Experiments are in progress to explore the scope of this reaction, the chemistry of **6** and its relatives, and to determine whether the ring-opening/hydrogen shift process is indeed intramolecular in nature.

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Supplementary Material Available: Tables of atomic coordinates and isotropic temperature factors for non-hydrogen atoms (Table 1S), bond lengths (Table 2S), bond angles (Table 3S), anisotropic temperature factors (Table 4S), and observed and calculated structure factor tables (Table 5S) (25 pages). Ordering information is given on any current masthead page.

Indenylmolybdenum Dicarbonyl and Indenylmolybdenum Tricarbonyl Dimers: A Clarification of Their Syntheses and Spectroscopic Characteristics, Including the Structure of the Previously Unrecognized Triply Bonded Species

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Summary: The reaction of indene with molybdenum hexacarbonyl in diglyme/octane at 165 °C generates indenylmolybdenum dicarbonyl dimer directly rather than the tricarbonyl dimer as had been previously reported. Spectroscopic characteristics of the dicarbonyl dimer as well as its single-crystal X-ray structure are presented. The indenyl ligands are bound in η^5 fashion, and the metal–metal distance is in the expected range for a Mo–Mo triple bond. The complex reacts readily with carbon monoxide to form the known tricarbonyl dimer.

The reactivity of the triple bond in $[CpMo(CO)_2]_2$ has been widely studied since this fascinating complex was first prepared.[1] It's high reactivity makes the dimer a useful starting material in the preparation of a variety of clusters.

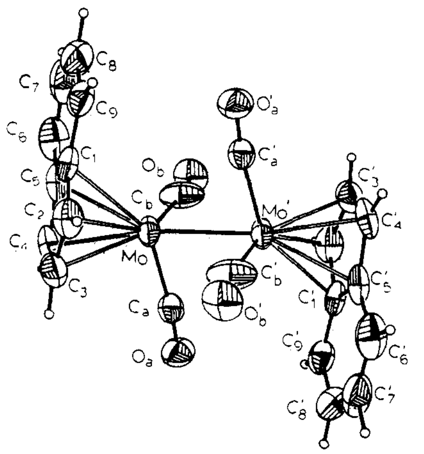

Figure 1. X-ray crystal structure of $[Mo(C_9H_7)(CO)_2]_2$, **1**. Selected interatomic distances (Å) and bond angles (deg): Mo–Mo′ = 2.500 (1), Mo–C_a = 1.953 (7), Mo–C_b = 2.098 (9), Mo–C_a' = 2.753 (7), Mo–C_b' = 2.692 (9), O_a–C_a = 1.155 (9), O_b–C_b = 1.107 (10), Mo–C_1 = 2.401 (6), Mo–C_2 = 2.332 (7), Mo–C_3 = 2.336 (7), Mo–C_4 = 2.348 (7), Mo–C_5 = 2.396 (7); C_a–Mo-Mo′ = 75.3 (2), C_b–Mo–Mo′ = 71.1 (3), Mo–C_a–O = 173.6 (5), Mo–C_b–O = 171.2 (8).

Table I. Infrared Carbonyl Stretching Frequencies and UV–Vis Band Maxima for $[Mo(C_9H_7)(CO)_2]_2$, 1, $[Mo(C_9H_7)(CO)_3]_2$, 2, and Their Cyclopentadienyl Analogues[a]

compound	IR, cm^{-1}	UV–vis, nm
$[Mo(C_9H_7)(CO)_2]_2$, **1**	1893 (s), 1858 (s)	349
$[Mo(C_5H_5)(CO)_2]_2$	1895 (s), 1855 (s)	322, 380 (sh)
$[Mo(C_9H_7)(CO)_3]_2$, **2**	2020 (w), 1958 (s), 1910 (s)	410, 510
$[Mo(C_5H_5)(CO)_3]_2$	2020 (w), 1959 (s), 1913 (s)	382, 507

[a] All spectra run in CH_2Cl_2 solvent under inert atmosphere.

Synthesis of the indenyl analogue would be particularly interesting, because of possible heightened reactivity at the molybdenum centers due to the "indenyl effect"[2] and because of the use of the indenyl complex as a precursor to other clusters in which the "indenyl effect" might be studied.

A logical approach to the synthesis of the previously unreported triply bonded dimer $[IndMo(CO)_2]_2$, **1**, appeared to be through the singly bonded dimer $[IndMo(CO)_3]_2$, **2**, which had been reported by several authors to be accessible via the direct reaction of $Mo(CO)_6$ with indene in high boiling solvents.[3-5] We have found that under one such set of conditions the triply bonded dimer **1** is produced directly and in fact suspect that the material previously characterized as the singly bonded dimer **2** was,

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at least in some cases, actually the triply bonded dimer 1. In the following we report reliable syntheses and full spectroscopic characterization for both dimers 1 and 2, along with the crystal structure of the triply bonded complex.

The reaction of $Mo(CO)_6$ with indene in a diglyme/heptane mixture at 165 °C[6] produces a dark orange–red reaction mixture from which deep maroon microcrystalline 1 can readily be isolated.[5] The correspondence between the infrared and electronic spectra of 1 and the known triply bonded cyclopentadienyl complex, as indicated in Table I, suggests that 1 is the triply bonded species rather than the expected singly bonded tricarbonyl dimer. Mass spectroscopy and elemental analysis[7] support this conclusion. In order to establish the mode of binding of the indenyl ligand (η^5 vs. η^3) and the carbonyl ligands, an X-ray diffraction study was carried out on a single red-brown crystal grown from methylene chloride/hexane solution.[8]

The structure of the triply bonded dimer 1 is shown in Figure 1, and selected bond length and bond angle data are given in the supplementary material. The two halves of the dimer are related by a crystallographically imposed inversion center midway between the two Mo atoms. The Mo–Mo distance of 2.500 (1) Å is nearly the same as the 2.448 (1) Å reported for the cyclopentadienyl analogue.[9] The nature of the CO bonding is also similar to that observed in the previous structure, with the carbonyls acting as four-electron donors, tipped over the metal–metal bond to form an asymmetric bridge. The details of the carbonyl bonding do, however, differ somewhat from those observed for the cyclopentadienyl complex. In the Cp complex, the carbonyl ligands were disordered, with Mo–C bond lengths ranging from 2.06 to 2.17 Å and Mo–Mo–C bond angles between 66 and 68.7°. In the current structure the indenyl ligands have broken the symmetry and the carbonyl ligands are well ordered. Two rather different carbonyls are observed, one which is slightly less tipped (Mo–Mo–C = 75.3°) with a shorter Mo–C bond (1.953 (7) Å) and the other more tipped (Mo–Mo–C = 71.1°) with a longer Mo–C bond (2.098 (9) Å). The bonding of the indenyl ligand to molybdenum is noteworthy in light of recent interest in distortions toward an η^3 mode of bonding for various indenylmetal complexes.[10] In that light, 1 represents an example of an essentially undistorted (η^5-indenyl)metal complex, with ΔM–C (the difference between the average M–C2, C3, C4 and M–C1, C5 bond lengths) being only 0.06 Å and with the indenyl ligand rigorously planar.

The ^{13}C NMR spectra of the indenylmolybdenum dimer 1 is rather straightforward displaying resonances at δ 80.9 (C2, C4), 93.6 (C3), 111.5 (C1, C5), 123.9 (C6, C9), 126.3 (C7, C8), and 235.4 (CO). The relatively low δ value for C1 and C5 in this complex is in keeping with the crystallographic determination of an essentially undistorted η^5-indenyl ligand.[11]

As in the cyclopentadienyl case,[1b] solutions of the triply bonded species 1 react readily with carbon monoxide at atmospheric pressure and room temperature to generate the singly bonded complex 2.[8] This conversion, which is complete in a matter of several minutes in methylene chloride solution, can be readily monitored by the shift of the carbonyl infrared bands to higher frequency and the change in the color of the solution from red-orange to a much darker red (see Table I). Dark red-black microcrystalline 2 can be isolated in essentially quantitative yield by addition of hexane to the CO treated solution of 1, followed by evaporation of methylene chloride under a slow argon stream.[8] Complex 2 displays resonances at δ 84.5 (C2, C4), 93.7 (C3), 110.5 (C1, C5), 124.5 (C6, C9), 126.5 (C7, C8), and 229.9 (CO). On the basis of the high field position of the resonance for C1 and C5, we would exect that the indenyl ligand in 2 is also undistorted η^5.[11]

The initial literature report of the synthesis of the tricarbonyl dimer 2[3] described a brown crystalline solid with IR bands at 2045 (w), 1970, and 1920 cm^{-1} in CS_2 solution, in keeping with our observations. however, a subsequent "improved synthesis"[4] described the product as having IR bands at 1894 (sh), 1876 (sh), and 1862 (s) cm^{-1} (halocarbon mull). These bands appear to be at too low a frequency to correspond to authentic tricarbonyl dimer 2 and are more likely due to the formation of the dicarbonyl dimer 1. The most recent reported synthesis of the tricarbonyl dimer[5] gives no spectroscopic information, but the reported dark violet color of the product, combined with our results using essentially the same synthetic procedure, suggests that here also the product was actually the triply bonded dicarbonyl dimer 1.

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Note Added in Proof. The structure of the indenylmolybdenum dicarbonyl dimer has also recently been reported by Curtis and Bakkar, 190th American Chemical Society Meeting, Chicago, IL, Sept 8–13, 1985, INOR 377.

Registry No. 1, 98540-88-6; 2, 12098-65-6; $Mo(CO)_6$, 56779-83-0; indene, 95-13-6.

Supplementary Material Available: Crystallography details, including tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and structure factors (18 pages). Ordering information is given on any current masthead page.

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(6) $Mo(CO)_6$ (5.0 g, 19 mmol) was added to a mixture of 25 mL of freshly distilled 2-methoxyethyl ether and 9 mL of heptane. This suspension was then degassed, and indene (7.0 mL, 60 mmol, Aldrich 99+%) added via syringe. All subsequent manipulations were carried out under an Ar atmosphere. The mixture was refluxed at 165 °C for 8 h. Solvents and excess hexacarbonyl were stripped from the dark orange-brown reaction mixture, leaving a tarry residue. This was extracted three times with a total of 50 mL of methylene chloride. Hexane (20 mL) was added and then a slow flow of argon used to evaporate the methylene chloride. The resulting maroon microcrystals were isolated by filtration, rinsed with hexane, and dried under vacuum; yield 1.2 g. Further purification was achieved by column chromatography utilizing a 3 × 5 cm column of silica with methylene chloride as eluent.

(7) Anal. Calcd for $C_{22}H_{14}O_4Mo_2$: C, 49.46; H, 2.64;, O, 11.98; Mo, 35.92. Found: C, 49.24; H, 2.67; O, 12.04; Mo, 36.11. Mass spectrum (positive ion CI, isobutane), $M + H^+$.

(8) $C_{22}H_{14}O_4Mo_2$: monoclinic $C2/c$; $a = 10.641$ (2) Å, $b = 8.545$ (5) Å, $c = 21.259$ (5) Å, $\beta = 103.25°$, $V = 1881.5$ (7) Å^3, $Z = 4$. $R = 0.040$ for 1202 independent data. Full crystallographic details are available as supplementary data. The structure analysis was carried out by Dr. C. S. Day of Crystalytics Co., Lincoln, NB.

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(12) Anal. Calcd for $C_{24}H_{14}O_6Mo_2$: C, 48.84; H, 2.39; O, 16.26; Mo, 32.51. Found: C, 48.32; H, 2.32; O, 16.76; Mo, 32.12. Mass spectrum (positive ion CI, isobutane), $M + H^+$.