high-pressure limit, which seems to be reasonable if one is interested in reactions in a condensed phase.

The calculated rate constants for tunneling at −50 and −10 °C are 8.08×10^4 and 4.65×10^5 s^{-1}, respectively. These are to be compared with the classical rate constants[13] of 1.01×10^2 and 4.82×10^3 s^{-1} at the same temperatures. The startling conclusion is that, assuming the validity of this model, *tunneling accounts for >97% of the total reaction below 0 °C.*

The combined tunneling and classical rate constants correspond to the activation parameters $\Delta H^{\ddagger} = 4.6$ kcal/mol, $\Delta S^{\ddagger} = -15$ cal/(mol K). Recent experiments suggested that the activation parameters for cyclobutadiene automerization,[14] measured over the same temperature span, must be in the range $1.6 \leq \Delta H^{\ddagger} \leq 10$ kcal/mol and $-32 \leq \Delta S^{\ddagger} \leq -17$ cal/(mol K). Given the crudity of the model used here and the probable underestimate of the tunneling contribution, the agreement seems to be quite good.

Two features of this analysis should be emphasized. First, the most striking consequence of the tunneling mechanism is the abnormally low activation entropy that one calculates. Second, the apparent $\Delta H^{\ddagger}$ for the reaction cannot be equated with the potential barrier calculated by any molecular orbital technique.

For the conclusions drawn here to be *qualitatively* incorrect, the model used for the calculation of the tunneling-rate constants would have to be seriously in error (and there is substantial experimental evidence to suggest that it is not[15]) or the numerical parameters (barrier width and oscillation frequency) would have to be wrong by considerable amounts.

While the discussion to this point has centered on cyclobutadiene, there is reason to believe that the bond-shift reaction in cyclooctatetraene might have a significant tunneling contribution as well. The activation entropy was recently measured[16] and found to be −9.7 cal/(mol K). While this is not as low as the one for cyclobutadiene, it must still be considered abnormal for a reaction in which no rotations are frozen out and no especially low-frequency vibrations are lost in the transition state. It is possible that the higher temperatures at which the measurements were made resulted in a larger contribution from the classical mechanism in this case.

When one considers the effect of substituents on the tunneling efficiency, it becomes clear that sterically demanding groups, which tend to force a planar annulene toward the regular polygonal structure,[17] should further reduce the barrier width and increase the tunneling rate constant.[18] This could be the reason that the automerization of tri-*tert*-butylcyclobutadiene cannot be frozen out in the ^{13}C NMR even at −185 °C.[19] Substituents seem to have a profound effect on the $\Delta S^{\ddagger}$ for bond shifting in cyclooctatetraenes[20] with values ranging from +2.3 to −23.6 cal/(mol K). Here, too, the effect could be a geometrical one in which the substituents increase or decrease the amount of tunneling by changing the effective barrier width in the planar structure.

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[13] In order to calculate the classical rate constant a value of $\Delta H^{\ddagger} = 10.8$ kcal/mol was used. The value for $\Delta S^{\ddagger}$ was calculated to be −0.4 cal/(mol K), reflecting a vibrational contribution of +1.0 (calculated from vibrational frequencies listed in ref 3 and 6) and a rotational contribution of −1.4 cal/(mol K). The latter was due in large part to the change in symmetry number during the bond-shift reaction.

[14] Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 6473–6474. This experiment was actually conducted on cyclobutadiene-d_2, but the extra mass makes a negligible contribution to the overall effect.

[15] For an example and some leading references see: Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 6803–6811.

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The Novel Reaction of Metal–Metal Triple-Bonded Complexes and Nitro Compounds. Decarbonylation and the Formation of High Oxidation State Molybdenum and Tungsten Complexes Bearing Bridging and Terminal Oxygen Ligands

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The fascinating chemistry of complexes containing metal–metal multiple bonds has been a subject of great interest in recent years.[2,3] One of the most widely investigated class of compounds is the (cyclopentadienyl)molybdenum dicarbonyl dimer and related complexes.[4] The metal–metal bond in such complexes undergoes intriguing reactions with nucleophilic (e.g., isocyanides)[5] and electrophilic (e.g., α-halo ketones)[6] reagents.

The reaction of nitro compounds with $[C_5H_5M(CO)_2]_2$ has not been investigated. It seemed conceivable that the nitro group would add to the triple bond to give a complex in which cleavage of at least one nitrogen–oxygen linkage has taken place. The occurrence of such a process is of relevance to the metal carbonyl catalyzed reduction[7] and reductive carbonylation[8] of nitro compounds. We now report the remarkable reaction of nitro compounds with $[(C_5H_4R)M(CO)_2]_2$, where M = Mo, W and R = H, CH_3.

Addition of *p*-nitrotoluene (**1**, Ar = *p*-$CH_3C_6H_4$, Scheme I) to an equimolar amount of the (cyclopentadienyl)molybdenum dicarbonyl dimer (**2**, M = Mo, R = H) in toluene at room temperature afforded the molybdenum complex **3**, M = Mo, R = H, Ar = *p*-$CH_3C_6H_4$. This reaction, and others described below, are exceedingly facile since they are essentially complete in 5 min (infrared spectral determination), although they generally were stirred for 3 h. Complex **3** could also be prepared by refluxing a mixture of **1** and (cyclopentadienyl)molybdenum tricarbonyl dimer overnight in toluene (**2** is generated under these conditions). The infrared spectrum of **3** (M = Mo, R = H, Ar = *p*-$CH_3C_6H_4$) showed $\nu_{\mathrm{Mo=O}}$ at 895 cm^{-1} while the μ-Mo–O stretching band appeared at 817 cm^{-1}.[9] The nuclear magnetic resonance spectral data (Table I) of the complex are also in accord wth structure **3**.

In order to establish the structure unambiguously, an X-ray determination[10] of **3**, M = Mo, R = H, Ar = *p*-$CH_3C_6H_4$, was

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[10] Single crystals of $(\mu\text{-}NC_6H_4CH_3)(\mu\text{-}O)([C_5H_5]MoO)_2$ were monoclinic, space group $C2/c$, with $a = 14.796$ (1) Å, $b = 15.999$ (1) Å, $c = 7.692$ (1) Å, and $\beta = 109.44$ (1)°. ρ_{calcd} $(Z = 4) = 1.838$ g cm^{-3}. X-ray diffraction intensity data were collected by the line profile analysis of 1517 reflections ($3° < 2\theta < 50°$) measured on a Picker FACS-I diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7093 Å). Non-hydrogen atoms were located by conventional methods and refined with anisotropic temperature factors. H atomic coordinates were determined geometrically but were not refined. An absorption correction ($\mu = 14.5$ cm^{-1}) was applied. Block-diagonal refinement of 108 variables [using 1364 reflections with $I > 2.30\sigma(I)$] gave $R = 0.022$, $R_w = 0.035$.

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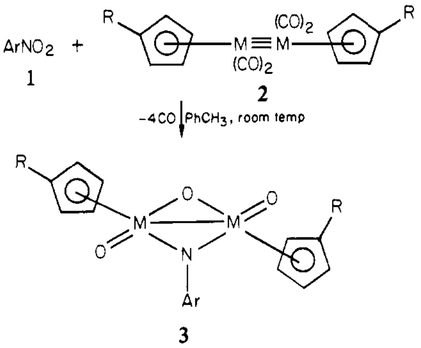
Table I. Pertinent Data for 3[a]

3, M, R, Ar	mp, °C	IR, cm^{-1} $\nu_{Mo=O}$	IR, cm^{-1} ν_{Mo-O}	^{1}H NMR, δ
Mo, H, p-$CH_3C_6H_4$	225	895	817	2.50 (s, 3 H, CH_3), 6.00 (s, 10 H, C_5H_5), 7.70 (d each, 4 H, J = 8 Hz, Ar H)
Mo, CH_3, p-$CH_3C_6H_4$	166	890	818	1.86 (s, 6 H, $CH_3C_5H_4$), 2.43 (s, 3 H, CH_3), 5.26, 5.70, 5.96 (m, 8 H, cyclopentadienyl ring protons), 7.23, 7.63 (d each, 4 H, J = 8 Hz, Ar H)
Mo, H, 1-naphthyl	164	897	801	5.83, 6.03 (s, 10 H, C_5H_5), 7.03 (m, 7 H, Ar H)
Mo, H, 1-fluorenyl	95	897	812	4.03 (s, 2 H, CH_2 of fluorene), 6.03 (s, 10 H, C_5H_5), 7.40, 7.90 (m, 7 H, remaining protons of fluorene)
W, H, p-$CH_3C_6H_4$	228	902	813	2.46 (s, 3 H, CH_3), 5.86 (s, 10 H, C_5H_5), 7.30, 7.70 (d each, 4 H, Ar H)

[a] Satisfactory C, H, N, Mo elemental analyses were obtained for 3.

Scheme I



made, and an ORTEP view of the molecule is given in Figure 1,together with pertinent bond distances and bond angles. The bridging and terminal molybdenum-oxygen distances are similar to those in other complexes having such structural features [e.g., $BaMo_2O_4(C_2O_4)_2{\cdot}5H_2O$].[11] The molybdenum-molybdenum bond distance of 2.6497 Å is consistent with the presence of a single bond between the two metal atoms and a Mo(V) oxidation state. While this bond distance is somewhat longer than that of ionic binuclear molybdenum(V) compounds bearing a Mo–Mo single bond ($Mo_2O_4^{2+}$ core 2.56 Å;[12] $Mo_2O_4(C_2O_4)_2^{2-}$ 2.541 Å),[11] complex 3 is uncharged. The trans disposition of the cyclopentadienyl and terminal oxygen groups is also noteworthy.

The reaction of p-nitrotoluene with the (cyclopentadienyl)molybdenum dicarbonyl dimer is not an isolated curiosity. It is a general process, applicable to the methyl-substituted molybdenum complex 2, M = Mo, R = CH_3, and to the tungsten complex 2, M = W, R = H, as well as to other nitro compounds. Melting points and spectral data for 3 are listed in Table I.

There are several novel features of the reaction of nitro compounds with the M≡M complexes. First, it is an unusual case of complete decarbonylation of 2 with retention of a metal-metal bond in the product. Second, we have succeeded in capturing a molybdenum-oxo containing a bridging μ-nitrene ligand (as well as a μ-oxo ligand). Third, complex 3 has, as noted above, several noteworthy structural features.

Finally, it is worth noting that hydrogenation of 3, M = Mo, R = H, Ar = p-$CH_3C_6H_4$, effected under phase-transfer conditions [5 N NaOH, $PhCH_2N(C_2H_5)_3{}^+Cl^-$, C_6H_6, room temperature, 1 atm, 15 h], afforded p-toluidine in quantitative yield.

The following general procedure was used: a toluene (10 mL) solution of the nitro compound (1.0 mmol) was added to 2 (1.0 mmol, generated from $[C_5H_4M(CO)_3]_2$ in 30 mL of refluxing toluene) at room temperature. The reaction mixture was stirred for 3 h and then concentrated by rotary evaporation of the solvent.

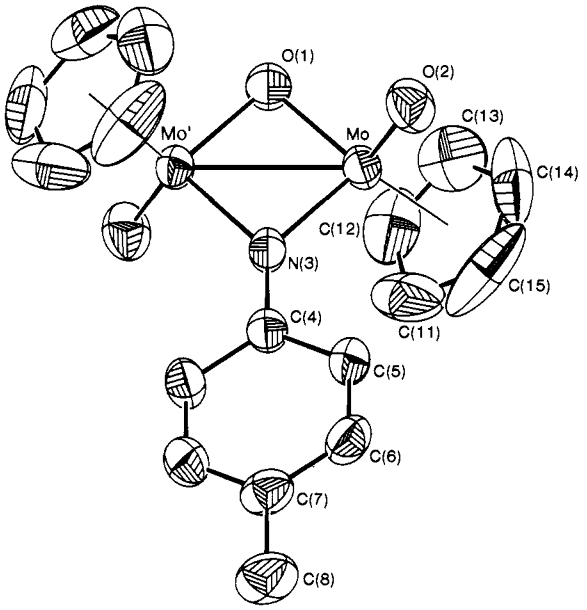


Figure 1. ORTEP diagram of 1. The molecule possesses a crystallographic 2-fold axis running through O(1), N(3), C(4), C(7), and C(8). Selectred distances (Å): Mo–Mo', 2.6497 (5); Mo–O(1), 1.933 (2); Mo–O(2), 1.708 (2); Mo–N(3), 1.958 (2). Selected angles (deg): Mo'–O(1)–Mo, 86.5 (1); Mo–N(3)–Mo', 85.2 (1); Mo'–Mo–O(2), 113.56 (9); O(1)–Mo–N(3), 94.14 (8).

Pure 3 was obtained by column chromatography on Florisil with ether as the eluant or by thin-layer chromatography (silica gel) using 2:1 ether/methylene chloride as the developing solvent mixture. The yields of 3 were 40–46%, with $[(C_5H_4R)M(CO)_3]_2$, which contains a metal-metal single bond, formed as a byproduct.

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Registry No. 1 (Ar = p-$CH_3C_6H_4$), 99-99-0; 1 (Ar = 1-naphthyl), 86-57-7; 1 (Ar = 1-fluorenyl), 22250-99-3; 2 (M = W; R = H), 62853-03-6; 2 (M = Mo; R = H), 56200-27-2; 2 (M = Mo; R = Me), 69140-73-4; 3 (Ar = p-$CH_3C_6H_4$; M = Mo; R = H), 84801-10-5; 3 (Ar = p-$CH_3C_6H_4$; M = Mo; R = CH_3), 84801-11-6; 3 (Ar = 1-naphthyl; M = Mo; R = H), 84801-12-7; 3 (Ar = 1-fluorenyl; M = Mo; R = H), 84801-13-8; 3 (Ar = p-$CH_3C_6H_4$; M = W; R = H), 84801-14-9; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Three tables listing atomic coordinates, thermal parameters, and bond distances and angles for μ-$NC_6H_4CH_3(\mu$-$O)[(C_5H_5)MoO]_2$ (4 pages). Ordering information is given on any current masthead page.

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