Inorganica Chimica Acta, 24 (1977) L49–L50

Carbon Dioxide–Transition Metals Complexes. III. Rhodium(I)–CO_2 Complexes

M. ARESTA and C. F. NOBILE

Istituto di Chimica Generale ed Inorganica, Università, Via Amendola 173, Bari 70126, Italy

Received July 4, 1977

Carbon dioxide activation via direct co-ordination to metal complexes can represent a way to CO_2 fixation [1]. In this light there appears justified the increasing interest in the synthesis and characterization of metal–CO_2 complexes and the attempts to put light on the mode of bonding of CO_2.

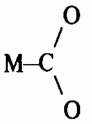
We have recently reported the synthesis and properties of $Ni(CO_2)(PCy_3)_2 \cdot 0.75\ C_7H_8$ (characterized crystallographically [2a]) and of a few other Ni(0) complexes [2b]. This report concerns the synthesis and properties of some Rhodium(I)–CO_2 complexes of formula $RhCl(CO_2)L_3$ (class A) and $RhCl(CO_2)L_2$ (class B) ($L = PR_nPH_{3-n}$) obtained either by reaction of $[RhCl(C_2H_4)_2]_2$ with the phosphorous ligand in toluene (or other hydrocarbon solvents) under CO_2 or by reaction of $RhClL_3$ with CO_2 either in solution (toluene, benzene, pentane) or in the solid state. $[RhCl(C_2H_4)_2]_2$ (I) in toluene at room temperature reacts with 2 equiv. of PBu^n_3 under CO_2 (1 atm) to give a low melting red–orange solid analyzing for $RhCl(CO_2)(PBu^n_3)_2$ (II) [3]. This compound shows in its i.r. spectrum two intense bands at 1668 and 1630 cm^{-1} attributable to $\nu(C{=}O)$ and bands at 1165 and 1120 cm^{-1} due to ν_{asym} and ν_{sym} (C–O) respectively [4]. The same compound is obtained when a pentane solution of $RhClL_3$ (from I and 6 equiv. of PBu^n_3 in benzene under nitrogen [5]) is exposed to 1 atm of CO_2 at room temperature. The $\nu(C{=}O)$ i.r. bands for II are at 1665(s) and 1627(s) cm^{-1} in a freshly prepared CH_2Cl_2 solution. On standing the i.r. spectrum shows the appearance of a new strong band at 1958 cm^{-1} due to a Rh(I) carbonyl species [6] and strong bands at 1147 and 1092 cm^{-1} due to the co-ordinated phosphine oxide formed according to:

$$RhCl(CO_2)L_2 \rightarrow RhCl(CO)(OL)L \qquad (1)$$

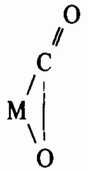
II exposed to the air converts into the bis(phosphineoxide)(1) complex ($\nu P{=}O$ at 1227(s), 1145(s), 1095(s) cm^{-1}] and CO_2 is retained. I with 6 equiv. of $PEtPh_2$ under CO_2 affords the yellow $RhCl(CO_2)L_3$ [3] (III; $\nu C{=}O$ at 1675vs and 1625w,sh cm^{-1}), which in the solid state releases CO_2 upon pumping *in vacuo* (90% of the CO_2 given off in 10 hours at room temperature). The CO_2 loss is complete in a short time when III is crystallized from benzene/pentane under nitrogen. Working with a ligand to metal molar ratio equal to two a pale yellow complex analysing for $RhCl(CO_2)L_2$ [3] is obtained ($\nu C{=}O$ at 1655vs and 1625vs cm^{-1}), which is much more stable to pumping in the solid state. Similarly I with PEt_2Ph (6 equiv.) in toluene under CO_2 affords the orange $RhCl(CO_2)L_3$ [3] ($\nu C{=}O$ at 1670vs, 1635sh, 1255m, 963m, 780m cm^{-1}) while with 4 equiv. of the phosphorous ligand $RhCl(CO_2)L_2$ [3] is obtained showing bands due to the co-ordinated CO_2 at 1658vs, 1620vs, 1238m, 827m cm^{-1}.

Analogous complexes are obtained with PMe_2Ph [$RhCl(CO_2)L_2$, red, CO_2 bands at 1657vs, 1627vs, 1217m, 996m, 823m cm^{-1}] and $PMePH_2$ [$RhCl(CO_2)L_3$, CO_2 bands at 1673vs, 1635sh, 1290m, 1000m, 822m, 760m cm^{-1}]. All the complexes lose CO_2 when treated with H_2SO_4 or when heated at temperatures above 80 °C.

The different spectra for class A and class B complexes can be tentatively explained assuming a different way of co-ordination for the CO_2 ligand. In class A complexes [pentacoordinate Rh(I)] CO_2 could be monodentate and in class B complexes it could be bidentate:



Class A bonding



Class B bonding

Such a picture has been proposed by us [2b] to explain the differences in the spectroscopic properties of $P_3Ni(CO_2)$ and $P_2Ni(CO_2)$ complexes. Similarly Herskovitz [7] proposes that CO_2 in [Ir(diars)-(CO_2)]Cl (diars = *o*-phenylenebis(dimethylarsine)] is bonded through the carbon atom (A class [8]; CO_2 i.r. bands at 1550 and 1220 cm^{-1}).

The noticeable difference of ν(CO) between the pentaco-ordinate Ir(I) (1550 cm^{-1}) and Rh(I) (about 1670 cm^{-1}) complexes can be explained taking into account that the lower energy of the Ir(I) *d* orbitals [with respect to Rh(I)] can allow a greater π-bond back donation from the metal *d* orbitals to antibonding $2\pi_u$ CO_2 [9] orbitals, thus reducing more effectively the CO_2 bond order. The important role played by the *d* orbitals energy is also demonstrated by the scarce tendency of the $[Rh(L_2)_2]^+$ moiety to bound CO_2 [7] under the same conditions as $[Ir(L_2)_2]^+$. The basicity and bulkiness of the phosphorous ligands, their π-acceptor character, the geometry of the complexes, the *trans*-effect of the *trans*-to-CO_2 ligands, can barely affect the stability of the CO_2–metal bond. Although at the moment it is difficult to make any definite correlation between bond order reduction of the co-ordinate CO_2 and strength of the metal–CO_2 bond, it appears to us that in the case of the class A Rh(I) complexes all those factors can make the CO_2 more loosely bonded than in the class B complexes, which retain CO_2 also in polar solvents such as acetone, CH_2Cl_2, ethanol [10].

Further studies are in progress on the reactivity of the complexes.

Acknowledgement

The Authors thank the C.N.R., Rome for financial support and Miss R. Micera for experimental assistance.

References

1 For a recent review see: M. E. Vol'pin and I. S. Kolomnikov, *Organometallic Reactions, 5,* 313 (1975).
b– T. Herskovitz and L. Guggenberger, *J. Am. Chem. Soc., 98,* 1615 (1976).

2 a) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, M. Manassero, *Chem. Comm.,* 636 (1975).
b) M. Aresta and C. F. Nobile, *J. Chem. Soc. Dalton,* 708 (1977).

3 C, H, Cl, P analyses agree with the proposed formula.

4 Unless otherwise stated the ν values are intended for Nujol mull through the whole paper.

5 M. Aresta and A. Sacco, Report to the, "Convegno sui Composti di Coordinazione", C.N.R., Rome, 17–19 April (1967).

6 $RhCl(CO)(PBu^n_3)_2$ presents the $\nu(C{=}O)$ band at 1957 cm^{-1}, ref. 5.

7 T. Herskovitz, *J. Am. Chem. Soc., 99,* 2391 (1977).

8 The similar complex $Ir(dmpe)_2Cl{\cdot}CO_2$ [7] displays bands at 1550 and 1230 cm^{-1}.

9 The CO_2–metal σ-bond should be formed by transfer of electrons density from a filled CO_2 π-orbital (one of the filled $1\pi_g$ anti-bonding orbitals) to one of the empty *d, s, p* metal orbitals (probably a dsp^3 hybrid). This bond should strengthen the C–O bond and, thus, the back π-bonding from the filled metal orbitals to the antibonding $2\pi_u$ orbitals plays an important role in CO_2 bond-order reduction.

10 As reported above in such polar solvents oxygen-transfer to the phosphine occurs. Such a tendency is more pronounced with the more basic phosphines in the order $PPh_2Et \cong PPh_2Me < PPhEt_2 \cong PPhMe_2 < PBu^n_3$.