

Heterobimetallic Carbene Complexes by a Single-Step Site-Selective Metalation of a Tricarbene Ligand

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Supporting Information

ABSTRACT: The unsymmetrical tris(imidazolium) salt $H_3-1(Br)_3$, featuring a 1,2,4-substitution pattern of the central phenyl ring, after triple imidazolium C2 deprotonation reacts in a one-pot reaction with $Pd(OAc)_2$ and $[M(Cp^*)(Cl)_2]_2$ ($M = Rh^{III}, Ir^{III}$) to yield heterobimetallic complexes [3] ($M = Rh$) and [4] ($M = Ir$), in which the Pd^{II} ion is chelated by two ortho N-heterocyclic carbene (NHC) donors while the third NHC donor coordinates to the M^{III} center, which orthometalates the central phenyl ring.

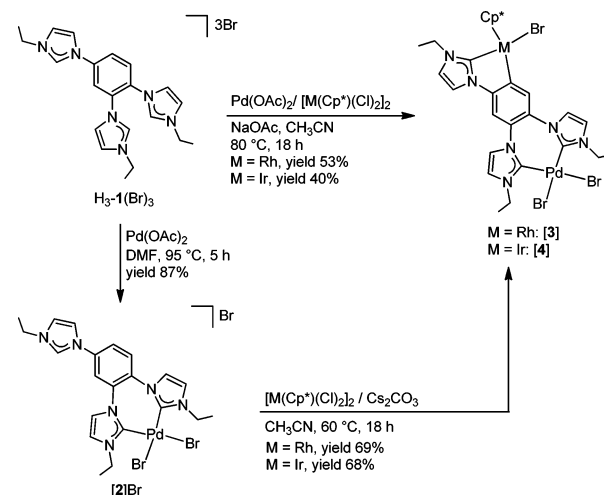
N-heterocyclic carbenes (NHCs) have emerged as a very useful class of ligands in organometallic chemistry over the last few decades.¹ NHCs have been used extensively as spectator ligands in catalytically active metal complexes,² in organocatalysis,³ and in biologically active compounds.⁴ Applications for NHCs may be further enhanced by incorporation of the NHC donor groups into poly-NHC ligands.⁵ Very recently, poly-NHC ligands have also been used for the generation of two- or three-dimensional metallosupramolecular assemblies.⁶

Since the emergence of the first poly-NHC ligands, the preparation of polymetallic and heterobimetallic carbene complexes with applications in cooperative or tandem catalysis has become a focus of interest. The first attempts were reported in 2000, when a 1,2,4-triazolidin-3,5-diylidene was doubly metalated with Ag^I , leading to a one-dimensional polymeric chain.⁷ Later, Arduengo et al.⁸ described a cyclopentadienyl-fused imidazolium cation that was employed to prepare a ruthenocene derivative by reaction with $[Ru(Cp^*)(MeCN)_3]-(CF_3SO_3)$. Subsequent oxidative addition of Pd^0 to the imidazolium C2–C1 bond gave the heterobimetallic complex featuring an η^5, η^5 -coordinated Ru^{II} and an NHC-coordinated Pd^{II} . Doubly metalated benzobiscarbenes bearing two identical metals have been described⁹ in addition to several dinuclear complexes derived from flexible bis(NHC) ligands,^{10a} some of which could be metalated stepwise with two different metals.^{10b,c} Probably the most promising approaches to heterobimetallic NHC complexes were described by Peris and co-workers, who attached two different complex fragments to a 1,2,4-triazolyldiylidene in a stepwise manner.¹¹ In addition, they prepared a Y-shaped tris(NHC) ligand derived from a 4,5-bis(NHC)-substituted imidazolin-2-ylidene. This ligand could be metalated in a stepwise fashion, leading to heterobimetallic complexes featuring one metal coordinated by two NHC

donors in a chelating fashion and a second metal center coordinated by only one NHC donor. The metalation pattern of this tris(NHC) ligand depended on the sequence of addition of the metal sources, underlining the stepwise nature of the metalation process.¹²

We became interested in the heterobimetallic metalation of polycarbenes in a one-pot procedure. We envisaged that an unsymmetrical tricarbene ligand could be metalated simultaneously with two different metals by utilizing the differences in their coordination chemistries. The 1,2,4-tris(imidazolium)-substituted NHC precursor $H_3-1(Br)_3$ reacts simultaneously with $Pd(OAc)_2$ and $[M(Cp^*)(Cl)_2]_2$ ($M = Rh, Ir$) to give complexes [3] ($M = Rh$) and [4] ($M = Ir$) in a one-pot synthesis (Scheme 1).

Scheme 1. Synthesis of the Monometalated Complex [2]Br and the Heterobimetallic Complexes [3] and [4]



The design of the ligand precursor $H_3-1(Br)_3$ was based on previous observations. It is known that 1,2-bis(NHC)-substituted benzenes react with Pd^{II} or Pt^{II} to form *cis*-dicarbene chelate complexes of type A (Figure 1).^{6h} Alternatively, 1,3,5-tris(NHC)-substituted benzenes react with $[M(Cp^*)(Cl)_2]_2$ ($M = Rh, Ir$) to yield complexes in which the metal center bears only one NHC ligand and in addition orthometalates the central phenyl group. Even trinuclear

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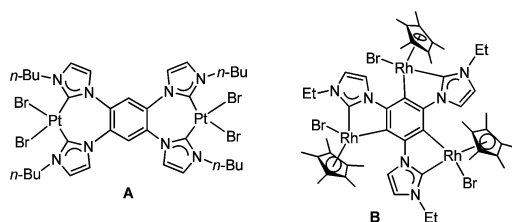


Figure 1. Coordination modes of 1,2- and 1,3,5-substituted poly-NHC ligands.

complexes such as **B** featuring a tris-orthometalated central phenylene group (Figure 1) have been prepared.¹³ Combining the 1,2- and 1,4-substitution patterns in one ligand led to the unsymmetrical 1,2,4-tris(imidazolium) NHC precursor **H₃-1(Br)₃** which was designed to react simultaneously with Pd(OAc)₂ and [M(Cp*)(Cl)₂]₂ in a one-pot reaction with regioselective metalation of the two different coordination sites.

The tris(imidazolium) salt **H₃-1(Br)₃** (Scheme 1) was prepared by heating a mixture of 1,2,4-tribromobenzene and imidazole in the presence of the base K₂CO₃ and CuSO₄ followed by alkylation of the free imine functions with ethyl bromide [see the Supporting Information (SI)]. The ¹H NMR spectrum of **H₃-1(Br)₃** shows three distinctly different resonances for the chemically nonequivalent imidazolium C2–H protons at 10.41, 10.07, and 9.91 ppm, with the resonance for the imidazolium moiety located at the 4-position of the aromatic ring at the lowest field.

The reaction of **H₃-1(Br)₃** with 1 equiv of Pd(OAc)₂ and 0.5 equiv of [M(Cp*)(Cl)₂]₂ (M = Rh, Ir) in a one-pot reaction in the presence of sodium acetate selectively gave the heterobimetallic complexes **[3]** and **[4]**, respectively, in yields of 40–53% (Scheme 1; also see the SI). No regioisomeric complexes were detected. The Pd(II) ion is selectively coordinated by the chelating 1,2-bis(NHC) moiety, whereas the M^{III} center is coordinated by a single NHC donor and orthometalates the phenyl ring at the sterically least encumbered ortho position next to this NHC donor.

Two geometric isomers of both complexes **[3]** and **[4]** were identified by NMR spectroscopy. Their formation is caused by the two possible orientations of the halogenato ligands relative to each other (*syn* or *anti*). The isomers were separated (*syn*:*anti* ratio ≈ 33:67) by column chromatography using a 4:1 (v/v) dichloromethane/acetone solvent mixture (see the SI).

The formation of heterobimetallic complexes **[3]** and **[4]** was confirmed by ¹H, ¹³C{¹H}, and 2D correlation NMR spectroscopy and mass spectrometry. The ¹H NMR spectra of *syn/anti*-**[3]** featured no imidazolium C2–H resonances. The ¹³C{¹H} NMR spectra of *syn/anti*-**[3]** also indicated the absence of any imidazolium groups, which were detected in **H₃-1(Br)₃** at 138.2, 138.1, and 135.9 ppm. The imidazolium resonances were replaced with the characteristic carbene resonances (*syn* isomer: 180.6 ppm, ¹J_{Rh,C} = 54.8 Hz for Rh–C_{NHC} and 159.9 and 159.8 ppm for Pd–C_{NHC}; *anti* isomer: 183.4 ppm, ¹J_{Rh,C} = 55.1 Hz for Rh–C_{NHC} and 162.2 ppm for Pd–C_{NHC}). These values fall in the typical range reported for Rh^{III}–C_{NHC}^{13,14} and Pd^{II}–C_{NHC}¹⁵ complexes. The ¹³C{¹H} NMR spectra of *syn/anti*-**[4]** also showed the characteristic resonances for the carbene carbon atoms for both isomeric complexes (*syn* isomer: 164.1 ppm for Ir–C_{NHC} and 159.8 and 159.6 ppm for Pd–C_{NHC}; *anti* isomer: 166.3 ppm for Ir–C_{NHC} and 162.1 and 162.0 ppm for Pd–C_{NHC}). Again, these values

match well with previously reported chemical shifts for related Pd^{II}¹⁵ and Ir^{III}^{13,14,16} complexes.

The orthometalation of the central aryl ring of the ligand in both **[3]** and **[4]** was confirmed by 2D correlation NMR spectroscopy. For the rhodium complexes *syn/anti*-**[3]**, the resonances for the orthometalated carbon atoms were observed at 160.6 ppm (¹J_{Rh,C} = 36.9 Hz) for the *syn* isomer and 162.4 ppm (¹J_{Rh,C} = 35.4 Hz) for the *anti* isomer. Two resonances at higher field were found for *syn/anti*-**[4]** at 144.1 and 146.5 ppm, respectively. For *syn/anti*-**[3]** the ¹J_{Rh,C} coupling clearly indicates the metalation of the central aryl ring of the ligand. The formation of complexes **[3]** and **[4]** was also confirmed by high-resolution electrospray ionization (ESI) mass spectrometry (positive ion mode), which showed peaks at *m/z* 903.9876 for [**[3]** – Br + CH₃CN]⁺ (calcd for [**[3]** – Br + CH₃CN]⁺, 903.9874) and *m/z* 994.0436 for [**[4]** – Br + CH₃CN]⁺ (calcd for [**[4]** – Br + CH₃CN]⁺, 994.0437).

The connectivity and overall geometry of complex *syn*-**[4]** was established by X-ray crystallography. Suitable crystals of *syn*-**[4]**·CHCl₃·3CH₃CN were obtained by slow evaporation of the solvents from a concentrated acetonitrile/chloroform solution of the complex at ambient temperature. The structure analysis confirmed the formation of the heterobimetallic complex and showed that two *o*-NHC donors are bonded to the Pd^{II} center in a chelating fashion while the Ir^{III} center is coordinated by only one NHC donor and orthometalates the central phenyl ring of the ligand (Figure 2).

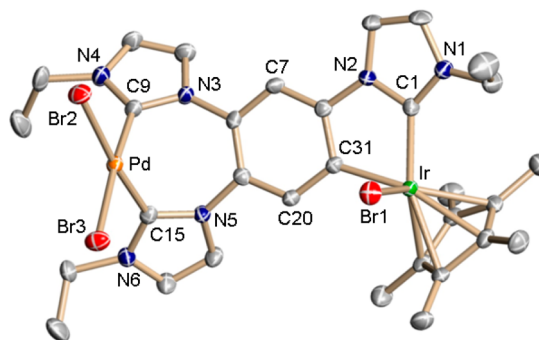


Figure 2. Molecular structure of *syn*-**[4]** in *syn*-**[4]**·CHCl₃·3CH₃CN (H atoms and solvent molecules have been omitted for clarity, 50% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ir–Br1, 2.5301(3); Ir–C1, 1.999(3); Ir–C31, 2.049(3); Pd–Br2, 2.4756(4); Pd–Br3, 2.4836(4); Pd–C9, 1.961(3); Pd–C15, 1.963(3); N1–C1, 1.349(4); N2–C1, 1.361(4); N3–C9, 1.359(4); N4–C9, 1.346(4); N5–C15, 1.348(4); N6–C15, 1.340(4); Br1–Ir–C1, 86.87(8); Br1–Ir–C31, 89.44(8); C1–Ir–C31, 77.22(11); Br2–Pd–Br3, 93.615(13); Br2–Pd–C9, 91.31(9); Br2–Pd–C15, 174.07(8); Br3–Pd–C9, 174.69(9); Br3–Pd–C15, 90.83(8); C9–Pd–C15, 84.12(12); N1–C1–N2, 104.3(2); N3–C9–N4, 105.6(2); N5–C15–N6, 105.8(2).

The coordination geometry at the Pd^{II} center is best described as slightly distorted square-planar, while that at Ir^{III} resembles a three-legged piano stool with the NHC, C_{aryl}, and bromo donors functioning as the legs. In *syn*-**[4]**, the bromine atoms bound to the Pd atom point in the same direction as the bromine atom bonded to the Ir center relative to the central aryl ring.

The Pd–C_{NHC} bond lengths are equidistant within experimental error [Pd–C9, 1.961(3) Å; Pd–C15, 1.963(3) Å] and slightly shorter than the Ir–C_{NHC} and Ir–C_{aryl} bond

lengths [Ir–C1, 1.999(3) Å; Ir–C31, 2.049(3) Å]. Interestingly, the Ir–C_{NHC} bond distance is shorter than the Ir–C_{aryl}^{III} separation. Similar observations have been made for an Ir^{III} complex bearing a benzyl-substituted NHC ligand that was also orthometalated, leading to a six-membered chelate ring.^{16c} However, the Ir–C_{NHC} and Ir–C_{aryl} distances in that complex [Ir–C_{NHC}, 2.014(7) Å; Ir–C_{aryl}, 2.068(8) Å] are distinctly longer than the equivalent distances in *syn*-[4]. The six-membered chelate ring also leads to a larger C_{NHC}–Ir–C_{aryl} bite angle of 85.7(3)° compared with the equivalent bite angle of 77.22(11)° found in *syn*-[4]. The Ir···Pd separation in *syn*-[4] measures 7.240 Å.

Complexes [3] and [4] can also be synthesized following a stepwise synthetic procedure. In this case, the monometallic intermediate [2]Br was prepared and isolated (Scheme 1). The reaction of tris(imidazolium) salt H₃-1(Br)₃ with 1 equiv of Pd(OAc)₂ in *N,N*-dimethylformamide (DMF) for 5 h at 95 °C resulted in the formation of the bis(NHC) Pd(II) chelate complex [2]Br in a good yield of 87%. We observed exclusive Pd^{II} coordination to the two NHC donors at the 1- and 2-position of the central aryl ring, while the remaining imidazolium moiety did not react (Scheme 1).

The formation of [2]Br was confirmed by ¹H and ¹³C{¹H} NMR spectroscopy and mass spectrometry. The resonance for the remaining imidazolium proton was detected at 10.19 ppm in the ¹H NMR spectrum. The ¹³C{¹H} NMR spectrum of complex [2]Br revealed two characteristic carbene resonances at 160.4 and 160.2 ppm for the *cis*-Pd(NHC)₂ moiety, while the resonance for the C2 carbon atom of the free imidazolium group was observed at 135.9 ppm. This value is identical to that for the same C2 carbon atom in the tris(imidazolium) salt H₃-1(Br)₃. The ESI mass spectrum (positive ion mode) showed the peak for the cationic complex [2]⁺ at *m/z* 626.9530 (calcd for [2]⁺, 626.9532) as one of the strongest signals (see the SI).

Reaction of the monometalated complex [2]Br with 0.5 equiv of [M(Cp*)(Cl)₂]₂ (M = Ir, Rh) in the presence of Cs₂CO₃ gave the heterobimetallic complexes *syn/anti*-[3] and *syn/anti*-[4] in good yields of 68–69% (total yield over the two reaction steps was 60%, compared with 40–52% in the one-pot synthesis). The ease of the one-pot procedure outweighs the slightly higher yields of the two-step synthesis. The ratio of the formed *syn* and *anti* isomers was not significantly affected by the synthetic protocol used.

We have prepared the novel tris(imidazolium) salt H₃-1(Br)₃, which can be metalated regioselectively with two different transition-metal complex fragments in a one-pot reaction. The ligand topology favors the binding of Pd^{II} in a chelating fashion by two NHC donors in *ortho* positions at the central aryl ring of 1, while the remaining NHC donor of the ligand binds to Rh^{III} or Ir^{III} with concurrent orthometalation of the central aryl ring. The differences in the reactivities of the metal centers together with the topology of the ligand (chelate formation vs carbene binding and orthometalation) allowed the regioselective one-pot formation of the heterobimetallic complexes. The formation of two isomeric complexes (*syn* and *anti*) posed no problem, as the isomeric complexes were easily separated by column chromatography. The separation of the two metal centers in [3] and [4] is rather large, although cooperative catalysis has been observed with heterobimetallic NHC complexes featuring an M···M' separation of up to 6.7 Å.^{11,12} The strategy employed for the preparation of [3] and [4] can be utilized to generate heterobimetallic complexes with a

shorter separation of the metal centers, and corresponding investigations are underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details for the synthesis of all compounds and X-ray crystallographic data (CIF) for [4]·CHCl₃·3CH₃CN. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849. (b) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677–3707. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172. (d) Kaufhold, O.; Hahn, F. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4057–4061.
- (2) (a) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676. (b) Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6786–6801. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (d) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29.
- (3) (a) Loh, C. C. J.; Enders, D. *Chem.—Eur. J.* **2012**, *18*, 10212–10225. (b) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000. (c) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655.
- (4) (a) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Chem. Rev.* **2009**, *109*, 3859–3884. (b) Sivaram, H.; Tan, J.; Huynh, H. V. *Organometallics* **2012**, *31*, 5875–5883.
- (5) (a) Edwards, P. G.; Hahn, F. E. *Dalton Trans.* **2011**, *40*, 10278–10288. (b) Corberán, R.; Mas-Marzá, E.; Peris, E. *Eur. J. Inorg. Chem.* **2009**, 1700–1716. (c) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610–641.
- (6) (a) Hu, X.; Castro-Rodríguez, I.; Meyer, K. J. *Am. Chem. Soc.* **2003**, *125*, 12237–12245. (b) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. *Chem.—Eur. J.* **2008**, *14*, 10900–10904. (c) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. *Organometallics* **2008**, *27*, 6408–6410. (d) Radloff, C.; Weigand, J. J.; Hahn, F. E. *Dalton Trans.* **2009**, 9392–9394. (e) Radloff, C.; Hahn, F. E.; Pape, T.; Fröhlich, R. *Dalton Trans.* **2009**, 7215–7222. (f) Rit, A.; Pape, T.; Hahn, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 4572–4573. (g) Rit, A.; Pape, T.; Hahn, F. E. *Organometallics* **2011**, *30*, 6393–6401. (h) Rit, A.; Pape, T.; Hepp, A.; Hahn, F. E. *Organometallics* **2011**, *30*, 334–347. (i) Conrady, F. M.; Fröhlich, R.; Schulte to Brinke, C.; Pape, T.; Hahn, F. E. *J. Am. Chem. Soc.* **2011**, *133*, 11496–11499. (j) Schmidendorf, M.; Pape, T.; Hahn, F. E. *Angew. Chem., Int. Ed.* **2012**, *51*, 2195–2198. (k) Schulte to Brinke, C.; Pape, T.; Hahn, F. E. *Dalton Trans.* **2012**, DOI: 10.1039/c2dt32905k.
- (7) (a) Guerret, O.; Solé, S.; Gornitzka, H.; Trinquier, G.; Bertrand, G. *J. Organomet. Chem.* **2000**, *600*, 112–117. (b) Guo, S.; Huynh, H. V. *Organometallics* **2012**, *31*, 4565–4573.
- (8) Arduengo, A. J., III; Tapu, D.; Marshall, W. J. *J. Am. Chem. Soc.* **2005**, *127*, 16400–16401.
- (9) (a) Khramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6186–6189. (b) Boydston, A. J.; Bielawski, C.

W. Dalton Trans. **2006**, 4073–4077. (c) Mercks, L.; Neels, A.; Albrecht, M. Dalton Trans. **2008**, 5570–5576.

(10) (a) Mercks, L.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. Dalton Trans. **2009**, 7168–7178. (b) Zamora, M. T.; Ferguson, M. J.; McDonald, R.; Cowie, M. Organometallics **2012**, 31, 5463–5477. (c) Zamora, M. T.; Ferguson, M. J.; Cowie, M. Organometallics **2012**, 31, 5384–5395.

(11) (a) Zanardi, A.; Corberán, R.; Mata, J. A.; Peris, E. Organometallics **2008**, 27, 3570–3576. (b) Zanardi, A.; Mata, J. A.; Peris, E. J. Am. Chem. Soc. **2009**, 131, 14531–14537. (c) Sabater, S.; Mata, J. A.; Peris, E. Organometallics **2012**, 31, 6450–6456.

(12) Gonell, S.; Poyatos, M.; Mata, J. A.; Peris, E. Organometallics **2012**, 31, 5606–5614.

(13) Maity, R.; Rit, A.; Schulte to Brinke, C.; Daniliuc, C. G.; Hahn, F. E. Chem. Commun. **2013**, 49, 1011–1013.

(14) (a) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. J. Am. Chem. Soc. **2005**, 127, 3516–3526. (b) Viciano, M.; Mas-Marzá, E.; Poyatos, M.; Sanaú, M.; Crabtree, R. H.; Peris, E. Angew. Chem., Int. Ed. **2005**, 44, 444–447.

(15) (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. Angew. Chem., Int. Ed. Engl. **1995**, 34, 2371–2374. (b) Heckenroth, M.; Neels, A.; Garnier, M. G.; Aebi, P.; Ehlers, A. W.; Albrecht, M. Chem.—Eur. J. **2009**, 15, 9375–9386. (c) Heckenroth, M.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. Inorg. Chim. Acta **2006**, 359, 1929–1938.

(16) (a) Hanasaka, F.; Tanabe, Y.; Fujita, K.-i.; Yamaguchi, R. Organometallics **2006**, 25, 826–831. (b) Tanabe, Y.; Hanasaka, F.; Fujita, K.-i.; Yamaguchi, R. Organometallics **2007**, 26, 4618–4626. (c) Corberán, R.; Sanaú, M.; Peris, E. J. Am. Chem. Soc. **2006**, 128, 3974–3979. (d) Raynal, M.; Cazin, C. S. J.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. Chem. Commun. **2008**, 3983–3985. (e) Corberán, R.; Sanaú, M.; Peris, E. Organometallics **2006**, 25, 4002–4008.