A Stable Dirhodium Tetracarboxylate Carbenoid: Crystal Structure, Bonding Analysis, and Catalysis

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Transition metal catalyzed reactions of α-diazo ketones (**1**) are a powerful means to synthesize complex polycyclic organic frameworks.[1] In particular, dirhodium(II) carboxylate and carboxamide catalysts mediate a wide range of synthetic transformations such as cyclopropanation,[2] C−H and X−H insertion,[3,4] aromatic substitution,[5] and ylide formation.[6] Enantioselective transformations promoted by chiral Rh(II) complexes allow construction of both carbocyclic and heterocyclic systems in optically active form,[7−10] and much effort has been directed toward understanding the factors that control both regio- and enantioselectivities.[7,11,12]

The critical intermediate presumed to unify this body of chemistry is an electrophilic rhodium carbenoid in which a metal−axial carbene adopts a linear Rh−Rh−C arrangement (**3**, $R_2 = COR_4$). A growing number of examples demonstrate that the reactivity of rhodium carbenoids is greatly affected by the electronic nature of the bridging ligand attached to the metal.[1] Accordingly, the reactivity-determining Rh−C interaction is regarded as highly polarizable,[7,13] although steric[14] and confor-

mational effects[15] inherent within a particular system can override electronic factors. When the latter operate, the selectivity of the rhodium carbenoid intermediate is less predictable.
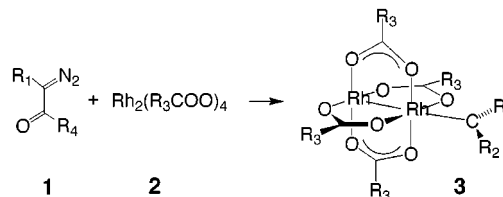
While resonance forms representing metal-stabilized carbocations and metal carbenes in the classical σ/π framework have been invoked to explain Rh-carbenoid chemistry,[11] the more recent formulation of a double "*half-bond*" model[12,16] appears to better describe the Rh−C linkage. To substantiate the independent existence of rhodium carbenoids and to more fully characterize the Rh−Rh−C bonding, we report a combined X-ray crystallographic and quantum chemical evaluation of the first stable rhodium carbenoid intermediate.

Since the observation of an imidazol-2-ylidene by the Arduengo group in 1991,[17] a number of stable crystalline carbenes have been described.[18] We reasoned that combination of a derivative of the latter and a dirhodium(II) tetracarboxylate catalyst would deliver the desired metal complex. Accordingly, admixture of carbene **4**[19] ($R_5 = $ Me) and the Rh(II) pivalate **5** delivered compound **6** as wine-red crystals suitable for X-ray structure determination.
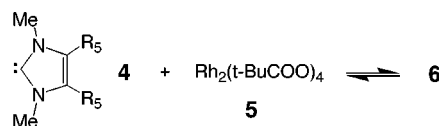
The molecular geometry is depicted in Figure 1 with selected variables given in Table 1. The overall structure of the dirhodium cage is faithful to that determined by X-ray crystallography for a series of Rh$_2$-tetracarboxylates.[20] One noteworthy difference is an expanded Rh−Rh distance of 0.05 Å in **6** by comparison with the average for **2**, R = H and C$_3$H$_7$ (2.424 vs 2.37 Å, respectively). A similar elongation upon formation of rhodium carbenoids has been predicted and rationalized by DFT calculations.[12,16]

To gain insight into the nature of the metal−carbon bonding in **6**, we have performed additional DFT calculations on alkyl-truncated variations of the structure (i.e. tetraformate or tetraacetate) with two different basis sets (Table 1). All geometry optimizations predict the overall structure and the bisection of the carboxylate bridges by the imidazoyl ring (N−C−Rh−O‡ = ca. 0°, Table 1). The latter feature is clearly steric in origin as indicated by the alternative energy minimum DFT conformers of the bis-*N*-demethyl analogue (**6**, N−R, R = H) and the parent carbenoid (**3**, $R_1 = R_2 = $ H), both of which orient the carbene moiety in a plane common to two of the bridging carboxylates.

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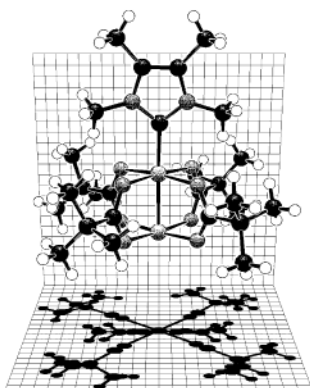
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Figure 1. KANVAS drawing[21] of the X-ray structure of dirhodium(II) carbenoid **6**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Rhodium Carbenoid **6** Derived from X-ray Crystallography and Alkyl-Truncated DFT Calculations with Two Basis Sets[a]

|	Rh−C	Rh−Rh	N−C−N	N−C−Rh−O[‡]
X-ray	2.057	2.424	102.0	0.5−2.8
3-21G/ECP[c,d]	2.089	2.465	104.4	−0.1
6-31G*/ECP[c,d]	2.110	2.461	104.3	−0.2

[a] All geometry optimizations were performed with G-98 (Frisch, M. J. et al. Gaussian 98, Revision A.3; Gaussian Inc.: Pittsburgh, PA, 1998). [b] O[‡] is the midpoint between two oxygens bound to a given Rh. [c] **3** (R_3 = Me, R_5 = H). [d] B3LYP on all atoms, LANL2DZ basis set and ECP-2 core potentials on Rh as implemented in G-98.

The effective core potential calculations slightly overestimate the Rh−C separation and the N−C−N bond angle (Table 1). Nonetheless, by comparison with previously optimized Rh−C bond distances for less stable carbene fragments (**3**, R_1 = H, R_2 = H, COR, 1.92−1.96 Å),[12,16] it is clear that the X-ray derived 2.057 Å metal−carbon distance in **6** is rather long. An understanding of this phenomenon follows from the double "*half-bond*" model in which half of the Rh−C bonding electrons in **3** (R_1 = R_2 = H) derive from the σ-donation of the H$_2$C: lone pair to Rh and half from π-back-donation at Rh to the empty carbon p-orbital.[12,16] In **6**, π-electron repulsion by the flanking nitrogen p-type lone pairs counteracts significant Rh-back-donation to the carbene center and is expected to weaken the Rh−C bond. NBO population analysis[22] confirms this viewpoint. At the 6-31G*/LANL2DZ level, **6** registers an Rh−C bond order of 0.5 (vs 1.0 for **3**, R_1 = R_2 = H) reflecting a bond−antibond interaction between σ-C$_{LP}$ and a virtual orbital centered on both Rh atoms. The well-developed π Rh−CH$_2$ interaction in **3** (R_1 = R_2 = H)[16] is, however, seriously diminished in **6** compatible with the 50% reduction in bond order. By contrast, both **4** and **6** exhibit partial π-character around the carbenoid carbon with identical N−C bond orders of 1.3.

An additional issue concerns the oxidation state of the Rh atoms in **6**. Formally, the two metal centers can be regarded as two Rh(II) atoms or a Rh(I)/Rh(III) pair. DFT/NBO assessment of electron configuration in **3** (R_1 = R_2 = H) and alkyl-truncated **6**

with or without an all-electron treatment[23] shows slight polarization of the 4d electron shell, but uniformly places 7.8−8.1 electrons in it. Both metal sites are thus predicted to be be Rh(II) with clear-cut d^8 configurations.

Is rhodium carbenoid **6** capable of catalyzing the transformations of α-diazo ketones analogous to ligand-free catalyst **2**? An intramolecular C−H insertion reaction (**7** → **8**) and two intramolecular alkyne cyclizations for diazo ketone substrates were performed separately (**9** → **10**; **11** → **12**) in the presence of 1 mol % of **2** (R_3 = CH$_3$), **5**, and **6** under the same reaction conditions. Products and yields were identical in all three cases. The most plausible mechanistic scenario is that the weak Rh−C bond engages in a dissociative equilibrium as pictured above followed by subsequent reaction of **5** and diazo ketone. The reactions then proceed normally. Although we have not recovered elements of complex **6**, we presume that the small quantity of freed carbene **4** (R = Me) reacts with diazo ketone to form the corresponding diazine as observed in related systems.[24]
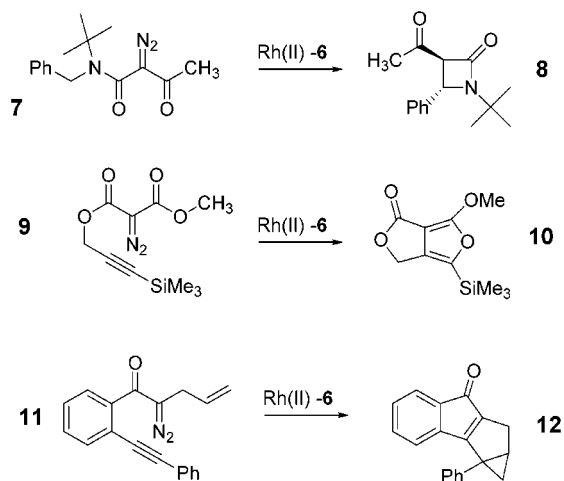
In conclusion, the first stable dirhodium(II) carbenoid **6** has been isolated and its structure determined by X-ray crystallography. The compound exhibits an increase in the Rh−Rh distance expected for carbene complexation, along with a somewhat long and weak Rh−C bond. NBO population analysis indicates the latter to be similar in character to that in systems incorporating more reactive carbenes, but with much reduced metal back-bonding. Catalytically, complex **6** most likely fragments to carbene **4** and the chemically active ligand-free Rh$_2$-carboxylate **5**. The postulated ease of dissociation is entirely consistent with previous proposals for catalytic action by **3** and its analogues.

Supporting Information Available: Synthesis and properties for **6** along with tables of X-ray structural data (CCDC No. 168865) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

(21) This drawing was made with the KANVAS computer graphics program based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, Germany) and modified by A. J. Arduengo, III to produce the back and shadowed planes. The planes depict a 50-pm grid. The lighting source is at infinity so that shadow size is meaningful.

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