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Synthesis, electrochemistry, and crystal and molecular structures of some molybdenum(0) arene derivatives with fluorinated and phenyl-substituted arene ligands ☆

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Abstract

Compounds of general formula Mo(η^6-arene)$(CO)_3$, arene = diphenyl, **1**; 1,3,5-triphenylbenzene, **2**; C_6H_5F, **3**; $C_6H_5CF_3$, **4**, have been prepared in good yields by reacting *fac*-Mo$(CO)_3(DMF)_3$, DMF = *N*,*N*-dimethylformamide, with $BF_3 \cdot OEt_2$ and the appropriate arene. The crystal and molecular structures of **1**, **3**, and **4**, are reported. The dinuclear derivative $Mo_2(\eta^6{:}\eta^6\text{-}C_6H_5\text{-}C_6H_5)(CO)_6$, **5**, was obtained by thermal reaction of Mo(η^6-toluene)$(CO)_3$ with Mo(η^6-diphenyl)$(CO)_3$. An electrochemical study has been performed on the new complexes, showing that the dimolybdenum complex undergoes a single two-electron reduction at about the same potential as the corresponding dichromium complex, the molybdenum dianion being less stable than the chromium analogue.

Keywords: Molybdenum; Arene; Electrochemistry; Structures

1. Introduction

Several transition metals (e.g. V, Cr, Mo, W, Fe, Co) form complexes with arenes, those of chromium being studied in a greater detail [1]. The chromium(0) derivatives of general formula Cr(η^6-arene)$(CO)_3$ are readily prepared by several methods, for example by treating the commercially available $Cr(CO)_6$ with the appropriate arene as a neat liquid or in a basic solvent such as dioxane or THF, or by reacting $Cr(CO)_3L_3$, L = NH_3 [2], α- or γ-picoline [3], with an excess arene. As a consequence of these high-yielding processes, a number of Cr(η^6-arene)$(CO)_3$ derivatives are known [1b,1c,1d] and some of them are commercially available. However, the molybdenum and tungsten congeners are not so common. This may be due to two reasons: the generally higher kinetic lability of the zerovalent complexes of 4d transition metals with respect to the corresponding complexes of 3d and 5d elements [4]; the formation of stronger bonds descending a vertical sequence of transition metals [4b,5], which makes $W(CO)_6$ more stable and less reactive than the molybdenum analogue in dissociative processes.

Even less frequent are the dinuclear complexes of condensed aromatics, those of polyphenyls, and the complexes of fluoro-substituted aromatics, due to steric and electronic effects, respectively. In this paper, we report the moderate- to high-yield preparation of η^6-arene tricarbonyl derivatives of molybdenum(0) containing polyphenyls and fluoro-substituted arenes as ligands,

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and their characterization. Moreover, the redox activity of the complexes is reported and discussed.

2. Results and discussion

2.1. Synthesis and characterization

2.1.1. Mononuclear compounds

Our first approach to the synthesis of molybdenum polyphenyl complexes was based on procedures successfully applied to the chromium analogues [6]. However, we have found that $Mo(CO)_6$ in melting diphenyl (70 °C) forms a metallic mirror. Alternative procedures consisting of treating a THF/Bu_2O mixture as reaction medium with the $Mo(CO)_6$/arene system or with the Lewis base adducts *fac*-$Mo(CO)_3(CH_3CN)_3$ [7–13] or *fac*-$Mo(CO)_3(DMF)_3$ were equally unsuccessful, due to extensive formation of a metallic mirror.

A synthetic approach different from thermal substitution on $Mo(CO)_6$ was therefore necessary. The arene derivatives have been obtained by reaction of *fac*-$Mo(CO)_3(DMF)_3$ with the stoichiometric amount of $BF_3 \cdot Et_2O$ in the presence of excess arene, see Eq. (1).

$$\begin{aligned} &\textit{fac}\text{-}Mo(CO)_3(DMF)_3 + 3BF_3 \cdot Et_2O + \text{arene} \\ &\quad \rightarrow Mo(\eta^6\text{-arene})(CO)_3 + 3BF_3 \cdot DMF + 3CO \\ &\quad (\text{arene} = \text{diphenyl}, 1,3,5\text{-triphenylbenzene}, \\ &\qquad C_6H_5F\ [14], C_6H_5CF_3) \end{aligned} \quad (1)$$

The methodology based on the Lewis acid $BF_3 \cdot Et_2O$ has been used in the past for the preparation of the $Cr(\eta^6\text{-arene})(CO)_3$ complexes (arene = bromo- and iodobenzene) from $Cr(CO)_3(\gamma\text{-picoline})_3$ [3], while alkyl-substituted arene derivatives of molybdenum(0) and tungsten(0) of general formula $M(\eta^6\text{-arene})(CO)_3$ were synthesized from *fac*-$M(CO)_3(L)_3$, L = DMF [15], py [16], pentamethyldiethylenetriamine [17].

Reactions proceed smoothly at room temperature and give the arene derivatives in satisfactory to good yields. The compounds form yellow crystals, stable in air in the solid state for short periods of time. They are sensitive to light, especially the fluorine-substituted arene derivatives, which have to be prepared and stored in the dark.

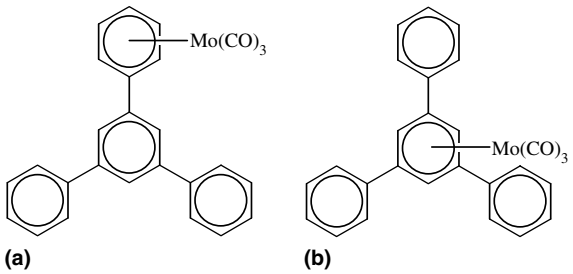
With the exception of 1,3,5-triphenylbenzene, vide infra, reaction (1) gives the best yields only in the presence of excess arene (diphenyl/Mo = 10) or in the arene as solvent (fluorinated derivatives). Unless an excess was used, extensive formation of molybdenum metal and $Mo(CO)_6$ took place. In the preparation of the 1,3,5-triphenylbenzene derivative **2**, an arene/Mo molar ratio of 1 was used, and no formation of $Mo(CO)_6$ was observed. Probably this is due to the presence of four possible coordination sites for molybdenum in the triphenylbenzene molecule, the probability of the $Mo(CO)_3$ moiety to escape from the hydrocarbon cage thus decreasing.

Table 1
IR carbonyl stretching vibrations of $Mo(\eta^6\text{-arene})(CO)_3$ derivatives in heptane

Arene	$\tilde{\nu}_{CO}$ (cm^{-1})
Diphenyl	1983s, 1915s
1,3,5-Triphenylbenzene	1982s, 1914s
Fluorobenzene	1995s, 1926s
Trifluoromethylbenzene	2002s, 1937s

Infrared and NMR spectra were recorded for all the compounds reported in this paper, see Table 1. The IR spectra are consistent with a C_{3v} local symmetry of the $\{Mo(CO)_3\}$ group (two carbonyl stretching vibrations $A_1 + E$), with higher wavenumber values for the fluorine-containing aromatic ligands C_6H_5F and C_6H_5–CF_3, in agreement with the higher electron-withdrawing power of the substituent. Noteworthy is the large shift observed for the stretching vibrations on going from heptane to toluene [the $\Delta\tilde{\nu}_{CO}$ is 12 and 19 cm^{-1} for $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$]. This large difference has been already pointed out [18] and suggested to be due to a preferential solvation by the aromatic medium [19].

The NMR spectra (^1H and ^{13}C) show the shift of the resonances towards high fields with respect to the uncoordinated arene, as usually observed for neutral arene derivatives of transition metals [20]. The ^1H NMR spectrum of the 1,3,5-triphenylbenzene derivative is noteworthy because it is indicative of the coordination of the polyarene molecule to molybdenum. As a matter of fact, 1,3,5-triphenylbenzene may give 1:1 arene complexes by coordination through the central C_6H_3 ring or through one of the three peripheric phenyl rings, and examples are known of both coordination types [21]. Due to the presence of two sets of signals at 7.64–7.49 and ca. 5.8 ppm with an intensity ratio of 13:5, we conclude that the $Mo(CO)_3$ fragment is bonded to one of the external C_6H_5 rings (**A** of Scheme 1) rather than to the central C_6H_3 ring (**B** of Scheme 1) for which the intensity ratio of the resonances should be 15:3. In this connection it is relevant that the 1:1 thermal reaction between $Cr(CO)_6$ and 1,3,5-triphenylbenzene affords a mixture of compounds where the $Cr(CO)_3$ fragment is



Scheme 1.

bonded to the external C_6H_5 ring and to the central C_6H_3 ring [21a,21b]. The formation of isomer **A** is probably due to the larger atomic radius of molybdenum (1.36 Å), whose coordination to the central ring is consequently less favourable than in the case of chromium (atomic radius, 1.25 Å) [10].

X-ray structural analyses have been performed on compounds **2**–**4**, derivatives **3** and **4** being the first examples of fluoro-substituted molybdenum-tricarbonyl to be structurally characterised. The three molecular structures are similar as far as the coordination of molybdenum is concerned and they belong to the *piano-stool* class of compounds, see Fig. 1. Selected bond distances and angles are reported in Table 2.

The unit cell of Mo(η^6-C_6H_5–C_6H_5)(CO)$_3$, **1**, contains two independent molecules which differ in the orientation of the phenyl substituent with respect to the plane of the coordinated ring, the dihedral angles being 28.2(2)° and −30.2(2)°. These values compare well with those reported for diphenyl complexes of transition metals such as Ti(η^6-C_6H_5–C_6H_5)($AlCl_4$)$_2$ (30.6°) [22], [K([2.2.2]cryptand)][Ti(η^6-C_6H_5–C_6H_5)$_2$] (31°) [23], Mn(η^6-C_6H_5–C_6H_5)Cp (24.4°) [24], and Ru_6C(η^6-C_6H_5–C_6H_5)(CO)$_{14}$ (34.2°) [25]. It is interesting to observe that the six-membered rings are practically coplanar in crystalline diphenyl [26].

The arene and the carbonyl groups are in a staggered orientation [28] with the following tilting angles: C21–centroid–Mo1–C1, −30.3(2) and −30.3(2)° and C41–centroid–Mo2–C5, −28.5(2)°.

Once the atomic radii of chromium and molybdenum are taken into consideration, the distances within Mo(η^6-C_6H_5–C_6H_5)(CO)$_3$, [Mo-ring: 2.381(3) Å, Mo–$C_{carbonyl}$: 1.949(4), mean values] are similar to those observed in Cr_2(η^6:η^6-C_6H_5–C_6H_5)(CO)$_6$ [Cr-ring: 2.20 Å, Cr–$C_{carbonyl}$: 1.85, mean values] [29], in Cr_2(η^6:η^6-C_6H_5–C_6H_5)(CO)$_4$(P_2Me_4) [Cr-ring: 2.207 Å, Cr–$C_{carbonyl}$: 1.818 Å, mean values] [30], and in Cr_2(η^6:η^6-C_6H_5–C_6H_5)(CO)$_4$[1,2-bis(diphenylphosphino)methane] Cr-ring carbon atoms: 2.209 Å, Cr–$C_{carbonyl}$: 1.815 Å, mean values] [31]. The mean C–C bond distances in the bonded C_6H_5 ring are longer than the corresponding distances in the uncoordinated one (1.410 vs. 1.380 Å, mean values) and correspond to those observed for structurally characterized diphenyl derivatives [22–25,29–31].

The fluoro- and the trifluororobenzene derivatives Mo(η^6-C_6H_5F)(CO)$_3$ and Mo(η^6-$C_6H_5CF_3$)(CO)$_3$ are the first structurally characterized fluoro-substituted derivatives of molybdenum(0) and belong to the restricted class of η^6-arene derivatives containing electron-withdrawing substituents. Although the chemistry of η^6-arene complexes is rather well developed [1b], compounds containing electron-withdrawing substituents on the aromatic ligand are rather rare. This is mainly due to the instability typical of these compounds (weakening of the arene–metal bond on increasing the electronegativity of the substituents) and to the reactivity of the C–X bond with low-valent transition metals (oxidative addition followed by decomposition) in the sequence I > Br > Cl > F. Some derivatives of manganese(I) containing electron-withdrawing substituents on the arene ring have been recently reported [32].

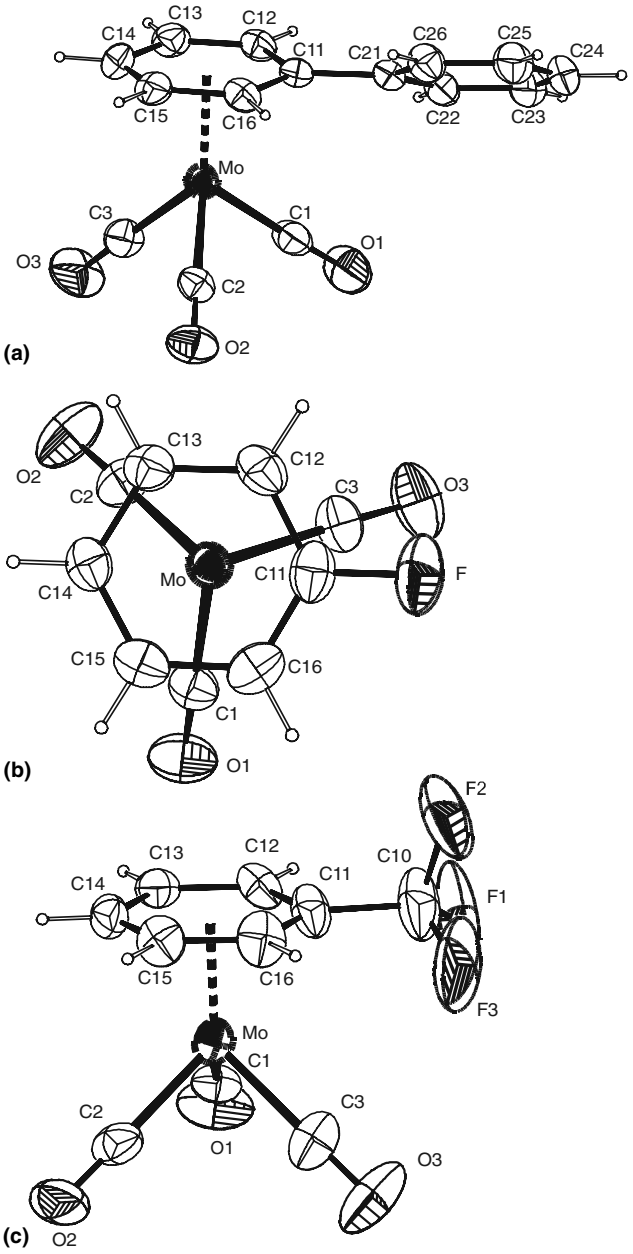


Fig. 1. Molecular structures [27] of: (a) one of the two independent molecules of Mo(η^6-C_6H_5–C_6H_5)(CO)$_3$; (b) Mo(η^6-C_6H_5F)(CO)$_3$, as viewed along the ring centroid–Mo direction; (c) Mo(η^6-$C_6H_5CF_3$)(CO)$_3$. Ellipsoids are drawn at 50% level.

The Mo–centroid distance in Mo(η^6-C_6H_5F)(CO)$_3$ is 1.91 Å and, as it appears from Fig. 1(b), the carbonyl groups are almost staggered with respect to the C–F bond in order to form a dihedral angle F–centroid–Mo–C3 of −19.85(9)°. The mean value of the C–C bond

Table 2
Bond distances (Å) and angles (°) for Mo(η^6-C_6H_5-C_6H_5)$(CO)_3$, Mo(η^6-C_6H_5F)$(CO)_3$, and Mo(η^6-$C_6H_5CF_3$)$(CO)_3$

Mo(η^6-C_6H_5–C_6H_5)$(CO)_3$			
Mo(1)–C(1)	1.945(4)	C(1)–Mo(1)–C(2)	85.94(16)
Mo(1)–C(2)	1.957(4)	C(1)–Mo(1)–C(3)	87.01(17)
Mo(1)–C(3)	1.957(4)	C(2)–Mo(1)–C(3)	84.74(15)
O(1)–C(1)	1.149(5)	C(1)–Mo(1)–C(11)	92.71(14)
O(2)–C(2)	1.143(4)	C(2)–Mo(1)C(11)	117.55(13)
O(3)C(3)	1.150(5)	C(3)–Mo(1)–C(11)	157.66(14)
C(11)–C(21)	1.482(5)		
Mo(2)–C(6)	1.952(4)	C(6)–Mo(2)–C(4)	87.19(17)
Mo(2)–C(4)	1.954(4)	C(6)–Mo(2)–C(5)	87.50(17)
Mo(2)–C(5)	1.955(4)	C(4)–Mo(2)–C(5)	85.56(15)
O(4)C(4)	1.152(4)	C(4)–Mo(2)–C(31)	119.12(14)
O(5)–C(5)	1.148(5)	C(5)–Mo(2)–C(31)	94.24(14)
O(6)–C(6)	1.144(5)	C(6)–Mo(2)–C(31)	153.69(16)
C(31)–C(41)	1.490(5)		
Mo(η^6-C_6H_5F)$(CO)_3$			
Mo–C(2)	1.960(2)	C(2)–Mo–C(3)	88.86(9)
Mo–C(3)	1.962(2)	C(2)–Mo–C(1)	85.96(8)
Mo–C(1)	1.969(2)	C(3)–Mo–C(1)	87.55(9)
Mo–C(11)	2.364(2)	C(2)–Mo–C(11)	149.44(9)
O(1)–C(1)	1.146(3)	C(3)–Mo–C(11)	90.74(9)
O(2)–C(2)	1.147(2)	C(1)–Mo–C(11)	124.56(9)
O(3)–C(3)	1.146(3)	F–C(11)–Mo	127.31(15)
Mo(η^6–$C_6H_5CF_3$)$(CO)_3$			
Mo–C(1)	1.961(4)	C(1)–Mo–C(3)	87.51(16)
Mo–C(3)	1.970(5)	C(1)–Mo–C(2)	85.84(15)
Mo–C(2)	1.975(4)	C(3)–Mo–C(2)	87.45(19)
O(1)–C(1)	1.146(4)	C(1)–Mo–C(11)	117.39(14)
O(2)–C(2)	1.144(5)	C(2)–Mo–C(11)	156.60(14)
O(3)–C(3)	1.158(5)	C(3)–Mo–C(11)	95.86(17)

Estimated standard deviations in parentheses refer to the least significant digit.

distances is 1.400 Å and the C(11)–F bond distance is 1.339(3) Å. The C–C and C–F bond distances of the arene ligand are comparable to those observed in Cr(η^6-C_6H_5F)$(CO)_2(SiCl_3)_2$ [C–C, mean value, 1.388 and C–F bond distance, 1.334(9) Å] within the 1:1 co-crystallite Cr(η^6-C_6H_5F)$(CO)_2(SiCl_3)_2 \cdot$ Cr(η^6-C_6H_5F)$(CO)(H)_2(SiCl_3)_2$ [33], and in Cr(η^6-C_6H_5F)$(CO)_2(SnPh_3)_2$ [C–C mean value, 1.402 Å and C–F bond distance, 1.32(2) Å] [34].

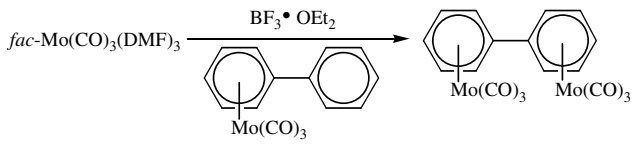
The molecular structure of the trifluoromethyl complex, Mo(η^6-$C_6H_5CF_3$)$(CO)_3$, is similar to that of the fluoro derivative with a Mo–centroid distance of 1.89 Å and a dihedral angle C(10)–centroid–Mo–C3 (see Fig. 1(c)) of 29.9(2)° larger than the angle observed in the fluoro derivative probably due to the higher steric hindrance of the $-CF_3$ group with respect to the fluoro substituent. The mean Mo–C and C–C distances (2.342 and 1.404 Å) are comparable with those observed in Cr(η^6-$C_6H_5CF_3$)(η^6-1,4-$C_6H_4Me_2$) (2.131 and 1.408 Å) [35] and in Cr(η^6-$C_6H_5CF_3)_2$ (2.136 and 1.408 Å) [36].

2.1.2. *$Mo_2(\eta^6{:}\eta^6$-C_6H_5–$C_6H_5)(CO)_6$*

The binuclear chromium derivative $Cr_2(\eta^6{:}\eta^6$-C_6H_5–$C_6H_5)(CO)_6$ was originally obtained by reacting $Cr(CO)_6$ with melted diphenyl [37] or in a THF/Bu_2O mixture [6c]. The structure consists of a diphenyl ligand bridging two {$Cr(CO)_3$} fragments in a *trans* arrangement [29].

We tried to extend the previously reported synthetic pathways for the chromium derivatives to the 4d analogue, but the higher thermal lability of the molybdenum derivatives $Mo(CO)_6$ and Mo(η^6-C_6H_5–$C_6H_5)(CO)_3$ caused the formation of a metallic mirror in both cases. Moreover, the reaction sequence reported in Scheme 2 gave a very low yield (from ^{1}H NMR, see Section 4) of the dinuclear compound, most of the molybdenum being present after the reaction as $Mo(CO)_6$ and starting material.

By taking into consideration the higher lability of the arene ligand in Mo(η^6-$C_6H_5CH_3$)$(CO)_3$ with respect to



Scheme 2.

CO in $Mo(CO)_6$ [1b,38], we decided to react $Mo(\eta^6\text{-}C_6H_5CH_3)(CO)_3$ with $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$ in boiling heptane (no reaction occurs at room temperature), see Eq. (2). The formation of the dinuclear derivative is presumably favoured by its low solubility. However, a maximum yield of 40% was obtained, further heating over longer reaction times leading to particular total decomposition.

$$Mo(\eta^6\text{-}C_6H_5CH_3)(CO)_3 + Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3 \rightarrow Mo_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6 + C_6H_5CH_3 \quad (2)$$

The dinuclear compound $Mo_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ is stable in air for short periods of time in the solid state, it is slightly soluble in aliphatic hydrocarbons and promptly reacts with Lewis bases with formation of diphenyl. Analytical data, and infrared and NMR spectra are in agreement with the presence of two tricarbonyl groups of C_{3v} symmetry, and a diphenyl ligand. The NMR spectra (^1H and ^{13}C) are similar to that reported by Top and Jouen [6c] for the analogous chromium derivative. The dinuclear nature of the compound is evidenced by the presence of resonances only in the region of metal-bonded aromatic groups (5.79, 5.65 and 5.58 ppm) at variance with the starting $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$ derivative which has resonances typical of bonded (6.02, 5.87 and 5.64 ppm) and uncoordinated phenyl rings (7.48, 7.43 ppm).

The low solubility of the dinuclear compound has not allowed the preparation of crystals for X-ray analysis and therefore we can only suggest that the system may adopt a *trans*-configuration of the two $Mo(CO)_3$ fragments as observed in $Cr_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$.

2.2. Electrochemistry

After the first paper by Dessy [39] on the redox properties of $Cr(\eta^6\text{-}C_6H_6)(CO)_3$, several papers have appeared concerning electrochemical studies on $Cr(\eta^6\text{-arene})(CO)_3$ derivatives. They have been reported to undergo mono-electronic oxidation to the $[Cr(\eta^6\text{-arene})(CO)_3]^+$ cations [40], whose stability increases with increasing methyl substitution on the aromatic ring [41]. As far as reduction is concerned, $Cr(\eta^6\text{-arene})(CO)_3$ derivatives can be bi-electronically reduced to dianions which are very reactive on the time-scale of cyclic voltammetry [42]. The presence of condensed aromatics or polyphenyls as ligands increases the stability of the anions [43] and $[Cr_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6]^{2-}$ has been isolated and characterized [44].

Due to the fact that most of the electrochemical studies have been performed on chromium derivatives, we decided to investigate the electrochemical behaviour of our arene molybdenum tricarbonyl derivatives and to compare them with the chromium analogues. Is it noteworthy that a paper has appeared reporting that in the case of $M(\eta^6\text{-arene})(CO)_3$, M = Cr, Mo, W, arene = estrone-3-methyl ether [45], the electrochemically oxidized species show the following stability trend: $[Cr(\eta^6\text{-arene})(CO)_3]^+ \gg [Mo(\eta^6\text{-arene})(CO)_3]^+ > [W(\eta^6\text{-arene})(CO)_3]^+$.

The typical redox behaviour of the mononuclear derivatives in CH_2Cl_2 solution is reported in Fig. 2(a), which refers to $Mo(\eta^6\text{-}C_6H_5CF_3)(CO)_3$ in the presence of an equimolar amount of $Fe(C_5Me_5)_2$ as an internal standard (starred peaks). The pertinent electrode potentials are compiled in Table 3.

They only exhibit an oxidation process at high potential without any associated return peak even at high scan rates (up to 5 $V\,s^{-1}$), suggesting that the oxidation is accompanied by fast decomposition; moreover, no reduction process was detected in the cathodic scan up to 2.1 V (maximum potential allowed in CH_2Cl_2). Although the controlled potential coulometry failed to determine the number of electrons involved in the anodic process because of electrode poisoning phenomena

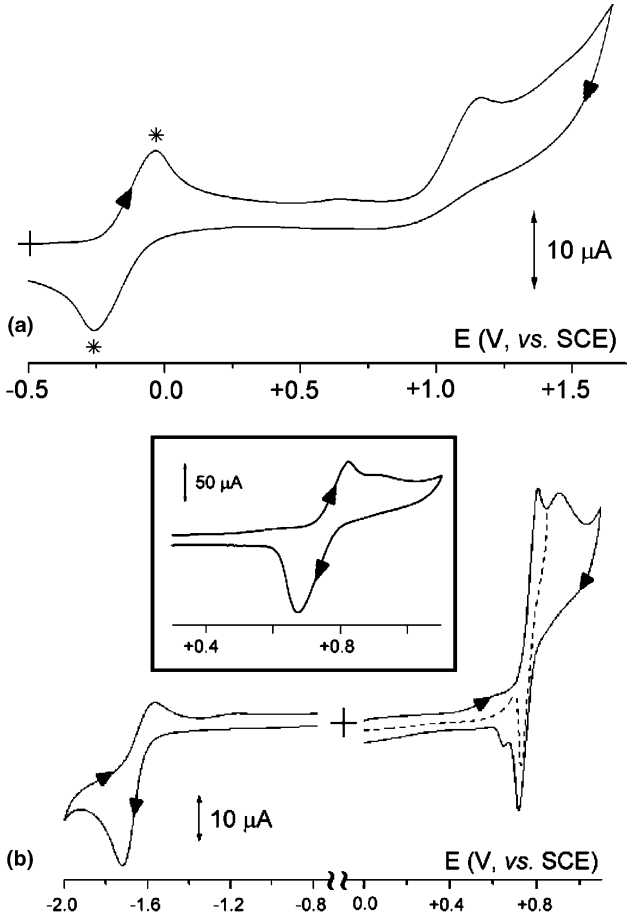


Fig. 2. Cyclic voltammograms recorded at a platinum electrode on a CH_2Cl_2 solution of: (a) $Mo(\eta^6\text{-}C_6H_5CF_3)(CO)_3$ (1.6×10^{-3} M) and $Fe(C_5Me_5)_2$ (1.7×10^{-3} M); (b) $Mo_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ (1.4×10^{-3} M); inset: scan rate 1.0 $V\,s^{-1}$; $[NBu_4][PF_6]$ (0.2 M) as supporting electrolyte. Scan rate 0.2 $V\,s^{-1}$, unless otherwise specified.

Table 3
Formal electrode potentials (V, vs. SCE), peak current ratios and peak-to-peak separations (mV) for the redox processes in CH_2Cl_2 solution

Complex	$E_{p_{(0/+)}}{}^{a,b}$	$E^{0\prime}_{(0/2+)}$	ΔE^b_p	i_{pc}/i^b_{pa}	$E^{0\prime}_{(0/2-)}$	ΔE^b_p	i_{pa}/i^b_{pc}
$Mo(\eta^6\text{-}C_6H_5\text{-}C_6H_5)(CO)_3$	+0.96						
$Mo(\eta^6\text{-}C_6H_5F)(CO)_3$	+0.96						
$Mo(\eta^6\text{-}C_6H_5CF_3)(CO)_3$	+1.17						
$Mo[\eta^6\text{-}C_6H_5\text{-}3,5\text{-}C_6H_3(C_6H_5)_2](CO)_3$	+0.91						
$Mo_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{-}C_6H_5)(CO)_6$		+0.77	77	0.8	−1.65	140	0.4
$Cr_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{-}C_6H_5)(CO)_6$					−1.65[c]		

[a] Peak potential value for irreversible processes.
[b] Measured at 0.2 $V\,s^{-1}$.
[c] In THF solution, recalculated from [43c].

(see below), we can assume the one-electron nature of the molybdenum-centred oxidation on the timescale of the voltammetric experiment. This assumption is based on the appearance of essentially similar peak heights for equimolar amounts of the complexes $Mo(\eta^6\text{-}C_6H_5\text{-}CF_3)(CO)_3$ and decamethylferrocene which, due to their substantially identical molecular weights (326.1 and 326.3, respectively), should have similar diffusion coefficients.

A close examination of Table 3 shows that the oxidation potentials of $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$, $Mo(\eta^6\text{-}C_6H_5F)(CO)_3$ and $Mo[\eta^6\text{-}C_6H_5\text{–}3,5\text{-}C_6H_3\text{-}(C_6H_5)_2]\text{-}(CO)_3$ are similar, suggesting that phenyl and fluoride substituents have similar effects on the oxidation of the central metal atom. On the other hand, the presence of the stronger electron-withdrawing CF_3 substituent in $Mo(\eta^6\text{-}C_6H_5CF_3)(CO)_3$ makes the oxidation more difficult, the oxidation potential shifting to more positive values.

The electrochemical behaviour of $Mo_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ is reported in Fig. 2(b). At a platinum electrode it exhibits both an oxidation and a reduction, with some degree of reversibility. The analysis [46] of the cyclic voltammograms of the oxidation process, with scan rates varying from 0.02 to 2.0 $V\,s^{-1}$, was complicated by both the reagent diffusion and the adsorption processes, resulting in an appreciable decrease of the $i_{pa}v^{-1/2}$ and the $i_{pa}v^{-1}$ functions upon increasing the scan rate. The adsorption phenomena, which are evident from the shape of the voltammogram, see inset of Fig. 2(b), increases the current ratio above unity, a value of 1.2 being obtained in the voltammogram recorded at 1.0 $V\,s^{-1}$. Changing the electrode material to gold or glassy carbon did not prevent the observed adsorption effects. Moreover, the formed cation rapidly decomposes, as confirmed by the absence of a directly associated reduction peak at low scan rates (from 0.02 to 0.05 $V\,s^{-1}$). Only by operating at high scan rates, the i_{pc}/i_{pa} ratio has finite values.

The analysis of the cyclic voltammograms of the cathodic process with increasing scan rate showed the current function $i_{pa}v^{-1/2}$ to be constant, whereas the current ratio i_{pa}/i_{pc} decreases. Such trend is diagnostic [46] of a relatively slow first-order reversible chemical process following a reversible electron transfer. As a matter of fact, a consumption of two electrons *per* molecule was evaluated by controlled potential coulometry ($E_w = -1.8$ V). Unfortunately, cyclic voltammetric tests on the exhaustively reduced solution did not clarify the nature of the reduction process, due to a series of oxidation processes in the range from 0.0 V to +1.5 V (Fig. 3, Supplementary material). This suggests that the electrochemically-formed reduced species is not stable under the experimental conditions at variance with the corresponding chromium derivative which affords the $[Cr_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6]^{2-}$ dianion. The latter has been independently obtained as the lithium salt by reduction of $Cr_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ with lithium anthracenide [44].

Comparison of the intensities of the oxidation and of the reduction peaks within the mononuclear complexes (Fig. 2(a)) with those of the dinuclear derivative $Mo_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ (Fig. 2(b)) suggests that the anodic process for the latter compound is bielectronic.

We can now compare the redox ability of the molybdenum complexes reported in this paper with that of the chromium analogue. First of all, the mononuclear chromium complexes afford irreversible reductions while the molybdenum complexes undergo irreversible oxidations. This fact suggests that the region of the HOMO–LUMO gap of the molybdenum species is shifted towards less positive (more negative) potentials with respect to the chromium analogues. As a consequence, access to oxidation processes is favoured whereas the reduction processes occur at negative potentials and are masked by the solvent discharge. As far as the dinuclear derivative is concerned, we observe that the dimolybdenum complex undergoes a single two-electron reduction at about the same potential as the dichromium complexes but the electrogenerated dianion is notably less stable. Moreover, the dimolybdenum derivative is oxidized giving a short-lived dication at variance with the dichromium complexes. Finally, we point out that, similar to the case of the dichromium complexes, the appearance of a single two-electron reduction for $Mo_2(\eta^6\text{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ means that no phenyl–phenyl interaction (or communication) in-

volving the two molybdenum centres occurs within the biphenyl ligand. This is further confirmed by the appearance of a single two-electron oxidation process.

3. Conclusions

This paper has shown that the thermal reaction is not a general method for the preparation of arene tricarbonyl derivatives of molybdenum from $Mo(CO)_6$, due to the thermal lability of the products. On the other hand, the DMF adduct *fac*-$Mo(CO)_3(DMF)_3$ in the presence of $BF_3 \cdot Et_2O$, has been shown to be a valuable starting material, leading to polyarene and fluoro derivatives of general formula $Mo(\eta^6\text{-arene})(CO)_3$. Moreover, we have prepared the dinuclear compound $Mo_2(\eta^6{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ through a thermal displacement of co-ordinated toluene in $Mo(\eta^6\text{-}C_6H_5\text{–}CH_3)(CO)_3$ in the presence of $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$.

The dimolybdenum complex $Mo_2(\eta^6{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ undergoes a single two-electron reduction at about the same potential as the dichromium complex $Cr_2(\eta^6{:}\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_6$ [44], but the electrogenerated dianion is notably less stable than that of the heavier metal. Moreover, the dimolybdenum compound gives the corresponding short-lived dication more easily than the dichromium complexes.

4. Experimental

4.1. General

Unless otherwise stated, all of the operations were carried out under an atmosphere of nitrogen. Solvents were dried by conventional methods prior to use. The compounds *fac*-$Mo(CO)_3(CH_3CN)_3$ [47], *fac*-$Mo(CO)_3(DMF)_3$ [15], and $Mo(\eta^6\text{-}C_6H_5CH_3)(CO)_3$ [15] were prepared according to literature.

IR spectra were recorded on a FT-1725X instrument on solutions or nujol mulls prepared under rigorous exclusion of moisture and air. NMR spectra were recorded with a Varian Gemini 200 BB spectrometer at 200, 50.31 and 188.1 MHz for ^1H, ^{13}C, and ^{19}F resonances, respectively. Chemical shifts are referred to TMS as external standard for ^1H and ^{13}C, and to $CFCl_3$ for ^{19}F. Materials and apparatus for electrochemistry have been described elsewhere [48]. The values of the electrochemical potentials are referred to the saturated calomel electrode (SCE) with the one-electron oxidation of ferrocene occurring at +0.39 V.

4.2. *fac*-$Mo(CO)_3(CH_3CN)_3CH_3CN$: crystal structure solution and refinement

Crystals of *fac*-$Mo(CO)_3(CH_3CN)_3 \cdot CH_3CN$ were obtained by slow cooling of a saturated acetonitrile solution. IR (nujol mull, cm^{-1}): 2276m-w, 2250s, 1909vs, 1779vs. Crystallographic data and details of the structure refinement are in Table 4. Data were collected at 223 K with the Mo K_α ($\lambda = 0.71073$ Å) radiation on a Enraf–Nonius-CAD4 diffractometer equipped with a graphite monochromator. A set of 5683 reflections with indices $-10 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 16$, $-18 \leqslant l \leqslant 17$, were collected with the θ/θ scan. No absorption correction was applied before averaging symmetry equivalent data. The structure was solved by direct methods [49], and the structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on F^2 [50]. Maximum and minimum from a final Fourier map were 1.033 and −0.891 e Å^{-3}.

4.3. Synthesis and characterization of $Mo(\eta^6\text{-arene})(CO)_3$ derivatives (arene = diphenyl; 1,3,5-triphenylbenzene; C_6H_5F; $C_6H_5CF_3$)

4.3.1. $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$, **1**

A suspension of *fac*-$Mo(CO)_3(DMF)_3$ (2.513 g, 6.3 mmol) and diphenyl (9.7 g, 63 mmol) in Et_2O (50 ml) was slowly added (1.5 h) at room temperature of a solution of $BF_3 \cdot OEt_2$ (2.4 ml, 18.9 mmol) in Et_2O (100 ml). After 8 h stirring at room temperature, the yellow solution was transferred to a sublimation apparatus, the solvent was removed in vacuo at room temperature, and the residue was gently warmed at ca. 40 °C/10^{-2} mmHg in order to remove the excess diphenyl. The residue of the sublimation was dissolved in heptane at 60 °C. By slow cooling, well shaped crystals of $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$ formed which were collected by filtration and shortly dried in vacuo at room temperature (1.2 g). Anal. Calc. for $C_{15}H_{10}MoO_3$: C, 53.9; H, 2.9. Found: C, 53.9; H, 3.7%. ^1H NMR (CD_2Cl_2): δ 7.48 (3H, m), 7.43 (2H, m), 6.02 (2H, d, 6.6 Hz), 5.87 (1H, t, 6.6 Hz), 5.64 (2H, t, 6.2 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 136.6, 129.1, 127.6, 115.3, 95.7, 94.5, 93.6. IR (nujol mull, cm^{-1}): 3083w, 3065w, 1962s, 1872vs-br, 1581w, 1526w, 1494m-w, 1401w, 1153m, 756m, 692m-f, 617m-f, 589m-f, 505m-f; (toluene, cm^{-1}): 1971s, 1896s; (cyclohexane, cm^{-1}): 1981s, 1912s; (heptane, cm^{-1}): 1983s, 1915s; (dichloromethane, cm^{-1}): 1970s, 1891s.

On cooling at ca. −30 °C, the mother liquor gave additional 0.635 g of $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$ for a total yield of 87%.

4.3.2. $Mo[\eta^6\text{-}C_6H_5\text{–}3,5\text{-}C_6H_3(C_6H_5)_2](CO)_3$, **2**

A suspension of *fac*-$Mo(CO)_3(DMF)_3$ (1.176 g, 2.94 mmol) and 1,3,5-triphenylbenzene (0.902 g, 2.94 mmol) in Et_2O (50 ml) was slowly added (2 h) at room temperature of a solution of $BF_3 \cdot OEt_2$ (1.1 ml, 8.8 mmol) in Et_2O (100 ml). Formation of an oily substance was observed at the end of the addition. After 3 h stirring at room temperature, the yellow suspension was filtered and the solution was dried in vacuo at room tempera-

Table 4
Crystallographic data and details of the structure refinement for *fac*-$Mo(CO)_3(CH_3CN)_3 \cdot CH_3CN$, $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$, $Mo(\eta^6\text{-}C_6H_5F)(CO)_3$, and $Mo(\eta^6\text{-}C_6H_5CF_3)(CO)_3$

Compound	*fac*-$Mo(CO)_3(CH_3CN)_3 \cdot CH_3CN$	**1**	**3**	**4**
Formula weight	344.2	334.2	276.1	326.8
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group (No)	*Pbcm*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	8.2659(9)	6.995(1)	6.6898(7)	6.786(2)
b (Å)	12.672(3)	12.615(3)	11.169(1)	7.758(3)
c (Å)	14.935(4)	15.765(3)	12.846(1)	11.299(3)
α (°)		70.30(2)		96.77(3)
β (°)		84.16(2)	103.24(3)	97.90(3)
γ (°)		79.06(2)		108.20(3)
V (Å^3)	1564.4(6)	1284.9(5)	934.3(2)	551.5(3)
Z	4	4	4	2
d_{calc} (g cm^{-3})	1.461	1.727	1.963	1.964
μ (cm^{-1})	0.846	1.020	1.394	1.222
$\theta_{min/max}$ (°)	2.1–27.0	2.5–27.0	2.45–27.44	3.08–26.97
Reflections unique	1769 ($R_{int} = 0.1600$)	5583 ($R_{int} = 0.0265$)	2135 ($R_{int} = 0.0202$)	2391 ($R_{int} = 0.0521$)
Variables refined	99	343	127	154
R indexes [$I > 2\sigma(I)$]				
R_1	0.0544	0.0334	0.0246	0.0328
wR_2	0.1015	0.0740	0.0616	0.0665
R indexes (all data)				
R_1	0.1088	0.0552	0.0278	0.0469
wR_2	0.1132	0.0801	0.0633	0.0703
Goodness-of-fit	1.016	1.006	1.097	1.072

$R_1 = \sum ||F_o| - |F_c|| / \sum F_o|$.
$wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

ture. The residue was dissolved in cyclohexane (150 ml) and filtered at ca. 70 °C. The volume of the solution was reduced to 20 ml and heptane (50 ml) was added which caused the precipitation of the yellow microcrystalline solid which was recovered by filtration and dried in vacuo at room temperature affording 0.575 g (40% yield) of $Mo[\eta^6\text{-}C_6H_5\text{–}3,5\text{-}C_6H_3(C_6H_5)_2](CO)_3$. Anal. Calc. for $C_{27}H_{18}MoO_3$: C, 66.6; H, 3.7. Found: C, 66.5; H, 3.9%. ^{1}H NMR ($CDCl_3$): δ 7.64–7.49 (13H, m), 6.01 (2H, d, 5.8 Hz), 5.82 (2H, t, 6.4 Hz), 5.56 (1H, t, 5.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.5, 127.3, 126.4, 116.2, 96.8, 93.2, 92.3. IR (Et_2O, cm^{-1}): 1973s, 1900s; (heptane, cm^{-1}): 1982s, 1914s; (dichloromethane, cm^{-1}): 1970s, 1891s.

4.3.3. $Mo(\eta^6\text{-}C_6H_5F)(CO)_3$, **3**, $Mo(\eta^6\text{-}C_6H_5CF_3)(CO)_3$, **4**

Only the preparation of $Mo(\eta^6\text{-}C_6H_5F)(CO)_3$ is described in detail, the trifluoromethylbenzene derivative being obtained in a similar way. A suspension of *fac*-$Mo(CO)_3(DMF)_3$ (1.892 g, 4.74 mmol) and a mixture of fluorobenzene (15 ml) and cyclohexane (25 ml) was slowly added (2 h) at room temperature to a solution of $BF_3 \cdot OEt_2$ (1.8 ml, 14.2 mmol) in Et_2O (100 ml). After 2 h stirring at room temperature, a yellow–brown suspension was obtained which was filtered. The solution was dried in vacuo at room temperature and the residue was dissolved in heptane (60 ml) and filtered at ca. 40 °C, thus obtaining a solid and a solution. The solution was stored for 64 h at ca. −30 °C obtaining yellow crystals (0.139 g) which where collected by filtration, shortly dried in vacuo at room temperature and identified as $Mo(\eta^6\text{-}C_6H_5F)(CO)_3$. Anal. Calc. for $C_9H_5FMoO_3$: C, 39.2; H, 1.8. Found: C, 38.3; H, 1.8%. ^{1}H NMR (C_6D_6): δ 4.46 (3H, m, 3.6 Hz), 3.81 (2H, m, 3.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 114.5 (d, 251.5 Hz), 94.5, 87.5, 80.1. ^{19}F NMR (C_6D_6): δ −129. IR (heptane, cm^{-1}): 1995s, 1926s.

The solid obtained from the filtration was suspended in heptane (50 ml), gently heated at ca. 60 °C and filtered when hot. After 14 h at room temperature, the yellow crystals thus obtained were shown to be identical with the previous crop analytically and spectroscopically (NMR). Total yield: 0.466 g, 36%.

$Mo(\eta^6\text{-}C_6H_5CF_3)(CO)_3$. Yield: 56%. Anal. Calc. for $C_{10}H_{15}F_3MoO_3$: C, 36.8; H, 1.5. Found: C, 36.2; H, 1.9%. ^{1}H NMR ($C_6D_5CD_3$): δ 4.81 (2H, d, 6.6 Hz), 4.37 (1H, t, 6 Hz), 4.20 (2H, t, 6 Hz). ^{19}F NMR (C_6D_6): δ −61.5. IR (heptane, cm^{-1}): 2002s, 1937s; (cyclohexane/Et_2O, cm^{-1}): 1996s, 1926s.

4.4. $Mo(\eta^6\text{-arene})(CO)_3$ derivatives: crystal structure solution and refinement

Arene = diphenyl. Crystals of $Mo(\eta^6\text{-}C_6H_5\text{–}C_6H_5)(CO)_3$ were obtained by slow cooling of a saturated

heptane solution. Crystallographic data and details of the structure refinement are in Table 4. Data were collected at 223 K with the Mo K_α ($\lambda = 0.71073$ Å) radiation on a Enraf–Nonius-CAD4 diffractometer equipped with a graphite monochromator on a crystal of approximate dimensions $0.30 \times 0.14 \times 0.07$ mm^3. A set of 6479 reflections with indices $-8 \leqslant h \leqslant 8$, $-16 \leqslant k \leqslant 2$, $-20 \leqslant l \leqslant 19$, were collected with the $\omega/2\theta$ scan method. A numerical absorption correction (minimum transition 0.843, maximum transition 0.934) was applied before averaging symmetry-equivalent data. The structure was solved by direct methods [49], and the structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on F^2 [50]. Maximum and minimum from a final Fourier map were 0.459 and −0.556 e Å^{-3}.

Arene = C_6H_5F. Crystals of Mo(η^6-C_6H_5F)(CO)$_3$ were obtained by slow cooling of a saturated heptane solution. Crystallographic data and details of the structure refinement are in Table 4. Data were collected at 213 K with the Mo K_α radiation ($\lambda = 0.71073$ Å) on a CCD area detector diffractometer equipped with a graphite monochromator on a crystal of approximate dimensions $0.30 \times 0.30 \times 0.20$ mm^3. A set of 6268 reflections with indices $-8 \leqslant h \leqslant 6$, $-14 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 16$, were collected with the ω-scan method. An empirical absorption correction (minimum transition 0.6799, maximum transition 0.7679) was applied before averaging symmetry-equivalent data. The structure was solved by direct methods [49], and the structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on F^2 [50]. Maximum and minimum from a final Fourier map were 0.462 and −0.379 e Å^{-3}.

Arene = $C_6H_5CF_3$. Crystals of Mo(η^6-$C_6H_5CF_3$)(CO)$_3$ were obtained by slow cooling of a saturated toluene/heptane solution. Crystallographic data and details of the structure refinement are in Table 4. Data were collected at 213 K on a crystal of approximate dimensions $0.39 \times 0.10 \times 0.09$ mm^3. A set of 3893 reflections with indices $-8 \leqslant h \leqslant 8$, $-9 \leqslant k \leqslant 4$, $-14 \leqslant l \leqslant 14$, were collected with the $\theta/2\theta$ scan method in the range $3.08 \leqslant \theta \leqslant 26.97°$. A numerical absorption correction (minimum transition 0.6472, maximum transition 0.8980) was applied before averaging symmetry equivalent data. The structure was solved by direct methods [49], and the structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on F^2 [50]. Maximum and minimum from a final Fourier map were 0.638 and −0.848 e Å^{-3}.

4.5. Synthesis of $Mo_2(\eta^6{:}\eta^6$-C_6H_5–$C_6H_5)(CO)_6$, **5**

A mixture of Mo(η^6-$C_6H_5CH_3$)(CO)$_3$ (0.388 g, 1.45 mmol) and Mo(η^6-C_6H_5–C_6H_5)(CO)$_3$ (0.486 g, 1.46 mmol) in heptane (55 ml) was heated at the reflux temperature for 3 h. The initial solution gave a yellow suspension. The solid was collected by filtration and shortly dried in vacuo at room temperature (0.302 g, 42% yield) of $Mo_2(\eta^6{:}\eta^6$-$C_6H_5C_6H_5)(CO)_6$, **5**. Anal. Calc. for $C_{18}H_{10}Mo_2O_6$: C, 42.0; H, 2.5. Found: C, 41.6; H, 2.5%. ^{1}H NMR ($CDCl_3$): $\delta = 5.79$ (2H, d, 6.0 Hz), 5.65 (2H, t, 6.4 Hz), 5.58 (1H, t, 5.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 94.6$, 93.8, 93.2, 93.0. IR (nujol mull, cm^{-1}): 3100w, 3083w, 1953s, 1870vs-br, 1498w, 1289w, 1150w, 609m-f, 578m-f, 502m-f; (toluene, cm^{-1}): 1969s, 1903s.

An attempt was made to prepare the dinuclear compound by reacting equimolar amounts of *fac*-Mo(CO)$_3$(DMF)$_3$ and Mo(η^6-C_6H_5–C_6H_5)(CO)$_3$ with a solution of $BF_3 \cdot OEt_2$ in Et_2O. After 16 h stirring at room temperature, an IR spectrum of the solution had absorptions typical of the starting materials and Mo(CO)$_6$. On work-up, traces only of the dinuclear compound $Mo_2(\eta^6{:}\eta^6$-$C_6H_5C_6H_5)(CO)_6$, were detected by ^{1}H NMR spectrometry.

5. Supplementary material

Fig. 3. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution of $Mo_2(\eta^6{:}\eta^6$-C_6H_5–$C_6H_5)(CO)_6$ (4.2×10^{-3} M) after exhaustive two-electron reduction at −1.8 V. [NBu_4][PF_6] (0.2 M) as supporting electrolyte. Scan rate 0.2 V s^{-1}.

6. Crystallographic material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 223579, Mo(CO)$_3$-(CH_3CN)$_3 \cdot CH_3CN$; CCDC No. 223580, Mo(η^6-C_6H_5–C_6H_5)(CO)$_3$; CCDC No. 223581, Mo(η^6-C_6H_5F)(CO)$_3$, CCDC No. 223582, Mo(η^6-$C_6H_5CF_3$)(CO)$_3$. Copies of the crystallographic data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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[7] During the preparation of *fac*-$Mo(CO)_3(CH_3CN)_3$, large yellow crystals of *fac*-$Mo(CO)_3(CH_3CN)_3 \cdot CH_3CN$ were obtained from the mother liquor. The IR spectrum (Nujol mull) showed absorptions at 2276(m-w) and 2250(s) cm^{-1}, assigned to Mo-coordinated and to uncoordinated acetonitrile, respectively [8]. Although the molybdenum system is not isostructural with the tungsten analogue, *fac*-$W(CO)_3(CH_3CN)_3$ [9] due to the presence of uncoordinated nitrile, the metrical data are similar in the two compounds as the atomic radii of molybdenum (1.36 Å) and tungsten (1.37 Å) [10] differ only slightly. The mean M–N and M–C bond distances are 2.231 and 1.923 Å, M = Mo, and 2.208 and 1.932 Å, M = W, respectively, and agree with those reported for other acetonitrile carbonyl derivatives of molybdenum(0) such as $Mo(CO)_2$(maleic aldehyde)$(CH_3CN)_2$ [2.206(3) and 1.982(3) Å] [11], $Mo(CO)_3$[bis(2–pyridyl)formamidine]$_2(CH_3CN)$ [2.255(3) and 1.932(4) Å] [12], and *fac*-$Mo(CO)_3$[1,1-bis(diphenylphosphino)ferrocene](CH_3CN) 0.5 H_2O [2.222(2) and 1.958(3) Å] [13]. The C–N distance [1.096(15) Å] of the lattice acetonitrile is shorter than those in the Mo-bonded ligand [N(1)–C(3), 1.134 Å].

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