Reversible Addition of Carbon Dioxide to Rhodium and Iridium Complexes

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Summary Crystalline *trans*-[$M(OH)(CO)(Ph_3P)_2$] (M = Rh, Ir) reacts with CO_2 under normal conditions to form addition compounds, [$(CO_2)M(OH)(CO)(Ph_3P)_2$], which, on pumping, release carbon dioxide and revert to the starting hydroxo complexes; the vibrational spectra of the bound CO_2 indicate a substantial lowering of symmetry and bond order from those of the free molecule.

THE reactions of carbon dioxide with metal complexes generally occur *via* insertion or ligand replacement,[1] and no authenticated direct CO_2 co-ordination to the central atom seems to have been reported. In the course of our studies of the interactions between carbon dioxide and some d^8 transition elements,[2] we have discovered what appears to be a new mode of CO_2-metal complex association.

Exposure of solid covalent hydroxo compounds, *trans*-[$M(OH)(CO)(Ph_3P)_2$], M = Rh, Ir,[3] to one atmosphere of carbon dioxide at 25° [equation (1)] results in gas uptake.

$$[M(OH)(CO)(Ph_3P)_2](\text{powder}) + CO_2(\text{gas}) \rightleftharpoons [(CO_2)M(OH)(CO)(Ph_3P)_2](\text{powder}) \qquad (1)$$

The Rh complex reacts virtually instantaneously with a stoicheiometry of CO_2: Rh = 1 as shown by volumetric and gravimetric measurements. Uptake of CO_2 by [$Ir(OH)(CO)(Ph_3P)_2$] is much slower and reaches an equilibrium after 5 h with *ca.* 65% conversion into the adduct. Both reactions are accompanied by substantial changes in vibrational spectra (Table). Continuous pumping on the CO_2 adducts at 25° yields carbon dioxide and the starting hydroxo complexes. Complete decarboxylation of [$(CO_2)M(OH)(CO)(Ph_3P)_2$] requires about 10 h and weeks for M = Ir and Rh, respectively.

TABLE. I.r. spectral data, cm^{-1}.[a]

Compound	ν_{CO}	$\Delta\nu_{CO}$[b]	ν_{CO_2}
CO_2 (gas)			2349, 667[c]
[$(CO_2)Rh(OH)(CO)(Ph_3P)_2$] ..	1966 vs	16	1602 s, 1351 s, 821 m
[$(CO_2)Ir(OH)(CO)(Ph_3P)_2$] ..	1958 vs	27	1636m, 1310s, 815m, 1618m

[a] Nujol or halocarbon mulls. [b] $\Delta\nu_{CO} = \nu_{CO}$ in [$(CO_2)M(OH)(CO)(Ph_3P)_2$] minus ν_{CO} in [$M(OH)(CO)(Ph_3P)_2$]. [c] K. Nakamoto 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley-Interscience, New York 1970, p. 83.

The following observations on this are noteworthy. (1) The positions and the number of absorption bands attributable to the vibrations of bound CO_2 indicate a marked decrease in both the carbon–oxygen bond order and symmetry of the triatomic species upon complexation. These frequency shifts are similar to those reported for chemisorbed carbon dioxide on metal and metal oxide surfaces, *e.g.*, Ni + CO_2: 1640, 1390; NiO + CO_2: 1620, 1360 cm^{-1},[4] and suggest a bent structure for the CO_2 group. On the other hand, the recently described carbon dioxide adducts with some Cu^{II} complexes apparently involve a physical interaction since the spectrum of the incorporated CO_2 (2350, 2380 cm^{-1})[5] differs only little from that of the free molecule (Table), implying a linear combination, $M \cdots O{=}C{=}O$.[6] (2) The ν_{OH} in $[M(OH)(CO)(Ph_3P)_2]$ disappear upon carbon dioxide addition which seems to reflect hydrogen bond formation to oxygen(s) of CO_2. Indeed, hydrogen bonding apparently is necessary for stabilizing the carbon dioxide co-ordination since analogous but non-hydroxo complexes of Rh and Ir {*e.g.*, $[MA(CO)(Ph_3P)_2]$; A = F, Cl, $OClO_3$}, either as solids or solutions, do not measurably react with CO_2 under normal conditions. (3) The carbon monoxide stretching frequencies shift to higher values (see $\Delta\nu_{CO}$ in the Table), but the change is relatively small, and thus the $[(CO_2)M(OH)(CO)(Ph_3P)_2]$ are best interpreted as containing univalent metals.[7]

$$[(CO_2)M(OH)(CO)(Ph_3P)_2] \xrightarrow{EtOH} [M(OCO_2H)(CO)(Ph_3P)_2] \qquad (2)$$

In ethanol solution, both carbon dioxide complexes are rapidly and quantitatively converted into bicarbonato derivatives[2] [equation (2)]; however, dissolution with simultaneous pumping causes partial decarboxylation to give the parent hydroxo compounds. These observations suggest that the formation of the metal bicarbonato complexes by reaction of $[M(OH)(CO)(Ph_3P)_2]$ with CO_2 in alcohol[2] proceeds *via* the species described here. Preliminary results show that the reversible addition of carbon dioxide also occurs in acetone solution, the reactivity order of the metals being the same as for solid-gas reactions [equation (1)], *i.e.*, Rh > Ir.

The presently available data do not allow a definite description of the mode of CO_2 co-ordination in these complexes, *i.e.*, whether the species is attached to the metal atom, C- or O-bonded, or is linked to the hydroxo group only. The i.r. spectra of bound carbon dioxide are different from those of carbonato and bicarbonato ligands,[3] and the *reversibility* of the reactions at mild conditions and in the solid state appears to be unique for all metal complex-CO_2 associations thus far reported {*e.g.*, pumping on crystalline $[M(OCO_2H)(CO)(Ph_3P)_2]$ for months produces no change}.

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