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ACETYL SUBSTITUTION OF THE CYCLOPENTADIENYL LIGAND IN MOLYBDENUM COMPLEXES; NUCLEOPHILIC ADDITIONS TO COORDINATED ALLYL GROUPS

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Summary

An unusual acetyl substitution of the cyclopentadienyl ligand is observed during the synthesis of allyl(η^5-Cp)Mo$(CO)_2$ (I) by nucleophilic displacement on Cl(allyl)Mo$(CO)_2(NCMe)_2$ with lithiocyclopentadiene according to Hayter. The origin of the acetyl group is established by deuterium labelling studies, and it is rationalized in terms of the activation of the coordinated acetonitrile to nucleophilic addition with LiCp. The X-ray crystal structure of (η^5-AcCp)Mo$(CO)_2$(η^3-allyl) (II) reveals a slightly distorted cyclopentadienyl ring and an effective enlargement (i.e., expanded locus) of the ligand as a result of acetyl substitution. The stereoelectronic consequences of the substituted cyclopentadienyl ligand (η^5-AcCp) are found in the relative populations of the *exo*- and *endo*-conformations of the coordinated allyl ligands in both II as well as in its derived cation IV (η^5-AcCp)Mo(CO)-(NO)(η^3-allyl)$^+$ by comparison with their unsubstituted analogues I and III, respectively. The stereochemistry resulting from this steric change is also examined in the course of nucleophilic additions to the cationic allyl complexes IV with hydride, thiolate anions and carbanions.

Introduction

Ring substitution of cyclopentadienyl (Cp) ligands is promoted by electrophiles [1], and it has been observed in the classical studies of both sandwich and open-sandwich Cp-metal complexes [2–7]. The failure of many other cyclopentadienyl complexes to undergo ring substitution generally results from the availability of other facile pathways, especially those centered on the metal [8]. Thus our observation of the metallation of cyclopentadienide with a coordinatively saturated molybdenum complex was unexpected. Accordingly in this study we have traced the origin of the acetyl group, and examined the stereoelectronic consequences of the substituted cyclopentadienyl ligand in a series of allylmolybdenum complexes.

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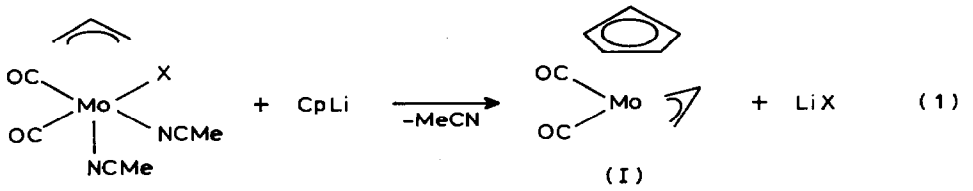
Results and discussion

The standard preparation of a series of allylmolybdenum complexes I η^5-$CpMo(CO)_2(\eta^3$-allyl) by Hayter's method [9] employs the nucleophilic displacement of halide (X) from the corresponding halo-bis-acetonitrile complex with lithiocyclopentadiene according to eq. 1.

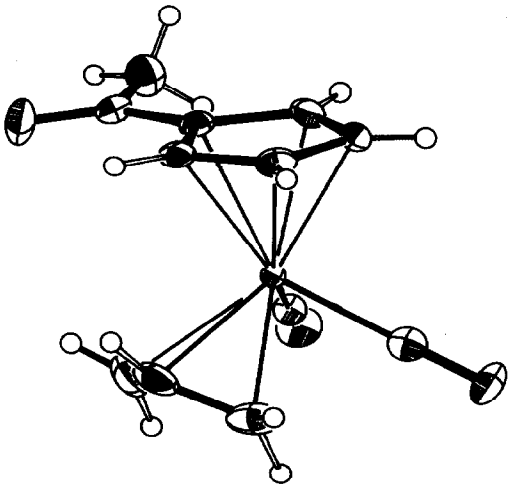


However during the careful purification of the product I, we noted the presence of a pair of similar yellow complexes on the column chromatogram. The major chromatographic band was readily eluted with hexane, and it proved to consist of I. The minor band was somewhat slower moving and was eluted with a mixture of dichloromethane and hexane. It yielded yellow crystal of a second allylmolybdenum compound II which clearly contained a substituted cyclopentadienyl ring, as judged by the presence of the characteristic doublet of triplets centered at $\delta \sim 5.5$ in the ^1H NMR spectrum [8]. (Note that the symmetry of the splitting for the symmetrical Cp resonance pattern is lost when the allyl ligand is unsymmetrically substituted.) A series of analogs were prepared with allyl Ia, 1-methallyl IIb and 2-methallyl IIc groups from the corresponding chloro-allyl precursors. The analogues IIa–c were all low-melting solids which were somewhat less prone to aerial degradation than their unsubstituted relatives Ia–c. They were generally formed as a minor constituent ($< 10\%$) in the synthesis of I.

A single crystal X-ray structure determination proved II to be the ring-substituted acetyl analogue of I. The ORTEP diagram of IIa is illustrated in Fig. 1. The pair of terminal CO ligands in II showed IR stretching bands at ~ 1960 and 1885 cm^{-1} together with a weaker low frequency band (~ 1675 cm^{-1}). The allylic protons in both the *syn* and *anti* forms were indicated in the ^1H NMR spectra similar to those observed in the unsubstituted analogues I [9]. The unique acetyl group was observed as a sharp singlet resonance at $\delta \sim 2.3$.

Since the acetyl substitution of Cp under these conditions was unprecedented, we traced briefly its origin. The activation of a coordinated acetonitrile, as a potential acetyl equivalent, was examined by synthesizing the deuteriated precursor $(CD_3CN)_2Mo(Cl)(CO)_2(\eta^3$-$C_3H_5)$ and converting it to IIa(d_3). Indeed the ^1H NMR of IIa(d_3) was identical to that of IIa except the acetyl singlet was missing. Furthermore the ^2H NMR spectrum established the presence of the CD_3CO group at δ 2.30 as a broad, unresolved singlet (at 13.7 MHz).

The conversion of an acetonitrile ligand to an acetyl group substituted onto Cp is intriguing. While strong nucleophiles such as Grignard reagents add directly to free nitriles [10,11], control experiments showed that LiCp did not react with a stoichiometric amount of acetonitrile under the reaction conditions employed in this study (See Experimental section). However it is known that coordination to transition metal centers can activate nitriles toward addition by nucleophiles as weak as aromatic amines and alcohols [12] which otherwise require acid catalysis [13]. We



(II a)

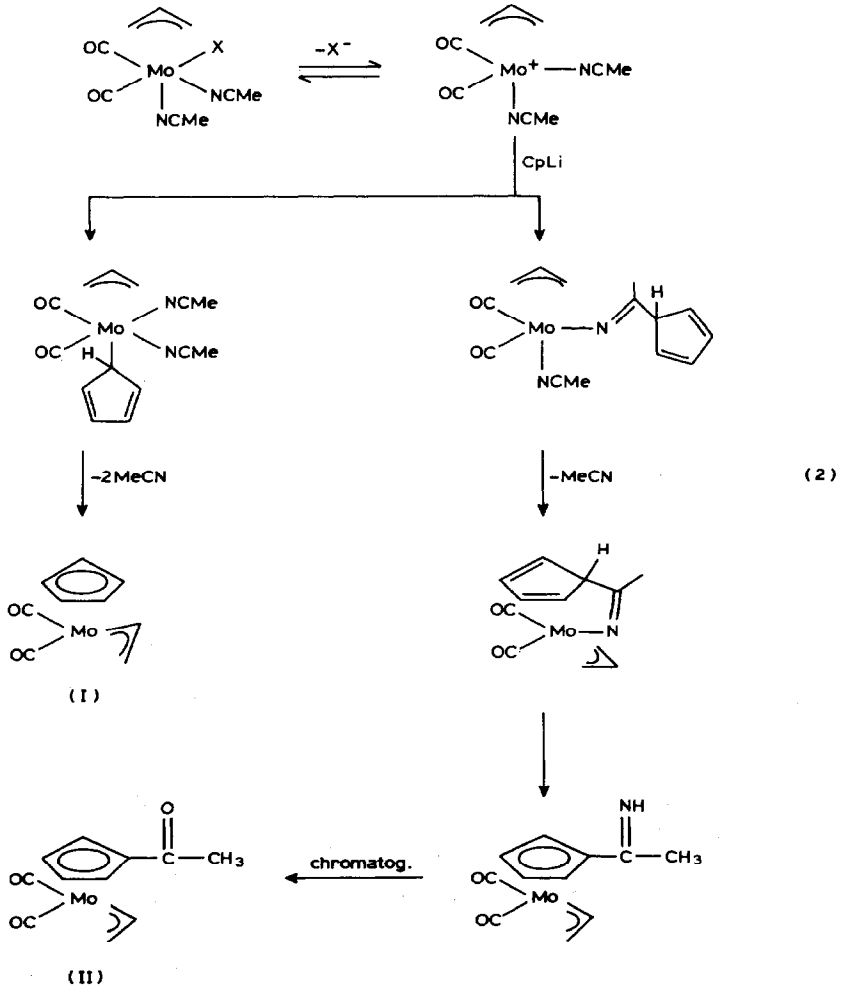
Fig. 1. ORTEP diagram of (η^5-AcCp)Mo(CO)$_2$(η^3-allyl) (IIa) showing the *exo*-conformation of the allyl ligand and the acetyl group coplanar with the Cp ring.

suspect that a similar activation occurs in competition with the synthesis in eq. 1, as depicted in Scheme 1.

According to Scheme 1, the production of I or II is determined by the nucleophilic atttack either at the metal center or at the coordinated acetonitrile ligand of the allylmolybdenum cation formed in eq. 2. Our inability to alter the relative yields of I and II in a significant way by varying the reaction conditions (see Experimental section) is consistent with such a common intermediate. If so, the instability of the imine intermediate resulting from the attack on the coordinated acetonitrile is reminiscent of that formed under the conditions of the Friedel–Crafts syntheses [13,14]. However under the anhydrous conditions employed in eq. 1, the hydrolysis probably occurred in the subsequent chromatographic workup. This conclusion is supported by the severe tailing of II observed when the crude reaction mixture was exposed directly to the thin-layer chromatographic plate. By contrast, no tailing was observed if IIa was first isolated and then rechromatographed under the same conditions. Furthermore the rate of elution increased from $R_f \sim 0.3$ for "crude" IIa compared to a value of ~ 0.5 for the pure complex. For convenience, the substituted cyclopentadienyl ligand will hereafter be referred to as η^5-AcCp.

Molecular structure of the (η^5-AcCp)molybdenum complexes II

The crystal structure of IIa in Fig. 1 provides useful insight into its behavior in solution. Thus the ORTEP diagram clearly defines the *exo* geometrical preference of the allyl ligand. This conformation is common to the parent series of complexes I containing cycloalkenyl groups [15], but it is generally considered to be the less favorable isomer in the solid state [16]. Most importantly, the acetyl substituent occupies the preferred conformation coplanar with the Cp ring, which provides an effectively larger umbrella to shield the Mo hemisphere. The acetyl substituent,



SCHEME 1

which exerts a moderately electron-withdrawing effect [17], distorts the Cp ring by elongating the pair of contiguous ring bonds to 1.43 Å (compared to 1.41 Å for the others in Table 1). A slight contraction of the ring angle at C(1) also occurs. The remaining structural parameters are essentially the same as those in the unsubstituted analog I.

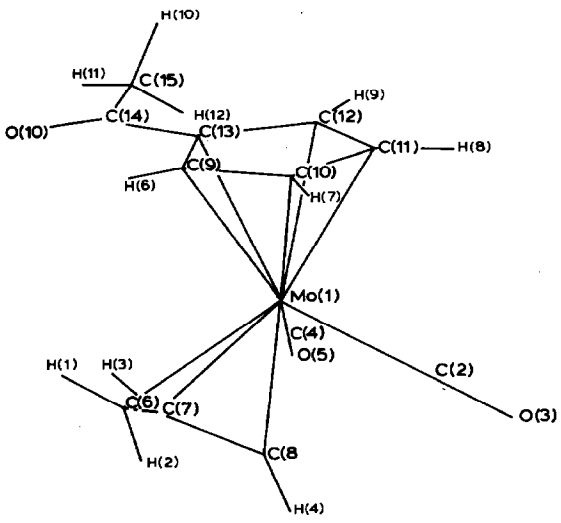
Independent synthesis of the acetylCpmolybdenum complexes II

The unusual stereochemical arrangement in II suggested that it could be a useful precursor in the synthetic methodology developed for I in allylic alkylations [18]. Accordingly we sought a more efficient procedure for the synthesis of the allylic complexes IIa–c. Thus the substituted cyclopentadienyl ligand was first prepared by treating LiCp with one equiv. of methyl acetate [8]. The subsequent admixture of acetylcyclopentadienyllithium with the series of $ClMo(NCMe)_2(CO)_2(\eta^3\text{-allyl})$ [9,19] afford complexes IIa–c in 50–60% yields.

TABLE 1

RELEVANT NON-HYDROGEN BOND DISTANCES (Å) AND ANGLES (°) IN (η^5-AcCp)-Mo(CO)$_2$(η^3-allyl) (with numbering scheme)

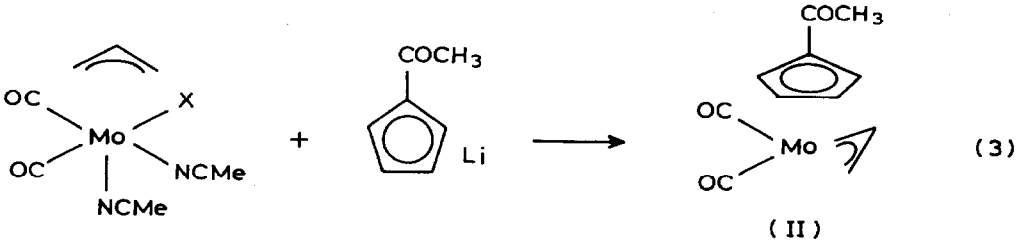
Mo(1)–C(2)	1.9524(22)		
Mo(1)–C(4)	1.9506(20)		
Mo(1)–C(6)	2.3296(23)		
Mo(1)–C(7)	2.2262(20)		
Mo(1)–C(8)	2.3376(21)		
Mo(1)–C(9)	2.3655(21)		
Mo(1)–C(10)	2.3901(19)		
Mo(1)–C(11)	2.3638(21)		
Mo(1)–C(12)	2.3253(19)		
Mo(1)–C(13)	2.3179(19)		
O(3)–C(2)	1.1585(26)		
O(5)–C(4)	1.1548(25)		
O(16)–C(14)	1.2205(24)		
C(6)–C(7)	1.401(3)		
C(7)–C(8)	1.399(3)		
C(9)–C(10)	1.409(3)		
C(9)–C(13)	1.4304(27)		
C(10)–C(11)	1.414(3)		
C(11)–C(12)	1.408(3)		
C(12)–C(13)	1.4342(27)		
C(13)–C(14)	1.4763(28)		
C(14)–C(15)	1.498(3)		
C(2)–Mo(1)–C(4)	80.83(8)	C(6)–C(7)–C(8)	119.53(21)
C(2)–Mo(1)–C(6)	114.07(9)	Mo(1)–C(8)–C(7)	67.86(12)
C(2)–Mo(1)–C(7)	105.26(9)	Mo(1)–C(9)–C(10)	73.73(11)
C(2)–Mo(1)–C(8)	70.89(9)	Mo(1)–C(9)–C(13)	70.41(10)
C(2)–Mo(1)–C(9)	140.00(8)	C(10)–C(9)–C(13)	108.08(18)
C(2)–Mo(1)–C(10)	105.57(8)	Mo(1)–C(10)–C(9)	71.82(11)
C(2)–Mo(1)–C(11)	89.18(8)	Mo(1)–C(10)–C(11)	71.68(11)
C(2)–Mo(1)–C(12)	107.80(8)	C(9)–C(10)–C(11)	108.34(18)
C(2)–Mo(1)–C(13)	143.68(8)	Mo(1)–C(11)–C(10)	73.71(11)
C(4)–Mo(1)–C(6)	73.94(8)	Mo(1)–C(11)–C(12)	71.04(11)
C(4)–Mo(1)–C(7)	106.41(8)	C(10)–C(11)–C(12)	108.53(18)
C(4)–Mo(1)–C(8)	109.12(8)	Mo(1)–C(12)–C(11)	74.03(11)
C(4)–Mo(1)–C(9)	133.68(8)	Mo(1)–C(12)–C(13)	71.73(10)
C(4)–Mo(1)–C(10)	152.02(8)	C(11)–C(12)–C(13)	107.88(18)
C(4)–Mo(1)–C(11)	120.63(8)	Mo(1)–C(13)–C(9)	74.04(11)
C(4)–Mo(1)–C(12)	93.91(8)	Mo(1)–C(13)–C(12)	72.29(10)
C(4)–Mo(1)–C(13)	100.16(8)	Mo(1)–C(13)–C(14)	118.59(12)
C(6)–Mo(1)–C(7)	35.73(9)	C(9)–C(13)–C(12)	107.17(17)
C(6)–Mo(1)–C(8)	62.44(9)	C(9)–C(13)–C(14)	124.53(18)
C(6)–Mo(1)–C(9)	97.36(9)	C(12)–C(13)–C(14)	128.30(18)
C(6)–Mo(1)–C(10)	124.49(8)	O(16)–C(14)–C(13)	120.54(19)
C(6)–Mo(1)–C(11)	155.19(9)	O(16)–C(14)–C(15)	121.22(19)
C(6)–Mo(1)–C(12)	133.36(8)	C(13)–C(14)–C(15)	118.23(18)
C(6)–Mo(1)–C(13)	100.78(9)	C(9)–Mo(1)–C(12)	58.86(7)
C(7)–Mo(1)–C(8)	35.59(9)	C(9)–Mo(1)–C(13)	35.55(7)
C(7)–Mo(1)–C(9)	85.67(8)	C(10)–Mo(1)–C(11)	34.61(7)
C(7)–Mo(1)–C(10)	98.22(8)	C(10)–Mo(1)–C(12)	58.12(7)
C(7)–Mo(1)–C(11)	132.51(8)	C(10)–Mo(1)–C(13)	58.41(7)
C(7)–Mo(1)–C(12)	143.45(7)	C(11)–Mo(1)–C(12)	34.94(7)
C(7)–Mo(1)–C(13)	109.10(8)	C(11)–Mo(1)–C(13)	58.78(7)
C(8)–Mo(1)–C(9)	106.00(8)	C(12)–Mo(1)–C(13)	35.98(7)



continued

TABLE 1 (continued)

C(8)–Mo(1)–C(10)	98.62(8)	Mo(1)–C(2)–O(3)	178.45(18)
C(8)–Mo(1)–C(11)	122.28(8)	Mo(1)–C(4)–O(5)	177.87(17)
C(8)–Mo(1)–C(12)	156.08(8)	Mo(1)–C(6)–C(7)	68.11(12)
C(8)–Mo(1)–C(13)	138.99(8)	Mo(1)–C(7)–C(6)	76.17(13)
C(9)–Mo(1)–C(10)	34.46(7)	Mo(1)–C(7)–C(8)	76.55(13)
C(9)–Mo(1)–C(11)	57.89(7)		



(II) (3)

The conformational preferences of the allyl ligands in IIa–c were based on the ^{1}H NMR spectral assignments (for details see Experimental section), by analogy with that established earlier in the parents Ia–c [20]. The results summarized in Table 2 indicate that one isomer was always favored over the other. The establishment of such a conformational "purity" differs from that of the unsubstituted analogs I which are usually formed as mixtures of *exo* and *endo* isomers [21]. This difference is readily apparent in the IR spectra of the carbonyl region (ν(CO)) in which the presence of *exo* and *endo* isomers gives rise to a doubling of the CO stretching bands [20,22], as illustrated in column 4 of Table 3. (Note that the relative amounts of *exo* and *endo* isomers of I can be variable owing to differing rates of equilibration [18d].) The observation of only one set of CO stretching bands for IIa and IIb indicates the preponderance of only the *exo* isomer (97 ± 5%). Similarly, the single set of carbonyl frequencies in the IR spectrum of IIc is consistent with the presence of only the *endo* isomer, i.e.

TABLE 2

CONFORMATIONAL PREFERENCE OF π-ALLYL LIGANDS IN II [a]

Complex	η^3-Allyl	Predominant conformation [b]	*exo*/*endo*
IIa		*exo*	> 20
IIb		*exo*	> 20
IIc		*endo*	< 0.05

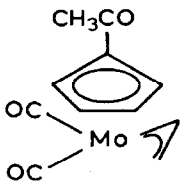
[a] In acetonitrile at 25°C. [b] Based on ^{1}H NMR assignments (see Experimental).

TABLE 3

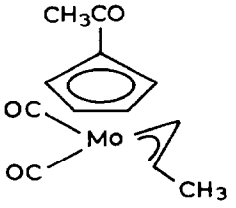
COMPARISON OF THE CARBONYL BANDS IN THE IR SPECTRA COMPLEXES I AND II

Complex II	ν(CO) [a]	Complex I	ν(CO) [b]
IIa	1949, 1867 (*exo*) [c]	Ia	1963, 1889 (*exo*) 1970, 1903 (*endo*)
IIb	1948, 1869 (*exo*) [d]	Ib	1953, 1879 (*exo* 1960, 1894 (*endo*)
IIc	1961, 1872 (*endo*) [e]	Ic	1962, 1895 (*endo*) sh 1886 (*exo*)

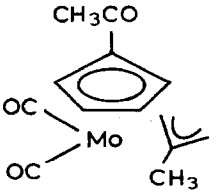
[a] In dichloromethane. [b] In cyclohexane from ref. 20. Acetyl band at [c] 1670 [d] 1673 and [e] 1676 cm^{-1}.



(IIa)



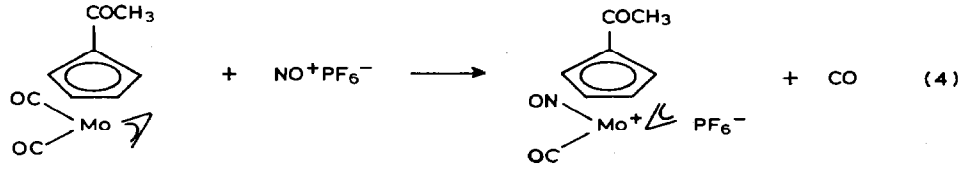
(IIb)



(IIc)

Oxidative nitrosation of the (η^5-AcCp)molybdenum complexes II

The standard method for the conversion of the neutral allylmolybdenum complexes I to their cations III entails the treatment with nitrosonium salts [15,18,23]. As applied to the η^5-AcCp analogs pertinent to this study, the oxidative nitrosation of II also proceeded in the same way, i.e.

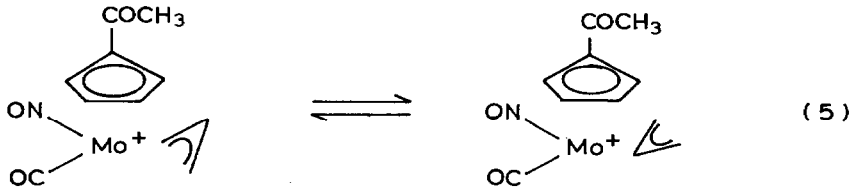


(IIa) (IVa)

In the formation of cation IVa the displacement of carbon monoxide was slow at temperatures below 0°C. This contrasted with the rapid rate of CO loss from the unsubstituted analogue IIIc even at −20°C [18c,d]. However when the temperature was allowed to rise from 0 to 20°C, one equiv. of carbon monoxide was evolved from IIa within 30 min in accord with the stoichiometry in eq. 4. Inspection of the ^{1}H NMR spectrum of the solution revealed a doublet of doublets centered at δ 6.61 and a triplet of equal intensity at δ 6.11. This pattern of chemical shifts is characteristic of the *endo* isomer of IVa (illustrated in eq. 4). Minor amounts of the *exo* isomer were indicated by the pair of multiplets centered at δ 6.45 and 5.91. (Note in the unsubstituted Cp-series of complexes the chemical shift of the *endo* allyl complex invariably occurs downfield relative to the *exo*-isomer [18b,d,23].) The integrations of these resonances yielded an *endo/exo* ratio of 6.7 for IIIa. (By comparison, the *endo/exo* ratio for the unsubstituted Cp-analogs was 0.42 [23].)

Such an inversion of the allyl moiety accompanying oxidative nitrosation of II follows the pattern established with the unsubstituted analogues I [23].

Upon standing, the resonances of IVa due to the *exo* isomer increased at the expense of those of the *endo* isomer. After 2 h at 25°C, the *endo/exo* ratio had decreased to 0.40, indicative of the attainment of the equilibrium in eq. 5.



(IVa - *endo*) (IVa - *exo*) (5)

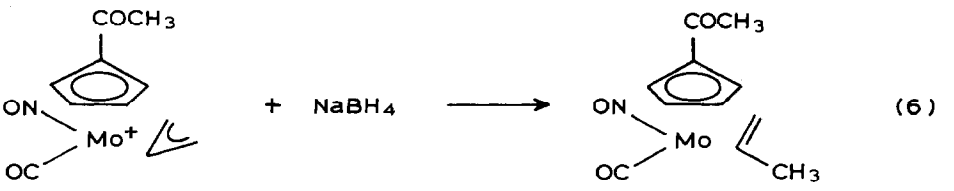
The thermodynamic *endo/exo* ratio of 0.4 is only slightly larger than that obtained in the equilibration of the unsubstituted analogue. This indicates that the acetyl substituent plays only a minor role in influencing the relative stabilities of the *exo* and *endo* isomers. In order to confirm this conclusion, we also examined the conversion of the 2-methallyl derivative IIc which exists predominantly in the *endo* conformation (see Table 2). The addition of one equiv. of $NO^+PF_6^-$ to IIc yielded a mixture of *endo* and *exo* cations IVc, the ratio of which was *endo/exo* = 4.0, as described in the Experimental section. This equilibrated ratio was essentially unchanged upon prolonged standing (2 h) at 25°C. Thus the cation IVc was formed close to the equilibrium population of *endo* and *exo* isomers. Alternatively, it may undergo a rapid *exo* → *endo* isomerization [18d]. In either case, the preponderance of the *endo* isomer from the more encumbered 2-methallyl ligand is consistent with steric factors of the cyclopentadienyl ligand playing an important role in determining conformational populations. However if this conclusion is applied to the neutral precursors, some factor other than steric constraints needs to be considered in order to account for the preponderant formation of the *exo* isomers of IIa and IIb. Among these, an electronic effect of the acetyl group (vide supra) may play an important role.

Nucleophilic addition to allylmolybdenum cations IV

The allylmolybdenum cations III derived from the oxidative nitrosation of I can undergo nucleophilic addition with higher regio- and stereoselectivity [15,18,24]. Such selectivities could be achieved even when the cation was formed close to the equilibrium population of *exo* and *endo* isomers, provided one reacted faster than the other. Conformationally pure *exo* and *endo* isomers have also been reported to undergo selective reactions despite the opposed kinetics preferences, if a nucleophile-assisted isomerization occurred [18]. In order to determine how (or whether) an acetyl substitution can alter this selectivity, we examined the addition to the cations IVa–c of three classes of nucleophiles.

A. Nucleophilic addition of hydride. The series of unsubstituted CpMo(η^3-allyl) cations III are converted to the corresponding neutral η^2-olefin complexes by hydride attack from sodium borohydride on the coordinated allyl ligand [18a–c]. Under the same conditions, the η^5-AcCp analogue IVa reacted with excess $NaBH_4$

at 0°C to produce the η^2-propene complex Va in 46% yield as an air-sensitive, yellow solid, i.e.



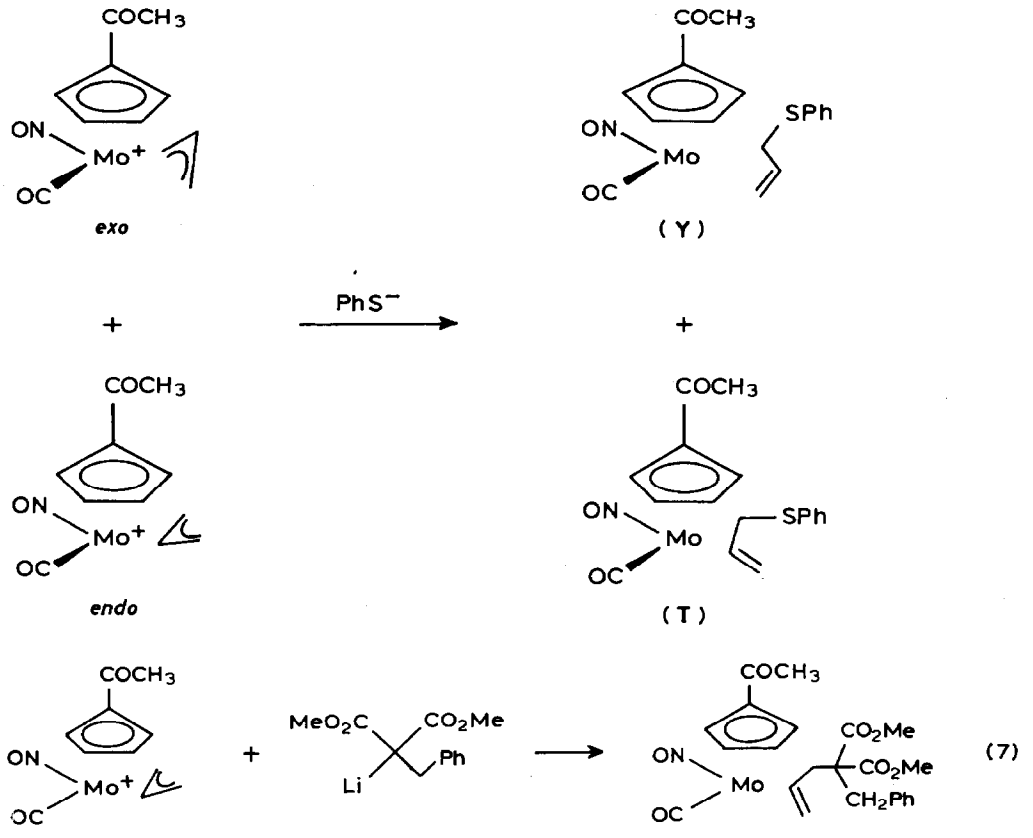
(IVa) (Va)

The product Va exhibited a single terminal CO stretch at 1973, a NO stretch at 1635 and a band at 1668 cm^{-1} characteristic of an intact acetyl group. Similarly the 2-methallyl analog IVc afforded a good yield of the η^2-isobutylene complex Vc. The low susceptibility of the acetyl group to borohydride reduction parallels the diminished reactivity of the η^5-AcCp complex II with excess $NaBH_4$. For example, the exposure of IIa to borohydride for 2 h in refluxing methanol led to only a 50% conversion to the η^2-propene complex Va.

The cationic 2-methallyl complex IVc was of particular interest since the unsubstituted CpMo cation IIIc was previously found to undergo a hydride addition from nitronate anions [18c]. Indeed the treatment of IVc with diethylammonium isopropylnitronate led to the η^2-isobutylene complex Vc which was the same as that derived from borohydride. The rather poor yields of Vc were due to admixture with a side product, which though not characterized, was unlikely to be the halonitrosylmolybdenum complex similar to that observed from IIIc [18c], as described in the Experimental section. Furthermore the same pair of products was observed when IVc was treated with sodium amalgam. Therefore it is likely the overall hydride addition from nitronate actually proceeded via a prior electron-transfer followed by hydrogen atom abstraction [18c,d].

B. Nucleophilic addition of thiolate anions. The cationic complexes III undergo a highly selective addition of thiolate anions such as thiophenoxide to both acyclic as well as cyclic allyl ligands. Similarly we found the addition of triethylammonium thiophenoxide to IVa to be rapid at 0°C. The formation of a pair of isomeric adducts VIa was indicated from an inspection of the IR spectrum. The major isomer **Y** showed intense stretching bands at 1990 and 1637 cm^{-1} characteristic CO and NO ligands, respectively, as well as the acetyl band at 1732 cm^{-1}. The minor isomer **T** showed similar CO and NO bands at 1944 and 1581 cm^{-1}, respectively, but the band due to the acetyl group was too weak to observe [18c]. The ratio of the two was estimated to be $\mathbf{Y}/\mathbf{T} \cong 3/1$, based on the relative intensities of the CO bands (see Experimental section). From our previous analysis of thiophenoxide additions to IIIa, we infer that the major isomer **Y** derived from the *exo*-isomer and **T** from the *endo*-isomer by addition at the terminus *cis* to NO [18,24], as illustrated in Scheme 2.

C. Nucleophilic addition of carbanions. In order to establish the structural assignments in thiophenoxide addition, we also examined the addition of the carbanion from an alkylmalonate ester to the cation IV. Thus the addition of dimethyl lithiobenzylmalonate to the cation IVa proved to be facile at 25°C. The single set of sharp IR bands characteristic of CO, NO, acetyl and ester stretching frequencies indicated that the η^2-olefin adduct VIIa was formed as one stereoiso-



SCHEME 2

mer. The ^{1}H NMR spectrum also accorded with the structure (see eq. 7) in which the temperature-dependent line broadening could be attributed to the existence of a pair of rotamers with a sizeable barrier to interconversion (see Experimental). The regioselective addition of the dimethyl benzylmalonate nucleophile to yield such an adduct is consistent with our previous studies with the unsubstituted cations III [18d]. Such a regio- and stereo-selective addition of the benzylmalonate nucleophile should encourage the further investigation of η^5-AcCp complexes for other carbanion additions to coordinated allyl ligands, particularly in chiral systems [25].

Summary and conclusions

Acetyl-substituted cyclopentadienyl ligand (η^5-AcCp) derives from the in situ activation of coordinated acetonitrile toward nucleophilic addition by cyclopentadienide. The allyl ligands in (η^5-AcCp)molybdenum complexes show conformational preferences which are exaggerated relative to the unsubstituted Cp analogues as a result of both steric and electronic influences of the acetyl substituent. An efficient, independent synthesis of (η^5-Ac) complexes is developed for nucleophilic additions to coordinated allyl groups without the competitive involvement of the acetyl group. The potential for the exploitation of this modified ligand to induce highly regio- and stereoselective allyl additions is discussed.

Experimental

Materials

Molybdenum hexacarbonyl (Pressure Chemicals) and nitrosyl hexafluorophosphate (Alfa) were used as received. The precursors *cis*-[(η^3-allyl)MoCl(NCMe)$_2$(CO)$_2$], *cis*[(η^3-1-methallyl)MoCl(NCMe)$_2$(CO)$_2$], and *cis*-[(η^3-2-methallyl)MoCl(NCMe)$_2$(CO)$_2$] were prepared by literature methods [9,19], and they have been previously characterized [9,19,20]. Methyl acetate (Fisher) and thiophenol (Fisher) were traditionally distilled at reduced pressures and stored under an argon atmosphere. Dimethyl benzylmalonate was prepared and purified according to literature methods [26]. Butyllithium (Aldrich) consisted of a 1.6 *M* solution in n-hexane and was used as received. Cyclopentadiene was freshly prepared by the thermal cracking of dicyclopentadiene (Matheson, Coleman and Bell).

All reactions were performed using standard inert atmosphere techniques with Schlenk ware. Solvents were purified as follows. Acetonitrile (Fisher) was refluxed over phosphorus pentoxide followed by fractional distillation under an atmosphere of argon. Tetrahydrofuran (Fisher) was refluxed with sodiobenzophenone under an atmosphere of argon and redistilled from lithium aluminum hydride immediately prior to use. Dichloromethane and hexane were dried over 4 Å molecular sieves and stored under argon.

Infrared spectra were recorded on either a Perkin–Elmer 597 or a Beckman 1100 FT-IR. Only the principal bands are listed. ^{1}H NMR measurements were made at 60, 90 and 360 MHz with a Varian T-60, JEOL JNM-FX-90Q and Nicolet NT-360 spectrometers, respectively. ^{13}C NMR measurements were made with pulsed FT techniques at 22.53 MHz using internal deuterium as a field frequency lock. Chemical shifts are reported in ppm relative to internal tetramethylsilane in the indicated solvent. Mass spectra were obtained using an AEI MS-12 spectrometer at 60 eV or greater, and only the most intense fragments are listed. The parent ions of the organo-molybdenum compounds were taken to be those due to ^{98}Mo (natural abundance, 23.78%).

Thin-layer chromatography (TLC) was performed with Eastman No. 6060 silica gel sheets using a fluorescent indicator. Developing solvents are as indicated, and visualization was achieved using either UV irradiation or by spraying with 50% (v/v) sulfuric acid in methanol. Column chromatographic separations were achieved using gravity flow columns packed with Fisher alumina (neutral or acid-washed, 80–200 mesh) or Florisil. "Flash" chromatography [27] was performed using pressurized columns packed with EM Reagents Kieselgel 60 (200–400 mesh) with a head pressure of argon. Preparative thin-layer chromatographic separations were obtained with precoated EM Reagents silica gel 60 preparative plates (F-254).

Isolation of the (η^5-AcCp) complexes IIa–c

In a typical procedure, a solution of 10.0 g (32.0 mmol) of *cis*-[(η^3-C_3H_5)Mo(Cl)(NCMe)$_2$(CO)$_2$] in 10 ml of tetrahydrofuran (THF) was stirred at −70°C under an argon atmosphere. Freshly distilled cyclopentadiene monomer (3.50 ml, ~42 mmol) was stirred in 15 ml of THF under argon at −70°C. To this solution was added 20.0 ml of 1.6 *M* n-butyllithium in hexane, and the solution stirred vigorously while allowing it to come to room temperature. After solvent removal in vacuo, the chalk-white lithiocyclopentadiene was redissolved and trans-

ferred to the reaction mixture with the aid of an additional 10 ml of THF. The THF solution of 32 mmol of cyclopentadienyllithium was added with the aid of a hypodermic syringe. After allowing the reaction mixture to warm to room temperature and stir for 16 h, most of the solvent was removed in vacuo, and the dark brown residue transferred to an acid-washed alumina column (act. II) with the aid of a minimum volume of THF. Elution with hexane afforded the major (unsubstituted Cp) product as a bright yellow band [20]. Subsequent elution with a mixture of hexane and dichloromethane (1/1) yielded a second yellow band which afforded, after solvent removal in vacuo, $[(\eta^5\text{-}C_5H_4COCH_3)Mo(CO)_2(\eta^3\text{-allyl})]$ (IIa) (530 mg, 6% yield). The products IIa, IIb and IIc were characterized as follows.

For IIa: m.p. (sealed tube): 98–101°C with decomp.; TLC (SiO_2, CH_2Cl_2): $R_f = 0.51$; IR (CH_2Cl_2): 3080w, 2940w, 2915w, 1949s, 1867s, 1670m, 809w cm^{-1}; Mass spectrum (EI), *m/z* (rel. int.): 302 (5), 274 (14), 260 (25), 232 (39), 204 (17), 195 (15), 154 (40), 43 (55), 42 (45), 41 (45), 28 (100), 15 (10); ^1H NMR ($CDCl_3$, 25°C): δ 5.70 (t, J 2.3 Hz, 2H), 5.36 (t, J 2.3 Hz, 2H), 3.82 (tt, J 10.5, 6.8 Hz, 1H), 2.76 (d, J 6.8 Hz, 2H), 2.30 (s, 3H), 1.25 (brd, J 10.5 Hz, 2H).

For IIb: m.p. (sealed tube): 95–97°C with slight decomp.; TLC (SiO_2, CH_2Cl_2): $R_f = 0.45$; IR (CH_2Cl_2): 3050w, 2920w, 1948s, 1869s, 1673m, 815w cm^{-1}; ^1H NMR ($CDCl_3$, 25°C): δ 5.72 (br dd, $J \cong 4$, 2 Hz, 2H), 5.38 (br t, J 2.2 Hz, 2H), 3.84 (m, 1H), 2.45 (m, 1H), 2.33 (s, 3H), 1.79 (br d, $J \cong 5$ Hz, 3H), 1.59 (br s, 1H), 0.96 (m, 1H).

For IIc: m.p. (sealed tube): 101–103°C with slight decomp.; TLC (SiO_2, CH_2Cl_2): $R_f = 0.55$; IR (CH_2Cl_2): 3050w, 2950w, 2905w, 1961s, 1872s, 1676m, 812w cm^{-1}; ^1H NMR ($CDCl_3$, 25°C): δ 5.71 (t, J 2.4 Hz, 2H), 5.32 (t, J 2.4 Hz, 2H), 2.91 (s, 2H), 2.29 (s, 3H), 1.78 (br s, 2H), 1.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 25°C): δ 237.6 (s), 194.7 (s), 105.6 (br s), 102.2 (s), 94.7 (d), 90.0 (d), 41.6 (t), 26.2 (q), 23.4 (q).

For IIa(d_3): TLC (SiO_2, CH_2Cl_2): $R_f = 0.50$; IR (CH_2Cl_2): 3020w, 2950w, 2670w, 1950s, 1867s, 1670m cm^{-1}; ^1H NMR ($CDCl_3$, 25°C): δ 5.70 (t, J 2.3 Hz, 2H), 5.36 (t, J 2.3 Hz, 2H), 3.82 (tt, J 10.5, 6.8 Hz, 1H), 2.76 (d, J 6.8 Hz, 2H), 1.25 (br d, J 10.5 Hz, 2H); ^2H NMR (13.75 MHz, $CDCl_3$, 25°C): δ 2.30 (br s).

Various attempts were made to alter the product distribution between I and II in the following way. (a) Using the procedure described previously, the formation of IIa was monitored by TLC (SiO_2, CH_2Cl_2). It was observed that no significant amount of IIa was formed until the reaction mixture had warmed to room temperature. As soon as the slow-moving (tailing) band characteristic of IIa was observed, 0.180 ml (10.0 mmol) of H_2O was added, and the resulting mixture stirred for 16 h. The product was isolated as before, affording only 250 mg of IIa, (2.6% yield), which was characterized by its ^1H NMR spectrum (vide supra). (b) Using the procedure described previously, 79 mg (1 mmol) pyridine was added via syringe as soon as the reaction mixture had reached room temperature. The resulting mixture was stirred 16 h and the product isolated as before affording 475 mg of IIa, (4.9% yield), which was characterized by its ^1H NMR spectrum (vide supra). (c) A solution of 10.0 g (32.0 mmol) of *cis*-$[(\eta^3\text{-}C_3H_5)MoCl(NCMe)_2(CO)_2]$ in 25 ml acetonitrile was stirred at −20°C under an argon atmosphere. Addition of a solution of 42 mmol of lithiocyclopentadiene in a total of 25 ml of THF (vide supra), followed by warming to room temperature, stirring for 16 h, and isolation as before, afforded 120 mg IIa, (1.4% yield), which was characterized by its ^1H NMR spectrum (vide supra).

Independent synthesis of (η^5-AcCp) complexes IIa–c

A solution of 10.0 mmol of lithiocyclopentadiene (vide supra) in THF was stirred under an argon atmosphere. Methyl acetate (750 mg, 10 mmol) was added via syringe and the solution heated to reflux. After 4 h, the solution was cooled and the solvent removed in vacuo. The light residue was identified as acetylcyclopentadienyllithium as previously reported [8]. IR (Nujol mull): 1695m cm^{-1}; ^1H NMR (D_2O quenched, 25°C): δ 6.42 (br t, $J \cong 3$ Hz, 2H), 5.93 (m, 2H). This lithium complex was redissolved in 10 ml of THF, and transferred with the aid of a cannula to a solution of 3.00 g (9.60 mmol) of *cis*-[(η^3-C_3H_5)$MoCl(NCMe)_2(CO)_2$] in 10 ml of THF stirred under an argon atmosphere. The reaction mixture was heated at reflux for 2 h and then stirred at room temperature for 16 h. Thereafter, the solvent was removed in vacuo, and the residue taken up in dichloromethane. Flash chromatography on silica gel with a mixture of hexane and dichloromethane (1/1) as the eluent afforded a single yellow band which yielded, after solvent removal, 1.59 g (55% yield) of [(η^5-$C_5H_4COCH_3$)$Mo(CO)_2$(η^3-C_3H_5)] (IIa) as a yellow, air-sensitive solid, identical in all respects to IIa previously isolated (vide supra).

Preparation of the η^5-AcCp cations IVa–c

In a typical preparation a solution of 50.0 mg (0.166 mmol) of IIa in 2 ml of acetonitrile was stirred at 0°C under an atmosphere of argon. Then, 0.20 ml of a 0.81 *M* nitrosyl hexafluorophosphate solution in acetonitrile was added. The mixture was stirred while slowly warming to room temperature (~ 30 min) at which time all the gas evolution had ceased. The solution was then sealed in a 5 mm o.d. Pyrex NMR tube in vacuo (together with an appropriate volume of CD_3CN to provide an internal lock). The ^1H NMR spectrum of the cationic complex was recorded immediately (within 15 min of the completion of reaction) and measured again after 2 h at 25°C.

For IVa: Initial ^1H NMR (CD_3CN, 25°C): *endo*-isomer, δ 6.61 (br dd, *J* 4.8, 2.1 Hz); 6.11 (br t, *J* 2.1 Hz); *exo*-isomer δ 6.45 (m), 5.91 (m); *exo/endo* = 0.15; Final ^1H NMR (CD_3CN, 25°C): *endo*-isomer, δ 6.61 (m), 6.11 (m); *exo*-isomer, δ 6.45 (br dt, $J \cong 2$, 1 Hz), 5.91 (br dd, *J* 4.8, 2.1 Hz); *exo/endo* = 2.50.

The mixture of *exo* and *endo* cations comprising IVc were characterized by ^1H NMR spectroscopy as follows. The major signals consisted of a broad triplet centered at δ 6.50 and a pair of double doublets centered at δ 5.98. Both comprised 80% of the total integral. A minor set of signals with the same splitting was centered at δ 6.33 and 5.63 and was assigned to the *exo*-isomer of IVc. The initially formed ratio of *exo/endo* isomers was 0.25 ± 0.05.

For IVc: Initial ^1H NMR (CD_3CN, 25°C): *endo*-isomer, δ 6.50 (br t, *J* 2.2 Hz), 6.03 (dd, *J* 5.0, 2.2 Hz), 5.93 (dd, *J* 5.0, 2.2 Hz); *exo*-isomer, δ 6.33 (br t, $J \cong 2$ Hz), 5.68 (dd, $J \cong 5$, 2 Hz), 5.58 (dd, $J \cong 5$, 2 Hz), *exo/endo* = 0.28; Final ^1H NMR (CD_3CN, 25°C): *endo*-isomer, δ 6.50 (br t, *J* 2.2 Hz), 6.03 (dd, *J* 5.0, 2.2 Hz), 5.93 (dd, *J* 5.0, 2.2 Hz); *exo*-isomer, δ 6.33 (br t, $J \cong 2$ Hz), 5.68 (dd, $J \cong 5$, 2 Hz), 5.58 (dd, $J \cong 5$, 2 Hz), *exo/endo* = 0.30.

Nucleophilic addition of hydride to the η^5-AcCp cations

A solution of 0.125 g (0.414 mmol) of IIa in 3 ml acetonitrile was stirred at 0°C under an atmosphere of argon. Conversion of IVa was accomplished by the addition of 0.50 ml of a 0.82 *M* $NOPF_6$ solution in CH_3CN, and the mixture warmed to

room temperature over a 30 min period. After recooling the solution of IVa to 0°C, a cold solution of 40 mg of sodium borohydride in 5 ml of a mixture of methanol and CH_3CN (1/1) was added, and the resulting solution stirred at 0°C for 2 h. Thereafter, the solvent was removed in vacuo, the residue taken up in dichloromethane, and quickly filtered through a bed of Florisil. Removal of solvent afforded 40 mg (31%) of [(η^5-$C_5H_4COCH_3$)Mo(NO)(CO)(η^2-propene)] (Va) as a yellow orange, air-sensitive semi-solid. TLC (SiO_2, CH_2Cl_2): $R_f = 0.60$; IR (CH_2Cl_2): 3020w, 2980w, 1973s, 1668m, 1635s, 835w cm^{-1}. ^1H NMR ($CDCl_3$, 25°C): δ 6.80 (br dd, $J \cong 8$, 4 Hz, 1H), 6.26 (m, 1H), 5.71 (br d, $J \cong 4$ Hz), 5.50 (m, 1H), 3.50 (br m, 1H), 2.54 (br d, J 9.2 Hz, 1H), 2.42 (br d, J 10.5 Hz, 1H), 2.32 (s, 3H), 1.62 (d, J 6.1 Hz, 3H).

A solution 0.140 g (0.443 mmol) of IIc in 3 ml of acetonitrile was stirred at 0°C under an atmosphere of argon. Conversion to IVc was accomplished in a manner similar to that described previously. After recooling the solution of IVc to 0°C, a cold solution of 40 mg of sodium borohydride in 5 ml of a mixture of methanol and CH_3CN (1/1) was added, and the resulting solution stirred at 0°C for 2 h. Work-up as before afforded 65 mg (46%) of [(η^5-$C_5H_4COCH_3$)Mo(NO)(CO)(η^2-isobutene)] (Vc) as a yellow, air-sensitive solid. TLC (SiO_2, CH_2Cl_2): $R_f = 0.55$; IR (CH_2Cl_2): 3020w, 2960w, 1969s, 1667m, 1632s, 835w, cm^{-1}; ^1H NMR ($CDCl_3$, 25°C): δ 6.75 (v brd, $J \cong 8$ Hz, 1H), 6.22 (m, 1H), 5.80 (m, 1H), 5.61 (br d, $J \cong 4$ Hz, 1H), 2.49 (br s, 1H), 2.37 (s, 1H), 2.30 (s, 3H), 1.81 (s, 3H), 1.50 (s, 3H).

A solution of 0.150 g (0.475 mmol) of IIc in 3 ml of acetonitrile was stirred at 0°C under an atmosphere of argon. Conversion to IVc was accomplished as described above. After recooling the solution to 0°C, 0.5 ml of a 1.0 *M* diethylammonium isopropylnitronate solution [18c] was added via syringe. The resultant mixture was warmed to room temperature, and stirred for 2 h. Most of the solvent was removed in vacuo, the residue taken up in dichloromethane, and then filtered quickly through a bed of Florisil. Removal of the solvent in vacuo afforded 250 mg of a red orange oil. Analysis of the crude product indicated the presence of two carbonyl complexes (IR (CH_2Cl_2): 1969, 1883 cm^{-1}). Fractionation by flash chromatography on silica gel (CH_2Cl_2 eluent) afforded (after solvent removal), 20 mg of a yellow solid found to be identical to Vc (13% yield, vide supra). The second constituent contained a terminal CO ligand as indicated by ν(CO) 1883 cm^{-1} together with a NO ligand with $\nu(CO) \cong 1640$ cm^{-1} which was between the principal NO stretch and the acetyl carbonyl stretching band. Complexes of the general structure (η^5-Cp)Mo(NO)Cl(η^3-allyl) exhibit NO stretching bands only [18c]. An identical (by IR spectral analysis) product mixture could be obtained by simply stirring a solution of cation IVc in acetonitrile over sodium amalgam at room temperature for a period at 16 h followed by the usual work-up.

Nucleophilic addition of thiophenoxide to the η^5-AcCp cation IVa

A solution of 0.125 g (0.414 mmol) IIa in 3 ml of acetonitrile was stirred at 0°C under an atmosphere of argon and converted to IVa as described above. A solution of 2.0 *M* triethylammonium thiophenolate was prepared from 2.20 g (20.0 mmol) of thiophenol dissolved in 7 ml acetonitrile and 3 ml of triethylamine. A 0.2 ml aliquot (0.40 mmol) of this solution was added to the solution of IVa maintained at 0°C. The mixture was stirred at that temperature for 30 min. Thereafter, the solvent was removed in vacuo, the residue taken up in dichloromethane, and quickly filtered

through a bed of Florisil. Removal of solvent in vacuo afforded 75 mg (38%) of [(η^5-$C_5H_4COCH_3$)Mo(NO)(CO)(η^3-allylphenylthioether)] (VIa) as a red-brown, amorphous solid. TLC (SiO_2, CH_2Cl_2): $R_f = 0.60$; IR (CH_2Cl_2): 3025w, 2982w, 1990s, sh. 1944, 1732w, 1637s, sh. 1581, 830m cm^{-1}, intensity (1990)/intensity (1944) = 3/1.

Nucleophilic addition of benzylmalonate to the η^5-AcCp cation IVa

A solution of 0.150 g (0.497 mmol) of IIa in 3 ml of acetonitrile was stirred at 0°C under argon atmosphere. Conversion to IVa was effected with one equiv. of $NOPF_6$. In a separate flask, 0.110 g (0.495 mmol) of dimethylbenzylmalonate was stirred with 5 ml of THF at 0°C under argon. n-Butyllithium (0.30 ml of a 1.6 *M* solution in hexane) was added dropwise with constant stirring. The resultant mixture allowed to warm to room temperature, then stirred for an additional 30 min. After recooling to 0°C, the mixture was transferred to the solution of IVa with the aid of an additional 5 ml of CH_3CN. The mixture was allowed to warm to room temperature, and stirred for 2 h. Thereafter, the solvent was removed in vacuo, the residue taken up in dichloromethane, and filtered quickly through a bed of Florisil. Most of the solvent was removed in vacuo, and the product was isolated by flash chromatography on silica gel with a mixture of CH_2Cl_2 and hexane (2/1) as the eluent. Removal of solvent in vacuo afforded 106 mg (43% yield) of [(η^5-C_5H_4CO-CH_3)Mo(NO)(CO)(η^2-dimethyl(allyl)benzylmalonate)] (VIIa) as an orange-yellow,

TABLE 4

EXPERIMENTAL DATA FOR X-RAY DIFFRACTION DATA OF (ACETYLCYCLOPENTADIENYL)DICARBONYL(η^3-ALLYL)MOLYBDENUM (IIa)

Crystal parameters at −159°C			
Space group	$P2_1/c$	V (Å^3)	1129.57
a (Å)	10.236(2)	Z	4
b (Å)	8.008(2)	mol. wt.	300.17
c (Å)	13.793(3)	$\rho_{calcd.}$ (g cm^{-3})	1.771
β (°)	92.42(1)		
Measurements of intensity data			
Radiation Mo-K_α		0.71069 Å	
Monochromator		graphite	
Detector aperture		3.0×4.0 mm	
Reflctns measd		$+h, +k, +l$	
max 2θ, (°)		45	
min 2θ, (°)		6	
Scan type		moving crystal-moving detector	
ω scan rate, (° min^{-1})		4.0	
ω scan width, (° min^{-1})		2.0+dispersion	
Background time, (s)		10 at extremes of scan	
Refls. measd.		3868	
Data used ($F > 3\sigma(F)$)		1891	
Treatment of data			
Abs coeff. μ (cm^{-1})		11.209	
Δ/σ final cycle (max)		0.05	
Final residuals $R(F)$, $R_w(F)$		0.0155, 0.0200	
Goodness of fit for last cycle		0.767	

air-sensitive, amorphous solid. A single sharp set of CO, NO, ester and acetyl (stretching) bands were observed in the solution spectrum of VIIa at 1673, 1640, 1732 and 1678 cm^{-1}, respectively. However the 360 MHz ^1H NMR spectrum was more complex. Four methoxy resonances representing a pair of diastereotopic environments were observed at 22°C together with broadened Cp multiplets and the acetyl resonance. The latter sharpened as the temperature was raised to 57°C but four methoxy resonances were still apparent. Above this temperature, VIIa decomposed. We believe that this NMR behavior is best accounted for as not a pair of diastereomers, as in product VIa, but as a single diastereomer existing as 2 rotamers with a large barrier to interconversion. The sharper definition of the Cp and Ac resonances with increasing temperature is consistent with an increased rotation about the metal-ring axis. However the barrier to olefin rotation appeared to be even higher. If a true diastereomeric mixture pertained, a doubling of the IR bands (compare Table 3) should have been apparent. The behavior of VIIa was: TLC

TABLE 5

FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR (η^5-AcCp)-$Mo(CO)_2(\eta^3$-ALLYL) (IIa) [a]

Atom	x	y	z	B_{iso}
Mo(1)	2138.9(1)	2222.2(2)	5595.0(1)	9
C(2)	799(2)	2884(2)	4621(1)	17
O(3)	9982(1)	3271(2)	4058(1)	24
C(4)	2228(2)	307(3)	4727(1)	15
O(5)	2263(2)	−857(2)	4234(1)	23
C(6)	4253(2)	2208(3)	5033(2)	24
C(7)	3866(2)	3810(3)	5310(2)	22
C(8)	2841(2)	4607(3)	4790(2)	23
C(9)	2710(2)	2642(3)	7257(1)	14
C(10)	1528(2)	3508(3)	7073(1)	15
C(11)	552(2)	2335(3)	6789(1)	15
C(12)	1118(2)	732(3)	6796(1)	14
C(13)	2475(2)	905(2)	7081(1)	14
C(14)	3482(2)	−410(3)	7174(1)	15
C(15)	3080(3)	−2179(3)	6973(2)	21
O(16)	4607(1)	−60(2)	7424(1)	22
H(1)	486(3)	170(4)	542(2)	26(5)
H(2)	424(3)	192(4)	437(2)	29(6)
H(3)	421(2)	430(3)	594(2)	21(5)
H(4)	275(3)	441(4)	409(2)	32(6)
H(5)	252(2)	565(3)	499(2)	16(4)
H(6)	348(2)	310(2)	745(1)	2(3)
H(7)	141(2)	464(3)	714(1)	11(4)
H(8)	972(2)	254(3)	661(2)	10(4)
H(9)	71(2)	−25(3)	665(1)	13(4)
H(10)	257(4)	−251(4)	741(3)	50(9)
H(11)	373(3)	−289(4)	697(2)	41(7)
H(12)	255(4)	−226(4)	647(3)	51(9)

[a] Fractional coordinates are ($\times 10^4$) for non-hydrogen atoms and ($\times 10^3$) for hydrogen atoms. B_{iso} values are ($\times 10$). Isotropic values for atoms refined anisotropically were calculated according to Hamilton [29].

(SiO_2, CH_2Cl_2): $R_f = 0.49$; IR (CH_2Cl_2): 3012w, 2920m, 2842w, 1973s, 1732s, 1678m, 1640s, 802w cm^{-1}; ^1H NMR ($CDCl_3$, +22°C): δ 7.26–7.08 (br m, 5H), 6.20 (br s, 1H), 5.82–5.65 (br m, 1H), 5.58 (br s, 1H), 5.52 (br s, 1H), 3.77, 3.75, 3.68, sh. 3.67, 3.65 (singlets, 6H total), 3.35 (br dd, $J \cong 12$, 9 Hz, 1H), 3.22 (d, J 1.8 Hz, 1H), 3.19 (d, J 1.8 Hz, 1H), 2.65 (br dd, J 12.5, 9.2 Hz, 2H), 2.28 (m, 2H), 2.23 (br s, 3H); (+57°C): δ 7.27–7.09 (br m, 5H), 6.18 (br s, 1H), 5.81 (br s, 1H), 5.58 (br s, 1H), 5.52 (br s, 1H), 3.77, 3.75, 3.67, 3.65 (singlets, 6H total), 3.35 (br dd, $J \cong 12$, 9 Hz, 1H), 3.22 (d, J 1.8 Hz, 1H), 3.19 (d, J 1.8 Hz, 1H), 2.65 (dd, J 12.5, 9.2 Hz, 2H), 2.28 (m, 2H), 2.22 (s, 3H).

X-Ray crystallography of (η^5-AcCp)Mo(CO)(η^3-allyl) (IIa)

Crystals of IIa were grown by slowly cooling a saturated solution of IIa in a mixture of hexane and dichloromethane (3/1) over a 16-h period from 25 to −15°C under an atmosphere of argon. The diffractometer utilized for data collection was designed and constructed locally [28]. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator was interfaced to a TI 980 mini-computer, with Slo-Syn stepping motors to drive angles. Measurements are taken using Mo-K_α radiation, and centering was accomplished using top/bottom-left/right slit assemblies. The mini-computer was interfaced by low-speed data lines to a CYBER 170-855 (NOS operating system) where all computations were performed.

A crystal of dimensions $0.13 \times 0.12 \times 0.12$ mm was selected and affixed to a goniometer with silicone grease, then transferred to the goniostat where it was cooled to −159°C for characterization and data collection (Table 4). A systematic search of a limited hemisphere of reciprocal space located the diffraction maxima which could be indexed as the monoclinic, unique space group $P2_1/c$. From a total of 3868 reflections, 1891 [$F > 3\sigma(F)$] were used in the structure solution and refinement. The structure was solved by direct methods (MULTAN 78) and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were clearly visible in a difference Fourier phased on the non-hydrogen atoms and were refined isotropically in the final cycles (non-hydrogens anisotropically). A final difference Fourier was featureless, the largest peak being 0.19 e $Å^{-3}$. Psi scans of several reflections were flat, indicating no absorption correction was necessary. Final atomic coordinates and thermal parameters are listed in Table 5.

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