

π -Back-Bonding in Bis(isonitrile) Complexes of Rhodium(II) Acetate: Structural Analogs for Rhodium Carbenoids

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Summary: $Rh_2(O_2CCH_3)_4 \cdot 2C \equiv NC_6H_4R$ ($R = (CH_3)_2N-$ (**1**), $-H$ (**2**), $-CF_3$ (**3**)) were synthesized and characterized by X-ray crystallography. The structures exhibited several common features: (i) a relatively short Rh–C bond (2.148(4) Å (**1**), 2.133(4) Å (**2**), and 2.122(4) Å (**3**)), (ii) an inversion center between the two rhodium atoms, (iii) coplanar aryl rings, and (iv) a significant deviation from linearity in the Rh–C–N bond angle. Comparison to other rhodium carboxylate complexes indicates the presence of π -back-bonding and, by extension, π -back-bonding in rhodium–carbenoid systems.

Introduction

Rhodium carboxylates and carboxamides are important catalysts for a variety of carbenoid transformations,¹ including cyclopropanations,² N–H³ and C–H⁴ insertion reactions, and dipolar cycloadditions.⁵ Rhodium carboxylates and carboxamides have been modified extensively to enhance and direct chemical reactivity, diastereoselectivity, and enantioselectivity. A question of vital importance in the rational design of selective catalysts is the structural and electronic makeup of the rhodium–carbenoid intermediate. Despite much interest in these catalysts, little is known about rhodium–carbenoid intermediates, largely due to their highly transient nature.

The debate regarding π -back-bonding in rhodium carboxylate complexes dates back to the original controversy regarding the Rh–Rh bond order of such complexes.⁶ While the Rh–Rh bond order is now firmly established as 1, the debate regarding π -back-bonding, particularly in rhodium–carbenoid complexes, contin-

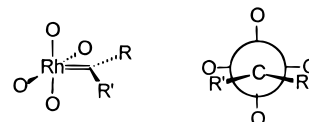


Figure 1. Eclipsing conformation of the rhodium–carbenoid complex.

ues.⁷ Crystal-field theory suggests that π -back-bonding is possible through donation of electron density from one of the two degenerate, filled metal π^* orbitals (arising from antibonding overlap of the two Rh d_{xz} (or Rh d_{yz}) orbitals) into the vacant, unhybridized, p orbital of the carbene. Consequently, π -back-bonding would result in a conformation in which the carbene eclipses two of the carboxylate ligands surrounding the metal core, as shown in Figure 1.

In an elegant series of linear free energy relationship experiments, Pirrung and Morehead demonstrated the importance of the polarizability and resonance contributions of the carboxylate (and carboxamide) ligands to the reaction selectivity of carbenoid transformations, suggesting that π -back-bonding is an important facet of these transformations.⁷ Spectroscopic studies published in the same report also suggest the importance of π -back-bonding in $Rh_2(O_2CR)_4 \cdot 2CO$ complexes and, by analogy, rhodium–carbene complexes.

Bear, Kadish, and co-workers found evidence for π -back-bonding in $Rh_2(OAc)_n(NHAc)_{4-n} \cdot CO$ complexes ($n = 0-4$; $Ac = -C(O)CH_3$).⁸ As n decreased, the binding constant for CO increased, the degree of bis-(CO adduct) formation increased, and $\nu(CO)$ decreased. These factors all point to π -back-bonding from the metal to the carbonyl. While Bear, Kadish, and co-workers drew no conclusions regarding π -back-bonding in rhodium–carbenoid systems, extending their conclusions to such systems appears logical given the similarity in the frontier molecular orbitals of CO and carbenes.

Doyle and co-workers, on the other hand, propose a “carbenoid” intermediate with no π -back-bonding and, thus, a formal Rh–C single bond.⁹ The electrophilic carbon is therefore more akin to that found in a

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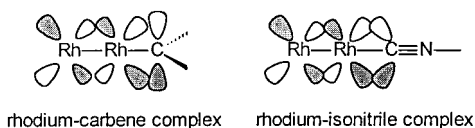
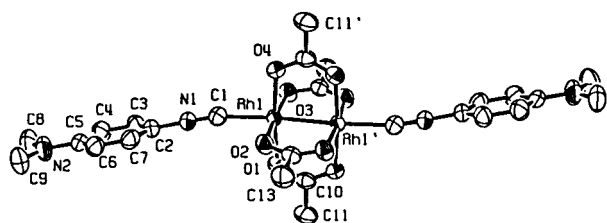
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**Figure 2.** Orbitals involved in π -back-bonding.**Figure 3.** ORTEP drawing of bis(*p*-(dimethylamino)phenyl isonitrile)rhodium(II) acetate.

carbocation than to the alkylidene carbon of a metal-carbenoid complex. Doyle et al. based this proposition on modeling studies of chiral rhodium-carboxamidate complexes. The structures were optimized with molecular mechanics, and the axial carbene ligand was then rotated as a rigid rotor. Each rotamer was then examined by extended Hückel calculations. Both molecular mechanics and extended Hückel calculations found a rotational barrier of less than 1 kcal/mol, suggesting a lack of double-bond character in the Rh-C bond.

Bursten and Cotton have performed $X\alpha$ -SW calculations on the bis(phosphine) adduct of rhodium formate.¹⁰ The $\text{Rh}_2(\text{O}_2\text{CH})_4 \cdot 2\text{PH}_3$ geometry was obtained from the X-ray crystal structure of the corresponding rhodium acetate adduct. These calculations also failed to show any significant π -back-bonding from metal to phosphine. Bursten and Cotton acknowledged that the applicability of these calculations to other π -acid complexes is a "moot point".

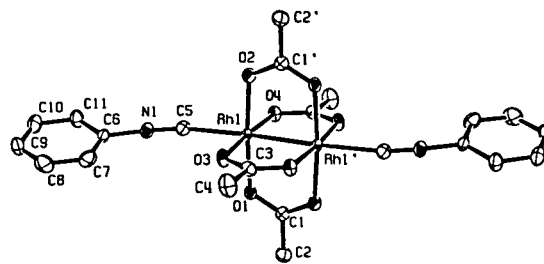
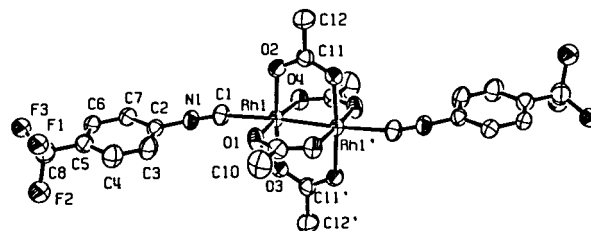
To shed more light on this important area, three bis(*para*-substituted-aryl isonitrile) adducts of $\text{Rh}_2(\text{OAc})_4$ were synthesized to serve as analogs for the rhodium-carbenoid complex. Herein we describe the structural features of the three isonitrile adducts.

Results and Discussion

Carbenes and isocyanides both have appropriate orbitals available to function as σ -donors and π -acids. In the case of carbenes, the π -acceptor orbital is the unhybridized p atomic orbital while, in the isocyanide, it is the CN π^* -molecular orbital (Figure 2).

The solid-state structures of the three bis(*para*-substituted-aryl isonitrile) adducts $\text{Rh}_2(\text{OAc})_4 \cdot 2\text{CNC}_6\text{H}_4\text{X}$, where X = $-\text{N}(\text{CH}_3)_2$ (**1**), $-\text{H}$ (**2**), and $-\text{CF}_3$ (**3**), were determined. ORTEP drawings of **1–3** are given in Figures 3–5, respectively. The structures exhibited several common features: (i) a relatively short Rh-C bond, (ii) an inversion center between the two rhodium atoms, (iii) coplanar aryl rings, and (iv) a significant deviation from linearity in the Rh-C-N bond angle. Interestingly, the bent Rh-C-N bond lies between the planes of the acetate ligands in **1** but largely in the plane of one pair of acetate ligands in **2** and **3**. Selected bond lengths and angles are given in Table 1 for **1–3**.

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**Figure 4.** ORTEP drawing of bis(phenyl isonitrile)rhodium(II) acetate.**Figure 5.** ORTEP drawing of bis(*p*-(trifluoromethyl)phenyl isonitrile)rhodium(II) acetate.**Table 1.** Selected Bond Lengths (Å) and Bond Angles (deg)

| | 1 | 2 | 3 |
|--------|-----------|-----------|-----------|
| Rh-Rh | 2.4245(4) | 2.4271(3) | 2.4182(3) |
| Rh-C | 2.148(4) | 2.133(3) | 2.122(3) |
| C-N | 1.139(5) | 1.153(4) | 1.141(5) |
| Rh-C-N | 166.8(4) | 158.7(2) | 155.4(3) |

One factor which is commonly used as an indication of π -back-bonding is the metal-to-ligand bond length. In this series, as the *para* substituent was varied from the strongly electron-donating dimethylamino ($(\text{CH}_3)_2\text{N}-$) group to the strongly electron-withdrawing trifluoromethyl ($-\text{CF}_3$) group, the degree of π -back-bonding was anticipated to increase and the Rh-C bond to shorten. While such a trend is evident here, translating it into evidence for π -back-bonding is problematic; analogous trends are expected, but not seen, in the variation of the Rh-Rh and C-N bond lengths.

The same factors which influence the degree of π -back-bonding also affect the strengths of the Rh-Rh and C-N σ -bonds in a complex, interdependent fashion. For example, the dimethylamino group is electron-donating from a resonance standpoint (diminishing π -acceptor ability of the isonitrile), while it is inductively electron-withdrawing (diminishing σ -donor ability of the isonitrile).¹¹ Consequently, the Rh-C bond will weaken and lengthen. Since the isonitrile is donating electron density into the Rh-Rh σ^* molecular orbital and accepting electron density from the Rh-Rh π^* molecular orbital, the net effect on the Rh-Rh bond will depend on the relative strengths of the two competing factors. Similarly, the effect on the C \equiv N bond will be mixed since the isonitrile is accepting electron density into a π^* molecular orbital yet is donating from a nonbonding

(11) This argument is simplistic in that resonance effects, while primarily a π molecular orbital phenomenon, also affect σ molecular orbitals, though to a lesser degree. Likewise, inductive effects are not limited to σ molecular orbitals but also affect π molecular orbitals. These complex interdependencies highlight the difficulties inherent in relying on bond lengths to measure the degree of π -back-bonding present in the isonitrile complexes.

Table 2. Crystallographic Data

| | 1 | 2 | 3 |
|---|---|---|--|
| formula | C ₂₆ H ₃₂ N ₄ O ₈ Rh ₂ | C ₂₂ H ₂₂ N ₂ O ₈ Rh ₂ | C ₂₄ H ₂₀ F ₆ N ₂ O ₈ Rh ₂ |
| fw | 734.38 | 648.24 | 784.24 |
| cryst descriptn | plate | plate | prismatic |
| color | orange | orange-red | red |
| cryst dimens (mm) | 0.50 × 0.31 × 0.02 | 0.32 × 0.30 × 0.03 | 0.31 × 0.29 × 0.15 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>a</i> | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> , Å | 12.018(2) | 8.562(1) | 8.4661(8) |
| <i>b</i> , Å | 8.119(2) | 13.954(2) | 8.257(1) |
| <i>c</i> , Å | 15.008(3) | 10.201(2) | 20.145(4) |
| α, deg | 90.00 | 90.00 | 90.00 |
| β, deg | 91.7(1) | 104.30(1) | 94.41(1) |
| γ, deg | 90.00 | 90.00 | 90.00 |
| <i>V</i> , Å ³ | 1463.7(9) | 1181.0(6) | 1404.0(6) |
| <i>Z</i> | 2 | 2 | 2 |
| <i>F</i> (000) | 740 | 644 | 772 |
| <i>T</i> , (K) | 294 | 160 | 294 |
| 2θ range (deg) | 3–52 | 3–52 | 2–52 |
| ρ _{calcd} , g cm ⁻³ | 1.67 | 1.82 | 1.85 |
| no. of rflns measd | 3081 | 2435 | 2958 |
| no. of rflns obsd (<i>I</i> > 3.0 σ(<i>I</i>)) | 2279 | 2024 | 2377 |
| <i>R</i> | 0.034 | 0.025 | 0.030 |
| <i>R</i> _w | 0.045 | 0.033 | 0.045 |
| goodness of fit | 1.470 | 1.190 | 1.610 |

σ molecular orbital lying coincident with the C–N σ^* .¹² On the other hand, the trifluoromethyl group is both electronically and inductively electron withdrawing and will enhance the π -acceptor ability while diminishing the σ -donor ability of the isonitrile.

To date, three other X-ray crystal structures of rhodium carboxylates with carbon in the axial sites have been reported: Rh₂(O₂CCF₃)₄·2CO,¹³ Rh₂(O₂CCF₃)₄·2((–)-*trans*-caryophyllene),¹⁴ and Rh₂(O₂CC(CH₃)₃)₄·(1,4-benzoquinone).¹⁵ The Rh–C bond length of the rhodium trifluoroacetate dicarbonyl adduct is 2.092(4) Å, only 0.03–0.06 Å shorter than those of the aryl isonitrile complexes. This small difference in bond lengths suggests that CO and CNR bond to the metal center in a similar fashion, pointing to π -back-bonding in the isonitrile complexes. In contrast, the alkene adducts exhibit Rh–C bond lengths 0.23–0.50 Å longer than those of the isonitrile complexes. Measuring from the centroid of the carbon–carbon double bond to the Rh metal produces rhodium–ligand distances 0.22–0.33 Å longer than those of the isonitrile complexes. Although these differences are probably due as much to steric repulsion as to the η^2 -bonding fashion of the alkenes, they do highlight the significantly longer bonds that result from the different bonding mode.

Comparing the relative metal–ligand bond lengths in the isonitrile complexes with those found in the complexes of the isolobal nitriles is also instructive. Given the smaller covalent radius of N versus C, in the absence of π -back-bonding, the Rh–N bond is anticipated to be shorter than the Rh–C bond. The converse, however, is true; the Rh–N bonds of Rh₂(O₂CCH₃)·2NCCH₃ are 2.249(7) and 2.258(6) Å, 0.1 Å longer than the Rh–C bonds of the isonitrile adducts.¹⁶ The most likely cause for the shorter Rh–C bonds is greater

π -back-bonding in the case of the isonitriles than in acetonitrile. This is not surprising, since isonitriles are generally better π -acceptors than nitriles, but it again supports the presence of π -back-bonding in the isonitrile complexes.

Additional evidence for π -back-bonding is found in the coplanarity of the aromatic rings. Conjugation through the extended π -network that would result from π -back-bonding would render the aromatic rings coplanar. In the absence of π -back-bonding, free rotation about the Rh–C σ bonds would give rise to solid-state structures in which the relative orientation of the aromatic rings would be dictated by packing forces, perhaps resulting in a random disposition of the axial aryl ligands. This random disposition is seen in a series of rhodium carboxylate–arylamine complexes synthesized by Cotton and Felthouse¹⁷ and Koh and Christoph.¹⁸ The planes of the aromatic amines are inclined to one another at angles of 68.4, 4.4, and 9.9° for the rhodium butyrate complexes of 7-azaindole, phenazine, and acridine, respectively.¹⁷ For the bis(pyridine) adduct of rhodium acetate, the pyridine rings are inclined at a 59° angle.¹⁸

The relatively short Rh–C bonds of the isonitrile complexes compared to other Rh–C bonds and Rh–N bonds and the coplanar arrangement of the aromatic rings indicate the presence of π -back-bonding in these complexes and, by extension, in rhodium–carbenoid systems.

Experimental Section

Commercial reagents were used as received, with no further purification. IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer. NMR spectra were recorded on either a Varian VXR-400 spectrometer or a Varian Gemini 2000 spectrometer. ¹H NMR spectra were referenced to residual protiochloroform in the solvent, while ¹³C NMR spectra were

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referenced to the central solvent peak. Crystal data were collected on an ENRAF-Nonius CAD4 diffractometer with Mo K α radiation and solved by direct methods.

Synthesis of Isonitriles. The isonitriles were synthesized by the dehydration of the respective formamides according to the procedure of Ugi and Meyr.¹⁹

Synthesis of Rhodium Acetate Isonitrile Adducts. Rh₂(O₂CCH₃)₄ (10 mg) was dissolved in 20 mL of ethanol and treated with approximately 25 mg of isonitrile without stirring. The resulting yellow solution was allowed to stand until crystals developed (1–2 days).²⁰ Rh₂(O₂CCH₃)₄·2CN(C₆H₄)N(CH₃)₂ (**1**): IR (KBr, cm⁻¹) ν (CN) 2133.0; ¹H NMR (400 MHz, δ , CDCl₃) 7.67 (d, 8.48 Hz, 4H), 6.68 (d, 8.8 Hz, 4H), 3.04 (s, 12H), 1.97 (s, 12H); ¹³C NMR (101 MHz, δ , CDCl₃) 194.9, 128.5, 111.7, 40.2, 24.3. Rh₂(O₂CCH₃)₄·2CNC₆H₅ (**2**): IR (KBr, cm⁻¹) ν (CN) 2138.7; ¹H NMR (300 MHz, δ , CDCl₃) 7.84 (m, 4H), 7.54 (m, 6H), 1.99 (s, 12H); ¹³C NMR (75 MHz, δ , CDCl₃) 194.9, 130.1, 129.6, 127.4, 24.3. Rh₂(O₂CCH₃)₄·2CN(C₆H₄)CF₃ (**3**): IR (KBr, cm⁻¹) ν (CN) 2133.9; ¹H NMR (400 MHz, δ , CDCl₃) 7.96 (d, 8.44 Hz, 4H), 7.81 (d, 8.44 Hz, 4H), 1.98 (s, 12H); ¹³C NMR (101 MHz, δ , CDCl₃) 195.0, 127.9, 127.0, 24.3.

X-ray Structure Determination. General Methods. A single crystal selected for data collection was mounted on a glass fiber in a random orientation. X-ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer in the ω -2 θ mode. Data were collected to a maximum 2 θ value of 52°. Lorentz and polarization corrections were applied to the data. Absorption effects were corrected by a semiempirical method on the basis of ψ scans. The structure was refined by full-matrix least squares on F using $F_o^2 > 3.0\sigma(F_o^2)$, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w was defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from the standard literature.²¹ Anomalous dispersion effects were included in F_c . The unweighted and weighted agreement factors are defined as $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. All calculations were performed on a VAX 3100 computer using MolEN.²²

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Structure Solution and Refinement. The position of the rhodium atom in the asymmetric unit was located by direct methods. The remaining atoms were located by repeated least-squares refinements followed by difference Fourier syntheses. The CF₃ group in **3** was disordered. The model refined contained three different positions for the F atoms. These atoms were refined with isotropic atomic displacement factors, and their occupancy was 1/3. For compounds **1** and **3**, the hydrogen atoms were calculated and included in the least-squares refinement as riding atoms; $U_{iso} = 1.3U_{eq}$ (bonding atom). In compound **2**, the hydrogen atoms were located by difference maps and refined with isotropic thermal parameters. All other atoms were refined with anisotropic thermal parameters. For compound **1**, the final cycle included 181 variable parameters and converged with $R = 0.034$ and $R_w = 0.045$. For compound **2**, the final cycle included 198 variable parameters and converged with $R = 0.025$ and $R_w = 0.033$. For compound **3**, the final cycle included 199 variable parameters and converged with $R = 0.030$ and $R_w = 0.045$. Further details relevant to the data collection and structure refinements are found in Table 2.

Acknowledgment. This research was supported by an award from Research Corp. and a Supplemental Award of the Camille and Henry Dreyfus Foundation Grant Program in Chemistry for Liberal Arts Colleges. We also thank Johnson Matthey Inc. for the loan of rhodium salts and the College of Arts and Sciences of the University of Toledo for generous financial support of the X-ray diffraction facility. We sincerely thank Kristin Kirschbaum for her assistance with the crystallographic details.

Supporting Information Available: Three X-ray crystallographic files for **1–3**, in CIF format, are available. Access information is given on any current masthead page.

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