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Supplementary Material Available: Tables for atomic coordinates, bond distances and angles, and observed and calculated structure factors for **9** (12 pages). Ordering information is given on any current masthead page.

Very Twisted η^4 -*trans*-Diene Complexes^{1,2}

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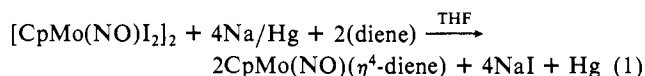
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Numerous, monomeric transition-metal complexes containing acyclic conjugated dienes have been synthesized since the first report of $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_3$ in 1930,³ and many of these have found applications in organic synthesis.⁴ In the vast majority of these compounds, the diene ligand is attached to the metal center in a planar η^4 -*s-cis* manner.⁵ Indeed, the only examples to date of η^4 -*s-trans* diene coordination to a single metal⁶ occur in $\text{Cp}_2\text{M}(\eta^4\text{-diene})$ complexes ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Zr}, \text{Hf}$).¹⁰ We now wish to report the preparation and characterization of three $\text{CpMo}(\text{NO})(\eta^4\text{-diene})$ compounds (**1**) which, in addition to being rare examples of (diene)nitrosyl complexes,¹¹ possess a novel type of diene-metal linkage.

The new molybdenum complexes **1** may be conveniently synthesized, albeit in low yields, by the general reaction



where diene = 2-methylbutadiene (**a**), 2,3-dimethylbutadiene (**b**), or 2,5-dimethyl-2,4-hexadiene (**c**). In a typical experiment, a red

solution of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ (2.00 g, 2.25 mmol) in THF (50 mL) containing the diene (2 mL, a 10- to 20-fold excess) was added to a sodium amalgam (0.23 g, 10 mmol of Na in 5 mL of Hg), and the mixture was stirred at room temperature. The supernatant solution immediately became yellow-brown in color. After 15 min, the final mixture was filtered through alumina (3 \times 6 cm, Woelm neutral, activity 1), and the filtrate was taken to dryness in vacuo. Crystallization of the resulting orange residue from hexanes at -10°C afforded ~ 0.15 g ($\sim 10\%$ yield) of the appropriate diene complex (**1a-c**) as yellow, somewhat air-sensitive crystals.¹³

Single-crystal X-ray crystallographic analysis of **1c**¹⁴ revealed it to possess a type of "three-legged piano stool" molecular structure (Figure 1)¹⁵ with normal Cp-Mo and Mo-NO geometries.¹⁶ The most chemically interesting feature of the structure involves the diene-Mo linkage in which the diene carbons adopt a transoidal, nonplanar arrangement with a torsion angle of $124.8(4)^\circ$ (Figure 1b). The central atoms are slightly closer to the metal center (Mo-C ~ 2.22 Å) than are the terminal carbons (Mo-C ~ 2.38 Å). Furthermore, the carbon-carbon bond lengths in the diene fragment are all similar (1.401-1.418 (4) Å) and classically intermediate to those expected for C-C and C=C bonds.¹⁷ This structural feature of **1c** stands in marked contrast to that found for $\text{Cp}_2\text{Zr}(\eta^4\text{-PhCH=CH-CH=CHPh})$ ¹⁸ (the only other structurally well-characterized monometallic η^4 -*trans*-diene complex) in which the analogous carbon-carbon bond distances exhibit the short (~ 1.40 Å)-long (~ 1.48 Å)-short (~ 1.40 Å) alternation characteristic of a diene. In molecular orbital terms,¹⁹ the unprecedented type of interaction between the dienes and the central molybdenum atoms in complexes **1** may thus be viewed as resulting from increased back-donation of electron density into the π_3^* MO's of the *trans*-diene ligands, a view supported by preliminary theoretical investigations.²⁰

The spectroscopic properties of all three complexes **1**¹³ indicate that they retain this twisted η^4 -*trans*-diene-Mo configuration in solution.²¹ In this connection, it may be noted that the ¹H NMR spectrum of **1c** in CDCl_3 displays a coupling constant for the meso hydrogens of the diene ligand (i.e., $^3J_{\text{HH}} = 12$ Hz) that is more in accord with those previously reported^{10,22} for the *cis*-diene

(12) Seddon, D.; Kita, W. G.; Bray, J.; McCleverty, J. A. *Inorg. Synth.* **1976**, *16*, 24.

(13) For **1c**. Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NOMo}$: C, 51.83; H, 6.36; N, 4.65. Found: C, 51.95; H, 6.44; N, 4.66. IR (CH_2Cl_2) ν_{NO} 1584 (s) cm^{-1} ; ¹H NMR (CDCl_3) δ 5.30 (s, 5 H, C_5H_5), 3.34 (d, 1 H, CH, $J = 12$ Hz), 2.71 (d, 1 H, CH, $J = 12$ Hz), 2.09 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3); low-resolution mass spectrum (probe 50°C), m/z 303 (P^+ , ⁹⁸Mo). Analogous data for **1a** and **1b** are presented in the supplementary material.

(14) X-ray diffraction data for $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\eta^4\text{-C}_8\text{H}_{14})$: monoclinic; space group $\text{P}2_1/c$; $a = 12.153(2)$ Å, $b = 9.275(1)$ Å, $c = 12.909(4)$ Å; $\beta = 117.31(2)^\circ$; $V = 1292.9$ Å³; $Z = 4$; absorption coefficient = 9.69 cm^{-1} ; diffractometer, Enraf-Nonius CAD4F; radiation, Mo $\text{K}\alpha$, graphite monochromator ($\lambda(\text{K}\alpha_1) = 0.70930$ Å); scan range = $0^\circ \leq 2\theta \leq 50^\circ$; reflections = 1862 with $I_0 \geq 3\sigma I_0$; $R = 0.021$, $R_w = 0.024$; error in observation of unit weight = 1.61 e. All atoms, including H atoms, were refined.

(15) 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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(19) Tatsumi, K.; Yasuda, H.; Nakamura, A. *Isr. J. Chem.* **1983**, *23*, 145.

(20) Bursten, B. E.; Gatter, M. G., personal communication.

(21) The ¹H NMR spectrum of **1a** in CDCl_3 at 30°C also reveals that the compound exists as a 3:1 mixture of isomers which presumably differ in the orientation of the 2-methyl substituent with respect to the Cp group. For purely steric reasons, the major isomer probably has the methyl group directed away from the Cp ring.

(22) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics*, **1982**, *1*, 388.

(1) Organometallic Nitrosyl Chemistry 24. For part 23, see: Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.*, in press.

(2) Taken in part from: Nurse, C. R. Ph.D. Dissertation, The University of British Columbia, Vancouver, Canada, 1983.

(3) Reihlen, H.; Grühl, A.; von Hessling, G.; Pfrengle, O. *Liebigs Ann. Chem.* **1930**, *482*, 161.

(4) Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: Oxford, England, 1982.

(5) See, for example: (a) Erker, G.; Engel, K.; Krüger, C.; Müller, G. *Organometallics* **1984**, *3*, 128. (b) Chinn, J. W., Jr.; Hall, M. B. *Organometallics* **1984**, *3*, 284 and references therein.

(6) Transoidal 1,3-butadiene is known to function as a bridging ligand between two metal centers in $[\text{CpMn}(\text{CO})_2]_2(\mu_2\text{-}\eta^4\text{-C}_4\text{H}_6)$,⁷ $[\text{Mn}(\text{CO})_4]_2(\mu_2\text{-}\eta^4\text{-C}_4\text{H}_6)$,⁸ and $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-}\eta^4\text{-C}_4\text{H}_6)$.⁹

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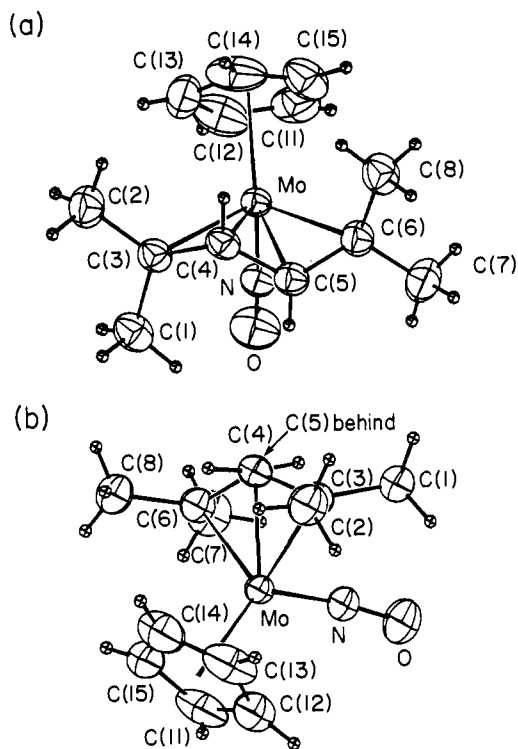


Figure 1. Views of the molecular structure of **1c** (a) along the axis bisecting the Cp-Mo-NO angle and (b) down the C(4)-C(5) bond. Selected bond lengths (Å) and angles (deg): Mo-N = 1.767 (2), N-O = 1.213 (3), Mo-N-O = 172.2 (2), C(3)-C(4) = 1.418 (4), C(4)-C(5) = 1.408 (4), C(5)-C(6) = 1.401 (4), Mo-C(3) = 2.390 (3), Mo-C(4) = 2.209 (3), Mo-C(5) = 2.234 (3), Mo-C(6) = 2.365 (3), C(Me)-C(av) = 1.510 (7), C(3)-C(4)-C(5) = 122.3 (3), C(4)-C(5)-C(6) = 122.1 (3), C(1)-C(3)-C(2) = 112.7 (3), C(1)-C(3)-C(4) = 121.7 (3), C(2)-C(3)-C(4) = 118.1 (3), C(3)-C(4)-H(4) = 115 (2), C(4)-C(5)-H(5) = 117 (2), C(5)-C(4)-H(4) = 120 (2), C(6)-C(5)-H(5) = 118 (2), C(5)-C(6)-C(7) = 117.9 (3), C(5)-C(6)-C(8) = 120.7 (3), C(7)-C(6)-C(8) = 112.6 (3).

complexes of Cp_2Zr ($^3J_{\text{HH}} \sim 10\text{--}11$ Hz) than their *trans*-diene analogues ($^3J_{\text{HH}} \sim 15\text{--}16$ Hz). This spectroscopic property thus reaffirms the partial double-bond character of the coordinated diene's central C-C link in **1c**.¹⁹ There is, however, no evidence in any case for isomerization of the bound dienes in **1** to their *cis* forms as occurs with $\text{Cp}_2\text{Zr}(\eta^4\text{-diene})$ species.¹⁰ Since there appears to be no steric restriction to such isomerization,²³ the factors responsible for the preferred linkage of dienes to the $\text{CpMo}(\text{NO})$ fragment in a twisted, *transoidal* fashion must be electronic in nature. Confirmation of this inference must obviously await a detailed theoretical analysis of the intramolecular bonding. In the interim, the characteristic reactivity of the bound dienes in **1** toward representative nucleophiles and electrophiles is currently under investigation.

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Supplementary Material Available: Elemental analysis and spectroscopic (IR, ^1H and ^{13}C NMR, mass spectral) data for **1a** and **1b** and tables of fractional coordinates and isotropic and anisotropic thermal parameters for **1c** (7 pages). Ordering information is given on any current masthead page.

(23) Indeed, this lack of steric crowding permits the isolation of complexes **1a** and **1b** which contain dienes that are sterically prohibited from attaining a *trans* configuration when coordinated to Cp_2Zr .¹⁹

Specific Long-Range Effects on Relaxation of Local Stress during a Solid-State Reaction

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Discussions of organic solid-state reactions have tended to stress the importance of the static structure of a reactant molecule and its environment. The environment's local mechanical properties should also be important, since some accommodation to reactant motion is essential. If it were adequate to approximate the medium as an isotropic continuum, one could treat mechanical properties with simple elasticity theory. But if the specific molecular mechanism by which stress is transmitted should be important, anisotropy would invalidate such a treatment. Here we report observations on the influence of crystal defects which demonstrate that mechanical effects can be both specific and of long range.

We have used FTIR spectroscopy to study pairs of CO_2 molecules generated by photolyzing single crystals of diundecanoyl peroxide (UP) at low temperature.¹ We previously found a characteristic sequence of IR patterns as stress resulting from bond cleavage was annealed.² The present work concerns UP crystals that were made defective by introducing 11.8% of decanoyl undecanoyl peroxide (DUP) as a solid solute.³ This means that 5.9% of the alkyl chains in the crystal were one-carbon short, leaving holes at the chain ends. Labeling one of the carboxyl carbons of DUP with ^{13}C made it possible to distinguish by FTIR spectroscopy between CO_2 pairs derived from DUP and those derived from UP.

Figure 1A shows $^{12}\text{CO}_2$ asymmetric stretching vibrations in such a crystal. There are 10 absorptions from 2329.3 to 2352.3 cm^{-1} . Nine of these can be assigned unambiguously to the first four stages of relaxation previously observed in pure UP crystals.⁴ We assign the new peak at 2330.9 cm^{-1} to the ^{12}C member of the $^{12}\text{CO}_2/^{13}\text{CO}_2$ pair from DUP. The isolated $^{13}\text{CO}_2$ peak at 2265.3 cm^{-1} (Figure 1B) is due to the other member of this pair. The assignment was confirmed by an analogous experiment in which the other carboxyl carbon of DUP was labeled. In this spectrum the guest $^{12}\text{CO}_2$ peak shifted down by 0.5 cm^{-1} to 2330.5 cm^{-1} , while the $^{13}\text{CO}_2$ peak shifted up by 0.5 cm^{-1} to 2265.8 cm^{-1} , as expected for isotopic exchange between CO_2 sites with frequencies differing by 0.5 cm^{-1} .

Under these conditions where CO_2 pairs from UP show a variety of structures, those from DUP guests show a single structure in which the CO_2 molecules do not exchange positions over a period of hours. Spectra of host and guest pairs remained distinct through further annealing, although CO_2 s in the guest sites began to exchange positions at higher temperature. Only after completing relaxation above 150 K did the strong peak from the host CO_2 (2333.7 cm^{-1}) correspond to that from the guest (2268.4 cm^{-1}). Until then the host always had at least one peak above 2338 cm^{-1} , higher than any guest peak.

(1) A Nicolet 7199 FTIR spectrometer was used with nominal resolution of 0.24 cm^{-1} to measure transmission through a sandwich of two crystal plates each about 5 mm wide and 0.1 mm thick. Absorbance subtraction was used to observe the effect of photolysis (<0.1% conversion, Osram 200W/2 Hg arc, CuSO_4 filter). Background absorption in the 2200-2400- cm^{-1} region was weak enough to give a reasonable base line, although the weak "triplet" near 2668 cm^{-1} in Figure 1B is probably artificial. The crystals were held in vacuum and cooled from the edges by a Displex CS-202 cryostat.

(2) For a preliminary account, see: McBride, J. M. *Acc. Chem. Res.* **1983**, *16*, 304.

(3) Crystals grown from methanol solution at 22 °C were shown to be single by examination with a polarizing microscope and to be solid solutions by their melting in a single exotherm upon differential scanning calorimetry. By X-ray diffractometry lattice constants were within 0.1% of those for pure UP. The concentration of DUP was estimated by 125.7-MHz ^{13}C NMR spectra in CD_2Cl_2 solution.

(4) There are 16 host absorptions some of which overlap or are too weak to observe. These arise because each stage consists of two slowly equilibrating structures, each with two different CO_2 molecules. Four stages are present simultaneously because of substantial temperature gradients in these crystals.