

Metal Cyclic Carbene Complexes. A Molybdenum Complex of 2-Oxacyclopentylidene: Synthesis and X-Ray Structure of $[\text{MoI}(\text{CO})_2(\text{C}_4\text{H}_6\text{O})(\eta\text{-C}_5\text{H}_5)]$

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Reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ with $\text{I}[\text{CH}_2]_3\text{I}$ in tetrahydrofuran (THF) or of $[\text{Mo}\{\text{[CH}_2\text{]}_3\text{Br}\}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ with LiI in THF affords the carbene complex

$[\text{MoI}(\text{CO})_2\{\text{C}\cdot\text{O}\cdot\text{[CH}_2\text{]}_2\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)]$, which has been characterised by X-ray diffraction, while treatment of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ with $\text{I}[\text{CH}_2]_4\text{I}$ leads to $[(\eta\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo}[\text{CH}_2]_4\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$.

Reactions of $\text{Br}[\text{CH}_2]_n\text{Br}$ ($n = 3, 4$) with $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ proceed by substitution of only one halide atom forming the complexes $[\text{Mo}\{\text{[CH}_2\text{]}_n\text{Br}\}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ ($n = 3, 4$)¹ while

treatment of $\text{Br}[\text{CH}_2]_n\text{Br}$ ($n = 3-6$) with $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ results in replacement of both halide atoms.² The product obtained from $[\text{Mn}(\text{CO})_5]^-$ and $\text{Br}[\text{CH}_2]_3\text{Br}$ has been identi-

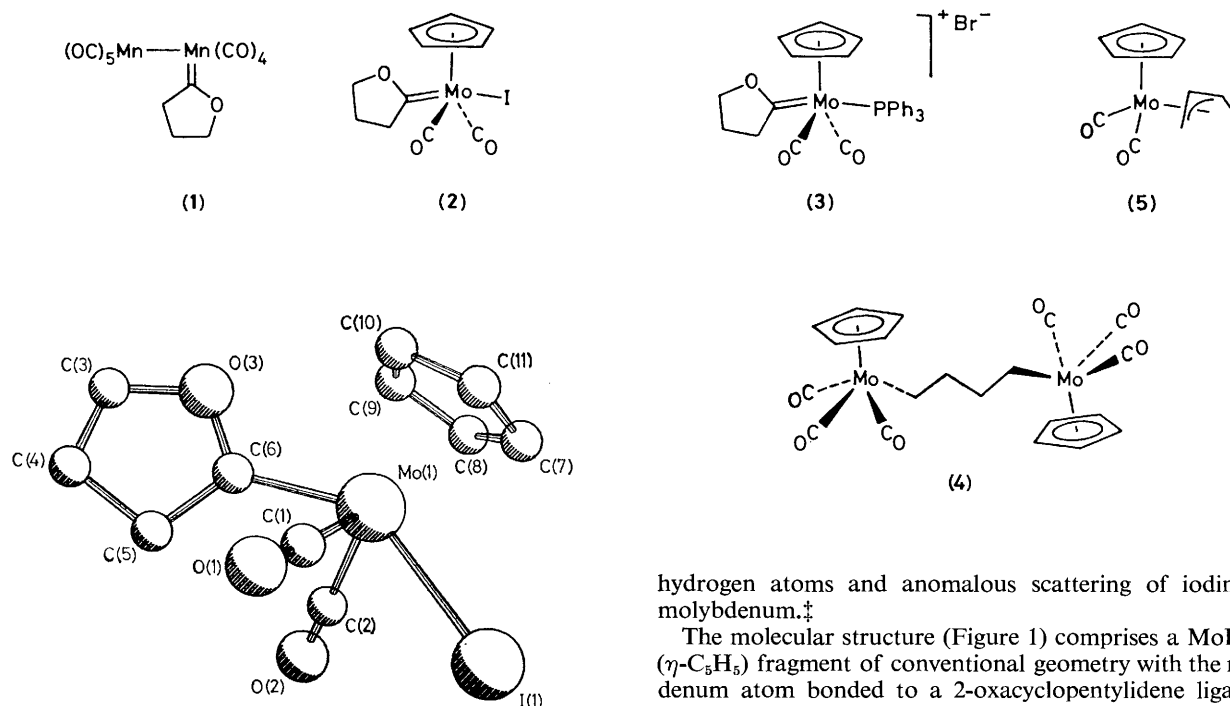


Figure 1. Molecular structure of $[\text{Mo}\{\text{C}(\text{O})\cdot[\text{CH}_2\text{]}_2\text{CH}_2\}\text{CO}_2(\eta\text{-C}_5\text{H}_5)]$ (2). Bond lengths Mo(1)–I(1) 2.862(1), Mo(1)–C(1) 1.991(9), Mo(1)–C(2) 2.007(9), Mo(1)–C(6) 2.086(8), O(3)–C(3) 1.454(15), O(3)–C(6) 1.337(11), C(3)–C(4) 1.448(18), C(4)–C(5) 1.507(16), C(5)–C(6) 1.453(13) Å. Angles: I(1)–Mo(1)–C(6) 140.3(2), C(1)–Mo(1)–C(2) 98.5(4), O(3)–C(6)–C(5) 108.1(7), O(3)–C(6)–Mo(1) 123.7(6), C(5)–C(6)–Mo(1) 128.2(6)°.

fied as a complex of 2-oxacyclopentylidene (1).³ We now report that α,ω -diiodoalkanes behave differently towards certain transition metal anions. Addition of $\text{I}[\text{CH}_2]_3\text{I}$ to a THF solution of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ leads to rapid formation of $[\text{Mo}\{\text{C}(\text{O})\cdot[\text{CH}_2]_3\}\text{CO}_2(\eta\text{-C}_5\text{H}_5)]$ which reacts further at reflux allowing eventual isolation of the orange-brown species

$[\text{Mo}\{\text{C}(\text{O})\cdot[\text{CH}_2]_2\text{CH}_2\}\text{CO}_2(\eta\text{-C}_5\text{H}_5)]$ (2) (55%).[†] The structure of (2) was determined by X-ray diffraction.

Crystal data: $\text{MoI}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{C}_4\text{H}_6\text{O})$; $\text{C}_{11}\text{H}_{11}\text{IMoO}_3$, $M = 414.01$, crystal dimensions $0.44 \times 0.30 \times 0.15$ mm, monoclinic, $a = 6.372(2)$, $b = 14.168(5)$, $c = 14.390(3)$ Å, $\beta = 98.12(2)^\circ$, $U = 1286.0(6)$ Å³, $D_m = 2.15$, $Z = 4$, $D_c = 2.138$ g cm⁻³, space group $P2_1/c$ (from systematic absences), Mo- K_α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 33.61$ cm⁻¹, $F(000) = 784$. The structure was solved by standard Patterson and Fourier techniques and refined by block diagonal least squares methods. The 1726 independent reflections for which $I/\sigma(I) > 3.0$ were collected on a Nicolet/Syntex R3 diffractometer in the range $3.5 < 2\theta < 50^\circ$ and corrected for 5% intensity loss, Lorentz, and polarisation effects. Hydrogen atoms were detected and placed in calculated positions (C–H 0.95 Å); their contributions were included in structure factor calculations ($B = 8.0$ Å²) but no refinement of positional parameters was permitted. Refinement converged at $R = 0.0355$ with allowance for anisotropic motion of all non-

[†] (2): m.p. 98–100 °C; $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ 1985 m and 1909 s cm⁻¹; ¹H n.m.r. (CDCl_3) δ 5.57 (s, 5 H), 4.60 (t, J 7 Hz, 2 H), 3.60 (t, J 7 Hz, 2 H), and 1.92 (quint., J 7 Hz, 2 H); ¹³C n.m.r. (CDCl_3) δ 316.6 (Mo=C), 223.4 (CO), 96.9 (C_5H_5), 82.0 (CH_2), 58.8 (CH_2), and 22.5 (CH_2) p.p.m.

hydrogen atoms and anomalous scattering of iodine and molybdenum.[‡]

The molecular structure (Figure 1) comprises a $\text{MoI}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ fragment of conventional geometry with the molybdenum atom bonded to a 2-oxacyclopentylidene ligand via a formal double (Mo–C) bond of length rather greater than to the carbonyl carbon atoms. The ring has an envelope conformation; atoms Mo(1), C(3), O(3), C(6), and C(5) are coplanar (r.m.s. deviation 0.0027 Å) while atom C(4) deviates by 0.41 Å from the mean plane. This, taken together with the absence of substituent hydrogen atoms on C(6) confirms the nature of the ligand. The 2-oxacyclopentylidene ligand found here is much less planar than that found in the two other molecular structures involving this ligand^{4,5} or in the two reported structures involving the related 2,5-dioxacyclohexylidene ligand.^{6,7}

Compound (2) is also available from the reaction of $[\text{Mo}\{\text{C}(\text{O})\cdot[\text{CH}_2]_3\text{Br}\}\text{CO}_2(\eta\text{-C}_5\text{H}_5)]$ with lithium iodide in refluxing THF but an analogous bromo-complex was not detected in a similar reaction using lithium bromide. It is likely that formation of (2) involves attack of I^- on $[\text{Mo}\{\text{C}(\text{O})\cdot[\text{CH}_2]_3\text{X}\}\text{CO}_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{X} = \text{Br}, \text{I}$) generating the intermediate acyl species $[\text{Mo}\{\text{C}(\text{O})\cdot[\text{CH}_2]_3\text{X}\}\text{CO}_2(\eta\text{-C}_5\text{H}_5)]^-$ (not detected) which undergoes rapid spontaneous intramolecular cyclisation to (2). This parallels suggestions concerning the formations of (1) and cation (3) where the incoming groups are $[\text{Mn}(\text{CO})_5]^-$ and PPh_3 respectively.⁸

Addition of $\text{I}[\text{CH}_2]_4\text{I}$ to a THF solution of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ followed by reflux does not lead to a 2-oxacyclohexylidene complex, rather to replacement of both iodine atoms by molybdenum generating the new complex $[(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Mo}[\text{CH}_2]_4\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (4) (32%).[§] Refluxing a mixture of $[\text{Mo}\{\text{C}(\text{O})\cdot[\text{CH}_2]_4\text{I}\}\text{CO}_2(\eta\text{-C}_5\text{H}_5)]$ and lithium iodide in THF leads only to $[\text{MoI}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ rather than a 2-oxacyclohexylidene complex.

[‡] Atomic co-ordinates 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 structure factor table is available as Supplementary Publication No. SUP 23251 (15 pp.) from the British Library. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, Index Issues.

[§] (4): m.p. 150–152 °C (decomp.); $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ 2015 m and 1919 s cm⁻¹; ¹H n.m.r. (C_6D_6) δ 4.50 (s, 10 H), 1.83 (m, 2 H), and 1.68 (m, 2 H).

Under certain conditions mixtures of cyclopropane and propene or butenes are released from $[(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Fe}[\text{CH}_2]_n\text{-Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($n = 3, 4$).⁹ However we find that u.v. irradiation of a toluene solution of (4) leads to some ethylene, butane, and the π -allyl species (5)¹⁰ but no butenes.

We conclude that di-iodoalkanes and dibromoalkanes exhibit different reactivity towards transition metal anions thus providing an entry into at least two new types of compounds.

We are grateful to the S.E.R.C. for support.

Received, 6th November 1981; Com. 1302

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