Angewandte
International Edition Chemie

Structure Elucidation

DOI: 10.1002/anie.201206175

Unconventional Reactivity of Imidazolylidene Pyridylidene Ligands in Iridium(III) and Rhodium(III) Complexes**

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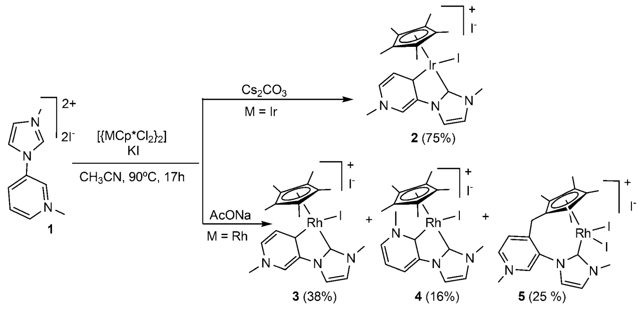
Pentamethylcyclopentadienyl (Cp*) and N-heterocyclic carbene (NHC) ligands are often regarded as spectator ligands in organometallic catalysis,[1] meaning that they rarely undergo modification during a reaction sequence. However, these types of ligands may sometimes undergo rearrangements which can be the source for the activation or deactivation processes. For example, Cp* ligands are known to undergo activation at the methyl groups on the ring to afford Cp* functionalizations on iridium,[2] rhodium,[2a,3] and ruthenium[4] complexes. For NHC chemistry, several reports have also highlighted ligand rearrangements, including migratory insertions,[5] reductive elimination,[6] heterocycle cleavage,[7] and C–C bond formation.[8] All in all, these examples are rare enough to be counted as exceptions.

In the course of our research we have recently been interested in the preparation of imidazolylidene pyridylidene ligands for the preparation of rhodium (III) and iridium (III) complexes.[9] Very few examples of such linked imidazolylidene (or triazolylidene) pyridylidenes have been described so far,[10] but they already have provided elegant examples of reactivity, such as the selective methyl transfer from a pyridinium unit to an unfunctionalized aryl carbon atom.[10c] Aiming to obtain complexes with unusual C–H activation properties, we now describe the coordination of a series of imidazolylidene pyridylidene ligands to [MCp*Cl$_2$] (M = Ir and Rh). Together with the expected bis(NHC) complexes, we obtained a series of metal complexes arising from unusual ligand rearrangements, including C–C couplings between the pyridyl and the Cp* rings, and C–N bond cleavage of the imidazolylidene.



Scheme 1.

The reaction of the imidazolium pyridinium salt [Him-pyH](I)$_2$ (**1**) with [{MCp*Cl$_2$}$_2$] (M = Rh, Ir) in refluxing acetonitrile in the presence of Cs$_2$CO$_3$ afforded two different reaction outcomes depending upon the nature of the metal (Scheme 1). For the reaction carried out with [{IrCp*Cl$_2$}$_2$], the reaction cleanly led to the formation of the corresponding [IrCp*I(*C*,*C*′-im-py)]$^+$ (**2**; Scheme 1), in which the pyridylidene coordinates to the metal through the *para*-carbon atom, thus affording a remote coordination mode rather than coordination through the carbon atom adjacent to the nitrogen center. For the reaction carried out with [{RhCp*Cl$_2$}$_2$], a mixture of complexes is obtained. Two of these complexes are the expected [RhCp*I(*C*,*C*′-im-py)]$^+$ isomers in which the pyridylidene is bound to the metal through the remote (**3**; major) and normal (**4**; minor) coordination modes. Only when AcONa is used, together with these two isomers, is a new and unexpected complex obtained; in this new complex the imidazolylidene is bound to the metal while the pyridinium ring is coupled to Cp*, thus affording a Cp* functionalized with a pendant imidazolylidene. All Cp*-functionalized NHCs reported to date have been obtained through the prior preparation of the hybrid Cp*/NHC ligands,[11] so this intramolecular coupling constitutes the first example of the formation of a NHC-containing cyclopentadienyl through the coupling of previously coordinated ligands. All compounds (**2**–**5**) were characterized by means of NMR spectroscopy and mass spectrometry (see the Supporting Information for full details). The ^{1}H NMR spectrum of **5** provides the first evidence that the activation of the Cp* ligand has been achieved. The spectrum shows the characteristic signals resulting from the protons of the four inequivalent methyl groups ($\delta = 2.26, 2.22, 1.85, 1.36$ ppm) and the two diastereotopic protons at the CH$_2$ linker (two doublets at $\delta = 3.61$ and 3.44 ppm, $^3J_{HH} = 15$ Hz). The ^{13}C NMR spectrum shows the signal corresponding to the C$_{carbene}$ atom at $\delta = 170.1$ ppm.

For the reactions carried out with the salt [Him-pyH](I)$_2$ wherein the C2 position of the imidazolium is blocked with one methyl group (**6**; Scheme 2), the reaction with [{IrCp*Cl$_2$}$_2$] led to the formation of a complex in which the chelate ligand is coordinated through the pyridylidene and a methylene group resulting from the C–H activation of the

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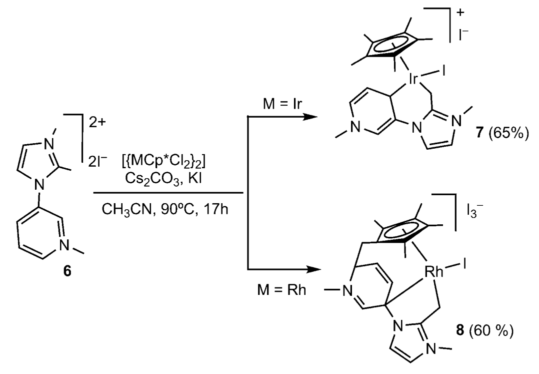
[**] We gratefully acknowlegde financial support from the MEC of Spain (CTQ2011-24055/BQU) and Bancaixa (P1.1B2010-02). We would also like to thank the Juan de la Cierva program (E.M.-M.). Candela Segarra thanks the Ministerio de Ciencia e Innovación for a fellowship. The authors are grateful to the Serveis Centrals d'Instrumentació Científica (SCIC) of the Universitat Jaume I for providing us with spectroscopic and X-Ray facilities. We thank Prof. D. Gusev from the Wilfrid Laurier University for the thoughtful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206175.



Scheme 2.

Me group at the C2 of the imidazolium ring (**7**). It has recently been suggested that the deprotonation of imidazoliums with methyl groups at the C2 position is more likely to occur at the Me group on the C2 than that on the backbone to afford an abnormal carbene.[12] This reactivity should actually explain many of previously reported examples in which the metalation through the methylene group is preferred over the formation of the abnormal carbene when imidazoliums with methyl groups at the C2 position are used.[9,13] For the reaction carried out with [{RhCp*Cl$_2$}$_2$], we obtained a complex in high yield (**8**), resulting from the reductive coupling between the Cp* and the pyridinium rings, and the imidazolium ring is bound to the metal as a result of the activation of the Me group at C2. The ^{1}H NMR spectrum of **8** shows first evidence that the coupling has proceeded, as indicated by the four distinct signals corresponding to the inequivalent methyl groups ($\delta = 2.15$, 1.82, 1.74 and 1.13 ppm). The ^{13}C NMR spectrum displays two doublets at $\delta = 66.5$ ppm ($^1J_{\mathrm{RhC}} = 15.1$ Hz) and $\delta = 1.8$ ppm ($^1J_{\mathrm{RhC}} = 26.9$ Hz), which correspond to the two metalated carbon atoms of the pyridine and methyl groups, respectively.

The molecular structures of complexes **3**, **5**, and **8** have been unambiguously determined by means of X-ray diffraction. Figures 1a and b show the molecular diagrams of molecules **5** and **8**, respectively.

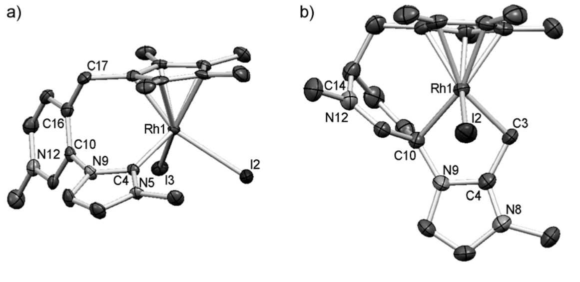


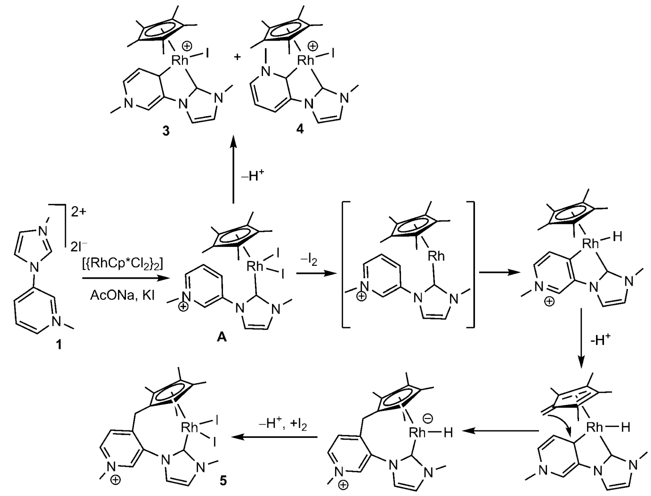
Figure 1. Molecular diagram of complexes **5** (a) and **8** (b). Only one enantiomer of each complex is displayed. Thermal ellipsoids shown at 50% probability. Hydrogen atoms and counter ions (iodide in **5**, triiodide in **8**) are omitted for clarity. Selected bond lengths [Å] and angles [°] in **5**: Rh(1)–I(2) 2.7063(4), Rh(1)–I(3) 2.7020(4), Rh(1)–C(4) 2.032(3), Rh(1)–C(centroid) 1.823(3). In **8**: Rh(1)–I(2) 2.7256(5), Rh(1)–C(3) 2.112(5), Rh(1)–C(10) 2.191(5), Rh(1)–C(centroid) 1.832(5), C(3)-Rh(1)-C(10) 78.85(19).[19]

The molecular structure of compound **5** verifies the C–C coupling between the pyridinium ring and one of the methyl groups of the Cp* ligand, therefore a chelating η5-(tetramethylcyclopentadienyl)/NHC ligand has been formed. Two iodides complete the coordination sphere about the Ir$^{\mathrm{III}}$ center. The molecular structure of complex **8** also confirms the coupling of the pyridinium ring to one of the methyl groups of the Cp* ligand, although in this case the pryridinium has been dearomatized and formed a pyridinium ring with two sp^3-carbon atoms at the 2- and 5-positions of the ring (Figure 1b; carbon atoms labeled C10 and C14). The C2 position of the pyridinium ring (labeled C14) is directly bound to the methylene group of the cyclopentadienyl ligand. The C5 carbon atom (labeled C10), is bound to the rhodium center [Rh(1)-C(19) distance = 2.191 Å]. The presence of the C=N double bond (1.317 Å) confirms the iminium character of the ring, which adopts a boat conformation with the carbon atoms labeled C10 and C14 out of the plane formed by the other four atoms of the pyridinium. The compound crystallized with a I$_3^-$ counter-anion, an indication of the existence of residual I$_2$ present in the reaction media, as will be discussed below.

We believe that the formation of both **5** and **8** occurs through the formation of tetramethylfulvene/Rh intermediates. It has been reported that whereas η^4-tetramethylfulvene complexes react with nucleophiles,[2b,4c,14] η^6-tetrafulvene complexes are more prone to react with electrophiles.[15] Although we are aware that the mechanisms we propose may be considered as speculative, we believe that they provide a plausible explanation of the processes under study.

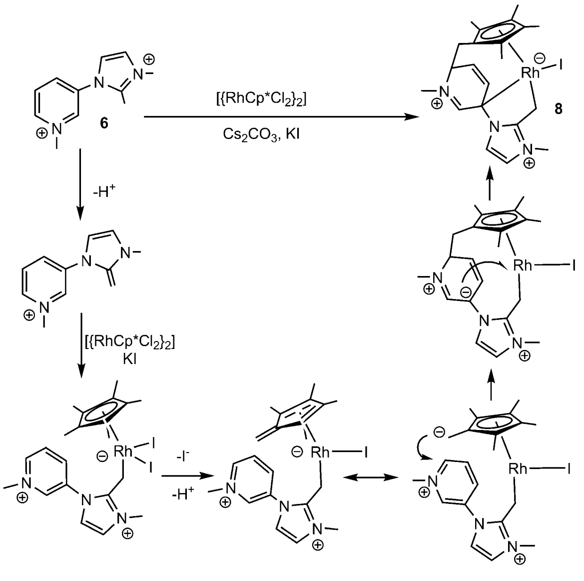
We initially thought that **5** could be formed by a rearrangement of complexes **3** and **4**. In this regard, several reactions employing **3** and **4** in refluxing acetonitrile in the presence of KI or I$_2$ did not produce any change in the starting compounds, so we believe that these two compounds are irreversibly formed by metal-mediated C–H activation of the pyridinium ring and subsequent deprotonation of the metal hydride intermediate with a base. This hypothesis is supported by our previous experimental and theoretical studies on the mechanisms of the formation of bis(NHC) complexes of Cp*M (M = Rh and Ir).[13,16] The formation of complex **5** may occur through the reductive elimination of diiodine from the reaction intermediate **A** (Scheme 3), and subsequent oxidative addition of the pyridinium ring to form a Rh$^{\mathrm{III}}$ hydride with a pyridylidene imidazolylidene ligand. The deprotonation of the Cp* ligand may induce a nucleophilic attack of the fulvene onto the pyridylidene carbon atom, thus affording the C–C coupling between the Cp* and the pyridinium rings. Finally, the oxidative addition of diiodine and deprotonation of the hydride would allow formation of the final product. In the course of the purification of complex **5** by column chromatography we observed the separation of a first band containing a small amount of diiodine. We have performed control experiments which show that the diiodine does not come from the oxidation of the KI present in the reaction medium, and therefore believe that it may be formed from the reductive elimination from **A**.

In the formation of complex **8**, we first may have the coordination of the imidazolium pyridinium salt through the methylene group resulting from the C–H activation of the Me



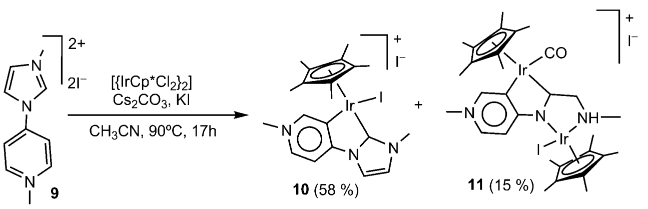
Scheme 3.

group on C2 of the imidazolium ring (Scheme 4). Deprotonation of this new species results in the formation of the tetramethylfulvene intermediate, which can undergo a nucleophilic attack at the carbon atom adjacent to the nitrogen center of the pyridinium ring. The nucleophilic attack of the carbon atom bound to the imidazolylilidene to the rhodium center generates a Rh–C bond in compound **8**. The overall process implies the dearomatization of the pyridinium ring through consecutive nucleophilic and electrophilic attacks to the ring.



Scheme 4.

The preparation of the rhodium and iridium complexes with the chelate C,C′-im-py ligands in which the pyridylidene is bound by the abnormal position could be achieved by using the [Him-pyH](I)$_2$ salt (**9**; Scheme 5).[9] The reaction of **9** with [{IrCp*Cl$_2$}$_2$] in refluxing acetonitrile in the presence of Cs$_2$CO$_3$ and KI allows the formation of the expected [IrCp*I(C,C′-im-py)]$^+$ (**10**), in which the pyridylidene ligand is coordinated to the iridium by an abnormal coordination mode. This result is consistent with our previous findings in which **9** reacted with [{IrCl(cod)}$_2$], thus affording the same type of coordination of the ligand.[9] Along with complex **10**, we could also isolate, in low yield (15%), the dimetallic species **11** in which the ring opening of the imidazole ring has been produced.



Scheme 5.

Both **10** and **11** were characterized by means of NMR spectroscopy and mass spectrometry. The molecular structure of **11** was confirmed by means of X-ray diffractometry. Figure 2 shows the molecular diagram of **11** in which the dimetallic nature of the molecule is observed. The bis(heterocyclic) ligand has been transformed into one pyridylidene amino amido ligand. The pyridylidene is bound to one iridium fragment through an abnormal coordination form, and the amino amido part of the ligand forms an N,N chelate with a second iridium fragment. The ethylene linker between the amino amido functionalities is metalated to the first iridium fragment by the α-carbon atom relative to the amido group, so in the same molecule we have both C,C- and N,N-chelating ligands to the two different iridium fragments. The iridium fragment with the C,C chelation is bound to a carbonyl group.

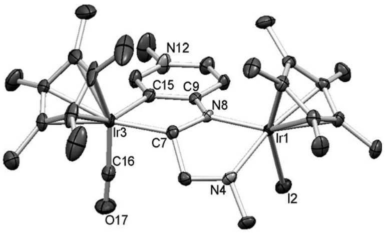
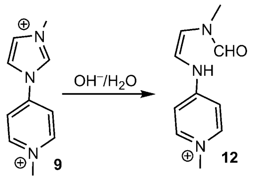


Figure 2. Molecular diagram of complex **11**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms, counter ions (iodide), and solvent (CH$_2$Cl$_2$ and diethyl ether) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–I(2) 2.7208(5), Ir(1)–N(4) 2.153(5), Ir(1)–N(8) 2.078(5), Ir(1)–C(centroid) 1.798(5), N(8)-Ir(1)-N(4) 78.8(2), Ir(3)–C(7) 2.099(6), Ir(3)–C(15) 2.056(7), Ir(3)–C(16) 1.837(8), Ir(3)–C(centroid) 1.903(5), C(7)-Ir(3)-C(15) 78.1(2).[19]

Imidazole-2-ylidenes can be hydrolyzed under basic conditions in the presence of small amounts of H$_2$O, thus allowing the formation of iminoformamides.[17] Although this process is a very slow for aromatic imidazolium derivatives,[17a,c] it is most probably of minor importance in all the reactions, involving the coordination of NHCs to metals, which are carried out at low temperatures and with short reaction times. In fact, in a very recent study, it has been reported that the attempt to coordinate one bis(imidazolium) salt to [{IrCl(cod)}$_2$] in the presence of Cs_2CO_3 (9 h of reaction in refluxing acetonitrile) afforded a mono-NHC/Ir^I species with a iminoformamide branch formed by hydrolysis of the formed free carbene.[18] In our case, the hydrolysis of the imidazolylidene should afford the ring-opened product **12** (Scheme 6), even though the reaction with [{IrCp*Cl$_2$}$_2$] suffers from further rearrangements involving a decarbonylation of the aldehyde to generate the carbonyl ligand and the amine branch of **11**, and the C=C double bond has been hydrogenated generating a saturated backbone. To prove the participation of **12** in the formation of **11**, we added an equimolecular amount of Cs_2CO_3 to a solution of **9** in CD_3CN. After five minutes of stirring at room temperature, we observed the formation of **12** (30%, estimated by ^{1}H NMR spectroscopy), and the reaction was quantitative only after 3 h at 90°C.



Scheme 6.

To provide additional support to the possible involvement of **12** in the process of the formation of the dimetallic complex **11**, we performed a reaction in which compound **9** hydrolyzed to form **12** in acetonitrile in the presence of Cs_2CO_3. Only after we confirmed that **12** was formed, we added the corresponding amount of [{IrCp*Cl$_2$}$_2$], and we observed that the yield in the formation of **11** increased up to 40%. Under these reaction conditions we did not detect the formation of complex **10**.

In summary, our work provides three different pieces of evidence for the nonconventional behavior of a series of pyridylidene imidazolylidene ligands. That is, we describe three unprecedented reactivities. The formation of the Cp*-functionalized NHC through the intramolecular coupling of two existing ligands in the molecule constitutes an interesting alternative to the methods which have been reported to date, thus implying the use of preformed Cp*/NHC precursors.[11] The reductive coupling of the Cp* and the pyridine opens the possibility for the use of "M^{III}Cp*" (M = Rh, Ir) complexes in the reduction of pyridiniums, a reaction that we are currently studying in our laboratory. Finally, the formation of the dimetallic complex **11** underlines the importance of the hydrolysis of free carbenes in the process of forming metal complexes, a reaction that is underestimated most of the time and should be taken under serious consideration in all reactions involving the use of imidazolylidenes in reactions run for long time periods in the presence of traces of water. Small changes within the imidazolylidene-pyridylidene ligands lead to great changes in the outcome of the reactions, therefore leading to unexpected products. These observations may be helpful for the design of Cp*M-based complexes as catalysts for C–H activation processes.

Received: August 1, 2012
Revised: August 16, 2012

Keywords: C–C coupling · cyclopentadienyl ligands · heterocycles · iridium · rhodium

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[1] R. H. Crabtree, *J. Organomet. Chem.* **2005**, *690*, 5451–5457.

[2] a) A. Millan, P. M. Bailey, P. M. Maitlis, *J. Chem. Soc. Dalton Trans.* **1982**, 73–77; b) K. Fujita, M. Nakamura, R. Yamaguchi, *Organometallics* **2001**, *20*, 100–105; c) R. M. Bellabarba, G. C. Saunders, *Polyhedron* **2004**, *23*, 2659–2664; d) K. Fujita, R. Yamaguchi, *Chem. Lett.* **1999**, 707–708; e) L. S. Park-Gehrke, J. Freudenthal, W. Kaminsky, A. G. DiPasquale, J. M. Mayer, *Dalton Trans.* **2009**, 1972–1983.

[3] a) M. Bernechea, J. R. Berenguer, E. Lalinde, J. Torroba, *Organometallics* **2009**, *28*, 312–320; b) R. M. Bellabarba, M. Nieuwenhuyzen, G. C. Saunders, *Organometallics* **2002**, *21*, 5726–5737; c) R. P. Hughes, D. C. Lindner, A. L. Rheingold, G. P. A. Yap, *Organometallics* **1996**, *15*, 5678–5686.

[4] a) D. R. T. Knowles, H. Adams, P. M. Maitlis, *Organometallics* **1998**, *17*, 1741; b) L. Fan, M. L. Turner, M. B. Hursthouse, K. M. Malik Abdul, O. V. Gusev, P. M. Maitlis, *J. Am. Chem. Soc.* **1994**, *116*, 385; c) R. M. Fairchild, K. T. Holman, *Organometallics* **2008**, *27*, 1823–1833.

[5] a) A. A. Danopoulos, N. Tsoureas, J. C. Green, M. B. Hursthouse, *Chem. Commun.* **2003**, 756–757; b) S. Fantasia, H. Jacobsen, L. Cavallo, S. P. Nolan, *Organometallics* **2007**, *26*, 3286–3288.

[6] D. J. Nielsen, A. M. Magill, B. F. Yates, K. J. Cavell, B. W. Skelton, A. H. White, *Chem. Commun.* **2002**, 2500–2501.

[7] A. W. Waltman, T. Ritter, R. H. Grubbs, *Organometallics* **2006**, *25*, 4238–4239.

[8] a) T. Steinke, B. K. Shaw, H. Jong, B. O. Patrick, M. D. Fryzuk, J. C. Green, *J. Am. Chem. Soc.* **2009**, *131*, 10461–10466; b) C. Romain, K. Miqueu, J. M. Sotiropoulos, S. Bellemin-Laponnaz, S. Dagorne, *Angew. Chem.* **2010**, *122*, 2244–2247; *Angew. Chem. Int. Ed.* **2010**, *49*, 2198–2201.

[9] C. Segarra, E. Mas-Marzá, J. A. Mata, E. Peris, *Organometallics* **2012**, *31*, 5169–5176.

[10] a) A. McSkimming, G. E. Ball, M. M. Bhadbhade, S. B. Colbran, *Inorg. Chem.* **2012**, *51*, 2191–2203; b) A. McSkimming, M. Bhadbhade, S. B. Colbran, *Dalton Trans.* **2010**, *39*, 10581–10584; c) R. Lalrempuia, H. Muller-Bunz, M. Albrecht, *Angew. Chem.* **2011**, *123*, 10144–10148; *Angew. Chem. Int. Ed.* **2011**, *50*, 9969–9972; d) R. Lalrempuia, N. D. McDaniel, H. Muller-Bunz, S. Bernhard, M. Albrecht, *Angew. Chem.* **2010**, *122*, 9959–9962; *Angew. Chem. Int. Ed.* **2010**, *49*, 9765–9768.

[11] B. Royo, E. Peris, *Eur. J. Inorg. Chem.* **2012**, 1309–1318.

[12] O. Hollóczki, L. Nyulászi, *Org. Biomol. Chem.* **2011**, *9*, 2634–2640.

[13] M. Viciano, M. Feliz, R. Corberan, J. A. Mata, E. Clot, E. Peris, *Organometallics* **2007**, *26*, 5304–5314.

[14] a) A. H. Klahn, B. Oelckers, F. Godoy, M. T. Garland, A. Vega, R. N. Perutz, C. L. Higgitt, *J. Chem. Soc. Dalton Trans.* **1998**, 3079–3086; b) L. Fan, M. L. Turner, H. Adams, N. A. Bailey, P. M. Maitlis, *Organometallics* **1995**, *14*, 676–684; c) U. Kölle, J. Grub, *J. Organomet. Chem.* **1985**, *289*, 133–139.

[15] O. V. Gusev, S. Sergeev, I. M. Saez, P. M. Maitlis, *Organometallics* **1994**, *13*, 2059–2065.

[16] M. Viciano, M. Poyatos, M. Sanau, E. Peris, A. Rossin, G. Ujaque, A. Lledos, *Organometallics* **2006**, *25*, 1120–1134.

[17] a) F. Bonnette, T. Kato, M. Destarac, G. Mignani, F. P. Cossio, A. Baceiredo, *Angew. Chem.* **2007**, *119*, 8786 – 8789; *Angew. Chem. Int. Ed.* **2007**, *46*, 8632 – 8635; b) M. K. Denk, J. M. Rodezno, S. Gupta, A. J. Lough, *J. Organomet. Chem.* **2001**, *617*, 242 – 253; c) O. Hollóczki, P. Terleczky, D. Szieberth, G. Mourgas, D. Gudat, L. Nyulászi, *J. Am. Chem. Soc.* **2011**, *133*, 780 – 789.

[18] W. W. Zuo, P. Braunstein, *Dalton Trans.* **2012**, *41*, 636 – 643.

[19] CCDC 894391 (**3**), 894392 (**5**), 894393 (**8**), 894394 (**10**), and 894395 (**11**) 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.