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PREPARATION OF DICYCLOPENTADIENYLDIPHENYLPHOSPHINE-HYDRIDOMOLYBDENUM(IV) CHLORIDE AND ITS REACTIONS WITH ELECTRON POOR ALKYNES RC≡CR′ (R = R′ = CF_3, CO_2Me; R = H, R′ = CN). FORMATION OF MOLYBDAPHOSPHACYCLOBUTANES AND X-RAY STRUCTURE OF $[(\eta^5\text{-}C_5H_5)_2\overline{\text{MoCH(CF}_3\text{)CH(CF}_3\text{)P}}\text{Ph}_2]\text{Cl}\cdot H_2O$

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Summary

Reactions of PPh_2Cl with $(\eta^5\text{-}C_5H_5)_2MH_2$ (M = Mo, W) in toluene give the ionic complexes $[(\eta^5\text{-}C_5H_5)_2MH(PPh_2H)]Cl$. The reactions of the molybdenum derivative with electron poor alkynes RC≡CR′ (R = R′ = CF_3 (hfb), CO_2Me (dmad); R = H, R′ = CN (mca)) were studied, and insertions of the alkynes into the Mo–H bond, leading to either the ionic complexes $[(\eta^5\text{-}C_5H_5)_2Mo(PPh_2H)(\sigma\text{-}CR{=}CHR')]^+$ (hfb, dmad, mca) or the molecular species $[(\eta^5\text{-}C_5H_5)_2MoCl(\sigma\text{-}CR'{=}CHR)]$ (dmad, mca), were observed. In the case of hfb and dmad the cationic metallaphosphacyclobutanes $[(\eta^5\text{-}C_5H_5)_2\overline{\text{MoCHRCHRP}}\text{Ph}_2]^+$ were formed. An X-ray diffraction study of the latter complex, derived from hfb, revealed an ionic structure with the presence of water of hydration in the centrosymmetric triclinic cell ($P\bar{1}$, *a* 7.919(8), *b* 9.689(7), *c* 16.613(11) Å, α 81.52(5), β 80.82(5), γ 82.44(5)°). The water molecules and the chloride ligands are involved in hydrogen bonding. The Mo–P bond length is 2.487(1) Å, that of Mo–C(sp^3) is 2.299(3) Å, and the C–Mo–P angle is 63.8(1)°.

Introduction

For some years we have been interested in the reactions of dicyclopentadienyl dihydrides of molybdenum and tungsten and their derivatives with alkynes activated by electron-withdrawing groups such as CN, CF_3 or CO_2Me [1–4]. In the course of this study we decided to prepare phosphido-bridged dimetallic dicyclopentadienyl complexes. The known complexes of this type possessing a molybdenum–phos-

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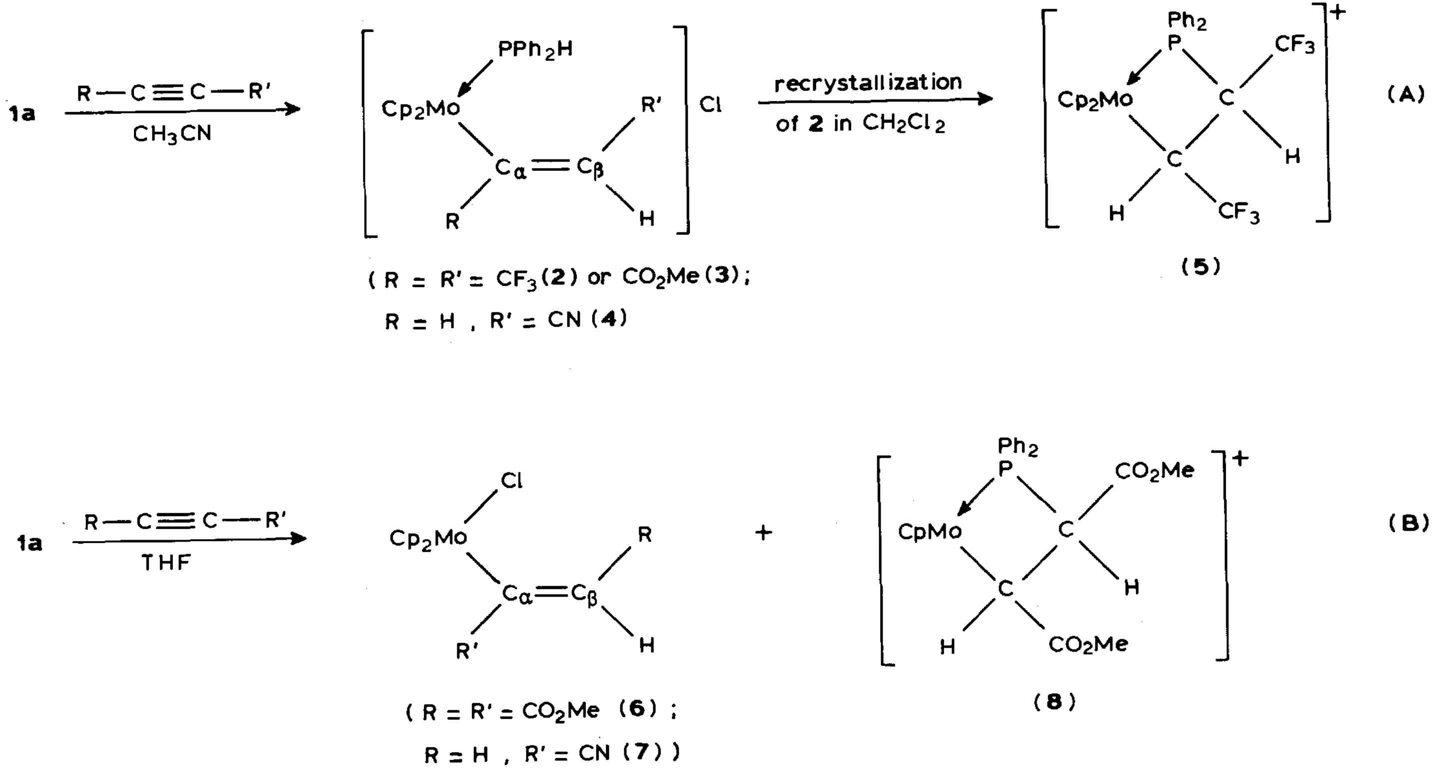

1a
R—C≡C—R'
CH3CN
Cp2Mo
PPh2H
Cα=Cβ
R
R'
H
Cl
(R = R' = CF3 (2) or CO2Me (3);
R = H, R' = CN (4)
recrystallization
of 2 in CH2Cl2
Ph2
P
CF3
C
H
(5)
(A)
1a
R—C≡C—R'
THF
Cl
(R = R' = CO2Me (6);
R = H, R' = CN (7))
+
CpMo
CO2Me
(8)
(B)

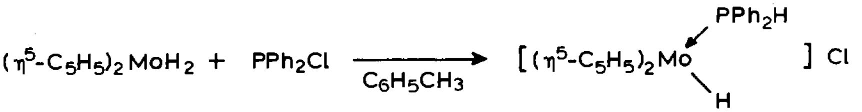
SCHEME 1

phorus bond generally contain tertiary phosphines [5–7], and thus are not of interest for our purpose as starting materials. One exception is the ionic complex $[(\eta^5\text{-}C_5H_5)_2MoBr(PPh_2H)]PF_6$ reported by Green [7] but the preparation of this complex from $(\eta^5\text{-}C_5H_5)_2MoH_2$ involves at least four steps, and because the presence of a halogenide ligand may reduce its reactivity we decided not to try to use it.

We thaught that potential precursors for phosphido-bridged complexes (e.g. $(\eta^5\text{-}C_5H_5)_2Mo \leftarrow PR_2H$, $(\eta^5\text{-}C_5H_5)_2Mo \leftarrow PR_2Cl$ or $(\eta^5\text{-}C_5H_5)_2MoHPR_2$) could be formed in a simple reaction between $(\eta^5\text{-}C_5H_5)_2MoH_2$ and PPh_2Cl. The complex obtained in this reaction is $[(\eta^5\text{-}C_5H_5)_2Mo(H) \leftarrow PPh_2H]Cl$ (**1**). The proximity of the hydride ligand on the metal and the hydrogen atom on phosphorus offers the interesting possibility of studying the separate or simultaneous reactions of these hydrogens, and we were encouraged by this and a recent observation of Seyferth on the two bond reduction of dimethylacetylene dicarboxylate by two sulphydryl bridges in $(\mu\text{-}SH)_2Fe_2(CO)_6$ [8]. We report here the results of studies of the reactions of **1** with alkynes activated by electron-withdrawing groups, and pay particular attention of the formation of metallaphosphacyclobutanes.

Results and discussion

Reaction of the dihydride complex $(\eta^5\text{-}C_5H_5)_2MoH_2$ with diphenylchlorophosphine in toluene gave a yellow precipitate of $[(\eta^5\text{-}C_5H_5)_2MoH(PPh_2H]Cl$ (**1a**) in nearly stoichiometric yield (eq. 1). The analogous tungsten complex **1b** was prepared



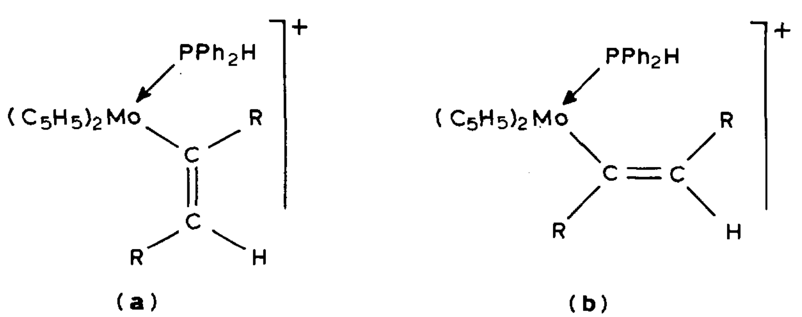
$$(\eta^5\text{-}C_5H_5)_2MoH_2 + PPh_2Cl \xrightarrow[C_6H_5CH_3]{} [(\eta^5\text{-}C_5H_5)_2\overset{PPh_2H}{\underset{H}{Mo}}]\,Cl \qquad (1)$$

(**1a**)

similarly. Complexes **1a** and **1b** are sparingly soluble in THF, benzene, $CHCl_3$ and CH_2Cl_2, but are sufficiently soluble in CH_3CN to permit recording of their ^1H and ^{31}P NMR spectra. The identity of **1** was elucidated from its IR and ^1H and ^{31}P NMR spectra (see Experimental). The IR bands observed at 2255 and 1875 cm^{-1} are assigned to the $\nu(P\text{-}H)$ and $\nu(Mo\text{-}H)$ vibrations, respectively. The ^{31}P resonance at 36.6 ppm is consistent with the presence of a coordinated PPh_2H ligand; ^{31}P in free PPh_2H is observed at -41.1 ppm [9a] and in free PPh_2Cl at $+81.1$ ppm [9b]. The hydrogen atom attached to phosphorus gives rise to a doublet with a normal value of $^1J(PH)$ of 386 Hz. The hydride resonance centered at -8.65 ppm exhibits a $^2J(PH)$ coupling (35 Hz) which is very close to that observed for the cation $[(\eta^5\text{-}C_5H_5)_2MoH(PPh_3)]^+$ – 33.5 Hz [7]. Attachment of the phosphine to the $(\eta^5\text{-}C_5H_5)_2Mo$ core is confirmed by the appearance of the C_5H_5 resonance as a doublet with $J(PH)$ equal to 2.5 Hz.

Treatment of the molybdenum complex **1a** in CH_3CN or THF with $F_3CC{\equiv}CCF_3$ (hfb), $MeO_2CC{\equiv}CCO_2Me$ (dmad), or $HC{\equiv}CCN$ (mca) leads to insertion of the alkyne into the Mo–H bond with or without retention of the phosphine ligand. The reactions are summarized in Scheme 1.

In the case of the ionic complexes **2** and **3** the presence in the ^1H NMR spectra of two doublets in the region of C_5H_5 ring resonances (see Experimental) suggests that they are present as mixtures of conformational isomers, **2a** and **2b** and **3a** and **3b** (Scheme 2).



(a)

(b)

(R = CF_3 (**2**) , R = CO_2Me (**3**))

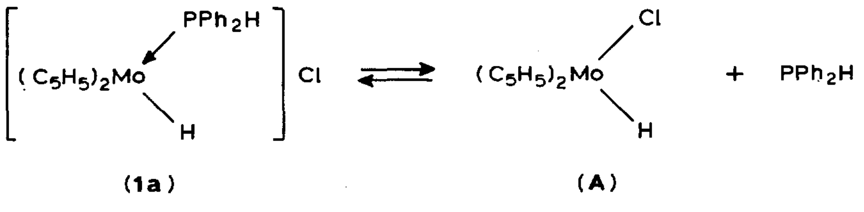
SCHEME 2

It has been previously shown that the insertion of (hfb) and (dmad) into one of the two Mo–H bonds of $(\eta^5\text{-}C_5H_5)_2MoH_2$ leads to σ-alkenyl complexes in which both conformations of the type **a** and **b** are present [4,10,11,12].

The positions of the σ-olefinic protons in the (mca) insertion complexes **4** and **7** can be assigned from the J(HH) coupling constants: complex **4**, ^3J(HH) 14 Hz; complex 7, ^2J(HH) 3 Hz. ^{13}C NMR data reveal the strong shielding effect of the CN group on the adjacent carbon atom: complex **4**; $\delta(C_\alpha)$ 182.3 ppm, $\delta(C_\beta)$ 146.6 ppm; complex **7**; $\delta(C_\alpha)$ 127.0 ppm, $\delta(C_\beta)$ 148.7 ppm. The sets of the NMR data indicate that each of the complexes **4** and **7** is present in only one conformation.

The molecular complexes **6** and **7** have been prepared previously by stirring of $[(\eta^5\text{-}C_5H_5)_2MoH(\sigma\text{-}CR{=}CHR')]$ with $CHCl_3$ for R = CN, R′ = H [12] and R = R′ = CO_2Me [4]. It seems that they do not arise from transformation of the ionic complexes **3** and **4** because in this case the same carbon atom of the σ-vinylic ligand would bear the nitrile group (C_β in **4** but C_α in **7**). However, such a transformation occurred when solid **3** was heated at 60°C under reduced pressure. The formation of molecular complexes **6** and **7** in THF can plausibly be attributed to the existence of an ionic–molecular equilibrium shown in Scheme 3.

The transient presence of $(\eta^5\text{-}C_5H_5)_2MoHCl$ is often detected during the recording of the ^{1}H NMR spectrum of $(\eta^5\text{-}C_5H_5)_2MoH_2$ in $CDCl_3$ [13]. The different electron densities in the nonbonding $1a_1$ orbital on the molybdenum center in **1a** and (A) could account for the different stereochemistry of the insertion reactions. The (mca) is polarized in the manner $H\overset{\delta+}{C}\equiv\overset{\delta-}{C}CN$, so the more positive carbon atom



(1a)

(A)

SCHEME 3

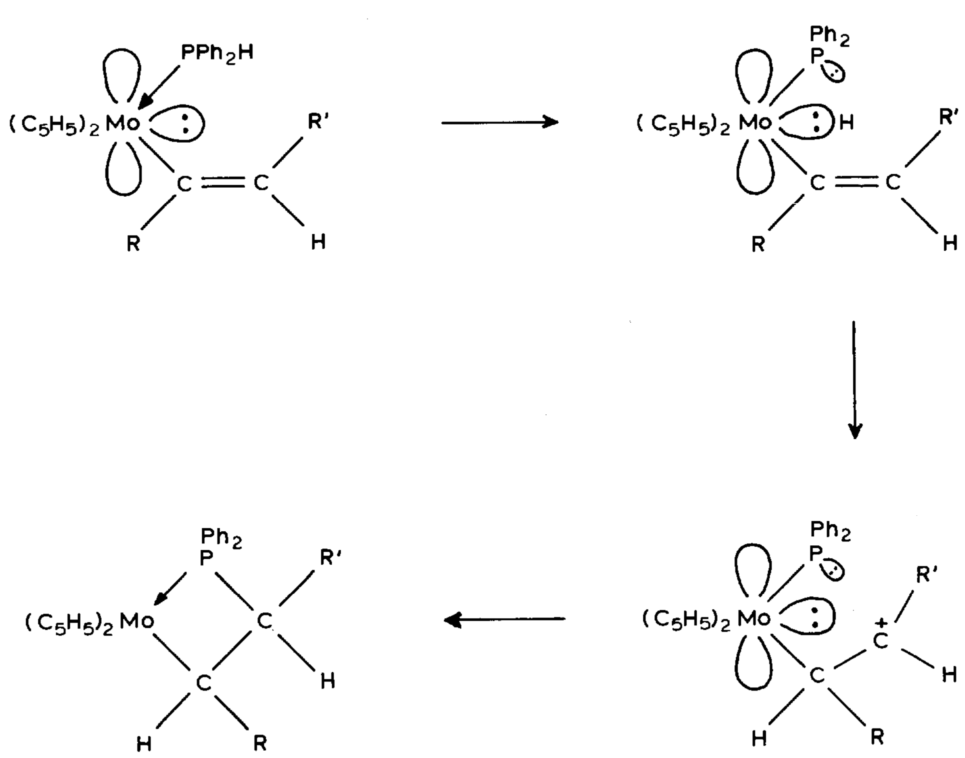
will be bound to molybdenum in **1a**, where it should have a higher electron density than in **A**, but the more negative carbon atom bearing the CN group will prefer the molybdenum atom rather than the hydride ligand in the case of **A**.

Recrystallization of the insertion complex **2** from CH_2Cl_2 solution gave orange-red crystals of the metallaphosphacyclobutane complex **5** in 45% yield based on **2**. Complex **5** is not soluble in CH_2Cl_2 or THF, but is sparingly soluble in methanol and chloroform. Its ^1H NMR spectra in these solvents are of poor quality, but four peaks are observed in the C_5H_5 region (see Experimental). They can be interpreted as two doublets arising as from the non-equivalence of the C_5H_5 rings. This suggests the presence of an asymmetric carbon atom in the coordination sphere of the metal. The resonance of the ^{31}P nucleus is observed at 19.7 ppm. Because the NMR data were not sufficient for elucidation of the structure of **5**, an X-ray structural analysis was carried out. This revealed a metallaphosphacyclobutane structure which is discussed later.

Attempts to recrystallize the (dmad) complex **3** similarly led to decomposition. However, the metallaphosphacyclobutane complex **8** was formed in the reaction of **1a** with (dmad) in THF (Scheme 1). The identity of **8** is based on the comparison of its ^1H and ^{31}P NMR data with those for **5**. The ^1H spectrum contains two doublets in the C_5H_5 region, and the ^{31}P resonance is observed at 19.4 ppm.

The reaction of (mca) with **1a** does not lead to formation of cyclobutane type structure in either CH_3CN or THF. This can be readily understood in terms of the electronic features of the σ-vinylic ligand of **4**. The C_β carbon atom bearing the CN group is too electron rich to interact with the phosphine ligand. The (mca) could give rise to a cyclic structure analogous to **5** and **8** if the CN group would be borne by the C_α atom as in **7**, but there is no phosphine. It seems that the formation of metallaphosphacyclobutanes described here must arise from some lability of the hydrogen atom bound to phosphorus. The simplest mechanism which would account for their formation, involving the migration of a hydrogen atom of the phosphine ligand via the non-bonding $1a_1$ orbital on molybdenum, is outlined in Scheme 4. We have previously discussed the participation of this orbital in the hydrogen atom transfer in the course of the reduction of σ-vinylic ligands in $[(\eta^5\text{-}C_5H_5)_2MoH(\sigma\text{-}CR{=}CHR')]$ complexes with protic acids HX [3].

In recent years, the chemistry of metallacyclobutanes has attracted great attention because these species are involved in a number of important organometal-assisted or -catalysed reactions [14], and in particular they are thought to be reactive intermediates in olefin metathesis reactions [15]. Various synthetic routes to the metallacyclobutanes have been developed; including oxidative addition of an olefin to a metal carbene [16], γ-hydrogen abstraction from a bulky alkyl ligand [17], oxidative addition of cyclopropane derivatives [18], cyclisation of carbanions [19], and protonation of a metal-coordinated allyl [20]. Some metallaphosphacyclobutanes have been prepared by intramolecular metallation of aryl- or alkyl-bulky phosphines coordinated to Pd, Pt [21], Rh [22], Ir [23], Ru [24] and Mn [25], or by reductive cycloelimination of phosphine complexes of Mn and Re with sodium amalgam [26]. In the class of dicyclopentadienyl complexes of Mo two molybdacyclobutanes have been reported. One of them was prepared by Green et al. by protonation of η-allylic ligand with $NaBH_4$ [20], and the second one, 1-molybda-3-silacyclobutane, by metathetical reaction of $[Mg(CH_2)_2SiMe_2]_n$ with $(\eta^5\text{-}C_5H_5)_2\text{-}MoI_2$ [14a]. The conversion of **2** into **5** described in the present report is the first



SCHEME 4. R = R' = CF_3, CO_2Me; R = H, R' = CN: no cyclobutane structure.

example of the formation of a metallacyclobutane from a σ-olefinic ligand. To the best of our knowledge, no hydride ligand bound to a transition metal has ever been involved in the formation of a metallacyclobutane, nor have metallocyclobutanes ever been obtained from alkynes. Alkynes are known to form metallacyclobutadienes, assumed to be intermediates in alkyne metathesis [27].

Structure of 5

The X-ray diffraction study of 5 revealed the presence of two metallaphosphacyclobutane cations, two chloride ions, and two water molecules in the centrosymmetric triclinic cell. The geometry around the molybdenum atom in the cation (Fig. 1) is typical of bent dicyclopentadienyl complexes. The four-membered ring MoPC(13)C(14) exhibits the expected (sp^3 hybridized P and C atoms) distortion from planarity; C(13) atom lies 0.58 Å below the PMoC(14) plane. The angle between this plane and that of (η^5-C_5H_5)Mo(η^5-C_5H_5) (centers of gravity of the C_5H_5 rings) is 90.8°. The nonplanarity of the metallacyclic part of the cation and the presence of the large PPh_2 group are responsible for the different values of the dihedral angles between the PMoC(14) plane and the best planes of the C_5H_5 rings (20.5 and 25.8°). The angle between the C_5H_5 planes is 133.7°.

Relevant interatomic distances and angles are given in Table 1. The Mo–P bond length of 2.487(1) Å is slightly longer than the Mo–P distance (2.473(3) Å) in an acetyl complex [(η^5-C_5H_5)$(CO)_2(PPh_3)$MoC(O)Me] of Mo^{II} [28], which indicates

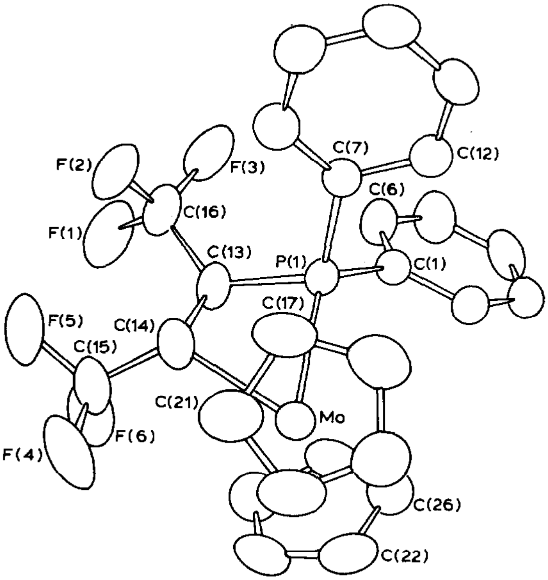


Fig. 1. ORTEP drawing of the cation in the structure of **5**. Hydrogen atoms are omitted for clarity.

that there is little π-back bonding between the Mo^{IV} and the phosphorus atom in **5**. This distance is however less than the sum of the covalent radii of Mo^{IV} in dicyclopentadienyl complexes, the value for "$(\eta^5\text{-}C_5H_5)_2\text{Mo}$" is 1.45–1.48 Å [13] and that for phosphorus (sp^3) is 1.10 Å [29]). The Mo–C(14) (sp^3) distance of 2.299(3) Å is effectively the same as that in $[(\eta^5\text{-}C_5H_5)_2\text{Mo(SPH)}\{\sigma\text{-CH(CN)CH}_3\}]$ (2.306(3) Å [20]) and in $[(\eta^5\text{-}C_5H_5)_2\text{MoCl}(\sigma\text{-CH}_2\text{CH}_3)]$ (2.284(10) Å [31]). The Mo–C(C_5H_5) distances are normal and vary from 2.240(3) to 2.372(3) Å. The P–Mo–C(14) angle of 63.8(1)° is the smallest observed to date for dicyclopentadienylmolybdenum(IV) complexes.

TABLE 1

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $[(\eta^5\text{-}C_5H_5)_2\text{MoCH(CF}_3\text{)CH(CF}_3\text{)PPh}_2]\text{Cl}\cdot H_2O$ (5)

Mo–P	2.487(1)	C(13)–H(13)	0.953(3)
Mo–C(14)	2.299(3)	C(14)–H(14)	0.938(3)
Mo–Cy(1)	1.972	O–H(0)(1)	0.832(2)
Mo–Cy(2)	1.983	O–H(0)(2)	0.727(2)
P–C(1)	1.811(3)	P–Mo–C(14)	63.8(1)
P–C(7)	1.823(3)	Cy(1)–Mo–Cy(2)	133.0
P–C(13)	1.856(3)	Mo–P–C(13)	87.7(1)
C(13)–C(14)	1.543(4)	P–C(13)–C(14)	95.9(2)
C(13)–C(16)	1.524(4)	Mo–C(14)–C(13)	94.9(2)
C(14)–C(15)	1.506(4)		

Cy(1) is the gravity center of C(17)–C(21) atoms.
Cy(2) is the gravity center of C(22)–C(26) atoms.

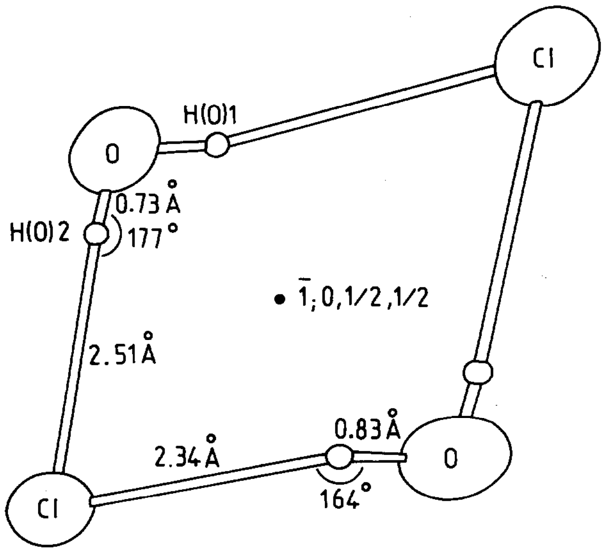


Fig. 2. Hydrogen bonds in **5**. The Cl---O distances are 3.147 and 3.234 Å.

Two chlorides and two molecules of water form hydrogen bonds around the symmetry center at 0, 1/2, 1/2 (Fig. 2).

Experimental

The reactions were performed under nitrogen by use of Schlenk tube techniques. Solvents were purified by standard methods and purged with nitrogen before use. $(\eta^5\text{-}C_5H_5)_2MH_2$ (M = Mo or W) were prepared by an established method [32]. Commercial ($CH_3CO_2C{\equiv}CCO_2CH_3$). ($CF_3C{\equiv}CCF_3$) and PPh_2Cl were used. Monocyanoacetylene was prepared by a published method [33]. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JNM-FX 100 spectrometer. Chemical shifts (δ values) are relative to an internal TMS (^1H, ^{13}C) or external aqueous H_3PO_4 (^{31}P).

Preparation of $[(\eta^5\text{-}C_5H_5)_2MH(PPh_2H)]Cl$ *(M=Mo (1a), M = W (1b))*

1.6 g (9 mmol) of PPh_2Cl were added to a solution of 2.0 g (8.8 mmol) of Cp_2MoH_2 dissolved in toluene (80 ml). The solution was stirred for 20 h at room temperature. The yellow precipitate of **1a** was filtered off (yield: 90–95%). Found: C, 57.7; Cl, 8.3; Mo, 20.2; P. 6.9. $C_{22}H_{22}ClMoP$ calcd.: C, 58.9; Cl, 7.9; Mo, 21.4; P. 6.9%. NMR, δ (ppm), (CD_3CN): ^1H: 7.28, P-*H*, d, ^1J(PH): 386 Hz; 5.13, C_5H_5, d, *J*(PH): 2.5 Hz; −8.65, Mo-*H*, d, ^2J(PH): 35 Hz; ^{31}P, ($CDCl_3$), 36.6. Infrared (Nujol), 2255, ν(P–H); 1875, ν(Mo–H).

The same procedure was used for preparation of **1b**, (yield: 65–70%). NMR, ($CDCl_3$); ^1H: 7.63, P-*H*, d, ^1J(PH): 387 Hz; 5.22, C_5H_5, d, *J*(PH): 3.0 Hz; −11.8, W-*H*, d, ^2J(PH): 26.4 Hz; ^{31}P: −0.6, *J*(WP): 152.6 Hz. Infrared (Nujol), 1950, ν(W–H).

Reaction of $[(\eta^5\text{-}C_5H_5)_2MoH(PPh_2H)]Cl$ *(**1a**) with* $CF_3C{\equiv}CCF_3$*: formation of complexes* $[(\eta^5\text{-}C_5H_5)_2Mo(PPh_2H)(\sigma\text{-}C(CF_3){=}CH(CF_3))]Cl$ *(2) and* $[(\eta^5\text{-}C_5H_5)_2MoCH(CF_3)\text{-}CH(CF_3)PPh_2]Cl\cdot H_2O$ *(5)*

Hexafluorobutyne ($CF_3C{\equiv}CCF_3$) (2.2 mmol) was added to a cold solution of 0.9 g (2 mmol) of **1a** in acetonitrile. The mixture was stirred for 20 h at room temperature and orange complex **2** then filtered off (yield: 40–45%). NMR, ($CDCl_3$), ^1H: 5.59, C_5H_5, d, J(PH): 3.0 Hz; 5.49, C_5H_5, d, J(PH): 3.0 Hz. Infrared (Nujol), 2255, ν(P–H).

Recrystallization of **2** from CH_2Cl_2 gave orange crystals of complex **5**. The X-ray structure determination shows that there is one molecule of H_2O and one chloride ion per cation. The water must have been present in the CH_2Cl_2. Found, C, 51.6; Cl, 5.6; F, 17.6; Mo, 14.5; P, 4.8. $C_{26}H_{24}ClF_6MoOP$ calcd.: C, 49.75; Cl, 5.64; F, 18.13; Mo, 15.26; P, 4.93%. NMR (CD_3OD) ^1H: 5.37; C_5H_5, d, J(PH) 2 Hz; 5.33, C_5H_5, d, J(PH) 2 Hz; ^{13}C: 96.1, C_5H_5; ^{31}P: 19.7; ($CDCl_3$), ^1H: 5.57, C_5H_5, d, J(PH) 2 Hz; 5.50, C_5H_5, d, J(PH) 2 Hz.

Reaction of $[(\eta^5\text{-}C_5H_5)_2MoH(PPh_2H)]Cl$ *(**1a**) with* $(CH_3CO_2C{\equiv}CCO_2CH_3)$*. Formation of the complexes:* $[(\eta^5\text{-}C_5H_5)_2MoCl(\sigma\text{-}C(CO_2CH_3){=}CH(CO_2CH_3))]$ *(6),* $[(\eta^5\text{-}C_5H_5)_2Mo(PPh_2H)(\sigma\text{-}C(CO_2CH_3){=}CH(CO_2CH_3))]Cl$ *(3) and* $[(\eta^5\text{-}C_5H_5)_2MoCH(CO_2CH_3)CH(CO_2CH_3)PPh_2]Cl$ *(8)*

A solution of equimolar amounts of **1a** and dimethylacetylenedicarboxylate in acetonitrile was stirred at room temperature for 20 h. The solvent was then evaporated off and the solid residue was dissolved in CH_2Cl_2 and chromatographed on a basic alumina column. A small amount of complex **6** was eluted with THF. Elution with methanol followed by evaporation of the solvent gave complex **3** as a red oil, which formed a red solid on stirring with pentane (yield: 30%).

Complex **6**: NMR ($CDCl_3$). ^1H: 6.75, $\equiv C\text{-}H$, s; 5.37, C_5H_5, s; 3.77, OCH_3, s; 3.65, OCH_3, s.

Complex **3**: NMR ($CDCl_3$), ^1H: 5.66, C_5H_5, d, J(PH): 2.5 Hz; 5.49, C_5H_5, d, J(PH): 2.5 Hz, other peaks not resolved.

The same reaction was carried out with THF as solvent. Complex **6** was eluted with THF (yield: 50%). A second band, obtained with methanol as eluant, contained some starting product **1a** together with the metallacyclobutane complex **8**: NMR (CD_3OD), ^1H: 5.17, C_5H_5, d, J(PH): 2.5 Hz; 5.15, C_5H_5, d, J(PH): 2 Hz; 3.58, OCH_3, s; 3.53, OCH_3, s; ^{31}P: 19.4.

Reaction of $[(\eta^5\text{-}C_5H_5)_2MoH(PPh_2H)]Cl$ *(**1a**) with* $(HC{\equiv}CCN)$*. Formation of the complexes:* $[(\eta^5\text{-}C_5H_5)_2Mo(PPh_2H)(\sigma\text{-}C_\alpha H{=}C_\beta H(CN))]Cl$ *(4) and* $[(\eta^5\text{-}C_5H_5)_2MoCl(\sigma\text{-}C_\alpha(CN){=}C_\beta H_2)]$ *(7)*

Reactions of **1a** with monocyanoacetylene were carried out as described above in both CH_3CN and THF. Complexes **4** (orange precipitate, yield: 50–60%) and **7** (elution CH_2Cl_2/THF (1/1), yield: 40%, recrystallization as a brown solid in CH_2Cl_2/heptane) were obtained. In both cases (CH_3CN and THF) elution with methanol gives unidentified products. Complex **4**: Found: C, 59.5; H, 4.7; Cl, 6.0; Mo, 18.7; P. 6.1. $C_{25}H_{23}ClMoNP$ calcd.: C, 60.1; H, 4.6; Cl, 7.1; Mo, 19.2; P, 6.2%. NMR ($CDCl_3$), ^1H: 8.45, $C_\alpha H$, d, ^3J(HH): 14 Hz; 6.25, $C_\beta H$, d, ^3J(HH): 14 Hz; 5.90, C_5H_5, s; ^{13}C: 182.3, C_α; 146.6, C_β; 96.7, C_6H_5; ^{31}P: 45.8. Infrared (Nujol), 2255, ν(P–H).

TABLE 2

ATOMIC COORDINATES FOR **5** [a]

Atom	*x*	*y*	*z*	$B(\text{Å}^2)$	Atom	*x*	*y*	*z*	$B(\text{Å}^2)$
Mo	0.35979(3)	−0.02996(2)	0.28243(1)	2.702(4)	C(21)	0.1666(4)	−0.0826(3)	0.2045(2)	4.74(6)
Cl	0.1022(1)	0.23010(9)	0.49843(6)	6.04(2)	C(22)	0.3380(4)	−0.1619(3)	0.408(2)	4.48(7)
O	0.1264(3)	0.546(2)	0.3942(1)	5.29(5)	C(23)	0.4527(5)	−0.2410(3)	0.3548(2)	4.82(7)
P	0.49337(8)	0.19024(6)	0.22971(4)	2.48(1)	C(24)	0.6000(4)	−0.1713(4)	0.3311(2)	4.54(7)
F(1)	0.9153(3)	0.0668(3)	0.0711(1)	6.81(6)	C(25)	0.5720(4)	−0.0463(3)	0.3671(2)	3.80(6)
F(2)	0.6895(3)	0.1498(2)	0.0193(1)	5.51(5)	C(26)	0.4094(4)	−0.0388(3)	0.4146(2)	4.03(6)
F(3)	0.8001(3)	0.2747(2)	0.0886(1)	7.02(5)	H(2)	0.3899	0.2588	0.3887	–
F(4)	0.5550(4)	−0.2723(2)	0.1490(2)	9.14(7)	H(3)	0.4911	0.3818	0.4775	–
F(5)	0.6937(4)	−0.1489(2)	0.0504(1)	7.58(6)	H(4)	0.7493	0.4806	0.4387	–
F(6)	0.7943(3)	−0.2049(2)	0.1642(2)	7.38(6)	H(5)	0.8989	0.4649	0.3055	–
C(1)	0.5876(3)	0.2837(2)	0.2950(2)	2.64(4)	H(6)	0.8011	0.3381	0.2174	–
C(2)	0.4960(4)	0.2985(3)	0.3719(2)	3.22(5)	H(8)	0.4279	0.2680	0.0558	–
C(3)	0.5568(4)	0.3728(3)	0.4245(2)	3.65(6)	H(9)	0.2501	0.4398	0.0090	–
C(4)	0.7064(4)	0.4312(3)	0.4013(2)	4.07(6)	H(10)	0.0822	0.6094	0.0627	–
C(5)	0.7968(4)	0.4198(3)	0.3241(2)	4.44(7)	H(11)	0.0965	0.6033	0.2033	–
C(6)	0.7386(4)	0.3459(3)	0.2708(2)	3.74(6)	H(12)	0.2778	0.4332	0.2688	–
C(7)	0.3734(3)	0.3307(3)	0.1693(2)	2.88(5)	H(13)	0.7646	0.0604	0.1883	–
C(8)	0.3617(4)	0.3349(3)	0.0870(2)	4.12(6)	H(14)	0.4806	−0.0184	0.1189	–
C(9)	0.2539(5)	0.4394(4)	0.0478(2)	5.00(8)	H(17)	0.2101	0.1218	0.1491	–
C(10)	0.1561(5)	0.5394(3)	0.0910(2)	4.74(7)	H(18)	0.0885	0.2015	0.2872	–
C(11)	0.1666(4)	0.5359(3)	0.1728(2)	4.36(7)	H(19)	0.0142	−0.0124	0.3848	–
C(12)	0.2735(4)	0.4337(3)	0.2124(2)	3.57(6)	H(20)	0.0908	−0.2235	0.3080	–
C(13)	0.6602(3)	0.0849(3)	0.1654(2)	3.18(5)	H(21)	0.2044	−0.1405	0.1606	–
C(14)	0.5478(4)	−0.0321(3)	0.1618(2)	3.57(5)	H(22)	0.2291	−0.1880	0.4362	–
C(15)	0.6456(5)	−0.1639(4)	0.1326(2)	5.62(8)	H(23)	0.4344	−0.3266	0.3363	–
C(16)	0.7655(4)	0.1452(4)	0.0861(2)	4.28(7)	H(24)	0.7015	−0.2013	0.2962	–
C(17)	0.1692(4)	0.0640(3)	0.1979(2)	4.31(6)	H(25)	0.6514	0.0226	0.3606	–
C(18)	0.1031(4)	0.1091(3)	0.2757(2)	4.73(8)	H(26)	0.3549	0.0355	0.4457	–
C(19)	0.0623(4)	−0.0111(4)	0.3293(2)	4.90(8)	H(0)(1)	0.071(5)	0.591(4)	0.430(2)	5.9(9) *
C(20)	0.1033(4)	−0.1277(3)	0.2863(2)	4.75(7)	H(0)(2)	0.124(4)	0.476(3)	0.416(2)	5.7(8) *

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab\cos\gamma B(1,2)+ac\cos\beta B(1,3)+bc\cos\alpha B(2,3)]$.

Complex 7: NMR ($CDCl_3$), ^1H: 6.66, Hb, d, J(HH): 3 Hz; 6.54, Ha, d, J(HH): 3 Hz (Ha and Hb being *trans* and *cis* to metal respectively); 5.29, C_5H_5, s; ^{13}C: 148.7, C_β; 127.0, C_α; 97.2, C_5H_5.

X-Ray structure analysis of 5

An orange-red crystal of dimensions 0.21 × 0.20 × 0.19 mm was mounted on an Enraf–Nonius CAD-4 four-circle diffractometer. The unit cell was determined and refined from 25 randomly selected reflections obtained by use of the CAD-4 automatic routines. Crystal data for **5**: triclinic, space group $P\bar{1}$, a 7.919(8), b 9.689(7), c 16.613(11) Å, α 81.52(5), β 80.82(5), γ 82.44(5)°, U 1237 Å^3, μ(Mo-K_α) 7.5 cm^{-1}, $Z = 2$. The intensities of 4220 independent planes measured in a ω–2θ scan (θ_{min} 2°, θ_{max} 28°) with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. All calculations were carried out using the Enraf–Nonius SDP library [34]. Neutral atom scattering factors and anomalous dispersion corrections applied to all non-hydrogen atoms were those given by Cromer and Waber [35]. The structure was solved and refined (325 variables) by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms of water molecule were found from a difference Fourier map and refined isotropically, and those of other hydrogen atoms were calculated by the "Hydro" program of SDP. In the final refinement the B_{iso} for these last atoms was fixed at 4.0 Å. The final residuals were $R = 0.028$, $R_w = 0.042$, GOF = 1.00. The weighting scheme employed was $w^{-1} = \sigma^2(F) = 1/4[\sigma(I)/(I) + 0.06^2(I)]$. The final atomic coordinates are listed in Table 2.

Lists of thermal parameters and structure factors are available from the authors.

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