Dalton Transactions

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

Revised DT-COM-10-2013-053025

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

Pengfei Ai,[a] Andreas A. Danopoulos [a,b]* and Pierre Braunstein [a] *

[a] Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg Cedex (France). E-mail: danopoulos@unistra.fr, braunstein@unistra.fr
[b] Institute for Advanced Study, USIAS, Université de Strasbourg.

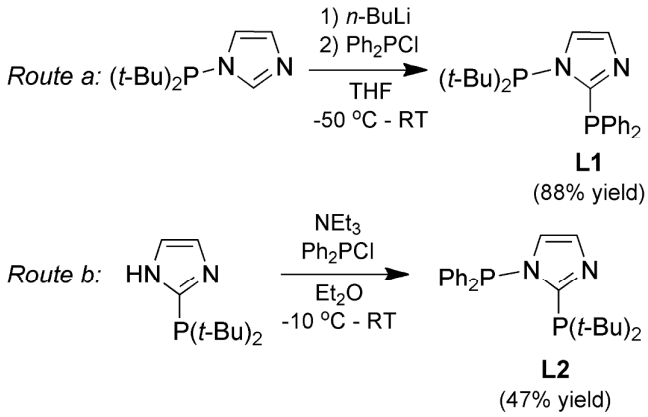
Abstract Two regioisomeric, nonsymmetric $P^{C2}P^{N}$-imidazoles, $t\text{-Bu}_2P\overline{NCH=CHNC}(PPh_2)$ (**L1**, P^{C2} = PPh_2, P^{N} = $P(t\text{-Bu})_2$); $Ph_2P\overline{NCH=CHNC}[P(t\text{-Bu})_2]$ (**L2**, P^{C2} = $P(t\text{-Bu})_2$, P^{N} = PPh_2), respectively, show dramatic differences 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.

† 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)

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-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, 11d, 12]

Due to our longstanding efforts in the chemistry of ligands with P-N bonds[13] we set out to study the chemistry of the chelating regioisomeric diphosphines $t\text{-Bu}_2\text{P}\overline{\text{NCH=CHNC}}(\text{PPh}_2)$ (**L1**) and $\text{Ph}_2\text{P}\overline{\text{NCH=CHNC}}[\text{P}(t\text{-Bu})_2]$ (**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-imidazol 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]



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

The high yielding and rational routes a and b (Scheme 1) can provide **L1** and **L2** in gram quantities and are based on the reaction of PPh_2Cl with C2 lithiated 1-(di-*tert*-butylphosphino)imidazole and 2-(di-*tert*-butylphosphino)-imidazole, respectively. 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 Ph_2P-N_{imid} bond and the formation of Ph_2P(*n*-Bu) (identified by ^{31}P NMR spectroscopy: δ -16 ppm). This demonstrated the weakness of 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 the 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).

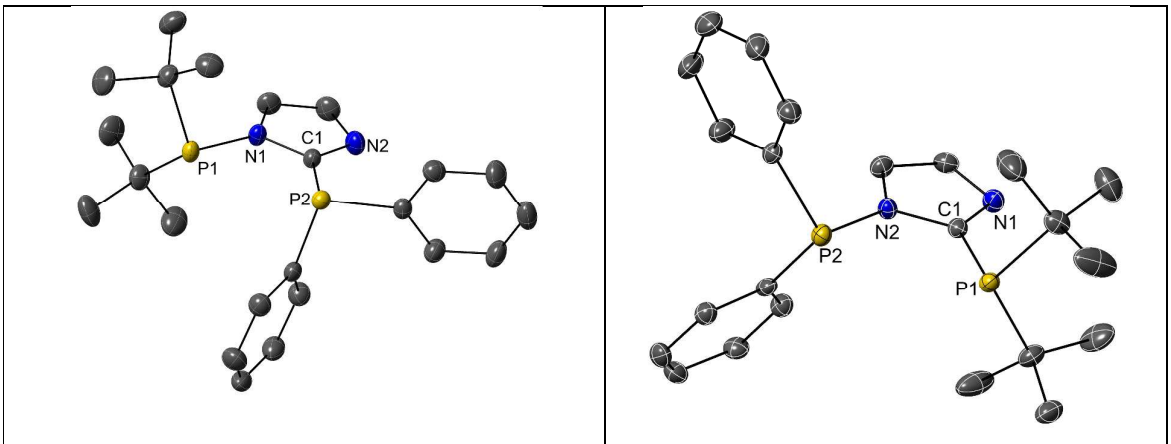
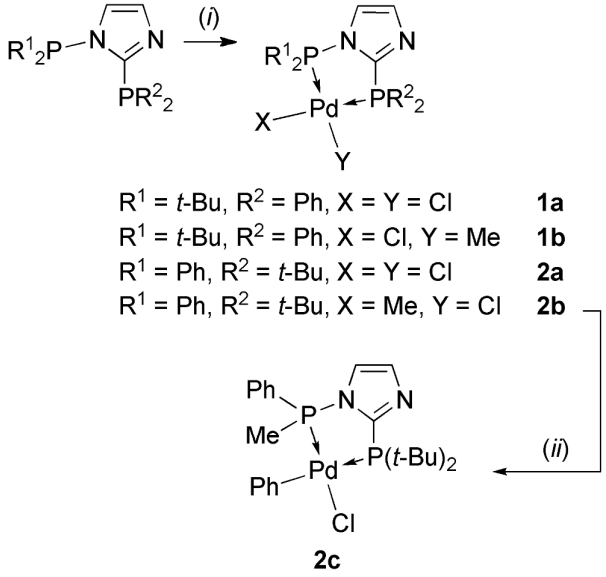


Figure 1. Thermal ellipsoid representation (30% probability level) of the structure of **L1** (left) and **L2** (right). Selected bond lengths (Å) and angles [°]: For **L1**: P1 N1 1.763(1), N1 C1 1.389(2), C1 P2 1.828(1), C1 N2 1.321(2); N2 C1 N1 111.6(1), N2 C1 P2 126.1(1), N1 C1 P2 122.16(9), C1 N1 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).

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



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

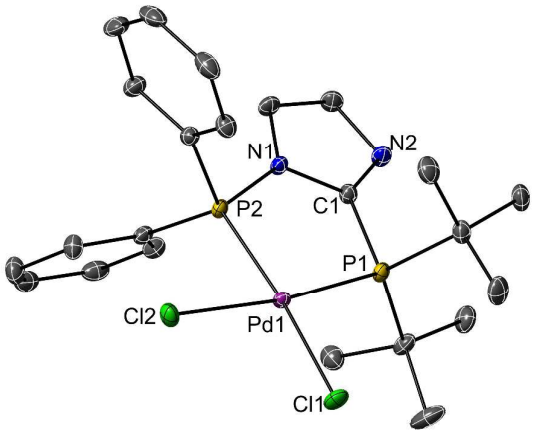


Figure 2. Thermal ellipsoid representation (30% probability level) of the structure of **2a**. Selected bond lengths (Å) and angles [°]: Pd1 P1 2.2850(4), Pd1 P2 2.2070(4), Pd1 Cl1 2.3507(3), Pd1 Cl2 2.3634(4); P1 C1 1.831(2), C1 N1 1.378(2), C1 N2 1.316(2), N1 P2 1.721(1); Cl1 Pd1 Cl2 91.12(2), P1 Pd1 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).

All characterisation data point to the retaining of the integrity of the basic ligand framework after complexation both in solution and the solid state. The Pd centre in **2a** shows 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 is noticeable on coordination. There is significant difference 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** wih [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-CH_3, in the ^{1}H-NMR spectrum due to ^3J-coupling of the methyl group protons with the P atoms are diagnostic for the complex formation. Attempts to obtain X-ray quality crystals were straightforward for **1b** but were complicated for **2b** due to a rearrangement reaction described below. Therefore, crystallisation of **2b** had to be carried out at -38 ^{o}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 Figs. 3 and 4.

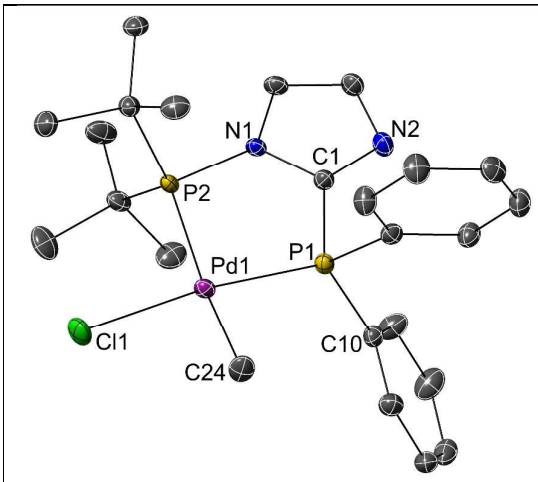


Figure 3. Structure of **1b**. Selected bond lengths (Å) and angles [°]: Pd1 C24 2.091(2), Pd1 Cl1 2.3792(7), Pd1 P1 2.2072(6), Pd1 P2 2.3632(6), C1 N2 1.317(3), C1 N1 1.378(3), C1 P1 1.817(2), N1 P2 1.749(2); N2 C1 N1 112.7(2), N2 C1 P1 127.4(2), N1 C1 P1 119.8(2), C1 N1 P2 121.4(2), C1 P1 Pd1 106.36(8),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

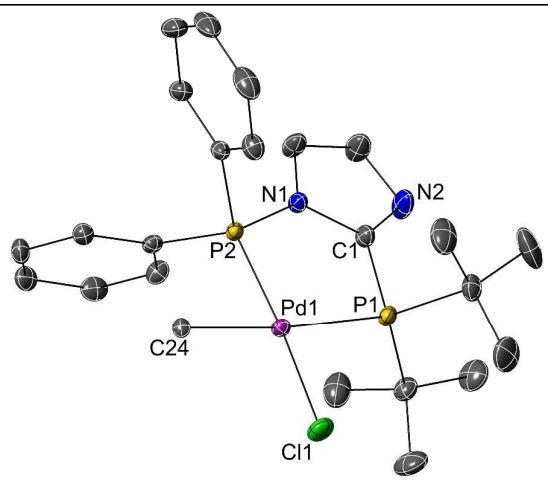


Figure 4. Structure of **2b**. Selected bond lengths (Å) and angles [°]: Pd1 C24 2.121(3), Pd1 Cl1 2.369(1), Pd1 P1 2.361(1), Pd1 P2 2.1808(9), C1 N2 1.324(5), C1 N1 1.377(5), C1 P1 1.824(4), N1 P2 1.736(3); N2 C1 N1 111.4(3), N2 C1 P1 130.1(3), N1 C1 P1 118.5(3), C1 N1 P2 123.0(3), C1 P1 Pd1 101.8(1),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

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 **1b**; Pd-P(*t*-Bu)$_2$ 2.2072(6) Å and Pd-PPh_2 2.3632(6) Å for **2b**].

Solutions of **2b** in THF or CH_2Cl_2 undergo a facile rearrangement ($t_{1/2}$ ~ 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 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.

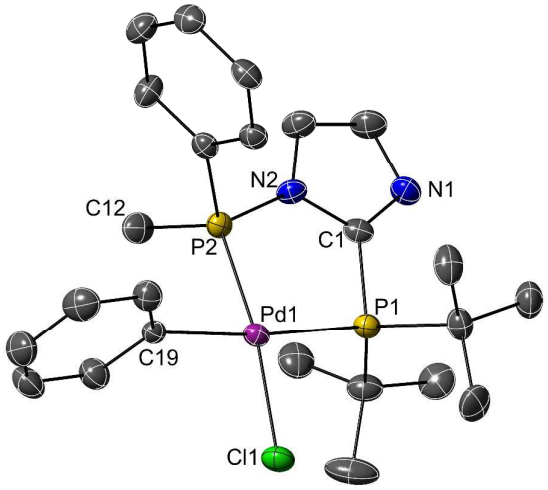


Figure 5. Thermal ellipsoid representation (30% probability level) of the structure of **2c**. Selected bond lengths (Å) and angles [°]: Pd1 C19 2.089(4), Pd1 Cl1 2.380(1), Pd1 P1 2.378(1), Pd1 P2 2.198(1), C1 N1 1.323(5), C1 N2 1.375(5), C1 P1 1.820(4), C12 P2 1.802(4), N2 P2 1.729(4); N1 C1 N2 111.7(4), 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).

In **2c** the Pd is adopting a square planar geometry (ligand bite angle 88.81(4)°). The chloride is still *trans* to PPh_2 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*-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*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 to homogeneous catalysis have been emphasised.[17] Recently the mechanistic diversity of the transition metal-mediated P-C/X exchange has been reviewed.[18] Out of the mechanistic scenario proposed, the intramolecular nucleophilic attack on the electrophilic P^N is plausible with the current ligand system. DFT calculations are in progress to rationalise our experimental observations on Pd-Me/P-Ph interchange which 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 A.P.), and the ucFRC (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, *Accounts 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.*, 2013, DOI: 10.1039/C3CC47370H; (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.

Two regioisomeric, nonsymmetric $P^{C2}P^{N}$-imidazoles, $t\text{-Bu}_2P\overline{NCH=CHNC}(PPh_2)$ (**L1**, P^{C2} = PPh_2, P^{N} = $P(t\text{-Bu})_2$); $Ph_2P\overline{NCH=CHNC}[P(t\text{-Bu})_2]$ (**L2**, $P^{C2} = P(t\text{-Bu})_2$, $P^{N} = PPh_2$), 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.