Mechanistic Studies of the Carbonylation of Nitrobenzene Catalysed by the $[Rh(CO)_4]^-$/bipy System. X-Ray Structure of $[PPN][\overline{Rh(CO)_2ON[C_6H_3Cl_2)C(O)O}]$; $[PPN^+ = (PPh_3)_2N^+$; bipy = 2,2′-bipyridyl]

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Reaction of $[PPN][Rh(CO)_4]$ with $C_6H_3Cl_2NO_2$ gives $[PPN][\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}]$, the X-ray structure of which is reported together with its reactivity.

The use of $[PPN][Rh(CO)_4]$ **1** $[PPN^+ = (PPh_3)_2N^+]$ as a catalyst for the carbonylation of nitrobenzene in the presence of alcohols, to afford phenylcarbamates has recently been independently reported by Liu and Cheng and us.[1] We also found that bipy (2,2′-bipyridyl) is a good cocatalyst for this reaction and we now report the preliminary results of a mechanistic study of the $[PPN][Rh(CO)_4]$/bipy system.

First we checked the possible reaction of **1** with bipy to afford a complex such as $[PPN][Rh(CO)_2(bipy)]$, but no reaction was observed in refluxing tetrahydrofuran (THF) or acetone, whereas rhodium metal and $[RhCl_2(CO)_2]^-$ were formed respectively in refluxing toluene and dichlorobenzene. Under the same conditions used in catalytic reactions (200 °C, P_{CO} = 60 atm, THF) some still unidentified compounds (probably cluster complexes) were formed, but they reacted with nitrobenzene much more slowly than **1** and cannot be intermediates in the catalytic cycle.

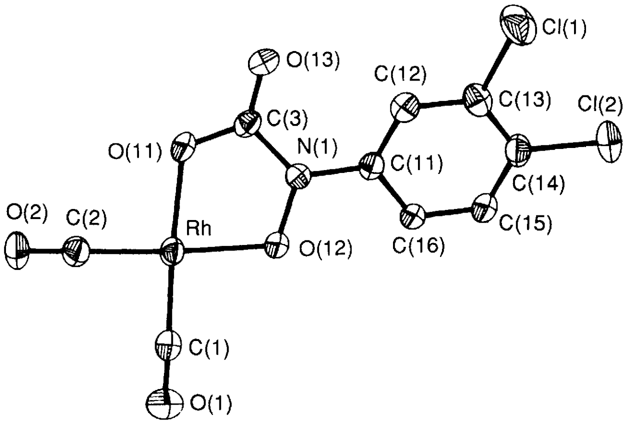

Fig. 1 ORTEP drawing of the $[\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}]^-$ anion. Thermal ellipsoids are drawn at 30% probability. Relevant bond distances (Å) are: Rh–C(1) 1.822(5), Rh–C(2) 1.830(4), C(1)–O(1) 1.132(5), C(2)–O(2) 1.136(4), Rh–O(11) 2.008(2), Rh–O(12) 1.989(2), N(1)–O(12) 1.398(3), N(1)–C(3) 1.384(4), C(3)–O(13) 1.218(4), C(3)–O(11) 1.299(4), N(1)–C(11) 1.401(4).

As it seems possible to exclude the direct interaction of bipy with **1**, we examined the reaction between **1** and nitrobenzene. A clean reaction was observed at 40 °C, affording a complex **2** showing three peaks in the IR spectrum at υ/cm^{-1} 2045(s), 1967(vs) and 1635(m) (THF). The same complex was also obtained by using nitrosobenzene in place of nitrobenzene, but 3 equiv. of nitrosobenzene were necessary and azoxybenzene was also formed. Use of smaller amounts of nitrosobenzene gave the same product together with unreacted **1**.† Unfortunately **2** was not stable enough to allow purification,

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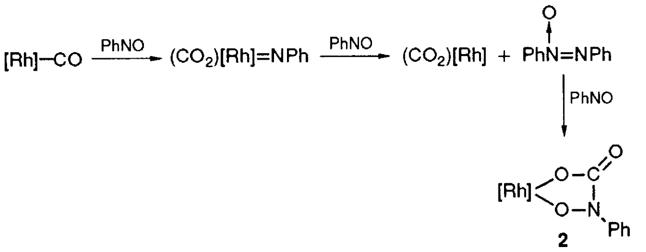
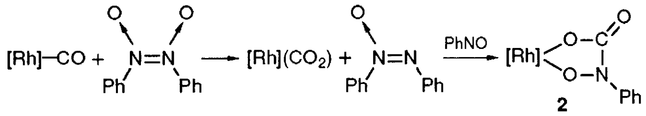
† In our previous paper on this topic,[1a] we tentatively formulated the product of the reaction of **1** with bipy in dichlorobenzene as $[Rh(CO)_2(bipy)]^-$. However we later discovered, as reported here, that this complex was indeed $[RhCl_2(CO)_2]^-$. So the original proposal must be considered erroneous. Also the previously reported reaction of this complex with nitrobenzene, to yield a still uncharacterized complex, is a reaction of $[RhCl_2(CO)_2]^-$ and not of a bipy complex. In the same paper we also reported that two different products (both at that time uncharacterized) were obtained by reaction of **1** with nitro- or nitroso-benzene. The products were considered to be different on the basis of slightly different IR spectra, recorded on an old Beckman IR spectrophotometer. However, when the same reactions were examined employing the more precise and reproducible FTIR spectrophotometer used in the course of this study, exactly the same spectrum was observed.



Scheme 1



Scheme 2

but, by use of 3,4-dichloronitrobenzene, an analogous, but more stable complex **3**‡ was obtained and its structure solved by X-ray diffraction§ (Fig. 1). The nitro group of the starting organic compound has been reduced to nitroso by a coordinated CO, but the so formed CO_2 molecule has not left the coordination sphere of the metal. It should be noted that CO_2 has surely rearranged from the original position in which the carbon atom was necessarily bound to rhodium. This is the first time that a metallacycle of this kind is observed during a deoxygenation reaction of nitrobenzene, although two similar metallacycles have been previously obtained by reaction of CO_2 with nitroso complexes.[2] In the present case, however, it is possible to exclude that CO_2 is delivered into the solution and then taken up again, since by performing the reaction while vigorously bubbling dinitrogen into the solution, no appreciable variation in the outcome of the reaction was observed.

Catalytic deoxygenation of nitrosobenzene to afford azoxybenzene has already been reported to be catalysed by rhodium[3] or ruthenium[4] complexes. In the case of rhodium a nitrene complex was suggested as an intermediate. Such a complex may be also formed in the present case when nitrosobenzene is used as a starting material (Scheme 1). However, since PhNO is in equilibrium in solution with its dimeric form, another possibility must be considered (Scheme 2). However, when the reaction with nitrosobenzene was performed in the presence of methanol, only 1 equiv. of nitrosobenzene was necessary to consume all of **1** and aniline was largely the dominant organic product. Only a trace of azoxybenzene was formed so the mechanism in Scheme 2 can be excluded, while the intermediate formation of a nitrene complex is strongly supported.¶

Once formed, **3** is relatively stable and does not show any tendency to lose CO_2; heating at 60 °C in THF solution is necessary to observe a reaction. The products are 3,4-dichloroaniline and an as yet unidentified insoluble material. No simple ntiroso complex is observed in solution during the reaction.

Compound **3** reacts with methanol at room temperature and atmospheric CO pressure affording 3,4-dichloroaniline and regenerating **1**. The regeneration of **1** is a very important point as it indicates that **1** is actually a part of the catalytic cycle and not simply a catalyst precursor. The reaction is faster if bipy or even pyridine are added to the solution, but, at the end of the reaction, only **1** is formed in every case. Pyridine was found to be an effective promoter even under catalytic conditions. This was unexpected since this base is completely ineffective when $Rh_4(CO)_{12}$ is used as a catalyst precursor.[6]

The absence of carbamate among the products of the reaction run under atmospheric CO pressure is not surprising, since carbamates are usually formed only under high CO pressure and at high temperature. In fact when an impure sample of **2** was added to a THF–MeOH solution preheated at 200 °C and under 60 atm. CO, carbamate was formed along with aniline.

Compound **3** reacts with bipy in THF only very slowly, to afford 3,4-dichloroaniline and an as yet unidentified insoluble material. Thus the rate enhancement caused by bipy in the reaction with methanol cannot be due to a direct interaction between **3** and bipy before the involvement of methanol and its effect must be found at a later stage of the reaction. Methanol probably acts by protonating **3** and further studies are in progress to ascertain the site of protonation and the remaining steps of the catalytic cycle.

Our results have shown that a metallacycle like **3** is a likely candidate as an intermediate during the catalytic reductive carbonylation of nitrobenzene and this was unpredictable considering that reaction between nitrobenzene and a bound CO should lead to carbon dioxide and nitrosobenzene. Together with recently isolated metallacycles of ruthenium[7] and palladium,[8] this rhodium derivative represents a further step in the understanding of the mechanism of the industrially important catalytic carbonylation of organic nitrocompounds.[9]

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‡ IR data for complex **3**: ν/cm^{-1} 2050s, 1973vs, 1638m (THF). Elemental analysis was satisfactory.

§ *Crystal data* for **3**: $C_{45}H_{33}Cl_2N_2O_5P_2Rh{\cdot}C_4H_8O$, M = 989.64, triclinic, space group $P\bar{1}$ (no. 2), a = 10.798(4), b = 9.889(6), c = 21.648(6) Å, α = 89.77(1), β = 96.00(1), γ = 92.71(1)°, U = 2296(2) Å^3, $F(000)$ 1012, Z = 2, D_c = 1.431 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 6.00 cm^{-1}. 8055 reflections with $2° < \theta < 25°$ were measured on a CAD4 diffractometer at room temperature. Data were corrected for Lorentz-polarization and absorption effects. 5299 independent reflections having $I > 3\sigma(I)$ were used in the structure refinement with anisotropical thermal parameters assigned to all non-hydrogen atoms. The final R value was 0.037 (R_w = 0.047).

Atomic coordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ During the reaction **2** was not formed, but a cluster compound showing an IR absorption pattern resembling closely that of $[NMe_4]_3[Rh_{11}(CO)_{23}]$[5] was present. This last cluster is often obtained after oxidative decomposition of **1**.

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