Synthesis and *X*-Ray Crystal Structure of $[Mo(CO_2)_2(PMe_3)_3(CNPr^i)]$: the First Structurally Characterized Bis(Carbon Dioxide) Adduct of a Transition Metal

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The reaction of *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ with isocyanides yields the new bis(carbon dioxide) complexes *trans,mer*-$[Mo(CO_2)_2(CNR)(PMe_3)_3]$, (R = Me, Pr^i, or Bu^t); the structure of the isopropyl derivative $[Mo(CO_2)_2(CNPr^i)(PMe_3)_3]$ has been determined by *X*-ray crystallography.

It is widely accepted that carbon dioxide is a very labile ligand that may be easily displaced when co-ordinated to a transition metal centre, or undergo a range of chemical transformations such as deoxygenation, dimerization, or disproportionation.[1] We have recently found that the interaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with CO_2 yields *trans*-$[Mo(CO_2)_2(PMe_3)_4]$, which has been unequivocally characterized by chemical and spectroscopic studies as the first stable bis(carbon dioxide) adduct of a transition metal.[1] However efforts to obtain crystals of this compound suitable for X-ray analysis were unsuccessful.

Recent work has shown a number of similarities between the complexes *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$[2] and *trans*-$[Mo(CO_2)_2(PMe_3)_4]$. Since the ethylene species reacts with isocyanides to yield the mono- and bis-substituted products, *trans,mer*-$[Mo(C_2H_4)_2(CNR)(PMe_3)_3]$ and all-*trans*-$[Mo(C_2H_4)_2(CNR)_2(PMe_3)_2]$, a similar behaviour was anticipated for the CO_2 complex. Indeed the interaction of *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ with various isocyanides affords new carbon dioxide complexes of composition *trans,mer*-$[Mo(CO_2)_2(CNR)(PMe_3)_3]$ according to equation (1):

$$[Mo(CO_2)_2(PMe_3)_4] + CNR \rightarrow [Mo(CO_2)_2(CNR)(PMe_3)_3] + PMe_3 \quad (1)$$

$$R = Me, Pr^i, \text{ or } Bu^t$$

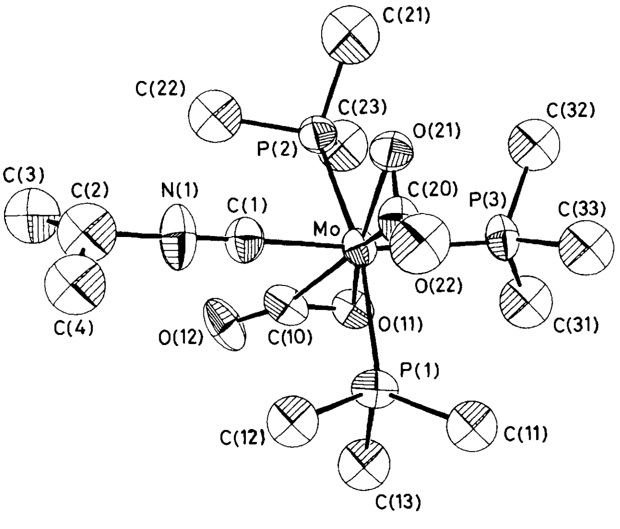

Figure 1. ORTEP perspective of *trans,mer*-$[Mo(CO_2)_2(PMe_3)_3(CNPr^i)]$, showing the atom numbering scheme. Important bond distances and angles: Mo–C(CO_2) 2.105(10) (av.), Mo–O 2.147(7)(av.), Mo–C(1) 2.07(2), Mo–P(1) 2.489(4), Mo–P(2) 2.535(4), Mo–P(3) 2.548(5) Å; O–C–O 133.5(10) (av.), C(10)–Mo–O(11) 34.5(4), C(20)–Mo–O(21) 34.3(4)°.

Only substitution of one PMe_3 ligand by CNR has been observed. The close similarity of the i.r. bands at 1670, 1155, and 1100 cm^{-1}, associated with the bound CO_2 in these complexes and in *trans*-$[Mo(CO_2)_2(PMe_3)_4]$, clearly indicates that the phosphine substitution reaction takes place without change in the co-ordination mode of the CO_2 molecules. The analogous reaction of the recently reported $[Mo(CO_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$[3] {which we believe is the bis(diphenylphosphino)ethane analogue of *trans*-$[Mo(CO_2)_2(PMe_3)_4]$[1]} with MeNC in boiling tetrahydrofuran, yields $[Mo(CNMe)_2(Ph_2PCH_2CH_2PPh_2)_2]$.[3]

The *X*-ray crystal structure of the isopropyl derivative has been determined. Figure 1 shows† an ORTEP view of $[Mo(CO_2)_2(CNPr^i)(PMe_3)_3]$. The molecule is essentially octahedral, with the CO_2 ligands bonded in a dihapto manner through one of the C=O bonds. The orientation of the co-ordinated double bonds is similar to that found in *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ and *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$, with the co-ordinated C=O bonds staggered with respect to one another, and eclipsing the *trans*-L–Mo–L vectors. The Mo–CO_2 bonding is relatively strong, as shown by the short Mo–C and Mo–O average bond distances of 2.105(10) and 2.147(7) Å respectively. Note for comparison that the average Mo–C(ethylene) distances in the analogous complexes *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ and *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$ are 2.270(5) and 2.29(3) Å respectively. The average value of 133.5(10)° obtained for the OCO angle of the co-ordinated CO_2 ligand is similar to that found in the complexes $[Ni(CO_2)(Pcy_3)_2]$[4] (cy = cyclohexyl) and $[Nb(C_5H_4Me)_2(CH_2SiMe_3)(CO_2)]$.[5] The bonding of the isocyanide ligand appears normal and the MoCNC entity is almost linear [MoC(1)N(1) 178.5(9)°, C(1)N(1)C(2) 177(1)°].

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† *Crystal data*: $C_{15}H_{34}MoNO_4P_3$, $M = 481.29$, monoclinic, space group $C2/c$, $a = 29.47(3)$, $b = 13.01(1)$, $c = 16.77(1)$ Å, $\beta = 132.41(3)°$, $U = 4747.5$ Å^3, $Z = 8$, $D_c = 1.347\ g\ cm^{-3}$, $\mu(Mo\text{-}K_\alpha) = 7.54\ cm^{-1}$, $F(000) = 2000$. A total of 4163 unique reflections were measured in the range $0 < \theta < 25°$ on an Enraf-Nonius CAD 4 diffractometer using ω-2θ scans and Mo-K_α radiation ($\lambda = 0.71069$ Å); 3493 reflections were considered observed $[F_o^2 \geqslant 3\sigma(F_o^2)]$ after data reduction, and used in subsequent calculations. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares procedures in the XRAY system to an R value of 0.076. The methyl carbon atoms were refined isotropically and the hydrogens were included in the refinement with fixed contributions at their calculated positions. Some disorder non-resolvable from thermal motion was found in the methyl groups attached to C(2) and P(3).

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.

The solid state structure of $[Mo(CO_2)_2(CNPr^i)(PMe_3)_3]$ is maintained in solution, as revealed by spectroscopic studies. The ^1H n.m.r. spectrum shows, in addition to the resonances due to the co-ordinated isocyanide, a virtually coupled triplet [δ 1.35 $J(P-H) + J(P-H')$ 6.8 Hz] and a doublet [1.15 $J(P-H)$ 6.8 Hz], in accord with a meridional distribution of the phosphine ligands. The co-ordinated CO_2 molecules in these $[Mo(CO_2)_2(CNR)(PMe_3)_3]$ derivatives exhibit ^{13}C n.m.r. resonances at δ 200—205, in the region found for other π-CO_2 complexes.[1,5]

The complexes *trans,mer*-$[Mo(CO_2)_2(CNR)(PMe_3)_3]$ show surprising thermal stability. Thus solid $[Mo(CO_2)_2(CNPr^i)(PMe_3)_3]$ can be heated for several hours *in vacuo* or under N_2 at 80 °C without noticeable decomposition, while toluene solutions only start decomposing at *ca.* 60 °C. It can therefore be concluded that two CO_2 molecules can be strongly bonded to a transition metal atom as independent ligands, and that these complexes are not necessarily unstable.

We thank the Comisión Asesora de Investigación Científica y Técnica (C.A.I.C.Y.T.) for generous support of this work (to E. C.). R. A. acknowledges a research grant by the Ministerio de Educación y Ciencia.

Received, 29th June 1984; Com. 924

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