VIP Single-Crystal Reactions

DOI: 10.1002/anie.201103316

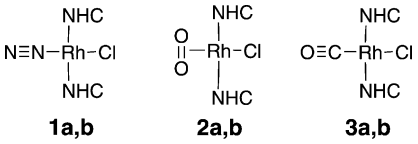
Double Single-Crystal-to-Single-Crystal Transformation and Small-Molecule Activation in Rhodium NHC Complexes**

*Olena V. Zenkina, Eric C. Keske, Ruiyao Wang, and Cathleen M. Crudden**

Dedicated to Professor Howard Alper on the occasion of his 70th birthday

Examples of chemical reactions that occur in the solid state without disruption of crystalline order are quite rare.[1] The most prevalent among these are photochemical reactions,[1j,2] absorption/desorption of solvents from porous materials,[3] or changes in coordination polymers.[1a,d,j,4] There are very few examples of single-crystal-to-single-crystal reactions of monomolecular species being reported[1e,5] and even fewer examples of such transformations of organometallic compounds. Notable exceptions include the recent elegant reports by van Koten,[6a,b] Brookhart,[7] and McKeown,[3a] which describe single-crystal-to-single-crystal transformations in which the coordination environment around a transition metal changes. These transformations are of significant interest in terms of crystal engineering, chemical sensing, and materials science in general.[1l,m,3b,d,4b,6b,8]

We have recently discovered an example in this rare series of organometallic single-crystal-to-single-crystal transformations. Furthermore, we will show that two sequential single-crystal-to-single-crystal transformations can occur back to back, such that one single crystal is converted into two new chemical entities without loss of crystallinity. These reactions involve the conversion of a rhodium dinitrogen complex, in which the N_2 unit is bound in an end-on fashion, into a rhodium dioxygen complex with the O_2 bound side-on, and finally to a rhodium carbon monoxide complex, with CO bound in the typical end-on fashion. These transformations were being studied as part of our program revolving around the chemistry of rhodium N-heterocyclic carbene (NHC) complexes.[9] These ligands have been employed for a wide variety of transition-metal-catalyzed reactions[9b,h,10] since their isolation by Arduengo et al. in 1991.[11] In particular, we were interested in the use of NHCs for their increased oxidative stability in comparison to phosphines. In particular, we and others have been interested in the reaction of rhodium complexes of bulky, electron-rich ligands with O_2.[9a,c,12] Interestingly, these types of ligands seem to promote the formation of what can best be described as rare examples of pseudo square-planar rhodium(I) complexes of singlet oxygen (**2**).[9a,c] These compounds could be prepared from a

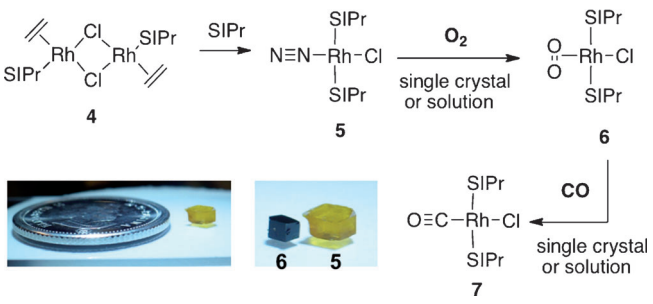


NHC = IPr (a) or IMes (b)

variety of precursors, but the cleanest reaction was observed using dinitrogen complexes **1**. Conversion of **1** into **2** is irreversible; however, O_2 complexes **2** can also be converted into CO complexes **3**.

As part of our attempts to understand why these relatively electron-rich rhodium species do not undergo oxidation to Rh^{III}, we began a study of rhodium complexes ligated by different NHC ligands. Since steric effects are postulated to play a key role in the reactivity of these and related rhodium species,[12a] we began with an NHC having similar electronic properties, but increased steric constraints, SIPr.[13] These studies have resulted in the isolation of key intermediates on the way to the final O_2 complex, as well as the discovery of single-crystal-to-single-crystal-to-single-crystal transformations in this series.

Our studies began with treatment of $[\{Rh(H_2C{=}CH_2)Cl\}_2]$ with the free carbene SIPr (Scheme 1). Depending on the ratio of NHC to rhodium, either ethylene adduct **4** or rhodium dinitrogen adduct **5** were obtained. Exposure of **5** to O_2 in solution results in a dramatic color change from yellow to blue, indicating the formation of rhodium dioxygen complex **6**, which is a new example of a Rh^I complex of singlet O_2. Interestingly, the interconversion of **5** into **6** also took place in



Scheme 1. Selective formation of rhodium complexes **4**–**7**. SIPr = *N*,*N*′-(2,6-*i*Pr$_2$C$_6$H$_3$)$_2$C$_3$H$_4$N$_2$.

[*] O. V. Zenkina, E. C. Keske, R. Wang, Prof. C. M. Crudden
Department of Chemistry, Queen's University
Chernoff Hall, 90 Bader Lane, Kingston, Ontario (Canada)
E-mail: cathleen.crudden@chem.queensu.ca
Homepage: http://www.cruddengroup.com

[**] The National Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for support of this research, and Johnson Matthey is acknowledged for a gift of $[\{Rh(C_2H_4)_2Cl\}_2]$.
NHC = N-heterocyclic carbene.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201103316.

the solid state, proceeding by a single-crystal-to-single-crystal transformation.[1–5,14] Herein we describe the details of these investigations and the full characterization of all of complexes **4**–**7** in addition to their decomposition products.

The reaction of $[\{Rh(C_2H_4)Cl\}_2]$ with 2 equivalents of SIPr in an organic solvent (such as benzene, THF) at room temperature results in the quantitative formation of complex **4**. This species was isolated and fully characterized by a combination of ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. Furthermore, the molecular structure of complex **4** was determined by single-crystal X-ray analysis (Figure 1). η^2-Coordination of

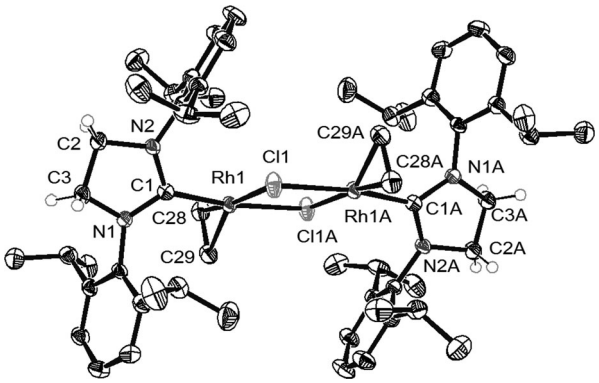


Figure 1. Crystallographically determined structure of $[\{Rh(SIPr)(C_2H_4)Cl\}_2]$ (**4**), with ellipsoids set at 50% probability. There is half of a molecule of complex **4** per asymmetric unit. Hydrogen atoms (except for those of the SIPr backbone) are omitted for clarity.

ethylene to each metal center is evident from the ^1H and ^{13}C NMR spectra.[15] At room temperature, the ^1H NMR spectrum of complex **4** shows very broad resonances for the ethylene protons (as well as for the saturated backbone of SIPr) that sharpen to clear doublets when the sample is cooled down below −30 °C. In the $^{13}C\{^1H\}$ NMR spectrum, a characteristic doublet ($^1J_{RhC} = 16.7$ Hz) ascribed to the η^2-C=C moiety is clearly observable at $\delta = 46.7$ ppm. The carbene peak appears at $\delta = 205.89$ ppm as a doublet with coupling to rhodium ($^1J_{RhC} = 58.0$ Hz). The observed coupling constant is almost identical to the structurally related species $[\{Rh(coe)(I\mathit{t}Bu)Cl\}_2]$[15b] (coe = cyclooctene; $^1J_{RhC} = 56.9$ Hz). Although a variety of rhodium olefin complexes, such as the latter, have been isolated and characterized, this is the first report we are aware of in which a dimeric ethylene–rhodium–NHC complex has been isolated. The dearth of these complexes is most likely due to the high lability of ethylene compared to other olefins.[15a]

Complex **4** exhibits a nearly planar geometry around each metal center, with both rhodium centers and chlorine atoms in one plane. The dihedral angle between the plane containing both rhodium centers (Rh1-Cl1-Rh1A-Cl1A) and the N1–C1–N2 plane of the heterocyclic rings of the corresponding carbene ligands is 58.47°. Deviation from planarity of the heterocyclic rings of the NHC is quite significant and is represented by the torsion angle (N1–C2–C3–N2) of 25.61°. The dihedral angle between the N1–C1–N2 plane and the Dipp groups of the carbene ligand is 69.18°. The distance between the two rhodium centers Rh1–Rh1A is 3.613 Å. Coordination to the rhodium centers induces significant lengthening of the C–C ethylene bond (that is, C28–C29, 1.383(4)) in comparison to uncomplexed ethylene 1.3391(13) Å.[16] The Rh–C=C bonds are 2.092–2.108 Å, which correlates well with the literature.[15c]

Treatment of complex **4** with an additional 2 equivalents of SIPr in a nitrogen atmosphere for 24 h yields the corresponding end-on dinitrogen complex **5**. This species was fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry, IR spectroscopy, elemental analysis, and X-ray crystallographic analysis (Figure 2). X-ray-quality crystals of this dinitrogen complex were obtained by slow diffusion of hexane into a concentrated THF solution of **5**. The N–N bond of bound dinitrogen in **5** has a bond length of 1.118(19)–1.110(10) Å (corresponding to two independent molecules with slightly different bond lengths observed by X-ray diffraction) versus 1.0975 Å in free dinitrogen,[17] and the ν(N-N) appears in the IR spectrum at 2107 cm^{-1}.

Exposure of a solution of compound **5** in THF to oxygen or air results in the formation of complex **6**, in which O_2 is

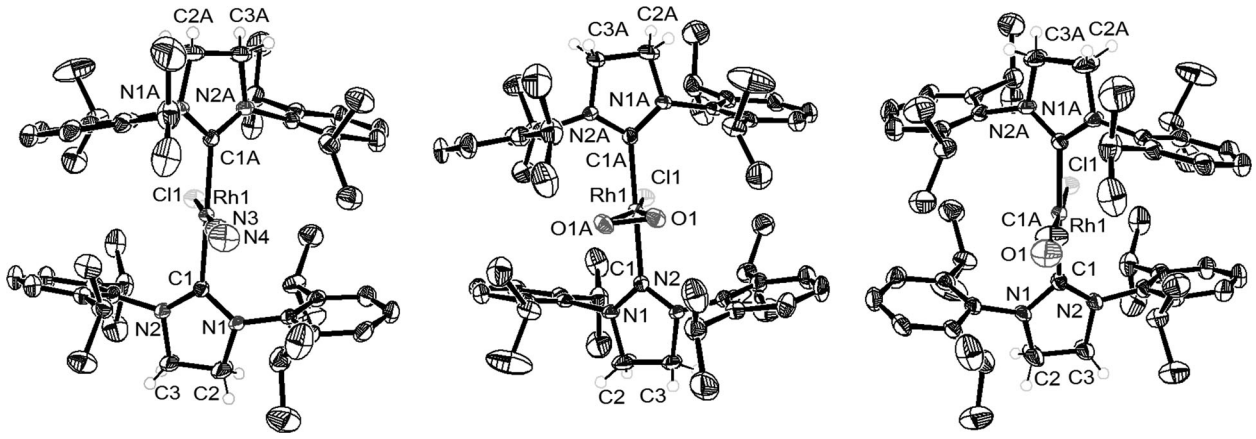


Figure 2. Crystallographically determined structures of $[Rh(SIPr)_2(N_2)Cl]$ (**5**, left), $[Rh(SIPr)_2(O_2)Cl]$ (**6**, middle), and $[Rh(SIPr)_2(CO)Cl]$ (**7**, right), with ellipsoids set at 50% probability. Hydrogen atoms (except for those of the SIPr backbone) are omitted for clarity. For details, see the Supporting Information.

bound side-on to rhodium. As expected based on our previous work,[9a–c] compound **6** is isolated as a square-planar complex of dioxygen with an oxygen–oxygen bond that is shorter than the characteristic peroxo bond of ca. 1.45 Å, as previously observed.[12b,d,17]

Compound **6** could also be synthesized by treating a THF solution of $[\{Rh(C_2H_4)_2Cl\}_2]$ with 4 equivalents of SIPr in a nitrogen atmosphere, and directly exposing the resulting yellow solution to air or oxygen. After 12 h under an atmosphere of oxygen, the resulting green residue was purified by column chromatography, yielding pure complex **6** as a deep blue powder.[18] Complex **6** has been isolated and characterized by the same means as **4**. NMR spectra of complex **6** are very similar to those obtained for the rhodium bis(IPr) analogue previously reported by our group.[9c]

Exposure of a THF solution of compound **5** to CO atmosphere generates complex **7**. Complex **7** has been isolated and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry, IR spectroscopy, and elemental analysis. The X-ray structures of complexes **5**–**7** are pseudo square-planar with slight distortions arising from a subtle tilting of the two rhodium carbene bonds towards the chloride ligand (Figure 2).

Dihedral angles between the heterocyclic rings of the *trans* carbene ligands are 52.19°, 53.09°, and 53.73° for **5**, **6**, and **7**, respectively. The heterocyclic rings of the carbene ligands are nearly planar, with minor deviation from planarity represented by the torsion angles (N1–C2–C3–N2) of 12.35° (**5**), 6.65° (**6**), and 12.26° (**7**). The heterocyclic rings of the carbene ligands are almost perpendicular to their corresponding Dipp groups, with a dihedral angle of 78.40° (**5**), 80.26°(**6**), and 77.17°(**7**). Complexes **5**, **6**, and **7** are essentially square-planar, with an angle between the carbene atoms and rhodium of 177.53° (**5**), 178.08° (**6**), and 178.44° (**7**).

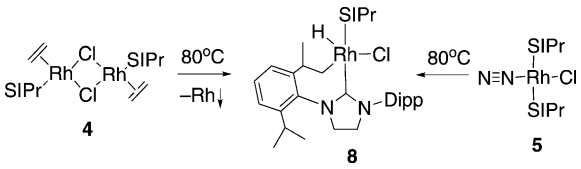
The rhodium–carbene bonds are nearly identical to structurally related rhodium bis(IPr) O_2 complexes.[9c] As previously noted, the O–O bond (O1–O1A) of complex **6** is shorter than typical peroxo bonds[12b,d,19] at 1.392(11) Å, which is consistent with other examples of related complexes.[9c] As the complex also has square-planar geometry, it is likely that complex **6** is another example of Rh^I singlet oxygen complexes. Despite the fact that NMR spectra appeared clean and sharp, small amounts of the paramagnetic $[Rh(SIPr)_2(Cl)_2]$ impurity often co-crystallized with the complexes **5**–**7**. Incorporation of $[Rh(SIPr)_2(Cl)_2]$ in the single crystals of **5**—**7** varies from 6–25%.

The transformations described above were also observed to take place in the single-crystal form. Exposure of yellow crystals of **5** to air or oxygen for an extended period of time (15 days) results in the selective conversion into single crystals of blue complex **6**, without cracking, yielding crystals suitable for X-ray diffraction analysis (Figure 2). Remarkably, following this, we were able to treat crystals of the rhodium O_2 complex **6** with CO for 7 days, resulting in the formation of the corresponding carbonyl complex in another single-crystal-to-single-crystal transformation without destruction of the crystal. X-ray analysis was conducted before and after each of these transformations.

All three crystalline forms of the yellow nitrogen adduct **5**, blue oxygen adduct **6**, and brown carbonyl adduct **7** (Figure 3) have an orthorhombic $P2_12_12$ space group with almost identical unit cells (Supporting Information, Table S1). Clearly, the loss of dinitrogen and the concurrent slow diffusion of oxygen (or loss of oxygen and concurent diffusion of CO) have minor effects on the molecular arrangement in the crystalline state.

Exposure of single crystals of complex **5** to an atmosphere for argon for 13 days resulted in no net loss of nitrogen, whereas exposure to oxygen for this same time period resulted in complete conversion into complex **6**. These results are consistent with a mechanism proposed by Brookhart, where the ligand exchange occurs within the crystal, rather than by dissociative displacement, however a dissociative mechanism cannot entirely be ruled out.

At elevated temperatures (80 °C) in solution, complex **4** converts slowly into another species (**8**) along with the formation of rhodium black. Formation of the paramagnetic complex **9** $[Rh(SIPr)_2(Cl)_2]$ was also observed. Although the presence of the paramagnetic impurity caused some broadness in the ^1H NMR spectra, the NMR data of **8** are consistent with its nonsymmetrical nature in which the metal center is bound to two SIPr ligands with cyclometalation at an isopropyl group of one of the SIPr ligands (Scheme 2).[15b]



Scheme 2. Selective formation of rhodium complex **8**. Dipp = 2,6-$iPr_2C_6H_3$.

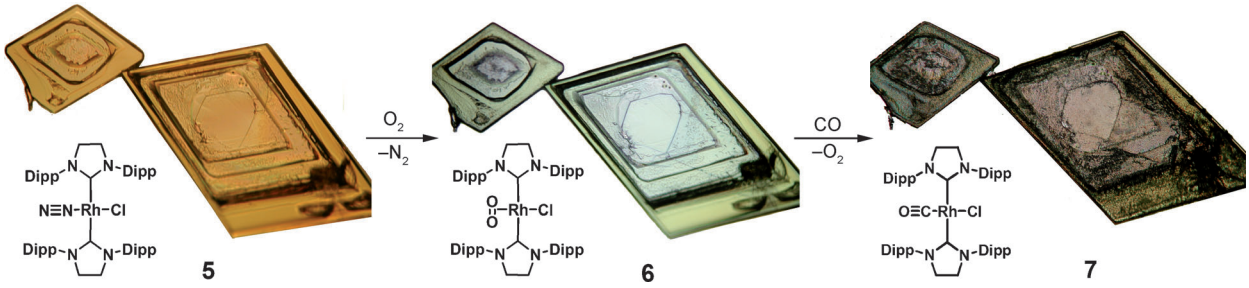


Figure 3. The structural conversion of complexes **5**→**6**→**7** in single-crystal form. Dipp = 2,6-$iPr_2C_6H_3$.

This result can be observed by ^{13}C NMR spectroscopy, as two distinctly different carbene peaks with equal intensity appear as doublets at $\delta = 197.90$ and $\delta = 191.89$ ppm with a coupling to rhodium of 48.28 and 50.53 Hz respectively. Furthermore, a characteristic signal for the cyclometalated CH_2 group appears at $\delta = 26.9$ ppm. Complex **8** exhibited an IR band for ν(Rh-H) at 1963 cm^{-1} that is characteristic of a rhodium hydride species. Although the ^1H NMR spectrum is very broad at room temperature, upon cooling, the characteristic hydride resonance becomes clearly visible as a doublet at $\delta = -23.38$ ppm ($^1J_{RhH} = 18$ Hz). T_1 measurements on this signal at 193 K give a relaxation time of 522.8 ms, confirming its hydridic nature.[20] Complex **8** could also be synthesized by heating a solution of complex **5** for 4 h at 80 °C in quantitative yield as determined by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Interestingly, when complex **8** was heated for 12 h under 2 atm. of deuterium gas, the only significant incorporation of deuterium observed occurred on the isopropyl groups of the SIPr ligand, as determined by ^2D and ^1H NMR spectroscopy. The hydride peak, which was observed at $\delta = -23.38$ ppm of the ^1H NMR spectrum, remains unaffected, and no deuterium incorporation occurred in this position as determined by ^2D and ^1H NMR.

In conclusion, we have synthesized several rhodium bis(NHC) complexes featuring the saturated SIPr ligand that are able to activate small molecules, such as N_2, O_2, and CO and also intramolecular C–H bonds from the SIPr ligand. As observed previously by our group, the rhodium complex does not undergo oxidation when reacted with O_2, which is presumably due to the significant steric bulk around the complex provided by the SIPr carbene ligands, preventing expansion of the coordination number from 4 to 6.[12a] The fact that CO binds better than N_2 or O_2 may make this system suitable for the detection of CO in air.[21] Finally, we have demonstrated that dinitrogen complex **5** can convert into the dioxygen complex **6** followed by conversion into carbonyl complex **7** by an unusual double single-crystal-to-single-crystal transformation.

Received: May 14, 2011
Published online: July 8, 2011

Keywords: hydrides · N-heterocyclic carbenes · rhodium · single-crystal reactions · X-ray diffraction

[1] a) D. Liu, Z.-G. Ren, H.-X. Li, J.-P. Lang, N.-Y. Li, B. F. Abrahams, *Angew. Chem.* **2010**, *122*, 4877; *Angew. Chem. Int. Ed.* **2010**, *49*, 4767; b) S. M. Mobin, A. K. Srivastava, P. Mathur, G. K. Lahiri, *Dalton Trans.* **2010**, *39*, 8698; c) H. J. Park, Y. E. Cheon, M. P. Suh, *Chem. Eur. J.* **2010**, *16*, 11662; d) S. Libri, M. Mahler, G. M. Espallargas, D. C. N. G. Singh, J. Soleimannejad, H. Adams, M. D. Burgard, N. P. Rath, M. Brunelli, L. Brammer, *Angew. Chem.* **2008**, *120*, 1717; *Angew. Chem. Int. Ed.* **2008**, *47*, 1693; e) S. Supriya, S. K. Das, *J. Am. Chem. Soc.* **2007**, *129*, 3464; f) N. L. Toh, M. Nagarathinam, J. J. Vittal, *Angew. Chem.* **2005**, *117*, 2277; *Angew. Chem. Int. Ed.* **2005**, *44*, 2237; g) K. Takaoka, M. Kawano, M. Tominaga, M. Fujita, *Angew. Chem.* **2005**, *117*, 2189; *Angew. Chem. Int. Ed.* **2005**, *44*, 2151; h) H. J. Choi, M. P. Suh, *J. Am. Chem. Soc.* **2004**, *126*, 15844; i) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 3331; *Angew. Chem. Int. Ed.* **2004**, *43*, 3269; j) G. S. Papaefstathiou, Z. Zhong, L. Geng, L. R. MacGillivray, *J. Am. Chem. Soc.* **2004**, *126*, 9158; k) C.-Y. Su, A. M. Goforth, M. D. Smith, P. J. Pellechia, H.-C. zur Loye, *J. Am. Chem. Soc.* **2004**, *126*, 3576; l) K. Biradha, M. Fujita, *Angew. Chem.* **2002**, *114*, 3542; *Angew. Chem. Int. Ed.* **2002**, *41*, 3392; m) J. D. Ranford, J. J. Vittal, D. Wu, X. Yang, *Angew. Chem.* **1999**, *111*, 3707; *Angew. Chem. Int. Ed.* **1999**, *38*, 3498; n) J. D. Ranford, J. J. Vittal, D. Wu, *Angew. Chem.* **1998**, *110*, 1159; *Angew. Chem. Int. Ed.* **1998**, *37*, 1114.

[2] M. A. Garcia-Garibay, *Acc. Chem. Res.* **2003**, *36*, 491.

[3] a) C. G. Bezzu, M. Helliwell, J. E. Warren, D. R. Allan, N. B. McKeown, *Science* **2010**, *327*, 1627; b) C.-D. Wu, W. Lin, *Angew. Chem.* **2005**, *117*, 1994; *Angew. Chem. Int. Ed.* **2005**, *44*, 1958; c) M.-H. Zeng, X.-L. Feng, X.-M. Chen, *Dalton Trans.* **2004**, 2217; d) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2002**, *114*, 3545; *Angew. Chem. Int. Ed.* **2002**, *41*, 3395; e) H. Li, M. Eddaoudi, M. O'Keeffe, M. Yaghi, *Nature* **1999**, *402*, 276.

[4] a) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109; b) E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798; c) X. Ouyang, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.* **2003**, *125*, 12400.

[5] a) A. Lennartson, M. Hakansson, S. Jagner, *New J. Chem.* **2007**, *31*, 344; b) D. Braga, F. Grepioni, *Angew. Chem.* **2004**, *116*, 4092; *Angew. Chem. Int. Ed.* **2004**, *43*, 4002.

[6] a) M. Albrecht, M. Lutz, A. L. Spek, G. van Koten, *Nature* **2000**, *406*, 970; b) M. D. Meijer, R. J. M. K. Gebbink, G. Van Koten, *Perspect. Supramol. Chem.* **2003**, *7*, 375.

[7] Z. Huang, P. S. White, M. Brookhart, *Nature* **2010**, *465*, 598.

[8] a) M. Kawano, M. Fujita, *Coord. Chem. Rev.* **2007**, *251*, 2592; b) D. Braga, G. Cojazzi, D. Emiliani, L. Maini, F. Grepioni, *Chem. Commun.* **2001**, 2272.

[9] a) J. M. Praetorius, R. Wang, C. M. Crudden, *Eur. J. Inorg. Chem.* **2009**, 1746; b) J. M. Praetorius, C. M. Crudden, *Dalton Trans.* **2008**, 4079; c) J. M. Praetorius, D. P. Allen, R. Wang, J. D. Webb, F. Grein, P. Kennepohl, C. M. Crudden, *J. Am. Chem. Soc.* **2008**, *130*, 3724; d) J. M. Praetorius, M. W. Kotyk, J. D. Webb, R. Y. Wang, C. M. Crudden, *Organometallics* **2007**, *26*, 1057; e) A. C. Chen, D. P. Allen, C. M. Crudden, R. Y. Wang, A. Decken, *Can. J. Chem.* **2005**, *83*, 943; f) D. P. Allen, C. M. Crudden, L. A. Calhoun, R. Y. Wang, A. Decken, *J. Organomet. Chem.* **2005**, *690*, 5736; g) D. P. Allen, C. M. Crudden, L. A. Calhoun, R. Y. Wang, *J. Organomet. Chem.* **2004**, *689*, 3203; h) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247.

[10] a) S. Diez-Gonzalez in *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools, RSC Catalysis Series No. 6*, Royal Society of Chemistry, London, **2011**; b) S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612; c) F. Glorius in *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer, Berlin, **2007**; d) S. P. Nolan in *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, Weinheim, **2006**; e) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; f) W. A. Herrmann, C. Kocher, *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162.

[11] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.

[12] a) C. M. Frech, L. J. W. Shimon, D. Milstein, *Helv. Chim. Acta* **2006**, *89*, 1730; b) A. Y. Verat, H. Fan, M. Pink, Y. S. Chen, K. G. Caulton, *Chem. Eur. J.* **2008**, *14*, 7680; c) X.-Y. Yu, H. Sun, B. O. Patrick, B. R. James, *Eur. J. Inorg. Chem.* **2009**, 1752; d) A. Vigalok, L. J. W. Shimon, D. Milstein, *Chem. Commun.* **1996**, 1673.

[13] a) R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 2485; b) A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig,

J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523.

[14] a) D. L. Reger, J. J. Horger, M. D. Smith, G. J. Long, F. Grandjean, *Inorg. Chem.* **2011**, *50*, 686; b) S. M. Mobin, A. K. Srivastava, P. Mathur, G. K. Lahiri, *Dalton Trans.* **2010**, *39*, 1447; c) M.-H. Zeng, S. Hu, Q. Chen, G. Xie, Q. Shuai, S.-L. Gao, L.-Y. Tang, *Inorg. Chem.* **2009**, *48*, 7070; d) B. D. Chandler, G. D. Enright, K. A. Udachin, S. Pawsey, J. A. Ripmeester, D. T. Cramb, G. K. H. Shimizu, *Nat. Mater.* **2008**, *7*, 229; e) B.-W. Hu, J.-P. Zhao, E. C. Sanudo, F.-C. Liu, Y.-F. Zeng, X.-H. Bu, *Dalton Trans.* **2008**, 5556; f) M. Shibakami, M. Tamura, A. Sekiya, *J. Am. Chem. Soc.* **1995**, *117*, 4499.

[15] a) E. Fooladi, B. Dalhus, M. Tilset, *Dalton Trans.* **2004**, 3909; b) R. Dorta, D. Stevens Edwin, P. Nolan Steven, *J. Am. Chem. Soc.* **2004**, *126*, 5054; c) P. Blazejewska-Chadyniak, M. Kubicki, H. Maciejewski, B. Marciniec, *Inorg. Chim. Acta* **2003**, *350*, 603; d) A. Vigalok, Y. Ben-David, D. Milstein, *Organometallics* **1996**, *15*, 1839.

[16] a) E. Hirota, Y. Endo, S. Saito, K. Yoshida, I. Yamaguchi, K. Machida, *J. Mol. Spectrosc.* **1981**, *89*, 223; b) J. Chatt, G. J. Leigh, *Chem. Soc. Rev.* **1972**, *1*, 121.

[17] X.-Y. Yu, B. O. Patrick, B. R. James, *Organometallics* **2006**, *25*, 4870.

[18] During this purification procedure, the yellow paramagnetic impurity $[Rh(SIPr)_2(Cl)_2]$ was separated from complex **6**, resulting in the change in color from green to blue.

[19] a) M. Ahijado, T. Braun, D. Noveski, N. Kocher, B. Neumann, D. Stalke, H.-G. Stammler, *Angew. Chem.* **2005**, *117*, 7107; *Angew. Chem. Int. Ed.* **2005**, *44*, 6947; b) K. Osakada, K. Hataya, T. Yamamoto, *Inorg. Chem.* **1993**, *32*, 2360; c) C. Busetto, A. D'Alfonso, F. Maspero, G. Perego, A. Zazzetta, *J. Chem. Soc. Dalton Trans.* **1977**, 1828; d) M. J. Bennett, P. B. Donaldson, *Inorg. Chem.* **1977**, *16*, 1581; e) H. L. M. Van Gaal, F. L. A. Van den Bekerom, *J. Organomet. Chem.* **1977**, *134*, 237; f) M. Laing, M. J. Nolte, E. Singleton, *J. Chem. Soc. Chem. Commun.* **1975**, 660.

[20] a) R. H. Crabtree, D. G. Hamilton, *J. Am. Chem. Soc.* **1986**, *108*, 3124; b) R. H. Crabtree, M. Lavin, *J. Chem. Soc. Chem. Commun.* **1985**, 1661.

[21] a) D. Benito-Garagorri, I. Lagoja, L. F. Veiros, K. A. Kirchner, *Dalton Trans.* **2011**, *40*, 4778; b) S. Heylen, J. A. Martens, *Angew. Chem.* **2010**, *122*, 7794; *Angew. Chem. Int. Ed.* **2010**, *49*, 7629; c) D. Benito-Garagorri, M. Puchberger, K. Mereiter, K. Kirchner, *Angew. Chem.* **2008**, *120*, 9282; *Angew. Chem. Int. Ed.* **2008**, *47*, 9142; d) A. Gulino, T. Gupta, M. Altman, S. Lo Schiavo, P. G. Mineo, I. L. Fragala, G. Evmenenko, P. Dutta, M. E. van der Boom, *Chem. Commun.* **2008**, 2900.

