Aerobic Oxidation of Carbon Monoxide in a Tetrametallic Complex

Cristina Tejel*, Sofía Sancho, José A. López, and Miguel A. Ciriano

Aerobic oxidation of CO is a very important prototypical heterogeneous catalytic process for both practical applications and fundamental catalysis research.^[1] Since Haruta's pioneering findings of very active catalysts, based on oxide-supported small Au nanoparticles (AuNPs), for this and other oxidation reactions at or below room temperature,^[2] a number of different effects and active sites have been proposed as responsible for their high activity. Accumulated experimental data indicate that the active sites are located at the particle support periphery and a maximum in the reactivity is reached if under-coordinated metal atoms, such as those at the edges and corners, serve as active sites for the reaction. However, mechanistic details and the way as oxygen is activated are still controversial.^[3] Current understanding of catalytic activity on oxide-supported AuNPs is based on highly model surface systems, but very few molecular compounds are reported to undergo or catalyze this reaction. Just a couple of η^2 -CO₂ complexes have been synthesized from the formal oxidation of a metal carbonyl complex with dioxygen.^[4] More common, but still rare, is the oxygenation of carbonyl groups to carbonate ligands in mononuclear complexes.^[5] On the other hand, replacement of metal-bound carbonyl groups by oxidation to CO₂ with trimethylamine N-oxide is a well-known reaction in the realm of cluster and organometallic chemistry.^[6] Nonetheless, complexes with different binding modes of CO₂ have been known for quite some time, a topic covered in excellent reviews.^[7]

From a mechanistic point of view, molecular compounds could possibly model some aspects of heterogeneous systems and we envisaged that complexes with the metals disposed linearly, such as found in metal-string compounds or EMAC's,^[8] could facilitate the interaction of different molecules (oxygen and CO for example) on adjacent metals. Herein, we report tetranuclear rhodium/iridium complexes with a linear metallic backbone, and only two bridging ligands ('semi-naked EMAC's') which undergo aerobic oxidation of carbonyl groups to CO₂ under very mild conditions.

Reaction of $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$ with 1,8-naphthyridine-2,7-dione $[(\text{HO})_2\text{napy}]$ in the presence of KOH in methanol gave a deep-purple solution of $\text{K}_2[\{\text{Rh}(\text{CO})_2(\mu\text{-O}_2\text{napy})\}_2]$ (**K₂[1]**). Subsequent addition of $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ caused the development of an intensely coloured navy blue solution, from which the hetero tetranuclear complex $[\{\text{RhIr}(\text{cod})(\text{CO})_2(\mu\text{-O}_2\text{napy})\}_2]$ (**2**) was isolated as a navy blue crystalline solid in good yield (Scheme 1). In an analogous way, by using $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$,

the complex $[\{\text{Rh}_2(\text{cod})(\text{CO})_2(\mu\text{-O}_2\text{napy})\}_2]$ (**3**) was isolated as an emerald green solid.

Scheme 1. Synthesis of tetranuclear complexes **2** and **3** and the equilibrium of **2** in solution. i) = $[\{\text{M}(\mu\text{-Cl})(\text{cod})\}_2]$

The molecular structures of **2** (Figure 1) and **3** consist in an essentially linear metallic backbone with two 'M(cod)' fragments at the ends of the chain and two 'Rh(CO)₂' moieties in the center.^[9] The metals are bridged by two tetradentate $[\text{O}_2\text{napy}]^{2-}$ ligands in a relative *cis*-position, with the 'M(cod)' fragments *O,O*-coordinated. One carbonyl ligand bridges two contiguous rhodium and iridium atoms in **2**, so that one of the iridium atoms is pentacoordinated in the solid state. On the contrary, the carbonyl ligands in **3** are terminal and the central rhodium atoms are essentially square-planar. The C–O distances in the $[\text{O}_2\text{napy}]^{2-}$ ligands (in the range 1.30–1.28 Å) are close to that found for double C=O bonds in ketones, so that the resonant form dione-diamide of the ligands, shown in Scheme 1, largely contributes to the electronic structure of the complexes. Apart from electronic effects, steric requirements are a primary cause of the stereoselectivity of the syntheses of **2** and **3**. The interior of the molecules is occupied by the less sterically demanding metal fragments, i.e., those possessing the carbonyl groups. The more sterically demanding 'M(cod)' fragments occupy the outer positions and create a cavity that protects, in some way, the internal metal atoms from attack by bulky molecules. Noticeably, the external metal atoms have an exposed face and, hence, these should be the most reactive sites (see below).

Figure 1. Structure (ORTEP at 50% level) of the heterometallic complex $[\{\text{RhIr}(\text{cod})(\text{CO})_2(\mu\text{-O}_2\text{napy})\}_2]$ (**2_B**).

Complex **2** is fluxional. The averaged structure observed shows equivalent $[\text{O}_2\text{napy}]^{2-}$ and carbonyl ligands in the ¹H and

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$^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively. This symmetrical structure can be easily reached by a concerted cleavage and formation of the carbonyl bridge on both sides of the molecule. In addition, both isomers **2_A** (with all terminal carbonyls) and **2_B** are detected in solution by IR, which indicates they are in equilibrium in solution (See Scheme 1). On the contrary, the structure of complex **3** in solution is analogous to that found in the solid state. DFT calculations indicate that the most stable configurations for **2** and **3** are those with 'all terminal' carbonyls. However, the bridging carbonyl isomer **2_B**, isolated in the solid state, is only 4.0 kcal·mol⁻¹ higher in energy than **2_A**, which explains the equilibrium observed in solution and makes reasonable to assume that solid state effects counterbalance the difference in energy calculated in gaseous phase.

Complexes **2** and **3** were found to be air-sensitive. Thus, dichloromethane solutions of **2** and **3** turned dark blue under an oxygen atmosphere while dark blue crystalline solids separated from the reaction media. The reaction for the heteronuclear Rh/Ir compound **2**, described in detail here, reaches completion in one day, while that of the rhodium complex **3** gives a similar result but it takes more than a week. The product of the reaction of **2** with oxygen, $[\{\text{RhIr}(\text{cod})(\text{CO})(\mu\text{-O}_2\text{napy})\}_2(\mu\text{-CO}_2\text{-}\kappa^2\text{-C,O})]$ (**4**), is diamagnetic and lacks symmetry, as shown by the ^1H NMR spectrum of saturated, but diluted, solutions of **4** in CDCl_3 . The molecular structure of **4** (Figure 2) retains the tetranuclear backbone of **2**, with two outer *O,O*-coordinated 'Ir(cod)' fragments and two central *N,N*-bonded 'Rh(CO)' moieties.^[9] These internal rhodium centres complete their coordination sphere with an unsymmetrical bridging CO_2 moiety bound through the carbon and one oxygen atom.^[10] Rhodium complexes with CO_2 ligands are extremely rare. Few mononuclear^[4d,11] compounds have been reported up to date and we are not aware of previous examples of a CO_2 group in a four-membered dirhodametallacycle. Moreover, this type of dimetallacycles are very uncommon with some examples characterized crystallographically.^[12] Nonetheless, dinuclear complexes with bridging CO_2 units in open arrangements, although scarce, have been previously reported.^[13]

Figure 2. Structure (ORTEP at 50% level) of $[\{\text{RhIr}(\text{cod})(\text{CO})(\mu\text{-O}_2\text{napy})\}_2(\mu\text{-CO}_2\text{-}\kappa^2\text{-C,O})]$ (**4**).

The structural data of the CO_2 moiety indicate a partial π -bond delocalization in the C–O bonds, with angles around the carbon (C35) close to 120° and quite different C–O bond lengths for the free (C35–O7 $\approx$ 1.24 Å) and coordinated (C35–O8 $\approx$ 1.35 Å) oxygen atoms. Moreover, these data, along with the chemical shift for the carbon (δ 173.4 ppm), suggest a description of this group as a dianionic formate ligand.^[12b] Accordingly, the $\nu(\text{CO}_2)$ band

for **4** at 1610 cm⁻¹, identified by the ^{13}C isotopically induced band shift (to 1574 cm⁻¹), lies in the frequency range of carboxylate groups. Hence, one can propose that in the reaction giving **4**, the tetrametallic backbone is oxidized by two electrons, which formally corresponds to the formation of a metal-metal bond. Certainly, the shortening of the rhodium-rhodium separation on going from **2_B** (2.678 Å) to **4** (2.493 Å) is very pronounced. Therefore, complex **4** can in principle be described as a species containing a metallic chain with the metals in an average oxidation state of + 1.5, displaying either a single, central $\text{Rh}^{\text{II}}\text{--Rh}^{\text{II}}$ bond or a delocalized 4c-2e bond involving the four metal centers. DFT calculations for complex **4** reproduce well the crystallographic data and show a LUMO mainly composed by the four d_z^2 atomic orbitals developing an antibonding character between every pair of adjacent metal atoms. The electron vacancy of this high-energy σ -MO is responsible for the metal-metal bonds. Therefore, a delocalized 4c-2e scheme seems to be the most appropriate description for the metal-metal bonding in **4**. Interestingly, the HOMO is mainly centred on the $\text{Rh}_2\text{--CO}_2$ moiety.

It is quite remarkable that the 1,5-cyclooctadiene ligands are not oxygenated with formation of metallaoxetanes or metalladioxolanes.^[14] Further, the reaction of **2** with oxygen was monitored by IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies, using additionally the labeled complex $[\{\text{RhIr}(\text{cod})(^{13}\text{CO})_2(\mu\text{-O}_2\text{napy})\}_2]$ (**2***). Apart from the disappearance of the starting complex and the increase of a signal for free $^{13}\text{CO}_2$ (δ = 125.4 ppm) as well as the resonances of the product, which precipitates in part, no other diamagnetic intermediates were observed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. When the reaction was carried out with $^{18}\text{O}_2$, complex **4** with one labeled 18-oxygen atom resulted, which proves that one oxygen atom from $^{18}\text{O}_2$ is incorporated into the product. The other 18-oxygen atom was found in the released carbon dioxide as evidenced from the peak at m/z = 46 in the MS of the gaseous phase. Moreover, no variation in pressure occurs if the reaction is carried out in a sealed vessel, which corroborates that all oxygen consumed is transformed into free and coordinated CO_2 .

The exact mechanism by which **2** is oxidized is not known and kinetic measurements are unfeasible because of the insolubility of the product.^[15] Nonetheless, given that the Ir(cod) fragments possess an exposed face, oxidation could be initiated by coordination of oxygen at one of these atoms, perhaps assisted by the close Rh center. (A, Scheme 2). Thus, the oxygen would become formally reduced to superoxide, a transformation for which recent examples have been reported both in the solid state and in complexes.^[16]

Scheme 2. A plausible mechanism for the oxygenation of **2** to the CO₂ bridged complex $[\{\text{RhIr}(\text{cod})(\text{CO})(\mu\text{-O}_2\text{napy})\}_2(\mu\text{-CO}_2\text{-K}^2\text{-C,O})]$ (**4**).

Attempts to observe dioxygen complexes in the reaction mixtures by rRaman spectroscopy were inconclusive, probably because of the low-concentration of these species. A Berry's pseudorotation on **A** would facilitate the nucleophilic attack of the superoxo to a carbonyl ligand to give the peroxoacyl complex **B**. Such couplings have been recently proposed based on DFT calculations on a complex of cobalt,^[5a] while a single precedent in osmium chemistry has been crystallographically characterized.^[5e] Extrusion of CO₂, observed experimentally, would give the oxo intermediate **C**, in which CO insertion into the Rh–O bond would complete the reaction to give complex **4**. Modeling complex **A** by DFT calculations is not simple because of the open-shell/closed-shell, triplet/singlet possibilities. Apart from that, the structures of **B**, **C**, and **4** converge to a minimum and their relative energies are smaller than the reactants in such a way that the reaction pathway is downhill from **2** to the products, being the overall process highly exothermic ($\Delta H \approx -94$ kcal).

In conclusion, we report the oxidation of coordinated carbonyl groups by oxygen in a polynuclear compound to free and coordinated CO₂ to two adjacent metals under very mild conditions. Both oxygen atoms in the molecule are transferred to two carbonyl ligands. Most probably, one of the metals activates dioxygen to react with a carbonyl group bound to an adjacent metal in such a way that metals work in a cooperative manner, cleaving and transferring both atoms of the molecule of oxygen to two carbonyl ligands in two distinct steps. These findings could provide additional information to the way in which carbon monoxide and oxygen are transformed into carbon dioxide on the periphery of supported NPs.

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Aerobic Oxidation of Carbon Monoxide in a Tetrametallic Complex

Semi-naked extended metal atom chains (EMACs) have been found to be suitable for the aerobic oxidation of CO to CO₂. One molecule of carbon dioxide remains attached to the metallic chain as a doubly

deprotonated formate group, shown in the Figure, while the other is released. The reaction involves the activation and cleavage of a molecule of oxygen with transfer of the atoms to two CO ligands.