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DISTORTIONS IN TRIHAPTO-ALLYLS INDUCED BY ELECTRONIC ASYMMETRY: A COMPARISON OF THE STRUCTURES OF $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)$ AND $(\eta^5\text{-}C_5H_5)Mo(NO)(I)(\eta^3\text{-}C_3H_5)$

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Summary

The electronic asymmetry induced by replacing two carbonyls by a nitrosyl and iodide ligand causes severe distortions in the allyl moiety. The allyl group in the nitrosyl complex is bound in a sigma-pi mode rather than the symmetrical mode found in the dicarbonyl. This change in ground state structure alters the *exo—endo* conformer interconversion mechanism from a rotation of the allyl in the dicarbonyl to a sigma-pi interconversion in the nitrosyl iodide.

Stereospecific nucleophilic addition at one terminus of the η^3-allyl ligand is observed in $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^3\text{-}C_3H_5)][PF_6]$ [1,2]. This implies a marked inequivalence in the reactivity of the termini of the η^3-allyl moiety with respect to nucleophilic attack. To ascertain whether this inequivalence might arise from ground state effects, we have examined the crystal and molecular structure of an analogous compound with two ligands of radically different electronic character, $(\eta^5\text{-}C_5H_5)Mo(NO)(I)(\eta^3\text{-}C_3H_5)$. To provide a basis for comparison, we have also determined the structure of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)$, which possesses a symmetrical allyl. NMR studies have shown that in solution these complexes undergo a rapid *endo—exo* conformational interconversion [1,3,4].

The compound, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)$ (I) crystallizes with the η^3-allyl ligand in the *exo* conformation. Thus, the *endo—exo* equilibrium, which occurs by rotation of the allyl [4], adjusts the solution concentrations as the *exo* isomer crystallizes; hence, on evaporation of the solvent only the *exo* conformer is obtained. As shown in Fig. 1, this molecule is rigorously symmetric and contains a crystallographic mirror plane which bisects the OC—Mo—CO angle, the allyl ligand, and the cyclopentadienyl ring. The molybdenum—allyl distances, as well as intraligand allyl distances are normal, Mo—C(1) 2.236(4) Å, Mo—C(2) 2.359(3) Å; C(1)—C(2) 1.380(4) Å. In contrast to I, $(\eta^5\text{-}C_5H_5)$Mo-

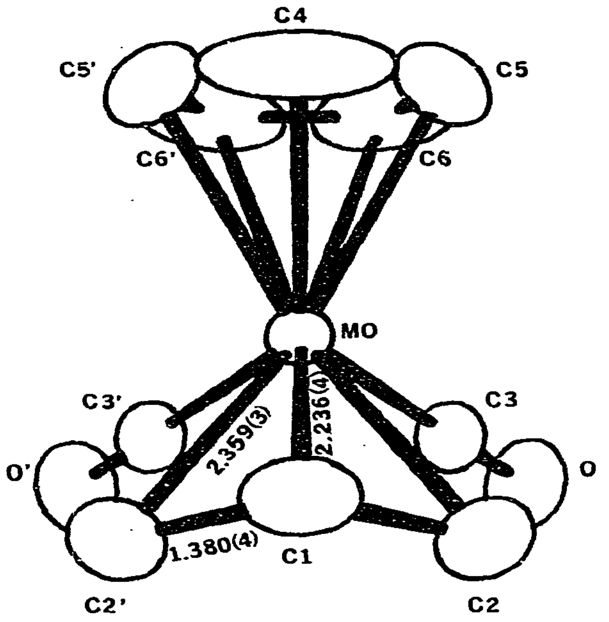

Fig. 1. An ORTEP view of $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_5)(CO)_2$ with 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

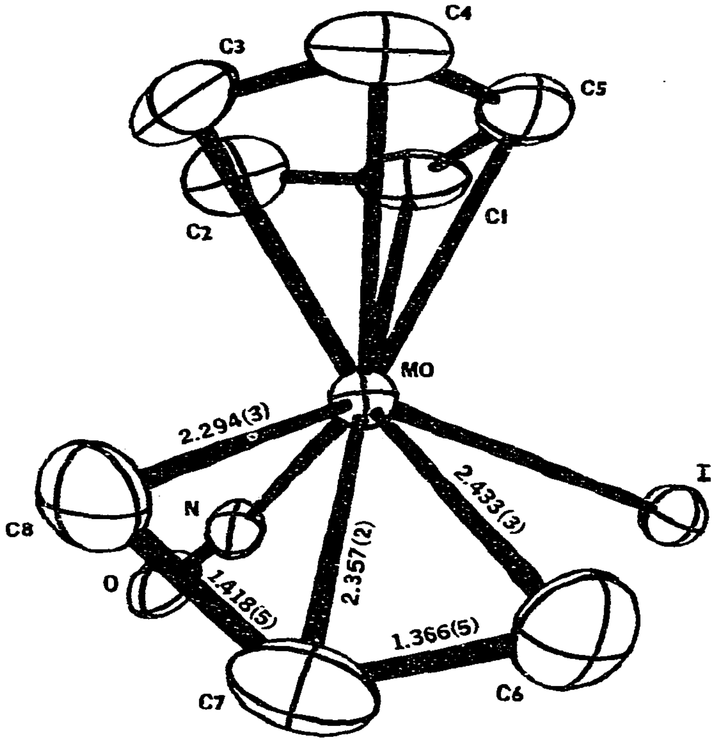

Fig. 2. An ORTEP view of $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_5)(NO)(I)$ with 50% probability ellipsoids. The hydrogen atoms have been omitted for clarity.

TABLE 1

INTRAMOLECULAR BOND DISTANCES AND ANGLES FOR CRYSTALLINE $(\eta^5\text{-}C_5H_5)\,Mo(CO)_2(\eta^3\text{-}C_3H_5)$

Atoms	Distance (Å)	Atoms	(Angles (degrees)
Mo—C(1)	2.236(4)	C(3)—Mo—C(3′)	82.5(2)
Mo—C(2)	2.359(3)	C(3)—MoC(1)	105.0(1)
Mo—C(3)	1.951(3)	C(3)—MoC(2)	72.2(1)
Mo—C(4)	2.348(6)	C(3)—Mo—C(2′)	111.5(1)
Mo—C(5)	2.340(4)	C(2)—Mo—C(2′)	61.3(2)
Mo—C(6)	2.321(4)	C(1)—Mo—C(2)	34.8(1)
C(3)—O	1.156(4)	Mo—C(3)—O	178.9(3)
C(1)—C(2)	1.380(4)	C(4)—Mo—C(5)	32.4(2)
C(4)—C(5)	1.307(9)	C(5)—Mo—C(6)	32.9(2)
C(5)—C(6)	1.322(9)	C(6)—Mo—C(6′)	35.2(4)
C(6)—C(6)	1.405(14)	C(4)—C(5)—C(6)	109.5(5)
		C(5)—C(6)—C(6′)	105.9(4)
		C(5)—C(4)—C(5′)	109.2(8)
		C(2)—C(1)—C(2′)	121.4(4)

(NO)(I)(η^3-C_3H_5) (II) shown in Fig. 2, which contains an *endo* allyl, shows a pronounced asymmetry in the allyl ligand.

The distortions induced by the electronic asymmetry of the NO and I ligands compared to two CO ligands can be quantitatively evaluated by reference to Tables 1—3 *. Although the allyl is in the *endo* conformation in II, the distances between the metal and the allyl carbons, as well as the carbon—carbon bond lengths within the allyl would be expected to be nearly identical to those in I in the absence of the perturbations induced by the differing electronic demands of the nitrosyl and iodide ligands **. In II, one half of the allyl has contracted and the other expanded a produce a σ—π type allyl *** which is also skewed and rotated by the asymmetric electronic environment. That is, the C—C distance *cis* to the nitrosyl is long [C(7)—C(8) 1.418(5) Å] compared to that *trans* to NO [C(6)—C(7) 1.366(5) Å]. Furthermore, the σ-bonded terminus is 0.14 Å closer to the metal atom than the other, Mo—C(6) 2.433(3) Å, Mo—C(8) 2.294(3) Å, and the allyl is rotated toward the iodide.

The distortion of the allyl in the iodide complex, II, has the drastic effect of changing the predominant mode of rearrangement between isomers from rotation, as found in I, to a σ—π rearrangement. Dynamic NMR studies using satu-

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* The dicarbonyl complex, I, crystallizes in the space group $P2_1/m$; a 6.372(1) Å, b 11.439(3) Å, c 7.257(2) Å, β 95.09(1)°, $Z = 2$, V 494.4(4) Å^3. The final values of the residuals R and R_w ($p = 0.03$) were 0.035 and 0.051, respectively. $(\eta^5\text{-}C_5H_5)Mo(NO)(I)(\eta^3\text{-}C_3H_5)$ crystallizes in the space group $P2_1/n$; a 7.537(1) Å, b 12.426(2) Å, c 11.168(2) Å, β 110.84(2)°, $Z = 4$, V 1041.9(5) Å^3; $R = 0.037$ and $R_w = 0.053$. The structures were solved by heavy-atom methods using the Enraf-Nonius SDP program library. Using monochromated Mo-K_α radiation 1485 and 2452 reflections with $F_0^2 > 3\sigma(F_0^2)$ for I and II respectively were collected with an Enraf-Nonius CAD-4 automated diffractometer.

** The structure of *endo* $C_5H_5W(NO)I$(allyl) has been determined by P. Legzdins [5] and shows comparable distortions.

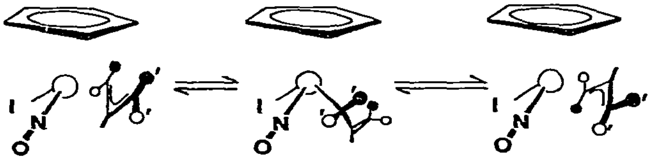
*** These distortions have been noted previously in square complexes of palladium [6,7].

TABLE 2

INTRAMOLECULAR BOND DISTANCES FOR CRYSTALLINE (η^5-C_5H_5) Mo(NO)(I)(η^3-C_3H_5

Atoms	Distance(Å)	Atoms	Distance (Å)
Mo—I	2.821(1)	Mo—C(8)	2.294(3)
Mo—N	1.783(2)	N—O	1.178(2)
Mo—C91)	2.310(3)	C(6)—C(7)	1.366(5)
Mo—C(2)	2.321(3)	C(7)—C(8)	1.418(5)
Mo—C(3)	2.332(3)	C(1)—C(2)	1.371(5)
Mo—C(4)	2.395(3)	C(1)—C(5)	1.364(5)
Mo—C(5)	2.366(3)	C(2)—C(3)	1.380(5)
Mo—C(6)	2.433(3)	C(3)—C(4)	1.350(5)
Mo—C(7)	2.357(2)	C(4)—C(5)	1.389(5)

ration transfer techniques [8] have demonstrated that the sigma bond forms at the terminus *cis* to nitrosyl and the rearrangement occurs stereospecifically such that the terminus *cis* to NO remains *cis* to NO during the process *.



The origin of some of these effects can be ascribed to the differential π accepting ability of NO and I. The π donor capacity of the metal parallel to the Mo—NO direction is depleted relative to that along the Mo—I direction; hence, the allyl rotates so as to tend to align itself in the plane with the Mo—I vector. This rotation occurs even though it increases the steric interaction of C(6) with I (C(6)—I 3.23 Å).

The steric repulsion of the iodide may partially account for the longer Mo—C(6) bond length. The asymmetry, however, arises predominantly from an electronic effect. This electronic origin is further demonstrated in our recently completed structure [9] of (+)-[neomenthylcyclopentadienyl-Mo(CO)(NO)-(allyl)]PF_6 for which the analogous bond lengths to those in Fig. 2 are: C(6)—C(7) 1.323(11); C(7)—C(8) 1.363(13); Mo—C(6) 2.396(9); Mo—C(7) 2.333(10); Mo—C(8) 2.357(7) Å **. In this compound, for which the steric differences between CO and NO are minimal, the short Mo—C bond is *cis* to NO and the shorter C—C bond is *trans* to NO.

Thus, differences in the electronic character of the other ligands can cause

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* These studies have been verified by deuterium substitution and the NMR assignments substantiated by comparisons with shift reagent studies of the isocyanate complexes. The ^1H resonances (δ, ppm) in $CDCl_3$ were observed as follows: major isomer, a(3.96), s(4.66), a'(2.36), s'(3.22). Minor isomer; a(4.05), s(4.74), a'(2.73), s'(3.53). Spin saturation transfer occurred between the following protons at 70° C: major a(3.96), minor a(4.05), major a'(2.36), minor s'(3.53), major s'(3.22), minor a'(2.73). The resonances at 4.66 and 4.74 ppm were too close to allow selective irradiation. The *syn—anti* interconversions are characteristic of π—σ rearrangement at one terminus. Rotations would allow only *anti—anti* and *syn—syn* interconversions.

** A summary of distortions and rotations in a series of seven compounds is in preparation.

TABLE 3

PERTINENT INTRAMOLECULAR ANGLES FOR CRYSTALLINE $(\eta^5\text{-}C_5H_5)$ Mo(NO)(I)$(\eta^3\text{-}C_3H_5)$

Atoms	Angle (degrees)	Atoms	Angle (degrees)
I—Mo—N	90.5(1)	C(1)—C(2)—C(3)	106.6(3)
I—Mo—C(6)	75.5(1)	Mo—C(3)—C(2)	72.3(2)
I—Mo—C(7)	100.5(1)	Mo—C(3)—C(4)	76.0(2)
I—Mo—C(8)	135.9(1)	C(2)—C(3)—C(4)	110.0(3)
N—Mo—C(6)	110.4(1)	Mo—C(4)—C(3)	70.9(2)
N—Mo—C(7)	86.9(1)	Mo—C(4)—C(5)	71.9(2)
N—Mo—C(8)	98.8(1)	C(3)—C(4)—C(5)	106.5(3)
C(6)—Mo—C(7)	33.1(1)	Mo—C(5)—C(1)	70.8(2)
C(6)—Mo—C(8)	61.3(1)	Mo—C(5)—C(4)	74.2(2)
C(7)—Mo—C(8)	35.5(1)	C(1)—C(5)—C(4)	108.5(3)
Mo—N—O	172.6(2)	Mo—C(6)—C(7)	70.4(2)
Mo—C(2)—C(2)	73.2(2)	Mo—C(7)—C(6)	76.5(2)
Mo—C(1)—C(5)	75.3(2)	Mo—C(7)—C(8)	69.9(2)
C(2)—C(1)—C(5)	108.3(3)	C(6)—C(7)—C(8)	120.0(3)
Mo—C(2)—C(1)—	72.3(2)	Mo—C(8)—C(7)	74.7(2)
Mo—C(2)—C(3)	73.2(2)		

appreciable variations in the bonding and, by inference, the charge delocalization in the termini of the allyl moiety. This suggests that electronic asymmetry in analogous compounds could be largely responsible for the stereospecificity of their reactions [10] **

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