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Quinone-Annulated N-Heterocyclic Carbene−Transition-Metal Complexes: Observation of π-Backbonding Using FT-IR Spectroscopy and Cyclic Voltammetry

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Since Arduengo's seminal isolation of 1,3-diadamantyl-imidazolylidene,[1] N-heterocyclic carbenes[2] (NHCs) have found extraordinary utility for modulating the activities of transition metals[3] and as versatile catalysts for promoting organic reactions.[4] We have recently launched a program that utilizes NHCs as building blocks for organometallic polymers, with an emphasis on tuning the electronic interactions between NHCs and their ligated transition metals.[5]

The complexation of NHCs to transition metals is strongly governed by σ-donation from the carbene to the metal center. π-Backbonding from the metal to the p-orbital of the carbene has historically been considered to be negligible owing to competing π-overlap of the electron-rich N atoms adjacent to the carbene.[6,7] However, recent theoretical analyses and synthetic advances have challenged this view. By corroborating computational models with key bond distances and angles observed in select ranges of metal−NHC X-ray crystal structures, Light, Meyer, Frenking, and Jacobsen concluded that π-backbonding contributes up to 30% of the overall bonding character.[8] However, Heinicke[9] demonstrated that metal complexes formed with carbo- and heterocyclic annulated NHCs did not adhere to these models. As a result, the nature of the NHC−metal interaction, including the existence of π-backbonding, remains controversial.[10]

The descrepancies between the aforementioned studies can be traced to challenges associated with separating σ- and π-contributions in NHC−metal complexes. An NHC featuring a functional group in conjugation with the carbene atom and sensitive to π-effects would be ideal for identifying π-backbonding in its respective metal complexes. We envisioned this could be accomplished by fusing a *p*-quinone moiety to the 4,5-positions of an imidazolylidene. With two carbonyl groups formally conjugated to the p-orbital at the carbene atom, a quinone-annulated NHC was anticipated to offer three distinct advantages for studying metal−NHC interactions: (1) Carbonyl stretching frequencies are sensitive to minute electronic changes in π-systems and can be conveniently measured using IR spectroscopy.[11] (2) The electron-withdrawing nature of the quinone should result in increased propensities for π-backbonding upon ligation to a transition metal. (3) *p*-Quinones exhibit reduction potentials that are sensitive to subtle electronic changes on their peripheries.[12] Collectively, this enables the use of IR spectroscopy and cyclic voltammetry to observe structural and electronic changes, including deconvoluting σ- versus π-effects, *on the NHC ligand* upon complexation. Herein, we report the synthesis of the first NHC annulated to a quinone and present evidence for π-backbonding in its respective transition-metal complexes.

Imidazolium salt **1** was synthesized in 74% isolated yield by reacting commercially available 2,3-dichloro-1,4-naphthoquinone with *N,N′*-dimesitylformamidine under mildly basic conditions (Scheme 1).[13] A signal assigned to the iminium proton was found at 12.8 ppm in the ^{1}H NMR spectrum (CDCl$_3$). To the best of our knowledge, this is the largest downfield shift reported for any known imidazolium compound and reflects the highly electron-withdrawing nature of the quinone moiety. Free carbene **2** was obtained in 73% yield by deprotonating **1** with sodium hydride (facilitated by adding a catalytic amount of potassium *tert*-butoxide). NHC **2** exhibited a signal at 232 ppm in the ^{13}C NMR spectrum (C$_6$D$_6$), which was similar to known benzimidazolylidenes and other annulated carbenes.[9] Combined with the ^{1}H NMR data for **1**, this result highlights the subtleties in using NMR spectroscopy to isolate σ- from π-effects in NHCs. To confirm the molecular structure of **2**, a crystal was obtained by slowly cooling a hot, saturated toluene solution and analyzed using X-ray diffraction analysis. The molecular structure of **2** revealed a planar ring system, relatively long N−C bond lengths (1.392(8) Å), and a narrow N−C−N bond angle (102.1°),[9c] which suggested that the π-system of the quinone moiety was effectively conjugated to the carbene.

Scheme 1. Synthesis of an NHC Annulated to a Quinone and its Rh Complexes

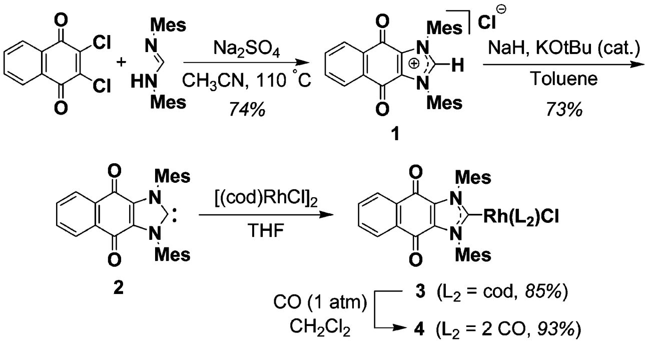

Table 1. Summary of Selected Physical Data for Compounds **1**−**5**

compd	^{13}C (ppm)^a	N–C (Å)^b	C═O (cm^{-1})^c	E$_{red}$ (V)^d
1	142	1.336(2)	1685 (1690)	−0.24
2	232	1.392(8)	1671 (^{e})	*e*
3	200	1.379(6)	1670 (1675)	−0.55
4	191	*e*	1680 (1680)	−0.49
5	193	1.352(4)	1681 (1683)	−0.49

^{a} Chemical shift of the carbene atom found in its respective ^{13}C NMR spectrum (C$_6$D$_6$). ^{b} Distance between the carbene atom and adjoining nitrogen atom. For **2**, the data reflects the longer N−C bond; the shorter N−C bond = 1.385(8) Å. All other compounds showed symmetric N−C bond lengths. ^{c} Carbonyl stretching frequencies were determined using IR spectroscopy for compounds in the solid-state (KBr); parenthetical values were determined for compounds in solution (CHCl$_3$). Values are ±1 cm^{-1}. ^{d} First reduction potentials as determined using cyclic voltammetry in CH$_3$CN, 1 mM analyte, 0.1 M (Bu$_4$N)(PF$_6$) as electrolyte, referenced to Fc$^+$/Fc (1 mM) at 507 mV vs Ag/AgCl/KCl (saturated) electrode; scan rate = 0.2 V s^{-1}. Values are ±0.01 V. ^{e} Not evaluated.

After isolation and characterization of **2**, its utility in the synthesis of organometallic complexes was investigated. With the goal of evaluating π-backbonding characteristics in mind, a metal complex was needed with ancillary ligands that were exchangeable without disrupting other physical characteristics of the complex (oxidation state, geometry, coordination number, etc.) In particular, we desired a system where a ligand with relatively little π-backbonding capability (e.g., an olefin) could be substituted with a ligand that is highly capable (e.g., carbon monoxide). Ancillary ligand exchange

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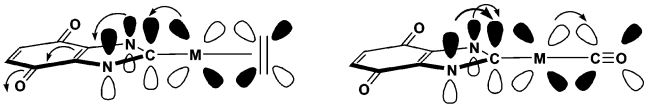
should result in detectable changes in the carbonyl stretching frequencies and reduction potentials of **2**. Thus, Rh complexes of the general type (NHC)RhCl(cod) (cod = *cis*,*cis*-1,5-cyclooctadiene) were targeted as the cod ligand is known to rapidly exchange with two units of carbon monoxide, with essentially no other change in the metal environment.[14]

Addition of [(cod)RhCl]$_2$ to a THF solution of **2** at ambient temperature resulted in the formation of Rh complex **3** as a brown solid, which was subsequently isolated in 85% yield. Bubbling carbon monoxide through a CH_2Cl_2 solution of **3** for 2 h afforded **4** as a green solid in 93% yield after the evaporation of the solvent.[15] While the structure of **3** was confirmed by X-ray diffraction analysis, the crystallization of **4** was frustrated by a competitive dimerization process where loss of carbon monoxide was concomitant with crystallization of [(**2**)(CO)RhCl]$_2$.

Once compounds **1**−**4** were synthesized, they were analyzed using IR spectroscopy in the solid-state (KBr) and in solution ($CHCl_3$). The *p*-quinone carbonyl stretching frequencies were recorded (see Table 1) and found to be dependent on the cationic character of the carbene atom. For example, positively charged **1** exhibited the highest stretching frequency of 1685 cm^{-1} (KBr) which was a reflection of strong N → C donation. In contrast, formally neutral NHC **2** required less N → C stabilization and exhibited a lower carbonyl stretching frequency of 1671 cm^{-1} (KBr). To isolate effects due to positive charge buildup upon ligation, any evaluation of π-backbonding character in metal complexes should compare the same metal center in similar oxidation states.[16] Since π-withdrawing effects from the cod and/or Cl ligands are relatively weak, complex **3** is well-suited for metal to NHC π-backbonding. In contrast, the Rh atom in complex **4** is bound to two π-acidic carbonyl groups which should greatly diminish its ability to π-backbond to the NHC. The quinone moieties of complexes **3** and **4** exhibited carbonyl stretching frequencies of 1670 and 1680 cm^{-1} (KBr), respectively; similar values were observed in solution ($CHCl_3$). These differences are consistent with the ability of complex **3** to donate π-electron density from Rh → C (i.e., π-backbond). On a relative scale, NHC **2** appears to be a stronger π-acid than an olefin but weaker than carbon monoxide (see Figure 1).[17,18]



3 **4**

Figure 1. Dominant resonance contributors for complexes **3** and **4**.

Next, we turned our attention toward using cyclic voltammetry as a means to evaluate the metal−NHC interaction. Electrochemical reductions of *p*-quinones are known to be inversely influenced by the electron-donating character of peripheral substituents.[12] As shown in Table 1, the first reduction potential of complex **3** (−0.55 V) was greater than complex **4** (−0.49 V), but within the range of known naphthoquinones.[19] This data supports the conclusion derived above that, as a result of Rh → C π-backbonding, the NHC ligand in complex **3** is more electron rich than in complex **4**.

To further study the π-system of NHC **2** in complexes **3** and **4**, a crystalline silver complex **5** ([(**2**)AgCl]) was prepared by condensation of Ag_2O with **1**.[20] As shown in Table 1, key physical charactristics of complex **4** were essentially identical to **5**, and therefore they could be accurately compared to complex **3**. The relatively short N−C bond distance observed for complex **5** supports the π-backbonding arguments described above. However, the use of N−C bond distances to evaluate π-backbonding in NHC−metal complexes is often challenging.[9a] For example, consider [(**2**)(CO)-RhCl]$_2$. This complex exhibits N−C bond distances that range from 1.356 to 1.397 Å which effectively covers all the respective distances shown in Table 1.

In summary, we have shown that an imidazolylidene annulated to a quinone can be readily synthesized from formamidines and 2,3-dichloro-1,4-naphthoquinone. The quinone moiety was found to be a unique and sensitive handle for analyzing the π-systems of NHC−metal complexes using FT-IR spectroscopy and cyclic voltammetry. Ultimately, unambiguous and non-negligible π-backbonding was experimentally observed in the NHC complexes reported herein.

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Supporting Information Available: Additional experimental data and spectra (pdf and cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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