Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 5419

www.rsc.org/dalton

COMMUNICATION

Oxidative addition of aryl halides: routes to mono- and dimetallic nickel amino-*bis*-phosphinimine complexes†

Renan Cariou, Todd W. Graham, Fatme Dahcheh and Douglas W. Stephan*

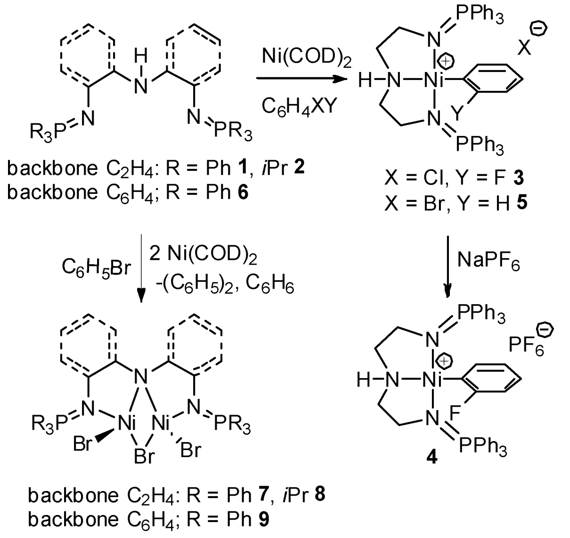
Received 28th February 2011, Accepted 31st March 2011
DOI: 10.1039/c1dt10341e

Oxidative addition of an aryl-halide to $Ni(COD)_2$ in the presence of an equivalent of amino-*bis*-phosphinimine ligand affords complexes of the form $[HN(CH_2CH_2N{=}PPh_3)_2Ni\text{-}Ar][X]$ ($Ar = C_6H_4F$, C_6H_5, $X = Cl$, Br) while the analogous reactions with 2 equivalents of Ni yield the amido-bridged complexes $N(CH_2CH_2N{=}PPh_3)Ni_2Br_3$ and $N(1,2\text{-}C_6H_4N{=}PPh_3)Ni_2Br_3$.

Tridentate or pincer ligand complexes have garnered much interest as they provide access to a broad range of tunable reactivity permitting applications as sensors, switches and catalysts.[1] Of the wide variety of such ligands,[1–4] PNP type ligands offer the electronic and steric features that accommodate a variety of highly reactive metal bound fragments. For example, alkylidene, phosphinidene,[3] metal hydrides,[4,5] and even three coordinate complexes[6,7] have been stabilized by PNP tridentate ligands. Such PNP pincer complexes also display interesting reactivity including oxidative addition of C–Halogen bonds,[8,9] C–H bond activation,[5] N_2 activation and homolytic cleavage of H_2.[7]

Much of this unique reactivity is attributable to the nature of the phosphine donors which are strong sigma donors and provide local steric shielding. While other authors have recently described analogous carbene-based CNC ligand systems,[10–17] it has only been recently that analogs incorporating phosphinimine donors have been reported.[18–21] Such donors are generally strong sigma donors, generally between phosphines and carbenes in terms of basicity. However, the nature of the phosphinimine linkage provides steric congestion that is removed from the metal center, thus providing steric shielding without crowding the metal environment; indeed the steric bulk is adjacent the metal binding coordination sphere. In a recent paper, we have described the coordination of such tridentate amino-*bis*-phosphinimine ligands to Ni(II) and Pd(II) precursors.[22] In this communication, we demonstrate that related organometallic Ni complexes are accessible from Ni(0) synthons *via* oxidative addition. Moreover, control of the stoichiometric offers a facile route to amido-bridged bimetallic Ni complexes.

We sought to exploit oxidative addition to intercept Ni(II) organometallic complexes with the use of tridentate amino-*bis*-phosphinimine ligands. To that end, *bis*-phosphinimine pincer ligands, $HN(CH_2CH_2N{=}PR_3)_2$ (R = Ph **1**, *i*Pr **2**) were combined with $Ni(COD)_2$ in THF. This gave only Ni metal. Similarly, combination of $Ni(COD)_2$ in THF and an aryl halide resulted in immediate formation of an Ni mirror. However, the reaction of **1** with $Ni(COD)_2$ in THF in the presence of 1,2-chlorofluorobenzene afforded a new Ni(II) complex **3**. Complex **3** displays a singlet at 36.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a ^{19}F NMR signal at −84.7 ppm. The aromatic protons of the fluorobenzene moiety were observed at 4.91 and 5.79 ppm in the ^1H spectrum. These data are consistent with the formulation of **3** as $[HN(CH_2CH_2N{=}PPh_3)_2Ni\text{–}C_6H_4F][Cl]$ **3** (Scheme 1). This presumably results from the oxidative addition of the C–Cl bond of 1,2-fluorochlorobenzene to a transient *bis*-phosphinimine pincer ligands Ni(0) complex. Salt methathesis of **3** with $NaPF_6$ in CH_2Cl_2 gave the analogous $[PF_6]$ salt, **4**. The spectroscopic signature of **4** is similar to **3** with the expected additional resonances at −142.3 ppm and −71.0 ppm in the $^{31}P\{^1H\}$ and ^{19}F NMR respectively, attributable to the PF_6 anion. The salt **4** was subsequently crystallographically characterized (Fig. 1(a)). The geometry at the Ni centre is best described as distorted square planar geometry with angles about the Ni centre of 173.45(9)° and 166.06(8)° for N(2)–Ni–C(41) and N(1)–Ni–N(3), respectively. The Ni–C(41) bond length is 1.900(2) Å. The aryl ring is orthogonal (89.24°) to the ligand plane. Ni–N bonds (1.9126(17) Å and 1.9264(18) Å)



Scheme 1 Synthesis of Ni complexes.

Department of Chemistry, 80 St. George St., University of Toronto, Toronto, Ontario, Canada M5S 3H6. E-mail: dstephan@chem.utoronto.ca

† CCDC reference numbers 815361–815363. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10341e

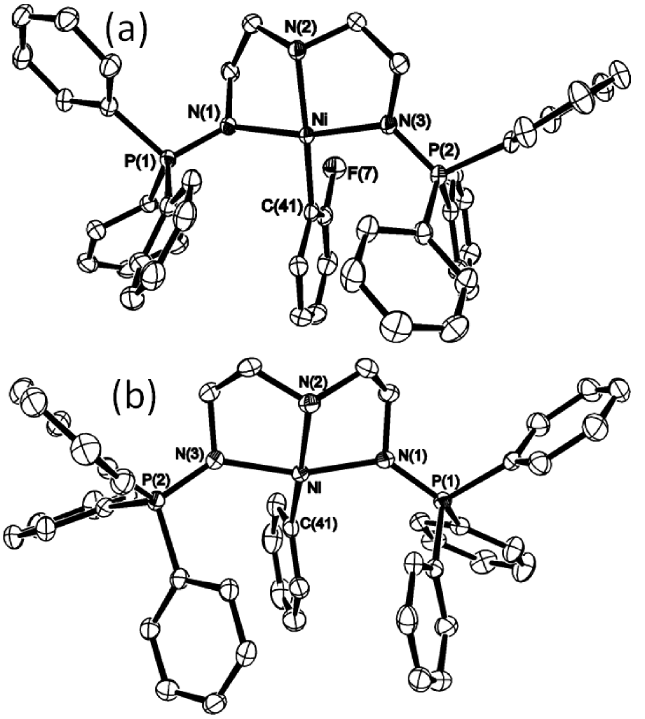


Fig. 1 ORTEP drawings of the cations (a) **4** and (b) **5**. Hydrogen atoms are omitted for clarity.

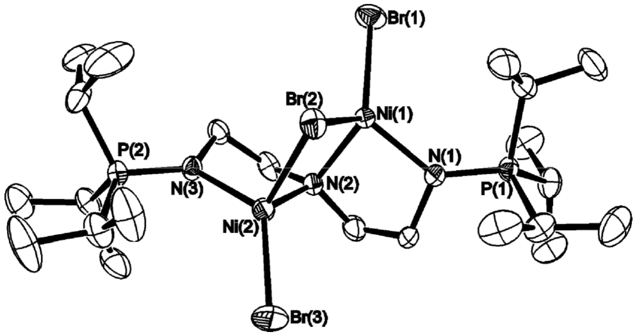


Fig. 2 ORTEP drawings of **8**. Hydrogen atoms are omitted for clarity.

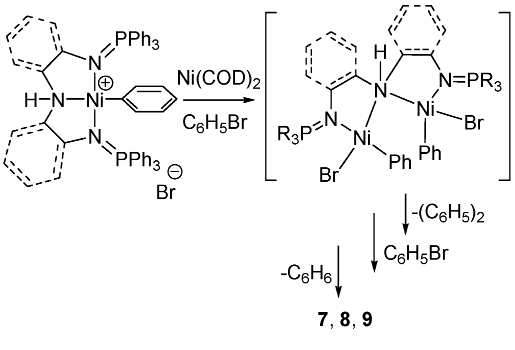
are in the range of previously reported bond length Ni–N(2) bond length of 1.9796(19) Å is slightly longer than that reported for $[HN(CH_2CH_2N{=}PPh_3)_2NiCl][PF_6]$ due to the *trans* influence of the aryl ligand.[22]

In the same vein, reaction of **1** with $Ni(COD)_2$ in bromobenzene afforded the new species **5**. This species exhibited NMR resonances that parallel those of **3** and **4**. A $^{31}P\{^1H\}$ NMR chemical shift was seen at 35.2 ppm and protons resonances observed between 5.30 and 5.80 ppm were attributed to the $Ni–C_6H_5$ fragment. X-ray quality crystals of **5**, grown from acetonitrile, revealed the expected square planar geometry at the Ni center (Fig. 1(b)). The metric parameters are similar to those seen in **4**, while the Ni–C(41) bond length of 1.8853(13) Å. Additionally, the Ni–N(2) bond length in **5** of 2.0314(11) Å is longer than the corresponding distance in **4**.

In marked contrast, use of two equivalents of $Ni(COD)_2$ in reactions with the ligands **1**, **2** and $HN(1,2\text{-}C_6H_4N{=}PPh_3)$ **6** with bromobenzene afforded nearly quantitative yields of new bimetallic complexes. In these cases, ligands **1**, **2** and **6** afforded the blue/purple, blue and brown species formulated as $N(1,2\text{-}CH_2CH_2N{=}PR_3)_2Ni_2Br_3$ (R = Ph **7**, R = *i*Pr **8**) and $N(1,2\text{-}C_6H_4N{=}PPh_3)Ni_2Br_3$ **9**. These species exhibited magnetic moments of 4.96, 4.43 BM and 5.02 BM, respectively. In the case of the reaction of ligand **2**, the paramagnetic complex **8** was unambiguously identified by X-ray crystallography (Fig. 2). These data revealed that **8** is a bimetallic species in which two Ni centers adopt pseudo-tetrahedral geometries and are bridged by the central amide of the ligand and a bromide atom. In addition, the coordination spheres of the Ni atoms are completed by a single phosphinimine N and a terminal bromide atom. The average bridging Ni–N(2) bond lengths were found to be 1.981(4) Å, while the Ni(1)–N(2)–Ni(2) angle is 99.75(17)°. The Ni phosphinimine-nitrogen bond lengths Ni(1)–N(1) and Ni(2)–N(3) were determined to be 1.961(4) Å and 1.965(4) Å respectively. The bridging Ni–Br bond distances were observed to be 2.4879(8) Å and 2.5054(8) Å, significantly longer than the terminal Ni–Br distances of 2.3580(8) Å and 2.3445(9) Å.

We have recently reported the analogous compound $N(1,2\text{-}C_6H_4N{=}PPh_3)Ni_2Cl_3$ bearing ligand **6**. This species was obtained by deprotonating the ligand with a base prior to its reaction with the Ni(II) source.[22] The Ni–N bond lengths in **8** are shorter than that of $N(1,2\text{-}C_6H_4N{=}PPh_3)Ni_2Cl_3$ and are consistent with ligand **2** being more electron donating as a result of the alkyl substituents on P.

In each of the reactions affording **7–9**, GC-MS analysis of the reaction mixture indicated the formation of biphenyl ($C_{12}H_{10}$) and benzene as the organic byproducts. It is also noteworthy that addition of $Ni(COD)_2$ to a solution of **5** in C_6H_5Br afford the blue/purple dinuclear complex **7**. These observations were consistent with consecutive oxidative additions of C_6H_5Br to Ni, suggesting a dinuclear Ni(II) intermediate that undergoes subsequent loss of the biaryl and arene (Scheme 2).



Scheme 2 Plausible intermediate en route to **7–9**.

In summary, we have shown that oxidative addition provides a convenient route to both aryl-monometallic Ni complexes containing amino-*bis*-phosphinimine ligands. These species are readily converted to related bimetallic amido-*bis*-phosphinimine complexes *via* reaction with additional arylhalide and $Ni(COD)_2$. An examination of the reactivity of these and related compounds is the current focus of our efforts.

Financial support of NSERC of Canada is gratefully acknowledged. DWS is grateful for the award of a Canada Research Chair and a Killam Research Fellowship for 2009–2011.

Experimental

General remarks

All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing an Innovative Technology glove box and a Schlenk vacuum-line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, toluene, CH_2Cl_2), or were dried over the appropriate agents and distilled. All solvents were thoroughly degassed after purification (repeated freeze-pump-thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly (CD_2Cl_2). Toluene and pentane were stored over potassium mirrors, while bromobenzene and dichloromethane were stored over 4 Å molecular sieves. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C on Varian 400 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residue solvent signal (^1H, ^{13}C) or relative to an external standard (^{31}P: 85% H_3PO_4). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Samples for GC-MS were filtered through activated Al_2O_3 prior to injection. GC-MS analysis were performed using an Agilent 7890A GC system coupled to a Agilent 5974C Mass Spectrometer.

Synthesis of $[HN(CH_2CH_2N{=}PPh_3)_2Ni\text{-}C_6H_4F][X]$ X = Cl 3, $[PF_6]$ 4 $[HN(CH_2CH_2N{=}PR_3)_2Ni\text{-}C_6H_5][Br]$ R = Ph 5

Compounds **3** and **5** were prepared in analogous manner, employing the reagents 1,2-chlorofluorobenzene and bromobenzene respectively. Thus, only one of these preparations is detailed. 350 mg (0.481 mmol) of $HN(CH_2CH_2N{=}PPh_3)_2$ was added to 132 mg (0.479 mmol) of $Ni(cod)_2$ and 101 mg (0.773 mmol) of 1,2-chlorofluorobenzene in *ca.* 5 ml of THF. The mixture was stirred for one hour resulting in the formation of an orange precipitate. The solvent was decanted and the solid was washed with ether (2 × 2 ml) and dried in vacuo. The solid was dissolved in CH_2Cl_2 (*ca.* 4 ml), filtered through Celite and then the solvent was removed in vacuo. The orange solid was triturated in ether until a powder formed which was then dried in vacuo. Yield 350 mg (77%). In the case of **4**, subsequent salt methathesis was performed using $NaPF_6$ (31 mg, 0.184 mmol) added to **3** (100 mg, 0.123 mmol) in *ca.* 2 mL of CH_2Cl_2. The mixture was stirred overnight and was then filtered through Celite. 10 mL of ether was added dropwise to precipitate a purple solid that was triturated for The solvent was decanted and the solid was washed with 2 × 5 mL of ether and dried in vacuo.

3. Yield 350 mg (77%). ^1H NMR (400 MHz, $CDCl_3$) 7.70 (m, 12H, C_6H_5); 7.45 (m, 18 H, C_6H_5); 6.14 (broad s, 1H, N*H*); 5.79 (dd, 1H, C_6H_4F); 5.26 (t, 2H, $^3J_{HH} = 7.4$ Hz, C_6H_4F); 4.91 (broad s, 1H, C_6H_4F); 3.25 (m, 2H, CH_2); 2.80 (m, 4H, CH_2); 2.61 (m, 2H, CH_2). ^{31}P NMR (162 MHz, $CDCl_3$): 36.0. ^{19}F NMR (377 MHz, $CDCl_3$): -84.7. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 168.2 (d, C_6H_4F, $^1J_{CF}$ = 223.4 Hz),143.1 (d, C_6H_4F, $^2J_{CF}$ = 19.4 Hz), 133.4 (d, *C*H, J_{CP} = 9.8 Hz), 131.3 (*C*q), 128.4 (d, *C*H, J_{CP} = 12.6 Hz), 127.5 (d, Ar*C*, $^1J_{CP}$ = 100.1 Hz), 123.5 (d, C_6H_4F, J_{CF} = 7.2 Hz), 119.2 (C_6H_4F), 115.3 (d, *C*H, J_{PC} = 21 Hz), 110.6 (d, C_6H_4F, J_{PC} = 29 Hz), 50.6 (*C*H_2), 50.1 (d, J_{PC} = 13 Hz). Anal. Calcd. for $C_{46}H_{43}FClN_3NiP_2$: C, 67.96; H, 5.33; N, 5.17. Found: C, 66.77; H, 5.61; N, 5.43.

4. Yield: 109 mg (96%). ^1H NMR (400 MHz, $CDCl_3$): 7.65 (m, 12H), 7.49 (m, 18H), 5.84 (m, 1H), 5.32 (dt, 2H), 4.84 (s br, 1H), 3.36 (m, 3H, CH_2 and NH overlapping), 3.10 (m, 2H, CH_2), 2.62 (m, 4H, CH_2).^{31}P NMR (162 MHz, $CDCl_3$): 36.8. ^{19}F NMR (377 MHz, $CDCl_3$): −71.0 (d, J_{PF} = 714 Hz), −84.9. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 167.8 (d, C_6H_4F, $^1J_{CF}$ = 223.6 Hz), 143.0 (d, C_6H_4F, $^2J_{CF}$ = 18.9 Hz), 139.0 (*C*H), 133.1 (d, *C*H, J_{CP} = 9.8 Hz), 132.0 (*C*q), 128.5 (d, *C*H, J_{CP} = 12.6 Hz), 127.1 (d, Ar*C*, $^1J_{CP}$ = 100.8 Hz), 123.8 (d, C_6H_4F, J_{CF} = 7.4 Hz), 119.6 (br, C_6H_4F), 110.7 (d, *C*H, J_{PC} = 29.7 Hz), 50.0 (*C*H_2), 49.9 (d, *C*H_2, J_{PC} = 13 Hz). Anal. Calcd. for $C_{46}H_{43}F_7ClN_3NiP_2$: C, 59.89; H, 4.70; N, 4.56. Found: C, 58.86; H, 4.77; N, 4.29.

5. Yield: 124 mg (84%) ^1H NMR (400 MHz, $CDCl_3$): 7.64 (t br, 12H, Ar*H*), 7.45 (m, 18H, Ar*H*), 5.85 (t br, 1H, C_6H_5), 5.62 (s br, 2H, C_6H_5), 5.30 (s br, 1H, N*H* + C_6H_5), 3.24 (m, 2H, CH_2), 2.81 (m br, 4H, CH_2), 2.69 (s br, 2H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 35.2. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): 141.4 (Ni-C_6H_5), 138.6 (Ni-C_6H_5), 133.5 (d, ArC, J_{CP} = 9.7 Hz), 131.7(Ar*C*), 128.4 (d, Ar*C*, J_{CP} = 12.5 Hz), 127.7 (d, Ar*C*q, $^1J_{CP}$ = 100.7 Hz), 122.9 (Ni-C_6H_5), 120.2 (Ni-C_6H_5), 50.4 (*C*H_2), 49.9 (d, *C*H_2, $^2J_{CP}$ = 12.3 Hz). Anal. Calcd. for $C_{46}H_{44}BrN_3NiP_2$: C, 65.82; H, 5.28; N, 5.01. Found: C, 62.52;‡ H, 5.26; N, 4.84.

Synthesis of $N(1,2\text{-}CH_2CH_2N{=}PR_3)_2Ni_2Br_3$ R = Ph 7, R = ^{i}Pr 8 and $N(1,2\text{-}C_6H_4N{=}PPh_3)Ni_2Br_3$ 9

These compounds were prepared in a similar fashion, thus only one preparation is detailed. $Ni(COD)_2$ (0.100 g, 0.364 mmol) was added to a solution of **1** (0.113 g, 0.182 mmol) in 3 ml C_6H_5Br while stirring. A color change from yellow to red was observed after a few hours and to brown when left stirring overnight. The solution was filtered and cooled to −35 °C before adding cold ether affording **6**.

7. Blue/purple solid. Yield: 263 mg (74%) $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ: 50.1. μ_{eff} = 4.96 BM. Anal. Calcd. for $C_{40}H_{38}Br_3N_3Ni_2P_2$: C, 49.03; H, 3.91; N, 4.29. Found: C, 49.41; H, 4.34; N 4.41.

8. Blue solid. Yield: 66 g (72%). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ: 78.3. μ_{eff} = 4.43 BM. Anal. Calcd. for $C_{22}H_{50}N_3P_2Ni_2Br_3.C_6H_5Br$: C, 36.06; H, 5.94; N, 4.51. Found: C, 35.74; H, 6.03; N, 4.28.

9. Brown solid. Yield: 96 mg (80%), Anal. Calcd. for $C_{48}H_{38}Br_3N_3Ni_2P_2$: C, 53.59; H, 3.56; N, 3.91. Found: C, 53.43; H, 3.86; N,3.43. μ_{eff} = 5.02 BM.

Notes and references

‡ In this case, repeated attempts to obtain satisfactory analysis led to consistently low analysis for C. This was attributed to the formation of Ni_2C during combustion.

1 D. Milstein, *Top. Catal.*, 2010, **53**, 915–923.

2 J. I. van der Vlugt and J. N. H. Reek, *Angew. Chem., Int. Ed.*, 2009, **48**, 8832–8846.

3 J. M. Serrano-Becerra and D. Morales-Morales, *Curr. Org. Synth.*, 2009, **6**, 169–192.

4 D. Benito-Garagorri and K. Kirchner, *Acc. Chem. Res.*, 2008, **41**, 201–213.
5 L.-C. Liang, P.-S. Chien and Y.-L. Huang, *J. Am. Chem. Soc.*, 2006, **128**, 15562–15563.
6 H. Fan, B. Fullmer, C. M. Pink and K. Caulton, G., *Angew. Chem., Int. Ed.*, 2008, **47**, 9112–9114.
7 M. Ingleson, H. Fan, M. Pink, J. Tomaszewski and K. G. Caulton, *J. Am. Chem. Soc.*, 2006, **128**, 1804–1805.
8 L. Fan, S. Parkin and O. V. Ozerov, *J. Am. Chem. Soc.*, 2005, **127**, 16772–16773.
9 S. Gatard, R. Çelenligil-Çetin, C. Guo, B. M. Foxman and O. V. Ozerov, *J. Am. Chem. Soc.*, 2006, **128**, 2808–2809.
10 R. E. Douthwaite, J. Houghton and B. M. Kariuki, *Chem. Commun.*, 2004, 698–699.
11 M. Peters and R. Breinbauer, *Adv. Synth. Catal.*, 2008, **350**, 1791–1795.
12 M. Poyatos, P. Uriz, J. A. Mata, C. Claver, E. Fernandez and E. Peris, *Organometallics*, 2008, **27**, 2268–2272.
13 M. Moser, B. Wucher, D. Kunz and F. Rominger, *Organometallics*, 2007, **26**, 1024–1030.
14 M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree and E. Peris, *Organometallics*, 2003, **22**, 1110–1114.
15 S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller and R. H. Crabtree, *Organometallics*, 2001, **20**, 5485–5488.
16 A. A. Danopoulos, J. A. Wright and W. B. Motherwell, *Chem. Commun.*, 2005, 784–786.
17 D. Pugh, N. J. Wells, D. J. Evans and A. A. Danopoulos, *Dalton Trans.*, 2009, 7189–7195.
18 C. A. Wheaton and P. G. Hayes, *Chem. Commun.*, 2010, **46**, 8404–8406.
19 C. A. Wheaton and P. G. Hayes, *Dalton Trans.*, 2010, **39**, 3861–3869.
20 K. R. D. Johnson and P. G. Hayes, *Organometallics*, 2009, **28**, 6352–6361.
21 M. J. Sgro and D. W. Stephan, *Dalton Trans.*, 2011, **40**, 2419–2421.
22 R. Cariou, F. Dahcheh, T. W. Graham and D. W. Stephan, *Dalton Trans.*, 2011, **40**, 4919–4926.