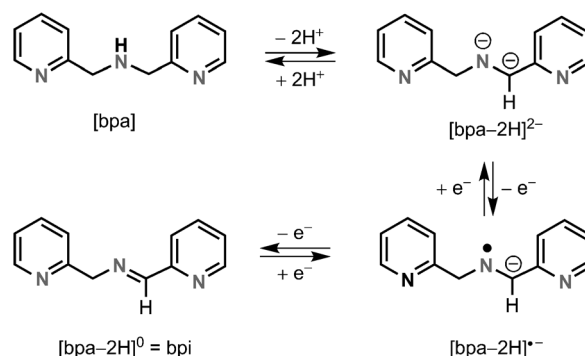


Developing Synthetic Approaches with Non-Innocent Metalloligands: Easy Access to Ir^I/Pd⁰ and Ir^I/Pd⁰/Ir^I Cores**

Cristina Tejel,* Laura Asensio, M. Pilar del Río, Bas de Bruin, José A. López, and Miguel A. Ciriano

The development of new, efficient, and selective synthetic methods is one of the major goals for future research in chemistry. An important and long-standing challenge in this field is to couple catalytic reactions with redox processes, which is expected to lead to interesting new reactions enabling (radical-type) transformations for substrates that are more difficult or impossible to activate otherwise. In this context, so-called redox-noninnocent ligands^[1,2] are expected to greatly facilitate access to new redox-coupled transformations. Key features that make these ligands unique are their ability to act as cooperative ligands^[3] and charge carriers in redox events,^[4] which is perfect for development of new redox-coupled catalytic transformations. The exploration of complexes with redox-active ligands aimed to facilitate electron-transfer (ET) processes to or from catalytically active transition metals is of crucial importance for such new developments. Among them, α -iminopyridine ligands, described for the first time by Vrieze and van Koten in 1983, are since long known to be redox-noninnocent.^[5] However, it took until 2008 before thorough investigations of the redox noninnocence of this class of ligands were complemented with detailed spectroscopic and X-ray crystallographic characterizations.^[6] Numerous examples of coordination compounds containing the neutral closed-shell form (L⁰) have been reported,^[7] some of which display catalytic activity.^[8] However, those incorporating the monoanionic radical form (L^{•−}) are restricted to a few first-row transition metals^[9] and lanthanides,^[10] while complexes with the closed-shell 2e[−]-reduced dianionic form (L^{2−}) are extremely rare.^[9a,11]

We recently reported a unique anionic iridium(I) complex containing the dianionic (bpa-2H)^{2−} ligand,^[12] which is the 2e[−]-reduced form of the α -iminopyridine ligand bpi (Scheme 1). We further investigated the redox pair (bpa-2



Scheme 1. Relationships between amine bpa, its doubly deprotonated form, monoanionic radical, and imine bpi.

H)^{2−}/(bpa-2H)^{•−} coordinated to iridium, and we hypothesized that a formal two-electron redox transformation from (bpa-2H)^{2−} to bpi occurs on binding rhodium(I) to produce a plausible rhodium(−I) species.^[13] Considering the importance of palladium in catalysis,^[14] and the very few studies on palladium chemistry incorporating noninnocent ligands,^[15] we decide to explore the potential reduction of Pd^{II} by the (bpa-2H)^{2−} ligand. Herein we report our success in developing this idea, which in addition opens new ways to prepare unprecedented heteronuclear Ir^I/Pd⁰ and Ir^I/Pd⁰/Ir^I complexes with an unusually π -coordinated α -iminopyridine ligand.

The doubly deprotonated bis(picoly)amine ligand (bpa-2H)^{2−} is not accessible from the free amine, but it can be generated if bpa is coordinated to a transition metal.^[11,12] Interestingly, the isolable iridium compound [Ir^I-(bpa-2H)^{2−}](cod)][−] (**1**[−]; cod = 1,5-cyclooctadiene) containing the closed-shell dianionic ligand can bind an additional transition metal to the ligand π system, while the redox activity of the complex makes it ideally suited to study ligand-to-metal ET processes. The pending pyridine arm of these complexes offers a valuable anchoring point for, for example, future electrode-modification purposes.

Reaction of **1**[−] with [PdCl₂(PPh₃)₂] took place immediately to give an intense red solution, from which heteronuclear complex [(cod)Ir^I(bpi)Pd⁰Cl(PPh₃)]**2** was isolated as red microcrystals in 70 % yield. In the X-ray structure of the dinuclear complex (Figure 1),^[16] the iridium(I) center displays a square-planar geometry with the metal atom bound to the central nitrogen atom N2, the nitrogen atom of one of the pyridine rings (N1), and a chelating cod ligand. The coordination geometry around palladium is best described as

[*] Dr. C. Tejel, L. Asensio, Dr. M. P. del Río, Dr. J. A. López, Prof. Dr. M. A. Ciriano
Instituto de Síntesis Química y Catálisis Homogénea (ISQCH)
CSIC—Universidad de Zaragoza
Pedro Cerbuna 12, 50009-Zaragoza (Spain)
E-mail: ctejel@unizar.es

Dr. B. de Bruin
Van't Hoff Institute for Molecular Sciences (HIMS)
University of Amsterdam (UvA)
Science Park 904, 1098 XH Amsterdam (The Netherlands)

[**] The generous financial support from MICINN/FEDER (Project CTQ2008-03860) and Gobierno de Aragón (GA, Project: PI 155/08) is gratefully acknowledged. L.A. and P.R. thank MICINN/FEDER for a fellowship and a post-doctoral contract, respectively.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201104045>.

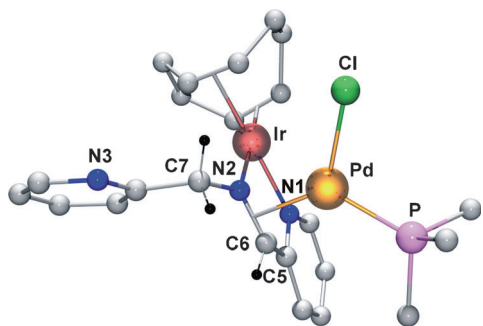


Figure 1. Structure (ORTEP at 50% probability) of dinuclear complex $[(\text{cod})\text{Ir}^{\text{I}}(\text{bpi})\text{Pd}^{\text{0}}\text{Cl}(\text{PPh}_3)]$ (**2**) (only the C_{ipso} atoms of the phenyl groups of PPh_3 are shown for clarity).

trigonal-planar, as defined by the metal atom, the phosphorus atom of triphenylphosphane, the chlorido ligand, and the η^2 -coordinated “imine” (C6-N2).^[17] Imines π -coordinated to palladium are uncommon with only four examples characterized crystallographically,^[18] which were mainly described as palladaazacyclopropanes. In our case, π coordination of the C6-N2 double bond to palladium is evident from Figure 1, from the trigonal-planar geometries around N2 and C6 (sp^2 hybridization), and from the short N2-C6 distance ($1.377(9) \text{ \AA}$) compared to the N2-C7 single bond ($1.489(10) \text{ \AA}$) in this compound. Nonetheless, the N2-C6 distance is longer than that expected for a neutral α -iminopyridine ligand (L^0 , Table 1) due to π backbonding from palladium.^[19] The $\text{C}_{\text{ipso}}-\text{C}_{\text{imine}}$ (C5-C6) and $\text{C}_{\text{ipso}}-\text{N}_{\text{pyridine}}$ (C5-N1) bond lengths fit well to those expected for α -iminopyridine ligands in their oxidized neutral form ($\text{L}^0 = \text{bpi}$ in this case).

Table 1: Characteristic bond lengths [$\text{\AA}$] for α -iminopyridine ligands (L)^[a] in different redox states and those in complexes **1**–**5**.^[b] **2**, and **5**.^[c]

	$\text{N}_{\text{imine}}-\text{C}_{\text{imine}}$	$\text{C}_{\text{ipso}}-\text{C}_{\text{imine}}$	$\text{C}_{\text{ipso}}-\text{N}_{\text{pyridine}}$
L^0	1.28	1.47	1.35
$\text{L}^{\cdot-}$	1.34	1.41	1.39
L^{2-}	1.45	1.36	1.42
1 [–]	1.383(13)	1.374(15)	1.406(13)
2	1.377(9)	1.470(10)	1.377(10)
5	1.392(10)	1.413(11)	1.378(10)

[a] Data taken from reference [6]. [b] Data taken from reference [12a].

[c] $\text{N}_{\text{imine}}-\text{C}_{\text{imine}}$, $\text{C}_{\text{ipso}}-\text{C}_{\text{imine}}$ and $\text{C}_{\text{ipso}}-\text{N}_{\text{pyridine}}$ correspond to N2-C6 , C5-C6 , and C5-N1 , respectively, for complexes **2** and **5**.

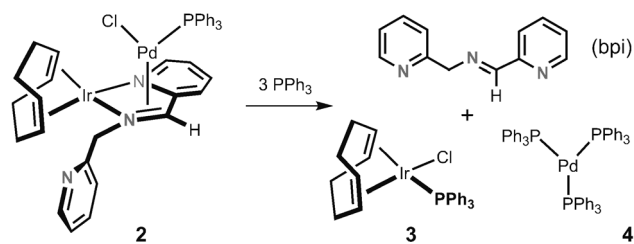
The structure of the palladium fragment is reminiscent of those of DFT-calculated tricoordinate anionic zerovalent palladium compounds $[\text{Pd}^0\text{X}(\text{PR}_3)_2]^-$, which were proposed by Amatore and Jutand to be the active species in Pd-catalyzed Heck and other cross-coupling reactions, but never isolated.^[20] The palladium center in **2** can be regarded as palladium(0), and in good agreement it adopts a trigonal-planar geometry, as expected for $\text{d}^{10}\text{-ML}_3$ complexes.

The above data suggest that coordination of palladium to **1**[–] triggers an internal two-electron transfer from the starting complex **1**[–] to the palladium(II) center. This ET

reaction transforms the dianionic ligand $(\text{bpa}-2\text{H})^{2-}(\text{L}^{2-})$ in **1**[–] into the oxidized ligand (L^0), the neutral imine $\text{PyCH}_2-\text{N}=\text{CHPy}$ (bpi). Simultaneously, palladium is formally reduced to a low-valent Pd^0 fragment that remains π -coordinated to the $\text{C}=\text{N}$ bond. Nevertheless, a palladaazacyclopropane resonance form could contribute in part to the electronic structure of **2** because of the expected strong π backdonation from electron-rich palladium(0) to the imine. Notably, the direction of the overall reaction regarding the ligand [from L^{2-} to L^0] is unique and opposite to the general trend in α -iminopyridine chemistry, in which ligands are reduced from the oxidized state L^0 to $\text{L}^{\cdot-}$ and to L^{2-} , with few cases reaching the dianionic form.

Complex $[(\text{cod})\text{Ir}^{\text{I}}(\text{bpi})\text{Pd}^{\text{0}}\text{Cl}(\text{PPh}_3)]$ (**2**) remains unaltered in THF and dichloromethane solution. The π coordination of palladium to the $\text{HC}=\text{N}$ bond is easily deduced from the coupling of the imine proton to the phosphorus atom ($J(\text{H},\text{P}) = 3.1 \text{ Hz}$). The imine carbon atom resonates at $\delta = 84.6 \text{ ppm}$ in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, which is substantially downfield shifted compared to the corresponding signals observed for the above-mentioned palladacycles ($\delta \approx 65 \text{ ppm}$). Additionally, the cod ligand bound to iridium gives just six resonances corresponding to its rotation (C_2 symmetry on the NMR timescale). This fluxional behavior, for which the slow-exchange spectrum cannot be observed on cooling to -80°C , can be explained by interaction of iridium with the nitrogen atom of the pendant pyridine ring. Coordination of N3 to iridium would facilitate a Berry pseudorotation accounting for the observed fluxional spectra. Similar behavior was found for the related square-planar $[\text{Ir}(\text{bpa}-\text{H})(\text{cod})]$, which also contains a pendant pyridine ring.^[12a] Other possibilities such as palladium changing π faces on the coordinated imine can be excluded, since this would lead to an averaged C_s -symmetric cod ligand on the NMR timescale.

Reaction of **2** with triphenylphosphane in $[\text{D}_6]$ benzene or $[\text{D}_8]$ THF leads to clean and quantitative fragmentation of the complex into the iridium(I) complex $[\text{Ir}^{\text{I}}\text{Cl}(\text{cod})(\text{PPh}_3)]$ (**3**), the palladium(0) complex $[\text{Pd}^0(\text{PPh}_3)_3]$ (**4**), and the free imine bpi (Scheme 2). Fast exchange of phosphane ligands between **3** and **4** prevented our unequivocally assigning the resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. However, crystallization of the reaction mixture gave yellow crystals of $[\text{Pd}^0(\text{PPh}_3)_3]$ (**4**), which were fully identified by X-ray diffraction (see Supporting Information). Notably, the whole reaction starting from **1**[–] can be considered as an example of how the non-



Scheme 2. Cleavage of complex **2** into $[\text{Ir}^{\text{I}}\text{Cl}(\text{cod})(\text{PPh}_3)]$ (**3**), $[\text{Pd}^0(\text{PPh}_3)_3]$ (**4**), and imine bpi by reaction with PPh_3 .

innocence of the ligand plays a key role in a full two-electron reduction of a late transition metal.

A second example in which complex $[1]^-$ acts as redox-noninnocent metalloligand is revealed in its reaction with $[PdCl_2(NCPh)_2]$. Two molar equivalents of complex $[1]^-$ are needed to consume all of the palladium precursor, and the product was found to be a highly insoluble black-green solid analyzing as $[Ir(PyCH_2NCHPy)(cod)]_2Pd$ (**5**). Single crystals of complex **5** were obtained by slow diffusion of THF solutions of $[1]^-$ and $[PdCl_2(NCPh)_2]$. Figure 2 shows the

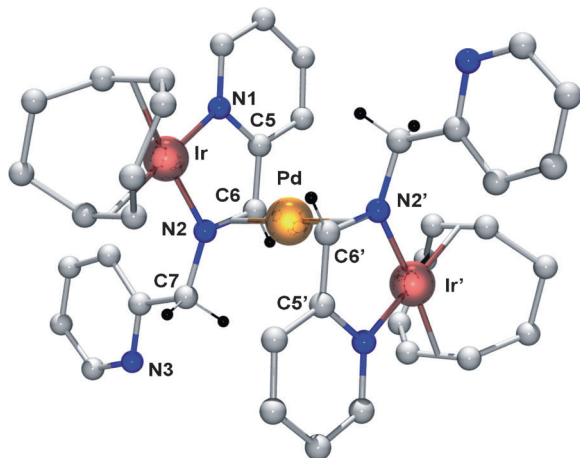
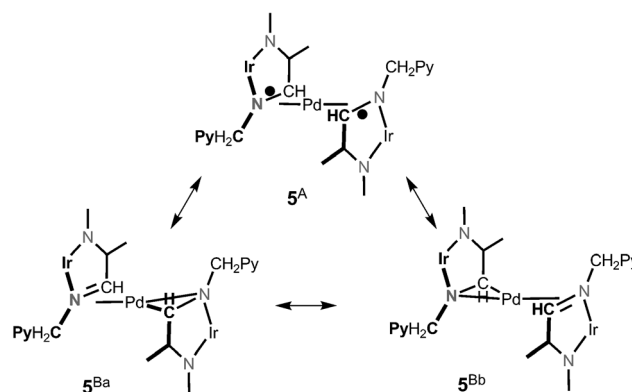


Figure 2. Structure (ORTEP at 50% probability) of heterotrinnuclear compound $[Ir(PyCH_2NCH_2Py)(cod)]_2Pd$ (**5**).

remarkable structure^[16] of **5**, which is a trinuclear compound in which two C6–N2 “imine” bonds, one from each iridium complex, coordinate in a π fashion to a palladium center in a fully linear arrangement. The relatively short Ir–Pd distances (2.8274(5) Å) suggest some kind of interaction between the metal centers, but this could just be the result of linear coordination of palladium by two bulky groups, which force the metal atoms to be in close proximity.

The description of the electronic structure of **5** is complicated. Assuming the palladium center to be zerovalent, as described above for **2**, two anionic iridium complexes are involved in this ET reaction, which allows different oxidation-state assignments of both ligands and metal centers. Identical contribution from both iridium metalloligands, each providing one electron, would in principle produce the biradical $[Ir^I\{(bpa-2H)^-\}(cod)]_2Pd^0$ (**5^A**, Scheme 3). This species would contain two $(bpa-2H)^-$ radicals, and could in principle have a triplet or a singlet biradical ground state. A closed-shell situation with fully paired electrons is another possibility. Such a closed-shell species would then be best described by the resonance structures **5^B** ($[Ir^I(cod)]_2\{(bpa-2H)^-\}(bpi)Pd^0$, Scheme 3), in which one ligand is oxidized by two electrons and the other is not. Both the biradical and the closed-shell possibilities are reasonable from a redox perspective.

Crystallographic bond lengths do not allow one to distinguish between an averaged $[Ir^I(cod)]_2\{(bpa-2H)^-\}(bpi)Pd^0$ description (**5^{Ba}**/**5^{Bb}**) and the symmetrical ligand-



Scheme 3. Possible resonance forms of trinuclear complex **5**.

based biradical possibility $[Ir^I\{(bpa-2H)^-\}(cod)]_2Pd^0$ (**5^A**), since both should have similar distances in the solid state. However, it is clear from the data in Table 1 that the $C_{ipso}-C_{imine}$ (C5–C6) and $C_{ipso}-N_{pyridine}$ (C5–N1) distances are slightly shorter and longer, respectively, relative to **2**, which suggests that the ligands in **5** are somewhat less oxidized than those in complex **2**. Accordingly, the $N_{imine}-C_{imine}$ (N2–C6) distance is longer in **5** than in **2**. Nonetheless, some caution should be taken when comparing these bond lengths (Table 1), because of the perturbation introduced by the additional C=N imine π coordination.^[19]

Unfortunately, complex **5** proved to be highly insoluble, and this prevented us studying its electronic structure in solution. Nonetheless, variable-temperature SQUID measurements on polycrystalline samples of **5** revealed it to be diamagnetic. Thus, plots of both the molar magnetization versus H and of $\chi_M T$ versus T gave straight lines with negative slope. Hence, complex **5** is clearly diamagnetic, and its electronic structure is best described by the closed-shell resonance structures of type **5^B** (Scheme 3). An open-shell biradical electronic structure of type $Pd(L^-)_2$ would be expected to result in paramagnetic behavior, as just reported for a related palladium complex.^[15a] Complex **5** is a rare example of a mixed-valent compound in which the mixed valency is based on the redox properties of the ligand.^[6]

In good agreement, DFT calculations show that **5** has a singlet ground state. The triplet state is substantially higher in energy, and all attempts to find a broken-symmetry open-shell singlet (singlet biradical) solution, both from the optimized singlet and triplet geometries, followed by full geometry optimizations, led simply to convergence to the same closed-shell singlet ground state (Table 2).

A similar situation occurs for complex **2**, which is in full agreement with the singlet ground state clearly established by NMR spectroscopy (sharp NMR resonances in the usual spectral range for diamagnetic compounds). The optimized triplet geometries are substantially higher in energy than the singlet ones, and their structures are different from that determined by X-ray diffraction (in particular, the Pd–C6 distances are clearly nonbonding in the triplet geometries) both at the BP86 and the b3-lyp levels of theory (see Table 2 and Supporting Information). Analysis of the frontier molecular orbitals of complexes **2** and **5** reveal a rather complicated

Table 2: Relative energies [kcal mol⁻¹] of the DFT-optimized geometries of **2** and **5** in their singlet and triplet states.

Complex	Closed-shell singlet b3-lyp ^[a] /BP86 ^[b]	Triplet ^[c] b3-lyp ^[a] /BP86 ^[b]
2	0/0	+ 21.3/ + 24.1
5	0/0	+ 17.8/ + 21.0

[a] Turbomole b3-lyp functional with def-TZVP basis set on all atoms; [b] BP86 functional with SV(P) basis set on all atoms. [c] The triplet geometries deviate strongly from the closed-shell ground-state geometries, especially at the b3-lyp TZVP level.

picture with several strongly delocalized orbitals (see Supporting Information).

In conclusion, we have described a unique synthetic route to π -imine Pd⁰ complexes from the redox-active metalloligand [Ir(bpa-2H)(cod)]⁻, in which (bpa-2H)²⁻ is the 2e⁻-reduced form of the α -iminopyridine ligand bpi. Subsequent 2e⁻ transfer from this L²⁻ ligand to palladium gives the neutral L⁰ valence state of the ligand, which remains π -coordinated to the thus formed palladium(0) center. Thus, the ligand redox couple (bpa-2H)²⁻/bpi coordinated to iridium is a versatile redox-active metalloligand that allows formation and stabilization of the unusual heterodinuclear Ir^I(bpi)Pd⁰ and heterotrinuclear Ir^I(bpi)Pd⁰{(bpa-2H)²⁻}Ir^I cores in complexes **2** and **5**. Furthermore, complex **5** is a rare example of a ligand-based two-electron mixed-valent complex wherein the two ligands have formally different redox states (L⁰ and L²⁻). Finally, in the light of the well-known catalytic activity of Pd⁰ in reactions such as cross-coupling, olefin polymerization, and oxidation, these results are highly promising for development of new redox-coupled catalytic reactions, which we are currently investigating.^[21]

Received: June 13, 2011

Published online: August 17, 2011

Keywords: electron transfer · iridium · noninnocent ligands · N ligands · palladium

- [1] Examples of general reviews: a) S. Sproules, K. Wieghardt, *Coord. Chem. Rev.* **2010**, *254*, 1358–1382; b) A. B. P. Lever, *Coord. Chem. Rev.* **2010**, *254*, 1397–1405; c) W. Kaim, B. Schwederski, *Coord. Chem. Rev.* **2010**, *254*, 1580–1588; d) P. Deplano, L. Pilia, D. Espa, M. L. Mercuri, A. Serpe, *Coord. Chem. Rev.* **2010**, *254*, 1434–1447; e) J. L. Boyer, J. Rochford, M.-K. Tsai, J. T. Muckerman, E. Fujita, *Coord. Chem. Rev.* **2010**, *254*, 309–330; f) K. Ray, T. Petrenko, K. Wieghardt, F. Neese, *Dalton Trans.* **2007**, 1552–1566; g) D. G. H. Hetterscheid, H. Grützmacher, A. J. J. Koekkoek, B. de Bruin, *Prog. Inorg. Chem.* **2007**, *55*, 247–253; h) B. de Bruin, D. G. H. Hetterscheid, *Eur. J. Inorg. Chem.* **2007**, 211–230; i) E. Evangelio, D. Ruiz-Molina, *Eur. J. Inorg. Chem.* **2005**, 2957–2971; j) M. D. Ward, J. A. McCleverty, *J. Chem. Soc. Dalton Trans.* **2002**, 275–288; k) C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *216*–217, 99–125.
- [2] Recent leading references involving noninnocent ligands: a) M. M. Khusniyarov, E. Bill, T. Weyhermüller, E. Bothe, K. Wieghardt, *Angew. Chem.* **2011**, *123*, 1690–1693; *Angew. Chem. Int. Ed.* **2011**, *50*, 1652–1655; b) W. I. Dzik, X. P. Zhang, B. de Bruin, *Inorg. Chem.* **2011**, DOI: dx.doi.org/10.1021/ic200043a; c) W. I. Dzik, S. E. Calvo, J. N. H. Reek, M. Lutz,

- M. A. Ciriano, C. Tejel, D. G. H. Hetterscheid, B. de Bruin, *Organometallics* **2011**, *30*, 372–374; d) H. Lu, W. I. Dzik, X. Xu, L. Wojtas, B. de Bruin, X. P. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8518–8521; e) Y. M. Badiei, M. A. Siegler, D. P. Goldberg, *J. Am. Chem. Soc.* **2011**, *133*, 1274–1277; f) A. I. Olivos Suarez, H. Jiang, X. P. Zhang, B. de Bruin, *Dalton Trans.* **2011**, *40*, 5697–5705; g) N. D. Paul, T. Krämer, J. E. McGrady, S. Goswami, *Chem. Commun.* **2010**, *46*, 7124–7126; h) A. L. Smith, K. I. Hardcastle, J. D. Soper, *J. Am. Chem. Soc.* **2010**, *132*, 14358–14360; i) A. Paretzki, R. Pattacini, R. Huebner, P. Braunstein, B. Sarkar, *Chem. Commun.* **2010**, *46*, 1497–1499; j) C. R. Hess, T. Weyhermüller, E. Bill, K. Wieghardt, *Inorg. Chem.* **2010**, *49*, 5686–5700; k) N. L. Wieder, M. Gallagher, P. J. Carroll, D. H. Berry, *J. Am. Chem. Soc.* **2010**, *132*, 4107–4109; l) F. F. Puschmann, J. Harmer, D. Stein, H. Ruegger, B. de Bruin, H. Grützmacher, *Angew. Chem.* **2010**, *122*, 395–399; *Angew. Chem. Int. Ed.* **2010**, *49*, 385–389; m) M. R. Ringenberg, M. J. Nilges, T. B. Rauchfuss, S. R. Wilson, *Organometallics* **2010**, *29*, 1956–1965; n) F. F. Puschmann, H. Grützmacher, B. de Bruin, *J. Am. Chem. Soc.* **2010**, *132*, 73–75; o) A. M. Tondreau, C. Milsmann, A. D. Patrick, H. M. Hoyt, E. Lobkovsky, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 15046–15059; p) E. Evangelio, M.-L. Bonnet, M. Cabañas, M. Nakano, J.-P. Sutter, A. Dei, V. Robert, D. Ruiz-Molina, *Chem. Eur. J.* **2010**, *16*, 6666–6677; q) W. I. Dzik, X. Xu, X. P. Zhang, J. N. H. Reek, B. de Bruin, *J. Am. Chem. Soc.* **2010**, *132*, 10891–10902; r) A. K. Das, B. Sarkar, C. Duboc, S. Strobel, J. Fiedler, S. Zális, G. K. Lahiri, W. Kaim, *Angew. Chem.* **2009**, *121*, 4306–4309; *Angew. Chem. Int. Ed.* **2009**, *48*, 4242–4245; s) C. R. Hess, T. Weyhermüller, E. Bill, K. Wieghardt, *Angew. Chem.* **2009**, *121*, 3758–3761; *Angew. Chem. Int. Ed.* **2009**, *48*, 3703–3706; t) R. G. Hicks, *Angew. Chem.* **2008**, *120*, 7503–7505; *Angew. Chem. Int. Ed.* **2008**, *47*, 7393–7395.
- [3] a) H. Grützmacher, *Angew. Chem.* **2008**, *120*, 1838–1842; *Angew. Chem. Int. Ed.* **2008**, *47*, 1814–1818; b) P. Chaudhuri, M. Hess, U. Flörke, K. Wieghardt, *Angew. Chem.* **1998**, *110*, 2340–2343; *Angew. Chem. Int. Ed.* **1998**, *37*, 2217–2220.
 - [4] a) W. I. Dzik, J. I. van der Vlugt, J. N. H. Reek, B. de Bruin, *Angew. Chem.* **2011**, *123*, 3416–3418; *Angew. Chem. Int. Ed.* **2011**, *50*, 3356–3358; b) P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794–795.
 - [5] a) T. Stahl, V. Kasack, W. Kaim, *J. Chem. Soc. Perkin Trans. 2* **1995**, 2127–2131; b) E. Uhlig, *Pure Appl. Chem.* **1988**, *60*, 1235–1240; c) G. van Koten, J. T. B. H. Jastrzebski, K. Vrieze, *J. Organomet. Chem.* **1983**, *250*, 49–61.
 - [6] C. C. Lu, E. Bill, T. Weyhermüller, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **2008**, *130*, 3181–3197.
 - [7] a) W. Massa, S. Dehghanpour, K. Jahani, *Inorg. Chim. Acta* **2009**, *362*, 2872–2878, and references therein; b) S. Dehghanpour, M. Khalaj, A. Mahmoudi, *Polyhedron* **2009**, *28*, 1205–1210; c) J. Kuwabara, D. Takeuchi, K. Osakada, *Polyhedron* **2009**, *28*, 2459–2465; d) A. Lavalette, F. Tuna, G. Clarkson, N. W. Alcock, M. J. Hannon, *Chem. Commun.* **2003**, 2666–2667; e) R. Ziesse, L. Douce, A. El-ghayoury, A. Harriman, A. Skoulios, *Angew. Chem.* **2000**, *112*, 1549–1553; *Angew. Chem. Int. Ed.* **2000**, *39*, 1489–1493; *Angew. Chem.* **2000**, *112*, 1549–1553.
 - [8] a) C. Alonso-Moreno, F. Carrillo-Hermosilla, J. Romero-Fernández, A. M. Rodríguez, A. Otero, A. Antiñolo, *Adv. Synth. Catal.* **2009**, *351*, 881–890; b) B. Moreau, J. Y. Wu, T. Ritter, *Org. Lett.* **2009**, *11*, 337–339; c) J. D. A. Pelletier, J. Fawcett, K. Singh, G. A. Solan, *J. Organomet. Chem.* **2008**, *693*, 2723–2731; d) S. Mori, M. Nambo, L.-C. Chi, J. Bouffard, K. Itami, *Org. Lett.* **2008**, *10*, 4609–4612; e) J. Song, Q. Shen, F. Xu, X. Lu, *Tetrahedron* **2007**, *63*, 5148–5153; f) J. Kuwabara, D. Takeuchi, K. Osakada, *Chem. Commun.* **2006**, 3815–3817.
 - [9] a) C. C. Lu, T. Weyhermüller, E. Bill, K. Wieghardt, *Inorg. Chem.* **2009**, *48*, 6055–6064; Cr complexes: b) C. C. Lu, S. D.

- George, T. Weyhermüller, E. Bill, E. Bothe, K. Wieghardt, *Angew. Chem.* **2008**, *120*, 6484–6487; *Angew. Chem. Int. Ed.* **2008**, *47*, 6384–6387; Zn complexes: c) M. van Gastel, C. C. Lu, K. Wieghardt, W. Lubitz, *Inorg. Chem.* **2009**, *48*, 2626–2632; d) A. Mondal, T. Weyhermüller, K. Wieghardt, *Chem. Commun.* **2009**, 6098–6100.
- [10] a) A. A. Trifonov, I. D. Gudilenkov, J. Larionova, C. Luna, G. K. Fukin, A. V. Cherkasov, A. I. Poddelsky, N. O. Druzhkov, *Organometallics* **2009**, *28*, 6707–6713; b) A. A. Trifonov, E. A. Fedorova, I. A. Borovkov, G. K. Fukin, E. V. Baranov, J. Larionova, N. O. Druzhkov, *Organometallics* **2007**, *26*, 2488–2491.
- [11] a) A. Malassa, C. Agthe, H. Görls, M. Friedrich, M. Westerhausen, *J. Organomet. Chem.* **2010**, *695*, 1641–1650; b) C. Stanciu, M. E. Jones, P. E. Fanwick, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2007**, *129*, 12400–12401; c) M. Westerhausen, A. N. Kneifel, I. Lindner, J. Grčić, H. Nöth, *Z. Naturforsch. B* **2004**, *59*, 161–166; d) M. Westerhausen, T. Bollwein, N. Makropoulos, S. Schneiderbauer, M. Suter, H. Nöth, P. Mayer, H. Piotrowski, K. Polborn, A. Pfitzner, *Eur. J. Inorg. Chem.* **2002**, 389–404.
- [12] a) C. Tejel, M. P. del Río, M. A. Ciriano, E. J. Reijerse, F. Hartl, S. Zális, D. G. H. Hetterscheid, N. Tschlis i Spithas, B. de Bruin, *Chem. Eur. J.* **2009**, *15*, 11878–11889; b) C. Tejel, M. A. Ciriano, M. P. del Río, D. G. H. Hetterscheid, N. Tschlis i Spithas, J. M. M. Smits, B. de Bruin, *Chem. Eur. J.* **2008**, *14*, 10932–10936.
- [13] C. Tejel, M. A. Ciriano, M. P. del Río, F. J. van den Bruele, D. G. H. Hetterscheid, N. Tschlis i Spithas, B. de Bruin, *J. Am. Chem. Soc.* **2008**, *130*, 5844–5845.
- [14] a) A. Brennfürer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176–4196; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114–4133; b) J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, 2nd ed., Wiley, Chichester, **2004**.
- [15] a) N. C. Tomson, L. A. Labios, T. Weyhermüller, J. S. Figueroa, K. Wieghardt, *Inorg. Chem.* **2011**, DOI: 10.1021/ic2005979; b) N. Deibel, D. Schweinfurth, R. Huebner, P. Braunstein, B. Sarkar, *Dalton Trans.* **2011**, *40*, 431–436; c) D. A. Smith, A. S. Batsanov, K. Costuas, R. Edge, D. C. Apperley, D. Collison, J.-F. Halet, J. A. K. Howard, P. W. Dyer, *Angew. Chem.* **2010**, *122*, 7194–7198; *Angew. Chem. Int. Ed.* **2010**, *49*, 7040–7044; d) C. Mukherjee, T. Weyhermüller, E. Bothe, P. Chaudhuri, *Inorg. Chem.* **2008**, *47*, 11620–11632; e) J. Zhou, H. Sun, K. Harms, J. Sundermeyer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1517–1521; f) I. J. S. Fairlamb, A. R. Kapdi, A. F. Lee, G. P. McGlacken, F. Weissburger, A. H. M. de Vries, L. Schmieder-van de Vondervoort, *Chem. Eur. J.* **2006**, *12*, 8750–8761; g) I. J. S. Fairlamb, C. T. O'Brien, Z. Lin, K. C. Lam, *Org. Biomol. Chem.* **2006**, *4*, 1213–1216.
- [16] CCDC 821731 (**2**), 821732 (**4**) and 821733 (**5**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [17] Angles around the palladium center are 126.4(2), 129.7(2), and 103.6(1)° for Cl-Pd-Ct, P-Pd-Ct, and Cl-Pd-P, respectively with $\Sigma^0 = 359.7(4)$ (Ct represents the midpoint of the C6–N2 bond).
- [18] a) W. Li, X. Zhang, A. Meetsma, B. Hessen, *Organometallics* **2008**, *27*, 2052–2057; b) C. C. Lu, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 15818–15832; c) G. R. Owen, R. Vilar, A. J. P. White, D. J. Williams, *Organometallics* **2003**, *22*, 3025–3027.
- [19] S. K. Russell, C. Milsman, E. Lobkovsky, T. Weyhermüller, P. J. Chirik, *Inorg. Chem.* **2011**, *50*, 3159–3169.
- [20] S. Kozuch, S. Shaik, A. Jutand, C. Amatore, *Chem. Eur. J.* **2004**, *10*, 3072–3080.
- [21] Preliminary catalytic studies on the standard Heck reaction ($\text{C}_6\text{H}_5\text{I} + \text{H}_2\text{C}=\text{CHCN}$) with complex **2** as catalyst precursor indicate moderate catalytic activity at 100°C in toluene.