Synthesis, Reactivity, and Stereochemistry of η^4-Diene–Molybdenum Complexes. Metallocyclopentene Intermediacy in an Intramolecular Trans–Cis Olefin Isomerization

Sir:

Transition metal complexes of η^4-conjugated dienes exhibit interesting intramolecular rearrangements[1] and provide important intermediates in synthetic applications. We wish to report the preparation and characterization of a new class of η^4-diene complexes which display a previously unobserved type of stereochemical nonrigidity and provide synthons for a variety of stereoselective olefin reactions and interconversions.

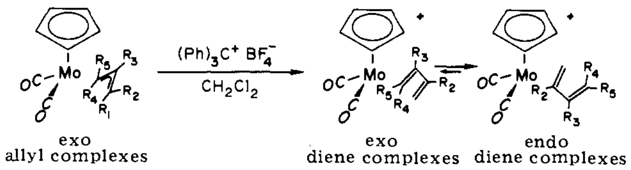
The coordinated butadiene cation **1** was readily prepared by hydride abstraction[2] from the *anti*-crotyl complex **2a** and was fully characterized by elemental analysis[3] and spectroscopic data. This reaction was extended to substituted derivatives as indicated in Chart I. For example, the 2,3-dimethyl and unsymmetrical 2- and 1-methylbutadiene cations **3, 4,** and **5** have been prepared through similar sequences involving **6, 7,** and **8.**

Cation **1** displays temperature-dependent ^{1}H NMR spectra consistent with its formulation as exo and endo conformational isomers, which equilibrate with a ΔG^* of 14.1 kcal/mol. The endo conformer is more stable based upon comparison of ^{1}H NMR results with the η^3-allyl complexes **9** and **10,** in which the anti and syn protons respectively resonate at lower and higher field in the endo conformers.[4,5] This assignment was confirmed by the low temperature ^{1}H NMR spectrum of the corresponding η^5-indenyl complex **11.**[6] Furthermore, the ^{1}H NMR assignments for **1** and its homologues compare favorably with those for related η^4-butadiene complexes (Table I).[7-12] Infrared spectra are consistent with the proposed equilibrium. Complex **1** displays two strong carbonyl bands at 2055 and 2005 cm^{-1} and a clearly discernable band of lower intensity at 1985 cm^{-1} in nitromethane.

At −60 °C the conformer ratio for **1** ($K_{\text{exo/endo}}$) is 0.21 ($(CD_3)_2CO$) as compared to neutral **9** where $K = 4.7$ or **10** where $K = 0.38$.[13]

Reduction ($NaBH_3CN$, THF, −78°C) of both **1** and **4** proceeds stereospecifically to return the starting allyl complexes **2a** and **7** in 55–60% yield. On the basis of steric effects, attack at C-4 would be expected in **4**[14] and the specificity was unexpected. As both η^3-allyl complexes **7** and **12** bear an *anti*-methyl substituent, relative energies of the endo conformers are comparable. Since a 2-methyl substituent tends to promote population of *endo*-allyl conformers and since *anti*-methyl substituents strongly favor the exo orientation, these opposing effects will tend to destabilize **12** and may determine the greater effective reactivity of C-1.

Chart I. Cationic Diene Complexes Derived from Allyl Complexes



Allyl Complexes

No.	R_1	R_2	R_3	R_4	R_5
2a	Me	H	H	H	H
2s	H	Me	H	H	H
6	Me	Me	Me	H	H
7	Me	Me	H	H	H
8sa	Me	H	H	H	Me
8ss	H	Me	H	H	Me
9	H	H	H	H	H
10	H	H	Me	H	H
12	Me	H	Me	H	H
13	Et	H	H	H	H
14	a	H	H	H	H

Diene Complexes

No.[a]	R_2	R_3	R_4	R_5
1	H	H	H	H
3	Me	Me	H	H
4	H	Me	H	H
5t	H	H	H	Me
5c	H	H	Me	H

[a] $R_1 = CH_2C(CH_3)_2CHO$.

Cation **5** appears to react with lower regioselectivity than **1** or **4** upon reduction, providing a 65% yield of isolated isomeric products. While **8sa** is the major product, 30% of the mixture is the *anti*-1-ethyl complex, **13.**[14,15]

Production of **13** may occur by either reduction of **5t** at C-4 or stereospecific attack on the isomeric cation **5c** at C-4. In the isomeric 1-*anti*-methylbutadiene cation, **5c,** reduction at C-1 would not be expected, as this would lead to an η^3-allyl complex bearing two *anti*-methyl substituents.[4] Thus, *under predictable conditions* this procedure permits the conversion of η^3-allyl complexes from the internal to the external mode while maintaining the anti configuration.

The use of complexes of type **1** in the preparation of functionalized 1-*anti*-allyl complexes is illustrated in the smooth enamine alkylation of **1** with isobutyraldehyde pyrrolidine enamine (CH_3CN, 0 °C). Complex **14** was formed stereospecifically in the anti configuration in 76% isolated yield.[16]

In addition to endo–exo conformational averaging, cation **5** executes an additional structural rearrangement which is manifested by further line broadening at high temperature. In the limiting spectrum of **5** (−50 °C, 270 MHz) resonances due to four isomeric complexes are observed. These are clearly

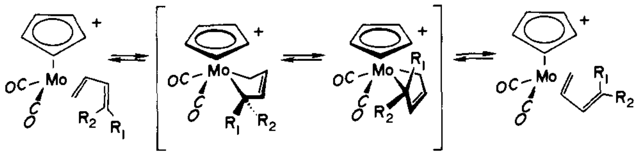
Table I. ^{1}H NMR Assignments for Selected η^4-Diene Cations as BF_4^- Salts[a]

			δ (J in Hz)			
Complex	Temp, °C	η^5-C_5H_5	H_a	H_s	H_c	CH_3
1 endo	−70	6.13	2.28 (d, 9.6)	3.07 (d, 7.4)	6.45	
1 exo	−70	6.13	2.09 (dd, 8.02, 2.0)	3.36 (dd, 7.4, 2.0)	6.17	
1 av	50	6.08	2.23 (d, 9.2)	3.18 (d, 7.4)	6.39 (m)	
3 av	20	5.98	2.03 (s)	3.09 (d, 1.5)		2.55 (s)
4 av	30	6.03	2.00	3.06 (dd, 7.3, 1.8)	6.29 (t, 8.6)	2.56 (s)
			2.22	3.12		
5t endo	−50	6.05	2.20 (d, 10.7)	2.98 (d, 7.8)	6.22 (m)	1.77 (d, 5.9)
			3.41 (m)		6.34 (m)	
5 av	60[b]	5.90		2.55	6.15 (m)	1.81 (d, 6.2)
			3.25		6.25 (m)	

[a] Only the shifts of the major isomer are given in the low temperature spectra. [b] At 60 °C the H_a and H_s resonances are coalesced to a broad signal ($\nu_{1/2}$ = 40 Hz).

indicated by the presence of four methyl doublets at δ 1.765, 1.740, 1.830, and 1.810 and four cyclopentadienyl singlets at δ 6.050, 6.034, 6.129, and 6.113 in the ratio of 222:93:22:1. The four sets of coordinated piperylene resonances are consistent with those expected based on the possibilities arising from exo-endo and cis-trans isomerism.

As the temperature was raised the signals assigned to endo-cis and exo-cis, as well as those assigned the endo-trans and exo-trans, isomers averaged pairwise. Thus at −32 °C two sets of resonances have averaged and one observes two methyl doublets at δ1.77 and 1.84 and two cyclopentadienyl singlets at δ 6.045 and 6.125, respectively, in the ratio of 11:1. Increasing the temperature results in further line broadening in the methyl and cyclopentadienyl regions. These signals coalesce at 20 °C to two sharp resonances, a doublet (6.0 Hz) and a singlet at δ 1.82 and 6.04, respectively. At this temperature the resonances assigned to the syn and anti protons on the unsubstituted terminal diene carbon atoms show broadening. A process by which this exchange may be accomplished is one involving the formation of a solvated metallocyclopentene intermediate.[17]



Configurational interconversion of syn and anti substituents in **5** may be achieved by flip of the metallocycle envelope followed by collapse to the η^4-butadiene structure. Passage through a metallocyclopentene intermediate also serves to interconvert conformational isomers, but it is a path of higher energy than the rotational motion corresponding to that observed for **1.** The ^{1}H NMR spectrum of cation **5** at 70 °C in the presence of 1 equiv of piperylene shows sharp resonances for the piperylene,[18] whereas the syn and anti protons are extremely broad. Thus we conclude that the configurational averaging is intramolecular.

In addition to the unusual stereochemical nonrigidity displayed by the η^4-diene cations, the η^3-allyl complexes derived by stereospecific addition reactions can be used as intermediates in homologation sequences by activation with $NOPF_6$.[13]

We are continuing to explore the stereochemistry associated with these species and to enlarge the scope of their reactivity.

References and Notes

(1) J. Takats and L. Kruczynski, *J. Am. Chem. Soc.*, **96,** 932 (1974); *Inorg. Chem.*, **15,** 3140 (1976).

(2) J. Y. Merour, C. Charrier, J. Benaim, J. L. Roustan, and D. Commereuc, *J. Organometal. Chem.*, **39,** 321 (1972). We have also observed formation of **1** and **5** by hydride abstraction from the *syn*-allyl complexes **2s** and **8ss.** Also an alternate path involving attack of Ph_3C^+ on the allyl group has been observed in addition to hydride abstraction. Cation **1** was obtained in 50% yield.

(3) Calcd for $C_{11}H_{11}O_2MoBF_4$ (1): C, 36.91; H, 3.10. Found: C, 36.57; H, 3.07.

(4) J. W. Faller, C. C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organometal. Chem.*, **52,** 361 (1972).

(5) The recent x-ray structure of η^5-$C_5H_5Mo(Ph_2PCH_2CH_2PPh_2)C_6H_8$ cation supports this assignment. The endo isomer is found in spite of the bulky ethano bridge. See J. A. Segal, M. L. H. Green, J. C. Darin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 766 (1976).

(6) At −43 °C under slow exchange conditions resonances for both conformers are observed for **11.** The upfield shift of the terminal protons in the endo conformer and those of the 2 and 3 protons in the exo conformer mirror the ring current induced shifts observed in **9** and **10** and their indenyl analogues.[4] The chemical shifts, δ (the ring current shifts relative to **1**), for the indenyl complex in acetone follow: endo, anti −0.34 (1.94), syn 3.18 (0.11), central 6.39 (−0.06); exo, anti 1.84 (0.25), syn 4.71 (1.35), central 5.27 (0.90).

(7) J. G. Preston, Jr., and J. C. Davis, Jr., *J. Am. Chem. Soc.*, **88,** 1535 (1966).

(8) M. L. H. Green, L. Pratt, and G. W. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

(9) P. Crews, *J. Am. Chem. Soc.*, **95,** 636 (1973).

(10) G. F. Emerson, J. E. Mahler, R. Kochar, and R. Pettit, *J. Org. Chem.*, **29,** 3620 (1964).

(11) E. Koerner von Gustorf, C. Jaenicke, and O. E. Polansky, *Angew. Chem., Int. Ed. Engl.*, **11,** 532 (1972).

(12) ^{1}H NMR assignments (δ) are given for selected η^4-diene cations as BF_4^- salts relative to internal acetone (δ 2.04).

(13) In CD_3CN at 0 °C. See J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, **98,** 3388 (1976).

(14) A. J. Pearson, *Aust. J. Chem.*, **29,** 1101 (1976).

(15) This is supported by the ^{1}H NMR spectrum where **13** displays an ABX_3 multiplet with the diastereotopic methylenes resonating at δ 0.96 and 1.30. The syn proton adjacent to the ethyl group is observed as a doublet of triplets at δ 2.83 (J = 7.0, 2.0 Hz).

(16) The allyl complex containing the aldehyde function showed the following characteristics: IR (cyclohexane) ν_{CO}, 1957, 1884 cm^{-1}, ν_{CHO} 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.40 (s, 1 H, CHO), 5.26 (s, 5 H, η^5-C_5H_5), 4.07 (dt, 1 H, H_c, J = 11.0, 7.5 Hz), 3.59 (complex t, 1 H, H_s), 2.87 (ddd, 1 H, H_s, J = 7.5, 2.5, 1.5 Hz), 2.06 (dd, 1 H, diastereotopic CH_2, J = 14.5, 3.0 Hz), 1.25 (dd, 1 H, H_a, J = 11.0, 1.5 Hz), 1.07, 104 (2 s, 6 H, diastereotopic CH_3), 0.26 (dd, 1 H, diastereotopic CH_2, J = 14.5, 12.5 Hz). ^{1}H NMR assignments were confirmed by spin decoupling at 270 MHz. We have not yet explored detailed methodology for decomplexation of the functionalized allkyl ligand from **14,** but note that protonation of **9** with CF_3COOH liberates propene.

(17) The geometric and electronic requirements necessary to accommodate the metallo cyclic intermediate in configurational and conformational rearrangements have not been fully delineated as piperylene iron tricarbonyl does not evidence line broadening to 100 °C. Intermediates of the type discussed herein may be important in the formation of 2-alkenes arising from pyrolysis of platinometallocycles: J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98,** 6521 (1976). A stable 3,4-platinometallocyclopent-3-ene of this type has been reported: M. Green, Conference on the Place of Transition Metals in Organic Synthesis, New York Academy of Science, New York, N.Y., Nov 10, 1976.

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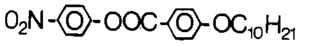
Effect of Molecular Structure on Mesomorphism. 3. 4-Nitrophenyl 4′-Decyloxybenzoate: A Liquid Crystal with Novel Mesomorphic Properties[1]

Sir:

As nonideal behavior of binary liquid crystal mixtures is of considerable current interest both from a theoretical viewpoint and in device technology, we wish to report the unusual x-ray diffraction of 4-nitrophenyl 4′-decyloxybenzoate (**1**) and its relation to nonlinear mixture properties of **1.** This compound



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was prepared by the reaction in pyridine of 4-nitrophenol and 4-decyloxybenzoyl chloride. Repeated recrystallization of crude product from ethanol-water afforded **1** as a white crystalline solid. It melts at 55 °C to a smectic A phase and at 77.5 °C transforms from the smectic A phase to an isotropic liquid. The smectic phase often appears, between microscope slide and coverslip, in a homeotropic texture, but can be obtained in a focal-conic fan texture. An x-ray photograph of **1** at 62 °C in its smectic phase showed two prominent diffraction rings. Using the relation $\lambda = 2\,d \sin\theta$, the outer diffuse ring corresponds to a D value of 4.65 Å, related to the intermolecular distance in the smectic layers. This value is consistent with current theory.[2] The sharp, intense inner ring corresponds to a d value of 31.4 Å—considerably greater than the length, l, of 27.4 Å for the most extended molecular configuration of **1.** This is quite unusual. Almost without exception this d value, thought[2] to be related to smectic layer thickness, tends to be several angstroms less than the molecular length. A notable