Direct gas-phase interaction of aryldiazoacetates and dirhodium catalysts†

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Interaction of two dirhodium catalysts $[Rh_2(O_2CR)_4]$ (R = CMe_3 and CF_3) with methyl-*p*-methoxyphenyldiazoacetate in the gas phase has resulted in the partial or complete loss of dinitrogen from diazo substrate and afforded two new hybrid products that are of interest for the further development of catalytic processes.

The intramolecular and intermolecular carbon–carbon bond formation reactions of diazocarbonyls with hydrocarbons catalyzed by dirhodium(II) tetracarboxylates, $[Rh_2(O_2CR)_4]$, have become general synthetic strategies for the stereoselective preparation of various carbocycles.[1] It has been generally assumed that these reactions involve a formation of reactive intermediates, rhodium–carbene complexes.[2] The information on the mechanisms of metal carbene formation is limited, with the questions on the role of the dinuclear structure of the catalyst and the nature and function of the bridging ligands being of fundamental interest.[3] The majority of previous reports on the dirhodium-catalyzed C–H activation and C–C formation reactions have focused on the applications in organic synthesis[4] with only a few studies aiming at the reaction mechanisms.[5,6]

To add more understanding on the role of the catalytically active rhodium centers in transformations of diazo compounds, we attempted to investigate the direct interaction of aryldiazoacetate substrates with dirhodium carboxylates in the vapor phase. The aryl donor group has been shown to add considerable stability to the rhodium carbenoid *via* resonance stabilization of the highly electrophilic carbene carbon. This stabilizing effect is not present in the more traditional carbenoids functionalized with only acceptor groups. Due to the moderating effect of the donor group, the chances of isolation of the presumed rhodium carbenoid intermediate are increased.[1c] The technique that we use relies on gas phase deposition, which is a very efficient route for studying donor–acceptor interactions in a solvent-free environment. This micro-scale technique has been tested for a variety of ligands, including thermally sensitive molecules.[7] It also provides a direct route for entrapment of molecular fragments and reaction intermediates in crystalline form,[7b] and therefore can serve as a viable approach to detect rhodium carbenoid species.[8] So far the gas-phase synthesis of metallocarbenoid compounds has relied only on high-energy methods utilizing electron impact or electrospray ionization.[9] Herein we report our findings on the use of the gas phase deposition to the systems comprising of dirhodium carboxylate catalysts $[Rh_2(O_2CR)_4]$, R = CMe_3 (**IA**) and CF_3 (**IB**), and methyl-*p*-methoxyphenyldiazoacetate (**II**) as a carbene source (Scheme 1).

The two selected dirhodium complexes are both volatile but differ significantly in their electrophilic properties with **IA** being a considerably weaker Lewis acid than **IB**. Sublimation–deposition reactions of dirhodium pivalate, $[Rh_2(O_2CCMe_3)_4]$ **IA**, with **II** were tested at different reagent ratios and different

Scheme 1
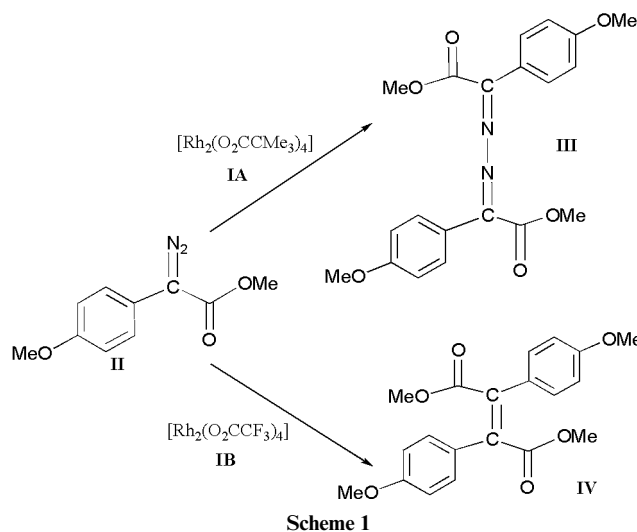
temperatures. Gas phase reactions performed in the range 130–150 °C for the ratios of **IA** to **II** of 1 : 1 and 2 : 1 have resulted in a clean formation of complex $[Rh_2(O_2CCMe_3)_4(CH_3OC_6H_4C-(COCH_3O)N)_2]$ (**1**), in moderate yield.†‡ The product **1** was isolated in the form of green crystals stable in air and moisture sensitive at room temperature. The IR data showed the presence of the bridging pivalate groups and several additional functionalities (C=O; C–O; Aryl). The X-ray diffraction study of **1** has revealed its composition and a structural motif.§ The structure of **1** consists of two building blocks, dirhodium complexes **IA** and dimeric azine molecules, $[CH_3OC_6H_4C(COCH_3O)N]_2$ (Scheme 1, **III**) that formed during the course of the reaction. The above units alternate in the structure of **1** to form an infinite 1D polymeric chain (Fig. 1).

The rhodium centers of the centrosymmetric dimetal complex are axially coordinated to the ligand **III** through the oxygen atom of its carbonyl functions with the Rh–O(5) distance
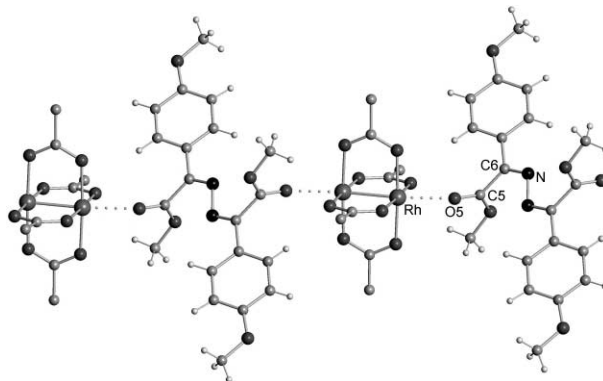

Fig. 1 A fragment of the 1D chain structure of **1** showing the coordination of **III** by the dirhodium units **IA**. Methyl groups of carboxylates are omitted. Selected distances (Å) and angles (°) are: Rh–Rh 2.3705(4), Rh–O(5) 2.420(2), O(5)–C(5) 1.213(3), C(5)–C(6) 1.516(3), N–C(6) 1.286(3), N–N′ 1.413(4), N′–N–C(6) 111.7(3), Rh–Rh–O5 175.3(4).

of 2.420(2) Å. The N–N separation in the entrapped centrosymmetric molecule **III** of 1.413(4) Å is consistent with a single bond between nitrogen atoms. The N–C(6) distance of 1.286(3) Å is indicative of a double bond character. The angles at the sp^2-hybridized C(6) atom average to 120.0(2)°, thus confirming its planar arrangement. Although we were unable to obtain satisfactory elemental analysis data for **1** (probably due to its moisture sensitivity), ^{1}H NMR results are consistent with the composition of **III** revealing the presence of two methoxy groups and two types of aromatic protons only.

The interaction of the carbene precursor **II** with dirhodium(II,II) tetrakis(trifluoroacetate) $[Rh_2(O_2CCF_3)_4]$ (**IB**) has also been studied. Complex **IB** is used as a catalyst in many organic processes, and is known to show an exceptional Lewis acidity at both metal centers when compared with other carboxylates. The gas phase interaction in this system afforded a new product $[Rh_2(O_2CCF_3)_4(CH_3OC_6H_4C(COCH_3O))_2]$ (**2**), in low yield.†¶ Although blue–green crystals of **2** are air stable, the low yield has prevented obtaining elemental analysis data, therefore the composition and structure of **2** were revealed by an X-ray diffraction study.‖ The structure of **2** is an infinite hybrid chain (Fig. 2) consisting of two alternating units: dirhodium complexes **IB** and newly formed dimeric ligands **IV** (Scheme 1).
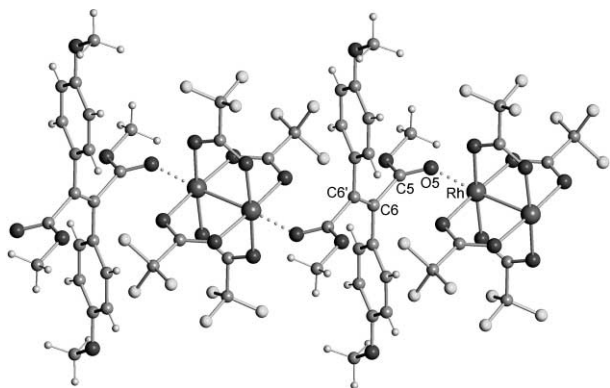

Fig. 2 A fragment of the 1D chain structure of **2** showing the coordination of **IV** by the dirhodium units **IB**. Selected distances (Å) and angles (°) are: Rh–Rh 2.398(1), Rh–O(5) 2.254(4), O(5)–C(5) 1.201(7), C(5)–C(6) 1.505(9), C(6)–C(6′) 1.292(12), C6′–C6–C5 119.3(9), Rh–Rh–O(5) 172.3(1).

In contrast to the formation of **1**, this reaction was accompanied by complete loss of dinitrogen, followed by dimerization of the two reactive carbene intermediates to form a molecule of the composition $[CH_3OC_6H_4C(COCH_3O)]_2$ (**IV**). The latter is bridging the dirhodium units **IB** to form an extended polymeric structure **2**. Again the rhodium centers of the centrosymmetric dimetal unit interact with the entrapped ligand **IV** through the O-atoms of the carbonyl groups. The axial Rh–O(5) distance of 2.254(4) Å in **2** is shorter than that in **1**. The C(6)–C(6′) separation in the centrosymmetric molecule **IV** is 1.292(12) Å, with the other two carbon–carbon distances around the C(6) atom being much longer, 1.505(9) and 1.511(6) Å. The angles at the sp^2-hybridized C(6) atom are averaged to 120.0(9)°.

In order to determine if the complexes **1** and **2** deposited from the gas phase relate to the solution phase chemistry, the dirhodium catalyzed decomposition of methyl-*p*-methoxyphenyldiazoacetate was examined in an inert solvent, 2,3-dimethylbutane. The $[Rh_2(O_2CCMe_3)_4]$ catalyzed reaction gave a mixture of carbene dimers **IV**, the azine **III** and starting material **II**, while the $[Rh_2(O_2CCF_3)_4]$ was a relatively clean reaction from which the azine **III** was isolated in 45% yield. As the gas phase reaction of $[Rh_2(O_2CCF_3)_4]$ generated the complexed carbene dimer **IV** rather than the azine **III**, it is conceivable that decomposition of the aryldiazoacetate and dimerization precedes coordination. The resulting organic

molecules are formed in the gas phase and then entrapped by dirhodium complexes to form **1** and **2** and this would explain why the solution and gas phase outcomes are different.

The most significant feature of these studies is the demonstration that the dirhodium(II) tetracarboxylates behave as oxophylic species. In the case of complex **1**, with the azine complexed to two $[Rh_2(O_2CCMe_3)_4]$ units, coordination of the azine molecule **III** occurs through oxygen rather than through nitrogen. This raises interesting questions about the initial interaction between the diazocarbonyl and the dirhodium catalyst. It has generally been assumed that coordination occurs at the diazo carbon, but our study suggests that possible coordination of the rhodium to the O-atom of carbonyl cannot be ignored.

In summary, by testing the gas phase reactions of dirhodium catalysts with methyl-*p*-methoxyphenyldiazoacetate the carboxylate ligand effect on the outcomes of transformation has been clearly detected. The two dirhodium complexes of different Lewis acidity, **1A** and **1B**, facilitate the partial or complete loss of dinitrogen from diazo substrate and this results in isolation of two new hybrid products **1** and **2**, respectively. These results reveal trends that should be of interest for the further development of catalytic processes and metal carbenoid chemistry.

Notes and references

‡ Synthesis of **1**. $[Rh_2(O_2CCMe_3)_4]$ (0.040 g, 0.066 mmol) was mixed with methyl-*p*-methoxyphenyldiazoacetate (0.12 g, 0.066 mmol) in a small glass ampoule. The ampoule was sealed under vacuum and then placed in an electric furnace at 145 °C. Green crystals of **1** that appeared air stable but moisture sensitive were deposited in about a week. Yield: 30–35%. IR (KBr, cm^{-1}): 2964m, 2933m, 2904w, 2869w, 2840w, 2363w, 2347w, 2331w, 2313w, 1745w, 1708s, 1602s, 1577s, 1518m, 1487m, 1459m, 1440w, 1416s, 1378m, 1366m, 1335m, 1301m, 1267s, 1223s, 1173s, 1027m, 1006w, 899w, 841m, 807w, 798w, 782w, 638m. ^{1}H NMR (CDCl$_3$, 22 °C): δ 0.99 (18H, CH$_3$), 3.71 (3H, CH$_3$O), 3.99 (3H, CH$_3$O), 6.91 (2H, Ar), 7.67 (2H, Ar).
§ Crystal data for **1**: Rh$_2$C$_{40}$H$_{56}$N$_2$O$_{14}$, M = 994.66, triclinic, a = 9.4127(9), b = 11.7589(11), c = 12.0273(11) Å, α = 61.582(2), β = 76.869(2), γ = 71.626(2)°, V = 1106.4(2) Å^3, T = 243(2) K, space group $P\bar{1}$ (no. 2), Z = 1, μ(Mo-Kα) = 0.811 mm^{-1}, 6994 reflections measured, 4925 unique (R_{int} = 0.015) which were used in all calculations. The final $R1$ = 0.0305, $wR2$ = 0.0756 (for 4436 reflections with $I > 2\sigma(I)$); $R1$ = 0.0353 and $wR2$ = 0.0782 (for all data). CCDC reference number 217509. See http://www.rsc.org/suppdata/dt/b3/b309809p/ for crystallographic data in CIF or other electronic format.
¶ Synthesis of **2**. Methyl-*p*-methoxyphenyldiazoacetate (0.008 g, 0.041 mmol) was loaded in a small glass capillary (6 mm od) and that was placed into a glass ampoule (13 mm od) containing $[Rh_2(O_2CCF_3)_4]$ (0.050 g, 0.078 mmol). This setup prevented direct contact of the two solids allowing their mixing only in the vapor phase. The ampoule was sealed under vacuum and placed into a tube electric furnace at 155 °C. In 24 h small blue–green crystals formed near the 'mouth' of the small open capillary. Yield: *ca.* 10%. IR (KBr, cm^{-1}): 2975w, 2955w, 2847w, 2364w, 2330w, 1799w, 1684m, 1669s, 1662s, 1611w, 1516m, 1439w, 1302m, 1260m, 1236s, 1194s, 1179m, 1166m, 1031w, 861m, 801w, 785w, 740m. ^{1}H NMR (CDCl$_3$, 22 °C): δ 3.79 (3H, CH$_3$O), 3.85 (3H, CH$_3$O), 6.94 (2H, Ar), 7.35 (2H, Ar).
‖ Crystal data for **2**: Rh$_2$C$_{28}$H$_{20}$F$_{12}$O$_{14}$, M = 1014.26, monoclinic, a = 10.064(3), b = 20.754(6), c = 8.544(2) Å, β = 107.010(4)°, V = 1706.6(8) Å^3, T = 173(2) K, space group $P2(1)/c$ (no. 14), Z = 2, μ(Mo-Kα) = 1.100 mm^{-1}, 10438 reflections measured, 2990 unique (R_{int} = 0.041) which were used in all calculations. The final $R1$ = 0.0521 and $wR2$ = 0.1056 (for 2431 reflections (with $I > 2\sigma(I)$); $R1$ = 0.0681 and $wR2$ = 0.1105 (for all data). CCDC reference number 217510. See http://www.rsc.org/suppdata/dt/b3/b309809p/ for crystallographic data in CIF or other electronic format.

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