Dalton Transactions

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 1957

Received 26th October 2013,
Accepted 25th November 2013

DOI: 10.1039/c3dt53025f

www.rsc.org/dalton

Non-symmetric diphosphines based on the imidazole scaffold: an unusual group interchange involving Pd–CH_3 and (imidazole)P–Ph cleavage†

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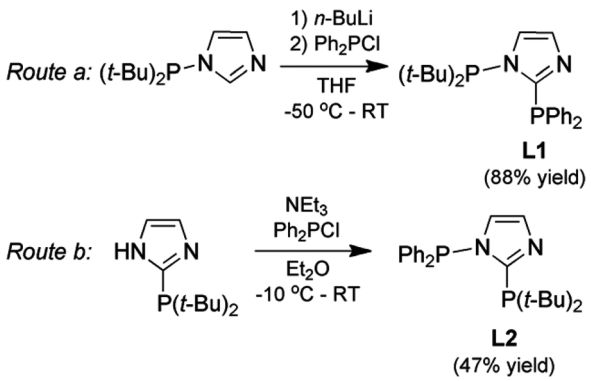
Two regioisomeric, non-symmetric $P^{C2}P^{N}$-imidazoles, *t*-$Bu_2PNCH{=}CHNC(PPh_2)$ (L1, P^{C2} = PPh_2, P^{N} = P(*t*-Bu)$_2$) and $Ph_2PNCH{=}CHNC[P(t\text{-}Bu)_2]$ (L2, P^{C2} = P(*t*-Bu)$_2$, P^{N} = PPh_2), respectively, show dramatic differences in the reactivity of the N-bound phosphine group; the L2 isomer is extremely sensitive to P–N bond cleavage by nucleophiles, and when coordinated to the PdCl(Me) fragment it undergoes facile interchange of one P^{N} phenyl with the methyl originating from Pd.

Functional phosphine ligands of the type $PR_n(Het)_{3-n}$, R = alkyl or aryl, Het = aza-heteroaryl, n = 0, 1, 2, are well studied for Het = *m*-pyridyl[1] (m = 2, 3, 4), but less so with other N-heteroaryls. $PR_n(m\text{-pyridyl})_{3-n}$ were used as ligands for the Pd-catalysed alkoxycarbonylation of propyne.[2] More recently 2-(di-alkyl- or -aryl-phosphino)-1*R*-imidazole ligands (R = H, alkyl or aryl) were employed for the hydration of alkynes,[3] the isomerisation of alkenes,[4] and for carbonylative cross-coupling reactions;[5] in the cases reported, catalytic performances were superior compared to non-heteroaryl analogues. Attempts to gain insight into the role of the N-heteroaryl group have pointed to its ability to be involved in the formation of small bite angle (P, N)-chelates with potential hemilability,[6] in intramolecular or intermolecular hydrogen bonding and to provide a basic site facilitating proton transfer during catalysis.[3c,7] Information on the donor characteristics of 2-(di-alkyl- or -aryl-phosphino)-1*R*-imidazoles is scarce but supports similarities (based on the electronic Tolman parameter) to analogous PR_2Ph ligands.[8] Recently, complexes with the chelating flexible 1,2-bis-(2-diphenylphosphino-imidazolyl)-benzene and 1,2-bis-(2-diphenylphosphino-imidazolium)-benzene have been reported.[9]

Ligands of the type 1-(di-*t*-butyl- or -aryl-phosphino)-imidazole, -imidazolium, and 1-(di-*t*-butylphosphino)-N-heterocyclic carbene (NHC), with a P–N covalent bond, belong to the broad class of aminophosphines[10] and have only recently become available,[11] attracting interest as ligands and as intermediates for the synthesis of imidazolium salts and NHCs.[11b,d,12]

Due to our long-standing efforts in the chemistry of ligands with P–N bonds[13] we set out to study the chemistry of the chelating regioisomeric diphosphines *t*-$Bu_2PNCH{=}CHNC(PPh_2)$ (**L1**) and $Ph_2PNCH{=}CHNC$-$[P(t\text{-}Bu)_2]$ (**L2**) shown in Scheme 1, which result from a swap of the PPh_2 and P(*t*-Bu)$_2$ donors between the 1- and 2-positions of the heterocycle. Such ligands offer a platform to explore rigid, chelating imidazole-based diphosphines, with one P–N and one P–C bond and thus one less donating, more π-acidic P donor and a more donating, less π-acidic P donor, respectively. There are two previous reports on bidentate $P^{C2}P^{N}$-imidazoles[11b,14] formed as undesired products from the coordination of 2-dimethylphosphanyl-imidazole on a W(0) carbonyl centre and the synthesis of *N*-phosphanyl-NHCs. More recently, the synthesis of the bis-(di-*t*-butyl) analogue of **L1** and **L2** has been reported.[15]

The high yielding and rational routes a and b (Scheme 1) can provide **L1** and **L2** in gram quantities and are based on the



Scheme 1 The ligands **L1** and **L2** and their synthesis.

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† Electronic supplementary information (ESI) available: Experimental details and full characterisation of all compounds; crystal structure data for **L1**, **L2**, **1b**, **2a**, **2b** and **2c**. CCDC 968367–968372. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53025f

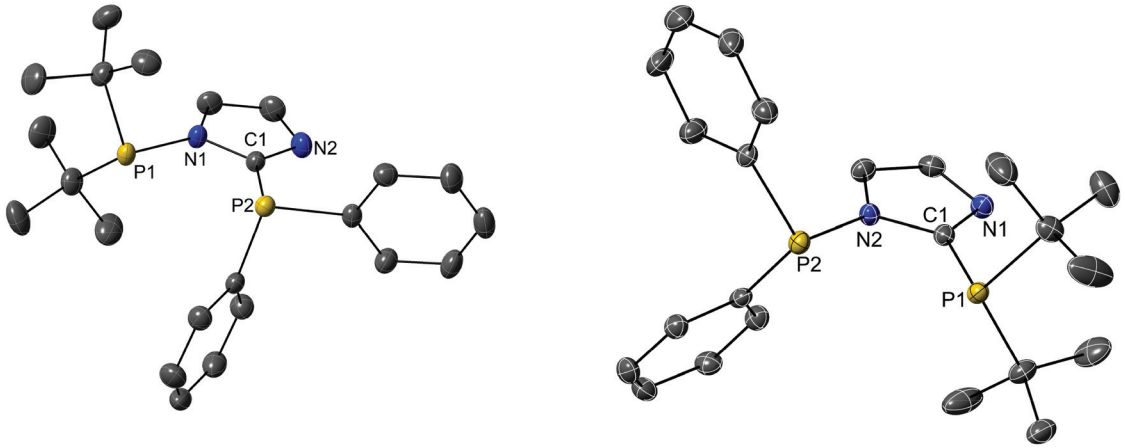


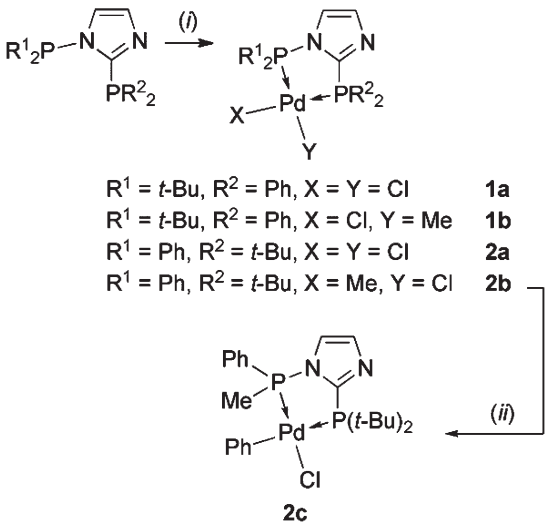
Fig. 1 Thermal ellipsoid representation (30% probability level) of the structure of **L1** (left) and **L2** (right). Selected bond lengths (Å) and angles [°]: for **L1**: P1–N1 1.763(1), N1–C1 1.389(2), C1–P2 1.828(1), C1–N2 1.321(2); N2–C1–N1 111.6(1), N2–C1–P2 126.1(1), N1–C1–P2 122.16(9), C1–N1–P1 122.17(9). For **L2**: P1–C1 1.828(3), C1–N1 1.321(3); C1–N2 1.396(4); N2–P2 1.751(2); N1–C1–N2 110.5(2), N1–C1–P1 128.4(2), N2–C1–P1 121.2(2), C1–N2–P2 125.6(2).

reaction of PPh_2Cl with C2 lithiated 1-(di-*tert*-butylphosphino)-imidazole and 2-(di-*tert*-butylphosphino)-imidazole. An indirect, less convenient formation of **L1** has recently been described.[11a] Interestingly, attempted preparation of **L2** by deprotonation of 1-(diphenylphosphino)imidazole with *n*-BuLi (in a sequence analogous to route a) led to the cleavage of the Ph_2P–N_{imid} bond and the formation of $Ph_2P(n\text{-Bu})$ (identified by ^{31}P NMR spectroscopy: δ −16 ppm). This demonstrated the weakness of the Ph_2P–N_{imid} bond (compared to $(t\text{-Bu})_2P$–N_{imid}) and its susceptibility to the presence of strong nucleophiles. Ligand **L1** is stable in air, while **L2** is very sensitive to both water and oxygen. Their different behaviour is not mirrored by major structural differences (*e.g.* P–N bond in **L1** (1.763(1) Å) and **L2** (1.751(2) Å) (see Fig. 1).

Preliminary comparative studies of the coordination chemistry of **L1** and **L2** gave some unexpected results (see Scheme 2).

All characterisation data point to the retaining of the integrity of the basic ligand framework after complexation both in solution and in the solid state (Fig. 2–4). The Pd centre in **2a** shows a typical distorted square planar coordination geometry; the ligand bite angle is 89.04(1)°. Slight shortening of the Ph_2P–*N* bond and reduction of the P2–N1–C1 angle are noticeable on coordination. There are significant differences between the two Pd–P bond distances, [Pd–PPh_2 (2.2070(4) *vs.* Pd–P(*t*-Bu)$_2$) (2.2850(4) Å], but not between the two Pd–Cl bonds.

Reaction of **L1** and **L2** with [PdCl(Me)(cod)] gave complexes **1b** and **2b** (see ESI†). The two doublets in ^{31}P NMR at δ 114.9 (d, $^{2+3}J_{PP}$ = 37.2 Hz, *P*(*t*-Bu)$_2$) and 27.4 (d, $^{2+3}J_{PP}$ = 37.2 Hz, *P*Ph_2), 85.9 (d, $^{2+3}J_{PP}$ = 35.4 Hz, *P*Ph_2) and 41.4 (d, $^{2+3}J_{PP}$ = 35.4 Hz, *P*(*t*-Bu)$_2$), respectively, in combination with the two doublets assignable to the Pd–C*H*$_3$, in the ^1H NMR spectrum due to ^3J-coupling of the methyl group protons with the P atoms are diagnostic for complex formation. Attempts to obtain X-ray quality crystals were straightforward for **1b** but were



$R^1 = t\text{-Bu}, R^2 = Ph, X = Y = Cl$ **1a**
$R^1 = t\text{-Bu}, R^2 = Ph, X = Cl, Y = Me$ **1b**
$R^1 = Ph, R^2 = t\text{-Bu}, X = Y = Cl$ **2a**
$R^1 = Ph, R^2 = t\text{-Bu}, X = Me, Y = Cl$ **2b**

2c

Scheme 2 Synthesis of palladium complexes **1a/b** and **2a/b/c**. Reaction conditions: (*i*) [$PdCl_2$(cod)] or [PdCl(Me)(cod)], THF; (*ii*) THF or CH_2Cl_2, room temperature, quantitative after 5 days.

complicated for **2b** due to a rearrangement reaction described below. Therefore, crystallisation of **2b** had to be carried out at −38 °C in the glove box. However, after successful isolation, the solids **1b** and **2b** are air-stable. The structures of **1b** and **2b** are shown in Fig. 3 and 4.

The coordination geometry around the Pd centre in both complexes is distorted square planar; the ligand bite angles are 88.62(2)° and 89.41(3)°, respectively. In both cases, the chloride is located *trans* to the PPh_2 group with Pd–Cl bond distances of 2.3792(7) and 2.369(1) Å and the *Pd*–*C*H_3 bond distances of 2.091(2) and 2.121(3) Å, respectively. There are significant differences between the two Pd–P bond lengths in each structure, [Pd–P(*t*-Bu)$_2$ 2.361(1) Å and Pd–PPh_2 2.1808(9) Å for **2b**; Pd–P(*t*-Bu)$_2$ 2.2072(6) Å and Pd–PPh_2 2.3632(6) Å for **1b**].

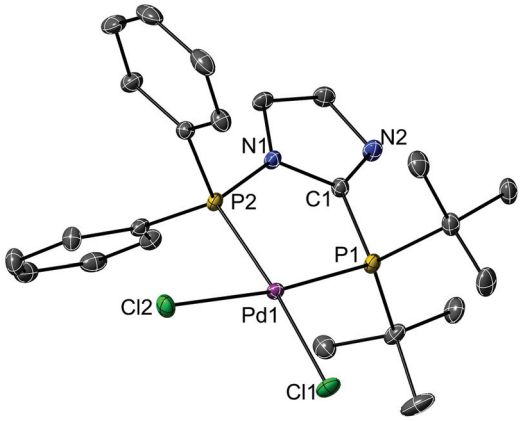


Fig. 2 Thermal ellipsoid representation (30% probability level) of the structure of **2a**. Selected bond lengths (Å) and angles [°]: Pd1–P1 2.2850(4), Pd1–P2 2.2070(4), Pd1–Cl1 2.3507(3), Pd1–Cl2 2.3634(4); P1–C1 1.831(2), C1–N1 1.378(2), C1–N2 1.316(2), N1–P2 1.721(1); Cl1–Pd1–Cl2 91.12(2), P1–Pd1–P2 89.04(1), P1–Pd1–Cl1 97.56(2), P2–Pd1–Cl1 173.34(2), P1–Pd1–Cl2 171.29(2), P2–Pd1–Cl2 82.28(1), N1–C1–N2 111.7(1), N1–C1–P1 117.7(1), N2–C1–P1 130.5(1), C1–N1–P2 121.9(1), C1–P1–Pd1 103.66(5), N1–P2–Pd1 107.26(4).

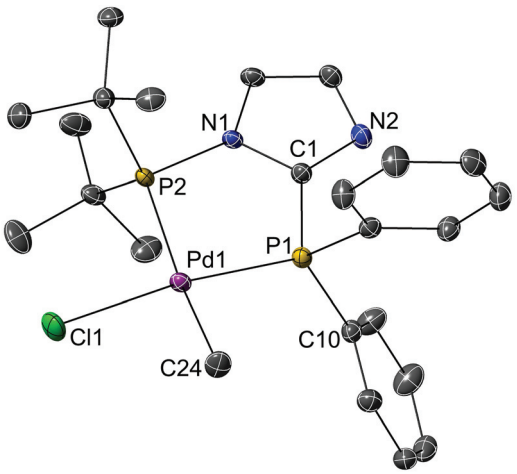


Fig. 3 Structure of **1b**. Selected bond lengths (Å) and angles [°]: Pd1–C24 2.091(2), Pd1–Cl1 2.3792(7), Pd1–P1 2.2072(6), Pd1–P2 2.3632(6), C1–N2 1.317(3), C1–N1 1.378(3), C1–P1 1.817(2), N1–P2 1.749(2); N2–C1–N1 112.7(2), N2–C1–P1 127.4(2), N1–C1–P1 119.8(2), C1–N1–P2 121.4(2), C1–P1–Pd1 106.36(8), N1–P2–Pd1 103.72(7), C24–Pd1–P1 88.73(8), C24–Pd1–P2 172.21(8), P1–Pd1–P2 88.62(2), C24–Pd1–Cl1 86.61(8), P1–Pd1–Cl1 172.57(3), P2–Pd1–Cl1 96.73(2).

Solutions of **2b** in THF or CH_2Cl_2 undergo a facile rearrangement ($t_{1/2} \sim 2$ days at room temperature), in which the methyl group bound to Pd exchanges with one of the Ph groups in PPh_2 to give the new complex **2c** cleanly and quantitatively after 5 days (Scheme 2). This could be confirmed by the appearance in the ^{31}P NMR of two new doublets at δ 72.1 (d, $^{2+3}J_{PP}$ = 35.3 Hz) and 42.0 (d, $^{2+3}J_{PP}$ = 35.3 Hz) and in the ^{1}H NMR the disappearance of the original two doublets

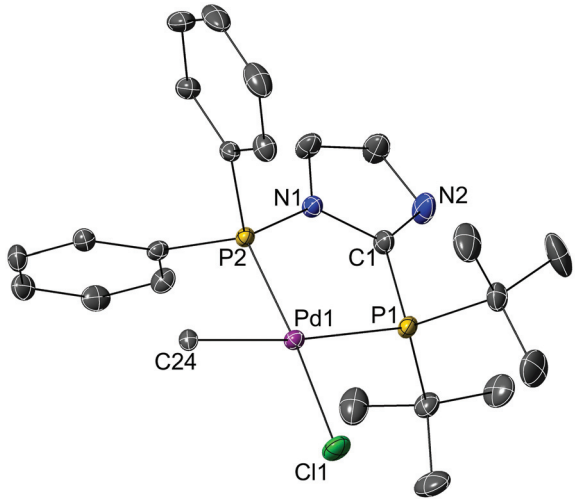


Fig. 4 Structure of **2b**. Selected bond lengths (Å) and angles [°]: Pd1–C24 2.121(3), Pd1–Cl1 2.369(1), Pd1–P1 2.361(1), Pd1–P2 2.1808(9), C1–N2 1.324(5), C1–N1 1.377(5), C1–P1 1.824(4), N1–P2 1.736(3); N2–C1–N1 111.4(3), N2–C1–P1 130.1(3), N1–C1–P1 118.5(3), C1–N1–P2 123.0(3), C1–P1–Pd1 101.8(1), N1–P2–Pd1 107.2(1), C24–Pd1–P2 84.5(1), C24–Pd1–P1 173.9(1), P2–Pd1–P1 89.41(3), C24–Pd1–Cl1 88.7(1), P2–Pd1–Cl1 172.78(4), P1–Pd1–Cl1 97.33(4).

assignable to the CH_3 and the appearance of one doublet at δ 2.04 (d, $^{2}J_{PH}$ = 9.7 Hz). The structure of the molecule is given in Fig. 5.

In **2c** the Pd is adopting a square planar geometry (ligand bite angle, 88.81(4)°). The chloride is still *trans* to P-phenyl and the Pd–Cl bond is longer compared to **2b**. The Pd–P bonds in **2c** are longer than those in **2b**. There is no significant difference between the N_{imid}–*P*PhMe and N_{imid}–*P*Ph_2 bond lengths.

Although the electronic characteristics of the P^N and P^C are not precisely known, it is reasonable to assume that the P^C-$(t\text{-Bu})_2$ is the strongest donor in the systems studied, and therefore should weaken in **2b** the Pd–Me bond that is *trans* to it; the rearrangement results in positioning the Ph (with stronger Pd–C_{aryl}) *trans* to the $P^C(t\text{Bu}_2)$. It also places the electron releasing Me on the electron deficient (and therefore electrophilic) P^N centre. A relevant rearrangement occurring in a Rh-methyl phosphine complex has been recently described,[16] and the implications of P–C/Pd–C bond cleavage/formation for homogeneous catalysis have been emphasised.[17] Recently the mechanistic diversity of the transition metal-mediated P–C/X exchange has been reviewed.[18] From the mechanistic scenario proposed, the intramolecular nucleophilic attack on the electrophilic P^N is plausible with the current ligand system. Our experimental observations on Pd–Me/P–Ph interchange may have relevance to reaction pathways or catalysts deactivation in *e.g.* cross-coupling reactions.

A. A. D. thanks the CNRS for support, the Région Alsace, the Département du Bas-Rhin and the Communauté Urbaine de Strasbourg for a Gutenberg Excellence Chair (2010–2011) and USIAS for a fellowship. We thank the CNRS, the MESR (Paris), the UdS, the China Scholarship Council (PhD grant to

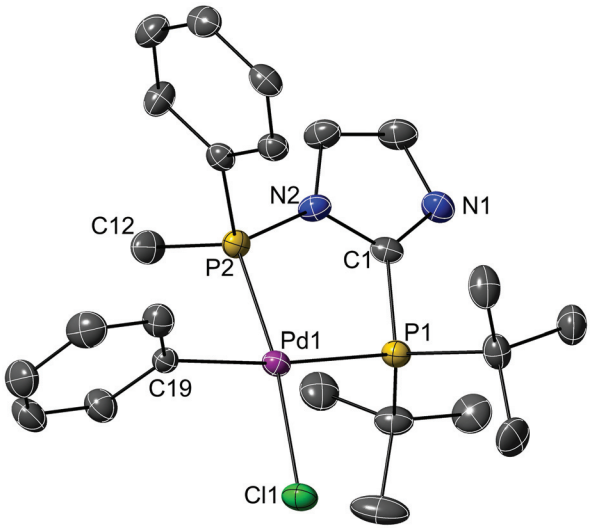


Fig. 5 Thermal ellipsoid representation (30% probability level) of the structure of **2c**. Selected bond lengths (Å) and angles [°]: Pd1–C19 2.089(4), Pd1–Cl1 2.380(1), Pd1–P1 2.378(1), Pd1–P2 2.198(1), C1–N1 1.323(5), C1–N2 1.375(5), C1–P1 1.820(4), C12–P2 1.802(4), N2–P2 1.729(4); N1–C1 N2 111.7(4), N1–C1–P1 130.6(4), N2–C1–P1 117.7(3), C1–N2–P2 124.0(3), C1–P1–Pd1 102.1(2), N2–P2–C12 103.7(2), N2–P2–Pd1 106.9(1), C12–P2–Pd1 115.2(2), C19–Pd1–P2 84.5(1), C19–Pd1–P1 173.2(1), P2–Pd1–P1 88.81(4), C19–Pd1–Cl1 88.0(1), P2–Pd1–Cl1 171.90(4), P1–Pd1–Cl1 98.53(4).

A.P.), and the ucFRC (http://www.icfrc.fr) for financial support and the Service de Radiocristallographie (Institut de Chimie, Strasbourg) for the determination of the crystal structures.

References

1 G. R. Newkome, *Chem. Rev.*, 1993, **93**, 2067.
2 E. Drent, W. W. Jager, J. J. Keijsper and F. G. M. Niele, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 2002.
3 (*a*) D. B. Grotjahn, C. D. Incarvito and A. L. Rheingold, *Angew. Chem., Int. Ed.*, 2001, **40**, 3884; (*b*) D. B. Grotjahn, Y. Gong, A. G. DiPasquale, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2006, **25**, 5693; (*c*) L. Hintermann, T. T. Dang, A. Labonne, T. Kribber, L. Xiao and P. Naumov, *Chem.–Eur. J.*, 2009, **15**, 7167.
4 D. B. Grotjahn, C. R. Larsen, J. L. Gustafson, R. Nair and A. Sharma, *J. Am. Chem. Soc.*, 2007, **129**, 9592.
5 X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 14596.
6 P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680.
7 (*a*) D. B. Grotjahn, *Dalton Trans.*, 2008, 6497; (*b*) E. Drent, P. Arnoldy and P. H. M. Budzelaar, *J. Organomet. Chem.*, 1994, **475**, 57; (*c*) E. Drent, P. Arnoldy and P. H. M. Budzelaar, *J. Organomet. Chem.*, 1993, **455**, 247; (*d*) G. Kiss, *Chem. Rev.*, 2001, **101**, 3435; (*e*) G. Franciò, R. Scopelliti, C. G. Arena, G. Bruno, D. Drommi and F. Faraone, *Organometallics*, 1998, **17**, 338.
8 D. B. Grotjahn, X. Zeng, A. L. Cooksy, W. S. Kassel, A. G. DiPasquale, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2007, **26**, 3385.
9 Y. Canac, N. Debono, C. Lepetit, C. Duhayon and R. Chauvin, *Inorg. Chem.*, 2011, **50**, 10810.
10 (*a*) D. Benito-Garagorri and K. Kirchner, *Acc. Chem. Res.*, 2008, **41**, 201; (*b*) J. Cheng, Y. Sun, F. Wang, M. Guo, J.-H. Xu, Y. Pan and Z. Zhang, *J. Org. Chem.*, 2004, **69**, 5428.
11 (*a*) P. Ai, A. Danopoulos, P. Braunstein and K. Monakhov, *Chem. Commun.*, 2014, **50**, 103; (*b*) A. P. Marchenko, H. N. Koidan, A. N. Huryeva, E. V. Zarudnitskii, A. A. Yurchenko and A. N. Kostyuk, *J. Org. Chem.*, 2010, **75**, 7141; (*c*) A. P. Marchenko, H. N. Koidan, I. I. Pervak, A. N. Huryeva, E. V. Zarudnitskii, A. A. Tolmachev and A. N. Kostyuk, *Tetrahedron Lett.*, 2012, **53**, 494; (*d*) P. Nägele, U. Herrlich, F. Rominger and P. Hofmann, *Organometallics*, 2012, **32**, 181.
12 (*a*) E. Kühnel, I. V. Shishkov, F. Rominger, T. Oeser and P. Hofmann, *Organometallics*, 2012, **31**, 8000; (*b*) A. P. Marchenko, H. N. Koidan, A. N. Hurieva, O. V. Gutov, A. N. Kostyuk, C. Tubaro, S. Lollo, A. Lanza, F. Nestola and A. Biffis, *Organometallics*, 2013, **32**, 718.
13 (*a*) S. Zhang, R. Pattacini and P. Braunstein, *Organometallics*, 2010, **29**, 6660; (*b*) R. Pattacini, G. Margraf, A. Messaoudi, N. Oberbeckmann-Winter and P. Braunstein, *Inorg. Chem.*, 2008, **47**, 9886; (*c*) P. Braunstein, *Chem. Rev.*, 2005, **106**, 134.
14 Z. Chen, H. W. Schmalle, T. Fox, O. Blacque and H. Berke, *J. Organomet. Chem.*, 2007, **692**, 4875.
15 M. Brill, L. Weigel, K. Rübenacker, F. Rominger and P. Hofmann, *Heidelberg Forum of Molecular Catalysis*, 28 June 2013, poster P60.
16 B. K. Shaw, B. O. Patrick and M. D. Fryzuk, *Organometallics*, 2012, **31**, 783.
17 (*a*) D. K. Morita, J. K. Stille and J. R. Norton, *J. Am. Chem. Soc.*, 1995, **117**, 8576; (*b*) F. E. Goodson, T. I. Wallow and B. M. Novak, *J. Am. Chem. Soc.*, 1997, **119**, 12441.
18 S. A. Macgregor, *Chem. Soc. Rev.*, 2007, **36**, 67.

