the transient Rh(NacNac)(η^1-P$_2$Ph$_4$) has a vacant coordination site permitting oxidative addition of H$_2$ to Rh. Subsequent reductive elimination of the secondary phosphine *via* P–P bond cleavage is proposed. Elimination of a second equivalent of phosphine regenerates the Rh(NacNac) fragment which then re-enters the catalytic cycle by reaction with P$_2$Ph$_4$.

In the case of the silylation reactions, an analogous catalytic cycle would generate equal amounts of Ph$_2$PH and Ph$_2$PSiR$_3$ for each P$_2$Ph$_4$ molecule activated. However, only low concentrations of Ph$_2$PH are observed by ^{31}P{^{1}H} NMR spectroscopy of the catalytic silylation reaction mixtures. This suggests that the second part of the catalytic cycle, where Ph$_2$PH must dehydrocouple with a second equivalent of silane, is more rapid than the initial P$_2$Ph$_4$ activation. Reaction of P$_2$Ph$_4$ and two equivalents of Ph$_2$SiH$_2$ in the presence of 10 mol% of **1** at 50 °C for 5 days affords a 74% yield of the silylphosphine Ph$_2$P(SiPh$_2$H) and a 23% yield of Ph$_2$PH.

Independent experiments demonstrated such activation of P–H bonds. For example, exposure of Ph$_2$PH to 4 atm of D$_2$ in the presence of 5 mol% **1** led to hydrogen for deuterium exchange resulting in 85% conversion to Ph$_2$PD. While treatment of **1** with excess Ph$_2$PH generates a species in solution formulated as Rh(NacNac)(Ph$_2$PH)$_2$, dissociation of phosphine and oxidative addition of D$_2$, followed by reductive elimination of HD and Ph$_2$PD accounts for the observed deuteration. Similarly, hetero-nuclear dehydrocoupling of Ph$_2$PH and silanes proceeds using 5 mol% of species **1**. For example, reaction of Ph$_2$PH and Ph$_2$SiH$_2$ gave quantitative yield of Ph$_2$P(SiPh$_2$H) in 18 h at 50 °C. Similarly, Ph$_2$P(SiPhMe$_2$) is formed in 84% yield under similar conditions, while Ph$_2$P(SiPh$_2$Me) is formed in 85% yield in 18 h at 100 °C. As with the diphosphines, bulkier silanes afford lesser yields as Ph$_2$P(SiPh$_3$) is formed in only 40% yield from Ph$_2$PH and Ph$_3$SiH and the homo-dehydrocoupling by-product P$_2$Ph$_4$ is observed in 10% yield.

Overall, these data support a mechanism in which hydrosilyla-tion of P$_2$Ph$_4$ affords both Ph$_2$PH and the silylphosphine; however the phosphine reacts further to form another equivalent of silylphosphine (Scheme 3). This latter P–Si dehydrocoupling is apparently faster than the initial P–P bond activation. Evidence for the nature of an intermediate was derived from stoichiometric reactions of **1** with Ph$_2$PH and Ph$_2$SiH$_2$. In this case a short-lived species was observed spectroscopically. The ^{1}H NMR resonance at −13.5 ppm was indicative of a Rh–hydride species, while the doublet at 5.05 ppm indicated the presence of the PH bond of coordinated phosphine. These data together with the ^{31}P{^{1}H} resonance at 47.4 ppm and the ^{29}Si{^{1}H} signal at 21.4 ppm were consistent with the formulation of **4** as
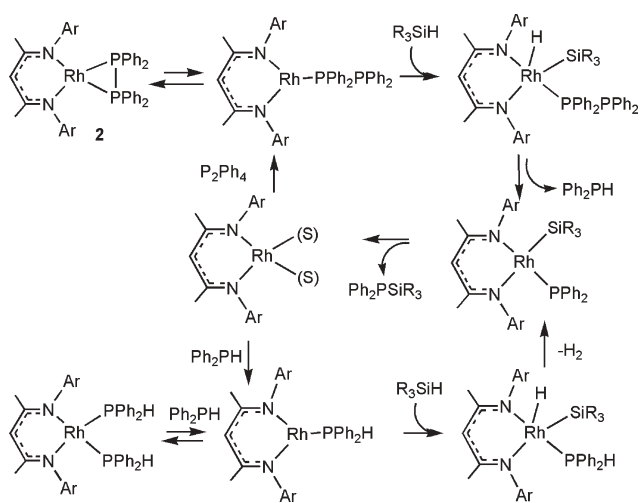
Scheme 3 Proposed mechanism of silylation of P₂Ph₄ and PPh₂H.

(NacNac)RhH(SiHPh₂)(PHPh₂) (Scheme 2). This Rh(III) inter-mediate is analogous to the Ir complexes (NacNac)IrH₂(PR₃) isolated previously by Chirik and co-workers.[30] This intermediate is also related to CpRhH(SiR₃)(PR₃) complexes reported by Marder and co-workers.[31] Loss of H₂ from this species would yield the proposed intermediate (NacNac)Rh(SiHPh₂)(PPh₂) which is proposed to undergo reductive elimination of the silyl–phosphide product. This proposition suggests that reductive Si–P elimination occurs more readily than ligand redistribution reactions.

In summary, the Rh-catalyst derived from **1** effects the catalytic hydrogenation and silylation of diphosphines. Inherent in this chemistry is the dehydrocoupling of secondary phosphines with silanes. Further studies of the mechanism, catalyst optimization and applications of these processes are ongoing.

Notes and references

‡ Preparation of **2** and **3**: these compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of 30 mg (0.081 mmol) P₂Ph₄ in 5 mL of toluene was added a solution of 50 mg **1** (0.079 mmol) in 5 mL of toluene. The mixture was allowed to stir overnight upon which the solvent was removed *in vacuo*. The dark-red residue was washed with 10 mL cold pentane to give 35 mg of the product **2** (0.039 mmol, 50% yield). ¹H NMR (C₆D₆) δ: 0.84 (6H, d, J = 6.5 Hz), 1.20 (6H, d, J = 6.5 Hz), 1.71 (6H, s), 4.45 (4H, sept, J = 6.5 Hz), 5.15 (1H, s), 6.73–7.19 (26H, br m). ³¹P{¹H} NMR (C₆D₆) δ: −51.4 (d, J_{P-Rh} = 140 Hz). ¹³C NMR (C₆D₆) δ: 24.0, 24.4, 28.6, 98.0, 124.0, 124.1, 127.5–128.6 (m, obscured by C₆D₆), 128.9, 134.9 (app. t, J = 7.5 Hz), 157.7, 159.6. EA anal. calcd for RhP₂N₂C₅₃H₆₁ (%) C: 71.21, H: 7.22, N: 3.13; found: C: 70.91, H: 7.22, N: 2.72. X-Ray quality crystals were grown by slow evaporation from a pentane solution. M = 890.89, space group: monoclinic, $P2_1/n$, a = 10.8591(11), b = 35.296(4), c = 12.6312(13) Å, β = 94.769(2)°, V = 4824.6(9) Å³, Z = 4, T = 273(2) K, data: variables 8472: 525, R = 0.0484, R_w = 0.1099, GOF = 1.053; CCDC 658230. **3**: ¹H NMR (C₆D₆) δ: 0.74 (8H, app. pent, J = 7.8 Hz), 1.26 (12H, t of d, J = 7.3 Hz, 2.9 Hz), 1.35 (12H, d, J = 6.9 Hz), 1.63 (12H, d, J = 6.9 Hz), 1.84 (6H, s), 4.19 (4H, sept, J = 6.9 Hz), 5.19 (1H, s), 7.15–7.29 (6H, m). ³¹P NMR (C₆D₆) δ: −64.51 (d, J = 127 Hz). ¹³C NMR (C₆D₆) δ: 9.8, 12.9, 22.4, 23.9 (d, J = 9.6 Hz), 28.3, 97.0, 123.2, 123.8, 127.3–130.5 (m, obscured by C₆D₆), 140.3, 156.7, 159.4. EA anal. calcd for RhP₂N₂C₃₇H₅₅ (%) C: 63.32, H: 9.19, N: 3.99; found: C: 63.55, H: 9.24, N: 4.12. X-Ray quality crystals were grown from a pentane

solution at −30 °C. M = 698.73, space group: monoclinic, $P\bar{1}$, a = 10.566(3), b = 11.676(4), c = 17.636(6) Å, α = 102.412(4), β = 93.045(4), γ = 114.125(4)°, V = 1914.7(11) Å³, Z = 2, T = 296(2) K, data: variables 6726: 381, R = 0.0459, R_w = 0.1233, GOF = 0.969; CCDC 658231. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b712972f

Generation of **4**: to 20 mg **1** (0.032 mmol) in 2 mL toluene was added 12 mg Ph₂SiH₂ (0.064 mmol). The solution was cooled to −30 °C upon which 6 mg Ph₂PH (0.032 mmol) was added. The solution was allowed to warm to room temperature, volatiles were removed *in vacuo* and the residue was washed with pentane (2 × 2 mL), leaving 12 mg of **4** (0.013 mmol, 43% yield). ¹H NMR (C₆D₆) δ: −13.5 (1H, d of d, J_{H-P} = 28.4 Hz, J_{H-Rh} = 15.4 Hz), 0.23 (3H, d, J = 6.6 Hz), 0.62 (3H, d, J = 6.6 Hz), 0.71 (3H, d, J = 6.6 Hz), 1.04 (3H, d, J = 6.6 Hz), 1.06 (3H, d, J = 6.6 Hz), 1.11 (3H, d, J = 6.6 Hz), 1.43 (3H, d, J = 6.6 Hz), 1.47 (3H, d, J = 6.6 Hz), 1.65 (3H, s), 1.88 (3H, s), 2.76 (1H, sept, J = 6.6 Hz), 2.82 (1H, sept, J = 6.6 Hz), 4.07–4.16 (2H, ov sept, J = 6.6 Hz), 5.00 (1H, d, J_{H-Rh} = 36 Hz), 5.05 (1H, d, J_{P-H} = 361 Hz), 5.34 (1H, s), 6.35–7.61 (26H, ov m). ³¹P{¹H} NMR (C₆D₆) δ: 47.4 (d of d, J_{P-H} = 361 Hz, J_{P-Rh} = 137 Hz). ²⁹Si{¹H} NMR (C₆D₆) δ: 21.4 (d of d, J = 23.5 Hz, J = 34.1 Hz).

1 T. P. Fehlner, *Inorganometallics*, Plenum Press, New York, 1992.
2 F. Gauvin, J. F. Harrod and H. G. Woo, *Adv. Organomet. Chem.*, 1998, **42**, 363.
3 J. Y. Corey, *Adv. Organomet. Chem.*, 2004, **51**, 1.
4 T. D. Tilley, *Comments Inorg. Chem.*, 1990, **10**, 37.
5 T. D. Tilley, *Acc. Chem. Res.*, 1993, **26**, 22.
6 N. Etkin, M. C. Fermin and D. W. Stephan, *J. Am. Chem. Soc.*, 1997, **119**, 2954.
7 N. Etkin, A. J. Hoskin and D. W. Stephan, *J. Am. Chem. Soc.*, 1997, **119**, 11420.
8 M. C. Fermin and D. W. Stephan, *J. Am. Chem. Soc.*, 1995, **117**, 12645.
9 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.
10 R. Shu, L. Hao, J. F. Harrod, H.-G. Woo and E. Samuel, *J. Am. Chem. Soc.*, 1998, **120**, 12988.
11 S. Xin, H. G. Woo, J. F. Harrod, E. Samuel and A.-M. Lebuis, *J. Am. Chem. Soc.*, 1997, **119**, 5307.
12 R. Waterman and T. D. Tilley, *Angew. Chem., Int. Ed.*, 2006, **45**, 2926.
13 V. P. W. Bohm and M. Brookhart, *Angew. Chem., Int. Ed.*, 2001, **40**, 4694.
14 L. Han and T. D. Tilley, *J. Am. Chem. Soc.*, 2006, **128**, 13698.
15 A. J. Roering, S. N. MacMillan, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2007, **46**, 6855.
16 J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 7052, and references therein.
17 G. Bai, P. Wei, A. Das and D. W. Stephan, *Dalton Trans.*, 2006, 1141.
18 J. D. Masuda and D. W. Stephan, *Can. J. Chem.*, 2005, **83**, 324.
19 L. J. Arnold, L. Main and B. K. Nicholson, *Appl. Organomet. Chem.*, 1990, **4**, 503.
20 M. R. Churchill, C. Bueno and D. A. Young, *J. Organomet. Chem.*, 1981, **213**, 139.
21 D. Rehder, *J. Organomet. Chem.*, 1977, **137**, C25.
22 K. Issleib and G. Schwager, *Z. Anorg. Allg. Chem.*, 1961, **310**, 43.
23 A. J. M. Caffyn and M. J. Mays, *J. Organomet. Chem.*, 2005, **690**, 2209.
24 H. Adams, A. Biebricher, S. R. Gay, T. Hamilton, P. E. McHugh, M. J. Morris and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 2000, 2983.
25 A. Martin, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Chem. Soc., Dalton Trans.*, 1993, 1431.
26 A. J. M. Caffyn, M. J. Mays, G. A. Solan, D. Braga, P. Sabatino, G. Conole, M. McPartlin and H. R. Powell, *J. Chem. Soc., Dalton Trans.*, 1991, 3103.
27 G. Conole, M. McPartlin, M. J. Mays and M. J. Morris, *J. Chem. Soc., Dalton Trans.*, 1990, 2359.
28 J. D. Korp, I. Bernal, J. L. Atwood, W. E. Hunter, F. Calderazzo and D. Vitali, *J. Chem. Soc., Chem. Commun.*, 1979, 576.
29 G. Fachinetti, C. Floriani and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, 1977, 2297.
30 W. H. Bernskoetter, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2005, **24**, 4367.
31 M. P. Campian, J. L. Harris, N. Jacin, R. N. Perutz, T. B. Marder and A. C. Whitwood, *Organometallics*, 2006, **25**, 5093.