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LETTER

Intramolecular –C–H···O– hydrogen bonding in Group 6 metal carbonyl complexes

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Intramolecular hydrogen bonding involving the –C–H functionality [1] can exert important and perhaps ubiquitous influences on stereochemistry and reactivity in metal carbonyl complexes [2, 3]**. In the synthesis of $(L)(L')M(CO)_4$ complexes from *cis*-$(pip)(L)M(CO)_4$ precursors (Scheme 1; M = Cr, Mo; solvent = chlorobenzene (CB)) [4, 5], where L = L′ (= phosphine, phosphite), the products are predominantly *trans*; where L is a phosphine and L′ is a phosphite, *cis*-$(L)(L')M(CO)_4$ (**I**) products are obtained, even where L, L′ possess large steric bulk. These observations [5] suggested possible internal M–P–C–H···O–P– hydrogen bonding involving L, L′ which would inhibit or alter the extent of intramolecular [6] isomerization in **I**. We wish to report structural evidence which supports this hypothesis and kinetics data which point to the more general importance of –C–H hydrogen bonding.

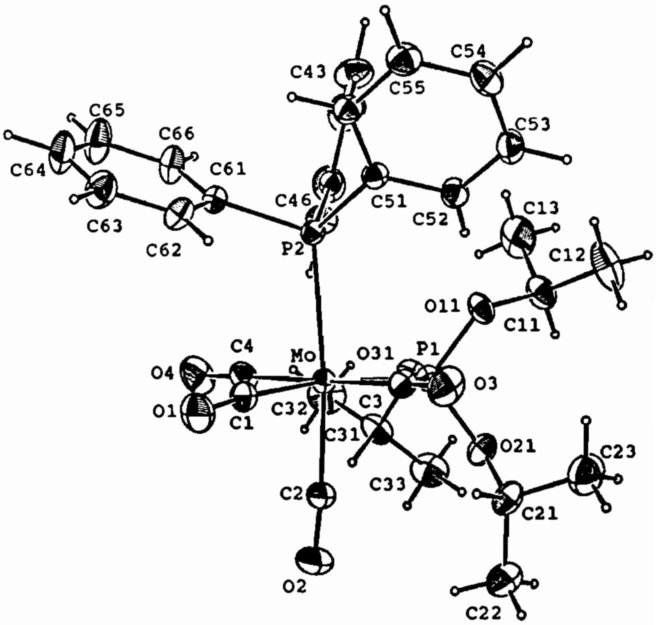

Fig. 1. Molecular structure of **II** showing the atom numbering scheme. Non-hydrogen atoms are drawn with 40% ellipsoids. Selected bond lengths and angles: Mo–P(1) 2.491(1), Mo–P(2) 2.557(1), Mo–C(1) 1.972(4), Mo–C(2) 1.974(4), Mo–C(3) 2.010(4), Mo–C(4) 2.014(4), O(11)···C(52) 3.35 Å; P(1)–Mo–P(2) 94.12(3)°.

The molecular structure for *cis*-$(PPh_3)(P(O\text{-}i\text{-}C_3H_7)_3)Mo(CO)_4$ (**II**)† synthesized from *cis*-$(pip)_2Mo(CO)_4$ (pip = piperidine) by the method of Darensbourg and Kump [7], determined employing single crystal X-ray diffraction methods††, is shown in Fig. 1, which also lists pertinent bond lengths and angles. The molybdenum is bonded to four carbonyl groups and the two phosphorus atoms at usual distances and with angles as expected on the basis of the steric demands of the various ligands [8]. The phenyl defined by C51–C56 is unusually [9] oriented, in such a fashion that it is virtually perpendicular to the other two rings. In this orientation, one of the *ortho* hydrogens (that bonded to C52) points directly toward one of the phosphite oxygens and the C52···O11 separation is 3.35 Å. Within this vector, the C–H and H···O distances are 0.88 and 2.49 Å, respectively, and the C52–H···O11

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**Darensbourg and co-workers have shown that intramolecular M–*N*–H···O–P– hydrogen bonding inhibits dissociation of pip relative to that observed in complexes which contain no P–O–R functionality; this interaction is clearly observed in *cis*-$(pip)(P(OMe)_3)M(CO)_4$ (M = Cr, Mo), the structures of which have been reported [2]. Basolo and co-workers have proposed that *inter*molecular C–H hydrogen bonding can influence reaction rates. They have attributed the observed decrease in the rate of CO displacement from $Co_4(CO)_{12}$ by trialkyl phosphites in chloroform to $Cl_3C\text{–}H\cdots O\text{–}P$ hydrogen bonding between $CHCl_3$ and the phosphite [3].

†Further characterization of **II**: *Anal.* (Midwest Microlabs, Inc., Indianapolis, IN): Calc. for $C_{31}H_{36}MoO_7P_2$: C, 54.87; H, 5.31. Found: C, 55.73, 5.34%. IR (cyclohexane solution): ν(CO) = 2026(m), 1936(s), 1914(vs), 1898(s) cm^{-1}.

††Structural data: space group $P2_1/n$, $a = 9.7416(7)$, $b = 22.558(3)$, $c = 15.481(2)$ Å, $\beta = 99.373(9)$°, $V = 3356.5(2)$ Å^3, $Z = 4$, $D_{calc} = 1.343$ g cm^{-3}. The structure was solved by Patterson methods and refined using full matrix least-squares based on *F*. All non-hydrogen atoms were refined anisotropically and two potentially interesting hydrogens were refined isotropically. Refinement of 3249 reflections ($I > 3\sigma(I)$) led to $R = 0.027$, $R_w = 0.030$. See also 'Supplementary material'.

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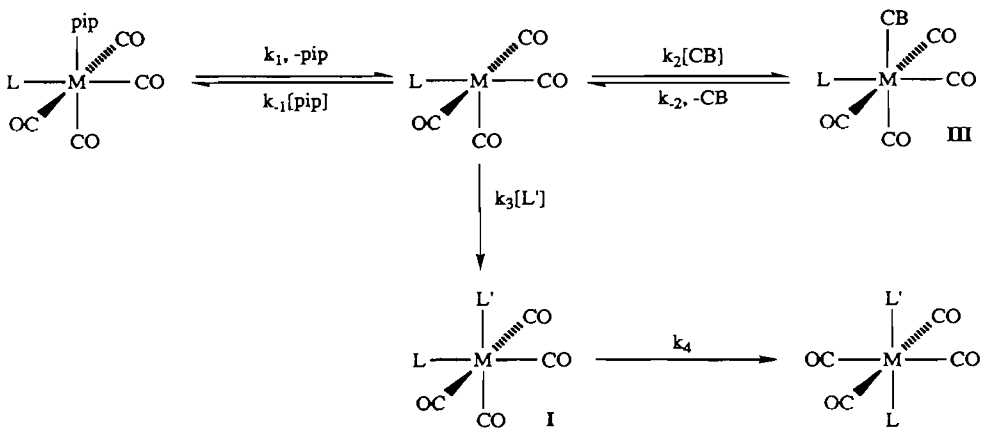
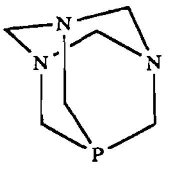


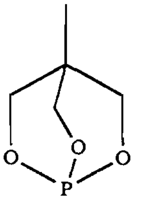
Scheme 1.

angle is 163°. These geometries are indicative of a weak –C–H···O– interaction [1].

Rates of CB displacement from *cis*-(CB)(L)Mo(CO)$_4$ intermediates (**III**), Scheme 1 [10]*, produced by pulsed laser flash photolysis from *cis*-(pip)(L)Mo(CO)$_4$, indicate that intramolecular –C–H···O– hydrogen bonding may also influence reactivity. Chlorobenzene loss from **III** to afford *cis*-(L)(L′)Mo(CO)$_4$ products (**I**, Scheme 1; $L' = P(O\text{-}i\text{-}C_3H_7)_3$), is largely steric in nature and is significantly accelerated (*c.* four-fold) where L is 3,5,8-triaza-1-7-phosphademantane, $P(CH_2NCH_2)_3$ (**IV**), rather than 4-methyl-2,5,7-trioxa-1-phosphabicyclo[2.2.1]octane, $P(OCH_2)_3CCH_3$ (**V**) [11, 12]**. Given the near identity of the cone angles for **IV** and **V** (101 and 102°, respectively) [12, 13] the difference in the rate of CB dissociation is most reasonably attributed to the structure of *cis*-(CB)($P(OCH_2)_3CCH_3$)Mo(CO)$_4$, in which the O in **V** is positioned to interact with a CB hydrogen *ortho* to Cl to afford intramolecular Mo–Cl–C–H···O–P hydrogen bonding in a manner analogous to that observed in **II**; in *cis*-(CB)($P(CH_2NCH_2)_3$)Mo(CO)$_4$, no such interaction can exist.



IV



V

Further studies designed to probe related intramolecular hydrogen bonding effects, particularly in metal carbonyl solvates [14]† are in progress.

Supplementary material

Tables of positional parameters and their e.s.d.s; general anisotropic displacement parameter expressions, *U*s; bond lengths in angstroms; bond angles in degrees; and structure factors are available from the authors upon request.

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[*] The kinetics data were obtained via pulsed laser flash photolysis studies of *cis*-(pip)(L)Mo(CO)$_4$ in chlorobenzene solution, which afforded **III** *in situ*, employing $P(O\text{-}i\text{-}C_3H_7)_3$ as the trapping nucleophile at 31.1 °C. The concentration range employed was $0.1 < [P(O\text{-}i\text{-}C_3H_7)_3] < 1.1$. Experimental details were similar to those cited in ref. 10.

[**] A multilinear regression [11] was employed to fit log $k = a\nu = b\theta = c$. In this equation, $\log k = k_{-2}k_3/k_2[CB]$ (Scheme 1) for dissociation of CB, θ is the Tolman steric parameter [12] and ν is the highest energy A′ carbonyl stretching mode (cyclohexane solution) for the *cis*-(pip)(L)Mo(CO)$_4$ photolysis precursors for five *cis*-(CB)(L)Mo(CO)$_5$ complexes ($L = P(OCH_2)_3CCH_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, $P(OC_6H_5)_3$. The regression fits the data as $\log k = 0.0218\theta - 0.0037\nu$ ($R = 0.979$), indicating that influences of L on k are predominantly steric in nature. The inclusion of the complex for $L = P(CH_2NCH_2)_3$ into the regression diminishes R to 0.050.

[†] For example, hydrogen bonding involving the –C–H functionality may also account for the greater rate (by a factor of about 2) for dissociation of n-heptane than cyclohexane from photogenerated (alkane)W(CO)$_5$ transients in which the alkane is bonded to W by an ‘agostic’ W–H–C– interaction [14]. A W–H–C–C–H···O–C– hydrogen bonding interaction involving a carbonyl *cis* to the alkane is expected to be stronger for cyclohexane that for n-heptane based on the greater rigidity of the ring system in the former. Activation parameters reported for alkane–W bond-breaking from cyclohexane and n-heptane indeed indicate that the difference in rates arises from an entropy effect, as would be expected on this basis. An examination of molecular models suggests that such interactions are sterically reasonable.

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