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Syntheses and structure of pseudooctahedral molybdenum-η^3-hexadienyl complexes

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Abstract

Compounds of the type $[MoX(\eta^3\text{-}C_5H_6Me)(CO)_2(MeCN)_2]$ where X = Cl (**1**) and Br (**2**) have been prepared by oxidative addition of 1-halohexa-2,4-dienes to $Mo(CO)_3(MeCN)_3$. Addition of the bisphosphine $Ph_2PCH_2CH_2PPh_2$ (dppe) or 2,2′-bipyridine (bipy) to **2** gives $[MoBr(\eta^3\text{-}C_5H_6Me)(CO)_2(dppe)]$ (**3**) or $[MoBr(\eta^3\text{-}C_5H_6Me)(CO)_2(bipy)] \cdot \frac{1}{2}MeCN$ (**4**), respectively, in high yields. 1,10′-phenanthroline and **1** afforded the bright red complex $[MoCl(\eta^3\text{-}C_5H_6Me)(CO)_2(phen)]$ (**5**). A crystallographic X-ray analysis showed the structure of **2** to be analogous to diether and diamine chelates previously reported. According to spectroscopic data the bisphosphine compound **3** adopts a different structure than **2**.

Introduction

The zerovalent molybdenum complex $[Mo(CO)_3(MeCN)_3]$ [1] has been shown readily to undergo oxidative additions with allylic halides, to give η^3-allyl complexes $[MoX(\eta^3\text{-allyl})(CO)_2(MeCN)_2]$ (X = Cl, Br; allyl = C_3H_5, C_3H_4Me, C_3H_4Cl, C_3Ph_3, C_6H_9) [2]. A variety of ligands readily displace the labile acetonitrile ligands in these complexes [3–6].

As part of an investigation into the chemistry of pentadienyl-transition-metal complexes, we have prepared similar hexadienylmolybdenum complexes and we compare them with their allyl analogues, which have been subject of extensive studies for many years. A recent report by Liu, Peng et al. describes the syntheses of some pentadienyl analogues by a similar method [7]. This work reports the use of 1-chloro- and 1-bromohexa-2,4-dienes as reagents for the syntheses of the novel

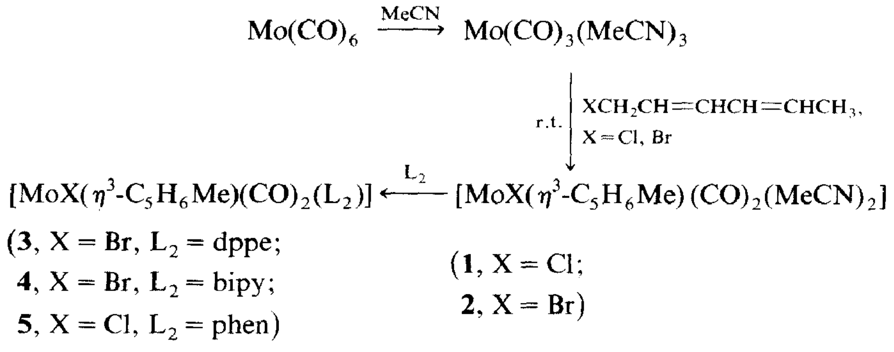
η^3-hexadienyl complexes [MoX(η^3-C_5H_6Me)(CO)$_2$(MeCN)$_2$] (X = Cl, Br), and the ready displacement of the acetonitrile ligands by the bidentate ligands, $Ph_2PCH_2CH_2PPh_2$ (dppe), 2,2′-bipyridine (bipy), and 1,10′-phenanthroline (phen).

Results and discussion

The η^3-hexadienylmolybdenum complexes were prepared by the route shown in Scheme 1. Oxidative addition of the conjugated halohexadienes to the intermediate complex [Mo(CO)$_3$(MeCN)$_3$] proved to be an accessible synthetic method [8]. In contrast, direct treatment of the halohexadienes with the molybdenum tetracarbonyl complex [Mo(CO)$_4$(bipy)] gave only decomposition products and insoluble solids, whose low solubilities precluded thorough investigations.

The complexes **1**, **2** were obtained as bright-orange crystals after slow evaporation of the solvent under nitrogen. They are air-sensitive in solution and they readily decompose as solids under air. The 1-chloro-2,4-hexadiene yielded the corresponding chloro-complex **1** rather more slowly than the bromo analogue **2** is obtained from 1-bromo-2,4-hexadiene. The orange solutions of **2** in acetonitrile were treated with bipy or dppe, as described in Scheme 1. The former gave a dark red microcrystalline product which was shown by elemental analysis to be [MoBr(η^3-C_5H_6Me)(CO)$_2$(bipy)] $\cdot \frac{1}{2}$MeCN (**4**). The latter yielded the chelate phosphine complex [MoBr(η^3-C_5H_6Me)(CO)$_2$($Ph_2PCH_2CH_2PPh_2$)] (**3**), which was also obtained using acetone as the solvent (see Experimental section). Under mild conditions, acetonitrile was displaced easily from **1** by the 1,10′-phenanthroline ligand, giving the bright-red complex [MoCl(η^3-C_5H_6Me)(CO)$_2$(phen)] (**5**). The analytical data are reported in Table 1.

Whereas the bidentate phosphine $Ph_2PCH_2CH_2PPh_2$ simply displaces the MeCN ligands without evidence of reduction of the metal, the monodentate ligand PPh_3 has been found to cause elimination of the hexadienyl ligand, with the formation of known [9] [Mo(CO)$_4$(PPh_3)$_2$]. The ligand PMe_2Ph however did give [MoBr(η^3-C_5H_6Me)(CO)$_2$(PMe_2Ph)$_2$] from an initial substitution of the acetonitrile ligands in **2**. There was no evidence of elimination of the hexadienyl group under longer reaction times, in contrast to observations on allyl derivatives [10]. However, if the phosphine ligand PMe_2Ph is in excess (4/1) with respect to the starting material **2**, a subsequent reduction reaction affords the final product [Mo(CO)$_2$(PMe_2Ph)$_4$]. It is



$$\begin{tikzcd} \mathrm{Mo(CO)_6} \arrow[r, "\mathrm{MeCN}"] & \mathrm{Mo(CO)_3(MeCN)_3} \arrow[d, "{\mathrm{XCH_2CH{=}CHCH{=}CHCH_3},\ \mathrm{X{=}Cl,\ Br}}", "\mathrm{r.t.}"'] \\ {[\mathrm{MoX}(\eta^3\text{-}\mathrm{C_5H_6Me})(\mathrm{CO})_2(\mathrm{L_2})]} & {[\mathrm{MoX}(\eta^3\text{-}\mathrm{C_5H_6Me})(\mathrm{CO})_2(\mathrm{MeCN})_2]} \arrow[l, "\mathrm{L_2}"'] \end{tikzcd}$$

(**3**, X = Br, L_2 = dppe;
4, X = Br, L_2 = bipy;
5, X = Cl, L_2 = phen)

(**1**, X = Cl;
2, X = Br)

Scheme 1

Table 1

Analytical data for the $[MoX(\eta^3\text{-}C_5H_6Me)(CO)_2L_2]$ complexes

Complex	Colour	M.p. (°C)	Yield (%)	Analysis (Found(calcd.)(%))		
				C	H	N
1	bright orange	79– 81 (dec)	48	41.10 (41.10)	4.30 (4.31)	8.01 (7.98)
2	bright orange	123–125 (dec)	62	35.88 (36.48)	3.73 (3.83)	7.03 (7.09)
3	dark red	[a]	83			
4	dark red	[a]	70	46.18 (46.60)	3.73 (3.80)	7.29 (7.15)
5	bright red	[a]	77	53.65 (53.53)	3.87 (3.82)	6.58 (6.24)

[a] Decomposes at 100 °C without melting.

suggested that the reduction involves initial nucleophilic attack on the hexadienyl ligand, according to studies by Mawby on the mechanism of reaction of the complexes $[MoCl(\eta^3\text{-}C_3H_4R)(CO)_2(PMe_2Ph)_2]$ (R = H, Me) [10]. The same patterns of reactivity have been shown by allylmolybdenum(II) complexes of the type $[MoX(\eta\text{-allyl})(CO)_2(MeCN)_2]$ [3a,4,6]. In the reaction between **2** and the monodentate triphenylphosphine, however, no intermediate Mo^{II} complex of the type $[MoBr(\eta^3\text{-}C_5H_6Me)(CO)_2(PPh_3)_2]$ or the species $[Mo(CO)_2(MeCN)_2(PPh_3)_2]$ (CO: 1814, 1745 cm^{-1}, MeCN) [6] was observed. From infrared data (CO stretching bands at 2021, 1949, 1910, 1856 cm^{-1}, MeCN) the molybdenum compound formed from this reaction is identified as the reduced product [*cis*-$Mo(CO)_4(PPh_3)_2$], which has been reported previously (2023, 1929, 1911, 1899 cm^{-1}, hexane) [9]. Brisdon et al. observed a similar product in their studies on allyl complexes [4]. The different reactivity of PPh_3 compared to $Ph_2PCH_2CH_2PPh_2$ and PMe_2Ph has been explained in terms of steric requirements, in which the PPh_3 has the greater cone angle [4].

The complex **2**, dissolved in the solvents MeOH or Me_2CO at −35 °C, was treated with trimethylphosphite in a similar manner to that reported for the preparation of the allylic complex $[MoX(\eta^3\text{-}C_3H_4R)(CO)_2(P(OMe)_3)_2]$ (X = halide; R = H, Me) [5]. However, no well-defined product could be isolated from the oily residues obtained after evaporation of the solvent.

Solid state structure of 2

The molecular structure of **2** was determined by an X-ray diffraction study. An ORTEP drawing is shown in Fig. 1. Crystal data, collection and refinement parameters are presented in Table 2. Bond lengths and angles are listed in Table 3 and the atomic coordinates and their temperature factors are in Table 4.

Compound **2** crystallizes in the *syn*-η^3-form similarly to $[MoBr(\eta^3\text{-}C_5H_7)(CO)_2(MeCN)_2]$ recently reported [7]. The complex has essentially a distorted octahedral arrangement of ligands with the mutually *cis*-carbonyl and acetonitrile ligands *trans* to each other. The η^3-pentadienyl group is *trans* to the bromine atom in the axial position. The structure of the hexadienyl ligand of **2** closely resembles

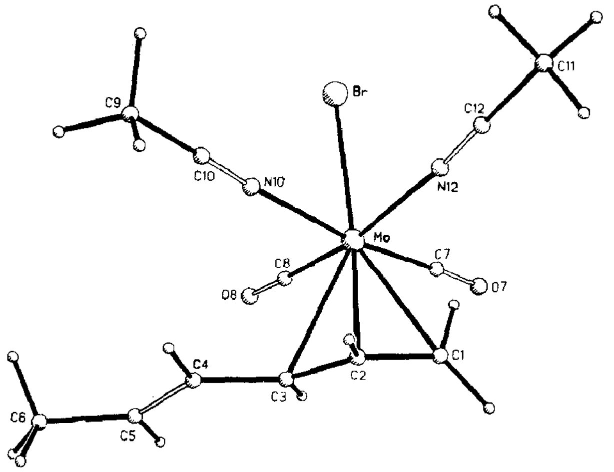


Fig. 1. Molecular structure of [MoBr(η^3-C_5H_6Me)(CO)$_2$(MeCN)$_2$] (**2**).

Table 2

Crystal data, collection and refinement parameters for [MoBr(η^3-C_5H_6Me)(CO)$_2$(MeCN)$_2$]

A. Crystal parameters	
chemical formula	$C_{12}H_{13}BrMoN_2O_2$
molecular weight	393.0986
crystal system	orthorhombic
space group	$P2_12_12_1$
crystal size, mm	0.9 × 0.08 × 0.08
crystal colour	orange
cell constants	
a, Å	7.113(2)
b, Å	13.567(5)
c, Å	15.804(10)
cell volume, Å^3	1525.1(12)
ρ(calc), g/cm^3	1.70
Z	4
F(000), e$^-$	768
B. Data collection parameters	
μ, cm^{-1}	102.62
scan width, below $K_{\alpha 1}$, above $K_{\alpha 2}$, deg	1.2–1.2
2θ limits, deg	3.0–110.0
scan speed (variable), deg min^{-1}	4.0–29.3
exposure time, h	28.5
total no. reflections collected	1164
no. unique reflections	1051
C. Structure refinement	
reflections for final refinement	1035
parameters refined	185
$R(F)$, %	4.00
$R_w(F)$, %	3.89
goodness of fit for the last cycle	1.007
final G	0.00153
residual electron density, (e$^-$/Å^3)	0.671

Table 3

Bond lengths (Å) and angles (deg.) for [MoBr(η^3-C_5H_6Me)(CO)$_2$(MeCN)$_2$]

Mo–Br	2.640(1)	Mo–C(1)	2.325(13)
Mo–C(2)	2.230(11)	Mo–C(3)	2.435(11)
Mo–C(7)	1.944(12)	Mo–C(8)	1.918(10)
Mo–N(10)	2.262(9)	Mo–N(12)	2.223(9)
C(1)–H(1a)	1.15(13)	C(1)–H(1b)	0.98(12)
C(1)–C(2)	1.392(18)	C(2)–H(2)	0.98(11)
C(2)–C(3)	1.425(16)	C(3)–H(3)	1.19(10)
C(3)–C(4)	1.444(15)	C(4)–C(5)	1.360(18)
C(5)–C(6)	1.481(17)	C(7)–O(7)	1.163(16)
C(8)–O(8)	1.156(14)	C(9)–C(10)	1.482(17)
N(10)–C(10)	1.112(14)	C(11)–C(12)	1.558(17)
N(12)–C(12)	1.095(14)		
Br–Mo–C(1)	152.5(3)	Br–Mo–C(2)	163.6(3)
C(1)–Mo–C(2)	35.5(5)	Br–Mo–C(3)	147.1(3)
C(1)–Mo–C(3)	60.0(4)	C(2)–Mo–C(3)	35.2(4)
Br–Mo–C(7)	91.3(3)	C(1)–Mo–C(7)	70.4(5)
C(2)–Mo–C(7)	103.3(5)	C(3)–Mo–C(7)	105.1(4)
Br–Mo–C(8)	86.0(3)	C(1)–Mo–C(8)	110.0(5)
C(2)–Mo–C(8)	103.4(4)	C(3)–Mo–C(8)	69.1(4)
C(7)–Mo–C(8)	80.8(5)	Br–Mo–N(10)	82.0(2)
C(1)–Mo–N(10)	114.9(4)	C(2)–Mo–N(10)	83.0(4)
C(3)–Mo–N(10)	81.9(3)	C(7)–Mo–N(10)	172.9(4)
C(8)–Mo–N(10)	101.0(4)	Br–Mo–N(12)	84.0(2)
C(1)–Mo–N(12)	79.2(4)	C(2)–Mo–N(12)	86.4(4)
C(3)–Mo–N(12)	120.1(4)	C(7)–Mo–N(12)	99.2(4)
C(8)–Mo–N(12)	170.0(4)	N(10)–Mo–N(12)	77.8(3)
Mo–C(1)–H(1a)	87.0(5)	Mo–C(1)–H(1b)	105.0(6)
H(1a)–C(1)–H(1b)	131.0(9)	Mo–C(1)–C(2)	68.5(7)
H(1a)–C(1)–C(2)	120.0(6)	H(1b)–C(1)–C(2)	108.0(7)
Mo–C(2)–C(1)	76.0(7)	Mo–C(2)–H(2)	109.0(5)
C(1)–C(2)–H(2)	128.0(6)	Mo–C(2)–C(3)	80.3(7)
C(1)–C(2)–C(3)	115.6(11)	H(2)–C(2)–C(3)	116.0(6)
Mo–C(3)–C(2)	64.5(6)	Mo–C(3)–H(3)	96.0(4)
C(2)–C(3)–H(3)	106.0(4)	Mo–C(3)–C(4)	118.5(7)
C(2)–C(3)–C(4)	124.2(11)	H(3)–C(3)–C(4)	127.0(4)
C(3)–C(4)–C(5)	121.9(11)	C(4)–C(5)–C(6)	125.2(13)
Mo–C(7)–O(7)	177.0(10)	Mo–C(8)–O(8)	174.7(9)
Mo–N(10)–C(10)	173.9(9)	C(9)–C(10)–N(10)	178.2(12)
Mo–N(12)–C(12)	175.2(9)	C(11)–C(12)–N(12)	176.4(12)

those of [MoBr(*syn*-η^3-C_5H_7)(CO)$_2$(MeCN)$_2$] (**6**) [7], [Fe(CO)(C_5H_5)(*syn*-η^3-C_5H_6Me)] (**7**) [11], [Mo(CO)$_2$(C_5H_5)(*syn*-η^3-C_5H_7)] (**8**) [12], [Co(CO)$_2$(*syn*-η^3-C_5H_7)(PPh_3)] (**9**) [13], [Mn(dmpe)$_2$(*syn*-η^3-C_5H_7)] (**10**) [14] and [Fe-*syn,syn*-bis(η^3-C_5H_7)(PMe_3)$_2$] (**11**) [15], in which the pentadienyl or hexadienyl ligand is bonded to the metal atom in an asymmetric fashion. The shortest and longest distances were observed for Mo–C(2) (2.230 Å) and Mo–C(3) (2.435 Å), respectively. The relatively long Mo–C(3) and C(2)–C(3) (1.425 Å) bonds relative to other η^3-systems suggest that the lack of symmetry is more pronounced for this complex. The methylvinyl group of the hexadienyl ligand points away from the rest of the complex, minimizing steric hindrance, with the angle between the methylvinylic

Table 4

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for [MoBr(η^3-C_5H_6Me)$(CO)_2$$(MeCN)_2$]

Atom	x	y	z	U_{eq} [a]
Mo	2988(1)	9705(1)	3719(1)	37(1)
Br	1496(2)	9088(1)	2284(1)	53(1)
C(1)	4175(22)	9445(10)	5072(8)	60(5)
H(1a)	2651(183)	9460(78)	5306(66)	74(27)
H(1b)	5067(188)	8900(81)	5011(64)	74(27)
C(2)	4969(16)	10275(9)	4697(7)	53(4)
H(2)	6223(167)	10344(67)	4445(54)	52(30)
C(3)	3756(17)	11105(8)	4618(7)	48(4)
H(3)	2516(153)	10975(64)	5115(57)	49(28)
C(4)	4283(18)	12022(8)	4220(7)	51(4)
C(5)	3224(22)	12852(9)	4301(7)	65(5)
C(6)	3681(21)	13822(9)	3926(8)	71(5)
C(7)	1216(18)	8924(8)	4373(7)	53(4)
O(7)	110(16)	8494(8)	4770(6)	97(4)
C(8)	937(15)	10621(7)	3763(7)	43(4)
O(8)	−389(14)	11114(7)	3774(6)	77(4)
C(9)	7495(17)	11252(9)	1839(8)	69(5)
N(10)	4966(13)	10489(6)	2823(5)	43(3)
C(10)	6043(15)	10807(8)	2392(7)	39(3)
C(11)	7911(18)	7328(9)	3076(8)	67(4)
N(12)	5134(13)	8552(7)	3461(6)	50(3)
C(12)	6242(17)	8026(7)	3295(7)	49(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor (except for H atoms).

plane (C(4), C(5), C(6)) and the allylic plane (C(1), C(2), C(3)) being 1.4°. The allylic (C(1), C(2), C(3)) angle is unusually narrow (115.6°) compared with **7** (121.7°), **8** (122.5°), and [MoCl(η^3-C_3H_5)$(CO)_2$$\{P(OMe)_3\}_2$] [5] (122.8°), but as expected is close to that in **6** (117.2°). The Mo–Br, Mo–C(carbonyl) and Mo–N distances are typical for molybdenum(II) structures [16]. The acetonitrile ligand is nitrogen-coordinated to the molybdenum. The Mo–N distances (2.262 and 2.223 Å) show a longer bond length for N(10) due to the presence of the methyl group in the hexadienyl ligand. The C–C distances of the acetonitrile ligands also reflect the opposite behaviour relative to Mo–N (C(9)–C(10) 1.482 and C(11)–C(12) 1.558 Å).

Infrared and NMR studies

The infrared spectra of complexes **1–5** in the CO stretching region contain two strong bands of approximately equal intensity, indicating a *cis*-arrangement of the carbonyl ligands. This assignment is confirmed by the crystal structure determination of **2** which has similar stereochemistry to several allyl [17–19] and pentadienyl [7] compounds of the type under investigation. The carbonyl stretching data of the complexes **1–5** are presented in Table 5 along with data for related complexes. It can be observed that the band position difference ($\Delta\nu$) values for complexes **1–4** are smaller than those for the corresponding analogues.

On account of the similarities in the spectra of all these closely related compounds with those of the dicarbonyl hexadienyl derivatives, it is reasonable to propose the same pseudo-octahedral structure of local C_s symmetry for the new complexes. Crystal structure determinations of various diamine analogues, such as

Table 5

Infrared data [a] for molybdenum complexes

Complex [b]	ν(CO) [c]		Analogous complexes	ν(CO)		Ref.
1	1927	1845	$[MoCl(\eta^3\text{-allyl})(CO)_2(MeCN)_2]$	1951	1855	25
			$[MoCl(\eta^3-C_5H_7)(CO)_2(MeCN)_2]$	1919 [f]	1849 [f]	7
2	1922	1840	$[MoBr(\eta^3\text{-allyl})(CO)_2(MeCN)_2]$	1953	1852	25
	1949 [d]	1860 [d]	$[MoBr(\eta^3\text{-}C_5H_7)(CO)_2(MeCN)_2]$	1925 [f]	1844 [f]	7
3	1942 [d]	1850 [d]	$[MoBr(\eta^3\text{-allyl})(CO)_2(dppe)]$	1953 [d]	1853 [d]	3
	1935 [e]	1858 [e]		1937	1842 1805(sh)	25
			$[MoCl(\eta^3\text{-}C_5H_7)(CO)_2(dppe)]$ [g]	1935 [f]	1843 [f]	7
4	1924	1861	$[MoBr(\eta^3\text{-allyl})(CO)_2(bipy)]$	1938	1845	25
				1927	1845	23
5	1929	1846	$[MoCl(\eta^3\text{-allyl})(CO)_2(phen)]$	1938	1859	23

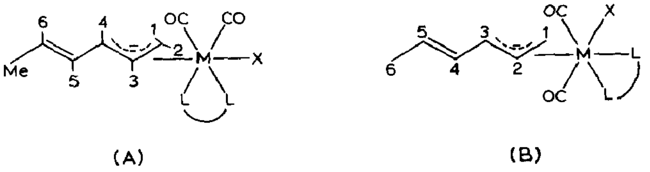
[a] Recorded as Nujol mulls (cm^{-1}). [b] Present work. [c] All bands have strong intensity. [d] In $CHCl_3$. [e] In CH_3CN. [f] In CH_2Cl_2. [g] ν(CO) not reported for the Br analogue.

$[MoX(\eta^3\text{-}C_3H_4R)(CO)_2L_2]^{n-1}$ (L_2 = bipy, R = H, X = NCS, $n = 1$; L_2 = bipy, X = py, R = H, $n = 2$; L_2 = phen, X = NCS, R = 2-Me, $n = 1$) [17–19] indicate that the chelate together with the carbonyl ligands form a horizontal plane, while above and below the plane in apical positions lie the allyl ligand and the X group, respectively. This suggests that the molecular structures of **4** and **5** have configuration **A** which was confirmed in complexes **1** and **2** (see Scheme 2). For the bisphosphine complex **3**, one can deduce from similarity between NMR and infrared data that the molecular structure is analogous to those of [MoCl(*syn*-η^3-C_5H_7)$(CO)_2$(dppe)] [7] (**12**) and of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(dppe)]$ [20] (**13**) with configuration **B** (vide infra).

The crude products of reaction between **2** and PMe_3 showed two strong bands in the CO stretching region at 1920 and 1830 cm^{-1} (CH_3CN), as do complexes **1**–**5**. However, ^{1}H NMR studies showed an impure product, which we have not been able to purify.

The chloro (**1**) and bromo (**2**) complexes, when dissolved in CD_3CN, have been found by ^{1}H NMR to ionize with concomitant liberation of free acetonitrile. A similar, but more pronounced effect had been observed for the allyl complexes $[MoX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ (X = Cl, Br) [21]. The ionization is much more evident for the chloro complex **1** than for the bromo complex **2**, and $CDCl_3$ is more efficient than CD_3CN for the formation of the ionic species. For **1** $\approx$ 70% ($CDCl_3$) and $\approx$ 10% (CD_3CN) dissociation was observed (referred to the H(3) signal).

The ^{1}H NMR studies of the allyl complexes [21] revealed three allyl containing species with chemical shifts characteristic of anionic, cationic and neutral com-



Scheme 2.

plexes. Confirmation that ionic species were formed in solution was obtained from conductivity measurements and NMR spectroscopy of analytically pure samples of $[Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]AsPh_4$ and of $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]PF_6$ [21b]. An equilibrium involving the liberation of free acetonitrile was proposed for the reversible formation of these ionic species [21b]:

$$3[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2] \rightarrow$$

$$[Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+ + [Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^- + 3\ MeCN$$

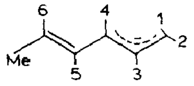
Assignments of the spectra of the η^3-hexadienyl complexes were made by comparison with the data of previously reported [7,21] analogous allyl and η^3-pentadienyl complexes. The ^1H NMR studies of **1** in deuterated acetonitrile solution at room temperature showed, as mentioned before, the presence of free acetonitrile ($\delta \approx 1.97$ ppm) along with a broad singlet at $\delta \approx 2.55$ ppm which resembles the cationic MeCN signal observed in the allylic complexes [21b]. Additionally, the spectrum shows barely detectable signals which could be assigned to ionic pentadienyl species. This ionization effect is not evident for **2**, which after remaining in solution for one year, shows the same pattern of signals. The ^1H NMR data of the neutral species **1** and **2** along with **3** are reported in Table 6.

The complex **1** in $CDCl_3$ solution exhibits resonances arising from at least two and probably three independent sets of hexadienyl signals. This is clear for the methyl protons at δ 1.80 and 1.88, the overlapped triplets at δ 2.49 and 2.68 and the signals of H(3) at 4.0 and 4.15. Higher intensities are found for the signals at higher fields, which suggests that the less intense signals may arise from cationic species. There is also clear evidence for the presence of ionic species from the H(5) and H(6) signals.

For the neutral complexes a *syn*-η^3-hexadienyl structure is assignable to **1**, **2** and **3** based on the coupling constants $J_{13} \approx J_{34} \approx 9$–11 Hz and $J_{23} \approx 6.6$ Hz. Thus,

Table 6

^1H-NMR data for $[MoX(\eta^3\text{-}C_5H_6Me)(CO)_2L_2]^a$ complexes

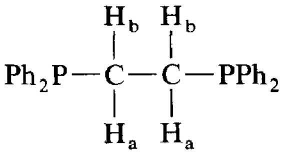


Complex	Solvent	Chemical shifts (δ)							
		H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	Me	L
1	CD_3CN (250 MHz)	1.13(dt) *J* 7.3, 9.1	3.17(s,br)	4.07(dt) *J* 6.8, 9.0	2.27(t) *J* 10	5.84(dq) *J* 15	6.12(m)	1.78(dd) *J* 1.6, 6.8	1.96(s,br) 2.56 (s, br, (4H)
1	$CDCl_3$ (250 MHz)	~1.3 [b]	3.41(dd) *J* 1.5, 6.5	4.0(dt)	~2.5 [b]	5.79(dq) *J* 15	6.30(m) *J* 1.7, 10.5	1.80(dd) *J* 1.5, 6.5	2.04(s,br)
2	CD_3CN (300 MHz)	1.1(d) *J* 8.4	3.13(s,br)	4.11(dt) *J* 6.6, 9.0	2.31(t) *J* 9.3	5.85(dq) *J* 15	6.06(m)	1.73(dd) *J* 6.0,15	1.93(s,br)
2	CD_3CN (90 MHz)	1.14(d) *J* 9	3.17(d,br) *J* 6.4	4.14(dt) *J* 6.8, 9.3	2.29(t) *J* 9.3	5.61–6.21(m)		1.68(d) *J* 6.0	1.93(s,br)
3	$CDCl_3$ (300 MHz)	1.81(d) *J* 11.2	3.63(m)	4.27(dt) *J* 11.2	3.32(t) *J* 11.2	5.91(m) *J* 11.2, 15	6.17(m) *J* 7.5, 15	1.68(d) *J* 7.5	2.37(m) [c] 2.99(m) [c] 6.9–8(m)

[a] Coupling constants in Hz. Measured relative to TMS. [b] Overlapped. [c] See text.

compound **2** has the same structure in solution and in the solid state. It is interesting to observe that the corresponding *syn* proton H(2) is observed as a broad signal for **1** and **2** when measured at 250 or 300 MHz. However, this signal is observed as a doublet (J 6.4 Hz) at 60 or 90 MHz for compound **2**, suggesting the presence of dynamic processes involving the hydrogens bound to allyl's terminal carbon atoms. This means that at higher fields the dynamic processes are close to a coalescence frequency [22].

In the dppe complex **3** all of the protons contained in the bidentate phosphine ligand displayed splitting by phosphorus. The ^1H NMR signals for the methylene protons appear as two multiplets at δ 2.37 and 2.99 ppm presumably corresponding to the a and b protons,



$$Ph_2P-\underset{H_a}{\overset{H_b}{C}}-\underset{H_a}{\overset{H_b}{C}}-PPh_2$$

(dppe)

according to Faller's studies in the allyl complex **13** [20]. A similar pattern has also been reported for $[MoCl(\eta^3\text{-}C_5H_7)(CO)_2(dppe)]$ [7] (**12**), which adopts configuration **B**. Evidence of a delocalized haxadienyl ligand adopting the *anti*-η^3-geometry was not observed, contrasting with the $[MoBr(\eta^3\text{-}C_5H_7)(CO)_2(dppe)] \cdot CHCl_3$ [7] complex.

The ^{13}C NMR spectral data show the inequivalence of the CO carbons (δ 227.2, 226.0 ppm) in **2** as a result of the unsymmetric allyl ligand. The central carbon atom C(2) of the allyl fragment is shifted ≈ 11 ppm downfield in the bisphosphine complex **3** compared with the acetonitrile compound **2**.

The insolubility of **4** and **5** prevented ^1H NMR studies. The analogues allyl compounds [23] are also sparingly soluble. The ^{31}P NMR spectrum of **3** shows $^{31}P\{^1H\}$ resonances at δ 47.3 (d) and 46.5 (d) with J 11 Hz, consistent with $[MoBr(syn\text{-}\eta^3\text{-}C_5H_7)(CO)_2(dppe)]$ (δ 46.9 (dd), 48.2 (dd), J 14.6 Hz) [7] and $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(dppe)]$ (δ 44.0) [20].

Experimental

All preparations were carried out under dry nitrogen gas using solvents and reactants freed from moisture and oxygen by standard procedures. Solution and mull IR spectra were recorded on Perkin Elmer 177 and 257, Unicam SP3-200 and Nicolet MX-1-FT spectrophotometers, and were calibrated with polystyrene film. ^1H NMR spectra were recorded using a Bruker 250 MHz instrument at King's College, London, ^1H and ^{13}C NMR spectra using Varian XL-300GS, EM-360, EM-390 spectrometers and ^{31}P NMR spectra using a Jeol FX-90 instrument at CINVESTAV, México. Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were performed by Butterworth Laboratories, Teddington, Middlesex, U.K. and Labor Pascher, Remagen, Federal Republic of Germany.

Bromo- and chloro-hexadiene. Esterification of hexa-2,4-dienoic acid with absolute methanol (2/9.3) in acid media followed by reduction of the ester with

$LiAlH_4$ (1/0.5) gave the corresponding 2,4-hexadien-1-ol (sorbyl alcohol). Bromination of the alcohol was carried out as described [24] and the product collected by distillation at 62–72° C/14 mmHg, while chlorination of the alcohol (0.26 *M*) was carried out in diethyl ether (100 cm^3) using concentrated HCl (100 cm^3). A mixture of isomers was obtained by distillation at 68–76° C/50 mmHg. Chlorination was also achieved by treatment of sorbyl alcohol (29.4 g, 0.3 *M*) with PPh_3 (87 g, 0.35 *M*) in carbon tetrachloride (200 cm^3), stirring at room temperature for 4 days. The precipitate of Ph_3PO was filtered off and the filtrate distilled through a 30 cm. fractionating column. Yield 15 g, b.p. 53–58° C/38 mmHg.

[MoX(η³-C₅H₆Me)(CO)₂(MeCN)₂] (1, X = Cl; 2, X = Br). $Mo(CO)_6$ 2.38 g, 9 mmol) was heated under reflux with MeCN (100 cm^3) for 4 h as reported by Brisdon [16]. The yellow solution was stirred and treated with the corresponding 1-chloro- or 1-bromo-2,4-hexadiene (9 mmol) at room temperature, giving an orange solution which was then evaporated to small volume under a slow stream of nitrogen. On standing for several days at 0° C, the product precipitated as bright orange crystals. The chloride derivative yielded the product rather more slowly and the solution was cooled to −23° C. The products were recrystallized from MeCN and the crystals washed with hexane and dried under vacuum. ^{13}C NMR (22.49 MHz, CD_3CN): Compound **2** δ 51.7 (C(1)), 78.8 (C(2)), 73.1 (C(3)), 133.0 (C(4)), 128.5 (C(5)), 18.6 (Me), 227.2 (CO), 226.0 (CO), 118.2 (Me*C*N), 1.77 (*Me*CN).

X-ray analysis of compound 2. Single crystals of **2** were grown by slow crystallization from acetonitrile. The X-ray data collection, structure resolution and refinements were done using a Nicolet R3m four circle diffractometer equiped with graphite monochromated Cu-K_α radiation (λ 1.54178 Å) which was operated in the $\theta/2\theta$ scanning mode. Cell parameters were established by least-squares adjustment of the setting angles of 25 machine centered strong reflections. The crystal data for compound **2** are summarized in Table 2. During the data collection two standard reflections were monitored after measurement of groups of 46 reflections and showed no significant intensity decay. The data measured were corrected for background, Lorenz and polarization effects as well as for absorption, for which the crystal was considered to have a pseudo-ellipsoid shape. The structure was solved by direct methods using the software package provided by the diffractometer manufacturer using data for which $I \geq 3\sigma(I)$. This provided all non-hydrogen atoms, which were refined anisotropically using the full matrix least-squares procedure. All hydrogen atoms bonded to carbons were placed at fixed positions (C–H, 1.09 Å) and included in the structure factor calculation with their isotropic contribution. After several full matrix least-squares cycles of refinement the idealised geometry for the four hydrogen atoms at C(1), C(2) and C(3) was slowly removed until, after several cycles of refinement, their most probable positions as completely free hydrogen atoms was acertained. The software package also tests for the correct enantiomorph of the noncentrosymmetric crystal. The least-squares weighing scheme used is $W = 1/\sigma^2(F_0) + G(F_0)^2$, were σ is the standard deviation of observed amplitudes based on counting statistics, and G is a variable adjusted after each cycle to minimize the function $\Sigma w(\Delta F)^2$. The final G value and other relevant refinement values are given in Table 2. The relevant bond distances and bond angles are given in Table 3 and the fractional atomic coordinates for all atoms, excepting those hydrogen atoms that were tied to the carbon atoms, are given in Table 4.

[MoBr(η³-C₅H₆Me)(CO)₂(bipy)] · ½MeCN (4). Complex **2** (0.33 g, 0.84 mmol) in

MeCN (45 cm^3) gave an orange solution which was filtered and cooled to −20 °C. Addition of bipyridine (0.131 g, 0.84 mmol) in MeCN (5 cm^3) gave immediately a red solution. After stirring for 15 min the temperature was increased to 0 °C. Some red-black impure solid precipitated. Recrystallization from MeCN was carried out by reducing the volume of the solvent with a slow stream of nitrogen to afford a dark-red microcrystalline product.

[MoCl(η^3-C_5H_6Me)(CO)$_2$(phen)] (5). As described for complex **4**, the chloro compound **1** (0.5 g, 1.43 mmol) and phenanthroline (0.257 g, 1.43 mmol) in MeCN (15 cm^3) afforded a bright red product, which has not been recrystallized.

[MoBr(η^3-C_5H_6Me)(CO)$_2$(dppe)] (3). As described for complex **4**, the bromo complex **2** (0.2 g, 0.5 mmol) and $Ph_2PCH_2CH_2PPh_2$ (0.2 g, 0.5 mmol) in 15 and 10 cm^3 of MeCN, respectively, were mixed and the resulting solution stirred for 1 h at room temperature. The solvent was removed under a stream of nitrogen. Recrystallization from CH_2Cl_2/hexane afforded a dark red powder. We were unable to fully purify the product. A similar synthesis using acetone (40 °C, 1.5 h) gave the same product **3**, but less pure. Chromatography on silica gel and CH_2Cl_2 afforded the product in very low yield. ^{13}C NMR (75.429 MHz, $CDCl_3$): δ 53.2 (C(1)), 90.2 (C(2)), 85.2 (C(3)), 18.4 (Me), 25.4–27.2 (br, CH_2), 127.5–134.0 (br, C_6H_5; C(4), C(5) overlapped in this region). ^{31}P NMR (36.23 MHz, $CDCl_3$): δ 46.5 (d), 47.3 (d), *J* 11 Hz.

[MoBr(η^3-C_5H_6Me)(CO)$_2$(PMe_2Ph)$_2$]. As described for complex **4**, the bromo complex **2** (0.2 g, 0.51 mmol) and PMe_2Ph (0.14 g, 1.02 mmol) in MeCN (15 cm^3) afforded after evaporation of the solvent a red product in low yield. IR (ν(CO)): 1926, 1837 cm^{-1} (CH_3CN); ^{1}H NMR (90 MHz, $CDCl_3$): δ 3.3–4.0 (m, H(2)), 4.5 (dt, H(3)), 2.7–3.3 (m, H(4)), 5.7–6.1 (m, H(5,6)), 1.8 (d, Me), 1.9–2.2 (br, P*Me*$_2$Ph), 7.5–7.8 (m, PMe_2*Ph*).

[Mo(CO)$_2$(PMePh)$_4$]. A solution of **2** (0.2 g, 0.51 mmol) in MeCN (15 cm^3) was treated with an excess of PMe_2Ph (0.282 g, 2.04 mmol) and then stirred to ensure complete mixing. A yellow powder was deposited in the reaction flask, which was filtered off, washed with MeCN, m.p. 125–127 °C in agreement with published data [10].

[Mo(CO)$_4$(PPh_3)$_2$]. A solution of **2** (0.2 g, 0.51 mmol) in MeCN (15 cm^3) was treated with PPh_3 (0.265 g, 1.01 mmol). The precipitated product was filtered off and washed with MeCN. The IR was in agreement with published data [9].

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