Polyhedron Vol. 8, No. 13/14, pp. 1810–1813, 1989
Printed in Great Britain

0277–5387/89 \$3.00+.00
Maxwell Pergamon Macmillan plc

TETRAPHENYLCYCLOPENTADIENONE COMPLEXES OF MOLYBDENUM: X-RAY CRYSTAL STRUCTURE OF $[Mo(CO)_3(C_4Ph_4CO)]_2$

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Abstract—The new complex $[Mo(CO)_3(C_4Ph_4CO)]_2$ has been prepared from $[Mo(CO)_6]$ and tetracyclone, and structurally characterized by X-ray diffraction. A high yield synthesis of $[Mo(CO)_2(C_4Ph_4CO)_2]$ is also described; one of the diene ligands of this complex is readily displaced by phosphines or alkynes.

We have recently reported[1] the synthesis and structural characterization of tetraphenylcyclopentadienoneruthenium dicarbonyl dimer (**1**). This complex functions as an effective catalyst precursor for hydrogenation and dehydrogenation reactions, owing to its facile dissociation in solution into two $16e^-$ $Ru(CO)_2(C_4Ph_4CO)$ units, which are thought to be the catalytically active species.[1,2] Since only one other dimer of this type, $[Fe(CO)_2(C_4H_4CO)]_2$, is known,[3] we were interested in preparing further examples. In this communication we report our preliminary studies of molybdenum cyclopentadienone chemistry, including the crystal structure of the dimer $[Mo(CO)_3(C_4Ph_4CO)]_2$.

Overnight reaction of $[Mo(CO)_6]$ with 2 equivalents of tetracyclone in refluxing toluene affords a 95% yield of bright yellow $[Mo(CO)_2(C_4Ph_4CO)_2]$ (**2**), isolated by column chromatography and characterized spectroscopically.† This complex was first prepared in low yield by Weiss and Hübel,[4] and presumably has a structure similar to that of the bis-cyclobutadiene complex, $[Mo(CO)_2(C_4Ph_4)_2]$.[5]

If 1 equivalent of tetracyclone is used with toluene as solvent, the yield of **2** becomes very low and the major product is a brown complex, which as yet we have been unable to characterize, as it decomposes to tetracyclone and insoluble material. However, its IR spectrum shows no peaks due to metal-bound carbonyls, and it therefore seems likely that it contains toluene as a ligand. In support of this view, when a 1 : 1 mixture of $[Mo(CO)_6]$ and C_4Ph_4CO was refluxed overnight in heptane, the brown material was not obtained; instead a precipitate was deposited consisting of a mixture of the new complex $[Mo(CO)_3(C_4Ph_4CO)]_2$ (**3**) (30% yield following chromatographic separation) and **2** (32% yield).

The nature of complex **3** was suggested by the presence of a peak at 1543 cm^{-1} in its IR spectrum in KBr (cf. 1535 cm^{-1} for **1**), indicative of the ketonic ring carbonyl bonding to a second metal atom; the NMR spectroscopic data† were also consistent with the proposed dimeric formulation, and

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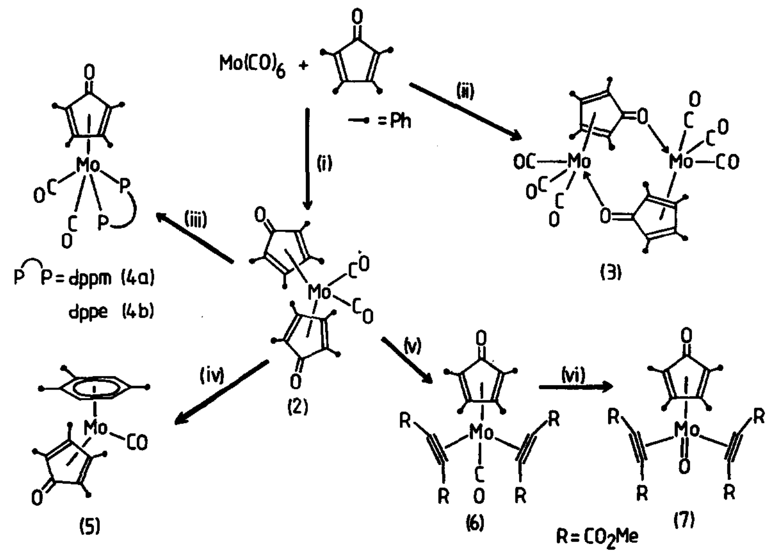
† Selected spectroscopic data (^1H and ^{13}C NMR spectra in $CDCl_3$ unless otherwise stated; shifts measured in ppm relative to TMS = 0.0 ppm, with coupling constants in Hz; phenyl resonances omitted): (**2**): $\nu(CO)$(KBr) 2008, 1960, 1651, 1634 cm^{-1}; ^{13}C NMR 228.9 (CO), 167.3 (ring CO), 108.9, 95.3 (CPh). (**3**): $\nu(CO)$(KBr) 2020, 1933, 1543 cm^{-1}; ^{13}C NMR (CD_2Cl_2) 242.7 (2CO), 225.3 (4CO), 155.2 (ring CO), 110.3, 104.7 (CPh). (**4a**): $\nu(CO)$(KBr) 1936, 1817, 1603 cm^{-1}; ^1H NMR 4.27 (t, 2H, J(HP) 9.5, CH_2). (**5**): $\nu(CO)(CH_2Cl_2)$ 1919, 1608 cm^{-1}; ^1H NMR 5.78 (d, 1H, J 2.4), 4.16 (s, 1H), 4.13 (d, 1H, J 2.4); ^{13}C NMR 237.9 (CO), 166.7 (ring CO), 114.3, 110.9, 109.5, 105.6, 100.9, 93.1, 84.6 (CPh), 100.2, 98.8, 91.5 (CH). (**6**): $\nu(CO)(CH_2Cl_2)$ 2000, 1735, 1720 cm^{-1}; ^1H NMR 3.98, 3.62, 3.58, 3.50 (Me); ^{13}C NMR 230.3 (CO), 193.1, 190.0 (CCO_2Me), 170.4, 168.5, 166.5, 156.1 (CO_2Me), 160.9 (ring CO), 155.2, 145.9 (CCO_2Me), 114.4, 102.8, 101.8, 100.5 (CPh), 53.2, 52.7, 52.0, 51.6 (Me). (**7**): $\nu(CO)(CH_2Cl_2)$ 1772, 1719 cm^{-1}; ^1H NMR 3.77, 3.75, 3.65, 3.58 (Me); ^{13}C NMR 170.1, 167.6, 165.3, 158.2 (CO_2Me), 167.2 (ring CO), 153.4, 149.8, 149.6, 142.3 (CCO_2Me), 120.3, 115.9, 114.7, 109.9 (CPh), 52.9, 52.6, 52.3, 52.0 (Me). Satisfactory analytical data were obtained for all new complexes.



Scheme 1. Reagents and conditions: (i) 1 : 2 ratio, refluxing toluene, 17 h; (ii) 1 : 1 ratio, refluxing heptane, 17 h; (iii) dppm or dppe, refluxing toluene, 8 h; (iv) PhC≡CH (5 equivalents), refluxing toluene, 17 h; (v) $C_2(CO_2Me)_2$ (5 equivalents), refluxing toluene, 17 h; (vi) air, or aged THF.

it was confirmed by an X-ray diffraction study.* The structure, shown in Fig. 1, consists of centrosymmetric dimers in which each molybdenum bears three terminal carbonyl ligands and an η^4-bonded tetracyclone ring, the ketonic carbonyl of which is joined to the second molybdenum atom. This carbonyl group is bent back from the diene plane at an angle of 9.6°, in common with other η^4-cyclopentadienone complexes,[1,6] and the C(3)—O(2) bond length of 1.271(8) Å (cf. 1.270 Å in **1**) indicates that this bond is still essentially double in character. These features may be contrasted with those in $[Mo_2(CO)_3(\mu\text{-}C_2Ph_2)(\eta\text{-}C_4Ph_4)(\mu\text{-}C_4Ph_4CO)]$,[7] where the five carbon atoms of the bridging tetracyclone are all coplanar, and the C—O bond length is considerably longer (1.38(2) Å), indicating an η^5-bonded ring.

Preliminary investigations into the reactivity of **2** and **3** indicate that **2** provides a convenient entry into further chemistry. For example, in refluxing toluene one of the tetracyclone ligands is readily replaced by chelating phosphines to give $[Mo(CO)_2(P⌒P)(C_4Ph_4CO)]$ (**4a**: P⌒P = dppm, 92%; **4b**, P⌒P = dppe, 90%); further substitution to give the known complexes $[Mo(CO)_2(P⌒P)_2]$ does not occur. Moreover, under similar conditions, **2** is reactive towards alkynes: thus phenylacetylene gives a red–brown complex, to which we assign the structure $[Mo(CO)(1,2,4\text{-}C_6H_3Ph_3)(C_4Ph_4CO)]$ (**5**) (54%), free 1,2,4-triphenylbenzene, 1,3,5-triphenylbenzene, and pentaphenylbenzene (formed through Diels–Alder condensation of phenylacetylene with the liberated tetracyclone). With dimethyl acetylenedicarboxylate, the sole organometallic product is the green bis-alkyne complex $[Mo(CO)(MeO_2CC{\equiv}CCO_2Me)_2(C_4Ph_4CO)]$ (**6**) (45%), which on standing in the solid state (or immediately on dissolution in THF containing peroxides) undergoes oxidation to the oxo–alkyne species $[MoO(MeO_2CC{\equiv}CCO_2Me)_2(C_4Ph_4CO)]$ (**7**); a strong peak in the IR spectrum at 937 cm^{-1} is assigned to the Mo═O group. These reactions are summarized in Scheme 1.

Further investigations into the reactivity of these complexes are in progress.

Acknowledgements—We thank the Universities of Manchester and Sheffield for support, and Dr B. F. Taylor for helpful NMR experiments.

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* The atomic coordinates for this work have been deposited at the Cambridge Crystallographic Data Centre. Crystal data for **3**: $C_{32}H_{20}O_4Mo$, $M = 564.4$ (for monomer), triclinic, space group $P\bar{1}$ (No. 2), $a = 8.980(3)$, $b = 11.332(4)$, $c = 13.516(5)$ Å; $\alpha = 77.55(3)$, $\beta = 71.94(3)$, $\gamma = 81.02(3)°$, $U = 1271$ Å^3, $D_c = 1.47$ g cm^{-3} for $Z = 2$ (monomer units), $F(000) = 636$, absorption. coefficient = 6.0 cm^{-1} ($\lambda = 0.71069$ Å, Mo-K_α). Final $R = 0.0535\%$ for 2194 unique, observed [$F > 3\sigma(F)$] intensity data, collected on an Enraf–Nonius CAD4 diffractometer to a maximum θ of 22°. As $\mu R < 0.11$, no absorption correction was applied, but a linear drift correction for a total intensity drop of 12% was used. The structure was solved by direct methods using the MULTAN 80 program, and eventually refined with anisotropic thermal parameters for all non-hydrogen atoms. A non-unit weighting scheme was used.

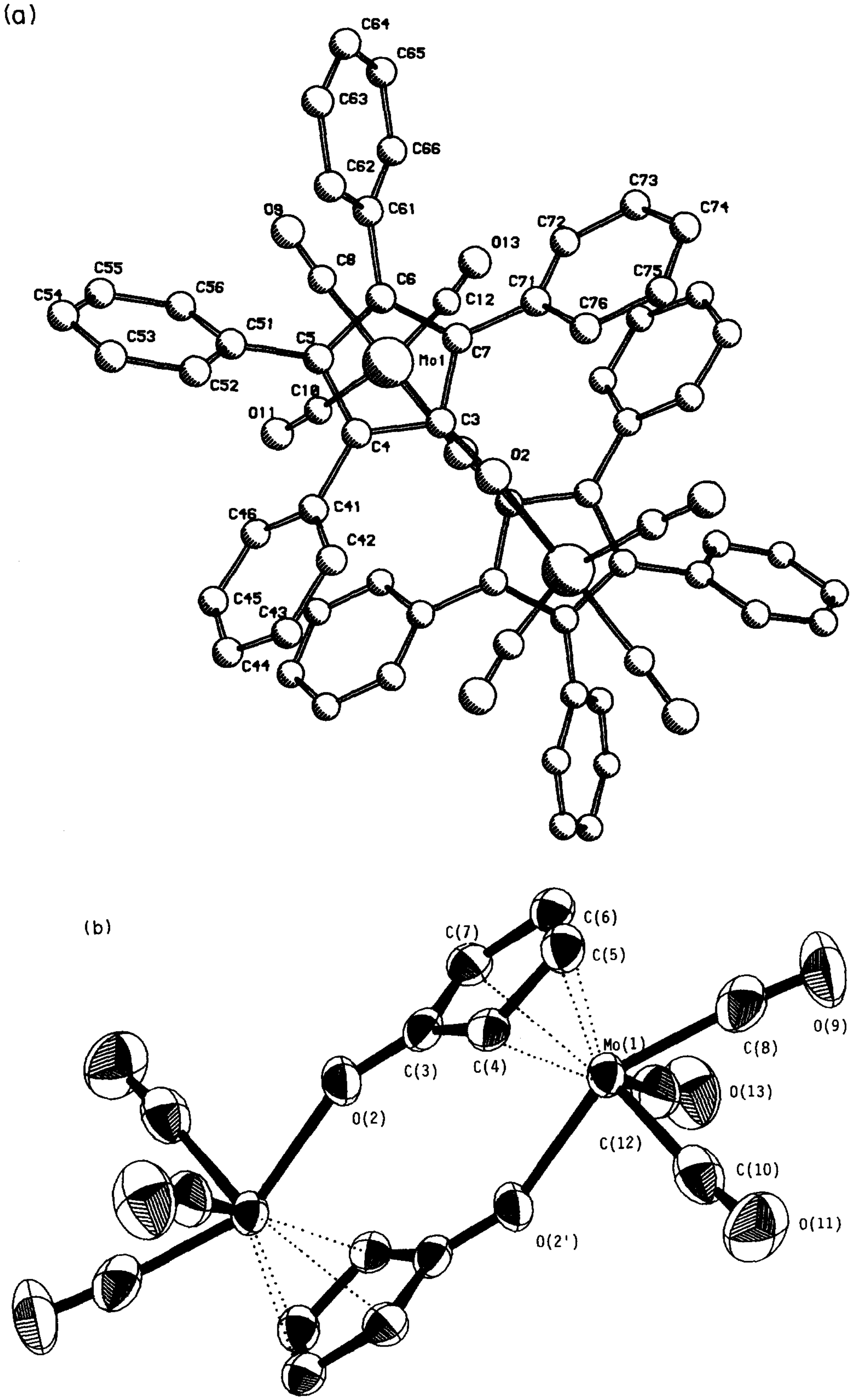

Fig. 1. (a) Molecular structure of 3. (b) ORTEP plot of 3 with phenyl groups omitted for clarity. Selected interatomic distances and angles: Mo(1)—O(2′), 2.168(5); Mo(1)—C(3), 2.531(7); Mo(1)—C(4), 2.367(7); Mo(1)—C(5), 2.320(8); Mo(1)—C(6), 2.281(8); Mo(1)—C(7), 2.365(8) Å. C(8)—Mo(1)—O(2), 151.1(3)°.

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