ARE CATIONIC η^3-ALLYL COMPLEXES GENERAL PRECURSORS TO METALLACYCLOBUTANES? SYNTHESIS AND STRUCTURE OF μ-CHLORO-BIS[(η^3-ALLYL)-2,2′-BIPYRIDYLDICARBONYLMOLYBDENUM(II)] TETRAFLUOROBORATE

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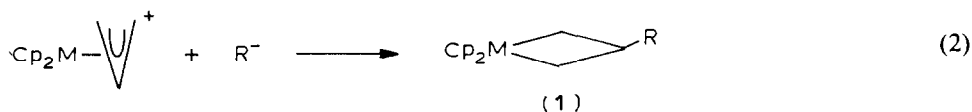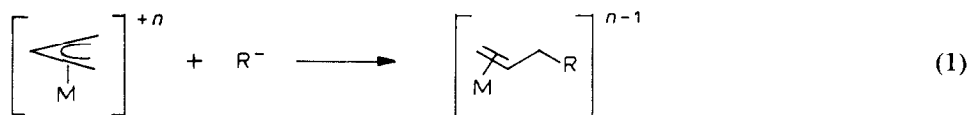*Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109 (U.S.A.)*
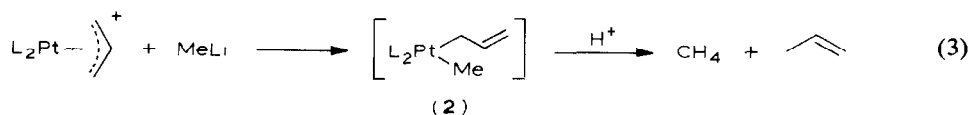
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Summary

Silver tetrafluoroborate reacts with $Cl(bipy)(CO)_2(\eta^3\text{-}C_3H_5)Mo$ in CH_2Cl_2 to give the dimeric cation, $(\mu\text{-}Cl)[(bipy)(CO)_2(\eta^3\text{-}C_3H_5)Mo]_2^+$, isolated as the crystalline BF_4^- salt with CH_2Cl_2 of solvation (5). Complex 5 crystallizes in the triclinic system (space group $P\bar{1}$, No. 2) with cell parameters: a 11.831(2), b 10.142(3), c 15.618(3) Å; α 93.96(2), β 104.33(2), γ 91.41(2)°, V 1809.5(8) Å^3, $Z = 2$, $\rho_{calc.}$ 1.60 g cm^{-3}. Full matrix refinement with all but three atoms anisotropic converged at $R_1 = 0.057$ and $R_2 = 0.073$ based on 3742 reflections with $I > 3\sigma(I)$. The two halves of the dimer are connected by a single chloride bridge (Mo–Cl 2.554(3), 2.519(3) Å, Mo–Cl–Mo 134.0(1)°). The η^3-allyl group is oriented so that its open face points toward the two *cis*-carbonyl groups, a feature common to all $L_2X(CO)_2Mo(\eta^3\text{-allyl})$ structures determined to date. A molecular orbital analysis shows that this rotational preference of the allyl group has its roots in the strong π-bonding character of the carbonyls. The MO analysis also provides a rationale for regioselectivity observed in the reactions of various η^3-allyl complexes with nucleophiles. In particular, the factors which determine whether the terminal carbons are attacked (giving olefin) or whether the central carbon is attacked (giving a metallacyclobutane) are exposed.

Introduction

η^3-Allyl complexes have proved to be valuable intermediates for the formation of new C–C bonds by way of nucleophilic attack on the coordinated allyl group (eq. 1) [1]. The cationic η^3-allyl complexes of Cp_2Mo and Cp_2W give metallacyclobutanes upon reaction with Grignard reagents, etc. (eq. 2) [2].

$$\left[\underset{M}{\diagdown\!\!\!\!\diagup\!\!\!\!=} \right]^{+n} + \ R^- \ \longrightarrow \ \left[\underset{M}{\diagup\!\!\!\!\diagdown\!\!\!\!\diagdown_R} \right]^{n-1} \tag{1}$$

$$Cp_2M-\diagup\!\!\!\!\diagdown^+ + \ R^- \ \longrightarrow \ Cp_2M\diamondsuit\!\!\!\!-R \tag{2}$$

(1)

At about the time Ephretikhine et al. published their results [2], we were also investigating the reactions of nucleophiles with 16-electron η^3-allyl complexes. Klingler [3] observed that MeLi reacted with η^3-allylnickel acetate in the presence of 2,2'-bipyridyl (bipy) to give an unstable, dark green complex, the instability and low solubility of which precluded its characterization. Also Dilgassa observed that MeLi attacked $L_2Pt(\eta^3\text{-}C_3H_5)Cl$ (L = Ph_3P) at Pt rather than at the allyl ligand (eq. 3) [4].

$$L_2Pt-\diagup\!\!\!\!\diagdown^+ + \ MeLi \ \longrightarrow \ \left[L_2Pt\diagdown\!\!\!\!\diagup_{Me} \right] \ \xrightarrow{\ H^+\ } \ CH_4 \ + \ \diagup\!\!\!\!\diagdown \tag{3}$$

(2)

Our goal at that time was the preparation of 16-electron metallacyclobutanes in order to study their behavior with respect to olefin metathesis [5]. To lessen the probability of nucleophilic attack at the metal, we therefore sought to prepare a cationic, 16-electron η^3-allyl complex with a coordination number greater than 4. Powell [6] had reported that treatment of $(bipy)Mo(CO)_2(\eta^3\text{-}C_3H_5)Cl$ (3) [7] with $AgBF_4$ in the presence of added ligands gave the 7-coordinate complexes $L(bipy)(CO)_2Mo(\eta^3\text{-}C_3H_5)^+$. We reasoned that the reaction of 3 with $AgBF_4$ in the absence of an added nucleophile might produce the desired complex, 4 (eq. 4).

$$3 + AgBF_4 \rightarrow AgCl + (bipy)(CO)_2Mo\big(\eta^3\text{-}C_3H_5\big)^+ BF_4^- \tag{4}$$

(4)
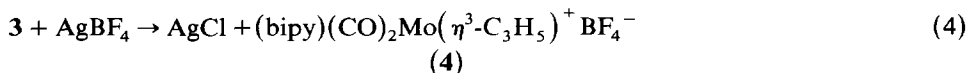
It was found, however, that the reaction of 3 with $AgBF_4$ in CH_2Cl_2 does not give isolable 4, but rather a chloro-bridged dimeric cation, 5, is formed, presumably according to eq. 5.

$$3 + 4 \rightarrow (\mu\text{-Cl})\big[Mo(CO)_2(bipy)\big(\eta^3\text{-}C_3H_5\big)\big]_2^+ BF_4^- \tag{5}$$
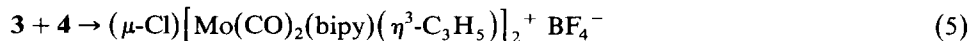
This report describes the synthesis and molecular structure of 5, which contains a relatively rare single chloride bridging ligand. A generalized MO analysis is used to explain the observed conformation of the allyl group in 5 and in related complexes. The regioselectivity of nucleophilic addition to the complexed allyl group (cf. eqs. 1 and 2) is also analyzed in terms of a generalized molecular orbital (MO) scheme.

Experimental

The starting material, $(bipy)Mo(CO)_2(\eta^3\text{-}C_3H_5)Cl$ (3) was prepared according to the methods of Brisdon or Hull and Stiddard [7]. Standard Schlenk techniques were used in all manipulations.

Synthesis of 5

Complex **3** (0.77 g, 2 mmol) and solid $AgBF_4$ (0.42 g, 2 mmol) were placed in a Schlenk flask under a nitrogen atmosphere. Methylene chloride (40 ml) was then added and the solution stirred for 20 min and then filtered to give ca. 1.3 mmol of AgCl. The filtrate was concentrated and cooled to $-20\,^{\circ}$C overnight. Filtration gave the product as a red, crystalline solid. Satisfactory elemental analyses were not obtained owing to varying amounts of solvation of the crystals (see below).

The product shows a complex pattern for the bipy protons in the region δ 9.1–7.3, a singlet due to CH_2Cl_2 of solvation at δ 5.3, and the π-allyl resonances occur at δ 3.2 (m) and 1.3 (d). The IR spectrum of **5** shows two $\nu(CO)$ bands at 1943 and 1850 cm^{-1} (KBr) and a $\nu(BF)$ at 1080 cm^{-1} (br).

Structure determination

Some difficulty was experienced in growing large crystals for diffractometry. Slow evaporation of a CH_2Cl_2 solution under N_2 gave marginally suitable crystals. A crystal was mounted on a automated Syntex P2$_1$ diffractometer (see Table 1 for relevant statistics). From rotation photographs and initial counter data it was determined that the crystal was triclinic with the assumed space group $P\bar{1}$ with $Z = 2$.

A Patterson [8] synthesis yielded the positions of 2Mo + Cl. The coordinates of these three atoms and the scale factor were refined once to give $R = 0.283$ and $R_w = 0.372$. A difference Fourier showed the positions of 28 non-hydrogen atoms. Following one more cycle of refinement on these 31 atoms, the remainder of the non-hydrogen atoms (excluding the solvent of crystallization) were located. Another cycle of refinement (x, y, z, B) was done, and on the 4th cycle the Mo and Cl atoms were refined anisotropically. At this point, the larger residuals were resolved as due to a CH_2Cl_2 of solvation. One η^3-allyl group and one CO had large thermal parameters and anomalous distances, probably as a result of poor crystal quality,

TABLE 1

CRYSTAL AND DATA COLLECTION SUMMARY FOR $[(\eta^3\text{-}C_3H_5)Mo(CO)_2\text{bipy}]_2(\mu\text{-Cl})$

Space group	$P\bar{1}$
a, b, c (Å)	11.831(2),10.142(3),15.618(3)
α,β,γ (°)	93.96(2), 104.33(2), 92.41(2)
V (Å^3), Z	1809.5(8), 2
ρ(calc) (g cm^{-3})	1.60
Crystal dimensions (mm)	$0.14 \times 0.29 \times 0.17$
Radiation	Mo-K_α, monochromatized from a graphite crystal
Scan speed (deg min^{-1})	2.5–12
Standard reflections	025, 12$\bar{6}$, 33$\bar{3}$
2θ limit (°)	50
Total reflections	6651
Reflection with $I > 3\sigma$	3742
R_1, R_2	0.057, 0.073
NV	427
NO/NV	8.76
$[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$	2.211

TABLE 2

FRACTIONAL ATOMIC COORDINATES

Atom	x	y	z
Mo(1)	0.0049(1)	0.0663(1)	0 2061(1)
Mo(2)	−0.2885(1)	0.1589(1)	0 3510(1)
Cl	−0.1043(2)	0.2005(3)	0.3019(2)
Cl(2)	0.3525(7)	−0.2480(6)	0.2802(5)
Cl(3)	0.4088(10)	−0.4710(9)	0.3786(5)
C(1)	−0.3482(10)	0.0222(12)	0.2565(8)
O(1)	−0.3836(9)	−0.0637(9)	0 2038(6)
C(2)	−0.2219(12)	0.0003(11)	0.4024(8)
O(2)	−0.1854(10)	−0.0988(9)	0.4278(6)
C(3)	−0.0379(11)	−0.1036(12)	0.2440(9)
O(3)	−0.0621(10)	−0.2035(9)	0 2647(8)
C(4)	0.1466(16)	0.0889(18)	0.3108(13)
O(4)	0.1721(22)	0.0532(23)	0.3699(13)
C(5)	−0.3772(11)	0.1050(13)	0.4640(8)
C(6)	−0.4404(10)	0.1947(13)	0.4086(9)
C(7)	−0.4918(10)	0.1429(13)	0.3205(9)
N(1)	−0.3231(7)	0.3499(8)	0.2857(5)
N(2)	−0.1981(7)	0.3241(8)	0.4509(5)
C(8)	−0.3754(9)	0.3523(11)	0.1992(7)
C(9)	−0.3737(11)	0.4686(13)	0.1551(8)
C(10)	−0.3165(11)	0.5811(12)	0 2014(9)
C(11)	−0.2645(11)	0.5779(11)	0.2918(8)
C(12)	−0.2679(9)	0.4608(11)	0.3318(7)
C(13)	−0.2080(9)	0.4490(10)	0.4255(7)
C(14)	−0.1626(12)	0.5598(11)	0.4828(8)
C(15)	−0.1020(12)	0.5369(13)	0.5701(9)
C(16)	−0 0855(12)	0.4076(15)	0.5947(8)
C(17)	−0.1359(10)	0.3059(12)	0.5334(7)
N(3)	−0.1555(7)	0.0894(8)	0.1005(5)
N(4)	0.0154(7)	0.2709(8)	0.1603(6)
C(18)	−0.2369(10)	−0.0117(11)	0.0675(7)
C(19)	−0.3421(11)	0.0083(13)	0.0035(8)
C(20)	−0.3617(11)	0.1316(15)	−0.0264(8)
C(21)	−0.2787(11)	0.2347(12)	0.0051(7)
C(22)	−0.1758(9)	0.2097(10)	0.0690(6)
C(23)	−0.0814(9)	0.3107(10)	0.1046(7)
C(24)	−0.0931(12)	0.4414(11)	0.0805(8)
C(25)	−0.0015(13)	0.5298(12)	0.1145(9)
C(26)	0.0972(12)	0.4943(12)	0.1721(9)
C(27)	0.1043(10)	0.3620(11)	0.1938(8)
C(28)	0.0473(13)	−0.1054(17)	0.1019(11)
C(29)	0.0927(19)	0.0005(21)	0.1059(13)
C(30)	0.1989(12)	0.0571(16)	0.1972(15)
C(31)	0.4331(20)	−0.3886(23)	0.2943(16)
B(1)	0.3254(13)	0.3480(14)	0.0583(10)
F(1)	0.2163(7)	0.3067(8)	0.0131(6)
F(2)	0.3357(7)	0.4830(7)	0.0739(6)
F(3)	0.3537(7)	0.2898(9)	0.1363(5)
F(4)	0.4018(8)	0.3109(9)	0.0100(6)
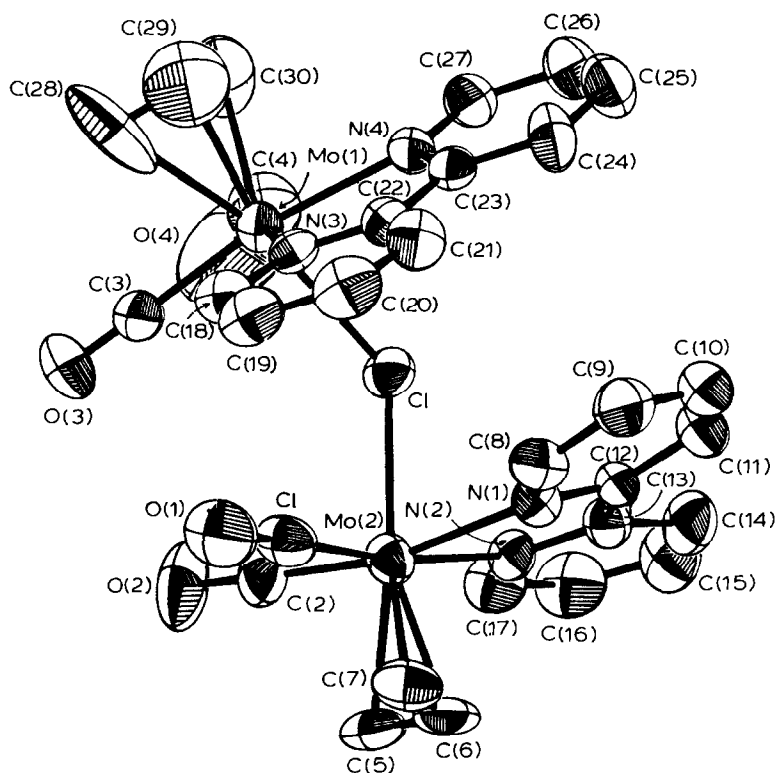
Fig. 1. ORTEP plot of the cation, [(bipy)(CO)$_2$(η^3-C$_3$H$_5$)Mo]$_2$(μ-Cl)$^+$ (5).

since a close inspection of the residuals did not reveal any reasonable model for disorder in the ill-behaved CO or η^3-allyl group.

After isotropic convergence (3 cycles), all atoms were refined anisotropically except three ill-behaved carbon atoms (one each in an η^3-allyl, a CO, and the CH$_2$Cl$_2$ of solvation). This model converged (2 cycles) to $R_1 = 0.057$ and $R_2 = 0.073$. The highest peak in the final difference map had ρ 1.31 e/Å^3 and was associated with the ill-defined η^3-allyl group. All other peaks had $\rho < 1.0$ e/Å^3 the largest two of which were associated with the chlorines of the CH$_2$Cl$_2$ of solvation. Tables 2 and 3 (supplementary material) contain the final positional and temperature factors, respectively. Figure 1 shows the molecule and its associated numbering scheme. Derived bond distances and angles are given in Tables 4 and 5, respectively. Table 6 (supplementary material) contains the structure factors.

MO schemes. The generalized molecular orbital schemes used to explain the rotational preference of the allyl group in L$_3$(CO)$_2$M(allyl) complexes and to explain the regioselectivity of nucleophilic addition are based on results calculated for particular complexes by standard Extended Hückel (EHMO) procedures. The calculational details are given in Ref. 17.

Results and discussion

Synthesis and structure of 5

X-ray crystallography established that the product of the reaction between

TABLE 4

SELECTED BOND DISTANCES

Bond	d (Å)	Bond	d (Å)
Mo(1)–Cl(1)	2.554(3)	N(1)–C(12)	1.35(1)
Mo(2)–Cl(1)	2.519(3)	N(2)–C(13)	1.35(1)
Mo(1)–C(3)	1.96(1)	N(2)–C(17)	1.34(1)
Mo(1)–C(4)	2.03(2)	N(3)–C(18)	1.37(1)
Mo(2)–C(1)	1.94(1)	N(3)–C(22)	1.35(1)
Mo(2)–C(2)	1.94(1)	N(4)–C(23)	1.35(1)
Mo(1)–N(3)	2.215(8)	N(4)–C(27)	1.36(1)
Mo(1)–N(4)	2.251(8)	C(8)–C(9)	1.41(2)
Mo(2)–N(1)	2.251(8)	C(9)–C(10)	1.37(2)
Mo(2)–N(2)	2.260(8)	C(10)–C(11)	1.40(2)
Mo(1)–C(28)	2.45(2)	C(11)–C(12)	1.38(1)
Mo(1)–C(29)	2.16(2)	C(12)–C(13)	1.47(1)
Mo(1)–C(30)	2.34(1)	C(13)–C(14)	1.40(1)
Mo(2)–C(5)	2.35(1)	C(14)–C(15)	1.41(2)
Mo(2)–C(6)	2.23(1)	C(15)–C(16)	1.40(2)
Mo(2)–C(7)	2.33(1)	C(16)–C(17)	1.37(2)
C(1)–O(1)	1.15(1)	C(18)–C(19)	1.42(2)
C(2)–O(2)	1.16(1)	C(19)–C(20)	1.37(2)
C(3)–O(3)	1.13(1)	C(20)–C(21)	1.39(2)
C(4)–O(4)	0.99(2)	C(21)–C(22)	1.41(1)
C(5)–C(6)	1.40(2)	C(22)–C(23)	1.47(1)
C(6)–C(7)	1.42(2)	C(23)–C(24)	1.40(1)
C(28)–C(29)	1.18(2)	C(24)–C(25)	1.36(2)
C(29)–C(30)	1.70(3)	C(25)–C(26)	1.36(2)
N(1)–C(8)	1.34(1)	C(26)–C(27)	1.41(2)

(bipy)Mo(CO)$_2$(η^3-C$_3$H$_5$)Cl (3) and AgBF$_4$ in CH$_2$Cl$_2$ is the dimeric cation, 5, which was isolated as the CH$_2$Cl$_2$-solvated BF$_4^-$ salt. Presumably, the dimer is formed by the reaction of the coordinatively unsaturated cation, 4, and the starting chloride complex, 3 (eq. 5). The ions, Fp$_2$X$^+$ (Fp = CpFe(CO)$_2$, X = Cl, Br, I) have been known for some time [9a–d]. More recently, Mattson and Graham have worked out the complete reaction sequence of Fp$_2$I with AgBF$_4$ and have delineated the role of Fp$_2$I$^+$ in the reaction scheme [9e]. It is interesting to note that the presumed intermediate, 4, is a sufficiently strong Lewis acid toward chloride to effectively compete with the Ag$^+$ for the available chloride. Recently, Beck et al. have shown that CpMo(CO)$_3^+$ is also an extremely strong Lewis acid [9f].

There is surprisingly little change in the ν(CO) frequencies in 5 as compared to the starting chloride, 3. Those of the former occur at 1943 and 1850 cm^{-1} while those of the latter complex are found at 1940 and 1840 cm^{-1}. This suggests that the degree of back-bonding to the carbonyls is comparable in the cationic dimer and the neutral monomer, which in turn suggests that a good portion of the positive charge on the cation is highly delocalized onto the ligands (or concentrated on the bridging halide) [10]. The isomer shifts in the ^{57}Fe Mössbauer spectra of FpX and Fp$_2$X$^+$ show a higher s-electron density on Fe in the former complexes [9c]. Increasing positive charge on the bridging halogen would lower the energy of the halogen orbitals which in turn would give less mixing of the Fe $3d$ and $4s$ orbitals. Thus, the

TABLE 5

SELECTED BOND ANGLES (°)

Mo(1)–Cl(1)–Mo(2)	134.0(1)	C(11)–C(12)–N(1)	121.0(1)
Mo(2)–C(1)–O(1)	176.0(1)	C(11)–C(12)–C(13)	122.0(1)
Mo(2)–C(2)–O(2)	175.0(1)	N(1)–C(12)–C(13)	116.6(8)
Mo(1)–C(3)–O(3)	178.0(1)	C(13)–N(2)–C(17)	118.4(9)
Mo(1)–C(4)–O(4)	136.0(2)	N(2)–C(13)–C(14)	123.0(1)
C(2)–Mo(2)–C(1)	77.3(5)	C(13)–C(14)–C(15)	117.0(1)
C(3)–Mo(1)–C(4)	90.9(7)	C(14)–C(15)–C(16)	120.0(1)
Cl(1)–Mo(2)–C(1)	93.3(3)	C(15)–C(16)–C(17)	118.0(1)
Cl(1)–Mo(2)–C(2)	88.7(4)	C(16)–C(17)–N(2)	124.0(1)
Cl(1)–Mo(1)–C(3)	94.0(3)	C(14)–C(13)–C(12)	122.0(1)
Cl(1)–Mo(1)–C(4)	87.0(5)	N(2)–C(13)–C(12)	115.5(8)
C(5)–C(6)–C(7)	115.0(1)	C(22)–N(3)–C(18)	118.5(9)
C(28)–C(29)–C(30)	120.0(2)	N(3)–C(18)–C(19)	122.0(1)
N(1)–Mo(2)–N(2)	72.6(3)	C(18)–C(19)–C(20)	119.0(1)
N(3)–Mo(1)–N(4)	72.6(3)	C(19)–C(20)–C(21)	120.0(1)
Mo(2)–N(1)–C(8)	121.9(7)	C(20)–C(21)–C(22)	119.0(1)
Mo(2)–N(1)–C(12)	116.9(6)	C(21)–C(22)–N(3)	122.0(1)
Mo(2)–N(2)–C(17)	124.2(7)	C(21)–C(22)–C(23)	123.0(1)
Mo(2)–N(2)–C(13)	117.5(6)	N(3)–C(22)–C(23)	114.9(9)
Mo(1)–N(3)–C(18)	123.0(7)	C(27)–N(4)–C(23)	117.9(9)
Mo(1)–N(3)–C(22)	118.5(6)	N(4)–C(23)–C(24)	122.0(1)
Mo(1)–N(4)–C(23)	116.4(6)	C(23)–C(24)–C(25)	118.0(1)
Mo(1)–N(4)–C(27)	125.1(8)	C(24)–C(25)–C(26)	121.0(1)
Cl(2)–N(1)–C(8)	119.7(9)	C(25)–C(26)–C(27)	118.0(1)
N(1)–C(8)–C(9)	121.0(1)	C(26)–C(27)–N(4)	122.0(1)
C(8)–C(9)–C(10)	119.0(1)	C(24)–C(23)–C(22)	121.0(1)
C(9)–C(10)–C(11)	119.0(1)	N(4)–C(23)–C(22)	116.6(9)
C(10)–C(11)–C(12)	119.0(1)		
N(3)–Mo(1)–C(3)	98.3(4)		
N(4)–Mo(1)–C(4)	96.9(6)		
N(1)–Mo(2)–C(1)	104.6(4)		
N(2)–Mo(2)–C(2)	103.5(4)		

Mössbauer spectra are also consistent with a higher positive charge on X in the bridged cations, Fp_2X^+.

Similarly, the ^{1}H NMR spectra for the η^3-allyl ligands in **5** and **3** are essentially identical within experimental error (see Ref. 7b and 11 for a full discussion of the ^{1}H NMR of these complexes). However, the resonances associated with the bipy ligand are very different in **5** and **3**. This effect is ascribed to the effect of the mutual diamagnetic shielding from the ring currents in the two bipy ligands which are overlapped (at least in the solid, see Fig. 1).

In the solid state, there are no significant contacts less than the Van der Waals distances between the cationic dimer and the BF_4^- anion or the CH_2Cl_2 of solvation. In the cation, the two molybdenums are bridged by a single Cl atom. The two Mo–Cl distances are 2.554(3) and 2.519(3) Å. Single halide bridges between molybdenum atoms are rather rare although Mo^V forms an extensive series of oxygen-bridged complexes, $[(LL)_2Mo^0]_2O$ (LL = bidentate dithiophosphate or dithiocarbamate) [12]. The Mo–O–Mo angle in these complexes is linear, a result of

extensive π-bonding between oxygen and Mo. In contrast, the Mo–Cl–Mo axis in **5** is bent: 134.0(1)°.

This Mo–Cl–Mo angle is considerably larger than normally found for chloride bridging Mo^{II} centers, viz. 102.9(1)° in $[(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)Mo]_2(\mu\text{-}Cl)_2$ [13b] or 86.5° (av.) in the anion, $[(CO)_2(\eta^3\text{-}C_3H_5)Mo]_2(\mu\text{-}Cl)_3$ [13c]. Although large angles about bridging atoms are often associated with p_π-multiple bonding [12–14], the average Mo–Cl distances (2.536 Å) in **5** is comparable to the Mo–Cl distances in Mo^{II} complexes of the type considered here [13], and the large Mo–Cl–Mo angle is ascribed to steric repulsion. In the compounds with small Mo–Cl–Mo angles, there are two or three bridging groups (edge or face-sharing of octahedra) so that steric effects are minimized and the presence of more than one bridging atom can draw the metal centers closer together, thereby decreasing the Mo–Cl–Mo angle. A large Fe–I–Fe angle (110.8(1)°) was also found in the solid state structure of Fp_2I^+ and was ascribed to steric repulsion between the bulky Fp groups [9d].

Probably because of poor crystal quality, one η^3-allyl and one CO group have large thermal parameters. The average Mo–C and C–O distances for the well-behaved carbonyls are 1.95 and 1.15 Å, respectively. These values are unexceptional. Likewise, the average distances and angles in the bipy ligands are very similar to those found elsewhere and deserve no further comment [15]. Three of the four Mo–N distances cluster around 2.25 Å, and the other, Mo(1)–N(3), is somewhat shorter, 2.215(8) Å. This Mo–N bond is *trans* to the ill-behaved carbonyl group and the apparent shortening may well be an artifact. The Mo–C and C–C distances associated with the η^3-allyl are also in accord with other structure determinations, as are the C–C–C angles [11,13c,15,16].

Electronic structure of η^3-allyl complexes

In all d^4-$L_2XMo(\eta^3\text{-}C_3H_5)(CO)_2$ complexes whose structures have been determined, the orientation of the η^3-allyl group is as shown in **6** or **7**. With $L_2X = (CH_3CN)_3$ [13c], (bipy)(SCN) [15a], (phen)(SCN) [15a], $PhB(pz)_3$ [16b], $Et_2B(pz)_2(py)$ [16c], Cl_3 [13c], $H_2B(3,5\text{-}Me_2pz)$ [16d], (bipy)(py) [15b], (bipy)Cl, Cp [16e] or $(MeOCH_2CH_2OMe)$ (CF_3CO_2), the structure is **6**. When L_2X is (diphos)(Cl), structure **7** is adopted in the solid state. Complex as well as simple allyl residues also adopt structure **6** [16b,16f]. In both **6** and **7**, the open face of the allyl group points toward the carbonyl ligands.

(6) (7)
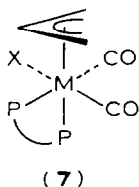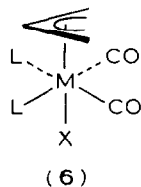
The electronic factors which control the conformational preference of the allyl ligand in d^4-$L_3(CO)_2M(allyl)$ complexes have been examined with the EHMO method [17]. The orbitals of the allyl group and the $X_3(CO)_2M$ fragment are shown in Fig. 2. It has been shown that strong π-bonding between the metal and the carbonyl ligands causes a mixing of the σ and d_{yz} orbitals of the metal fragment to
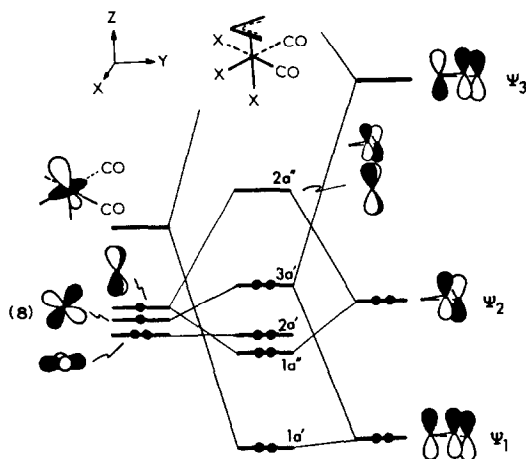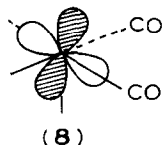
Fig. 2. Molecular orbital energy level diagram for the interaction of η^3-allyl orbitals with the orbitals of an $X_3(CO)_2M$ fragment.

give a d_{yz}-hybrid (8) which is tilted toward the y- and z-axes as compared to a pure d_{yz} orbital.

(8)

This tilted hydbrid (8) interacts strongly with the filled ψ_1-MO of the allyl group, and since orbital 8 is at a higher energy than ψ_1, orbital 8 is destabilized (i.e. pushed to higher energy) by its interaction with ψ_1. The overlap of ψ_1 and 8 is larger when the central carbon of the allyl group points toward the carbonyls than when the allyl group has its open face toward the carbonyls. Thus, the HOMO of the complex is destabilized to greater degree when the allyl group has its central carbon pointed toward the carbonyls. These interactions are diagramed in Fig. 3 [18]. The remaining orbitals of the complex show little variation in energy as the allyl group is rotated.

Regioselectivity of nucleophilic addition to η^3-allyls

Our calculations have also shown that the regioselectivity of the addition of nucleophiles to coordinated allyl groups is Frontier Orbital Controlled (FOC) rather than charge controlled [17]. In all cases examined, the central carbon of the η^3-allyl group is calculated to be positively charged with respect to the terminal carbons. Thus, charge control would always direct an incoming nuclophile to the central carbon [19], a prediction which is not borne out by experiment.

The LUMO of $L_3(CO)_2M$(allyl) complexes is the anti-bonding combination labelled $2a''$ in Fig. 2. This orbital is the only energetically accessible acceptor orbital in the complex, so FOC predicts that the complex would suffer attack at the terminal carbons since these have large "lobes" which can interact with an incoming nucleophile. In fact, it has been shown that carbanions do add to $L_3(CO)_2Mo$(allyl)
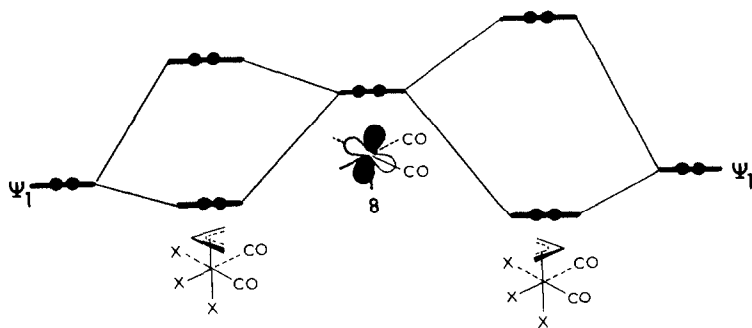
Fig. 3. Interaction of the allyl, ψ_1-orbital with the tilted hybrid, **8**, for two orientations of the allyl group.

complexes to give olefins which are formed as a result of attack on the terminal carbons (cf. eq. 1) [20].

Since the ψ_2-MO of the allyl fragment lies close in energy to the d orbitals of metals, there is always a strong interaction between the ψ_2-allyl MO and some d_π orbital on the metal. Such an interaction gives a filled bonding level and an empty anti-bonding level, e.g. the $2a''$ orbital of $L_3(CO)_2M(allyl)$ shown in Fig. 2. Normally, this anti-bonding level is the LUMO in allyl metal complexes and will be the usual acceptor orbital for an attacking nucleophile. Consequently, the usual mode of addition of nucleophiles to η^3-allyl complexes will be to the terminal carbons.

Nucleophilic addition to the central carbon of η^3-allyl groups will occur only when there is a low energy acceptor orbital with a large "lobe" on the central carbon. This condition will be met only if the metal fragment has a high energy, symmetric (a') d_π orbital to interact strongly with the ψ_3-MO of the allyl fragment. Such an interaction can result in a symmetric (a') level lying above the highest occupied orbital $(1a'')$, but below $2a''$ as shown in Fig. 4. In this case, the acceptor orbital $(1a')$ features a large lobe on the central carbon and nucleophilic addition can occur to the central carbon to give a metallacyclobutane (cf. eq. 2).

Typically, a high energy a' orbital as shown in Fig. 4 will only be produced if the metal fragment has ligands located with respect to the allyl group as shown in **9**. In
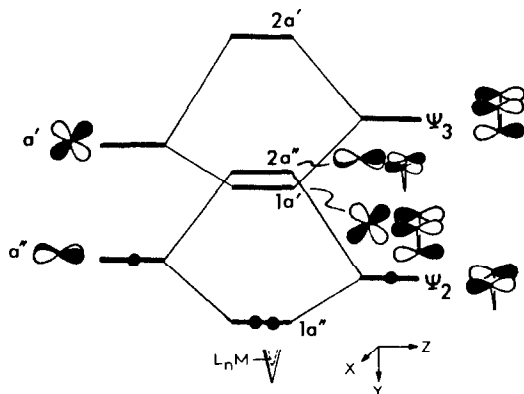

Fig. 4. Interaction of a high-energy, a'-orbital on a metal with the allyl ψ_3-orbital to create a LUMO which directs nucleophilic attack to the central carbon of the allyl group.

this case, ligand field effects (i.e. metal–ligand anti-bonding) will push the d_{yz} orbital to high energy. Such a disposition of ligands is precisely that found in $Cp_2M(allyl)^+$ (M = Mo, W), and these complexes are the only ones which are known to add nucleophiles to the central carbon (eq. 2).

(9)
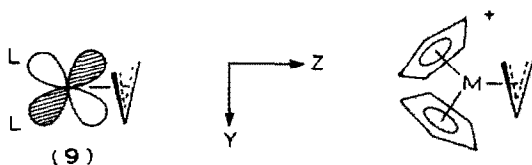
Conclusions

The cation, $(bipy)(CO)_2Mo(\eta^3\text{-}C_3H_5)^+$ (4) is a strong Lewis acid and reacts with the chloride, $(bipy)(CO)_2ClMo(\eta^3\text{-}C_4H_5)$ (3) to give a chloride-bridged dimer, 5. The allyl group in dimer 5 and in related $L_3(CO)_2M(\eta^3\text{-allyl})$ complexes displays a distinct conformational preference in which the open face of the allyl group points toward the carbonyl ligands. This rotational preference has its roots in the strong π-bonding between the metal fragment and the carbonyls.

The regioselectivity of nucleophilic addition to coordinated η^3-allyl groups is frontier orbital controlled. Normally, the frontier acceptor orbital is composed from the ψ_2-MO of the allyl and directs attacking nucleophiles to the terminal carbons. Only in exceptional circumstances will the frontier acceptor orbital be composed from the ψ_3-MO of the allyl, and hence very few allyl complexes will be suitable precursors for metallacyclobutane formation.

Acknowledgements

Supplementary Material Available: Table 3 (anisotropic thermal parameters) and Table 6 ($F_{obs.}$ vs. $F_{calc.}$) may be obtained from the principal author upon request (17 pages).

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