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# Structural and electronic properties of (2,2-*trans*)-dirhodium(II) tetrakis(*N*-phenylacetamidate)

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**Abstract**

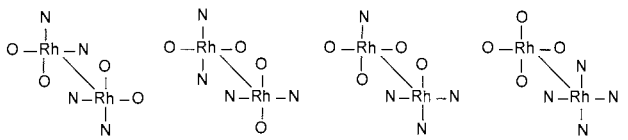
We have synthesized and characterized the first known 2,2-*trans* isomer of the *N*-substituted dirhodium(II) tetrakisacetamidate, $Rh_2(RNAc)_4$, class of compounds. The bis benzonitrile adduct exhibits a unique orthogonal arrangement of the axial aromatic rings in the solid state. Structural and electronic features suggest the presence of π-backbonding. 

*Keywords:* Aromatic rings; π-Backbonding; Rhodium acetate

## 1. Introduction

Rhodium acetate was first discovered to catalyze carbenoid transformations more than 25 years ago [1]. Since that discovery, the dirhodium(II) tetrakis(carboxylate) core has been extensively modified to develop selective carbenoid catalysts [2]. Such modifications have included altering the electronic demand of the metal, making electron-deficient catalysts by using perfluorocarboxylate ligands and electron-rich catalysts through the use of carboxamidate ligands [3]. Other modifications involve the production of enantioselective catalysts using chiral carboxylate and carboxamidate ligands [4] and axially chiral complexes derived from achiral orthometallating aryl phosphines [5]. These modifications have been driven largely by guesswork and chemical intuition due to the paucity of information regarding the structural and electronic composition of the rhodium carbenoid intermediate.

In the course of our efforts to shed light on this elusive, highly transient intermediate, we have synthesized the heretofore unreported 2,2-*trans* isomer of a rhodium carboxamidate. Dirhodium(II) tetrakis(carboxamidate) complexes can form four different isomeric structures: 2,2-*cis* (**I**); 2,2-*trans* (**II**); 3,1 (**III**); and 4,0 (**IV**).




Bear and co-workers characterized (by cyclic voltammetry and UV–vis spectroscopy) two dirhodium acetamidates, $Rh_2(NHC(O)CF_3)_4$ [6] and $Rh_2(PhNAc)_4$ [7], where $Ac = C(O)CH_3$. The trifluoroacetamidate complex was synthesized as a single isomer and presumed to be the 2,2-*cis* isomer. Synthesis of the *N*-phenyl acetamidate complex produced two isomers, assigned as the 2,2-*cis* and 3,1 isomers. Later synthesis and structural analysis of (2,2-*cis*)-$Rh_2(NHAc)_4$, (2,2-*cis*)-$Rh_2(NPhAc)_4$ and (3,1)-$Rh_2(NPhAc)_4$ indicated that the conformation of these acetamidate analogs, and by extension, previous analogs, were correctly assigned [8].

Doyle and co-workers recently isolated and obtained solid-state structures for their chiral rhodium acetamidate analogs with the 3,1 ($Rh_2(4S\text{-}MACIM)_4$) [9] and

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Table 1
Comparison of bond lengths of several isomeric analogs [a]

| | 2,2-*trans*-$Rh_2(PhNAc)_4 \cdot 2NCPh$ | 2,2-*cis*-$Rh_2(NPhAc)_4 \cdot 2DMSO$ | 3,1-$Rh_2(NPhAc)_4 \cdot 2DMSO$ | 2,2-*cis*-$Rh_2(MACIM)_4 \cdot 2NCCH_3$ | 3,1-$Rh_2(MACIM)_4 \cdot 2NCCH_3$ | 4,0-$Rh_2(MACIM)_4 \cdot 2NCCH_3$ |
|---|---|---|---|---|---|---|
| Rh–Rh | 2.4220 | 2.448 | 2.397 | 2.4586 | 2.4597 | 2.4447 |
| Rh–O | 2.039 [b] | 2.038 | 2.055 | 2.081 | 2.059 | 2.047 |
| $Rh–N_{(eq)}$ | 2.061 [b] | 2.059 | 2.037 | 2.009 | 2.023 | 2.039 |
| $Rh–N_{(ax)}$ | 2.2047 | | | 2.199 | 2.215 | 2.179 |
| | 2.2478 | | | 2.241 | 2.230 | 2.268 |

[a] All bond lengths are given in Å.
[b] Rh–O and $Rh–N_{(eq)}$ bond lengths are given as average lengths.

4,0 ($Rh_2(4S\text{-MACIM})_4$) [10] isomeric orientations. Synthesis of each of these complexes, as well as two other chiral carboxamidates, produced three isomers, the 2,2-*cis*, 3,1 and 4,0.

## 2. Discussion

### 2.1. Synthesis

We report herein the first isolation and structural characterization of the 2,2-*trans* isomer of a rhodium carboxamidate analog: 2,2-*trans*-dirhodium(II) tetrakis(*N*-phenylacetamidate) [$Rh_2(PhNAc)_4$] (**1**). This isomer was synthesized, along with the 2,2-*cis* and 3,1 isomers, by refluxing a mixture of rhodium acetate and *N*-phenylacetamide in chlorobenzene, over 7 days, using a Soxhlet extractor. The thimble of the Soxhlet extractor was charged with sodium carbonate and sand, and replaced every 24 h [11]. The isomers were separated by flash chromatography on silica gel. This differs significantly from the method used by Bear and coworkers, who allowed the rhodium acetate to react in a melt of the acetamide.

Doyle and co-workers, on the other hand, conducted their syntheses in a manner analogous to that employed by us. However, their reflux rate was such that the Soxhlet cycling time was as frequent as every 30 s, resulting in reaction times of 2–22 h. Doyle and coworkers report three isomeric products from their reactions, the 2,2-*cis*, 3,1 and 4,0 isomers, while we observe only the 2,2-*trans*, 2,2-*cis* and 3,1 isomers. In the synthesis of $Rh_2(4S\text{-MACIM})_4$, Doyle and co-workers report the 4,0 isomer is initially formed, but disappears after 18 h of heating at reflux. This suggests that the previously observed isomers may be kinetic products, while the 2,2-*trans* isomer is a thermodynamic product, evidenced only after extended reaction periods. Additional studies in this area are on-going.

### 2.2. Structural analysis

The crystal structure of **1** was obtained as the bis benzonitrile adduct (Fig. 1). The structural features of the 2,2-*trans* isomer are similar in many respects to those of other, previously characterized, isomeric analogs (Table 1). The Rh–Rh bond length (2.422 Å) is similar to those reported by Bear and Doyle. The Rh–N bonds of the equatorial acetamide ligands are slightly longer than those reported by Bear and Doyle; while the Rh–O bonds are slightly shorter.

The acetamide bridges are twisted slightly from planarity, with N–Rh–Rh–O dihedral angles from 9.03 to 11.89. This twisting, which is likely due to crystal packing forces, is present in Doyle's chiral rhodium acetamidate complexes and Bear's (3,1)-$Rh_2(NPhAc)_4$ complex, but is essentially absent in Bear's less sterically encumbered $Rh_2(NHAc)_4$ and (2,2-*cis*)-$Rh_2(NPhAc)_4$ analogs. The phenyl rings attached to the acetamide bridges are nearly perpendicular to the plane of the amide bridge. While this arrangement effectively eliminates conjugation between the two fragments, it is necessitated for steric reasons. A co-planar arrangement would not only block the axial site from coordination, but more importantly, would result in the *ortho* protons

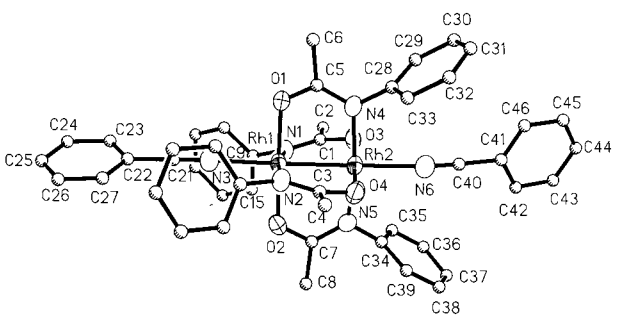


Fig. 1. ORTEP of $Rh_2[N(C_6H_5)C(O)CH_3]_4 \cdot 2NCC_6H_5$ (**1**) showing the co-planar arrangement of the axial benzonitrile ligands with the proximal nitrogen atoms of the acetamidate ligands.

of the phenyl rings approaching within 0.7 Å of the $CH_3$ moiety of the acetamide.

The most intriguing structural feature is the perpendicular disposition of the axial benzonitrile ligands. The planes of the aromatic rings are essentially perpendicular to one another. This is in contrast to a series of phenyl isonitrile adducts of rhodium acetate characterized by Eagle et al., in which the aromatic rings are co-planar [12]. Fenske–Hall calculations on the rhodium acetate isonitrile complexes indicate that the observed co-planarity is a consequence of extended conjugation between the axial ligands, through the rhodium–rhodium core via π-backbonding [13]. The orthogonal arrangement of the benzonitrile fragments is also likely to be a consequence of π-backbonding. The Rh–Rh core of the $Rh_2(NPhAc)_4$ fragment is isolobal with $Rh_2(OAc)_4$, containing an orthogonal pair of filled d–π* molecular orbitals (MOs). Likewise, the benzonitrile fragments are isolobal with the phenylisonitrile fragments, containing a pair of vacant π* orbitals available to receive electron density from the rhodium's filled π* orbital. The Fenske–Hall calculations show π-backbonding from both of the filled d–π* MOs to each of the vacant isonitrile π* MOs, indicating that extended conjugation can occur between the nitrile fragments even with the orthogonal arrangement of the aromatic rings.

The perpendicular arrangement of the aromatic rings of **1** renders each ring co-planar with the pair of equatorial nitrogens on the proximal rhodium atom. This orientation maximizes possible overlap of the π-type MOs of the benzonitrile fragment with the more electron-donating nitrogen atoms (relative to the oxygen atoms) of the acetamide fragments. Thus, the conformation of the axial ligands could be electronic in nature, a consequence of favorable orbital overlap. Alternatively, the conformation could result from an electrostatic attraction between the electropositive benzonitrile aryl hydrogens and the electronegative phenyl amidate π-cloud.

Steric explanations for the perpendicular orientation of the axial ligands are unconvincing. It is unlikely that both rings would be co-planar with the proximal pair of nitrogens, rather than have a random disposition, as seen in several rhodium acetate arylamine complexes [14], especially in light of the lack of symmetry in **1**.

### 2.3. Cyclic voltammetry

The cyclic voltammetric behavior of **1** in 1,2-dichloroethane and acetonitrile is reminiscent of that reported for Bear's 2,2-*cis*-$Rh_2(PhNAc)_4$ isomer [7]. In the non-coordinating 1,2-dichloroethane, two oxidations are observed within the potential window afforded by the solvent/supporting electrolyte. The first oxidation appears at a half-wave potential ($E_{1/2}$) of $+554$ mV. Diagnostic criteria applied to the oxidation shows that the peak separation ($E_{p,a} - E_{p,c}$ or $\Delta E_p$) increases from 85 to 196 mV with scan rates increasing from 50 to 2000 mV $s^{-1}$. However, the value of $E_{1/2}$ is independent of scan rate, as is the current function, $i_{p,a}/v^{1/2}$. The ratio of cathodic to anodic peak currents declines from unity at low scan rates to a value of 0.89 at 2000 mV $s^{-1}$. These criteria indicate a quasi-reversible electron transfer mechanism for this oxidative process, i.e. one characterized by moderately slow electron-transfer kinetics.

The second oxidation appears at an $E_{1/2}$ of $+1798$ mV (average value) versus $Ag|Ag^+$. This potential increases with increasing scan rate, from 1779 (50 mV $s^{-1}$) to 1824 mV (2000 mV $s^{-1}$). The value of $\Delta E_p$ increases from 91 (50 mV $s^{-1}$) to 202 mV (2000 mV $s^{-1}$). The current ratio increases with increasing scan rate; the current function drops slightly with increasing scan rate. Taken together, these criteria indicate a chemical reaction following the generation of the $+2$ ion, or an EC mechanism.

In acetonitrile, coordination of the solvent to the axial sites on the rhodium ions results in a shift in potential for the observed oxidations relative to the same complex observed in 1,2-dichloroethane. The first oxidation is shifted to an $E_{1/2}$ value of $+310$ mV, a cathodic shift of $+244$ mV relative to that observed in the non-coordinating solvent. Again, $E_{1/2}$ values were invariant with increasing scan rate. The value of $\Delta E_p$ increased from 77 (50 mV $s^{-1}$) to 101 mV (2000 mV $s^{-1}$), much smaller values than were observed in 1,2-dichloroethane. The current ratio declined from unity at low scan rates to 0.87 at 2000 mV $s^{-1}$, while the current function was relatively invariant with scan rate. The electron-transfer mechanism of this first oxidation was, of course, unchanged, although it appears that coordination of the nitrile ligands has increased the rate of electron transfer for the formation of the $+1$ ion.

The mechanism of the second oxidation was also not changed by altering the solvent, though the same potential shift was observed. The value of $+1566$ mV (average value) was 232 mV cathodic of the $E_{1/2}$ observed in 1,2-dichloroethane. The value of $\Delta E_p$ shifted to a maximum of 125 mV at 2000 mV $s^{-1}$, only 62% of the value observed in 1,2-dichloroethane. Other diagnostic criteria were unchanged; the current ratio still increases with increasing scan rate, while the current function decreases by a small amount over the same range. This indicates a chemical reaction following the generation of the $+2$ ion.

### 2.4. Visible spectroscopy

The complex exhibits a broad visible absorption which varies depending on the solvent used. In 1,2-dichloroethane, a featureless absorption at $\lambda_{max} = 497.8$

nm is observed. In acetonitrile, this absorption is centered at $\lambda_{max} = 510.4$ nm, a shift of 12.6 nm. This red shift is consistent with our cyclic voltammetric observations, indicating reduced energy of the HOMO for the complex in the π-donor solvent.

## 3. Experimental

NMR spectra were obtained with a Varian Gemini 2000 spectrometer (300 MHz) using $CDCl_3$ as solvent. Spectra were referenced to solvent. Elemental analysis was performed by Galbraith Laboratories. Visible spectra were obtained using a Shimadzu UV-2401PC UV–vis spectrophotometer. Cyclic voltammetry was performed with a BioAnalytical Systems, Inc. model 100 B Workstation.

X-ray crystallography data: molecular formula, $C_{46}H_{42}N_6O_4Rh_2$, $M_r = 948.68$, $T = 294(1)$ K, monoclinic $C2/c$ (No. 15), $a = 30.444(6)$, $b = 10.657(2)$, $c = 26.138(5)$ Å, $\beta = 90.39(3)$ °, $V = 8480(4)$ Å$^3$; $Z = 8$; $D_{calc.} = 1.49$ Mg m$^{-3}$; $F(000) = 3856$. Data were collected in a red platelet crystal of size $0.048 \times 0.12 \times 0.14$ mm$^3$ using a Rigaku AFC7R (18 kW) diffractometer with graphite-monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å), in the $\theta$ range 2.5–25°. A total of 8799 reflections were measured, 7526 unique ($R_{int} = 0.025$), and 4693 observed ($I > 2\sigma(I)$); empirical absorption correction, $\mu = 0.83$ mm$^{-1}$, transmission factors = 0.93–1.00. The structure was solved by direct methods and refined by full-matrix least-squares on $F$. Final residual values were $R = 0.045$, $R_w = 0.043$ for observed data and $R = 0.085$, $R_w = 0.050$ for all data.

Cyclic voltammetric measurements were made under a blanket of dry nitrogen gas using 0.1 M *tetra-N*-butylammonium hexafluorophosphate as supporting electrolyte. This had been purified by recrystallizing three times from ethanol and was dried prior to use. Electrochemical solvents were 1,2-dichloroethane or acetonitrile. The latter was distilled over $CaH_2$ under inert atmosphere immediately prior to use. The working electrode was a Pt disc and the auxiliary electrode consisted of a Pt coil. All electrochemical measurements were referenced against the $Ag \mid Ag^+$ couple. Potentials were not corrected for liquid junction, but were instead calibrated daily against an internal standard (ferrocene).

$Rh_2(N\{C_6H_5\}COCH_3)_4$ was prepared from $Rh_2(O_2CCH_3)_4$ [15] (1.00 g) and phenylacetamide (15.00 g), which were added to 150 ml of chlorobenzene, dried according to standard methods. The mixture was heated to reflux, and the reflux apparatus fitted with a Soxhlet extractor. The thimble was charged with sand and sodium carbonate (dried at 100°C for 2 days). The thimble was replaced every 24 h. After 7 days, the solvent was removed by vacuum distillation and the phenylacetamide was removed by sublimation, leaving a purple residue. This residue was purified by flash column chromatography (silica, hexane–ethyl acetate). Three colored bands eluted in the order: green (1), blue (2), and green (3). No detectable traces of a fourth band were evident. The eluting solvent was removed from each fraction under reduced pressure. Each fraction was then dried in a vacuum oven at 80°C for 8 h. Total yield of product from $Rh_2(O_2CCH_3)_4$ was 69%; of that 18% was fraction 1, 71% was fraction 2, and 11% was fraction 3. $^1$H-NMR: $\delta$ 1.67 (s, 12H), 7.00 (d, 8H), 7.14 (t, 4H), 7.29 (t, 4H). $^{13}$C-NMR: $\delta$ 21.41, 124.58, 126.01, 129.44, 149.23, 179.21. Elemental Analysis for $C_{32}H_{32}N_4O_4Rh_2$: Calc. C, 51.77; H, 4.34; N, 7.55. Anal. C, 51.38; H, 3.99; N, 7.65%.

$Rh_2(N\{C_6H_5\}COCH_3)_4 \cdot 2NCC_6H_5$ was obtained as red crystals by adding benzonitrile, without mixing, to a solution of **1** in acetone and allowing crystal growth over several days.

## 4. Supplementary material

X-ray crystallographic material has been deposited with the Cambridge Crystallographic Centre, deposition number CCDC 134587. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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