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Metal dimer chemistry: Me_3NO induced substitution reactions of $(\eta^5\text{-}C_5H_5)MoMn(CO)_8$. X-ray structure determination of $(\eta^5\text{-}C_5H_5)MoMn(CO)_7[P(OMe)_3]$

Wayne L. Ingham, David G. Billing, Demetrius C. Levendis and Neil J. Coville*
Applied Chemistry and Chemical Technology Unit, Department of Chemistry, University of the Witwatersrand, P.O. WITS 2050, Johannesburg (South Africa)

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Abstract

Reaction of $(\eta^5\text{-}C_5H_5)MoMn(CO)_8$ (**1**) with $P(OMe)_3$ and t-BuNC in the presence of Me_3NO results in facile Mo–Mn bond cleavage products as well as the synthesis of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_4[P(OMe_3)]$ (**3**) in which the $P(OMe)_3$ occupies a site *trans* to the Mo–Mn bond. The crystal structure of **3** is reported (space group $P2_1/c$, $a=13.064(4)$, $b=7.1325(8)$, $c=22.227(5)$ Å $\beta=104.91(1)°$. Final R and R_w values were 0.058 and 0.048 ($w=K\sigma^2(F)$). The non-bridged Mo–Mn bond length is the largest reported to date (3.112(1) Å) and the equatorial Mn–CO bond lengths are longer than those in the parent unsubstituted dimer (**1**).

Introduction

The substitution chemistry of metal carbonyl dimer complexes, with particular emphasis on the site selectivity problem, has been investigated by us [1] and other groups [2] in some detail. From these studies it is clear that a CO substitution reactivity sequence can be generated [3] and that this sequence correlates well with a knowledge of the reactivity of the monometallic fragments.

Recently Pope and Wrighton reported on the low temperature photochemical reactions of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5]$ (**1**) [4] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_5]$ (**2**) [5] and reported the synthesis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_4L]$ ($L=P(n\text{-}Bu)_3$, PPh_3) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_4L]$ ($L=P(OPh)_3$, PPh_3). These results contrasted with our findings on the reaction of **2** with group 15 donor ligands [3]. In our study we observed that the reaction of $[(\eta^5\text{-}C_5H_5)FeMn(CO)_7]$ with group 15 donor ligands, L, yielded:

(i) cleavage products $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[Mn_2(CO)_8L_2]$ when the reaction was carried out in the presence of Me_3NO;

(ii) the salt $[(\eta^5\text{-}C_5H_5)Fe(CO)L_2]^+$ when thermal, room temperature reaction conditions were employed.

It is thus apparent that a change in the synthetic strategy has a major impact on the chemistry of the $Mn(CO)_5$ group. To further investigate the chemistry of these dimers we have carried out the Me_3NO assisted substitution reaction of **1** with t-BuNC and $P(OMe)_3$ and report our results herein.

Experimental

General

$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and $[Mn_2(CO)_{10}]$ were purchased from Strem Chemicals. Me_3NO was purchased from Aldrich and dried by azeotrope in toluene. $[(\eta^5\text{-}C_5H_5)MoMn(CO)_8]$ was prepared by the literature method [6]. Solvents were distilled from appropriate drying agents and degassed prior to use. Elemental analyses were performed by the Division of Energy and Technology Laboratories, CSIR, Pretoria, South Africa. NMR spectra were recorded on a Bruker 200 MHz spectrometer and IR spectra on a Perkin-Elmer 580B spectrometer.

Reaction of $[(\eta^5\text{-}C_5H_5)MoMn(CO)_8]$ with L (L = t-BuNC, $P(OMe)_3$)

$[(\eta^5\text{-}C_5H_5)MoMn(CO)_8]$ (0.2 mmol) and L (1.1 equiv.) were dissolved in CH_2Cl_2 (20 ml). Dry Me_3NO (1.5 equiv.) was added as a solid and the solution stirred for 1 h. After solvent removal the products

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*Author to whom correspondence should be addressed.

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were purified by column chromatography on silica (C_6H_6/hexane mixtures as eluent).

L = t-BuNC

A red and pale yellow band were eluted from the column. After solvent removal the products from the bands were identified as $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (25% yield) and $[Mn(CO)_4(t\text{-}BuNC)]_2$ [7] (37% yield) by comparison with IR and NMR spectra of independently synthesised samples.

L = P(OMe)₃

A red and two yellow bands were eluted from the column. The red material was identified as $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_3]_2$ (20% yield) as described above. The first pale yellow product was identified as $[Mn(CO)_4P(OMe)_3]_2$ (35% yield) by comparison of IR and NMR spectral data with an independently prepared sample [8]. The second yellow material was recrystallised from a C_6H_6/hexane mixture at 5 °C (20% yield). The orange crystals obtained were characterised by NMR spectroscopy (C_6D_6: ^1H, 4.77 ppm (5H) and 3.19 ppm (d, 9H, J(PH) 12 Hz) (internal TMS standard); ^{31}P, 187.9 ppm (external $PO_4{}^{3-}$ standard)), IR spectroscopy (CH_2Cl_2: ν(CO) 2056 w, 2018 m, 1995 vs, 1963 m, 1885 (sh), 1876 m) and elemental analysis (Calc: C, 33.61; H, 2.63. Found: C, 33.58; H, 2.45%).

Crystal structure determination of $[(\eta^5\text{-}C_5H_5)MoMn(CO)_7P(OMe)_3]$

Crystal data

$C_{15}H_{14}O_{10}PMoMn$, $M = 536.1$, monoclinic, space group $P2_1/c$, $a = 13.064(4)$, $b = 7.1325(8)$, $c = 22.227(5)$ Å, $\beta = 104.91(1)°$, $V = 2001.4$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections with range $17 \leqslant \theta \leqslant 23$), $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 1.78$ g cm^{-3}, orange rectangle, crystal dimensions $0.07 \times 0.09 \times 0.05$ mm, $F(000) = 1063.79$, $\mu = 12.69$ cm^{-1}.

Data collection and processing

Oscillation and Weissenberg photographs were used to establish crystal quality, preliminary cell constants and space group. Nonius CAD4 diffractometer, ω scan, graphite-monochromated Mo Kα radiation; 5565 reflections measured ($3 \leqslant \theta \leqslant 25$, $-15 \leqslant h \leqslant 14$, $-8 \leqslant k \leqslant 8$, $0 \leqslant l \leqslant 26$) 3238 unique (merging $R_{int} = 0.04$), giving 2531 with $F_0 \geqslant 3\sigma(F_0)$. Empirical absorption corrections [9] were applied. Linear and approximate isotropic crystal decay, *c.* 6%, was corrected for, during processing.

Structure analysis and refinement

Patterson (Mo and Mn), and difference Fourier techniques were used to solve the structure using SHELXS86 [10a]. The structure was refined with SHELX76 [10b] in two blocks, with all non-hydrogen atoms anisotropic and hydrogen in calculated positions with one common refined U_{iso} ($= 0.33(6)$ Å^2). The weighting scheme used was $\omega = K\sigma^2(F)$. Final R and R_w were 0.058 and 0.048. Final fractional coordinates and equivalent isotropic temperature factors, as well as selected bond lengths and angles are given in Tables 1 and 2. Geometrical calculations and graphical output were produced with the PC version of the program NRCVAX [11].

Results and discussion

The reaction of **1** with t-BuNC in the presence of Me_3NO did not yield the expected substituted dimer. Rather the products obtained from the reaction were $[Mn_2(CO)_8(CNBu\text{-}t)_2]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ which were characterised by IR

TABLE 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å$^2 \times 10^3$) for **3**

	x/a	y/b	z/c	U_{eq}
Mo	2865(1)	834(1)	298(0)	47(0)
Mn	2164(1)	602(2)	1532(1)	48(0)
C10	2817(7)	−1701(13)	1681(4)	61(2)
C13	3400(7)	1912(11)	1763(4)	53(2)
C11	906(8)	−636(14)	1301(4)	67(3)
C12	1414(7)	2719(13)	1231(4)	58(2)
C7	1616(7)	−852(13)	186(4)	60(2)
C8	4026(8)	−355(13)	883(4)	65(3)
C6	3231(9)	−1167(14)	−237(4)	75(3)
C1	3786(8)	3681(12)	274(5)	70(3)
C2	2828(9)	4167(11)	429(4)	74(3)
C3	1963(7)	3589(10)	−110(4)	51(2)
C4	2392(9)	2805(12)	−567(4)	63(3)
C5	3525(9)	2837(12)	−339(5)	67(3)
C16	3846(7)	−175(13)	3172(4)	73(3)
C14	1083(8)	−971(14)	3254(4)	99(3)
C15	1694(9)	4396(12)	2718(5)	96(4)
O10	3177(6)	−3126(8)	1784(3)	87(2)
O13	4170(5)	2760(9)	1949(3)	93(2)
O11	91(6)	−1401(10)	1181(3)	114(2)
O12	897(6)	4007(9)	1059(3)	65(2)
O7	902(6)	−1816(10)	41(3)	110(2)
O8	4818(6)	−1049(11)	1197(3)	78(3)
O6	3431(7)	−2275(10)	−550(3)	118(3)
O16	2956(4)	1104(8)	3045(2)	73(2)
O14	1320(5)	−848(8)	2651(3)	86(2)
O15	1271(5)	2535(8)	2631(3)	68(2)
P1	1962(2)	836(3)	2471(1)	47(1)

$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j(\mathbf{a}_i \cdot \mathbf{a}_j)$. Starred items are isotropic temperature factors.

TABLE 2. Selected bond lengths (Å) and angles (°) for **1** (L=CO) and **3** (L=P(OMe)$_3$)

	1	3
Bond lengths		
Mo–Mn	3.083(8)	3.112(1)
Mo–C6	1.980(7)	1.993(11)
Mo–C7	1.960(7)	1.991(10)
Mo–C8	2.010(2)	1.922(9)
Mn–C10	1.739(6)	1.841(9)
Mn–C11	1.743(2)	1.820(10)
Mn–C12	1.752(6)	1.831(9)
Mn–C13	1.747(2)	1.821(9)
Mn–L	1.704(6)	2.176(2)
Mo–C–5 av.	2.326(8)	2.355(9)
C1–C5 av.	1.421(7)	1.436(12)
Bond angles		
C6–Mo–Mn	123.2(3)	131.2(3)
C7–Mo–Mn	76.3(3)	70.1(3)
C8–Mo–Mn	70.85(5)	74.9(3)
C6–Mo–C7	69.11(11)	78.9(4)
C7–Mo–C8	106.65(4)	107.2(4)
C6–Mo–C8	77.68(12)	79.6(4)
C10–Mn–Mo	100.2(4)	88.7(3)
C11–Mn–Mo	77.83(3)	103.0(3)
C12–Mn–Mo	77.5(3)	83.4(3)
C13–Mn–Mo	99.04(9)	77.3(3)
C10–Mn–L	87.5(3)	93.5(3)
C11–Mn–L	92.59(1)	89.1(3)
C12–Mn–L	95.0(3)	95.9(3)
C13–Mn–L	91.67(6)	90.5(3)
C10–Mn–C12	177.36(2)	168.8(4)
C11–Mn–C13	177.08(2)	178.1(4)
Mo–Mn–L	167.09(5)	167.7(1)

and NMR spectroscopy and thin layer chromotography [7]. The results suggest that substitution did indeed occur at Mn (as expected from the known reactivities of [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ and Mn$_2$(CO)$_{10}$ with t-BuNC [12, 13]) but that the product fragmented into monometallic radicals at room temperature. These radicals then recombined to form the homometallic dimers.

By contrast reaction of **1** with P(OMe)$_3$ in the presence of Me$_3$NO yielded the cleaved products, [Mn(CO)$_4$P(OMe)$_3$]$_2$ and [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ as well as the new stable product [(η^5-C$_5$H$_5$)MoMn(CO)$_7$P(OMe)$_3$] (**3**) which was characterised by IR and NMR spectroscopy and elemental analyses. Pope and Wrighton [4] have previously shown that the analogous complexes [(η^5-C$_5$H$_5$)MoMn(CO)$_7$L] (L=P(n-Bu)$_3$, PPh$_3$), synthesised via a photochemical route, had the L group attached to the Mn atom.

To rationlise the above results obtained on reaction of **1** with t-BuNC and P(OMe)$_3$, a crystal structure determination of **3** was undertaken.

Crystal structure determination

The crystal structure of **3** is shown in Fig. 1. This Figure also indicates the numbering scheme used. Features of the structure pertinent to this study include the following.

(1) The P(OMe)$_3$ ligand occupies an axial site on the Mn atom. Since P(OMe)$_3$ is a small ligand (Tolman cone angle $\theta = 107°$ [14]) it may have been expected to occupy the electronically preferred equatorial site. Also, the preferential substitution of a CO ligand on Mn rather than on Mo is consistent with expected reactivity trends and the earlier study by Pope and Wrighton [4].

(2) The Mo–Mn bond length (3.112(1) Å) is slightly longer than in the unsubstituted dimer (3.083(5) Å) [15]. This is not unexpected as a general bond lengthening occurs on replacement of a CO group by an axial ligand in metal dimer carbonyl complexes [16]. The bond length is the longest Mo–Mn distance reported to date. Most of the other structures have Mo–Mn bonds which contain bridging groups which result in shortened Mo–Mn distances typically in the range 2.68–3.09 Å [17].

(3) The Mo–Mn bond length is close to the average bond length (3.074 Å) for Mn$_2$(CO)$_8$(PR$_3$)$_2$ (*d*(Mn–Mn)=2.912(3) Å) [18] and [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$(*d*(Mo–Mo)=3.235(1) Å) [19].

(4) The cyclopentadienyl ring shows normal bond lengths and angles, as was found previously for **1** [15].

(5) The P(OMe)$_3$ ligand has normal bond lengths and angles [20].

(6) There is a marked increase in the Mn–CO (equatorial CO) bond lengths on going from **1** to **3**. It thus appears that the two axial ligands on Mn activate the remaining CO groups.

(7) The plane containing the Mn atom and the four equatorial CO groups is not perpendicular to the Mn–Mo bond, but bends in towards the cyclopentadienyl ring. This is also observed for structure **2**. This phenomenon has been commented on previously [5] and relates to the size of the cyclopentadienyl ligand. The cyclopentadienyl ring occupies less space than three CO groups. Figure 2(a) and (b) indicates the positions of the various ligands in **1** and **3**, respectively, which highlight this bonding phenomenon.

(8) The above plane bending results in a nonlinear Mo–Mn–P bond angle (167.7°). This is also observed in **1** (angle=167.4°). The axial group bends in towards the cyclopentadienyl side of the molecule.

Product stability

The crystal structure determination permits a rationalisation of the different products formed in the

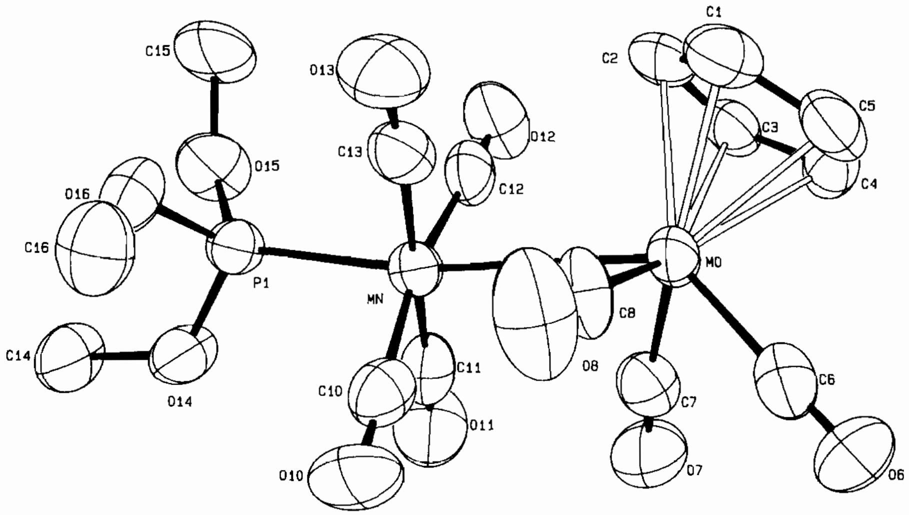

Fig. 1. ORTEP diagram of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{P(OMe)}_3]$.

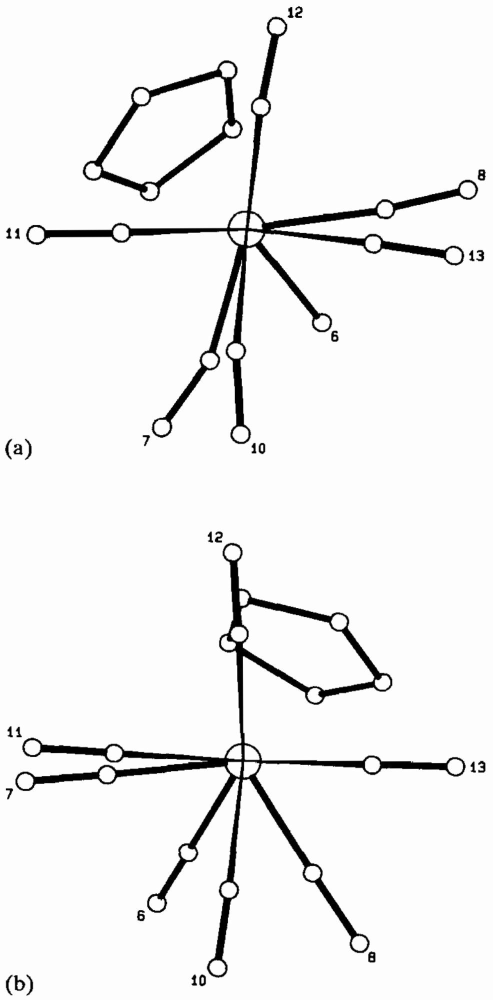

Fig. 2. Projection down the Mo–Mn bond showing the positions of the CO ligands relative to the cyclopentadienyl ligand for: (a) structure **1**; (b) structure **3** (the axial ligand on Mn is omitted for clarity).

reactions of **1** with L (L=t-BuNC and P(OMe)_3) in the presence of Me_3NO. If L is small, and nucleophilic, equatorial substitution on Mn is favoured both electronically and sterically. However, the metal fragment attached to the Mn atom will influence the size of the ligand that can fit into the equatorial site on Mn. In **2**, replacement of CO by t-BuNC is permitted sterically, but the larger size of the $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3$ fragment in **3**, relative to the $(\eta^5\text{-C}_{51\text{H}5})\text{Fe(CO)}_2$ fragment in **2**, results in extreme steric crowding and metal–metal bond cleavage.

Substitution of CO by the large P(OMe)_3 in the Me_3NO assisted reaction results in a further mechanism to relieve steric strain namely axial–equatorial isomerisation. Thus, replacement of CO by P(OMe)_3 in **1** results in P(OMe)_3 isomerisation as well as Mo–Mn bond cleavage. This is possible since the P(OMe)_3 is less electron donating than t-BuNC and its isomerisation can be influenced by steric considerations [21]. Replacement of CO by P(OMe)_3 in **2**, however, reveals that Fe–Mn bond cleavage takes precedent over axial–equatorial isomerisation. It is possible that in **2** the more 'open' equatorial site permits the P(OMe)_3 to occupy the equatorial site but the instability associated with this complex results in Fe–Mn bond fragmentation rather than the isomerisation reaction. This would suggest that $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Mn(CO)}_4\text{P(OMe)}_3]$, in which P(OMe)_3 is in an axial position, could be synthesised by indirect routes, e.g. by photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$ and diax-$[\text{Mn}_2\text{(CO)}_8]\text{P(OMe}_3)]_2]$ [5].

In summary the substitution reactions of **1** suggest that we are observing a type of 'inverse' steric effect in which small ligands lead to product instability. This unusual phenomenon is a direct consequence of having two metals in close proximity to each other and further highlights the unexpected chemistry that is associated with metal dimers.

Conclusions

The reaction of **1** with $P(OMe)_3$ in the presence of Me_3NO gives cleavage products as well as the axial Mn substituted complex $[(\eta^5\text{-}C_5H_5)MoMn(CO)_7(P(OMe)_3)]$ which has been completely characterised by IR and NMR spectroscopy and X-ray crystallography. The reaction of **1** with t-BuNC/Me_3NO has also been investigated but in this reaction only Mo–Mn cleavage products are obtained. The results from the Me_3NO induced substitution reaction can be explained by an 'inverse' steric effect in which both the electronic and steric characteristics of the ligands determine the overall products generated in the reaction.

Acknowledgements

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