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THE CRYSTAL STRUCTURE OF BENZYLTRICARBONYL-η^5-CYCLOPENTADIENYLMOLYBDENUM(II) AND RELATED SUBSTITUTED BENZYL COMPLEXES

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Summary

The crystal structures of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_5)]$, $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4\text{-}2\text{-}Me)]$ and $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_2\text{-}2,4,6\text{-}Me_3)]$ have been determined. With increases in intramolecular interaction arising from the degree of *ortho*-substitution in the benzyl group, the molybdenum–methylene carbon bond length (Mo–C(11)) and the bond angle, (Mo–C(11)–C(1)), around the methylene carbon generally increase. The structural features are compared with rates of CO insertion into the molybdenum–carbon bonds in these molecules.

Introduction

Steric factors have been observed [1,2] to have a strong influence on the reactivity of molybdenum–carbon σ bonds towards carbon monoxide insertion induced by tertiary phosphines, e.g.

$$[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_5)] + PPh_3 \rightarrow [(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Mo(COCH_2C_6H_5)] \quad (1)$$

Specifically, there is considerable enhancement of the k_1 rate stage of the overall reaction in polar solvents when the size of an alkyl substituent, in an *ortho*-position in a benzyl ligand, is increased [1]. Substitution of both *ortho*-benzyl positions by methyl groups results in a k_1 rate increase over single methyl substitution but di-substitution by the isopropyl group causes complete inhibition of reaction. The

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rate increases have been interpreted in terms of the release of strain in the transition state in which the molybdenum–benzylic carbon bond is partially broken, and the inhibition by very large groups in both *ortho*-positions in terms of a locking of the system which would prevent the required migration of the benzylic carbon atom to an adjacent carbon monoxide group [1]. In an attempt to understand better these reactivity differences, the solid-state structural characteristics of three pertinent compounds, $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_5)]$ (I), $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4\text{-}2\text{-}Me)]$ (II); and $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_2\text{-}2,4,6\text{-}Me_3)]$ (III) have been determined by X-ray diffraction.

Results and discussion

The structures of I, II and III (Fig. 1) involve a distorted pseudo-square pyramidal geometry around molybdenum with the η^5-C_5H_5 group in the apical position and the CO and benzyl ligands in the plane. In this respect they closely resemble $[(\eta^5\text{-}C_5H_5)(CO)_3MoC_2H_5]$ [3], $[(\eta^5\text{-}C_5H_5)(CO)_3MoC_3F_7]$ [4], $[(\eta^5\text{-}C_5H_5)(CO)_3MoCl]$ [5] and $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2COOH)]$ [6]. In each benzyl complex, the methylene group lies above the plane of the three carbonyl carbon atoms and towards the cyclopentadienyl group. The *ortho*-methylbenzyl compound, contains two distinct, but similar, molecules IIa and IIb, in the asymmetric unit. Structural data are collected in Table 2.

Although the Mo–C(11) distance (2.387(3) Å) in the unsubstituted compound, I, and in the 2-methyl compound, II, (2.390(6) Å) are the same, within experimental error, there is a significant increase in the 2,4,6-trimethylbenzyl complex III, (2.417(7) Å). The distances are comparable with those observed in $[(\eta^5\text{-}C_5H_5)(CO)_3MoC_2H_5]$ (2.40(2) Å), $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2COOH)]$ (2.36(2) Å) and $[(\eta^5\text{-}C_5H_5)(CO)_3MoC_3F_7]$ (2.29(1) Å). The Mo–C(11)–C(1) bond angle also increases with the degree of *ortho*-substitution, (I, 113.7(2)°; II, 123.1(3) Å; III, 122.3(5) Å) and is similar to that in the related compounds, $[(\eta^5\text{-}C_5H_5)(CO)_3MoC_2H_5]$ (120.9°) and $[(\eta^5\text{-}C_5H_5)(CO)_3MoC_3F_7]$ (123.3°). The methylene carbon to phenyl ring carbon distance, C(11)–C(1), also increases, but more regularly, across the series. For the unsubstituted benzyl, I, the phenyl group is inclined towards the cyclopentadienyl group whereas in the substituted compounds, II and III, the phenyl and cyclopentadienyl rings are oppositely disposed with respect to the molybdenum centre. (Torsion angles, C(8)–Mo–C(11)–C(1): I, +132°; II, +87°; III, +89°). The dihedral angle between the cyclopentadienyl ring and the least-squares plane through the carbonyl carbon atoms increases steadily across the series (I, 8.93°; II, 10.74°; III, 13.73°). In II, the Mo–C(11) bond is staggered with respect to the cyclopentadienyl ring carbons, but in I and III it is near-eclipsed as is the case for the non-carbonyl ligand in the basal plane of $[(\eta^5\text{-}C_5H_5)(CO)_3MoC_3F_7]$ [4] and $[(\eta^5\text{-}C_5H_5)(CO)_3MoCl]$ [5]. Although there is some variation in the observed cyclopentadienyl ring carbon–carbon distances and in metal–ring carbon distances within each of I, II and III, uncertainties are high; there is no systematic trend which would indicate localisation of ring–metal bonding in, say, a η^3-allyl-η^2-ene structure. Some disorder in the cyclopentadienyl rings, probably resulting indirectly from intramolecular interactions deriving from *ortho*-substitution, is indicated by high thermal parameters (up to 0.22 Å^2 for II and 0.15 Å^2 for III).

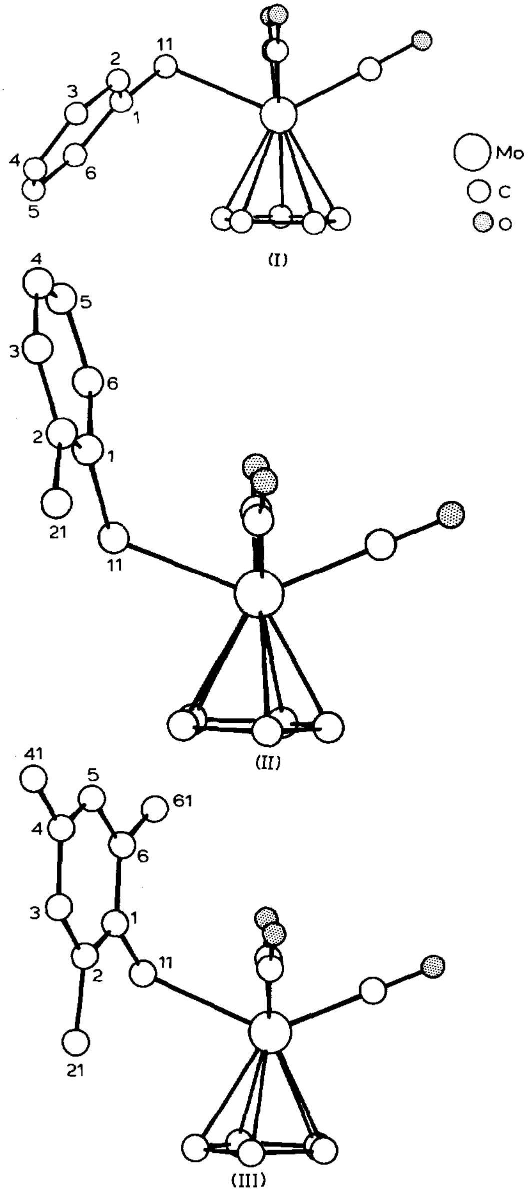

Fig. 1. Molecular configuration and atom numbering scheme for I, II and III (unless otherwise indicated, atoms are carbons).

The general trends, for I, II and III, in the Mo–C(11) bond length, the bond angle Mo–C(11)–C(1), and the dihedral angle C(8)–Mo–C(11)–C(1), are compatible with expected increases in intramolecular interactions associated with an increas-

(Continued on p. 122)

TABLE 1

CRYSTAL DATA AND DATA COLLECTION PARAMETERS FOR I, II AND III

	I	II	III
Formula	$C_{15}H_{10}MoO_3$	$C_{16}H_{12}MoO_3$	$C_{18}H_{18}MoO_3$
M_r	334.2	348.2	378.3
a (Å)	8.863(3)	14.929(5)	20.867(3)
b (Å)	18.080(5)	14.418(5)	11.088(2)
c (Å)	16.806(4)	6.918(2)	7.132(1)
α (°)		100.29(2)	
β (°)		90.55(2)	
γ (°)		94.68(3)	
V (Å^3)	2693.0	1459.8	1650.2
d_{measd} (g cm^{-3})	1.61	1.58	–
d_{calcd} (g cm^{-3})	1.65	1.58	1.52
Z	8	4	4
$F(000)$	1328	696	768
μ (cm^{-1})	9.59	8.88	7.92
Space group	$Pbca$	$P\bar{1}$	$P2_12_12_1$
Diffractometer	Nicolet $P2_1$	Nicolet $P2_1$	Nicolet $P2_1$
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
Wavelength (Å)	0.71069	0.71069	0.71069
2θ max (°)	50	60	60
Crystal size (mm)	0.50×0.50×0.25	0.40×0.25×0.12	0.50×0.15×0.15
Structure solution	Patterson	Patterson	Patterson
R	0.03	0.032	0.034
R_w	unit weights	0.032	0.036
$w = [A\sigma^2F_0 + B(F_0)^2]^{-1}$			
A	–	2.8	0.6
B	–	2×10^{-4}	7×10^{-4}
data used in refinement	2787	3387	1860
$I > n\sigma(I)$ where $n =$	2.5	2.5	2.5

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR I, II AND III

	I	IIa	IIb	III
Mo–C(11)	2.387(3)	2.394(6)	2.386(6)	2.417(7)
Mo–C(7)	1.978(3)	1.978(6)	1.987(6)	1.981(8)
Mo–C(8)	1.969(3)	1.998(6)	1.967(6)	1.979(7)
Mo–C(9)	1.987(3)	1.985(6)	1.970(6)	1.971(8)
Mo–Cp(1)	2.325(3)	2.373(6)	2.333(8)	2.358(9)
Mo–Cp(2)	2.327(3)	2.361(6)	2.355(9)	2.331(9)
Mo–Cp(3)	2.340(3)	2.311(7)	2.301(9)	2.326(8)
Mo–Cp(4)	2.371(3)	2.341(9)	2.317(10)	2.377(8)
Mo–Cp(5)	2.353(3)	2.326(7)	2.302(7)	2.406(8)
C(11)–C(1)	1.477(4)	1.483(8)	1.482(8)	1.493(11)
C(11)–Mo–C(7)	75.5(1)	77.8(2)	73.5(2)	72.8(3)
C(11)–Mo–C(8)	73.9(1)	74.9(2)	77.9(2)	76.4(3)
C(11)–Mo–C(9)	131.8(1)	135.6(2)	133.9(2)	133.8(3)
C(11)–Mo–Cp(1)	91.2(1)	82.3(2)	83.7(3)	98.1(3)
C(11)–Mo–Cp(2)	125.8(1)	112.4(3)	112.0(3)	132.8(3)
C(11)–Mo–Cp(3)	140.3(1)	138.6(3)	139.5(3)	138.0(3)
C(11)–Mo–Cp(4)	109.1(1)	116.7(3)	118.2(4)	104.4(3)
C(11)–Mo–Cp(5)	82.6(1)	84.9(3)	86.9(3)	82.2(3)
Mo–C(11)–C(1)	113.7(2)	123.7(4)	122.5(3)	122.3(5)

TABLE 3

ATOMIC COORDINATES ($\times 10^4$) FOR I, II AND III

Atom	x	y	z
Structure I			
Mo	2350(1)	3939(1)	5911(1)
C(1)	2371(4)	5689(2)	6410(2)
C(11)	1259(3)	5121(2)	6176(2)
C(2)	2634(5)	5858(2)	7208(2)
C(3)	3721(5)	6379(2)	7430(2)
C(4)	4546(4)	6740(2)	6867(2)
C(5)	4273(4)	6605(2)	6074(2)
C(6)	3218(4)	6087(2)	5852(2)
C(7)	2771(4)	4526(2)	4943(2)
O(7)	3024(3)	4837(1)	4362(2)
C(8)	130(4)	3785(2)	5920(2)
O(8)	−1137(3)	3679(2)	5938(2)
C(9)	2054(4)	3233(2)	5033(2)
O(9)	1854(4)	2832(2)	4509(2)
Cp(1)	4421(4)	4215(2)	6707(2)
Cp(2)	4753(4)	3558(2)	6290(2)
Cp(3)	3729(4)	3009(2)	6549(2)
Cp(4)	2800(4)	3322(2)	7133(2)
Cp(5)	3225(4)	4065(2)	7226(2)
Structure IIa			
Mo	2279(1)	1309(1)	1082(1)
C(1)	4214(4)	2229(4)	3733(8)
C(11)	3701(4)	2197(5)	1873(9)
C(2)	4871(4)	1622(5)	3863(10)
C(21)	5106(6)	889(6)	2189(15)
C(3)	5363(5)	1715(6)	5671(15)
C(4)	5195(6)	2411(7)	7238(11)
C(5)	4562(5)	3035(6)	7065(11)
C(6)	4078(4)	2920(4)	5348(9)
C(7)	2903(4)	495(4)	2581(9)
O(7)	3215(3)	−28(3)	3398(7)
C(8)	2016(4)	2425(4)	3091(9)
O(8)	1838(3)	3061(3)	4177(8)
C(9)	1298(4)	788(4)	2596(8)
O(9)	734(3)	483(3)	3468(7)
Cp(1)	2839(5)	1134(6)	−2151(8)
Cp(2)	2249(7)	338(6)	−2056(9)
Cp(3)	1389(6)	683(8)	−1669(9)
Cp(4)	1458(6)	1646(8)	−1571(11)
Cp(5)	2346(6)	1922(6)	−1809(9)
Structure IIb			
Mo	1353(1)	7064(1)	6097(1)
C(1)	2445(4)	5308(3)	7582(7)
C(11)	2025(4)	5603(4)	5865(8)
C(2)	3347(4)	5495(4)	8093(10)
C(21)	3998(5)	5956(5)	6827(14)
C(3)	3648(5)	5210(5)	9802(12)
C(4)	3098(6)	4733(5)	10914(11)
C(5)	2234(6)	4503(4)	10337(11)
C(6)	1912(4)	4795(4)	8738(9)
C(7)	2393(4)	7419(4)	7969(8)
O(7)	2968(3)	7683(3)	9080(6)

continued

TABLE 3 (continued)

Atom	x	y	z
C(8)	510(4)	6214(4)	7271(9)
O(8)	−18(3)	5738(4)	7936(8)
C(9)	874(4)	7941(4)	8281(8)
O(9)	594(3)	8456(3)	9531(6)
Cp(1)	1811(7)	6976(7)	2859(11)
Cp(2)	1854(7)	7911(6)	3645(10)
Cp(3)	982(10)	8104(6)	4113(9)
Cp(4)	437(5)	7266(10)	3507(13)
Cp(5)	989(8)	6611(6)	2803(11)
Structure III			
Mo	982(1)	695(1)	1028(1)
C(1)	1713(3)	3410(7)	2064(11)
C(11)	1788(3)	2260(7)	995(11)
C(2)	1369(3)	4375(7)	1301(11)
C(21)	1069(5)	4301(10)	−643(13)
C(3)	1317(4)	5449(7)	2325(15)
C(4)	1602(3)	5599(7)	4067(15)
C(41)	1532(5)	6774(8)	5156(20)
C(5)	1952(4)	4652(6)	4786(14)
C(6)	1995(3)	3551(7)	3831(12)
C(61)	2372(4)	2540(7)	4697(13)
C(7)	1758(4)	24(6)	2242(11)
O(7)	2202(3)	−407(5)	2887(11)
C(8)	648(3)	1905(7)	2819(10)
O(8)	412(3)	2574(4)	3852(10)
C(9)	615(4)	−331(7)	3014(11)
O(9)	410(3)	−913(5)	4181(9)
Cp(1)	1165(4)	−85(11)	−2001(12)
Cp(2)	675(4)	−756(9)	−1161(10)
Cp(3)	144(4)	34(8)	−862(11)
Cp(4)	311(4)	1155(9)	−1568(11)
Cp(5)	955(4)	1123(10)	−2278(10)

ing extent of *ortho*-substitution in the benzyl groups and are in line with the trend in k_1, the rate constant for the first stage of the CO insertion process induced by triphenylphosphine in acetonitrile solution (I: k_1 3.2×10^{-4} s^{-1}; II: k_1 7.3×10^{-4} s^{-1}; III: k_1 8.5×10^{-4} s^{-1}) [1]. A longer Mo–C(11) bond suggests a lower bond energy and a correspondingly lower activation energy in this reaction stage in which partial breaking of the bond takes place. The effect of the increasing bond angle Mo–C(11)–C(1) on reactivity may arise through an increase in steric interactions in the ground state, relative to the transition state of the k_1 process, which again would serve progressively to lower the activation energy.

Experimental

Compounds were prepared as described previously [1]. Crystals of I and III were grown from dichloromethane/hexane at −15°C and III from acetonitrile at −15°C.

Crystal data, and details of structure solution and refinement, are given in Table 1. The structures were solved, and all non-hydrogen atoms anisotropically refined, using SHELX-76 [7], on an IBM 3083 computer. Hydrogen atoms were allowed to refine isotropically. Neutral atom scattering factors were used [8] while heavy atoms were corrected for anomalous dispersion. Final residuals, R and R_w, are defined as $R = [\Sigma\{ |F_0| - |F_c| \}/|F_o|]$ and $R_w = [(\Sigma w\{ |F_0| - |F_c| \}^2/\Sigma w|F_0|^2)^{1/2}]$.

Relevant bond distances and angles are in Table 2 and atomic coordinates in Table 3. Full tables of bond lengths and angles, thermal parameters, and observed and calculated structure factors are available from CHLK.

Acknowledgements

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