Developing Synthetic Approaches with Non-Innocent Metalloligands: Easy Access to Ir\(^{1}/\)Pd\(^{0}\) and Ir\(^{1}/\)Pd\(^{0}/\)Ir\(^{1}\) cores**

Cristina Tejej, 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 non-innocent’ 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 the 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, \(\alpha\)-iminopyridine ligands, described for the first time by Vrieze and van Koten in 1983, are since long known to be ‘redox non-innocent’.\(^{5}\) However, it took until 2008 before thorough investigations of the redox non-innocence of this class of ligands were complimented with detailed spectroscopic and x-ray crystallographic characterizations.\(^{6}\) Numerous examples of coordination compounds containing the neutral closed-shell form \((L)^{0}\) have been reported,\(^{7}\) some of which display catalytic activity.\(^{8}\) However, those incorporating the monoanionic \(\pi^{\ast}\) radical form \((L)^{\ast}\) of the ligand are restricted to a few bis(ligand)-metal complexes of the first-row transition metal ions,\(^{9}\) and lanthanides,\(^{10}\) and complexes with the closed-shell 2\(e^{-}\) reduced dianionic form of these ligands \((L)^{2}\) are extremely rare.\(^{11}\)

We recently reported a unique method to prepare an anionic iridium(I) complex containing dianionic \((bpa-2H)^{2-}\) ligand\(^{12}\) which is the 2\(e^{-}\) reduced form of the \(\alpha\)-iminopyridine ligand bpi (Scheme 1). We further investigated the redox pair \([bpa-2H]^{2-}/[bpa-2H]^{+}\) coordinated to iridium, and we hypothesized that a formal two-electron redox transformation from \((bpa-2H)^{2-}\) to bpi occurs upon binding rhodium(I) to produce a plausible rhodium(−1) species.\(^{13}\) Considering the importance of palladium in catalysis,\(^{14}\) and the very few studies on palladium chemistry incorporating non-innocent ligands,\(^{15}\) we decide to explore the potential reduction of Pd\(^{0}\) 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 \(\text{Ir}/\text{Pd}\) and \(\text{Ir}/\text{Pd}/\text{Ir}\) complexes with an unusually \(\pi\)-coordinated \(\alpha\)-iminopyridine ligand.

The doubly deprotonated \(\text{bis(picolyl)amine}\) ligand \([bpa-2H]^{2-}\) is not accessible from the free amine, but it can be generated if bpa is coordinated to a transition metal.\(^{16,17}\) Interestingly, the isolable iridium compound \([\text{Ir}^3(bpa-2H)^{2-}]^2\) (I) (containing a square-planar iridium(I) centre and the closed-shell dianionic ligand) can bind an additional transition metal to the ligand \(\pi\) system, while the redox activity of the complex makes this system ideally suited to study ligand-to-metal ET processes. The pending pyridine arm of these complexes offers a valuable anchoring point for e.g. future electrode modification purposes.

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

[1] Reaction of [I\(^{-}\)] \(^{-}\) with [PdCl\(_2\)(PPh\(_3\)]\(_2\)) takes place immediately to give an intense red solution, from which the heteronuclear complex [[(cod)Ir\(^{3+}\)(bpi)]Pd\(_2\)Cl\(_2\)(PPh\(_3\)]\(_2\)) \(_2\) was isolated as red microcrystals in 70\% yield after work-up. In the X-ray structure of the dinuclear complex \(_{16}\) (Figure 1) the iridium(I) centre displays a square-planar geometry with the metal bound to the central nitrogen N2, the nitrogen of one of the pyridine rings (N1) and a chelating cod ligand. The coordination geometry around palladium is best described as trigonal planar, as defined by the metal, the phosphorous of the triphenylphosphane, the chloride and the \(\eta^{2}\)-coordinated ‘imine’
(C₆–N₂), imines π-coordinated to palladium are uncommon with only four examples characterized crystallographically, which were mainly described as pallada-aza-cyclopropanes.

In our case, the π-coordination of the C₆–N₂ double bond to palladium is evident from Figure 1, from the almost trigonal planar geometries around N2 and C6 (sp²-hybridisation), and from the short N2–C6 distance (1.377(9) Å) compared to the single N2–C7 bond (1.489(10) Å) in this molecule. Nonetheless, the N2–C6 distance is longer than that expected for a neutral α-iminopyridine ligand (L₀, Table 1). This is due to strong π-back bonding from the π-coordinated palladium. The Cₐₙ₉-Cᵦₙ₉ (C₅–C₆) and Cₐₙ₉-Nₚ_yₙⁱᵈᵦₑ (C₅–N₁) bond distances fit well to those expected for α-iminopyridine ligands in their oxidized neutral form (L₀ = bpi in this case).

### Table 1. Characteristic bond distances (Å) for α-iminopyridine ligands (L) in different redox-states and those in complexes [1–4] 2 and 5.[14]

<table>
<thead>
<tr>
<th>L₀</th>
<th>Cₐₙ₉-Cᵦₙ₉</th>
<th>Cₐₙ₉-Cᵦₙ₉</th>
<th>Cₐₙ₉-Nₚ_yₙⁱᵈᵦₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>L⁻</td>
<td>1.28</td>
<td>1.47</td>
<td>1.35</td>
</tr>
<tr>
<td>L⁻⁺</td>
<td>1.34</td>
<td>1.41</td>
<td>1.39</td>
</tr>
<tr>
<td>L⁻²</td>
<td>1.45</td>
<td>1.36</td>
<td>1.42</td>
</tr>
<tr>
<td>[1]⁻</td>
<td>1.383(13)</td>
<td>1.374(15)</td>
<td>1.406(13)</td>
</tr>
<tr>
<td>2</td>
<td>1.377(9)</td>
<td>1.470(10)</td>
<td>1.377(10)</td>
</tr>
<tr>
<td>5</td>
<td>1.392(10)</td>
<td>1.413(11)</td>
<td>1.42</td>
</tr>
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</table>


The structure of the palladium fragment is reminiscent with those of DFT-calculated tricoordinate anionic zero-valent palladium [PdX(PR₃)]⁻⁻⁻ compounds, which have been proposed by Amatore and Jutanud[20] (but never isolated) being the active species in Pd-catalyzed Heck and other cross-coupling reactions. The palladium centre in complex 2 can be considered as palladium(0), and in good agreement it adopts a typical trigonal planar geometry expected for d¹⁰-ML₃ complexes.

![Figure 1. Structure (ORTEP at 50% level) of the dinuclear complex [(cod)Ir(bpi)PdCl(PPh₃)] (2) (only the Csp³ atoms of the phenyl groups from PPh₃ are shown for clarity).](image)

The above data suggest that coordination of palladium to [I⁻] tigers an internal two-electron transfer from the starting complex [I⁻] to the palladium(II) centre. This ET reaction transforms the dianionic ligand {bpa–2H}⁻⁻⁻ (L⁻²⁻⁻) in [I⁻] into the oxidized ligand (L⁰⁻⁻⁻), the neutral imine PyCH₂–N=CPyH (bpi). Simultaneously, the palladium is formally reduced to a low-valent Pd⁰ fragment that remains π-coordinated to the C≡N bond. Nonetheless, the strong back-donation from the electron-rich metal to the imine makes that a pallada-aza-cyclopropane resonance form contributes in part to the electronic structure of the complex. Noticeably, the direction of the overall reaction regarding the ligand [from (L₀⁻⁻⁻) to (L⁰⁻⁻⁻)] is unique and opposite to the general trend in α-iminopyridine chemistry in which ligands are reduced from the oxidized state L⁰⁻⁻⁻ to L⁻⁻⁻ and to L⁻⁻⁻, with few cases reaching the dianionic form.

Complex [cod]Ir(bpi)PdCl(PPh₃)] (2) remains unaltered in thf and dichloromethane solutions. The π-coordination of the palladium to the HC≡N bond is easily deduced from the coupling of the imine proton to the phosphorus (J(H,P) = 3.1 Hz) in the ¹H NMR spectrum. The imine carbon was found at δ 84.6 ppm in the ¹³C NMR spectrum, which is substantially downfield shifted compared to the corresponding signals observed for the above mentioned palladacycles (ca. δ 65 ppm). Additionally, the cod ligand bound to iridium does not reveal the expected twelve resonances but just six, corresponding to a ‘rotating’ cod fragment (C₃v symmetry on the NMR time scale). This fluxional behaviour, for which the slow-exchange spectrum cannot be observed on cooling to −80º C, can be explained from the interaction of iridium with the nitrogen of the pendant pyridyl ring. Coordination of N₃ to iridium would facilitate Berry-pseudo-rotation accounting for the observed fluxional spectra. A similar behaviour was found for the related square-planar [Ir(bpa–H)(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 C₃ symmetry cod ligand on the NMR time scale (see Supporting Information).

Complex 2 reacts with triphenylphosphine in [D₆]benzene or [D₃]thf causing a clean and quantitative fragmentation of the complex into the iridium(I) complex [IrCl(cod)(PPh₃)] (3), the palladium(0) complex [Pd⁰(PPh₃)] (4), and the free imine bpi (Scheme 2). The fast exchange of the phosphate ligands between 3 and 4 prevents us from unequivocal assignment of the resonances belonging to palladium compound 4 in the ³¹P{¹H} NMR spectrum. However, crystallization of the reaction mixture gave yellow crystals of [Pd⁰(PPh₃)] (4) which were fully identified by X-ray diffraction (see Supporting Information). Noticeably, the whole reaction starting from [I⁻] can be considered as an example of how the non-innocence of the ligand plays a key role in a full two-electron reduction of a late transition metal.

![Scheme 2. Cleavage of complex 2 into [IrCl(cod)(PPh₃)] (3), [Pd⁰(PPh₃)] (4) and the imine bpi by reaction with PPh₃.](image)

A second example in which complex [I⁻] acts as ‘redox non-innocent metallo-ligand’ is revealed in its reaction with [PdCl₄(NCPh₃)] as palladium source. Two molar-equiv. of complex [I⁻] are needed to consume all the palladium precursor and the product was found to be a highly insoluble black-green solid.
analyzing as \([\text{Ir(PyCH2NCHPy})(\text{cod})]_2\text{Pd}\) (5). Single crystals of complex 5 were obtained by slow diffusion of the solutions of \([\text{Ir}^-]\) and \([\text{PdCl}_2(\text{NCHPh})]_2\) at the porous frit of a H-tube. Figure 2 shows the remarkable structure\(^{[16]}\) of 5 being a trinuclear compound in which two C6-N2 'imine' bonds, one from each iridium complex, coordinate in a \(\pi\)-fashion a palladium centre in a fully linear arrangement. The relatively short Ir-Pd distances (2.827±5 Å) suggest some kind of interaction between the metals, but this could just be the result of the linear coordination of palladium by two bulky groups, thus forcing the metals to be placed in close proximity.

Unfortunately, the trinuclear complex 5 proved to be highly insoluble, preventing us from properly studying its electronic structure in solution experimentally. Nonetheless, variable temperature SQUID measurements on powdered polycrystalline samples of 5 revealed it to be diamagnetic. Thus, plots of both, the molar magnetization versus \(H\) and that of \(\chi_M\) versus \(T\) give straight lines with a negative slope (see Supporting Information).

Hence, complex 5 is clearly diamagnetic, and its electronic structure is best described by the closed-shell resonance structures of type \(S^0\) (Scheme 3). An open-shell biradical electronic structure of the type \(\text{Pd}([\text{L}]^\ast)\) \(_2\) would be expected to result in paramagnetic behavior (by either having a triplet ground state or by thermal population of a triplet excited state from a singlet ground state with antiferromagnetically coupled unpaired electrons on the ligands, as just reported for a related palladium complex\(^{[15d]}\). 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 possesses 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).

**Figure 2.** Structure (ORTEP at 50% level) of the heterotrinuclear compound \([\text{Ir(PyCH2NCHPy})(\text{cod})]_2\text{Pd}\) (5).

The description of the electronic structure of 5 is complicated. Assuming the palladium center to be zero-valent as described above for 2, two anionic iridium complexes are involved in this ET reaction and in the stabilization of the product, which allows different oxidation state assignments of both the ligands and metals. Identical contribution from both iridium metalloligands, each providing one electron, would in principle produce the bi-radical \(S^4\) \(\left(\text{[Ir}^2([\text{bpa-2H}]^\ast)(\text{cod})]_2\text{Pd}\right)\), Scheme 3). This species would contain two (bpa-2H)\(^\ast\) radicals, and could in principle have a triplet (ferromagnetic coupling) or a singlet biradical (antiferromagnetic coupling) 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 \(S^8\) \(\left(\text{[Ir}^2(\text{cod})]_2([\text{bpa-2H}]^\ast)(\text{bpi})\text{Pd}\right)\), 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 distances do not allow us to distinguish between an averaged \(\left(\text{[Ir}^2(\text{cod})]_2([\text{bpa-2H}]^\ast)(\text{bpi})\text{Pd}\right)\) description (\(S^8\)) and the symmetrical ligand-bonded biradical possibility \(\left(\text{[Ir}^2([\text{bpa-2H}]^\ast)(\text{cod})]_2\text{Pd}\right)\) (\(S^4\)), since both should give similar distances in the solid state. However, it is clear from the data in Table 1 that the C\(_{imine}\)-C\(_{imine}\) (C5-C6) and C\(_{imine}\)-N\(_{pyridine}\) (C5-N1) are slightly shorter and longer, respectively, relative to 2, suggesting that averaged ligands in 5 are somewhat less oxidized than the ligand in complex 2. Accordingly, the N\(_{pyridine}\)-C\(_{imine}\) (N2-C6) bond distance is longer in 5 relative to 2. Nonetheless, some caution should be taken when comparing these bond distances (Table 1) because of the relevant perturbation introduced by the additional \(\pi\)-C=N imine coordination.\(^{[19]}\)

![Scheme 3. Possible resonance forms of the trinuclear complex 5.](image)

A similar situation occurs for complex 2, which is in full agreement with the clearly established singlet ground state of 2 by NMR (sharp NMR resonances in the usual spectral range for diamagnetic molecules). The optimized triplet geometries are substantially higher in energy than the singlet ones, and their structures are substantially different from that determined by X-ray diffraction (in particular, the Pd-C6 distances are clearly not bonding distances 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 (FMO’s) of complexes 2 and 5 reveal a rather complicated picture with several strongly delocalized orbitals (see Supporting Information).

**Table 2.** Relative energies (kcal-mol\(^{-1}\)) of the DFT optimized geometries of 2 and 5 in their singlet and triplet states.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Closed-shell singlet</th>
<th>Triplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0 / 0</td>
<td>+21.3 / +24.1</td>
</tr>
<tr>
<td>5</td>
<td>0 / 0</td>
<td>+17.8 / +21.0</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Turbomole b3-lyp functional using the def-TZVP basis set on all atoms; \(^{[b]}\) BP86 functional using the 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.
In conclusion, we describe here a unique synthetic route to π-imine coordinated Pd²⁻ complexes from the redox active metalloid ligand, \([\text{Ir(bpa-2H)cod}]^+\), in which the \([\text{bpa-2H}^\text{2+}]\) ligand is the 2e⁻ reduced form of the \(\alpha\)-iminopyridine ligand bpa. Subsequent 2e⁻ transfer from this \(L^2\) ligand to palladium gives access to the neutral \(L^0\) valence state of the bpa ligand, which remains π-coordinated with its imine moiety to the thus formed palladium(0) centre. Hence, the ligand redox couple \([\text{bpa-2H}^\text{2+}]\)-\(\text{bpa}\) coordinated to iridium constitutes a versatile redox active metalloid ligand that allows the formation and stabilisation of the unusual heterobinuclear '\(\text{Ir}^3\)(bpa)\(\text{Pd}^0\)' and heterotrinuclear '\(\text{Ir}^2\)(bpa)\(\text{Pd}^0\)(\(\text{bpa-2H}^\text{2+}\))' \(L^2\) cores in the complexes 2 and 5. Furthermore, complex 5 represents a rare example of a ligand-based two-electron mixed-valent complex wherein the two ligands have formally different redox states, \((L^0)\) and \((L^2)\). Finally, in the light of the well-known catalytic activity of Pd²⁻ in several reactions ranging from cross-coupling, olefin polymerisation and oxidation reactions, these results are highly promising for the development of new redox-coupled catalytic or electrocatalytic reactions, which we are currently investigating in our laboratory.

**Experimental Section**

2: Solid \([\text{PdCl}_2(\text{PPh}_3)]\) (140.8 mg, 0.2 mmol) was added to a thf solution (8 mL) of \([\text{Ir(bpa-2H)}(\text{cod})]\) (0.2 mmol) \((\text{in situ prepared by reacting } \text{Ir(bpa-H)}(\text{cod})\text{))\) (100.0 mg, 0.2 mmol) with \(\text{KO}2\text{Bu}\) (225.5 mg, 0.2 mmol) in thf for 1h). The initial dark-brown solution of \([\text{Ir(bpa-2H)}(\text{cod})]\) evolved to red almost immediately while a red solid started to crystallize. After stirring for 30 min, the solution was concentrated to 4 mL, carefully layered with diethyl ether (12 mL) and kept undisturbed overnight. The mother-liquid was decanted and the solid was washed with diethyl ether \((3 \times 5\text{ mL})\) and vacuum-dried. It was verified that the expected 15.0 mg of KCl remains in solution in the above thf-diethyl ether mixtures. Yield: 126.2 mg \((70\%)\). Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a solution of complex 2 in thf. \(\text{H}^0\text{NMR (500.13 MHz, CD}_2\text{Cl}_2, 25\degree\text{C})}: \delta = 8.52 \text{ (br d, } J_{\text{H,H}} = 4.8 \text{ Hz, } 1\text{H, H}^2\text{)}, 7.90 \text{ (d, } J_{\text{H,H}} = 7.9 \text{ Hz, } 1\text{H, H}^6\text{)}, 7.69 \text{ (d, } J_{\text{H,H}} = 5.5 \text{ Hz, } 1\text{H, H}^8\text{)}, 7.57 \text{ (td, } J_{\text{H,H}} = 7.7 \text{ Hz, } J_{\text{H,H}} = 1.8 \text{ Hz, } 1\text{H, H}^2\text{)}, 7.38 \text{ (m, } 6\text{H, } \text{Ph}\text{H}), 7.30 \text{ (m, } 9\text{H, } \text{Ph}\text{H}), 7.12 \text{ (dd, } J_{\text{H,H}} = 7.4 \text{ Hz, } J_{\text{H,H}} = 4.9 \text{ Hz, } 1\text{H, H}^1\text{)}, 6.84 \text{ (dd, } J_{\text{H,H}} = 7.1 \text{ Hz, } J_{\text{H,H}} = 6.1 \text{ Hz, } 1\text{H, H}^6\text{)}, 5.28 \text{ (d, } J_{\text{H,H}} = 3.1 \text{ Hz, } 1\text{H, H}^1\text{)}, N.52 \text{ (d, } J_{\text{H,H}} = 8.3 \text{ Hz, } 1\text{H, H}^1\text{)}, 4.48 \text{ (\(\delta_n\) \(J_{\text{H,H}} = 3.2 \text{ Hz, } 1\text{H, H}^4\text{)}), 4.11 \text{ (\(\delta_n\) \(J_{\text{H,H}} = 6.4 \text{ Hz, } \text{J(AB)}\))} = 15.6 \text{ Hz, } 1\text{H, H}^4\text{)}, 3.43 \text{ (m, } 2\text{H, } \text{H}^2\text{C}^\text{a}\text{)}, 3.86 \text{ (m, } 2\text{H, } \text{H}^2\text{C}^\text{a}\text{)}, 2.44 \text{ (m, } 2\text{H, } \text{H}^2\text{C}^\text{a}\text{)}, 2.36 \text{ (m, } 2\text{H, } \text{H}^2\text{C}^\text{a}\text{), 1.89 \text{ (m, } 2\text{H, } \text{H}^2\text{C}^\text{a}\text{), 1.74 \text{ (2H, } \text{H}^2\text{C}^\text{a}\text{, cod)}, 1.08 \text{ (PPh}_3\text{)}\text{]}\text{NMR (201.6 MHz, CD}_2\text{Cl}_2, 25\degree\text{C})}: \delta = 29.8 \text{ (s, } \text{PPh}_3\text{)}, 17.3 \text{ (s, } \text{PPh}_3\text{)}, 159.8 \text{ (d, } J_{\text{C,C}} = 5.5 \text{ Hz, } \text{C}^\text{a}\text{)}, 149.3 \text{ (s, } \text{C}^\text{b}\text{)}, 146.0 \text{ (s, } \text{C}^\text{b}\text{)}, 138.2 \text{ (s, } \text{C}^\text{a}\text{)}, 137.0 \text{ (s, } \text{C}^\text{a}\text{)}, 134.8 \text{ (d, } J_{\text{C,C}} = 13.5 \text{ Hz, } \text{PPh}_3\text{)}, 134.4 \text{ (d, } J_{\text{C,C}} = 9.8 \text{ Hz, } \text{PPh}_3\text{)}, 123.2 \text{ (m, } J_{\text{C,C}} = 12.6 \text{ Hz, } 1\text{C}^\text{a}\text{)}, 120.1 \text{ (d, } J_{\text{C,C}} = 11.6 \text{ Hz, } \text{H}^2\text{C}^\text{a}\text{)}, 84.6 \text{ (SCH}^\text{a}\text{)}, 61.1 \text{ (d, } J_{\text{C,C}} = 4 \text{ Hz, } 1\text{C}^\text{a}\text{)}, 66.1 \text{ (\(\delta_n\) \(J_{\text{C,C}} = 66.0 \text{ Hz, } \text{C}^\text{a}\))}, 32.4 \text{ (s, } \text{C}^\text{a}\text{), 31 \text{ (s, } \text{C}^\text{b}\text{, cod}}, \text{elementary analysis calced }\% \text{ for } \text{C}_{29}\text{H}_{40}\text{N}_{2}\text{P}_{1.8} \text{ (901.8): C} = 50.55, \text{ H} = 4.35, \text{ N} = 4.65; \text{found: C} = 50.51, \text{ H} = 4.30, \text{ N} = 4.63 (\text{see supporting information for labelling of protons and carbons).}}

5: A thf solution (5 mL) of \([\text{PdClO}_2(\text{NCH}_3\text{P})_3]\) (37.1 mg, 0.1 mmol) was allowed to diffuse into a solution in the same solvent of \([\text{Ir(bpa-2H)cod}]^+\) (0.2 mmol) \((\text{in situ prepared as described above).}}

After two days of diffusion, dark purple crystals, suitable for diffraction studies, were formed at the porous frit of the H-tube. The mother-liquid was decanted and the crystals were washed with diethyl-ether \((3 \times 5\text{ mL})\) and vacuum-dried. Yield: 77.5 mg \((70\%\)).

Acknowledgement (calcd \% for \(\text{C}_{29}\text{H}_{40}\text{N}_{2}\text{P}_{1.8})\text{C} = 50.55, \text{ H} = 4.35, \text{ N} = 4.65; \text{found: C} = 50.51, \text{ H} = 4.30, \text{ N} = 4.63 (\text{see supporting information for labelling of protons and carbons).}}

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CCDC 821731 (2), 821732 (4) and 821733 (5), contain the supplemental 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.

[16] Angles around the palladium are 126.4(2), 129.7(2) and 103.6(1)º for Centre via www.ccdc.cam.ac.uk/data_request/cif.


[20] Preliminary catalytic essays on the standard Heck reaction (C₆H₅CH + H₂C=CHCN) using complex 2 as catalyst precursor indicate a moderate catalytic activity at 100 ºC in toluene.
Cristina Tejel,* Laura Asensio, M. Pilar del Río, Bas de Bruin, José A. López, and Miguel A. Ciriano

**Guilty as charged** is the anionic iridium [Ir(bpa-2H)(cod)] complex in its reactions with palladium(II) compounds. Net transfer of two electrons from the iridium complex to palladium allows the easy preparation of di- and trinuclear π-imine coordinated Pd⁰ compounds (see Figure).

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