Carbon Dioxide Co-ordination Chemistry: Preparation and *X*-Ray Crystal Structure of the Methoxycarbonyl Complex $[IrCl(CO_2Me)(Me_2PCH_2CH_2PMe_2)_2]FSO$ from a CO Adduct[1]

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Summary $[IrCl(CO_2Me)\,(dmpe)_2]FSO_3$ (dmpe = $Me_2PCH_2CH_2PMe_2$) is made by the reaction of $Ir(dmpe)_2Cl{\cdot}CO_2$ with $MeFSO_3$ and its structure has been determined by *X*-ray crystallography; this is the first transformation of a well defined CO_2 ligand into an organic species.

There is much current research activity on the interaction of carbon dioxide with transition metal complexes, owing in part to interest in exploring potential routes to organic molecules from abundant CO_2. Isolable CO_2–transition metal adducts[1,2] and methods of incorporating CO_2 into organic molecules[3] have both been reported. We now report the utilization of a well defined CO_2 adduct in a novel preparation of the methoxycarbonyl ligand.

$Ir(dmpe)_2Cl{\cdot}CO_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$),[1] suspended in toluene under nitrogen, was treated with 1 equiv. of methyl fluorosulphate. Stirring for several hours resulted in a light-brown solid which was recrystallized from methylene chloride–toluene. This product (**1**) showed loss of the i.r. bands at 1550 and 1230 cm^{-1} (CO_2 adduct) and new bands at 1630s and 1065s cm^{-1}.

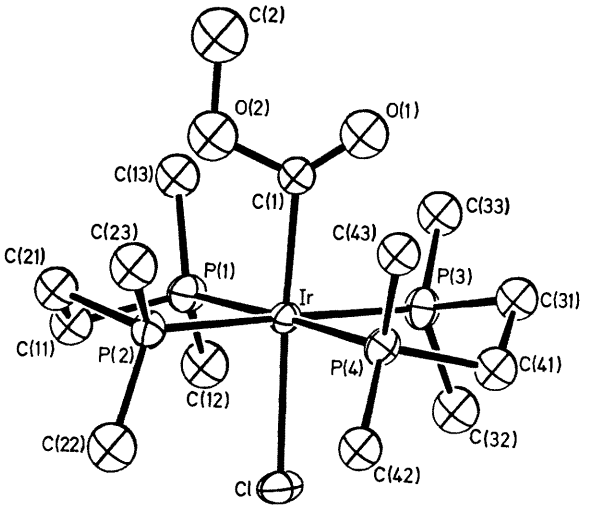

FIGURE ORTEP drawing of (**1**) with the atom-labelling scheme Some of the more interesting bond distances and angles are Ir–Cl, 2 469(2), Ir–P(1), 2 340(2), Ir–P(2), 2 341(2), Ir-P(3), 2 350(2), Ir–P(4), 2 342(2), Ir–C(1), 2 073(8), C(1)–O(1), 1 151(10), C(1)–O(2), 1 366(10), O(2)–C(2), 1 459(13) Å, Cl–Ir–P(1), 89 68(7), Cl–Ir–P(2), 89 79(8) Cl–Ir–P(3), 89 25(8) Cl–Ir–P(4), 88 54(7) Cl–Ir–C(1), 177 0(2), P(1)–Ir–P(2), 84 31(8) P(1)–Ir–P(3), 96 16(8) P(1)–Ir–P(4), 178 22(8) P(1)–Ir–C(1), 91 8(2), P(2)–Ir–P(3), 178 93(8) P(2)–Ir–P(4) 95 59(8) P(2)–Ir–C(1), 93 0(2), P(3)–Ir–P(4) 83 91(7) P(3)–Ir–C(1), 88 9(2) P(4)–Ir–C(1), 90 0(2), Ir–C(1)–O(1), 125 3(7) Ir–C(1)–O(2), 111 6(5), O(1)–C(1)–O(2), 123 0(8) C(1)–O(2)–C(2) 112 2(8)°

The molecular structure of $[Ir(Cl)(CO_2Me)(dmpe)_2]$-FSO_3 (**1**) was determined by a single-crystal *X*-ray diffraction study†, the result of which is shown in the Figure The metal–carbon bond length of this methoxycarbonyl complex, 2 073(8) Å, agrees well with the previously reported values of 2 059(7) for an ethoxycarbonylplatinum complex[4] and 2 05(2) Å for a methoxycarbonyliridium complex [5] The remaining bond distances and angles of the alkoxycarbonyl ligand are also in reasonable agreement (see Table 3 of ref 5), with some slight variations

Alkoxycarbonyl complexes have previously been prepared either by reaction of alkoxide ion with a carbonyl complex or by treating anionic carbonyls with chloroformate esters [6] The i r spectral characteristics ν(C=O) and ν(C–O) of these products closely resemble those of complex (**1**)

(*Received*, 22*nd February* 1980, *Com* 192)

† *Crystal data* monoclinic space group *I*2/*c* (no 15), at −50 °C, a = 15 481(2), b = 17 724(4), c = 18 019(4) Å, β = 90 36(1)°, U = 4944 Å^3, Z = 8, Syntex *P*3 diffractometer, graphite monochromator, Mo-K_α radiation, λ = 0 71069 Å, ω scans of 1 0°, 4° $< 2\theta <$ 48°, 3848 reflections The structure was solved by the heavy-atom method FSO_3^- anions are located on crystallographic 2-fold axes and are disordered The O and F atoms around each S atom were represented by 4 oxygen atoms, each with an occupancy of 0 5 the positions of the hydrogen atoms were calculated and agreed closely with peaks found in a difference-Fourier synthesis The structure was refined by the full-matrix least-squares method (anisotropic thermal parameters for Ir, Cl, S, P, isotropic for O and C, hydrogen atoms not refined) with 157 variables and 3007 reflections with $I > 3\sigma(I)$ to R = 0 037, all the major peaks in the final difference Fourier are located near the S atoms The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

Photographs taken at room temperature clearly indicated that the crystal system at 23 °C is orthorhombic, not monoclinic, with unit cell parameters which closely agree with those found at −50 °C The possible space groups for the room-temperature phase are *Ima*2 and *Imma* It is probable that the transition occurs when the temperature is lowered because of an ordering of the dmpe ligands which are disordered at room temperature

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[3] See for example, A Musco, C Perego, and V Tartiari, *Inorg Chim Acta*, 1978, **28**, L147, G O Evans and C J Newell *ibid* , **31**, L387, Y Inoue, Y Itoh and H Hashimoto, *Chem Lett* , 1978, 633

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