A 1,1′-ferrocenyl phosphine-borane: synthesis, structure and evaluation in Rh-catalyzed hydroformylation†‡§

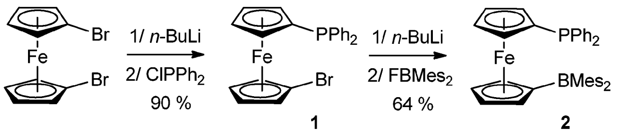
Magnus W. P. Bebbington,¶[a] Sébastien Bontemps,‖[a] Ghenwa Bouhadir,[a] Martin J. Hanton,[b] Robert P. Tooze,[b] Hendrick van Rensburg[b] and Didier Bourissou*[a]

Received (in Montpellier, France) 12th February 2010, Accepted 18th March 2010
DOI: 10.1039/c0nj00117a

The new ambiphilic ligand Ph_2P–(1,1′-ferrocenyl)–$BMes_2$, prepared by sequential lithiation/electrophilic trapping of 1,1′-dibromoferrocene, adopts a monomeric structure free of dative P → B and Fe → B interactions. This flexible phosphine-borane and the related *o*-phenylene bridged system have been evaluated in Rh-catalyzed hydroformylation.

There has been growing interest in ambiphilic derivatives over the last few years. The range of applications of phosphine-boranes (PB), for example, has grown considerably: *e.g.* π-conjugated systems,[1] ligands for transition metals able to adopt different coordination modes,[2] metal-free systems capable of H_2 activation and transfer,[3] precursors for photo-isomerizable systems,[4] and molecular probes for putative reaction intermediates.[5]

These developments have stimulated the preparation of an increasing variety of PB compounds differing in the number of accompanying donor buttresses, in the substitution pattern at phosphorus and boron, and in the nature of the spacer group, which permits the P–B distance and the rigidity of the system to be altered.[6] In this respect, purely organic linkers have been so far largely preferred, and only a few metallocene-bridged phosphine-boranes have been reported.[7–9] This includes the recent preparation of Ph_2P–(1,2-ferrocenyl)–$BMes_2$ (Mes = 2,4,6-trimethylphenyl).[9] Here, we report the synthesis and complete characterization of the position isomer Ph_2P–(1,1′-ferrocenyl)–$BMes_2$ **2**. This new phosphine-borane and the related rigid system Ph_2P–(*o*-phenylene)–$BMes_2$ **3**[10] have been evaluated in Rh-catalyzed hydroformylation of 1-octene.



Scheme 1

The target ligand **2** was prepared by sequential lithiation/electrophilic trapping of 1,1′-dibromoferrocene (Scheme 1), a very similar strategy to that used to prepare PB derivatives with conventional aromatic spacer groups. Borylation of the 1-bromo,1′-diphenylphosphinoferrocene **1**[11] afforded **2**, which was isolated as a purple powder after work up (64% yield). The ^{31}P NMR chemical shift for **2** (δ = −17.5 ppm) is very similar to that of **1** (δ = −18.1 ppm), and the ^{11}B NMR chemical shift (δ = 84.7 ppm) is in the typical range for a free triarylborane, suggesting a monomeric structure without P → B interaction.[12] This was unambiguously confirmed by an X-ray diffraction study (Fig. 1).** Despite the free rotation of the two Cp rings, the phosphorus and boron groups do not position themselves *anti* to one another, but even so they are still shifted markedly from an eclipsed arrangement (the C1P axis is rotated by 45.2° with respect to the C6B axis). Due to steric repulsion of the two bulky functional substituents, the two Cp rings are not exactly parallel (tilt angle = 7.8°). The large PB distance (4.87 Å, compared with 3.75 Å for the sum of the van der Waals radii),[13] and the planar environment around boron (the sum of CBC bond angles ΣB_α = 359.7°) rule out any significant P → B interaction. The absence of any

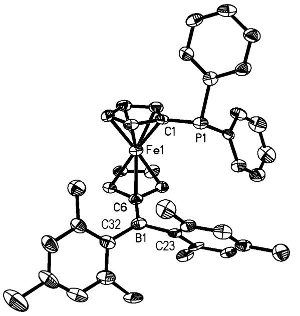


Fig. 1 Molecular view of **2** in the solid state (thermal ellipsoids at 50% probability). The phenyl and mesityl groups are simplified. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–P(1) 1.814(6), C(6)–B(1) 1.565(9), C(6)–B(1)–C(32) 122.4(5), C(6)–B(1)–C(23) 115.2(5), C(32)–B(1)–C(23) 122.1(5).

---

[a] *Université de Toulouse, UPS, LHFA, and CNRS, LHFA UMR 5069, 118 route de Narbonne, 31062 Toulouse, France. E-mail: dbouriss@chimie.ups-tlse.fr; Fax: +33 5-6155-8204; Tel: +33 (0)561557737*
[b] *Sasol Technology UK, Purdie Building, North Haugh, St Andrews, UK KY16 9ST*

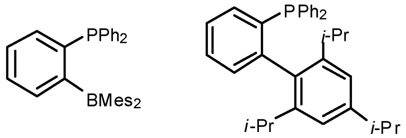
† Dedicated to the memory of Pascal Le Floch, a brilliant scientist and a great person.

‡ This article is part of a themed issue on Main Group chemistry.

§ Electronic supplementary information (ESI) available: Experimental details and characterization data for **2**. CCDC reference number 766316. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00117a

¶ Present address: School of Engineering and Physical Sciences, William Perkin Building, Heriot-Watt University, Edinburgh EH14 4AS, UK.

‖ Present address: CNRS, LCC, 205 route de Narbonne and Université de Toulouse, UPS, INPT, 31077 Toulouse, France.



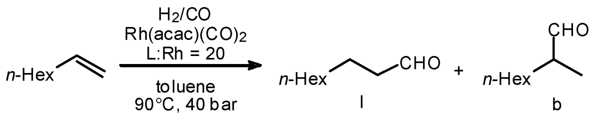
3 4

Chart 1

Fe → B interaction is also apparent from the long FeB distance (3.37 Å) and from the slight deviation of the $C_{ipso}B$ bond out of the plane of the Cp ring (by 7°).[14]

Until now, phosphine-boranes and related ambiphilic ligands have only been rarely evaluated in transition metal-mediated catalysis.[7,8,15,16] Here, we decided to study the rhodium-catalyzed hydroformylation of 1-octene and evaluated both **2** and the related phosphine-borane Ph_2P–(*o*-phenylene)–$BMes_2$ **3** described previously (Chart 1).[10] The reactions were performed in toluene at 90 °C and 40 bar of syngas with $[Rh(acac)(CO)_2]$, 20 equiv. of the ligand and 1-octene : Rh ratio ≈ 4000. With the flexible ligand **2**, the rhodium concentration was fixed at 0.5 mM in order to maintain the temperature at 90 °C. Under these conditions, complete conversion was reached in about 45 min (TOF 6400 h^{-1}) and the linear product was obtained with 72% selectivity. The related borane-free ligand, namely diphenylphosphinoferrocene, afforded the same rate and product distribution within experimental error (Table 1). This indicates that the $BMes_2$ group of **2** does not play any role in this case, most probably as the result of the flexibility of the 1,1′-ferrocenyl spacer. The properties of the related rigid phosphine-borane **3** were then evaluated in order to assess the influence of the linker. The 1-octene was completely consumed within about 150 min under the same conditions (except for [Rh] = 1 mM and 1-octene : Rh ≈ 2000) to afford a 54 : 46 mixture of linear and branched aldehydes. Thus, the presence of a $BMes_2$ group maintained in close proximity to the metal coordination sphere induces a decrease of both activity and selectivity. In order to determine whether the influence of the $BMes_2$ group was essentially steric or electronic in origin, the related sterically encumbered Buchwald-type biarylphosphine **4**[17] was tested under the same conditions.[18] Quasi-identical rates (TOF ≈ 1700–1800 h^{-1}) and product distributions (l : b 1.2–1.3) were found for both ligands (Table 1), suggesting that the $BMes_2$ group of **3** does not participate as a Lewis acid, but rather as a sterically demanding substituent.[20]

Table 1 Catalytic results for the hydroformylation of 1-octene. Reactions were carried out in toluene at 90 °C and 40 bar (1 : 1 feed syngas)



Ligand	TOF/h^{-1} [c]	K/h^{-1}	l : b[f]	Linearity (%)
2[a]	6400[d]	2.74	2.5	72
$FcPPh_2$[a]	6240[d]	2.57	2.6	73
3[b]	1700[e]	1.56	1.2	41
4[b]	1785[e]	1.78	1.3	46

[a] With [Rh] = 0.5 mM. [b] With [Rh] = 1 mM. [c] Average turnover frequency. [d] Calculated from 0 to 30 min. [e] Calculated from 0 to 60 min. [f] Linear to branched product distribution.

In conclusion, the phosphine-borane Ph_2P–(1,1′-ferrocenyl)–$BMes_2$ **2** has been prepared and characterized both spectroscopically and crystallographically. Precatalysts based on the combination of this new ambiphilic ligand or the related system Ph_2P–(*o*-phenylene)–$BMes_2$ **3** with $[Rh(acac)(CO)_2]_2$ promote the hydroformylation of 1-octene. The higher activity and selectivity in favor of the linear product are found with the flexible 1,1′-ferrocenyl *vs.* *o*-phenylene bridge. The phosphine-borane **3** and Buchwald-type biarylphosphine **4** were shown to behave very similarly, and future investigations will seek to compare the properties of these two classes of ligands in other transformations such as Pd-catalyzed cross-coupling reactions.

Experimental

General considerations

All reactions were performed using standard Schlenk techniques under an Argon atmosphere. NMR spectra were recorded at 293 K on a Bruker Avance 300 spectrometer. Chemical shifts are expressed with a positive sign, in parts per million, relative to residual ^1H (7.24 ppm) and ^{13}C (77.16 ppm) solvent signals and external $BF_3{\cdot}OEt_2$ (0 ppm) and 85% H_3PO_4 (0 ppm), respectively. The mass spectrum was recorded on a Hewlett Packard 5989A apparatus. Pentane was dried over CaH_2, tetrahydrofuran and toluene over sodium and distilled prior to use. All organic reagents were obtained from commercial sources and used as received. The 1,1′-dibromoferrocene,[11a] 1-bromo,1′-diphenylphosphinoferrocene **1**,[11b] 1-dimesitylboryl-2-diphenylphosphinobenzene[10] and biaryl diphenylphosphine ligand **4**[17] were prepared according to literature procedures.

Preparation of 1-dimesitylboryl-1′-diphenylphosphinoferrocene (2)

A solution of *n*-butyllithium (1.4 M in hexanes, 357 μL, 0.50 mmol) was added dropwise to a solution of 1-bromo-1′-diphenylphosphinoferrocene (224 mg, 0.50 mmol) in THF (2.5 mL) at −70 °C. After 10 min, a yellow precipitate appeared. After a further hour at this temperature, a solution of Mes_2BF (135 mg, 0.50 mmol) in THF (1 mL) was added dropwise. The mixture was then brought to room temperature over 30 min and the solvent was then removed at reduced pressure. The residue was dissolved in toluene (3 mL) and filtered by cannula to remove Li salts. The product **2** was recrystallised at −40 °C from pentane and isolated as a purple powder (198 mg, 64% yield). Mp 155–156 °C (dec.). ^1H NMR (300.1 MHz, $CDCl_3$): δ = 7.45–7.30 (m, 10H, H_{Ph}), 6.85 (s, 4H, H_{Mes}), 4.65 (s, 2H, H_{Ferr}), 4.50 (s, 2H, H_{Ferr}), 4.46 (s, 2H, H_{Ferr}), 4.08 (s, 2H, H_{Ferr}), 2.39 (s, 12H, *o*-CH_3), 2.34 (s, 6 H, *p*-CH_3); ^{13}C NMR: δ = 142.7 (C_q), 139.1 (C_q), 138.7 (d, J_{CP} = 10 Hz, C_q), 137.1 (C_q), 133.6 (CH), 133.4 (CH), 128.6 (CH), 128.2 (CH), 80.1 (CH), 77.3 (d, J_{CP} = 9 Hz, C_q), 75.4 (CH), 73.9 (d, J_{CP} = 14 Hz, CH), 72.5 (CH), 24.6 (*o*-CH_3), 21.1 (*p*-CH_3), the quaternary carbon atom of ferrocene bearing the boron atom is not observed; ^{11}B NMR (96.3 MHz, CDCl$_3$): δ = 84.7; ^{31}P NMR (121.5 MHz, CDCl$_3$) δ = −17.5; m/z (EI): 618 (M$^{+\bullet}$), 432 (M$^{+\bullet}$ − PPh$_2$), 368 (M$^{+\bullet}$ − BMes$_2$), 313 (M$^{+\bullet}$ − PPh$_2$-Mes).

Catalytic experiments

A 50 mL s/s autoclave equipped with gas entraining stirrer and sampling valve, was charged with [Rh(acac)(CO)$_2$] and placed under an atmosphere of N$_2$. Dry, de-gassed (d/d) toluene (10 mL) was then added. In a glovebox, a Schlenk was charged with ligand (L : Rh = 20), then transferred to Schlenk line. Toluene (d/d, 10 mL) was added to the ligand and the solution added to the autoclave under flow of N$_2$. At room temperature, the vessel was pressurised to 20 bar with 1 : 1 syngas, then heated to 90 °C. Once the reaction temperature was reached, 1-octene (d/d, 10 mL) was injected and the reactor pressure increased to 40 bar. During the reaction, the pressure in the vessel was maintained *via* a temperature compensated ballast vessel and the rate of catalysis was assessed by measuring the pressure drop in the ballast vessel which was logged with a polling frequency of 1 s. When gas uptake had ceased, the vessel was cooled to RT, the excess pressure vented, the vessel opened to air and a sample taken for GC-MS analysis. GC-MS analysis was performed on an Agilent Technologies 6890N GC system equipped with MDN12 (60 m × 0.25 mm × 0.25 μm) column, coupled to an Agilent Technologies 5973N MSD Mass Spectrometric instrument equipped with EI source.

Acknowledgements

Financial support from the Centre National de la Recherche Scientifique, the Université de Toulouse and the Agence Nationale de la Recherche (ANR-06-BLAN-0034) are gratefully acknowledged. D. B. thanks the COST action CM0802 PhoSciNet for supporting this work, and M. W. P. B. thanks the European Union for a Marie Curie Intra-european Postdoctoral Fellowship. We also thank Dr P. W. Dyer for helpful discussions and Dr H. Gornitzka for his assistance with the X-ray analysis.

Notes and references

** X-Ray crystal data for **2**: M = 618.35, monoclinic, space group $P2_1/c$, colourless blocks, a = 8.2786(11), b = 42.999(5), c = 9.2730(12) Å, β = 93.458(3)°, V = 3294.9(7) Å^3, Z = 4, T = 173 K.§

1 (*a*) Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz and L.-T. Cheng, *J. Chem. Soc., Chem. Commun.*, 1990, 1489–1492; (*b*) S. Sasaki, F. Murakami, M. Murakami, M. Watanabe, K. Kato, K. Sutoh and M. Yoshifuji, *J. Organomet. Chem.*, 2005, **690**, 2664–2672; (*c*) T. Agou, J. Kobayashi and T. Kawashima, *Org. Lett.*, 2005, **7**, 4373–4376; (*d*) A. Fukazawa, H. Yamada and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2008, **47**, 5582–5585.

2 (*a*) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu and D. Bourissou, *Angew. Chem., Int. Ed.*, 2006, **45**, 1611–1614; (*b*) S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 12056–12057; (*c*) D. J. H. Emslie, J. M. Blackwell, J. F. Britten and L. E. Harrington, *Organometallics*, 2006, **25**, 2412–2414; (*d*) S. R. Oakley, K. D. Parker, D. J. H. Emslie, I. Vargas-Baca, C. M. Robertson, L. E. Harrington and J. F. Britten, *Organometallics*, 2006, **25**, 5835–5838; (*e*) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron and D. Bourissou, *Angew. Chem., Int. Ed.*, 2007, **46**, 8583–8586; (*f*) S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu and D. Bourissou, *Chem.–Eur. J.*, 2008, **14**, 731–740; (*g*) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. Ozerov and D. Bourissou, *J. Am. Chem. Soc.*, 2008, **130**, 16729–16738; (*h*) A. Fischbach, P. R. Bazinet, R. Waterman and T. D. Tilley, *Organometallics*, 2008, **27**, 1135–1139; (*i*) J. Vergnaud, M. Grellier, G. Bouhadir, L. Vendier, S. Sabo-Etienne and D. Bourissou, *Organometallics*, 2008, **27**, 1140–1146; (*j*) D. J. H. Emslie, L. E. Harrington, H. A. Jenkins, C. M. Robertson and J. F. Britten, *Organometallics*, 2008, **27**, 5317–5325.

3 (*a*) G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126; (*b*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46–76.

4 M. W. P. Bebbington, S. Bontemps, G. Bouhadir and D. Bourissou, *Angew. Chem., Int. Ed.*, 2007, **46**, 3333–3336.

5 S. Moebs-Sanchez, G. Bouhadir, N. Saffon, L. Maron and D. Bourissou, *Chem. Commun.*, 2008, 3435–3437.

6 (*a*) H. Schmidbaur, M. Sigl and A. Schier, *J. Organomet. Chem.*, 1997, **529**, 323–327; (*b*) H. Braunschweig, R. Dirk and B. Ganter, *J. Organomet. Chem.*, 1997, **545–546**, 257–266; (*c*) S. Bontemps, G. Bouhadir, P. W. Dyer, K. Miqueu and D. Bourissou, *Inorg. Chem.*, 2007, **46**, 5149–5151; (*d*) M. W. P. Bebbington, G. Bouhadir and D. Bourissou, *Eur. J. Org. Chem.*, 2007, 4483–4486; (*e*) S. G. Thangavelu, K. E. Hocker, S. R. Cooke and C. N. Muhoro, *J. Organomet. Chem.*, 2008, **693**, 562–566; (*f*) S. Chikkali, S. Magens, D. Gudat, M. Nieger, I. Hartenbach and T. Schleid, *Eur. J. Inorg. Chem.*, 2008, 2207–2213; (*g*) P. Spies, R. Fröhlich, G. Kehr, G. Erker and S. Grimme, *Chem.–Eur. J.*, 2008, **14**, 333–343; (*h*) P. Spies, G. Kehr, K. Bergander, B. Wibbeling, R. Fröhlich and G. Erker, *Dalton Trans.*, 2009, 1534–1541.

7 1-Phosphino-1′-boryl-titanocenes and zirconocenes were found to be very efficient precatalysts for olefin polymerization: (*a*) K. A. Ostoja Starzewski, W. M. Kelly, A. Stumpf and D. Freitag, *Angew. Chem., Int. Ed.*, 1999, **38**, 2439–2443; (*b*) K. A. Ostoja Starzewski, B. S. Xin, N. Steinhauser, J. Schweer and J. Benet-Buchholz, *Angew. Chem., Int. Ed.*, 2006, **45**, 1799–1803; (*c*) K. A. Ostoja Starzewski, N. Steinhauser and B. S. Kin, *Macromolecules*, 2008, **41**, 4095.

8 1,1′-Bis(diphenylphosphino)ferrocenes featuring a pendant benzoxazaborolidine moiety were evaluated in Rh-catalyzed hydrogenation and hydroformylation of alkenes, with the aim of benefiting from secondary interactions between the pendant Lewis acid and the substrates: B. F. M. Kimmich, C. R. Landis and D. R. Powell, *Organometallics*, 1996, **15**, 4141–4146.

9 I. R. Morgan, A. Di Paolo, D. Vidovic, I. A. Fallis and S. Aldridge, *Chem. Commun.*, 2009, 7288–7290.

10 T. W. Hudnall, Y.-M. Kim, M. W. P. Bebbington, D. Bourissou and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2008, **130**, 10890–10891.

11 (*a*) T.-Y. Dong and L.-L. Lai, *J. Organomet. Chem.*, 1996, **509**, 131–134; (*b*) T.-Y. Dong, P.-H. Ho and C.-K. Chang, *J. Chin. Chem. Soc.*, 2000, **47**, 421–424.

12 Intramolecular P → B interactions were evidenced in phosphine-borane ligands featuring o-(C$_6$H$_4$),^{2b} (CH$_2$)$_n$ (n = 2–4)^{6a,g} and group 4 metallocene^{7} spacers.

13 S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871–885.

14 In ferrocenylboranes, the boron atom is generally tilted towards the metal center as the result of a delocalized through-space Fe→B interaction: (*a*) M. Scheibitz, M. Bolte, J. W. Bats, H. -W. Lerner, I. Nowik, R. H. Herber, A. Krapp, M. Lein, M. C. Holthausen and M. Wagner, *Chem.–Eur. J.*, 2005, **11**, 584–603; (*b*) K. Venkatasubbaiah, L. N. Zakharov, W. S. Kassel, A. L. Rheingold and F. Jäkle, *Angew. Chem., Int. Ed.*, 2005, **44**, 5428–5433; (*c*) H. Braunschweig, I. Fernández, G. Frenking and T. Kupfer, *Angew. Chem., Int. Ed.*, 2008, **47**, 1951–1954.

15 Boron-containing analogs of DIOP have been simultaneously and independently investigated by Kaganand Jacobsen: (*a*) A. Börner, J. Ward, K. Kortus and H. B. Kagan, *Tetrahedron: Asymmetry*, 1993, **4**, 2219–2228; (*b*) L. B. Fields and E. N. Jacobsen, *Tetrahedron: Asymmetry*, 1993, **4**, 2229–2240.

16 With the phosphino-alane ligand Me$_2$PCH$_2$AlMe$_2$, spectacular rate enhancements were observed in the Ni-catalyzed

dehydrogenative oligomerization of $PhSiH_3$: F.-G. Fontaine and D. Zargarian, *J. Am. Chem. Soc.*, 2004, **126**, 8786–8794.

17 T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 4685–4696.

18 Biaryl-bridged mono- and di-phosphines have been found to be extremely efficient ligands for the Rh-catalyzed hydroformylation of olefins,[19] but to the best of our knowledge, Buchwald-type biarylphosphines such as **4** have not been evaluated so far in this context.

19 (*a*) K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi and H. Takaya, *J. Am. Chem. Soc.*, 1997, **119**, 4413–4423; (*b*) Z. Hua, V. C. Vassar, H. Choi and I. Ojima, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 5411–5416; (*c*) C. J. Cobley, R. D. J. Froese, J. Klosin, C. Qin, G. T. Whiteker and K. A. Abboud, *Organometallics*, 2007, **26**, 2986–2999.

20 Secondary interactions between the π system of the Mes group and the metal may also intervene, by analogy with that demonstrated for biarylphosphines within various Pd complexes: (*a*) J. W. Faller and N. Sarantopoulos, *Organometallics*, 2004, **23**, 2008–2014; (*b*) S. D. Walker, T. E. Barder, J. R. Martinelli and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2004, **43**, 1871–1876; (*c*) T. E. Barder, M. R. Biscoe and S. L. Buchwald, *Organometallics*, 2007, **26**, 2183–2192; (*d*) B. P. Fors, D. A. Watson, M. R. Biscoe and S. L. Buchwald, *J. Am. Chem. Soc.*, 2008, **130**, 13552–13554; (*e*) D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. García-Fortanet, T. Kinzel and S. L. Buchwald, *Science*, 2009, **325**, 1661–1664.