N-Heterocyclic Carbene−Transition Metal Complexes: Spectroscopic and Crystallographic Analyses of π-Back-bonding Interactions

Dimitri M. Khramov, Vincent M. Lynch, and Christopher W. Bielawski*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

Received June 16, 2007

The ability of N-heterocyclic carbenes (NHCs) to participate in π-back-bonding interactions was evaluated in a range of transition metal complexes. Rh chloride complexes containing a systematic series of various 1,3-dimethyl-4,5-disubstituted-imidazol-2-ylidenes and either 1,5-cyclooctadiene (cod) or two carbon monoxide ligands were synthesized (i.e., (NHC)RhCl(cod) and (NHC)RhCl$(CO)_2$, respectively) and studied using ^{1}H NMR and IR spectroscopies. In the former series, the ^{1}H NMR chemical shifts of the signals attributable to the olefin *trans* to the NHC ligand were found to shift downfield by up to 0.17 ppm as the π-acidity of the substituents on the 4,5-positions increased (i.e., H → Cl → CN). Similarly, in the latter series, the IR stretching frequencies of the carbonyl groups *trans* to the NHC ligands were found to increase by 11 ± 0.5 cm^{-1} as π-acidity increased over the same series. Using the nitrile group as a diagnostic handle, the CN stretching frequency of (1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene)-(cod)RhCl was found to be 4 ± 0.5 cm^{-1} higher than 1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene)-$(CO)_2$RhCl, a more π-acidic analogue. X-ray analysis of the aforementioned series of (NHC)(cod)RhCl complexes indicated changes in N−$C_{carbene}$ bond lengths that were consistent with greater π-donation from complexes containing 4,5-dihydroimidazol-2-ylidene relative to the their 4,5-dicyano analogues. Collectively, these results suggest not only that imidazol-2-ylidenes are capable of π-back-bonding but that this interaction may be tuned by changing the π-acidity of the substituents on the imidazole ring.

Introduction

Since the discovery of transition metal complexes containing N-heterocyclic carbene (NHC) ligands by Wanzlick,[1] Öfele,[2] and Lappert,[3] an impressive number of new catalysts for facilitating synthetically useful transformations have been developed.[4] Continued interest in these ligands has been extraordinary and driven by their abilities to often significantly enhance the catalytic activities of a broad range of transition metals upon complexation.[4,5] To understand and ultimately control these unique features, the nature of the metal−NHC interaction has been intensely investigated by a number of research groups.[6] A general consensus is that N-heterocyclic carbenes (NHCs) are strong, two-electron σ-donors that coordinate to transition metals in a fashion analogous to, and in some cases better than, trialkylphosphines.[7] For example, *trans* carbonyl stretching frequencies are generally lower in metal complexes containing NHC ligands than analogous complexes containing trialkylphosphines.[8,9]

Although there are many distinguishing features between NHCs and phosphines, the former possess an empty p-orbital at the carbene atom poised to accept π-electron density from a complexed transition metal (i.e., π-back-bonding). However, due to competing π-overlap of electron-rich nitrogen atoms adjacent to the carbene atom, the extent to which NHCs are capable of

---

* Corresponding author. E-mail: bielawski@cm.utexas.edu.

(1) Wanzlick, H. W.; Schönherr, H. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141.

(2) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42.

(3) Cardin, D. J.; Çetinkaya, B.; Çetinkaya, E.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 514.

(4) For recent reviews of catalytically active transition metal complexes containing N-heterocyclic carbenes, see: (a) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (b) Cavell, K. J.; McGuiness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (d) Hillier, A. C.; Gasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C. L.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.

(5) For representative examples, see: (a) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101. (b) Navarro, O.; Marion, N.; Oonishi, Y.; Kelly, R. A., III; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 685. (c) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188. (d) Jørgensen, M.; Lee, S.; Liu, X.; Wolkowski, J. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 12557. (e) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (f) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.

(6) For representative examples, see: (a) Hahn, F. E.; Jahnke, M. C.; Pape, T. *Organometallics* **2007**, *26*, 150. (b) Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2006**, 3959. (c) Kuhn, N.; Al-Sheikh, A. *Coord. Chem. Rev.* **2005**, *249*, 829. (d) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978. (e) Lappert, M. F. *J. Organomet. Chem.* **2005**, *690*, 5467. (f) Oldham, W. J.; Oldham, S. M.; Scott, B. L.; Abney, K. D.; Smith, W. H.; Costa, D. A. *Chem. Commun.* **2001**, 1348. (g) Abernethy, C. D.; Clyburne, J. A. C.; Cowley, A. H.; Jones, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 2329. (h) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. J. *Chem.−Eur. J.* **1996**, *2*, 1627. (i) Enders D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J. P.; Ebel, K. Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021. (j) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (k) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725.

(7) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163. (b) Frölich, N.; Pidun, U.; Stahl, M.; Frenking, G. *Organometallics* **1997**, *16*, 442. (c) Herrmann, W. A.; Runte, O.; Artus, G. *J. Organomet. Chem.* **1995**, *501*, C1. (d) Herrmann, W. A.; Öfele, K.; Elison, M.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1994**, *480*, C7.

(8) (a) Perrin, L.; Clot, E.; Eisenstein, O.; Loch, J.; Crabtree, R. H. *Inorg. Chem.* **2001**, *40*, 5806. (b) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (c) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219. (d) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261. (e) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Priermeier, T.; Kiprof, P. *J. Organomet. Chem.* **1995**, *498*, 1. (f) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177.

10.1021/om700591z CCC: \$37.00 © 2007 American Chemical Society
Publication on Web 10/20/2007

participating in this type of bonding interaction has been under debate. Using photoelectron spectroscopy, Green found[10] that the π-systems of free NHCs were similar to their transition metal complexes. Combined with the results in the aforementioned studies involving NHC versus phosphine metal carbonyl complexes, Herrmann concluded that π-back-bonding in NHC−transition metal complexes was "negligible",[7a,11] a conclusion supported theoretically by a number of groups.[12]

A general consensus of negligible π-back-bonding in NHC−metal complexes is challenged by numerous anomalies reported in the literature.[13] In 1975, Clarke and Taube reported spectroscopic evidence for π-interactions in carbon-bound xanthine Ru complexes.[14] Arduengo found increased π-electron density on the NHC moieties in a series of (1,3-dimesitylimidazol-2-ylidene)$_2$M (M = Ni, Pt) complexes (**1**) and attributed this phenomenon to a greater degree of π-back-bonding relative to analogous cationic group 11 complexes.[15] By corroborating DFT calculations with X-ray crystal structure data obtained from a range of NHC−metal complexes, Meyer determined that π-back-bonding accounted for up to 30% of the metal−ligand interaction.[16] Using well-designed annulated NHCs (e.g., **2**), Heinicke found[17] that π-back-bonding interactions could be effectively increased by extending the π-system of the NHC ligand. Likewise, Albrecht[18] designed an elegant series of half metallocene NHC complexes (**3**) and then utilized a combination of cyclic voltammetry, NMR spectroscopy, and DFT calculations to experimentally show that NHCs exhibit π-back-bonding capabilities on the same order as pyridine, a well-known π-acidic ligand.[19] At the extreme, Nolan found[20] π-donation from a NHC was responsible for the high stability of a low-valent, 14-electron Ir complex (**4**). Theoretical support for π-back-bonding and π-donation in a variety of other NHC−metal complexes was subsequently reported.[21] Manifesting these fundamental studies, strong correlation between π-electronics and catalytic activities can be found in a range of NHC−metal complexes reported by Organ.[22]

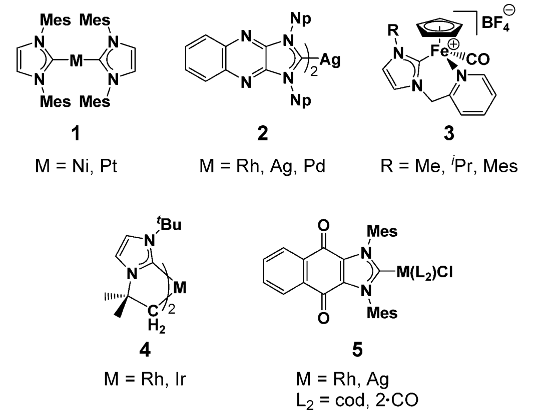


Figure 1. Examples of metal complexes used to study π-back-bonding interactions in NHCs. Np = *neo*-pentyl, Me = methyl, ^{i}Pr = isopropyl, Mes = 1,3,5-trimethylbenzene, ^{t}Bu = *tert*-butyl, cod = 1,5-cyclooctadiene.

Our interest in understanding the nature of the NHC−metal interaction, and in particular the existence and potential tunability of π-back-bonding, stems from a different perspective. We have recently launched a program that utilizes the affinities of NHCs for transition metals to create unique classes of main chain organometallic polymers.[23] With applications in electronics and catalysis in mind, understanding the role of π-back-bonding is essential for enhancing conductivities, thermal stabilities, catalytic functions, and other physical properties of these materials. For example, we found that copolymerization of a bis(NHC) with various group 10 metals (i.e., Pd, Pt, Ni) resulted in polymeric materials that exhibited modest bathochromic shifts relative to small molecule models.[24] Gaining insights into key factors that govern NHC−metal π-back-bonding interactions, including developing parameters for fine-tuning, should help guide future efforts for optimizing electronic characteristics and other physical properties of such materials.

Many of the aforementioned experimental approaches for studying NHC−metal interactions involve coordinating a NHC to a transition metal complex followed by monitoring spectroscopic changes in ancillary ligands (e.g., recording changes in *trans* carbonyl stretching frequencies upon ligation). Individual σ- versus π-contributions in the NHC−metal interaction are then deconvoluted through comparison with other types of ligands. We recently introduced a new approach for studying NHC−metal interactions by examining spectroscopic changes that occur *at the NHC ligand* upon coordination of ancillary ligands with varying degrees of π-back-bonding capabilities. In particular, various naphthoquinone-annulated NHC (NqMes) transition metal complexes (**5**) were synthesized and characterized.[25]

---

(9) For related studies that compare NHC−metal bond dissociation energies to phosphine analogues, see: (a) Dorta, R.; Stevens, D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485. (b) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322. (c) Huang, J.; Jafarpour, L.; Hillier, A. C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 2878. (d) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370.

(10) (a) Green, J. C.; Herbert, B. J. *Dalton Trans.* **2005**, *7*, 1214. (b) Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N. *Chem. Commun.* **1997**, 1963.

(11) (a) Öfele, K.; Herberhold, M. *Z. Naturforsch.* **1973**, *28b*, 306. (b) Öfele, K.; Kreiter, C. G. *Chem. Ber.* **1972**, *105*, 529.

(12) (a) Lee, M.; Hu, C. *Organometallics* **2004**, *23*, 976. (b) Niehues, M.; Erker, G.; Kehr, G.; Schwab, P.; Fröhlich, R.; Blacque, O.; Berke, H. *Organometallics* **2002**, *21*, 2905. (c) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801. (d) Fröhlich, N.; Pidun, U.; Stahl, M.; Frenking, G. *Organometallics* **1997**, *16*, 442.

(13) For a recent and excellent review of the nature of the bond formed between N-heterocyclic carbenes and transition metals, see: Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874.

(14) Clarke, M. J.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 1397.

(15) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391.

(16) (a) Hu, X.; Castro-Rodriguez I.; Olsen, K; Meyer, K. *Organometallics* **2004**, *23*, 755. (b) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, *22*, 612.

(17) (a) Saravanakumar, S.; Kindermann, K. M.; Heinicke, J.; Kockerling, M. *Chem. Commun.* **2006**, 640. (b) Saravankumar, S.; Oprea, A. I.; Kindermann, M. K.; Jones, P. G.; Heinicke, J. *Chem.−Eur. J.* **2006**, *12*, 3143.

(18) Mercs, L.; Labat, G.; Neels A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006**, *25*, 5648. For an earlier study that supports π-interactions in pyridine-N-functionalized NHC complexes, see: Tulloch, A. D. D.; Danopoulous, A. B.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027.

(19) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988.

(20) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516.

(21) (a) Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. *J. Organomet. Chem.* **2006**, *691*, 4350. (b) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407. (c) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, *23*, 3640. (d) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029.

(22) Hadei, N.; Assen, B.; Kantchev, B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 1991.

(23) (a) Boydston, A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073. (b) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496.

(24) Boydston, A. J.; Rice, J. D.; Sanderson, M. D.; Dykhno, O. L.; Bielawski, C. W. *Organometallics* **2006**, *25*, 6087.

(25) Sanderson, M. D.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2006**, *128*, 16514.

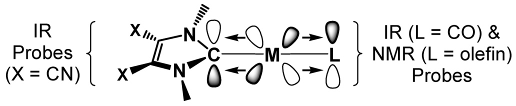


Figure 2. Basic design for evaluating π-back-bonding in a range of NHC−metal complexes using IR and NMR spectroscopies.

The quinone group, which contains two equivalent carbonyl moieties formally conjugated to the carbene atom, provided a distinct spectroscopic handle for studying π-interactions using IR spectroscopy. Furthermore, the redox-active character of this same group provided an independent means to measure ligand electronics using cyclic voltammetry. Using these spectroscopic techniques, (NqMes)RhCl(cod) (cod = 1,5-cyclooctadiene) was found to exhibit lower quinone carbonyl stretching frequencies and higher reduction potentials than (NqMes)RhCl$(CO)_2$. These results, supported by a comprehensive X-ray crystallographic analysis, suggested that the π-back-bonding capability of NqMes lies in between an olefin and a carbon monoxide, two ligands with well-established π-back-bonding capabilities.[19]

In this contribution, we supplement this approach by evaluating a series of NHC−metal complexes with differing degrees of π-back-bonding capabilities using a variety of spectroscopic techniques. As illustrated in Figure 2, the basic design utilizes IR- and NMR-active functional groups on both the NHC and other ancillary ligands complexed to a transition metal. Corroborating changes in π-acidity of one ligand with spectroscopic changes at the other should not only establish the existence of π-back-bonding but also demonstrate that this interaction is tunable. In particular, the synthesis of 4,5-dicyanoimidazol-2-ylidene metal complexes that feature two nitrile groups formally conjugated to the carbene atom are described. Similar to the aforementioned quinone carbonyl groups in NqMes, these IR-sensitive groups were envisioned to function as probes for evaluating the π-electronics of its respective metal complexes. For example, observation of an increased nitrile IR stretching frequency upon replacement of an ancillary olefinic ligand (i.e., 1,5-cyclooctadiene) with carbon monoxide would suggest that π-back-bonding is operative in this NHC architecture. If this could be established, then systematic replacement of the nitrile groups with functional groups of varying π-acidities should cause corresponding electronic changes in the ancillary olefin and/or carbon monoxide ligands, and observed using NMR spectroscopy and IR spectroscopy, respectively. Additional evidence for the existence and tunability of π-back-bonding interactions may be obtained through the observation of distinctive bond length changes using X-ray crystallography.

With the goals of evaluating and tuning π-back-bonding characteristics of NHCs in mind, we targeted a series of transition metal complexes fulfilling two key requirements: (1) The transition metals must be capable of coordinating to a series of NHCs with a range of π-back-bonding capabilities. As such, 1,3-dimethylimidazol-2-ylidenes with functional groups of varying π-acidities were designed. We envisioned that imidazol-2-ylidene derivatives possessing nitro and cyano groups in 4- and/or 5-positions should show differing degrees of π-back-bonding in their respective metal complexes and may be conveniently compared against its parent (4,5-dihydro) NHC. To deconvolute inductive σ-effects due to the installation of electronegative atoms, the plan also included synthesis and study of a 4,5-dichloro derivative. (2) Ancillary ligands coordinated to the NHC−transition metal complex must be readily exchanged without perturbing other physical characteristics of that same complex (oxidation state, geometry, coordination number, etc.) Ligand exchange should also influence the π-system of the respective complexes, manifesting in distinct spectroscopic and/or structural changes. In particular, a system was required such that an ancillary ligand with modest π-back-bonding capability (e.g., an olefin) could be readily substituted with a ligand that is highly capable (e.g., carbon monoxide). Building upon our experiences with using Rh complexes for the purposes of studying NHC π-back-bonding interactions, Rh complexes of the general type (NHC)RhCl(cod) were targeted, as the cod ligand is known to rapidly exchange with two units of carbon monoxide, with essentially no other change in the metal environment.[26,27]

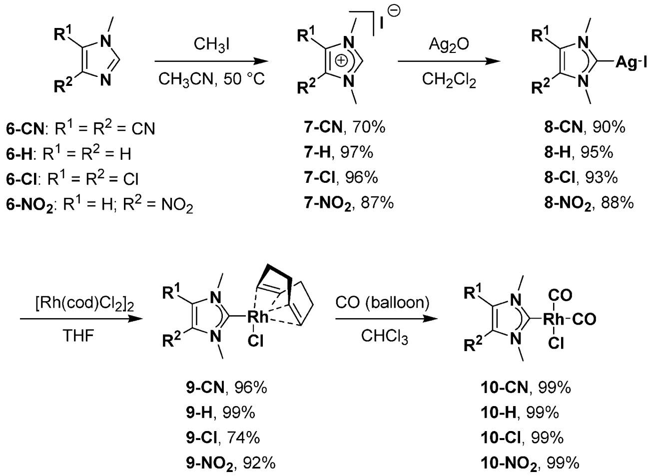


Figure 3. Synthesis of various metal complexes containing 4,5-disubstituted-imidazol-2-ylidenes.

Results and Discussion

The synthetic outline of various complexes meeting the aforementioned requirements is summarized in Figure 3. Independent treatment of commercially available 1-methyl-4,5-disubstituted-imidazoles (**6**) with excess methyl iodide in CH_3CN at 50 °C (sealed tube) resulted in the respective imidazolium salts **7** in yields ranging from 70 to 97%.[28] Although organometallic complexes containing NHCs are commonly prepared through direct treatment of the desired neutral ligand, this approach can be problematic, as it requires isolation of the free NHC or the use of strong bases to generate the NHC in situ. To circumvent the need for free NHCs, Lin developed a practical and operationally straightforward protocol that involves NHC−Ag complexes capable of transmetalation.[29] Following this procedure, Ag complexes **8** were prepared in 88−95% yields through treatment of the respective imidazolium salts with Ag_2O. Subsequent transmetalation to $[Rh(cod)Cl_2]_2$ afforded Rh complexes **9** in 74−99% yields. Finally, bubbling carbon monoxide

---

[26] Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.

[27] Transition metals in higher oxidation states may induce more positive charge buildup at the carbene atom, which may be a decisive factor for NHCs to undergo π-back-bonding; see: (a) Shukla, P.; Johnson, J. A.; Vidovic, D.; Cowley, A. H.; Abernethy, C. D. *Chem. Commun.* **2004**, 360. (b) Abernethy, C. D.; Codd, G. M.; Spicer, M. D.; Taylor, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 1128.

[28] All attempts at synthesizing 1,3-dimethyl-4,5-dinitroimidazolium via methylation of 1-methyl-4,5-dinitroimidazole were unsuccessful. Similar results were observed by Katritzky; see: Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *New J. Chem.* **2006**, *30*, 349.

[29] (a) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642. (b) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

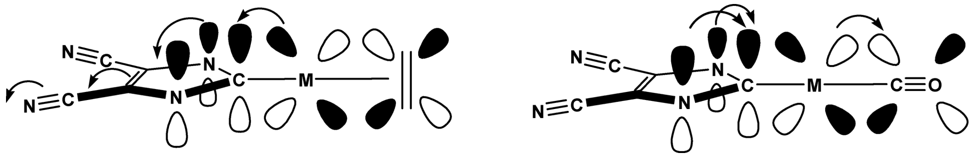


Figure 4. Dominant resonance contributors for complexes **9-CN** (left) and **10-CN** (right).

Table 1. Selected IR Stretching Frequencies of CN Groups in a Variety of NHC−Metal Complexes[a]

compound	ν_{CN} (cm^{-}1)
7-CN	2250
11	2247
8-CN	2239
9-CN	2238
10-CN	2242

[a] Carbonyl stretching frequencies were determined for compounds in the solid state using IR spectroscopy (KBr). Reported values are ±0.5 cm^{-1}. Compound **11** = (1,3-dimethyl-4,5-dicyanoimidazolylidene)$_2$Ag·BF$_4$.[32]

Table 2. ^{1}H NMR Chemical Shifts of the Protons on the Olefin *trans* to the NHC Ligand

complex	**δ(═CH) (ppm)**[a]
9-H	5.00
9-Cl	5.03
9-NO$_2$	5.12
9-CN	5.17

[a] Chemical shifts were determined using ^{1}H NMR spectroscopy (solvent = CDCl$_3$), reported downfield to tetramethylsilane, and referenced to residual protio solvent.

through solutions of Rh(cod) complexes **9** produced the respective Rh carbonyl complexes **10** in excellent yields (≥99%).[26,30]

Once compounds **7**−**10** were synthesized, they were studied using a variety of spectroscopic techniques. Initial attention was directed toward using solid-state (KBr) IR spectroscopy to examine the nitrile-substituted compounds **7-CN**−**10-CN**; selected data are summarized in Table 1. As expected, imidazolium salt **7-CN** exhibited a relatively high nitrile stretching frequency (ν_{CN}) of 2250 cm^{-1}.[31] Since the imidazolium proton has no π-back-bonding capability, this compound served as a comparative model. Reflecting relative charge densities and M→C electron-donating abilities, complexes **8-CN**, **9-CN**, and **10-CN** exhibited lower nitrile stretching frequencies to differing degrees. For example, the bis(NHC) cationic Ag complex (1,3-dimethyl-4,5-dicyanoimidazolylidene)$_2$Ag·BF$_4$ (**11**)[32] exhibited a $\nu_{\mathrm{CN}} = 2247$ cm^{-1}, whereas Ag complex **8-CN** registered a $\nu_{\mathrm{CN}} = 2239$ cm^{-1}.

While study of the aforementioned azolium and Ag complexes highlighted the sensitivity of IR spectroscopy for studying π-electronics, Rh complexes **9-CN** and **10-CN** were examined to probe for the existence of π-back-bonding in NHC−metal complexes. Since π-withdrawing effects from the cod and Cl ligands are relatively weak, complex **9-CN** was poised for NHC π-back-bonding. In contrast, the two carbon monoxide ligands in complex **10-CN** should greatly diminish the ability of the Rh to π-back-bond to the NHC. Dominant resonance contributors describing these two limiting cases are illustrated in Figure 4 and were supported by observed nitrile stretching frequencies of 2242 and 2238 cm^{-1} for complexes **9-CN** and **10-CN**, respectively. Interestingly, the ν_{CN} of Rh complex **9-CN** was comparable to Ag complex **8-CN**, which suggests that these two metal complexes may participate in π-back-bonding with NHCs to similar degrees.

Subsequent attention was directed toward using other spectroscopic tools to evaluate relative π-back-bonding abilities in a related series of NHC−transition metal complexes. Crabtree and Quirk demonstrated that NMR spectroscopy is a powerful technique for measuring electron densities in Ir−olefin complexes.[33] In relatively electron-deficient systems, coordinated olefins act as conventional two-electron donors and maintain a significant degree of C═C double bond character. As electron density on the metal increases, the olefin adopts metallocyclopropane character due to M→olefin π-back-bonding. By monitoring chemical shifts of the protons on the olefin, relative contributions from these two extreme states can be measured using ^{1}H NMR spectroscopy. We envisioned that evaluation of Rh complexes **9** and **10** using NMR spectroscopy should provide a relative scale for measuring π-back-bonding in NHC−transition metal complexes.

The ^{1}H NMR chemical shifts of the olefin *trans* to the NHC ligand in complexes **9** were recorded and are summarized in Table 2. Relative to **9-H**, downfield shifts were observed for each of the 4,5-disubstituted derivatives studied. In particular, electron-deficient complex **9-Cl**, which contains two electronegative chlorine atoms in the 4- and 5-positions of the imidazol-2-ylidene, was found to exhibit a chemical shift nearly identical to **9-H** (5.03 versus 5.00 ppm, respectively). In contrast, relatively significant downfield shifts were observed for compounds **9-NO$_2$** and **9-CN** (5.12 versus 5.17 ppm, respectively), which contain π-acidic nitro and cyano groups with group electronegativities similar to Cl.[34] In other words, the Rh centers in metal complexes **9-CN** and **9-NO$_2$** were apparently more electron-deficient than not only its parent complex **9-H** but also dichloro derivative **9-Cl**.

To help deconvolute π-withdrawing from σ-inductive effects in **9**, Hammett σ_{meta} parameters were calculated from experimentally derived acidity constants for 3-nitrobenzoic acid (pK_a = 3.46), 3,5-dichlorobenzoic acid (pK_a = 3.54), and benzoic acid (pK_a = 4.19).[35] Specifically, the inductive effect of one NO$_2$ group ($\sigma_{\mathrm{meta}} = 0.73$) is approximately the same as two Cl groups (additive $\sigma_{\mathrm{meta}} = 0.65$). Consequently, if the relative metal electron deficiencies in the series of NHC complexes studied were due solely to diminished σ-donation, and not π-back-bonding, one would expect the *trans* olefins in **9-Cl** and **9-NO$_2$** to show similar ^{1}H NMR chemical shifts. As shown in Table 2, a significant difference was observed between these two complexes, whereas only a small difference was observed between **9-H** and **9-Cl**. Since these results could not be readily rationalized in terms of σ-induction, we propose the observed

---

(30) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Chem.−Eur. J.* **1996**, *2*, 772.

(31) 1,3-Dimethyl-4,5-dicyanoimidazolium tetrafluoroborate exhibited a $\nu_{\mathrm{CN}} = 2264$ cm^{-1} (KBr).

(32) Complex **11** was prepared by treating 1,3-dimethyl-4,5-dicyanoimidazolium tetrafluoroborate with Ag$_2$O.

(33) Crabtree, R. H.; Quirk, J. M. *J. Organomet. Chem.* **1980**, *199*, 99.

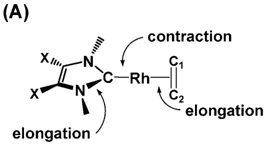
(34) Group electronegativities: H, 2.1; Cl, 3.0; CN, 3.3; NO$_2$, 3.4, see: (a) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111. (b) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006; p 16.

(35) Tehana, B. G.; Lloyda, E. J.; Wong, M. G.; Pitt, W. R.; Montana, J. G.; Manallack, D. T.; Gancia, E. *Quant. Struct.-Act. Relat.* **2002**, *21*, 457. For an extended compilation of pK_a values for substituted benzoic acids, see: Kalfus, K.; Kroupa, J.; Vecera, M.; Exner, O. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3009.

Table 3. Selected Carbonyl Stretching Frequencies for a Series of (NHC)Rh(CO)$_2$Cl Complexes[a]

complex	ν_{CO} (cm^{-}1)
10-H	2087, 2004
10-Cl	2091, 2010
10-NO$_2$	2094, 2012
10-CN	2099, 2017

[a] Carbonyl stretching frequencies were determined using IR spectroscopy for compounds in solution (CDCl$_3$). Values reported are ±0.5 cm^{-1}. The two frequencies correspond to in-plane and out-of-plane vibrational modes.



(B)

	X = H	X = Cl	X = NO$_2$	X = CN
C-Rh (Å):	2.023	2.021	2.005	2.006
C-N (Å):	1.352	1.360	1.360	1.369
Rh-C$_1$ (Å):	2.175	2.195	2.196	2.204
Rh-C$_2$ (Å):	2.204	2.218	2.226	2.205

Figure 5. (a) Expected changes in key bond lengths as the π-back-bonding ability of the NHC ligand increases. (b) Summary of key bond lengths observed for a series of (NHC)Rh(cod)Cl complexes with NHC ligands of varying degrees of π-acidity; the data reported were taken from Table 5. Note: average C−N bond lengths are reported.

trend in spectroscopic data is due to the relative π-withdrawing effects of the NHC ligands.

Having evaluated relative π-back-bonding contributions in a series of (NHC)Rh(cod)Cl complexes using ^{1}H NMR spectroscopy, attention turned toward using IR spectroscopy to study analogous interactions in a related series of (NHC)Rh(CO)$_2$Cl complexes. As summarized in Table 3, *trans* carbonyl stretching frequencies (ν_{CO}'s) were recorded for complexes **10**. For each complex analyzed, two unique CO stretching frequencies were observed, corresponding to in-plane and out-of-plane stretching CO vibrational modes. In accord with the aforementioned NMR data, ν_{CO}'s correlated with the π-acidities of the NHC ligands. For example, complexes **10-H** and **10-Cl**, which contained imidazol-2-ylidenes with hydro and chloro substituents in the 4,5-positions, respectively, exhibited almost identical ν_{CO}'s. In contrast, complexes **10-CN** and **10-NO$_2$**, which contained π-acidic cyano and nitro groups, respectively, exhibited significantly higher values. Since it is well-known that the interaction between a transition metal and carbon monoxide involves a considerable degree of M→CO π-donation, the higher ν_{CO}'s observed for Rh complexes containing π-acidic NHCs were suggestive of competitive π-back-bonding interactions.

To obtain additional support for π-back-bonding in NHC−transition metal complexes, attention was directed toward studying the solid-state structures of Rh complexes **9**. In general, three distinct structural changes were expected as the relative π-back-bonding ability of the NHC ligand increased: (1) the average C$_{carbene}$−N bond length should elongate due to population of the carbene p-orbital with electrons, (2) the Rh−C$_{carbene}$ bond length should contract due to a stronger interaction being formed between these two atoms, and (3) the length of the bond formed between the Rh atom and the olefin *trans* to the NHC ligand should elongate due to decreased electron density at the Rh center. All other bond lengths and angles in the respective metal complexes should remain relatively constant. For clarity, expected changes are summarized in Figure 5A.

Crystals of **9-Cl**, **9-CN**, and **9-NO$_2$** suitable for X-ray diffraction analysis were independently obtained. Selected crystallographic data as well as bond lengths and angles are summarized in Tables 4 and 5, respectively. For comparison, key data for known[30] **9-H** have been included. As shown in Figure 6, the ORTEP diagrams for each of these complexes are remarkably similar. In general, increased π-acidities of the NHC ligand resulted in elongated C$_{carbene}$−N and Rh−olefin bond lengths with concomitant contractions in the Rh−C$_{carbene}$ bond length (summarized in Figure 5B). Other bond lengths and angles remained relatively constant within this same series. Furthermore, complexes **9-H** and **9-Cl** exhibited comparable C$_{carbene}$−Rh bond lengths (2.023(2) and 2.021(2) Å, respectively), whereas analogous bond lengths in complexes **9-NO$_2$** and **9-CN** were relatively short (2.005(3) and 2.006(6) Å, respectively). Combined with the IR and NMR spectroscopic data described above, these results suggest not only that NHCs are capable of π-back-bonding but that the extent of this interaction is dependent on its π-acidity.

Conclusions

A range of new Rh and Ag complexes containing 1,3-dimethylimidazol-2-ylidenes with varying degrees of π-acidity were synthesized and then studied using NMR spectroscopy, IR spectroscopy, and X-ray crystallography. A new NHC ligand featuring two nitrile groups formally conjugated to the carbene atom, 1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene, was found to be useful for studying π-back-bonding using FT-IR spectroscopy. In particular, the ν_{CN} of (1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene)Rh(cod)Cl was found to be 4 ± 0.5 cm^{-1} higher than its respective Rh(CO)$_2$Cl complex, suggesting that this NHC was a stronger π-acid than an olefin but weaker than carbon monoxide. Using the 4,5-dicyano derivative as a reference, NMR and IR spectroscopies were employed to study a range of Ag- and Rh-containing imidazol-2-ylidenes. In general, chemical shifts of the coordinated olefin and the stretching frequencies of the carbonyl group *trans* to the NHC correlated with the π-acidity of this ligand. Furthermore, σ-inductive effects were found to be relatively minimal, as determined by comparison to complexes containing 4,5-dichloroimidazol-2-ylidenes. Finally, structural analysis of a series of (NHC)Rh(cod)Cl complexes possessing NHCs with varying degrees of π-acidities supported the NMR and IR spectroscopic data. In particular, the average N−C$_{carbene}$ and Rh−(olefin) bond lengths elongated while the Rh−C$_{carbene}$ bond length contracted as the π-acidity of the NHC ligand increased. Collectively, these results suggest that π-back-bonding in NHC−metal complexes is not only non-neglible but tunable. This information should help guide efforts toward fine-tuning transition metal-based catalysts for facilitating synthetically useful transformations and/or optimizing the electronic properties of organometallic polymers containing NHCs.

Experimental Section

Materials and Methods. All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox. Dichloromethane was distilled from calcium hydride and degassed by two freeze−pump−thaw cycles. Tetrahydrofuran and toluene were distilled from Na/benzophenone and degassed by two freeze−pump−thaw cycles. [(cod)RhCl]$_2$ and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride were purchased from Strem Chemicals and used without further purification. 1,3-Dimethylimidazolium iodide (**1-H**) was prepared according to literature procedures.[30,36] All other reagents were purchased from Aldrich or Acros and were used without further purification. ^{1}H NMR spectra were recorded using a Varian Gemini (300 or 400

---

(36) Benac, B. L.; Burgess, E. M.; Arduengo, A. J., III. *Org. Synth.* **1986**, *64*, 92.

Table 4. Selected Crystal Data for Rh Complexes 9

	9-H[a]	**9-Cl**	**9-NO$_2$**	**9-CN**
CCDC no.	109494	650155	650157	650156
empirical formula	$C_{13}H_2ClN_2Rh$	$C_{13}H_{18}Cl_3N_2Rh$	$C_{13}H_{19}ClN_3O_2Rh$	$C_{15}H_{18}ClN_4Rh$
fw	342.67	411.55	387.67	392.69
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	P21/*n*	*C*2/*c*	P21/*c*	P21/*n*
a, Å	10.162(2)	18.6430(3)	14.3364(9)	14.4910(8)
b, Å	11.137(1)	12.0050(2)	8.0561(5)	11.0430(5)
c, Å	13.223(2)	14.9100(2)	14.0038(10)	20.0880(10)
α, deg	90	90	90	90
β, deg	112.400(10)	113.8410(9)	109.016(2)	96.598(3)
γ, deg	90	90	90	90
V, Å^3	1383.6(4)	3052.25(8)	1529.12(17)	3193.3(3)
T, K	223(3)	153(2)	233(2)	153(2)
Z	4	8	4	8
D_{calc}, Mg/m^3	1.6450(5)	1.791	1.684	1.634
cryst size, mm	0.23 × 0.209 × 0.356	0.19 × 0.18 × 0.11	0.25 × 0.09 × 0.07	0.37 × 0.26 × 0.14
no. of reflns collected	4131	20 443	5470	11 522
no. of indep reflns	2583	3464	3448	7227
R_1, wR_2 $\{I > 2\sigma(I)\}$	0.021, 0.017	0.0249, 0.0552	0.0340, 0.0773	0.0536, 0.1157
goodness of fit	NA	1.090	1.014	1.028

[a] Data for **9-H** were reproduced from ref 30. NA = information not available.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Rh Complexes 9[a]

parameter	**9-H**[b]	**9-Cl**	**9-NO$_2$**	**9-CN**
C1−Rh	2.023(2)	2.021(2)	2.005(3)	2.006(6)
Rh−Ca	2.175(3)	2.195(2)	2.196(4)	2.205(6)
Rh−Cb	2.204(3)	2.218(2)	2.226(3)	2.204(6)
N2−C1	1.349(2)	1.363(3)	1.366(4)	1.366(9)
N1−C1	1.356(3)	1.358(3)	1.354(4)	1.372(7)
N1−C4	1.385(4)	1.383(3)	1.367(5)	1.371(7)
N2−C2	1.387(3)	1.384(3)	1.387(5)	1.391(7)
C2−C4	1.333(4)	1.340(3)	1.334(5)	1.344(8)
N1−C1−N2	104.06(16)	104.55(18)	105.1(3)	104.4(7)

[a] ORTEP diagrams are shown in Figure 6. [b]Data for **9-H** were reproduced from ref 30.

MHz) spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protio solvent as an internal standard ($CDCl_3$, 7.24 ppm; C_6D_6, 7.15 ppm; CD_2Cl_2, 5.32 ppm; DMSO-d_6, 2.49 ppm). ^{13}C NMR spectra were recorded using a Varian Gemini (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as an internal standard ($CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm; CD_2Cl_2, 53.8 ppm, DMSO-d_6, 39.5 ppm). ^{13}C NMR spectra were routinely run with broadband decoupling. Coupling constants are expressed in hertz (Hz). IR spectra were recorded using a Perkin-Elmer Spectrum BX FT-IR system. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument and are reported as *m*/*z* (relative intensity). X-ray crystal structure data for compounds **9-Cl** (CCDC 650155), **9-NO$_2$** (CCDC 650157), and **9-CN** (CCDC 650156) were deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

1,3-Dimethyl-4,5-dichloroimidazolium Iodide (7-Cl). A 30 mL pressure vessel was charged with 4,5-dichloro-1-methylimidazole (7.5 g, 49.7 mmol), CH_3I (5.0 mL, 80.2 mmol), CH_3CN (60 mL), and a stir bar. After sealing the vessel, the reaction mixture was stirred at 60 °C for 12 h. Subsequent cooling to 0 °C caused solids to precipitate, which were collected by filtration and washed with Et_2O (30 mL). Removal of residual solvent under reduced pressure afforded the desired product (14.0 g, 96% yield) as a white crystalline solid. ^1H NMR (DMSO-d_6): δ 9.39 (s, 1H), 3.82 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 136.6, 118.9, 34.9. HRMS: $[M]^+$ calcd for $C_5H_7Cl_2N_2$, 164.9981; found, 164.9981.

1,3-Dimethyl-4,5-dicyanoimidazolium Iodide (7-CN). A 30 mL pressure vessel was charged with 4,5-dicyano-1-methylimidazole (1.0 g, 7.57 mmol), CH_3I (2 mL, 32.1 mmol), CH_3CN (15 mL), and a stir bar. After sealing the vessel, the reaction mixture was stirred at 80 °C for 24 h. The mixture was then cooled to ambient temperature and poured into Et_2O (50 mL). The precipitated solids were collected by filtration and dried under reduced pressure to afford the desired product as yellow crystals (1.45 g, 70% yield). IR (KBr): 2250 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.76 (s, 1H), 4.05 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 142.5, 115.6, 106.1, 37.2. HRMS: $[M]^+$ calcd for $C_7H_7N_4$, 147.0665; found, 147.0672.

1,3-Dimethyl-4-nitroimidazolium Iodide (7-NO$_2$). A 30 mL pressure vessel was charged with 1-methyl-4-nitroimidazole (3.6 g, 28.3 mmol), CH_3I (5.0 mL, 80.2 mmol), CH_3CN (25 mL), and a stir bar. After sealing the vessel, the reaction mixture was stirred at 50 °C for 12 h. Subsequent cooling to 0 °C caused solids to precipitate, which were collected by filtration and washed with Et_2O (30 mL). Removal of residual solvent under reduced pressure afforded the desired product as an orange crystalline solid (6.61 g, 87% yield). Spectroscopic data were in accord with literature values.[37]

1,3-Dimethyl-4,5-dicyanoimidazolium Tetrafluoroborate. A vial was charged with $Me_3O{\cdot}BF_4$ (0.62 g, 4.2 mmol), CH_3CN (4 mL), 4,5-dicyano-1-methylimidazole (0.50 g, 3.79 mmol), and a stir bar.[38] After stirring for 1 h at ambient temperature, white flakes precipitated from the reaction mixture. The solids were then collected by filtration and dried under reduced pressure to afford the desired product as white crystals (0.89 g, 70% yield). IR (KBr): 2264 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.66 (s, 1H), 4.05 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 142.6, 115.6, 106.1, 37.0. HRMS: $[M]^+$ calcd for $C_7H_7N_4$, 147.0665; found, 147.0672.

Ag Complex 8-H. A 30 mL pressure vessel was charged with 1,3-dimethylimidazolium iodide (**1-H**)[30,36] (2.14 g, 9.8 mmol), Ag_2O (1.13 g, 4.9 mmol), CH_2Cl_2 (10 mL), and a stir bar. After sealing the vessel, the reaction mixture was stirred at 50 °C for 10 h. Subsequent cooling to ambient temperature caused solids to precipitate, which were collected by filtration. Removal of residual solvent under reduced pressure afforded the desired product as a gray powder (3.0 g, 95% yield). Spectroscopic data were in accord with literature values.[39]

Ag Complex 8-Cl. A 30 mL pressure vessel was charged with 1,3-dimethyl-4,5-dichloroimidazolium iodide (**7-Cl**) (1.05 g, 3.57 mmol), Ag_2O (0.41 g, 1.78 mmol), CH_2Cl_2 (15 mL), and a stir

---

(37) Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J. *Chem. Mater.* **2005**, *17*, 191.

(38) For additional examples of facilitating anion metathesis reactions with oxonium salts, see: Vu, P. D.; Boydston, A. J.; Bielawski, C. W. *Green Chem.* **2007**, in press (DOI: 10.1039/b705745h).

(39) Chen, W.; Liu, F. *J. Organomet. Chem.* **2003**, *673*, 5.

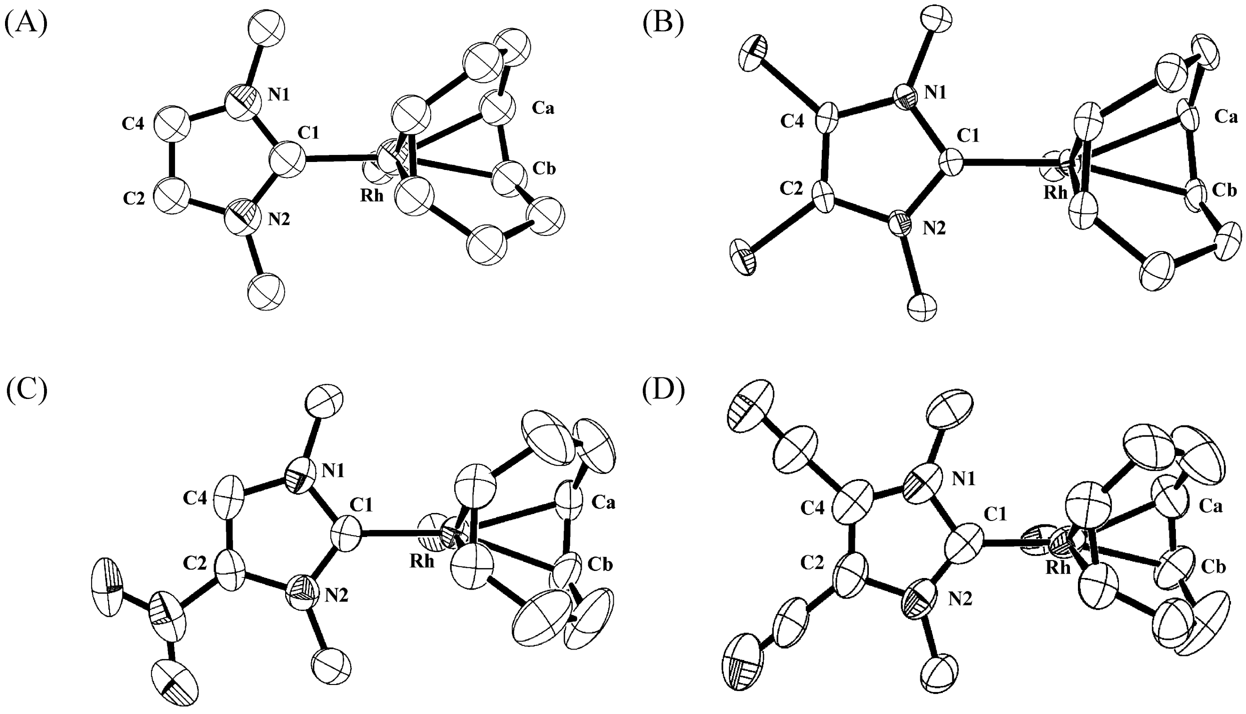


Figure 6. ORTEP diagrams of (A) **9-H**, (B) **9-Cl**, (C) **9-NO$_2$**, and (D) **9-CN**. Ellipsoids were drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Data for **9-H** were reproduced from ref 30.

bar. After sealing the vessel, the reaction mixture was stirred at 50 °C for 2 h. Subsequent cooling to ambient temperature caused solids to precipitate, which were collected by filtration. Removal of residual solvent under reduced pressure afforded the desired product as a gray powder (1.33 g, 93% yield). HRMS: [M]$^+$ calcd for $C_5H_6Cl_2N_2AgI$, 397.8004; found, 397.8000. This complex exhibited extremely poor solubilities in common organic solvents and therefore was used directly without further purification or characterization.

Ag Complex 8-CN. A 30 mL pressure vessel was charged with 1,3-dimethyl-4,5-dicyanoimidazolium iodide (**7-CN**) (0.19 g, 0.68 mmol), Ag_2O (78 mg, 0.34 mmol), CH_2Cl_2 (5 mL), and a stir bar. After sealing the vessel, the reaction mixture was stirred at 50 °C for 4 h. Subsequent cooling to ambient temperature caused solids to precipitate, which were collected by filtration. Removal of residual solvent under reduced pressure afforded the desired product as a gray powder (0.24 g, 90% yield). IR (KBr): 2239, 1449, 1384, 885, 490 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 4.04. ^{13}C NMR (DMSO-d_6): δ 192.7, 115.5, 107.7, 39.0.

Ag Complex 8-NO$_2$. A 30 mL pressure vessel was charged with 1,3-dimethyl-4-nitroimidazolium iodide (**7-NO$_2$**) (0.67 g, 2.47 mmol), Ag_2O (0.29 g, 1.24 mmol), CH_2Cl_2 (7 mL), and a stir bar. After sealing the vessel, the reaction mixture was stirred at 50 °C for 3 h. Subsequent cooling to ambient temperature caused solids to precipitate, which were collected by filtration. Removal of residual solvent under reduced pressure afforded the desired product as a green-yellow powder (0.82 g, 87% yield). ^{1}H NMR (DMSO-d_6): δ 8.79 (s, 1H), 4.12 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 188.2, 139.1, 126.8, 39.4.

Ag Complex 11. A 30 mL pressure vessel was charged with 1,3-dimethyl-4,5-dicyanoimidazolium tetrafluoroborate (0.12 g, 0.5 mmol), Ag_2O (60 mg, 0.25 mmol), CH_3CN (5 mL), and a stir bar. The vessel was then sealed and the reaction mixture was stirred at 80 °C for 16 h. After cooling to ambient temperature, the reaction mixture was filtered through a 0.2 μm PTFE filter. Residual solvent was then removed under reduced pressure to afford the desired product as a white foam (0.24 g, 98% yield). Note: the product is extremely hydrophilic and rapidly turns into an oil upon exposure to air. IR (KBr): 2247, 1457, 1260, 890 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 3.97. ^{13}C NMR (DMSO-d_6): δ 190.3, 115.6, 107.7, 38.7. HRMS: [M]$^+$ calcd for $C_{14}H_{12}AgN_8$, 399.0230; found, 399.02304.

Rh Complex 9-Cl. A 20 mL flask was charged with Ag complex **8-Cl** (0.29 g, 0.72 mmol), $[Rh(cod)Cl]_2$ (0.16 g, 0.33 mmol), THF (10 mL), and a stir bar. The resulting reaction mixture was then stirred at 60 °C for 3 h. Afterward, the reaction mixture was cooled to ambient temperature and then filtered through a 0.2 μm PTFE filter. Removal of residual solvent under reduced pressure afforded the desired product as yellow solid (0.2 g, 74% yield). ^{1}H NMR ($CDCl_3$): δ 5.03 (br, 2H), 4.04 (s, 6H), 3.26 (br, 2H), 2.40−2.37 (br, 4H), 1.97−1.93 (br, 4H). ^{13}C NMR ($CDCl_3$): δ 188.2 (d, $J_{\mathrm{Rh-C}} = 52.3$ Hz), 116.3 (d, $J_{\mathrm{Rh-C}} = 1.4$ Hz), 99.5 (d, $J_{\mathrm{Rh-C}} = 6.7$ Hz), 68.4 (d, $J_{\mathrm{Rh-C}} = 15.0$ Hz), 36.4, 32.8, 28.8. HRMS: [M]$^+$ calcd for $C_{13}H_{18}Cl_3N_2Rh$, 409.9591; found, 409.9596.

Rh Complex 9-CN. A 20 mL flask was charged with Ag complex **8-CN** (0.1 g, 0.26 mmol), $[Rh(cod)Cl]_2$ (60 mg, 0.12 mol), THF (5 mL), and a stir bar. The resulting reaction mixture was stirred at 50 °C for 6 h and then filtered hot through a 0.2 μm PTFE filter. Removal of residual solvent under reduced pressure afforded the desired product as an orange powder (98 mg, 95% yield). IR (KBr): 2238 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.17 (br, 2H), 4.26 (s, 6H), 3.29 (br, 2H), 2.42−2.40 (br, 4H), 2.03−2.01 (br, 4H). ^{13}C NMR ($CDCl_3$): δ 196.6 (d, $J_{\mathrm{Rh-C}} = 53.0$ Hz), 115.4, 106.8, 102.4 (d, $J_{\mathrm{Rh-C}} = 6.7$ Hz), 68.5 (d, $J_{\mathrm{Rh-C}} = 14.2$ Hz), 38.3, 33.0, 29.0. HRMS: [M]$^+$ calcd for $C_{15}H_{18}ClN_4Rh$, 392.0275; found, 392.0272.

Rh Complex 9-NO$_2$. A 20 mL flask was charged with Ag complex **8-NO$_2$** (0.3 g, 0.8 mmol), $[Rh(cod)Cl]_2$ (0.16 g, 0.33 mmol), THF (5 mL), and a stir bar. The resulting reaction mixture was then stirred at 60 °C for 1 h. Afterward, the reaction mixture was cooled to ambient temperature and then filtered through a 0.2 μm PTFE filter. Removal of residual solvent under reduced pressure afforded the desired product as a yellow solid (0.29 g, 92% yield). ^{1}H NMR ($CDCl_3$): δ 7.82 (s, 1H), 5.12 (br, 2H), 4.48 (s, 3H), 4.19 (s, 3H), 3.33 (br, 2H), 2.45−2.39 (br, 4H), 2.01−1.98 (br, 4H). ^{13}C NMR ($CDCl_3$): δ 192.8 (d, $J_{\mathrm{Rh-C}} = 53.0$ Hz), 125.1, 101.28 (d, $J_{\mathrm{Rh-C}} = 6.6$ Hz), 101.25 (d, $J_{\mathrm{Rh-C}} = 6.8$ Hz), 69.2 (d, $J_{\mathrm{Rh-C}} = 14.2$ Hz), 69.0 (d, $J_{\mathrm{Rh-C}} = 14.2$ Hz), 39.6, 39.0, 33.1, 33.0, 29.05, 28.98. HRMS: $[M]^+$ calcd for $C_{13}H_{19}ClN_3O_2Rh$, 387.0221; found, 387.0224.

General Procedures for the Synthesis of Rh Carbonyl Complexes 10. Rh complex **9** was dissolved in $CDCl_3$ (∼0.07 M) and then placed under an atmosphere of carbon monoxide (balloon). Ligand exchange was monitored using ^1H NMR spectroscopy and accompanied with a gradual loss in color. In general, reactions were complete in less than 10 min. Concentration of the reaction solutions resulted in decomposition of the desired product.[25]

Rh Complex 10-H. IR ($CDCl_3$): 2087, 2004 cm^{-1}. NMR data were in accord with literature values.[30]

Rh Complex 10-Cl. IR ($CDCl_3$): 2091, 2010 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.89 (s, 6H). ^{13}C NMR ($CDCl_3$): 184.7 (d, $J_{Rh-C} = 54.6$ Hz), 182.2, 174.7 (d, $J_{Rh-C} = 44.6$ Hz), 117.9, 37.1.

Rh Complex 10-CN. IR (KBr): 2242, 2085, 2007 cm^{-1}. IR ($CDCl_3$): 2252, 2099, 2017 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.13 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 186.9 (d, $J_{Rh-C} = 45.2$ Hz), 183.8 (d, $J_{Rh-C} = 55.8$ Hz), 181.2 (d, $J_{Rh-C} = 72.0$ Hz), 115.8, 105.9, 38.9. HRMS: $[M]^+$ calcd for $C_9H_6ClN_4O_2Rh$, 339.9234; found, 339.9229.

Rh Complex 10-NO$_2$. IR ($CDCl_3$): 2094, 2012 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.96 (s, 1H), 4.31 (s, 3H), 4.03 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 184.4 (d, $J_{Rh-C} = 54.6$ Hz), 182.8 (d, $J_{Rh-C} = 45.6$ Hz), 181.6 (d, $J_{Rh-C} = 73.0$ Hz), 139.6, 125.1, 40.1, 39.4. HRMS: $[M]^+$ calcd for $C_7H_7ClN_3O_4Rh$, 334.9180; found, 394.9181.

Acknowledgment. We are grateful to the National Science Foundation (CHE-0645563), the U.S. Army Research Office (W911NF-05-1-0430 and W911NF-06-1-0147), the Petroleum Research Fund as administered by the American Chemical Society (44077-G1), the Welch Foundation (F-1621), and the University of Texas at Austin for their generous financial support of this work. D.M.K. gratefully acknowledges the Dorothy A. Banks and Welch Foundations for graduate fellowships.

Supporting Information Available: Crystallographic information files (CIF) for complexes **9-Cl**, **9-NO$_2$**, and **9-CN** as well as spectral data (PDF) are available free of charge via the Internet at http://pubs.acs.org.

OM700591Z