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Cationic (pentamethylcyclopentadienyl)molybdenum complexes: improved synthesis and characterization

Ali Asdar, Marie-José Tudoret and Claude Lapinte *

Laboratoire de Chimie des Organométalliques, UA CNRS 415, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex (France)

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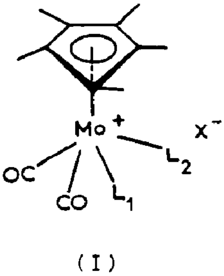
Abstract

The synthesis of the known pentamethylcyclopentadienylmolybdenum compounds $[Mp^\star]_2$ (**1**), $Mp^\star Cl$ (**3**), and $Mp^\star H$ (**7**) ($Mp^\star = Mo(\eta^5\text{-}C_5Me_5)(CO)_3$) has been improved. The cyclic voltammetry of **1** shows a behaviour close to that of $[Mp]_2$ ($Mp = Mo(\eta^5\text{-}C_5H_5)(CO)_3$) with a shift of potentials towards more negative values by 0.30 to 0.50 V. The $[Mp^\star CO]^+PF_6^-$ (**4**) has been synthesized by reaction of (a) $Mp^\star Cl$ (**3**) with CO (100 atm, 95 °C) and $AlCl_3$ followed by treatment with HPF_6 or (b) $Mp^\star H$ (**7**) with $Ph_3C^+PF_6^-$ under CO (1 atm, 20 °C) via the coordinatively unsaturated species $[Mp^\star]^+PF_6^-$. This reaction provides a convenient general route to $[Mp^\star L]^+PF_6^-$ ($L = PR_3$ (**8a–8d**); $P(OPh)_3$ (**9**), CH_3CN (**10**)). The new complexes have been obtained in overall yields ranging from 53 to 82% based on the C_5Me_5H initially taken. The *cis*- and *trans*-dicarbonyls species $[Mo(C_5Me_5)(CO)_2L^1L^2]^+PF_6^-$ (L^1L^2 = dppe (**13**) and $L^1 = PMe_3$, $L^2 = PMePh_2$ (**12**)) have been stereospecifically prepared. Cyclic voltammetric and ^1H, ^{13}C, ^{31}P NMR, and IR data are discussed.

Introduction

Cyclopentadienyltricarbonylmolybdenum (Mp) derivatives form one of the most studied series of complexes in organometallic chemistry [1], whereas the pentamethylcyclopentadienyl analogues I are little known. Until now the only examples known



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were the dimers $[Mo(C_5Me_5)(CO)_n]_2$ ($n = 2,3$) [2] and some neutral compounds such as $Mo(C_5Me_5)(CO)_3X$, ($X = H$, CH_3, CH_2XCl, I, SO_2H) [2,3]. Since this permethylated ligand has proved useful in the organometallic chemistry of many other transition metals, we decided to undertake the synthesis of the species $[Mo(C_5Me_5)(CO)_2L_1L_2]^+PF_6^-$. Our main objective was to make formyl, and carbene complexes stabilized by the $[Mo(C_5Me_5)(CO)L^1L^2]$ organometallic moiety. Some preliminary results were presented recently [4] and other findings will be described in subsequent articles.

Results and discussion

1. Synthesis of [Mp★CO]⁺ (4), using a Fischer type ligand exchange reaction

The dimeric complex $Mp^\star_2$ is often the starting point for syntheses in transition metal pentamethylcyclopentadienyl chemistry [5]. Adopting this strategy we have improved King's preparation of $Mp^\star_2$ (**1**) (involving reaction of $(Mo(CO)_6$ with $Cp^\star H$ in n-decane under reflux, followed by chromatography on Florisil, to give a 9% yield) [6a] by using the mixture of $[Cp^\star Mo(Co)_2]_2$ and $Mp^\star_2$ obtained from the reaction under CO (3 atm, 25 °C); this avoids the chromatography step and gives the desired dimer in 50% yield. A more useful procedure, based on Manning's synthesis [2c], starts from $Mp^\star Li$ (**2**) [3b], which is oxidized with $Fe_2(SO_4)_3$, to give $Mp^\star_2$ in 90% yield. The halide derivative $Mo(C_5Me_5)(CO)_3Cl$ (**3**), is then easily prepared by oxidative cleavage of the Mo–Mo bond of **1** with $FeCl_3$ or directly from **2** by oxidation with the same reagent [7*]. $[Mp^\star CO]^+PF_6^-$ (**4**) was obtained (in 40% yield of crude product) from a Fisher-type reaction, from **3**, i.e. by treatment with an excess of $AlCl_3$ under 100 atm of CO, as for the η^5-C_5H_5 analogue [6b,8]. Direct halide displacement from MpCl by a ligand L has been reported ($L = PEt_3$, PPh_3, diphos, diars, etc.) [9] and $AlCl_3$-promoted halide expulsion has also been employed [10], but these routes fail for the permethylated series. However, complex **5** was prepared under photochemical conditions in 90% yield (eq. 1) (See also section 4). Disproportionation with substitution of Mp_2 also affords substituted dicarbonylmolybdenum cation [11], but this reaction does not work for $Mp^\star_2$.

2. Redox properties of Mp★₂ (1)

Oxidative cleavage of the metal–metal bond is a key step in the synthesis of the cationic complexes $[Mo(C_5Me_5)(CO)_3L]^+X^-$. However, in the C_5Me_5 series use of the more common reagents (ferricinium, $FeSO_4$) either failed or led to the isolation of the molybdenum halide $[Mo(C_5Me_5)(CO)_3Cl]$ (**3**) ($FeCl_3$). In order to throw light on a possible synthetic strategy we carried out electrochemical studies of $Mp^\star_2$ with the aim of improving understanding of the reactivity of the dimer and related species.

The cyclic voltammetry data for $[Mo(CO)_3(C_5H_5)]_2$ (which has been fully studied [12]) and $[Mo(CO)_3(C_5Me_5)]_2$ in CH_2Cl_2, with 0.1 *M* of tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrode, are very similar (Fig. 1). For both dimers, four sets of peaks are observed either for initial oxidation

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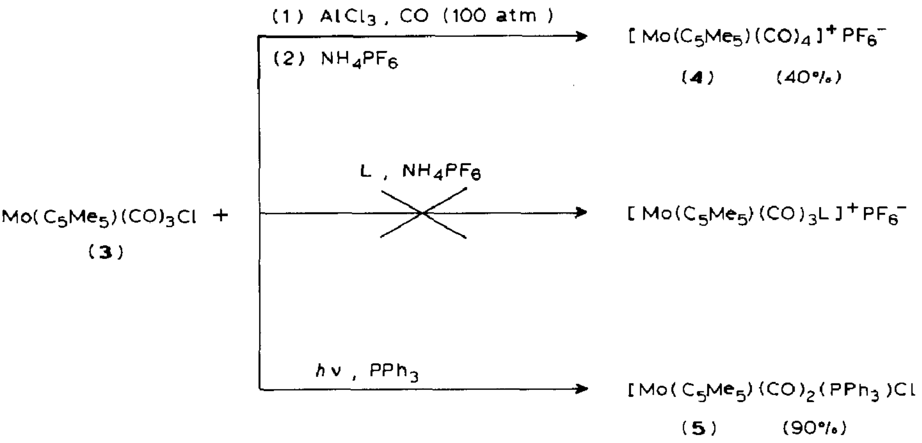
* Reference number with asterisk indicates a note in the list of references.



(1)

or for initial reduction. The permethylation of the Cp ring causes a shift of the potential peaks towards the more negative values of 0.33 to 0.50 (Table 1) [13*].

As in the case of the Cp parent dimer [12], all four electrode reactions are interrelated and give a reversible cyclic process, as shown by eq. 2–5, which

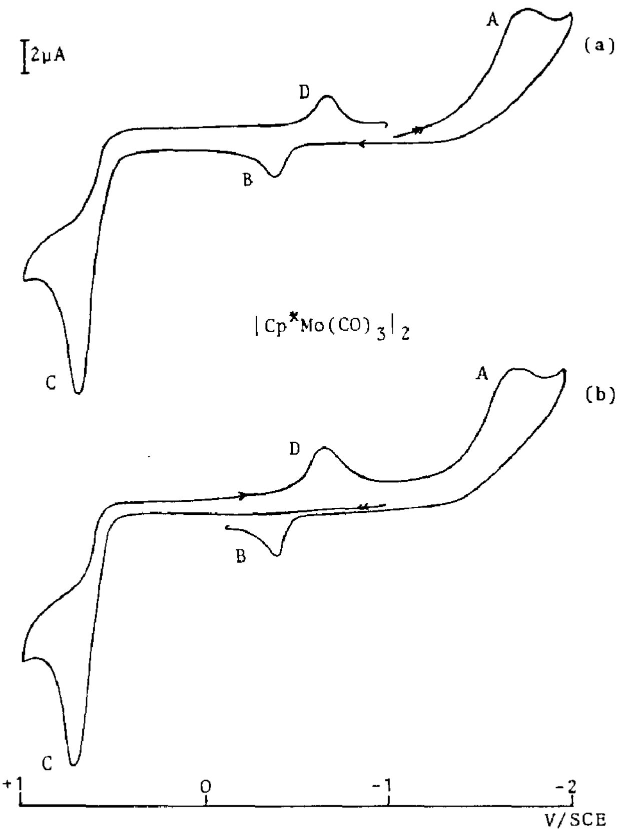


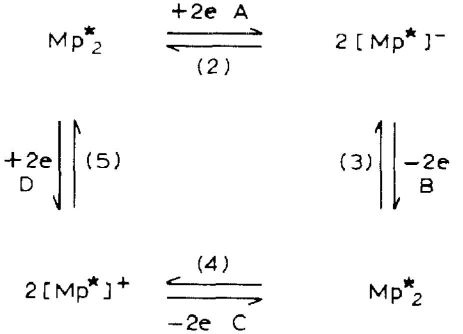
Fig. 1. Cyclic voltammograms of $[Mp^*]_2$ in dichloromethane with 0.1 *M* TBAH at 20 °C. Scan rate V s^{-1}. (a) initial reduction; (b) initial oxidation.

Table 1

Peak potentials for oxidation and reduction of $[Mp^\star]_2$, $[Mp^\star]^-$, and $[Mp^\star]^+$ and the corresponding Mp derivatives

Ligand	M_2L^2 oxidation C	M_2L^2 reduction A	$[ML]^-$ oxidation B	$(ML)^+$ reduction D
C_5H_5 [12]	1.00	−1.21	−0.09	−0.42
C_5Me_5	0.67	−1.71	−0.34	−0.62

correspond respectively to the waves A–D (Fig. 1). A two electron ECE mechanism involving a 17-electron intermediate has already been established for both reduction and oxidation processes [12].



Moreover the cyclic voltammograms of the isolated $[Mp^\star]^+PF_6^-$ (see section 2) allowed the observation for the initial reduction process of the waves corresponding to the formation of $[Mp^\star]_2$ (wave D) and its subsequent reduction to $[Mp^\star]^-$ (wave A) at the electrode. The reverse oxidation into $[Mp^\star]_2$ and $[Mp^\star]^+$ were also successively observed.

The difficulty of finding an efficient and readily available oxidizing reagent with a redox potential as high as +0.7 V led us to direct our synthetic strategy towards chemical generation of $[Mp^\star]^+X^-$ (**6**), in line with the procedure described by Beck [14].

3. Synthesis and characterization of the cation $[Mp^\star]^+PF_6^-$ (6)

Because the known metal hydride $Mp^\star H$ (**7**) [3], prepared from $[Mo(CO)_3(C_7H_8)]$ and C_5Me_5H (60%), is a key compound we decided to improve its synthesis. Our more efficient preparation involves the three-step one-pot procedure represented by eq. 6–8.

$$C_5Me_5H + Bu^nLi \xrightarrow{C_5H_{12}} C_5Me_5Li + Bu^nH \qquad (6)$$

$$C_5Me_5Li + Mo(CO)_6 \xrightarrow{THF} \underset{\textbf{(2)}}{[Mo(C_5Me_5)(CO)_3]^-Li^+} + 3CO \qquad (7)$$

$$\underset{\textbf{(2)}}{[Mo(C_5Me_5)(CO)_3]^-Li^+} + CH_3COOH \rightarrow \underset{\textbf{(7)}}{Mo(C_5Me_5)(CO)_3H} + CH_3CO_2Li \qquad (8)$$

On a 10–30 mmol scale this approach gives a 90% yield of **7**, which is isolated as pure yellow microcrystals. The deep purple salt $[Mp^{\star}]^+PF_6^-$ (**6**) was synthesized from **7** by hydride abstraction involving use of 1 equivalent of $Ph_3C^+PF_6^-$ in dichloromethane at 0 °C (eq. 9). The thermally stable but very air sensitive compound **6** was isolated by crystallization from a dichloromethane/pentane mixture. It displays two infrared stretches at 1980 and 2045 cm^{-1}, and a single ^1H NMR resonance at δ 1.92 ppm for the permethylated C_5 ring.

$$\underset{(\mathbf{7})}{Mo(C_5Me_5)(CO)_3H} + Ph_3C^+PF_6^- \xrightarrow[0\,^\circ C]{CH_2Cl_2} \underset{(\mathbf{6})}{[Mo(C_5Me_5)(CO)_3]^+PF_6^-} + Ph_3CH \qquad (9)$$

4. *Synthesis and characterization of [Mp★L]⁺ PF₆⁻*

Dichloromethane dissolves **6** to give a deep red solution, which on treatment with two-electron ligands such as PPh_3 gives **8a** (eq. 10).

$$\underset{(\mathbf{6})}{[Mo(C_5Me_5)(CO)_3]^+PF_6^-} + PPh_3 \rightarrow \underset{(\mathbf{8a})}{[Mo(C_5Me_5)(CO)_3PPh_2]^+PF_6^-} \qquad (10)$$

The salt $[Mp^{\star}]^+PF_6^-$ (**6**) is thus an excellent precursor for the complexes $[Mp^{\star}L]^+PF_6^-$, ($L = CO$ (**4**); $L = PR_3$ (**8a–8d**); $L = P(OPh)_3$ (**9**); $L = CH_3CN$ (**10**) (Scheme 1)). The general procedure consists of adding an excess (1–1.25 molar equivalent) of L to a dichloromethane solution of **6**. The cleaner and easier method is to carry out the hydride abstraction (eq. 9) and the ligand addition (eq. 10) in the same pot. The salts $[Mp^{\star}L]^+PF_6^-$ are obtained in high yield by this way for L = CO, acetonitrile, or phosphorus ligands. In particular, this method affords an excellent route to $[Mp^{\star}CO]^+PF_6^-$ (**4**) under ambient conditions with an overall yield of 81% with respect to C_5Me_5H. It is noteworthy that reaction of **6** with chloride salts does not yield **3**.

Cyclic voltammograms of $[Mp^{\star}L]^+PF_6^-$ in CH_2Cl_2 show an irreversible wave for the initial oxidation process. The potential of the first reduction wave is, dependent on L, as expected, it decreases with the electron-donating ability of the ligand L (Table 2), and is indicative of the electron density on the metal atom.

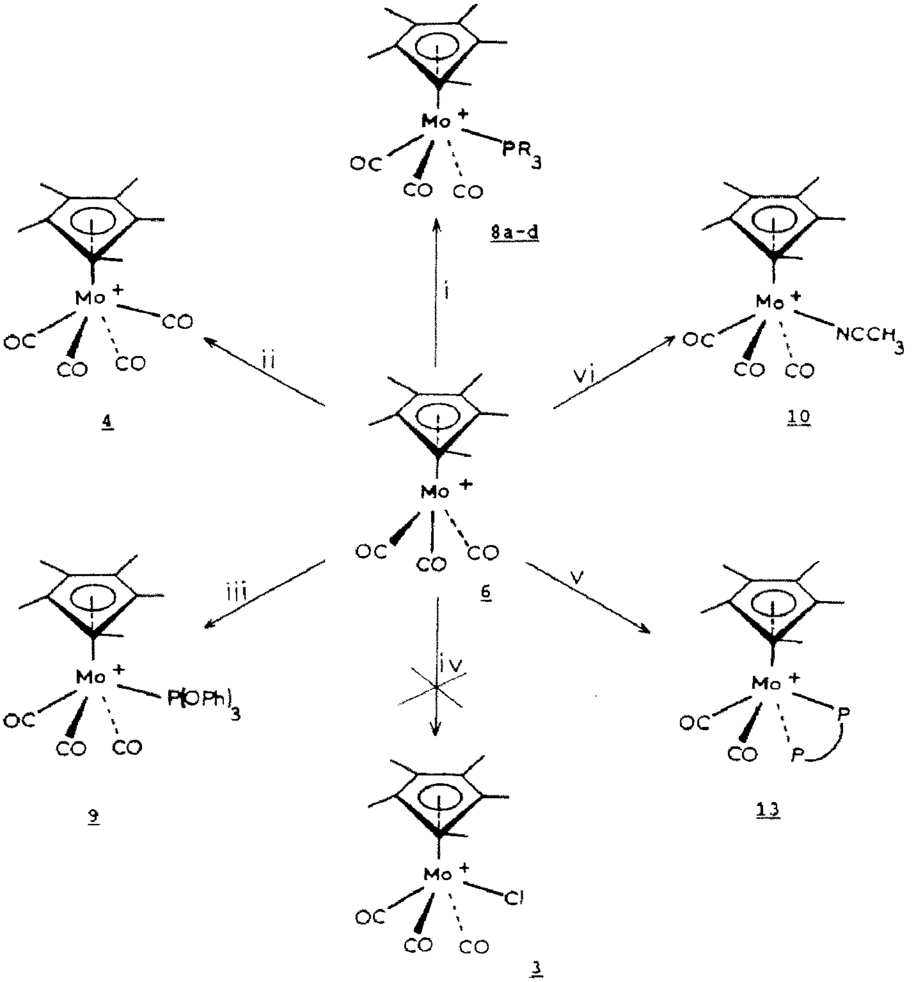
In contrast, the product waves are identical for all the derivatives and correspond to the formation of the anionic compounds $[Mp^{\star}]^-$ (**2**) with specific loss of L (eq. 11) [15*]. Further evidence for the occurrence of this reaction is provided by the

$$[Mp^{\star}L]^+ + 2e \rightarrow [Mp^{\star}]^- + L \qquad (11)$$

appearance in the voltammograms (Fig. 2) during the reverse oxidation of two waves, at −0.34 and 0.67 V, corresponding respectively to the oxidation of $[Mp^{\star}]^-$ to $[Mp^{\star}]_2$ (eq. 3) and to the oxidation of $[Mp^{\star}]_2$ to $[Mp^{\star}]^+$ (eq. 4).

Loss of the more electron-donating ligand during an irreversible reduction process is well known, but usually this reaction is followed immediately by dimerization of the radical. In contrast with the observations for the reduction of the coordinatively unsaturated $[Mp^{\star}]^+PF_6^-$, no dimerization occurs, suggesting that the leaving ligand must be involved in formation of the anion.

Except in the case of **8d** ($L = PBu^n{}_3$), the ^1H NMR chemical shift of the C_5Me_5 ligand is also a measure of the electron density at the molybdenum centre: the



Scheme 1. i, PMe_3 (**8a**), $PMePh_2$ (**8b**), PPh_3 (**8c**), PBu^n_3 (**8d**); ii, CO, 1 atm (**4**); iii, $P(OPh)_3$ (**9**); iv, KCl; v, dppe (**13**), CH_3CN (**10**).

Table 2

Peak potentials for oxidation and reduction of the cationic complexes $[Mo(C_5Me_5)(CO)_2L^1L^2]^+ PF_6^-$ at a platinum electrode, (V/ECS); CH_2Cl_2, $NBu^n_4PF_6$, 0.1 M)

L^1/L^2	$E_{p,a}$ (V/ECS)	$E_{p,c}$ (V/ECS)
CO/CO	1.89	−0.62
$P(OPh)_3$/CO	1.96	−1.08
$PMePh_2$/CO	1.78	−1.12
PBu_3/CO	1.74	−1.28
PMe_3/CO	1.72	−1.29
CH_3CN/CO	1.45	−0.84
dppe	1.35	−1.70
$PMe_3/PMePh_2$	1.31	−1.86

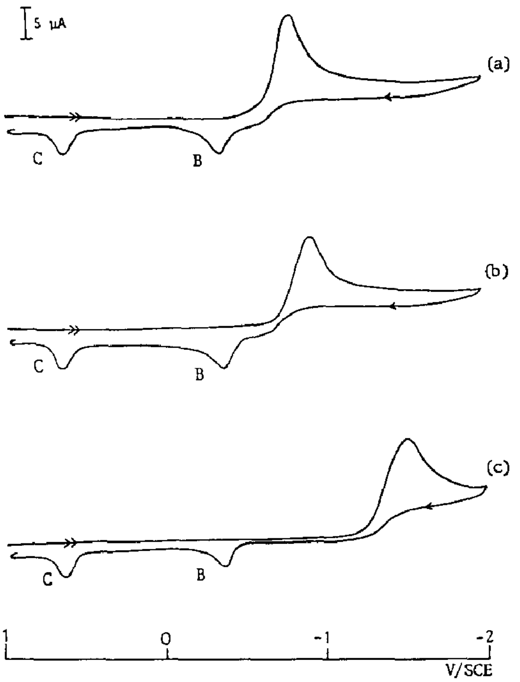


Fig. 2. Cyclic voltammograms of $[Mp^{\star}L]^+ PF_6^-$ in dichloromethane with 0.1 *M* TBAH at 20 °C. Scan rate V s^{-1}. (a) L = CO (**4**); (b) L = CH_3CN (**10**); L = PBu^n_3 (**8d**).

higher the δ value the lower is the electron density (Table 3). PBu^n_3 is a bulky ligand and the unusual chemical shift of the $Cp^{\star}$ ligand in **8d** must be attributed to steric effects [16]. On the other hand, the ^{13}C NMR chemical shifts are quite similar for all the $[Mp^{\star}L]^+$ compounds. Two doublets are attributed to the CO ligands: the signal with a large coupling constant $^2J(CP)$ (ca. 30 Hz) is attributed to the CO-*cis* to the phosphorus ligand, and that with a coupling constant close to zero is attributed to the CO *trans* of the phosphorus atom (Table 3).

The difference between the mull and solution infrared spectra of the complexes **8** is as great as if they came from different compounds. The solution spectra exhibit two C–O bond stretches in contrast with the spectra of Nujol mulls, where three stretches are observed in the same region (Table 4). Since the solubility of the solid complex in Nujol is low, the mull spectrum is that of the solid state, as was shown to be the case in the C_5H_5 series [17].

5. *Synthesis and characterization of* $[Mo(C_5Me_5)(CO)_2\ L^1L^2]^+PF_6^-$

The disubstituted dicarbonyl complexes $[Mo(C_5Me_5)(CO)_2L^1L^2]^+PF_6^-$ are prepared by a thermal ligand exchange reaction starting from the monosubstituted $[Mp^{\star}L^1]^+PF_6^-$ (eq. 12).

$$[Mp^{\star}L_1]^+PF_6^- + L_2 \rightarrow [Mo(C_5Me_5)(CO)_2L^1L^2]^+PF_6^- + CO \qquad (12)$$

$$(L^1 = PMe_3,\ L^2 = PMePh_2,\ T\ 135\,°C\ (\mathbf{12});\ L^1L^2 = dppe,\ T\ 40\,°C,\ (\mathbf{13}))$$

The displacement of the carbonyl group occurs under mild conditions in the case of the intramolecular chelation of the dppe ligand, leading in 2 h to the complex **13**, with *cis* configuration (80% yield). Intermolecular ligand exchange requires more drastic conditions (135 °C, 24 h), and affords the disubstituted cationic complex **12**, with *trans* configuration, in a lower yield (40%).

The cyclic voltammogram of **12** and **13** in dichloromethane show an almost reversible wave for the initial oxidation process with $i_a/i_c = 0.8$ for a scan rate of 0.5 V s^{-1} at 20 °C. For the initial reduction, the cyclic voltammograms show an irreversible cathodic peak at -1.7 V (Table 2).

The ^1H and ^{13}C NMR spectra of the disubstituted compounds exhibit the resonances expected for a single isomer. Analysis of the $^2J(CP)$ coupling constants for these dicarbonylmolybdenum complexes permit the determination of discrimination between the *cis–trans* isomers. The halide compound **5** exhibits two doublets at δ 246.8 ($^2J(CP)$ 5.3 Hz) and 260.2 ppm ($^2J(CP)$ 26 Hz) for the carbonyl resonances. The large difference between the two observed coupling constants shows that one CO is *trans* and the other *cis* with respect to the phosphine ligand, allowing assignment of the *cis* geometry to **5**. In compound **13** the two magnetically equivalent carbonyl ligands are coupled to the two phosphorus atoms of the dppe, and give a triplet in the ^{13}C NMR spectrum centred at δ 242.2 ppm ($^2J(CP)$ 14 Hz). This coupling constant corresponds to the average of $^2J(CP)$ *trans* and $^2J(CP)$ *cis* constants usually observed in the monosubstituted series (see Table 3), and indicates a *cis* geometry for **13**. The carbonyl resonances for the complex **12** exhibit an AB system centred at δ 240.4 ppm, with two $^2J(CP)$ coupling constants of 30.0 and 35.5 Hz. Such a pattern is consistent with a *trans* geometry for **12**. Similarly, the IR spectrum in each case, shows only two $\nu(CO)$ absorptions in the region 1850–2000 cm^{-1}, and the higher frequency band is much more intense in **5** and **13**, whereas the inverse pattern is observed for **12**. These data are consistent with a *cis* configuration for compounds **5** and **15** and the *trans* configuration for **12** [17,19]. We have also used the relative $\nu(CO)$ IR intensities to calculate the OC–Mo–CO angle [20*] from the relationship $\tan^2\theta = I_{as}/I_s$, where I_{as} and I_s are the areas under the antisymmetric (lower wavenumber) and symmetric (higher wavenumber) bands respectively [17]; since angles calculated in this way have been shown to be in good agreement with X-ray crystal data [19]. The angles thus determined for complexes **12** and **13** are 120° and 91°, respectively. The calculate angle for the neutral compound **5** is 88°. These values, characteristic of a "four-legged piano stool" geometry, are in good agreement with a *trans* geometry for **12** and *cis* geometry for **13** and **5**, and are nicely consistent with the X-ray data available for $Mo(C_5Me_5)(CO)_3H$ [3b,20*,21–25,26*].

Compound having the general formula $Mo(C_5Me_5)(CO)_2LX$ or $[Mo(C_5Me_5)(CO)_2L^1L^2]^+$ may be formally regarded as seven-coordinate molybdenum complexes with the cyclic ligand occupying three coordination sites. Crystallographic data are available to establish that the idealized lowest energy configuration would have the remaining ligands located approximately at the corners of a square [25]. In the C_5H_5 series an equilibrium between the two geometric isomers, made possible by the square pyramidal structure, has been observed for many analogous compounds [25]. In the permethylated series only one isomer is generally observed, except for formyl complexes with X = CHO, for which we observed formation of both isomers [4], but interconversions between these two forms were never observed. The permethylation of the Cp ring evidently increases the barrier to this intramolecular rearrangement.

Concluding remarks

A range of $[Mp^{\star}L^1]^+X$ complexes can be made by routes analogous to those previously used for $[MpL]^+X^-$ complexes. Such routes include hydride abstraction from Mp*H with the trityl reagent. Synthesis of [Mp*CO]$^+$X$^-$ via the coordinatively unsaturated [Mp*] species is a good substitute for the Fischer-type synthesis, since it proceeds quantitatively under 1– 3 atm of CO, and is generally applicable as a convenient route to various [Mp*L]$^+$X$^-$. The preparation of disubstituted cations, [Mo(C_5Me_5)$(CO)_2$L^{1}L^2]$^+$X$^-$ is conveniently achieved by thermal ligand exchange, which affords stereospecifically the *cis* isomer when the chelating dppe is present and the *trans* isomer when two independant phosphine ligands are present. The reactivity of the salts [Mp*L]$^+$X$^-$ is significantly different from that of the [MpL]$^+$X$^-$ series; in particular, we showed previously that the permethylation of the C_5 ring increases the stability of formyl complexes [4].

Experimental

General data. All manipulations were performed under argon by standard Schlenk techniques or in a BS531 Jacomex dry box filled with nitrogen. Solvents were dried, distilled, and de-aerated before use. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane, were distilled from sodium benzophenone ketyl immediately before use; CH_2Cl_2 was distilled from P_2O_5. C_5Me_5H [27] $Ph_3C^+PF_6^-$ [28] $PMePh_2$ [29], PMe_3 [30], $Ph_2P(CH_2)_2PPh_2$ [31] were synthesized by published methods. All other chemicals were used as received. Infrared spectra were recorded on a Pye Unicam SP 1000 spectrophotometer using 0.1 mm cells with KBr windows for solution and KBr pellets for Nujol mulls, and were calibrated with polystyrene film. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker WP80 FT or AM 300 WB intrument. Photolyses were performed with a Hanovia lamp (250 nm, 450 W) at room temperature under a stream of argon. Cyclic voltammetry studies were carried out with a Princeton Applied Research 362 instrument. Potentials were measured in V/SCE. All chemical shifts, δ, are in parts per million relative to Me_4Si for ^{1}H NMR signals, and CD_2Cl_2 (δ 53.8 ppm); C_6D_6 (δ 128.0 ppm) or CD_3CN (δ 1.26 ppm) for ^{13}C signals, and 85% H_3PO_4 for ^{31}P signals. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon. NMR, IR, yield and elemental analysis data for the 18-electron cationic complexes are summarized in Tables 3, 4, 5.

Mp$^\star_2$ (1). A. To a solution of 5.0 mmol (0.890 g) of C_5Me_5Li in 20 ml of THF was added 1.20 g (5.0 mmol) of $Mo(CO)_6$. The mixture was refluxed for 48 h, and the resulting dark yellow solution was cooled to 0 °C then treated dropwise with a solution of 0.760 g (5.0 mmol) of $Fe(SO_4)_3$ in 30 ml of a water 5/1 water/acetic acid mixture. [Mp*]$_2$ separated from the red solution and was filtered off, washed with water, methanol and pentane and dried under vacuum. Recrystallization from a toluene/pentane mixture (1/2) gave [Mp*]$_2$ in 90% yield as pure microcrystals. Spectroscopic data for **1** agree with those in the literature [2a].

B. To 5.0 mmol (0.890 g) of C_5Me_5H and 1.20 g (15.0 mmol) of $Mo(CO)_6$ was added 50 ml of n-decane, and the mixture was refluxed overnight. The solid formed was filtered off and its solution in heptane was kept under CO presure (3 atm, 25 °C) for 4 h. The [Mp*]$_2$ was recrystallized as in A and isolated in 55% yield.

Mp*Cl (3). A. To 3 mmol (0.426 g) of C_5Me_5Li in 50 ml of THF was added 3 mmol (0.792 g) of $Mo(CO)_6$. The mixture was refluxed for 48 h then cooled to 0 °C and 6 mmol (0.975 g) of anhydrous $FeCl_3$ were added, the yellow solution immediately turning red. After 1 h stiring, the THF was removed in vacuo, and the

Table 3. ^{1}H, ^{13}C and ^{31}P NMR of $[(C_5Me_5)Mo(CO)_2L^1L^2]^+ PF_6^-$

L^1L^2	^{1}H δ(ppm)/TMS	^{31}P δ(ppm)/TMS	^{13}C δ(ppm)/TMS
CO/CO	2.33(s; 15H; C_5Me_5) [a]	−143.5(sept; J(PF) 708 Hz; PF_6)	11.1(s; C_5Me_5); 112.6(s; C_5Me_5); 220.3(s; CO)
CO/PPh_3	1.91(s; 15H; C_5Me_5); 7–7.8(m; 15H; Ph) [b]	44.4(s; PPh_3); −143.4(sept; J(PF) 707; PF_6)	10.9(s; C_5Me_5); 110.3(s, C_5Me_5); 130.6(d; ^4J(CP) 11 Hz; C_{para}); 130.9(d; J(CP) 47.9 Hz C_{ipso}); 133.3(d; ^3J(CP) 21, C_{meta}); 134.2(d; ^2J(CP) 11 Hz C_{ortho}); 229.5(d; ^2J(CP) 27.8 Hz CO(*cis*)); 232.9 (d; ^2J(CP) 2.6 Hz CO (*trans*))
CO/$PMePh_2$	1.90(s; 15H; C_5Me_5); 2.30(d; 3H; ^2J(HP) 9.0 Hz; PMe); 7–8(m; 15H; Ph) [b]	26.4(s; $PMePh_2$); −143.6(sept; J(PF) 707; PF_6)	10.4(s; C_5Me_5); 18.1(d; J(CP) 31.6 Hz; $PMePh_2$); 109.1(s; C_5Me_5); 130 –134(m, Ph); 228.6(d; ^2J(CP) 28.8 Hz CO_{cis}); 231.7(s; CO_{trans})
CO/$PBu^n{}_3$	2.08(s; 15H; C_5Me_5); 0.9–2.0(m; 27H; Bu^n) [b]	23.1(s; $P(Bu^n{}_3)$; −142.7(sept; J(PF) 708 Hz; PFi_6	11.0(s; C_5Me_5); 22.0–29.0(m; Bn^n); 108.8(s; C_5Me_5); 229.3(d; ^2J(CP) 29.0 Hz; CO_{cis}); 231.7(d; ^2J(CP) 3.0 Hz; CO_{trans})
CO/P(OPh)	2.18(d; 15H; ^4J(HP) 1.2 Hz; (C_5Me_5); 7–7.5(m; 15H; Ph) [c]	156.2(s; $P(OPh)_3$); −144.3(sept; J(PF) 708 Hz; PF_6)	10.8(s, C_5Me_5); 109.8(s; C_5Me_5); 120.8(d; ^3J(CP) 4.0 Hz; C_{ortho}); 126.9(s; C_{para}), 130.5(s; C_{meta}); 150.6(d; ^2J(CP) 13.0 Hz; C_{ipso}); 225.3(s; CO_{trans}); 226.9(d; ^2J(CP) 40.0 Hz; CO_{cis})
CO/PMe_3	1.73(d; 9H; ^2J(PH) 10.1 Hz; (PMe_3); 2.11(s; 15H; C_5Me_5) [b]	6.2(s; $P(Me)_3$); −143.7(sept; J(PF) 712 Hz; PF_6)	10.8(s; C_5Me_5); 18.1(d; J(CP) 34.0 Hz; PMe_3); 108.7(s; C_5Me_5); 228.0(d; ^2J(CP) 31 Hz; CO_{cis}; 230.0(d; ^2J(CP) 4.0; CO_{trans})
CO/CH_3CN	2.05(s; 15H; C_5Me_5); 2.65(s; 3H; $NCCH_3$) [c]	−143.7(sept, J(PF) 711 Hz PF_6)	6.2(s; $NCCH_3$); 11.0(s; C_5Me_5); 118.8(s; C_5Me_5); 111.3(s; $NCCH_3$); 228.8(s; CO_{cis}); 238.6(s; CO_{trans})
PMe_3/$PMePh_2$	1.45(d; 9H; ^2J(PH) 10.4 Hz; PMe_3); 1.85(s; 15H; C_5Me_5); 2.29(d; 3H; ^2J(PH) 9.6 Hz; $PMePh_2$); 7.40–7.80(m; 15H; Ph) [b]	17.4(d; ^2J(PC) 24.4 Hz; PMe_3); 40.9(d; ^2J(PF) 19.5; $PMePh_2$) −144.3(sept; J(PF) 710; PF_6)	11.2(s; C_5Me_5); 17.1(d, J(CP) 34 Hz; PMe_3); 18.5(d; J(CP) 30.5 Hz; $PMePh_2$); 106.2(s, C_5Me_5); 132.5–128.0(m, Ph); 240.4(dd; ^2J(CP) 30 Hz; J(CP) 33.5 Hz; CO) ^2J(CP)
dppe	1.45(s; 15H; C_5Me_5); 2.52–2.58(m; 4H; $P(CH_2)_2P$); 7.0–7.6(m; 20H; Ph) [b]	74.0(s; $P(CH_2)_2P$); −143.5(sept, J(PF) 708 Hz; PF_6)	9.8(s; C_5Me_5); 26.6(t; J(CP) 15.0 Hz; $P(CH_2)_2P$); 106.0(s; C_5Me_5) 135 –127(m, Ph); 242.2(t; ^2J(CP) 14.0 Hz; CO)

[a] In acetone-d_6. [b] In chloroform-d_1. [c] In methylene chloride.

Table 4

Yields and IR data for $[\text{Mo}(\text{C}_5\text{Me}_5)(\text{CO})_2\text{L}^1\text{L}^2]\text{PF}_6$

L^1/L^2	Time (h)	Yield (%)	IR (cm^{-1})
CO/CO	12	91	2115(vs); 2038(s) ^{a}; 2050(s); 1970(s); 1945(vs) ^{b}
CO/PPh_3	10	70	2060(s); 1975(vs) ^{a}; 2070(s); 1995(s); 1955(vs) ^{b}
CO/PMePh_2	12	70	2080(s); 1955(vs) ^{a}; 2040(s); 1960(s); 1935(vs) ^{b}
$\text{CO/PBu}^n{}_3$	12	60	2055(s); 1962(vs) ^{a}; 2080(s); 2000(s); 2085(vs) ^{b}
CO/P(OPh)_3	12	59	2080(s); 1990(vs) ^{a}; 2050(s); 1965(vs); 1955(vs) ^{b}
CO/PMe_3	3	96	2055(s); 1965(vs) ^{a}; 2075(s); 1990(vs); 1960(w) ^{b}
$\text{CO/CH}_3\text{CN}$	12	70	2075(s); 1990(vs) ^{a}
$\text{PMe}_3/\text{PMePh}_2$	24	40	1955(s); 1870(vs) ^{a,b}
dppe	5	80	1975(s); 1900(s) ^{a,b}

^{a} CH_2Cl_2. ^{b} Nujol; (s) strong; (vs): very strong; (w) weak.

solid residue was extracted with ether and chomatographed on an alumina column. Initial elution with hexane removed the by-products, and **3** was then eluted with CH_2Cl_2. Recrystallization from a CH_2Cl_2/hexane mixture gave **3** as red needles (60% yield).

B. To a solution 2 mmol (0.632 g) of Mp*H in 20 ml of pentane at 20 °C was added 5 mmol (0.710 g) of CCl_4. The solution immediately became red. It was stirred for 10 min and the solvent then removed under vacuum. The residual Mp*Cl was recrystallized from 1/1 dichloromethane/hexane as red needles (86% yield).

MoCp**(CO)*$_2$*(PPh*$_3$*)Cl (5).* A solution of 2 mmol (0.701 g) of Mp*Cl in toluene (200 ml) containing 2 mmol (0.524 g) of PPh_3 was irradiated for 0.5 h. The solvent

Table 5

Analyses data for $[(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_2(\text{L}_1)(\text{L}_2)]^+ \text{PF}_6^-$

L_1L_2	Analyses (Found (calcd) (%))		
	C	P	H
CO/CO	34.68	6.27	2.99
	(34.65)	(6.34)	(3.09)
CO/PPh_3	51.45	8.43	4.20
	(51.54)	(8.58)	(4.18)
CO/PMePh_2	47.29	9.38	4.27
	(47.12)	(9.61)	(4.13)
$\text{CO/PBu}^n{}_3$	45.67	9.46	6.47
	(45.32)	(9.35)	(6.39)
CO/P(OPh)_3	48.13	8.09	3.78
	(48.33)	(8.04)	(3.92)
CO/PMe_3	35.87	11.55	4.88
	(35.84)	(11.55)	(4.51)
$\text{CO/CH}_3\text{CN}$	35.97	5.62	3.62
	(35.94)	(6.19)	(3.62)
$\text{PMe}_3/\text{PMePh}_2$	47.34	13.45	5.16
	(47.47)	(13.12)	(5.26)
dppe	34.80	11.23	4.70
	(34.92)	(11.19)	(4.73)

was then removed under vacuum and the solid residue was washed with diethyl ether and recrystallized from hot hexane to give red microcrystals of **5** (90%).; IR (CH_2Cl_2), 1960 (vs), 1880 (s) cm^{-1}. ^1H NMR (C_6D_6), 1.59(s, 15 H, C_5Me_5); 7.50–7.70(m, 15 H, Ph). ^{31}P NMR (C_6D_6) 48.5(s, PPh_3). ^{13}C NMR (C_6D_6), 10.5(s, C_5*Me_5*); 106.2(s, *C_5*Me_5); 134.0–128.0(m, Ph); 246.8 (d, ^2J(CP) 5.3 Hz; CO *trans*/PPh_3); 260.2 (d, ^2J(CP) 26.4 Hz; CO_{cis}/PPh_3). Anal. Found: C, 61.55; H, 5.13; Cl, 6.11; P, 5.22. $C_{30}H_{30}O_2PClMo$ calcd.: C, 61.60; H, 5.17; Cl, 6.06; P, 5.29%.

[Mp★CO]$^+$$PF_6$$^-$ (4) using a Fischer type ligand exchange. In an autoclave were placed 10 mmol (3.51 g) of Mp★Cl, 50 ml of dearerated heptane, and 30 mmol (3.20 g) of $AlCl_3$. The autoclave was charged with 100 atm of CO and then kept at 95 °C for 16 h. The cooled mixture was hydrolysed at 0 °C then treated with HPF_6, to give a yellow precipitate. This was filtered off, washed with ether, recrystallized from acetone/ethanol, and dried under vacuum. 4 mmol (1.95 mmol) of **4** were recovered (40% yield).

[Mp★]$^+$$PF_6$$^-$ (6). To a solution of 1 mmol (0.388 g) of $Ph_3C^+PF_6^-$ in 20 ml of dichloromethane at 0 °C was slowly added 1 mmol (0.316 g) of Mp★H (7). The initial yellow colour changed to purple. After 5 min stirring, the solution was slowly concentrated under vacuum to about 3 ml and, cold pentane (−40 °C) was then added to precipitate **5**. The solid was washed with cold pentane (3 × 30 ml) and dried under vacuum at 0 °C, to give a 90% yield of a purple solvate of **5** containing 1 mole of CH_2Cl_2 per mol. IR (nujol), 2070 (s); 1975 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2), 1.92 (s, C_5Me_5). Anal. Found, C, 30.59; H, 3.22 $C_{13}H_{15}F_6MoO_3P$ calcd.: C, 30.85; H, 3.14%.

Mp★H (7). To a solution of 30 ml (4.26 g) of C_5Me_5Li in 100 ml of THF, were added 30 mmol (7.92 g) of $Mo(CO)_6$. The mixture was refluxed for two days, and the dark yellow solution then cooled to 0 °C and treated with 45 mmol (1.8 g) of acetic acid. The solution was stirred for 2 h, the THF removed under vacuum, and **7** extracted with pentane (4 × 45 ml). After evaporation of the extract and sublimation of the remaining $Mo(CO)_6$ at 40 °C, **7** was isolated as a pure product in 90% yield; its spectroscopic data agree well with literature values [3,6].

[Mp★L]$^+$$PF_6$$^-$, standard procedure. To a solution of 2 mmol (0.776 g) of $Ph_3C^+PF_6^-$ in 20 ml of methylene chloride cooled to 0 °C were slowly added 2 mmol (630 mg) of Mp★H; the yellow solution turned purple. After 5 min stirring, 2.5 mmol of the ligand L were added and the temperature increased to 20 °C. After the reaction time listed in Table 4 the solution was concentrated to 5 ml and 15 ml of ether was added to precipitate the complex. The yellow solid obtained was filtered off and chromatographed on alumina with chloroform as eluant. The eluate was concentrated to 5 ml and ether was slowly added (30 ml) to give crystals of the complex (See Tables 3, 4, 5).

[Mo(C_5Me_5)($CO)_2$(dppe)]$^+$$PF_6$$^-$ (12). To a solution of 2 mmol (0.776 g) $Ph_3C^+PF_6^-$ in 30 ml of dichloromethane at 0 °C were added 2 mmol (0.630 g) of Mp★H. The solution was stirred for 5 min and 2.5 mmol (0.995 g) of dppe then added. The temperature was allowed to rise to 20 °C and the mixture was stirred for 3 h then refluxed for 2 h. The solution was concentrated under vacuum and **12** then precipitated by addition of ether. After purification by chromatography on alumina with chloroform as eluant, evaporation of the eluted solution under vacuum and recrystallization of the residue from a choroform/ether mixture gave **12** as pure yellow crystals.

$[Mo(C_5Me_5)(CO)_2(PMe_3)(PMePh_2)]^+PF_6^-$ (13). A mixture of 2 mmol (1.072 g) of $[Mp^{\star}(PMe_3)]^+PF_6^-$ (**8b**) and 2.5 mmol (0.5 g) of $PMePh_2$ in *o*-dichlorobenzene (30 ml) was heated at 135 °C for 24 h then cooled to room temperature. The solvent was removed by trap-to-trap distillation and the solid residue was washed with ether then chromatographed on an alumina column with chloroform as eluant. Slow evaporation of the eluate under vacuum, gave pure yellow crystals of **13**.

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