

Expanding the scope of solvent-free synthesis: entrapment of thermally unstable species

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Received 6 May 2003

Abstract

The use of the acetone monoadduct, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)]$, instead of unligated dirhodium(II) tetrakis(trifluoroacetate) in sublimation–deposition reactions allowed us to study coordination of thermally sensitive 1,4-diiodo-1,3-butadiyne. A new mixed-ligand organometallic compound, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)]_2 \cdot (\text{C}_4\text{I}_2)$, has been isolated in crystalline form and shown by X-ray diffraction study to have an $\eta^2(1,2):\eta^2(3,4)$ -bridging mode of diyne. This has demonstrated the donor ability of the diiodobutadiyne that was previously known to act as a π -acceptor through the Lewis acidic iodine atoms. This work has expanded the temperature limits of the solvent-free synthesis strategy for potential study of thermally unstable species.

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Keywords: Dirhodium(II) carboxylate; 1,4-Diiodo-1,3-butadiyne; Crystal structures

1. Introduction

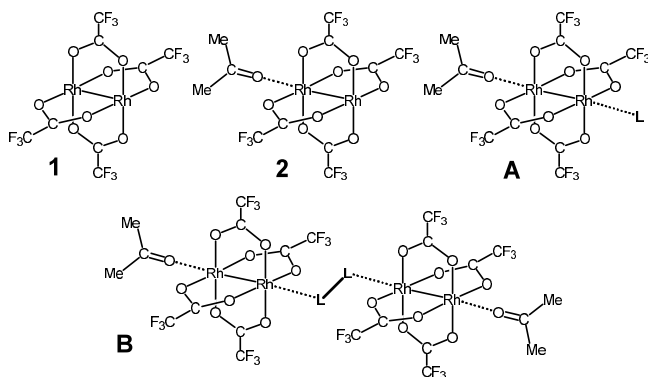
Coordination of unsaturated carbon–carbon bonds by metal centers is of fundamental importance, with wide use in various catalytic reactions. Dirhodium complexes are of particular interest in this context due to extensive use as catalysts [1]. We have recently introduced a solvent-free synthesis strategy for studying weak donor interactions through coordination using a strong two-ended Lewis acid, the volatile dirhodium tetrakis(trifluoroacetate) complex $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ (**1**) [2–4]. This method is based on sublimation of the components followed by deposition of an adduct from the gas phase, thus excluding any solvent participation in the reactions and avoiding competition of solvent molecules with weak donors for coordination. This micro-scale procedure is proved to be a very effective technique to isolate the corresponding donor–acceptor adducts in crystalline form. It has expanded the coordination limits of several weak donor molecules

including diiodine [2], octa-sulfur [3], ethylene [4] and corannulene [5], and has revealed their new coordination modes. We report here a modification of this technique that broadens its applications. The acetone monoadduct of **1**, namely complex $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)]$ (**2**, Scheme 1), has significantly greater volatility than bare **1**, allowing us to examine the coordination of thermally sensitive Lewis bases. We demonstrate this new methodology in the formation of a novel organometallic donor–acceptor complex from **2** and 1,4-diiodo-1,3-butadiyne (**3**).

Previous reactions of **1** have required relatively high temperatures to achieve substantial mass-transfer (crystal growth) rates. To create sufficient concentration of dirhodium molecules in the vapor phase, the adduct formation reactions have been performed at temperatures of 100–180 °C, depending on the volatility of donor partners. There are two major consequences of this temperature requirement: (a) at high temperatures some molecules of interest start to react with **1** in an oxidative (Br_2 , XeF_2) or reductive (CO , cyclooctadiene) manner and (b) some donor molecules start to decompose. For the latter transformations, we have been able to trap some volatile decomposition products and to isolate them as crystalline adducts of **1** [6]. Thermally

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Scheme 1. Representation of **1** and **2**, and **A** and **B**.

unstable substrates can deliberately be used as a source of target molecules: for example, **1** traps gas-phase ethylene, formed via decomposition of 1,2-diiodoethane at 105 °C [4].

As other metal trifluoroacetates show lower reduction and oxidation limits and limited structural rigidity at elevated temperatures compared to **1**, a selection of appropriate Lewis acid traps for thermally unstable and highly reactive molecules has been a challenge. We have been looking for analogues of **1** operating at low temperatures, in the range 35–100 °C, and have chosen the acetone monoadduct of **1**, namely $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)]$ (**2**). In general, the volatility of such species increases in the order: unligated **1** < mono-adduct < bis-adduct [7,8]. The bis-adduct complex has both axial positions blocked, while the mono-acetone adduct **2** has one open axial site and can be considered as a strong one-ended Lewis acid. Therefore by using **2** as a trap instead of **1**, we are able to study for the first time thermally unstable molecules at temperatures below their decomposition. It is expected that **2** may afford either a mixed-ligand bis-adduct (**A**), if the molecule of interest is a monodentate donor, or a sandwich-type structure (**B**), if the molecule has more than one donor site.

This work presents a solvent-free study of complexation of **2** with a thermally unstable carbon-rich molecule C_4I_2 (**3**) [9]. Compound **3** is of interest for preparation of carbonaceous materials [10] and due to its ambidentate character. Polarization of the carbon–iodine bonds toward carbon makes the iodine atoms Lewis acidic [11,12]. At the same time, C_4I_2 also has two electron-rich carbon–carbon triple bonds that are potentially attractive donor sites for metal centers. There have been several studies of the interactions of iodoalkynes with Lewis bases [12,13], but relatively little work has focused on their donor properties. Stahl and Dehnicke [14] demonstrated by IR and ^{13}C -NMR spectroscopy that **3** can act as a four-electron donor toward the two tungsten(IV) centers. However, they did not obtain direct structural data.

2. Results and discussion

Using the coordinating properties and good volatility of **2**, we have prepared the novel organometallic donor–acceptor complex $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)]_2 \cdot (\text{C}_4\text{I}_2)$ (**4**). Complex **4** forms in very small air stable crystals upon sublimation–deposition at ca. 55 °C. The yield was low, as even at this temperature partial thermal decomposition of ligand was observed, resulting in the formation of non-volatile and non-crystalline residues. An X-ray structural study of **4** confirmed the composition of product and provided the geometrical parameters of this donor–acceptor complex.

The structure of **4** consists of discrete centrosymmetric molecules, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)]_2 \cdot (\text{C}_4\text{I}_2)$, in which C_4I_2 is sandwiched between two dirhodium complexes (Fig. 1). Both carbon–carbon triple bonds are coordinated, each to one end of a dirhodium unit. For each triple bond, the two Rh–C_{alkyne} distances are long and slightly different, 2.604(13) and 2.632(13) Å. The diyne is disposed approximately perpendicular to the metal–metal axis of **1** at the angle of 86.8°. There is no significant lengthening of the carbon–carbon triple bond in **4** (1.18(2) Å). This bond distance implies a very weak metal– π interaction, preserving the triple-bond character of the carbon–carbon bond. The angle of C(2)–C(1)–I(1) is 166(2)°, while the angle of C(1)–C(2)–C(2A) is 173(2)°. Alkynes in general show low barriers to distortions away from linearity, and in this case the bending most likely results from steric interactions with the trifluoroacetate ligands.

These structural data can be compared to diphenylacetylene adducts of **1**, namely $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{Ph}_2\text{C}_2)_n]$ ($n = 1$ and 2) [15]. The alkyne coordination in both complexes is of η^2 -type, without disruption of the triple-bond system. The C≡C distances are 1.204(6) and

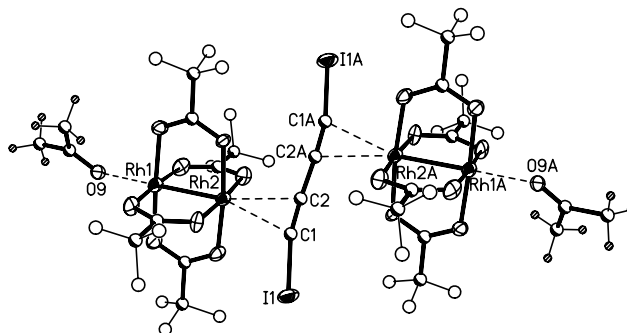


Fig. 1. A perspective drawing of the mixed-ligand complex $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)]_2 \cdot (\text{C}_4\text{I}_2)$ (**4**). Dashed lines indicate axial coordination of rhodium atoms. Selected bond distances (Å) and bond angles (°) are as follows: Rh(1)–Rh(2), 2.413(1); Rh(1)–O(9), 2.214(8); Rh(2)–C(1), 2.604(13); Rh(2)–C(2), 2.632(13); C(1)–C(2), 1.18(2); C(2)–C(2A), 1.43(2); C(1)–I(1), 1.985(1); C(2)–C(1)–I(1), 166(2); C(1)–C(2)–C(2A), 173(2); Rh(1)–Rh(2)–C(1), 164.9(3); Rh(1)–Rh(2)–C(2), 168.7(3).

1.208(8) Å for $n = 1$ and 2, respectively. The axial Rh–C_{alkyne} contacts are ca. 0.1 Å shorter than those in **4**.

The carbon–carbon triple bonds in π complexes formed by the dirhodium(II) molecule **1** stand in contrast to known rhodium(I)-diyne complexes. Werner and coworkers have found, e.g., that bis(triisopropylphosphine)rhodium chloride reacts with diynes to form η^2 complexes in which the ligand carbon–carbon triple bond lengthens significantly to 1.26–1.27 Å. Those carbon–carbon bonds also show greater deviation from linearity, with bond angles of approximately 150° [16]. Several transition metal complexes with disubstituted butadiynes of the type R–C≡C–C≡C–R (where R = H, Me, Ph, *t*-Bu, SiMe₃) have been structurally characterized [17] to exhibit a bridging $\eta^2(1,2):\eta^2(3,4)$ coordination, but that was accompanied by a significant elongation of the carbon–carbon triple bonds and a noticeable change in bond angles upon metal complexation. In comparison, complex **4** shows very little perturbation of the alkyne bonds.

3. Conclusions

Using the acetone monoadduct **2**, we have demonstrated here the donating properties of the ambidentate diiodobutadiyne ligand. In contrast to the above-mentioned butadiynes, under most circumstances, iodoalkyne **3** behaves as a Lewis acid. However, in the presence of electrophilic complex **2**, sublimation and deposition at mild temperatures afforded single crystals of novel product, in which the 1,4-diiodo-1,3-butadiyne is acting as a $\mu^2-\eta^2(1,2):\eta^2(3,4)$ -donor. Although this is the first structurally characterized example of this coordination for **3** toward metal centers, the most important outcome of this work is expanding the temperature limits of the solvent-free deposition strategy. The use of volatile compound **2** in sublimation–deposition reactions provides a new method for forming organometallic adducts under very mild conditions with ligands that are thermally unstable.

4. Experimental

4.1. Preparation of complex **2**

A mixture of **1** (0.035 g, 0.05 mmol) and bis-acetone adduct, [Rh₂(O₂CCF₃)₄·(OCMe₂)₂] (0.006 g, 0.008 mmol), has been sealed under vacuum in a glass ampoule. The ampoule was then placed in the electric furnace having small temperature gradient along the length of the tube. After keeping the ampoule for 3 days at 160 °C, a product of the composition [Rh₂(O₂CCF₃)₄·(OCMe₂)] (**2**) has been isolated in a form of green block-shaped crystals. Yield: 0.022 g,

45%. ¹H-NMR (300 MHz, chloroform-*d*, 22 °C): δ 2.72 ppm. Compound **1** was prepared according to [7]; the bis-acetone adduct of **1** was synthesized as described in [8].

4.2. Preparation of complex **4**

A mixture of **2** (0.045 g, 0.06 mmol) and **3** (0.018 g, 0.06 mmol) was loaded in a small glass ampoule, the ampoule was sealed under vacuum and placed in the electric furnace at 55 °C. Dark, almost black crystals of **4** appeared in 20 h in the middle section of the tube where the temperature was set a few degrees lower, ca. 52–50 °C. Grey unidentified non-volatile powder was left in the hot end of the tube. Yield of **4**: ca. 20%. ¹H-NMR (300 MHz, chloroform-*d*, 22 °C): δ 2.73 ppm.

4.3. Crystal structure determination of complex **4**

Crystal data for Rh₄C₂₆H₁₂F₂₄I₂O₁₈: crystal dimensions 0.10 × 0.10 × 0.10 mm³, $F_w = 1733.80$, monoclinic, $P2_1/n$, $a = 9.116(1)$ Å, $b = 15.928(2)$ Å, $c = 16.343(1)$ Å, $\beta = 92.58(2)^\circ$, $V = 2370.6(4)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.429$ g cm⁻³, $\mu = 2.830$ mm⁻¹, $T = 213(2)$ K. Nonius FAST area detector system, Mo–K α radiation, $\lambda = 0.71074$ Å, 3074 reflections measured, data corrected for Lorentz and polarization effects, solution by direct methods (SHELXTL V.5), full-matrix refinement of F^2 (SHELXL-97). The final R value was 0.0583 for 2391 reflections with $I > 2\sigma(I)$ ($wR_2 = 0.1309$ for all 3074 data), GOF = 1.09. The CF₃ disorder was modeled over three rotational orientations.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 209711 for compound **4**. Copies of the information may be obtained free of charge from The Director, CCDC 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We are very grateful to LMSB at Texas A&M University for access to the X-ray facilities, and to Dr. P.-H. Liu for preparation of **3**. We thank the University at Albany (FRAP-2002) and the National Science Foundation (CHE-9984937) for support of this work.

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