Structural and Electronic Consequences of Coordinating Butadienes to (η5-C5H5)Mo(NO)[1]

Allen D. Hunter and Peter Legzdins*

Department of Chemistry
The University of British Columbia
Vancouver, British Columbia, Canada V6T 1Y6

Frederick W. B. Einstein* and Anthony C. Willis

Department of Chemistry, Simon Fraser University
*Burnaby, British Columbia, Canada V5A 1S6*

Bruce E. Bursten*† and Michael G. Gatter

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Currently, the only monometallic fragments known to be capable of coordinating acyclic conjugated dienes in a transoidal fashion are Cp_2M (Cp = η^5-C_5H_5 or η^5-C_5Me_5; M = Zr, Hf)[2] and CpMo(NO) (Cp = η^5-C_5H_5).[3] For the Cp_2M systems, the η^4-*trans*-diene complexes are generally less thermodynamically stable under ambient conditions than their η^4-*cis*-diene isomers but are often isolable because of their kinetic stability.[2,4] We now wish to present evidence that in the case of CpMo(NO) this thermodynamic stability order is dramatically reversed and to offer a molecular-orbital rationale for the pronounced preference of this fragment to coordinate butadienes in an η^4-trans manner.

When reaction 1 is effected at 0 °C (rather than at room

$$[CpMo(NO)I_2]_2 + 4Na/Hg + 2(diene) \xrightarrow{THF}$$
$$2\ CpMo(NO)(\eta^4\text{-diene}) + 4\ NaI + Hg \quad (1)$$
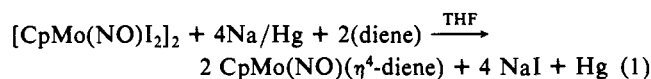
temperature)[3] with diene = 2,3-dimethylbutadiene,[5] monitoring of its progress by IR spectroscopy reveals the initial formation of the novel η^4-*cis*-diene **1** (ν_{NO} 1567 cm^{-1}) and the well-defined[3] η^4-*trans*-diene **2** (ν_{NO} 1608 cm^{-1}) product complexes in a molar ratio of ~4:1. This ratio diminishes continually with the passage of time. Nevertheless, by fractional crystallization of the dried final reaction mixture from Et_2O–hexanes at 0 °C, **1** and **2** may be isolated in yields of 13% and 37% as analytically pure, orange and yellow crystals, respectively.[6]

Single-crystal X-ray crystallographic analysis of **1**[7] established that it possesses a type of "three-legged piano stool" molecular structure having a crystallographically imposed mirror plane in the solid state (Figure 1).[8] The Cp–Mo linkage is normal,[3,9] and the Mo–N–O geometry (particularly the angle at N of 161.0

†Camille and Henry Dreyfus Foundation Teacher–Scholar (1984–1989) and Fellow of the Alfred P. Sloan Foundation (1985–1987).

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(5) 2,3-Dimethylbutadiene coordinates to Cp_2Zr exclusively in a cisoidal manner.[2]

(6) Complete details presented in the supplementary material.

(7) Crysals of **1** are orthorhombic; space group *Pnma*; *a* = 17.414 (3) Å, *b* = 9.116 (4) Å, *c* = 7.280 (1) Å; *V* = 1155.67 Å^3; *Z* = 4; absorption coefficient = 10.78 cm^{-1}; diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator ($\lambda(K\alpha_1)$ = 0.709 30 Å); scan range = 0° ≤ 2θ ≤ 60°; reflections = 1352 with $I_o \geqslant 3\sigma I_o$; R = 0.028, R_w = 0.028; error in observation of unit weight = 1.73 e. All atoms, including H atoms, were refined.

(8) Thermal ellipsoids enclose 50% probabilities. H atoms are shown as spheres with arbitrarily small radii. Davies, E. K. *'CHEMGRAF Users' Guide*; Chemical Crystallography Laboratory; University of Oxford, England, 1983.

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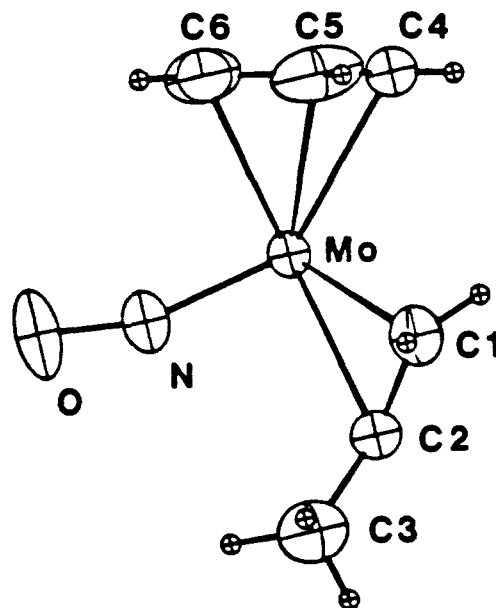
(a)
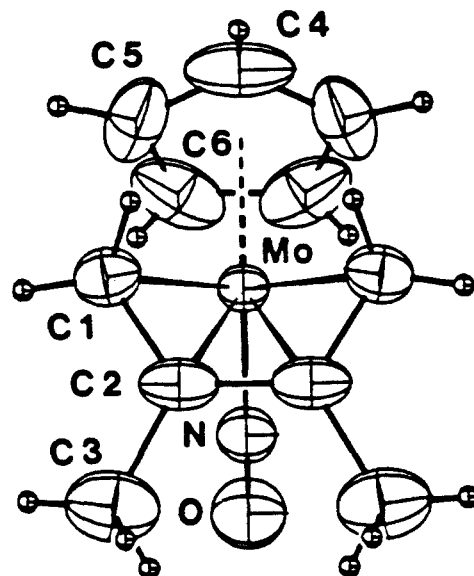
(b)

Figure 1. Views of the molecular structure of **1** (a) along the mirror plane and (b) perpendicular to the mirror plane. Selected bond lengths (Å) and angles (deg): Mo–N = 1.773 (3), N–O = 1.218 (4), Mo–N–O = 161.0 (3), C1–C2 = 1.410 (4), C2–C2' = 1.414 (6), Mo–C1 = 2.220 (3), Mo–C2 = 2.338 (2), C2–C3 = 1.504 (5), C1–C2–C2' = 122.0 (2), C1–C2–C3 = 117.3 (3), C3–C2–C2' = 119.8 (3), Mo–Cp(centroid) = 2.017 (2).

(3)°)[10] is indicative of considerable Mo→NO back-bonding. [That this back-bonding is greater in **1** than in **2** is suggested by the lower ν_{NO} values evident in the IR spectra of **1** (vide supra).] Furthermore, the intramolecular dimensions of the diene–Mo linkage (representable as [⊂–Mo)⁴ may be viewed as resulting from increased back-donation of electron density from Mo into the π_3* MO of the planar *cis*-diene ligand. The spectroscopic properties of **1**[6] (particularly the geminal coupling constant of 5.04 Hz evident in its ^{1}H NMR spectrum in C_6D_6) are consistent with this view and also indicate that **1** retains its η^4-*cis*-diene–Mo configuration initially in solutions. However, that **1** is the kinetic product of

(10) For comparison, the Mo–N–O linkage in CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) has similar Mo–N and N–O bond lengths, but the Mo–N–O angle is 172.2 (2)°.[3]
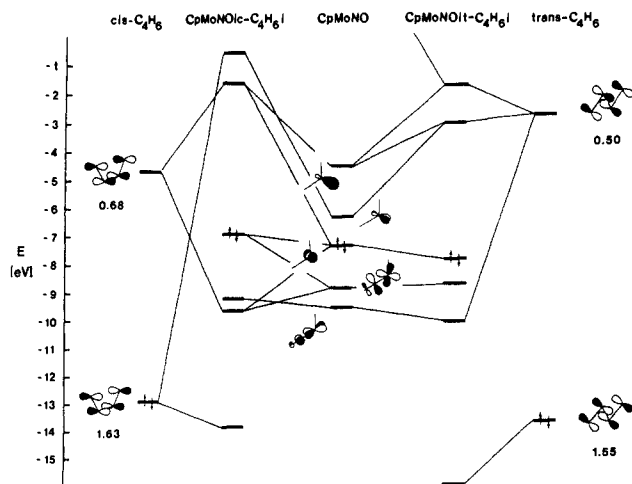
Figure 2. Molecular orbital diagram showing the interaction of the π_2 and π_3* orbitals of cis- and trans-butadiene with the frontier orbitals of the CpMo(NO) fragment. The Mulliken populations of the diene orbitals after complexation are given below the sketch of each (free ligand populations: π_2 = 2.0; π_3* = 0.0). The paired electrons indicate the HOMO of each species.

reaction 1 is established by the fact that it isomerizes irreversibly to 2 (with some attendant decomposition) in these solutions. This isomerization is rapid at 20 °C in donor solvents such as THF ($t_{1/2}$ ~ 5 min) but slower in nondonor solvents such as benzene ($t_{1/2}$ ~ 1 day). Once formed, the bound trans-diene in 2 (or in any other known CpMo(NO)(η^4-trans-diene) complex)[3] does not revert to its cis form even upon heating to the decomposition point of the complex in various solvents.

To rationalize the unprecedented stability of 2 over 1 in terms of their electronic structures, we have performed Fenske-Hall MO calculations[11] on the model systems containing cis- and trans-butadiene bound to CpMo(NO) in the fashion found in 1 and CpMo(NO)(η^4-trans-2,5-dimethyl-2,4-hexadiene),[3] respectively.[12] These calculations lead to the orbital interaction diagrams and Mulliken populations presented in Figure 2. In both model complexes there is substantial donation from the diene π_2 orbital to the metal and back-donation from the metal to the diene π_3* orbital. The cis-diene is calculated to be both a weaker donor and stronger acceptor than the trans-diene; in spite of this, the NO 2π population is greater in the cis complex (1.57 e) than in the trans complex (1.51 e), in accord with the IR data for 1 and 2. The greater stability of the trans complex, as evidenced by a HOMO energy ca. 0.9 eV lower than that of the cis complex, results from the asymmetry of the trans-diene ligand which is better able to stabilize the high-lying occupied orbitals of the CpMo(NO) fragment.

Finally, the results of these calculations (taken in conjunction with those performed on the related $Cp_2Zr(\eta^4$-butadiene) complexes)[4] suggest the following electronic criteria which a monometallic fragment (L_nM) must satisfy in order to coordinate butadienes preferentially in a trans manner: (1) L_nM must possess valence orbitals such that its HOMO and LUMO are coplanar and have σ and π rotational symmetry, respectively, with respect to the centroid of the diene ligand, and (2) L_nM must be relatively electron deficient to minimize electron donation from its HOMO and to maximize acceptance of electron density into its LUMO and higher lying unoccupied molecular orbitals. Experiments are currently in progress to test the general applicability of these criteria.

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Fluorescence of 6-Dodecyl-2-naphthol in Monolayers at the Air-Water Interface

F. Grieser, P. Thistlethwaite,* and P. Triandos

Department of Physical Chemistry, Melbourne University
Parkville, Victoria 3052, Australia

A number of different sorts of measurements have demonstrated that the apparent dielectric constant of the interfacial region of micelles, bilayers, and microemulsions is substantially lower than that of bulk water.[1-10] Although it has not always been recognized,[11] one result of this will be a pK_a shift for acid groups located at the interfaces of uncharged micelles.[1,2] By comparing the observed shifts with those obtained in suitable mixed solvents of known dielectric constant, an estimate of interfacial dielectric constant can be made.[1] Measurements with probe molecules whose absorption (solvatochromic probes)[4-6] or fluorescence spectrum[3,7,8] is sensitive to polarity provide independent confirmation of an interfacial dielectric constant ranging from 15 to 55 for various systems. Kinetic measurements on the hydrated electron in microemulsions are also in accord with these estimates.[9] The shift in pK_a of acid groups due to nonelectrostatic effects is also seen in cast monolayer films on solid substrates[2,12,13] but has not to date been demonstrated in air-water monolayers. It is not clear whether this reduced dielectric constant is entirely explicable in terms of the reduced concentration of water in an interface consisting of water and head groups[14] or whether there is an additional contribution due to water structuring associated with the proximity of the hydrocarbon tail groups.[14,6] Recent work on excited-state proton dissociation[15,16] has emphasized the importance of the molecular structure and dynamics of water and suggests that the dielectric constant may not be the most ap-

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