32.4, 28.9, 28.0, 26.2, 24.9, 24.4, 21.5, 12.7, 12.3 (C3), (C20), (C17), (C14), (C9), (C5), (C13), (C12), (C1), (C8, C10), (C4), (C7), (C6), (C2), (C16), (C15), (C21), (C11), (C18), (C19). For the butyryl moiety: ^{13}C NMR δ 172.8, 36.7, 18.9, 13.7. Anal. Calcd for $C_{25}H_{42}O_3$: C, 76.92; H, 10.76. Found: C, 76.76; H, 10.63.

Preparation of 5α-Pregnan-3β-ol-20-one. An amorphous solid of 3β-(monobutyryl ester) of **14**, obtained as described above prior to silica gel column chromatography, was dissolved in 180 mL of CH_2Cl_2. Then 3 g of pyridinium chlorochromate[18] was added, and the suspension was stirred at room temperature for 1 h, followed by washing with 100 mL of both a saturated solution of NaCl in water and water. Afterward, the solution was dried with anhydrous $MgSO_4$ and the solvent evaporated in a rotary evaporator. The solid residue was dissolved in 50 mL of MeOH containing 5% KOH, and the solution was refluxed for 30 min. The solvent was subsequently evaporated, and the oily residue was dissolved in $CHCl_3$ and washed with both 0.1 N HCl and with water. Following drying and evaporation of the solvent, the remaining solid was subjected to silica gel column chromatography (chloroform-methanol (99:1) as the solvent). The white crystalline product formed was pure by GC, TLC, and ^{13}C NMR: mp 195-196 °C; $[\alpha]^{25}_D$ +94.4° (*c* 0.5, $CHCl_3$); ^{13}C NMR (67.9 MHz, $CDCl_3$, TMS as the internal reference) δ 209.7, 71.2, 63.8, 56.6, 54.2, 44.8, 44.2, 39.0, 38.1, 37.0, 35.5, 32.0, 31.5, 31.4, 28.6, 24.4, 22.8, 21.2, 13.4, 12.3 (C20), (C3), (C17), (C14), (C9), (C5), (C13), (C12), (C4), (C1), (C8), (C2), (C7, C10), (C21), (C6), (C15), (C16), (C11), (C18), (C19). Anal. Calcd for $C_{21}H_{34}O_2$: C, 79.25; H, 10.69. Found: C, 79.30; H, 10.92. These melting points, $[\alpha]^{25}_D$, and ^{13}C NMR data were in agreement with those obtained for the authentic steroid purchased from Sigma.

Communications to the Editor

The Synthesis and Structure Determination from Powder Diffraction Data of $LaMo_5O_8$, a New Oxomolybdate Containing Mo_{10} Clusters

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Received January 6, 1988

The formation of metal clusters in mixed oxides in which molybdenum is present in a low formal oxidation state is now well established.[1] Examples include $Zn_2Mo_3O_8$, which contains triangular Mo_3 units,[2] $NaMo_4O_6$, which exhibits infinite chains of edge-sharing Mo_6 octahedra,[3] and $In_{11}Mo_{40}O_{62}$, with finite chains of four and five edge-sharing Mo_6 octahedra.[4] Structures containing more than one type of metal-metal bonded unit are also known, e.g., $La_3Mo_4SiO_{14}$.[5] In a careful survey of the system La-Mo-O by analytical electron microscopy[6] using a Jeol 2000FX TEMSCAN instrument, we found evidence for a new phase with a La:Mo ratio of 2:9. Oxygen analysis by X-ray emission spectroscopy[7] suggested the composition $La_2Mo_9O_{12}$, and a sample with this composition was prepared[8] for subsequent interrogation by powder diffraction methods.

Recent developments in both instrumental and computational aspects of powder diffractometry have made possible the precise determination of unknown structures from powder data. Examples include $FeAsO_4$,[9] determined from neutron data, $ZrKH(PO_4)_2$[10] and $AlPO_4$-12[11] from laboratory X-ray data, and α-$CrPO_4$,[12] I_2O_4,[13] and $MnPO_4 \cdot H_2O$[14] from synchrotron X-ray data. In the present work, high resolution synchrotron powder X-ray data were collected on the X13A beam line at the NSLS, Brookhaven National Laboratory, and neutron data were obtained on the diffractometer D2b at the ILL, Grenoble. The unit cell, $a = 9.912$ (1) Å, $b = 9.093$ (1) Å, $c = 7.575$ (1) Å and $\beta = 109.05$ (5)°, was determined by auto-indexing of the X-ray data[15] and con-

Table I. Neutron (N) and X-ray (X) Atomic Coordinates for $LaMo_5O_8$[a,b]

		x	*y*	*z*
La	N	0.0399 (8)	−0.001 (1)	0.255 (1)
	X	0.0420 (5)	0.0037 (7)	0.2609 (7)
Mo1	N	0.490 (1)	0.1161 (9)	0.610 (1)
	X	0.4863 (7)	0.1155 (9)	0.606 (1)
Mo2	N	0.5848 (8)	0.124 (1)	−0.004 (1)
	X	0.5845 (6)	0.1249 (7)	−0.0019 (9)
Mo3	N	0.3845 (9)	0.128 (1)	0.182 (1)
	X	0.3826 (7)	0.1269 (9)	0.1772 (9)
Mo4	N	0.2939 (9)	0.1271 (9)	0.808 (1)
	X	0.2970 (7)	0.1283 (9)	0.8083 (9)
Mo5	N	0.6805 (9)	0.122 (1)	0.387 (1)
	X	0.6769 (7)	0.119 (1)	0.3850 (8)
O1	N	0.848 (1)	−0.008 (2)	0.397 (1)
	X	0.844 (4)	−0.002 (7)	0.398 (5)
O2	N	0.934 (1)	0.227 (1)	−0.003 (2)
	X	0.932 (6)	0.230 (4)	0.01 (1)
O3	N	0.116 (1)	0.249 (1)	0.799 (2)
	X	0.118 (6)	0.253 (4)	0.80 (1)
O4	N	0.213 (1)	0.243 (1)	0.199 (2)
	X	0.215 (7)	0.255 (4)	0.21 (1)
O5	N	0.231 (1)	0.001 (1)	−0.008 (1)
	X	0.232 (4)	0.004 (4)	−0.003 (5)
O6	N	0.018 (2)	0.2484 (9)	0.399 (2)
	X	0.017 (8)	0.247 (4)	0.40 (1)
O7	N	0.826 (2)	0.241 (1)	0.602 (2)
	X	0.826 (7)	0.235 (4)	0.61 (1)
O8	N	0.329 (1)	0.004 (2)	0.382 (1)
	X	0.321 (4)	0.017 (8)	0.392 (5)

[a] $Z = 4$; space group $P2_1/a$. [b] R-factors: neutrons: $R_1 = 11.0\%$, $R_p = 17.3\%$, $R_{wp} = 19.9\%$, $R_{exp} = 12.6\%$, $\chi^2 = 2.5$; X-rays: $R_1 = 11.4\%$, $R_p = 23.2\%$, $R_{wp} = 27.0\%$, $R_{exp} = 15.5\%$, $\chi^2 = 3.0$.

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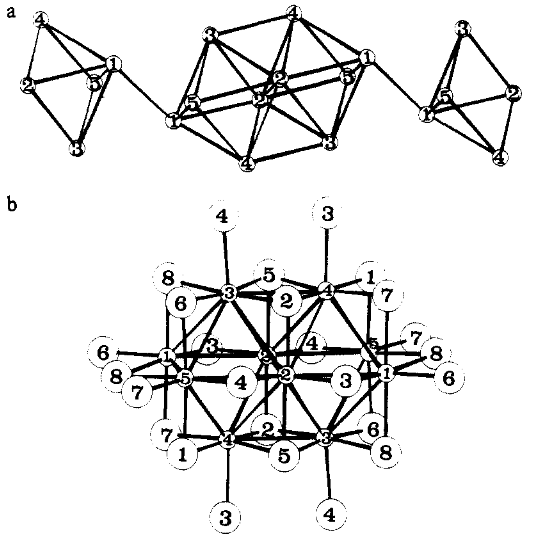

Figure 1. (a) The Mo_{10} cluster and its linkages to two identical units; (b) the $Mo_{10}O_{16}$ unit (Mo, small circles; O, large open circles).

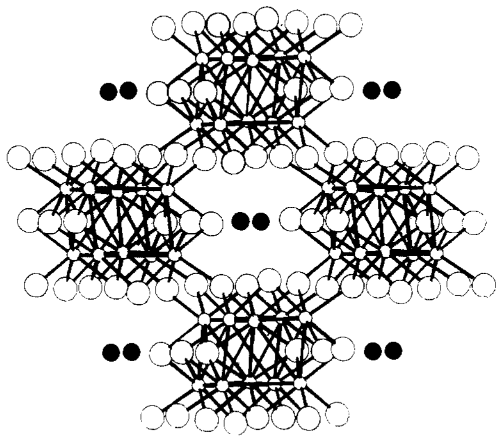

Figure 2. The $LaMo_5O_8$ structure viewed down z (La, solid circles; Mo, small circles; O, large open circles).

firmed by electron diffraction. The space group, $P2_1/a$, was determined from systematic absences in the X-ray and electron diffraction patterns. After removing impurity peaks due to molybdenum metal, the X-ray data were decomposed into 297 I_{hkl} values; the intensities of the overlapping reflections were broken up by considering electron diffraction patterns, of which 19 zones have been found. The heavy atoms were located by direct methods with negative quartets[16] and used as the starting model for Rietveld profile refinement.[17] Oxygen atoms were found from subsequent difference Fourier calculations, giving the composition $LaMo_5O_8$. Final details and atomic coordinates are given in Table I, which also contains the results of a Rietveld analysis of the neutron data (1237 reflections); the latter forms the basis of the discussion below. The La:Mo ratio of $LaMo_5O_8$ is slightly different from that used in the preparation (2:9), and a careful microanalytical examination of the sample has revealed a second new phase of approximate composition $La_5Mo_7O_{18}$. The presence of this minor impurity is presumably responsible for the rather high R-factors.

$LaMo_5O_8$ contains the first example of Mo_{10} clusters, consisting of two edge-shared octahedra, linked by two additional Mo–Mo bonds to form infinite chains (Figure 1). The chains are connected by bridging oxygens to define tunnels which contain lanthanum ions with 11-coordination (Figure 2). With the exception of Mo(2), which is shared by both octahedra, the molybdenum atoms are bonded to five oxygens in approximately square-pyramidal coordination. Mo–Mo distances within the cluster range from 2.676 to 2.836 Å. The shortest intercluster metal–metal bond is Mo(1)–Mo(1), 2.733 Å, but Mo(1) also forms weaker intercluster bonds to Mo(5), 2.921 Å, and Mo(3), 3.065 Å. Molybdenum–oxygen bonds fall in the range 1.984–2.163 Å. Calculation of Mo–O bond strengths[18] confirms Mo(2) as the Mo atom of lowest valency: 2.446. The valencies of the other Mo atoms are calculated as the following: Mo(1), 2.720; (Mo(3), 2.785; Mo(4), 2.895; and Mo(5), 3.087. The relative values for waist (shared edge) and apex molybdenums are comparable to those found for infinite edge-shared Mo_6 clusters found in $NaMo_4O_6$ and related compounds.

Acknowledgment. A part of this research was carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Division of Chemical Sciences, U.S. Department of Energy. We thank the S.E.R.C. for the provision of neutron facilities at ILL, Grenoble. S.J.H. and A.K.C. thank British Petroleum plc for an EMRA grant.

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Palladium-Catalyzed Arylation of Siloxycyclopropanes with Aryl Triflates. Carbon Chain Elongation via Catalytic Carbon–Carbon Bond Cleavage

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Received November 30, 1987

Activation of a carbon–carbon bond by homogeneous transition-metal complexes has been a challenge for chemists.[1] Although the preparation of stable complexes[2] and the rearrangement of highly strained molecules initiated by C–C bond cleavage have been extensively studied,[3] little is known about the utility of C–C bond activation for carbon chain elongation, not to mention its catalytic use.[4,5] The purpose of this communication is to disclose the first example of a *catalytic reaction of general synthetic utility*, in which a C–C bond is cleaved by an organopalladium complex to create a new C–C bond. Namely, the present reaction demonstrates the general synthetic utility of homoenolate[6] A as the inverse-polarity synthon[7] of a Michael acceptor B (see below),

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