Carbon Dioxide Coordination Chemistry. The Structure and Some Chemistry of the Novel CO_2 Addition Product $IrCl(C_2O_4)(PMe_3)_3$

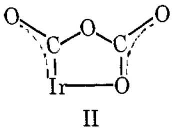
Sir:

There has been much recent interest in the interaction of carbon dioxide with transition metal systems.[1] Some of the impetus is the goal of CO_2 fixation into organic compounds via transition metal catalysts. Adducts of carbon dioxide have been proposed in various studies, and the structure of $Ni(PCy_3)_2(CO_2)\cdot 0.75(C_7H_8)$ (Cy = cyclohexyl) was recently reported.[2] We report here the preparation and structure of a novel "adduct" and propose a scheme for CO_2 activation and transformation consistent with our observations and those of others.

The reaction of $Ir_2Cl_2(C_8H_{14})_4$ in benzene with 6 equiv of trimethylphosphine (PMe_3) affords air-sensitive yellow crystals of chloro(cyclooctene)[tris(trimethylphosphine)]iridium(I), $IrCl(C_8H_{14})(PMe_3)_3$.[3] Upon exposure to a carbon dioxide atmosphere, benzene solutions of $IrCl(C_8H_{14})(PMe_3)_3$ deposit white crystals of $IrCl(C_2O_4)(PMe_3)_3\cdot 0.5C_6H_6$ (I). This complex shows infrared bands at 1725 (s), 1680 (s), 1648 (sh), 1605 (m), 1290 (s), 1005 (m), and 790 (m) cm^{-1}, which have been confirmed to be due to the bound CO_2 using isotope labeling ($^{13}CO_2$ and $C^{18}O_2$). The band at 1290 cm^{-1} is a composite of several vibrational modes.

The crystal structure of I was determined from 4071 reflections measured on an automatic diffractometer using the θ-2θ scan technique and Zr-filtered Mo radiation. Crystals are triclinic, space group $P\bar{1}$, with a = 16.142 (6), b = 16.626 (7), c = 9.335 (14) Å, α = 96.8 (3), β = 98.3 (3), and γ = 115.6 (2)°. The data were corrected for absorption effects. The structure was solved by Patterson and Fourier techniques and refined by least-squares to a conventional R of 0.049 for 3567 reflections with $F_o > 2.0\sigma(F_o)$; the hydrogen atoms were not included in this model and all atoms had anisotropic thermal parameters.

There are two symmetry independent molecules per cell but both have the same structure (Figure 1). The interatomic distances and angles in Figure 1 were averaged for the two independent molecules and the errors estimated from the observed differences in the two molecules (angle errors estimated to be 0.5°). The iridium is basically octahedrally coordinated with the angle deviations consonant with the ligand steric constraints. The unusual feature is the CO_2 coordination which appears to be best described by the valence bond structure (II). The C-O multiple bonds in II are like the short bonds in carboxylic acids and esters (1.233 (5) Å) whereas the C-O single bonds are like the long bonds in carboxylic acids and esters (1.358 (5) Å).[4] For comparison the C-O distance in CO_2 is 1.16 Å and in carbonates about 1.29 Å. There are the usual trans ligand bonding compensations; for example, the Ir-P(3) distance is shorter than usual,[5] whereas the Ir-O(1) distance is on the long side (compared to the values of 1.99 (1) Å[6] in *trans*-$[Ir(t\text{-}Bu_2PC_6H_4O)_2]$ and 2.00-2.06 Å in Ir-O_2 complexes[7]). Likewise, the Ir-Cl distance is longer than expected for a single bond (2.360 (9) Å[9] in $IrCl(O_2)(CO)(PPh_2Et)_3$ and 2.371 (10) Å[10] in $IrCl(SO_2)(CO)(PPh_3)_2$), whereas the Ir-C(2) distance is shorter. The Ir-C(2) distance is perhaps most like the second- and third-row group 8 transition metal carbene distances.[11]



II

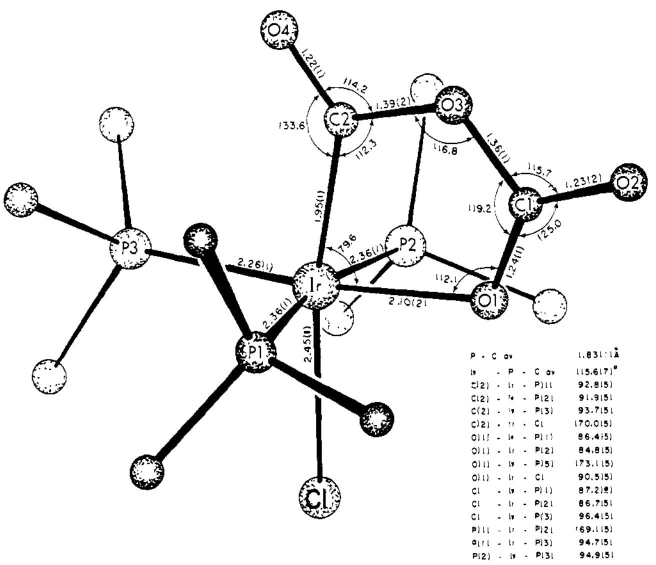
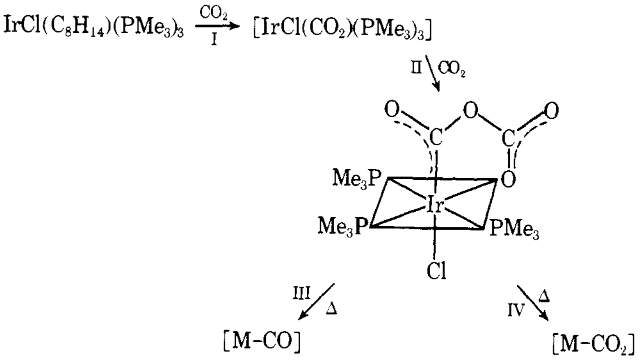


Figure 1. The molecular configuration of $IrCl(C_2O_4)(PMe_3)_3$.

Thermal decomposition of solid $IrCl(C_2O_4)(PMe_3)_3$ at 150° afforded a mixture of products including a carbonyl complex (ν_{CO} at 1930 cm^{-1}) and a 1:1 Ir:CO_2 adduct ($\nu_{coord.CO_2}$ at ~1620, 1230 cm^{-1}).[12] Plausible routes to the above compounds involve cleavage of the C(2)-O(3) or the equidistant C(1)-O(3) bond to yield bound carbon monoxide or carbon dioxide (reactions III and IV in Scheme I).

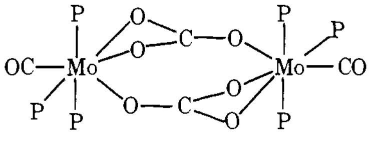
Scheme I[a]



[a] Brackets denote species not fully characterized.

Reaction of $IrCl(C_8H_{14})(PMe_3)_3$ with less than 2 equiv of CO_2 yielded $IrCl(C_2O_4)(PMe_3)_3$ and a species displaying ir bands at 1600 and 1260 cm^{-1}, ascribable to a mono-CO_2 adduct.[12] We postulate that $IrCl(C_2O_4)(PMe_3)_3$ is formed from $IrCl(C_8H_{14})(PMe_3)_3$ via stepwise uptake of two CO_2 molecules with concomitant displacement of cyclooctene. Presumably the reaction is initiated by addition of the nucleophilic $IrCl(C_8H_{14})(PMe_3)_3$ to CO_2 (O(3)C(2)O(4)) and the resultant more basic oxygen (O(3)) binding a second CO_2 molecule (O(2)C(1)O(1)) through C(1). Cyclization via Ir-O(1) bond formation affords the product. The reactions postulated are outlined in Scheme I.

The reported formation of $Mo_2(PMe_2Ph)_6(CO)_2(CO_3)_2$, V, from *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ and carbon dioxide[13]



V

may involve a pathway analogous to Scheme I above. An intermediate $Mo(PMe_2Ph)_n(C_2O_4)$ species may be cleaved at the C(2)–O(3) bond of the metallocycle to yield carbonyl and carbonate containing fragments prior to product formation. Likewise, the report by Aresta et al.,[2] that $Ni(PCy_3)_2(CO_2)$ upon decomposition affords carbonyl and carbonate species, may reflect a mechanism like that of Scheme I.

References and Notes

(1) M. E. Volpin and I. S. Kolomnikov in *Organomet. React.*, **5**, 313–386 (1975).
(2) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 636 (1975).
(3) A 60% yield after recrystallization from hexane. Anal. Calcd for $C_{17}H_{41}P_3ClIr$: C, 36.07; H, 7.30. Found: C, 35.91; H, 7.12.
(4) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18**, S20s (1965).
(5) G. R. Clark, B. W. Skelton and T. N. Waters, *J. Organomet. Chem.*, **85**, 375 (1975), and references therein.
(6) R. Mason and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 612 (1974).
(7) M. Laing, M. J. Nolte, and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 660 (1975), and references therein.
(8) Ir–C(Me) distances of 2.202 (22) and 2.126 (17) Å were observed for $(C_8H_{12})(PhMe_2P)_2Ir(Me)$ and $(C_8H_{12})(diphos)Ir(Me)$, respectively: M. R. Churchill and S. A. Bergman, *J. Organomet. Chem.*, **31**, C43 (1971).
(9) M. S. Weiniger, I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1172 (1971).
(10) S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).
(11) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972); D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
(12) See forthcoming paper by T. Herskovitz on other similar CO_2 adducts.
(13) J. Chatt, M. Kubota, G. J. Leigh, F. C. March, R. Mason, and D. J. Yarrow, *J. Chem. Soc., Chem. Commun.*, 1033 (1974).

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Detection of Covalent Intermediates by Nucleophile Trapping in the Hydrolysis of Phenyl Tetrahydrofurfuryl Sulfite Catalyzed by Pepsin

Sir:

From a consideration of both kinetic studies and chemical modification data, the mechanism illustrated in Scheme I involving the formation of an anhydride intermediate, V, has been proposed for the pepsin-catalyzed hydrolysis of sulfite esters.[1,2] Recently, it has been demonstrated that in the hydrolysis of sulfite esters mediated by model carboxylate catalysts mixed anhydride intermediates can be detected by the use of nucleophile trapping agents.[3] This finding encouraged us to test the application of this approach to the elucidation of the mechanism of the pepsin-catalyzed hydrolysis of sulfite esters. We now wish to report that with the use of hydroxylamine as a trapping agent we have been able to obtain the first direct evidence for the intermediacy of mixed anhydrides in the pepsin-catalyzed hydrolysis of sulfite ester and to identify the active site carboxyl groups involved in the formation of the anhydrides.

Scheme I. Proposed Mechanism for the Pepsin-catalyzed Hydrolysis of Sulfite Esters

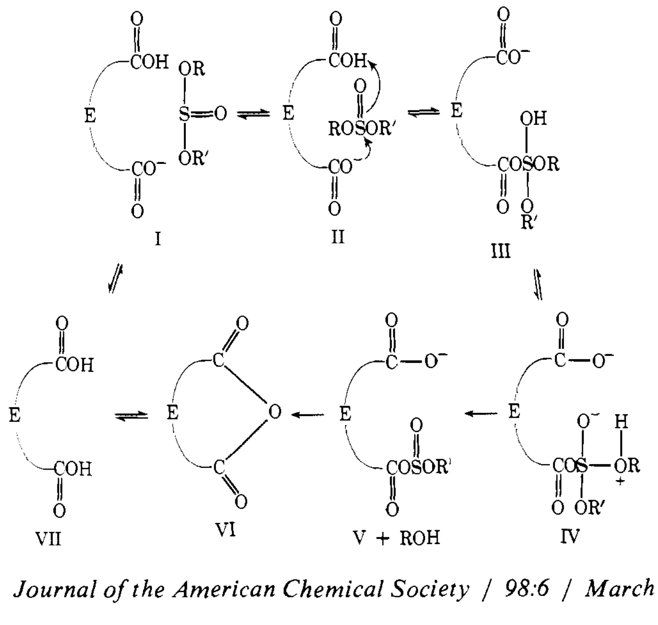
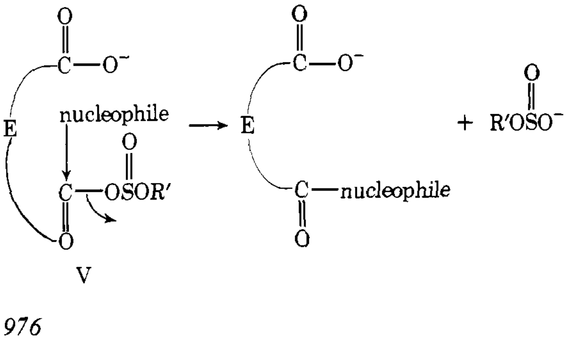


Table I. Hydroxamate Incorporation and Remaining Catalytic Activity in the Pepsin-Catalyzed Hydrolysis of Phenyl Tetrahydrofurfuryl Sulfite in the Presence of Hydroxylamine[a]

Mole ratio of PTFS to pepsin	No. of incubations[b]	Remaining pepsin activity %	Mol of hydroxamate/ mol of pepsin
2.5	1	81.9	1.2
2.2	2	61.2	3.3
5.0	1	59.5	1.4
5.0	2	52.0	3.8
9.2	1	57.2	1.4
11.7	9	53.3	3.2

[a] Solutions containing porcine pepsin (Worthington PM 8HA and PM 2LB) were purified by passing them through a column of Sephadex G-25 which had been equilibrated with 0.01 M 2-(*N*-morpholino)ethanesulfonic acid (MES) buffer, pH 5.3. Phenyl tetrahydrofurfuryl sulfite (PTFS) in CH_3CN was added to the pepsin solution containing 0.01 M hydroxylamine (pH 5.3), and the resultant solution was equilibrated for 30 min at room temperature. Control experiments for the measurement of pepsin activity were carried out in parallel in the presence of CH_3CN only. Experiments on the incubation of hydroxylamine with pepsin in the absence of the sulfite ester revealed no significant incorporation of hydroxylamine during time periods comparable to those employed for the experiments summarized in this table. [b] Additional substrate was added at 30-min intervals for multiple incubation experiments. At the end of the experiments the enzyme solution was dialyzed against 3 l. of 0.01 M sodium acetate buffer, pH 4.0, for 72 h with five changes. Hydroxamic acid was quantitatively analyzed by the method of F. Bergmann and R. Segal, *Biochem. J.*, **62**, 542 (1956). Pepsin activity was determined by the hemoglobin assay method described by R. B. Chow and B. Kassell, *J. Biol. Chem.*, **243**, 1718 (1968).

In Table I the results obtained by incubating various amounts of phenyl tetrahydrofurfuryl sulfite (PTFS) with pepsin in the presence of 0.01 M hydroxylamine at pH 5.3 are given. At a molar ratio of PTFS/pepsin = 2.5 in a single incubation experiment about 20% of the peptic activity was lost and concomitantly 1 mol of hydroxamate per mole of pepsin was found. This observation is consistent with the scheme of eq 1 in which the potent nucleophile hydroxylamine is postulated to attack the mixed anhydride intermediate V. With increases in the number of incubations performed with PTFS or increases in the concentration of PTFS, the peptic activity was seen to decrease and there was an increase in the number of enzyme-bound hydroxamate groups produced, up to a maximum value of 3–4 mol per mole of pepsin.



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