

Syntheses and structures of molybdenum and tungsten pentabenzylcyclopentadienyl complexes: new chlorination reactions

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Received 30 January 2004; accepted 21 April 2004

Abstract

[M(CpBz)(CO)₃CH₃] (M = Mo, **2a**, W, **2b**; CpBz = C₅(CH₂Ph)₅) have been prepared and reacted with PCl₅ and PhI·Cl₂. Depending on the metal and on the chlorinating reagent used [Mo(CpBz)(η²-COCH₃)Cl₃], **3**, [W(CpBz)Cl₄], **4**, [Mo(CpBz)(CO)₃Cl], **5** and [Mo(CpBz)Cl₄], **6** have been obtained. The molecular structures of all compounds are reported and two conformations have been characterised for the benzyl substituents. In complexes **2a**, **2b** and **5** one phenyl ring bends towards the metals while in **3** and **4** the five phenyls point opposite to the metals.

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Keywords: Molybdenum; Tungsten; Pentabenzylcyclopentadienyl; Oxidation; Chlorination; Carbonyl insertion

1. Introduction

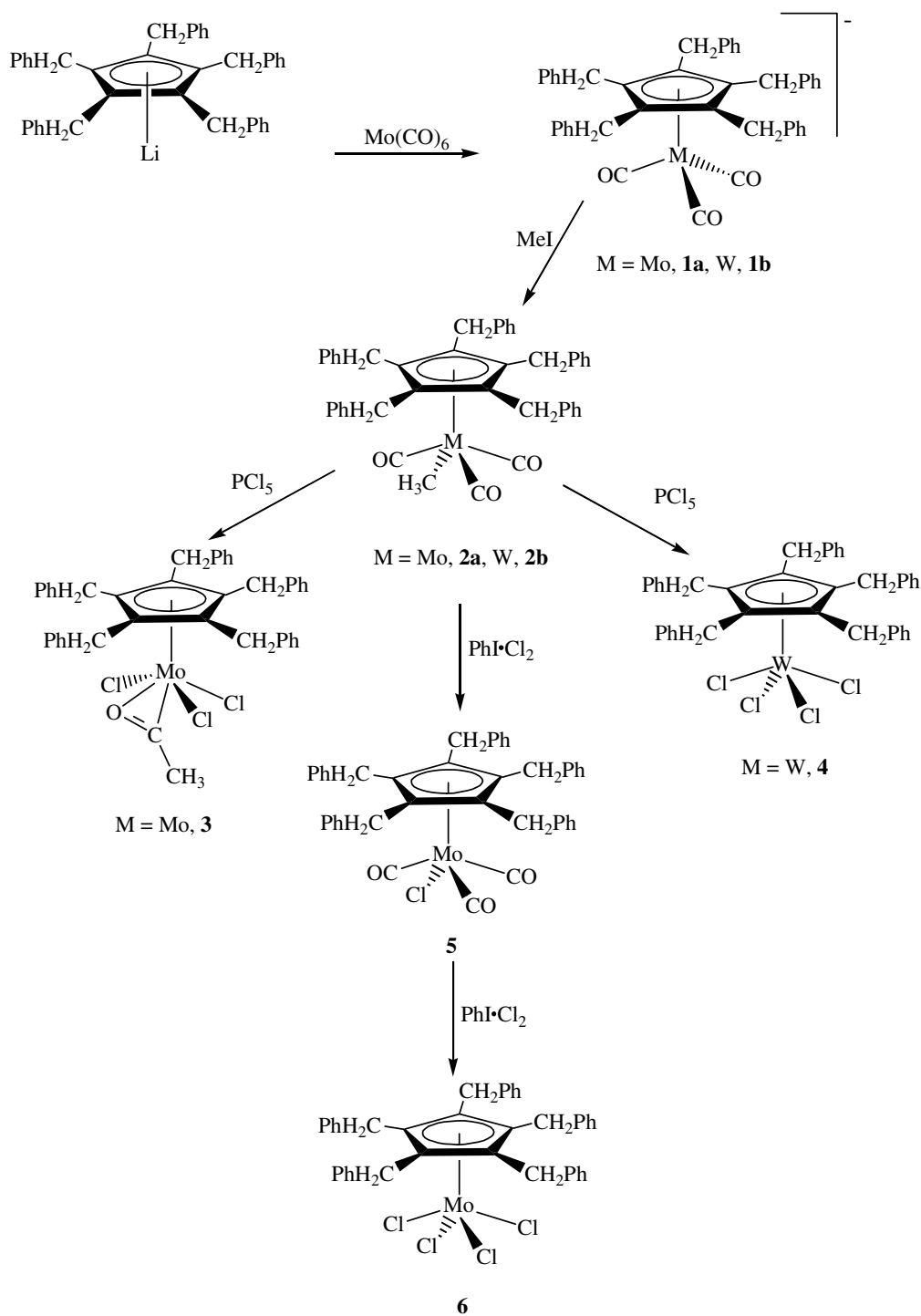
Bulky and polyfunctional cyclopentadienyl ligands have been widely used as support of transition metal complexes since they provide extra thermodynamic stability and kinetic control. Due to stereochemical peculiarities, bulky ligands shield the metal centres and make possible the stabilisation of unusual metal oxidation states and coordination geometries [1]. On the other hand, polyfunctional ligands are able to support specific reactivity patterns and structures that extended the applications of transition metal complexes [2]. Pentabenzylcyclopentadienyl is simultaneously bulky and polyfunctional since it may coordinate as a cyclopentadienyl ligand but also as an arene [3]. These features led us to the syntheses of pentabenzylcyclopentadienyl molybdenum and tungsten complexes aiming to evaluate the specific properties that the ligand confers to the chemistry of half-sandwich molybdenum and tungsten derivatives. Our first results on this subject focused on the synthesis of monocyclopentadienyl chloride compounds by oxidative decarbonylation reactions here presented.

2. Results and discussion

All new compounds presented in this contribution are summarised in Scheme 1. Following a synthetic procedure well established for the syntheses of [MCp'(CO)₃CH₃] (M = Mo, W; Cp' = C₅H₅, Ind and derivatives), treatment of [M(CO)₆] (M = Mo, W) with LiC₅(CH₂Ph)₅ (abbreviated LiCpBz), prepared in situ from reaction of HCpBz [4] with LiBu, led to Li(S)_n-[M(CpBz)(CO)₃] (M = Mo, **1a**, W, **1b**; S = THF, dyglime) that upon reactions with MeI in THF gave [M(CpBz)(CO)₃CH₃] (M = Mo, **2a**, W, **2b**). Reactions of **1a** with a bulkier alkyl group as (CH₃)₃CH₂Br did not lead to the alkyl derivative. Probably due to stereochemical constrain, no reaction was observed. When **1b** was prepared in dyglime and then extracted in THF, its reaction with MeI in THF did not proceed as expected and [Li(CH₃OCH₂CH₂OCH₂CH₂OCH₃)] [W(CpBz)-(CO)₃] has been recovered. The yield of **2b** obtained in these conditions was only 6%, whereas when **1b** was prepared in THF, in analogous experimental conditions, **2b** was prepared in 38% yield.

The reactions of **2a** and **2b** with PCl₅ led to high yield syntheses of a η²-acyl molybdenum complex [Mo-(CpBz)(η²-COCH₃)Cl₃], **3**, and to the expected product

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Scheme 1.

$[\text{W}(\text{CpBz})\text{Cl}_4]$, **4**, in the case of tungsten. By analogy with $[\text{MCp}'(\text{CO})_3\text{CH}_3]$ ($\text{M} = \text{Mo, W}$; $\text{Cp}' = \text{C}_5\text{H}_5$ and derivatives) [5–7] that reacts with PCl_5 to give $[\text{MCp}'\text{Cl}_4]$, we did not expect to obtain complex **3** as the oxidation product of **2a** with PCl_5 . Actually, acyl intermediates have never been claimed to form for Mo or W half-sandwich compounds under similar experimental

conditions and, furthermore, similar reactivity patterns have always been displayed by Mo and W complexes in chlorination reactions. Although acyl derivatives of general formula $[\text{MoCp}'(\text{CO})_3(\sigma\text{-COR})]$ have been described [8,9], alkyl migrations to CO have not been observed in $[\text{MoCp}'(\text{CO})_3\text{CH}_3]$ ($\text{Cp}' = \text{C}_5\text{H}_5, \text{Cp}^*, \text{Ind}$), under pressure of carbon monoxide [10]. In the presence

of AlBr_3 , however, $[\text{MoCp}(\text{CO})_3\text{Me}]$ readily undergoes methyl migration to give $[\text{MoCp}(\text{CO})_2\{\text{C}(\text{OAlBr}_2\text{Me})\}]$ that reacts with CO to give $[\text{MoCp}(\text{CO})_3\{\text{C}(\text{OAlBr}_3)\text{Me}\}]$ and hydrolyses to $[\text{MoCp}(\text{CO})_2(\text{COMe})]$ [11]. Analogous $[\text{MoCp}(\text{CO})_2(\text{PPh}_2\text{R})(\sigma\text{-COMe})]$ ($\text{R} = \text{H}, \text{Ph}$), are formed by reactions of $[\text{MoCp}(\text{CO})_3\text{Me}]$ with the appropriate phosphines [12] and related η^2 -acyl complexes, $[\text{MTp}(\text{CO})_2\{\eta^2\text{-C}(\text{O})\text{R}\}]$ ($\text{M} = \text{Mo}, \text{W}$) have been reported to form by reaction of $[\text{MTp}(\text{CO})_3]^-$ with alkylating reagents [13,14]. The different behaviours shown by CpMo and TpMo based complexes have been reasoned on both stereochemical and electronic arguments [13]. Complex **3** is reminiscent of that reported by Kreissl and co-workers on the protonation of $[\text{WCp}(\text{CO})_2(\equiv\text{CTol})]$ with HCl that leads to $[\text{WCp}(\text{CO})\{\eta^2\text{-C}(\text{O})\text{CH}_2\text{Tol}\}\text{Cl}_2]$ by insertion of CO in a W–C bond [15] and also of $[\text{WCp}(\text{CO})(\text{NCMe})_2(\eta^2\text{-COEt})](\text{BF}_4)_2$ reported by Tilset and co-worker [16] as the oxidation product of $[\text{WCp}(\text{CO})_3\text{Et}]$ in acetonitrile.

The unexpected result obtained with PCl_5 led us to perform reactions of $[\text{Mo}(\text{CpBz})(\text{CO})_3\text{CH}_3]$ with $\text{PhI}\cdot\text{Cl}_2$ as a chlorinating reagent. The reaction of equimolar amounts of **2a** and $\text{PhI}\cdot\text{Cl}_2$ led to the synthesis of $[\text{Mo}(\text{CpBz})(\text{CO})_3\text{Cl}]$, **5**, whereas the use of an excess of $\text{PhI}\cdot\text{Cl}_2$ gave $[\text{Mo}(\text{CpBz})\text{Cl}_4]$, **6**. These results show that the reactivity of $[\text{Mo}(\text{CpBz})(\text{CO})_3\text{CH}_3]$ with $\text{PhI}\cdot\text{Cl}_2$ pursue via (i) the replacement of a Me by a Cl ligand and (ii) decarbonylation of the metal centre in consequence of its oxidation, a pattern that has been commonly observed for similar complexes [7,17].

The different mechanisms displayed by the chlorination reactions described and that compound **3** is not a precursor of **6** are also corroborated by the lack of reactivity between $[\text{Mo}(\text{CpBz})(\eta^2\text{-COCH}_3)\text{Cl}_3]$ and an excess of PCl_5 or $\text{PhI}\cdot\text{Cl}_2$.

The characterisation of all complexes by IR shows a common pattern due to the pentabenzylcyclopentadienyl fragment and characteristic peaks attributable to terminal CO and acyl ligands. The IR acyl frequency in **3** is shifted to higher wavenumbers compared to values for Mo(II) η^2 -acyl compounds [13].

The ^1H NMR spectra of the diamagnetic complexes (**1a**, **1b**, **2a**, **2b** and **5**) show one singlet for the methylene protons and the usual 2:2:1 patterns for the benzyl aromatic protons of the pentabenzylcyclopentadienyl ligand, indicating that there are no constraints to the free rotation of the benzyl groups. Complexes **2a**, **2b** and **5** present two carbon resonances for the carbonyl carbons that integrate 2:1, according to their relative positions to the methyl or chloride ligands.

The molecular structures of $[\text{M}(\text{CpBz})(\text{CO})_3\text{CH}_3]$ ($\text{M} = \text{Mo}$, **2a**; W , **2b**), $[\text{Mo}(\text{CpBz})(\eta^2\text{-COCH}_3)\text{Cl}_3]$, **3**, $[\text{W}(\text{CpBz})\text{Cl}_4]$, **4** and $[\text{Mo}(\text{CpBz})(\text{CO})_3\text{Cl}]$, **5** have been determined by X-ray diffraction. Relevant bond lengths and angles are presented in Table 1 (for complexes **2a**, **2b**, and **5**), and Table 2 (for complexes **3** and **4**). Figs. 1–5

Table 1

Relevant bond distances and angles as well as torsion angles for compounds **2a**, **2b** and **5**

	$[\text{M}(\text{CpBz})(\text{CO})_3\text{Me}]$		$[\text{Mo}(\text{CpBz})(\text{CO})_3\text{Cl}]$, 5
	2a ($\text{M} = \text{Mo}$)	2b ($\text{M} = \text{W}$)	
M–C(6)/Cl(1)	2.290(6)	2.306(3)	2.8041(18)
M–C(7)	1.981(4)	1.999(3)	1.997(6)
M–C(8)	2.048(5)	1.985(3)	2.047(8)
M–C(9)	1.971(4)	1.970(3)	1.983(6)
C(7)–O(1)	1.139(5)	1.150(3)	1.145(7)
C(8)–O(2)	1.034(6)	1.151(3)	0.995(8)
C(9)–O(3)	1.121(5)	1.153(4)	1.125(7)
M–CT	2.023(8)	2.022(5)	2.018(8)
Cl(1)/C(6)–M–C(7)	75.9(2)	74.67(12)	78.5(2)
Cl(1)/C(6)–M–C(8)	127.7(2)	130.00(11)	129.02(19)
Cl(1)/C(6)–M–C(9)	72.4(2)	71.57(12)	71.18(19)
C(7)–M–C(8)	74.1(2)	76.13(11)	74.4(3)
C(7)–M–C(9)	105.4(2)	104.35(11)	107.0(2)
C(8)–M–C(9)	75.7(2)	77.61(12)	76.6(3)
CT–M–Cl(1)/C(6)	116.5(9)	112.5(8)	115.4(9)
CT–M–C(7)	130.6(8)	131.2(7)	129.9(9)
CT–M–C(8)	115.9(8)	117.3(7)	115.1(9)
CT–M–C(9)	123.8(8)	129.1(7)	123.2(9)
M–C(1)–C(10)–C(11)	–11.1(5)	10.0(3)	–11.6(7)
M–C(2)–C(20)–C(21)	–173.5(3)	–157.1(2)	–172.3(4)
M–C(3)–C(30)–C(31)	171.8(3)	–169.3(2)	172.0(4)
M–C(4)–C(40)–C(41)	170.5(3)	–171.8(3)	171.3(4)
M–C(5)–C(50)–C(51)	157.9(3)	173.4(3)	158.5(4)

CT – CpBz centroid.

depict ORTEP representations of the complexes presenting the corresponding atomic labelling scheme.

The metal co-ordination geometry in complexes $[\text{M}(\text{CpBz})(\text{CO})_3\text{X}]$ ($\text{M} = \text{Mo}$, $\text{X} = \text{CH}_3$, **2a**, **Cl**, **5**; $\text{M} = \text{W}$, $\text{X} = \text{CH}_3$, **2b**) is very similar and can be best described as four-legged piano-stool, usually observed for $\text{M}(\text{Cp}')\text{L}_4$ complexes. As expected and registered in Table 1, the CpBz(Centroid)–M–X angles are larger than the corresponding basal angles. In these complexes the metal to basal mean square plane distances are 1.086(2), 1.057(2) and 1.099(3) Å for **2a**, **2b** and **5**, respectively, while the distances to the CpBz mean square plane are 2.022(2), 2.021(2) and 2.017(2) Å, respectively. The CpBz mean square and the basal planes define dihedral angles of 5.4(2)°, 5.1(2)° and 7.6(3)° respectively in **2a**, **2b** and **5**. The phenyl rings of four benzyl fragments are directed opposite to the metal and one is bended down towards the metals but sufficiently far apart to prevent any bonding interaction. This arrangement is also observed in the solid state structure of $[\text{Mo}(\text{CpBz})(\text{CO})_3\text{I}]$ [4]. To better characterize the relative conformation of the phenyl rings we present in Table 1 the torsion angles of the pending benzyl arms defined as M–C(CpBz ring)–C(CH₂ bridge)–C_{ipso}. In all compounds the phenyl rings bending towards the metals define torsion angles of 10–11°, while the others present

Table 2
Relevant bond distances, angles as well as torsion angles for compound **3** and **4**

	Mo(CpBz ₅)(η ² -COMe)Cl ₃ , 3 (M = Mo)	W(CpBz ₅)Cl ₄ , 4 (M = W)
M–C(6)	2.041(13)	–
M–O(1)	2.156(9)	–
M–Cl(1)	2.399(3)	2.279(7)
M–Cl(2)	2.364(3)	2.308(7)
M–Cl(3)	2.425(3)	2.263(6)
M–Cl(4)	–	2.247(8)
C(6)–O(1)	1.201(14)	–
C(6)–C(7)	1.435(18)	–
M–CT1	2.078(9)	2.028(7)
M–CT2	2.01(1)	–
Cl(1)–M–C(6)	73.6(4)	–
Cl(1)–M–O(1)	79.8(3)	–
C(6)–M–O(1)	33.1(4)	–
Cl(1)–M–CT2	76.2(4)	–
Cl(2)–M–C(6)	98.5(4)	–
Cl(2)–M–O(1)	131.7(2)	–
Cl(2)–M–CT2	115.6(6)	–
Cl(3)–M–C(6)	71.6(4)	–
Cl(3)–M–O(1)	79.8(3)	–
Cl(3)–M–CT2	75.2(5)	–
Cl(1)–M–Cl(2)	85.82(13)	78.9(5)
Cl(1)–M–Cl(3)	141.79(12)	131.8(2)
Cl(1)–M–Cl(4)	–	82.9(6)
Cl(2)–M–Cl(3)	84.15(13)	80.6(4)
Cl(2)–M–Cl(4)	–	138.6(3)
Cl(3)–M–Cl(4)	–	84.5(6)
CT1–M–Cl(1)	108.3(5)	113.5(7)
CT1–M–Cl(2)	111.1(6)	111.1(7)
CT1–M–Cl(3)	109.7(6)	114.6(7)
CT1–M–Cl(4)/CT2	133.4(7)	110.2(7)
M–C(1)–C(10)–C(11)	–163.3(9)	–161.8(9)
M–C(2)–C(20)–C(21)	–150.9(9)	–163.8(9)
M–C(3)–C(30)–C(31)	–150.0(9)	–161.3(9)
M–C(4)–C(40)–C(41)	–158.3(9)	–176.1(9)
M–C(5)–C(50)–C(51)	–170.4(9)	–158.7(9)

CT1 – CpBz centroid; CT2 – medium point in the bond C(6)–O(1).

angles that range from 157° to 173°. The M–C bond lengths and the bond distances and angles within the ligands in complexes **2a**, **2b** and **5** are similar to those reported for other cyclopentadienyl carbonyl compounds as [Mo(CpBz)(CO)₃I] [4], [M(C₅H₅)(CO)₃Cl] (M = Mo, W) [16], [Mo(CO)₃][Mo(CO)₃Cl](η⁵, η⁵:η¹-C₅H₄CH₂C₅H₃) [17]. However, the Mo–Cl distance encountered in **5** is much longer (2.8041(18) Å) than the typical values for this bond in similar compounds (ca. 2.5 Å) [17,18] and as long as the Mo–I distance in [Mo(CpBz)(CO)₃I] [4]. Similar distances have been determined for bimetallic metal–metal bonded molybdenum complexes as Mo₂(hpp)₄Cl (hpp = anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine) [19] where the long Mo–Cl distance has been taken as indicative of a less significant bonding contribution. Yet, the long Mo–Cl distance found in **5** is surprising and,

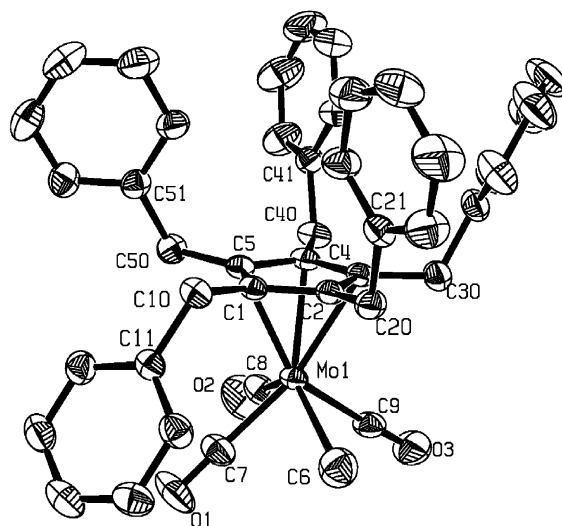


Fig. 1. Molecular structure of complex **2a**. H atoms were excluded for clarity, thermal ellipsoids at 30% probability level.

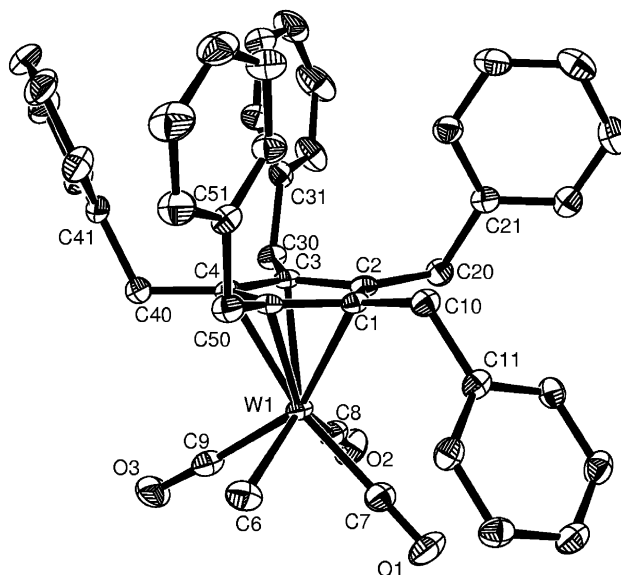


Fig. 2. Molecular structure of complex **2b**. H atoms were excluded for clarity, thermal ellipsoids at 50% probability level.

since it is not accompanied by other unusual features in the structure, it may reflect the disorder in the basal ligands. The CO ligand *trans* to the Mo–Cl bond in **5** displays a slightly different geometry with a longer M–C distance (Mo(1)–C(8), 2.047(8) Å) and a shorter C≡O distance, 0.995(8) Å (See Table 1).

Table 2 presents relevant bond distances and angles for complexes **3** and **4**. The molecular structure of [Mo(CpBz)(η²-COCH₃)Cl₃], **3**, shows the five phenyl rings of the pentabenzylcyclopentadienyl ligand opposite to the molybdenum as can be geometrically confirmed by the torsion angles presented in Table 2 that range from 150.0(9)° to 170.4(9)°. Considering the medium point of the C–O bond of the η²-C(O)CH₃ ligand

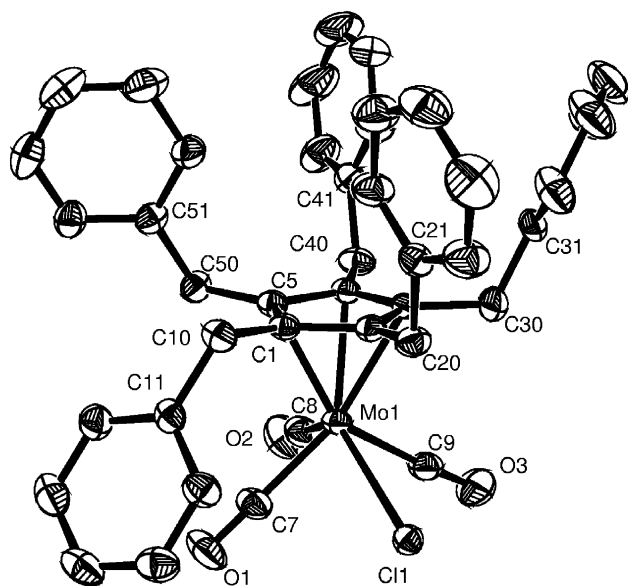


Fig. 3. Molecular structure of complex 5. H atoms were excluded for clarity, thermal ellipsoids at 30% probability level.

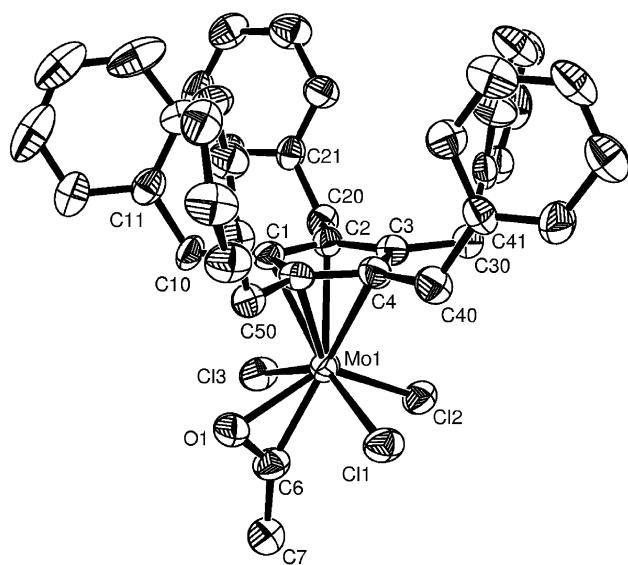


Fig. 4. Molecular structure of complex 3. H atoms were excluded for clarity, thermal ellipsoids at 30% probability level.

(CT2), the metal co-ordination may be described as four-legged piano stool, with a metal CpBz mean square plane distance of 2.068(5) Å and a Mo basal plane distance of 0.961(2) Å. The two planes are practically parallel to each other with an angle of 1.5(7)° between them. Again the basal bonding angles present values smaller than the ones involving the CpBz (see Table 2). The distances between the molybdenum and the five carbons of the Cp ring may be separated in two ranges. Shorter bond lengths are formed between the metal and carbons C(1) and C(5) (2.324(10) and 2.323(11) Å) that are closer to the acyl ligand. The other Mo–C distances

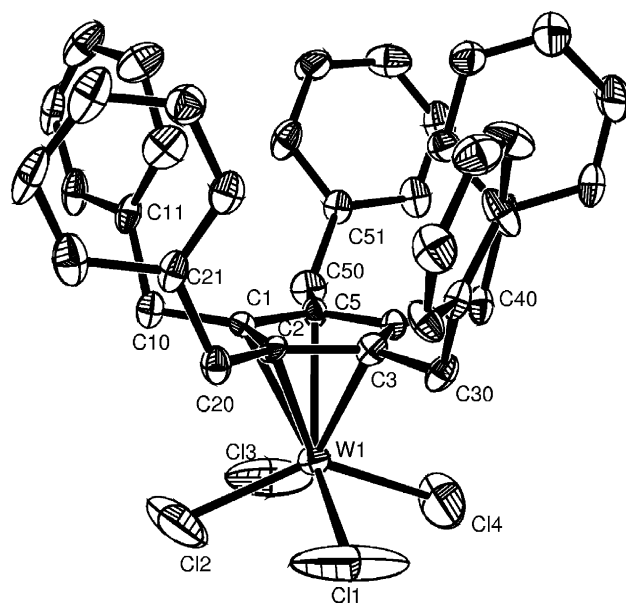


Fig. 5. Molecular structure of complex 4. H atoms were excluded for clarity, thermal ellipsoids at 30% probability level.

(Mo–C(2), Mo–C(3) and Mo–C(4)) reflect the *trans* effect of the η^2 -C(O)CH₃ ligand, particularly striking in the Mo–C(3) bond length (2.512(10) Å). The Mo–C(6), C(6)–O(1) and Mo–O(1) distances (2.041(13), 1.201(14) and 2.156(9) Å) are close to the values reported for octahedral Mo(II) compounds, [MoTp(CO)_nL_m(η^2 -C(O)R)] (*n* = 2, *m* = 0, R = Me, Ph; *n* = *m* = 1, L = P(OMe)₃, PEt₃, R = Me) [13].

[W(CpBz)Cl₄], **4**, also exhibits a four-legged piano stool geometry with angles between the basal ligands in the range 78.9(5)° to 84.5(6)° (see Table 2). The basal plane is parallel to the mean square plane of the CpBz ring with an angle of 1.0(2)° between them. The W atom is 2.028(5) Å away from the CpBz mean square plane and 0.864(3) Å from the basal plane. The benzyl phenyl groups are all directed opposite to the metal with torsion angles between 158.7(9)° and 176.1(9)°. The W–CpBz(cent) distance 2.028(7) Å and the W–Cl bond lengths vary between 2.247(8) and 2.308(7) Å. The data found for the molecular structure of **4** are close to those reported for [W(C₅Et₅)Cl₄] [7] that also point the five ethyl groups to the same side, opposite to the metal.

3. Conclusions

The compounds described have been prepared by oxidative decarbonylation of half-sandwich molybdenum and tungsten with PCl₅ and PhI·Cl₂. Likewise other WCp' derivatives in similar conditions, [W(CpBz)(CO)₃CH₃] led to [W(CpBz)Cl₄]. The behaviour of [Mo(CpBz)(CO)₃CH₃] is less straightforward since, depending on the chlorinating reagent used,

[Mo(CpBz)(η^2 -COCH₃)Cl₃] or [Mo(CpBz)Cl₄] have been obtained. The formation of a η^2 -acyl ligand by insertion of CO into the Mo–CH₃ bond implies that the oxidation of the metal by PCl₅ precedes the replacement of the methyl ligand by Cl, as observed in the reaction of **2a** with PhI·Cl₂. The stage at which the methyl migration takes place and the role of the CpBz ligand in the stabilisation of possible intermediates are unknown. However, it is plausible to envisage that, if a cationic intermediate plays a key role in the methyl migration, as proposed by Tilset and co-worker [16], the stabilisation of such compound may, in the case of **2a**, be achieved by intramolecular assistance of a phenyl ring through η^2 -coordination. This kind of interaction has been recognized in [MoCp(CO)₂(PPh₃)⁺] where one of the triphenylphosphine rings bends to coordinate the metal centre [20]. The molecular structures of all classes of compounds reported have been determined by single crystal X-ray diffraction. The pentabenzylcyclopentadienyl ligand adopts two arrangements for the phenyl rings. In complexes **2a**, **2b** and **5** four phenyls point opposite to the metals and one bends down to the metals, while in **3** and **4** the phenyl rings are directed up, opposite to the metals.

4. Experimental

4.1. General procedures

All manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk techniques except those where O₂ from air was used as an oxidant. Solvents were predried and distilled from the following drying agents: hexane and dichloromethane (CaH₂), d₆-benzene, toluene, THF, diglyme and diethyl ether (Na). Literature methods were used to prepare HCpBz [4]. NMR spectra were recorded on a Varian Unity 300 instrument at room temperature and were referred to the residual ¹H and ¹³C NMR resonances of the solvents. Mass spectra were recorded on a Finnegan MAT System 8200 spectrometer. Elemental analyses were performed on a Fisons Instruments 1108 device.

4.2. [Li(CH₃OCH₂CH₂OCH₂CH₂OCH₃)] [W(η^5 -C₅Bz₅)-(CO)₃] (**1b**)

To a solution of HCpBz (1.24 g, 2.40 mmol) in about 10 ml of diglyme, a 1.6 M solution of BuLi in hexanes (1.50 ml, 2.40 mmol) was added dropwise. After 20 min of reaction, the resulted purple solution was added to W(CO)₆ (0.87 g, 2.40 mmol) in about 10 ml of diglyme, resulting a yellow mixture after 5 min of reaction. After refluxed for 24 h, the reaction mixture was evaporated to dryness, and the resulted black oil was dissolved in about 10 ml of THF. Then a solution of MeI (0.30 ml,

4.81 mmol) in THF was added. After refluxed for 2 h, the solvent was removed. A red fraction was extracted in diethyl ether, which was cooled at –20 °C and yielded 0.12 g (6%) yellow crystals of [W(η^5 -C₅Bz₅)(CO)₃CH₃] (**2b**). The fraction insoluble in ether was extracted in toluene yielded by cooling at –20 °C a white solid identified by NMR as [LiMeOCH₂CH₂OCH₂CH₂OMe][W(η^5 -C₅Bz₅)(CO)₃]. ¹H NMR (C₆D₆, 300 MHz): δ 7.07–6.95 (m, 25H, *o*-C₆H₅, *m*-C₆H₅, *p*-C₆H₅), 4.12 (s, 10H, CH₂Ph), 3.42 (s, 6H, CH₃O), 3.17, 3.13 (d, 8H, CH₃OCH₂CH₂OCH₂CH₂OCH₃). ¹³C NMR (C₆D₆): δ 231.5 (CO), 142.1 (*i*-C₆H₅), 129.4 (*o*-C₆H₅), 128.0 (*m*-C₆H₅), 125.7 (*p*-C₆H₅), 106.1 (C₅Bz₅), 70.6, 69.2 (H₃CO–CH₂CH₂OCH₂CH₂OCH₃), 59.4(CH₃O), 33.7 (CH₂).

4.3. [Mo(CpBz)(CO)₃CH₃], **2a**

A solution of HCpBz (1.54 g, 2.98 mmol) in 15 ml of THF was treated, at 0 °C, with a 1.6 M solution of BuLi in hexanes (1.92 ml, 3.07 mmol). The mixture was stirred for 1 h and added to a suspension of [Mo(CO)₆] (0.79 g, 2.98 mmol) in THF. The mixture was then refluxed for 24 h and MeI (0.81 ml, 13.00 mmol) diluted in ca. 5 ml of THF was added. The reflux was kept for more 3 h and the volatiles were then evaporated off. The residue was extracted in diethyl ether leading to a brown solution that was filtered off, concentrated and cooled to –20 °C to yield yellow crystals of [Mo(CpBz)(CO)₃CH₃] (1.80 g, 85%). ¹H NMR (C₆D₆): δ 6.87 (m, 15H, *m*-C₆H₅, *p*-C₆H₅), 6.60 (m, 10H, *o*-C₆H₅), 3.55 (s, 10H CH₂Ph), 0.59 (s, 3H, CH₃). ¹³C{¹H}NMR (C₆D₆): δ 242.3, 227.4 (CO) 139.4 (*i*-C₆H₅), 129.0 (*o*-C₆H₅), 128.3 (*m*-C₆H₅), 126.4 (*p*-C₆H₅), 110.1 (C₅(CH₂Ph)₅), 32.3 (CH₂Ph), –9.7 (CH₃). IR (KBr): ν (C≡O), cm^{–1}: 2011(s), 1934(s), 1919(s), 1904(s). MS (FAB⁺): 712 (M + 1)⁺, 654 (M–2CO)⁺, 626 (M–3CO)⁺, 611 (M–3CO–CH₃)⁺, 515 (C₅Bz₅)⁺. Anal. Calc. for C₄₄H₃₈O₃Mo: C, 74.36; H, 5.39. Found: C, 74.46; H, 5.79.

4.4. [W(CpBz)(CO)₃CH₃], **2b**

A 1.6 M solution of BuLi in hexanes (2.30 ml, 3.69 mmol) was added dropwise, at 0 °C, to a solution of HCpBz (1.91 g, 3.69 mmol) in 15 ml of THF. The reaction proceeded for 1 h and the solvent was then evaporated to dryness. The product obtained was dissolved in DMF and added to a suspension of [W(CO)₆] (1.31 g, 3.73 mmol) in the same solvent. The mixture was refluxed for 3.5 h. Removal of the solvent led to a black oil that was dissolved in THF. MeI (1.00 ml, 16.00 mmol) dissolved in THF (8–10 ml) was then added to and the solution was refluxed for 3 h. The volatiles were removed and the residue extracted in diethyl ether and filtered. Yellow crystals of **2b** formed from diethyl ether solution at –20 °C (yield 1.11 g, 38%). ¹H NMR (C₆D₆):

δ 6.86 (m, 15H, *m*-C₆H₅, *p*-C₆H₅), 6.63 (m, 10H, *o*-C₆H₅), 3.58 (s, 10H CH₂Ph), 0.69 (s, 3H, CH₃). ¹³C{¹H}NMR (C₆D₆): δ 232.5, 218.0 (CO), 139.2 (*i*-C₆H₅), 129.0 (*o*-C₆H₅), 128.3 (*m*-C₆H₅), 126.5 (*p*-C₆H₅), 108.8 (C₅(CH₂Ph)₅), 32.4 (CH₂Ph), -22.1 (CH₃). IR (KBr): ν (C≡O), cm⁻¹: 2009(s), 1926(s), 1893(s). Anal. Calc. for C₄₄H₃₈O₃W: C, 66.17; H, 4.80. Found: C, 66.16; H, 4.90.

4.5. [Mo(CpBz)(COCH₃)Cl₃], 3

A dichloromethane solution of [Mo(CpBz)(CO)₃-CH₃] (0.90 g, 1.26 mmol) was added to a suspension of PCl₅ (0.66 g, 3.15 mmol) in dichloromethane. The

solution rapidly changed colour to dark purple. The mixture was heated under reflux for 8 h and the solvent was then evaporated off. The dark red oil obtained was extracted in diethyl ether and the solution was filtered and concentrated leading to dark red crystals. Yield, 0.87 g, 90%. IR (KBr): ν (C=O), cm⁻¹: 1625(m). Anal. Calc. for C₄₂H₃₈Cl₃OMo: C, 66.28; H, 5.03. Found: C, 66.67; H, 5.04.

4.6. [W(CpBz)Cl₄], 4

A solution of [W(CpBz)(CO)₃CH₃] (0.80 g, 0.99 mmol) in dichloromethane was added to a suspension of PCl₅ (0.52 g, 2.50 mmol) in the same solvent. A dark red

Table 3
Experimental details on X-ray data collection and structure refinement

	Compound 2a	Compound 2b	Compound 3	Compound 4	Compound 5
Empirical formula	C ₄₄ H ₃₈ O ₃ Mo ₁	C ₄₄ H ₃₈ O ₃ W ₁	C ₄₂ H ₃₈ Cl ₃ O ₁ Mo ₁	C ₄₀ H ₃₅ Cl ₄ W ₁	C ₄₃ H ₃₅ Cl ₁ O ₃ Mo ₁
Formula weight	710.68	798.59	761.01	841.33	731.10
Temperature (K)	293(2)	120(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069	1.54184	0.71069	0.71069
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P2 ₁ /n	P $\bar{1}$
Unit cell dimensions	$a = 9.955(4)$ Å, $b = 9.992(4)$ Å, $c = 18.327(6)$ Å, $\alpha = 91.38(2)^\circ$, $\beta = 91.46(2)^\circ$, $\gamma = 102.75(2)^\circ$	$a = 9.8295(10)$ Å, $b = 9.8894(10)$ Å, $c = 18.178(2)$ Å, $\alpha = 89.926(2)^\circ$, $\beta = 88.271(4)^\circ$, $\gamma = 77.808(4)^\circ$	$a = 9.867(5)$ Å, $b = 10.909(5)$ Å, $c = 19.068(5)$ Å, $\alpha = 101.70(2)^\circ$, $\beta = 97.13(3)^\circ$, $\gamma = 114.66(3)^\circ$	$a = 10.699(5)$ Å, $b = 16.173(5)$ Å, $c = 20.338(5)$ Å, $\beta = 94.03(2)^\circ$	$a = 9.958(5)$ Å, $b = 9.988(5)$ Å, $c = 18.264(7)$ Å, $\alpha = 91.33(2)^\circ$, $\beta = 91.57(2)^\circ$, $\gamma = 103.09(2)^\circ$
Volume (Å ³)	1776.6(12)	1726.4(3)	1775.5(13)	3510(2)	1767.9(14)
Z	2	2	2	4	2
Calculated density (Mg/m ³)	1.328	1.536	1.423	1.592	1.373
Absorption coefficient (mm ⁻¹)	0.408	3.386	5.342	3.623	0.486
F(000)	736	800	782	1668	752
Crystal size	0.60 × 0.30 × 0.09 mm	0.49 × 0.18 × 0.15 mm	0.5 × 0.3 × 0.1 mm	0.9 × 0.6 × 0.2 mm	0.9 × 0.65 × 0.15 mm
Crystal morphology	Parallelepiped	Parallelepiped	Parallelepiped	Parallelepiped	Parallelepiped
Colour	Yellow	Yellow	Dark red	Dark red	Red
Theta range for data collection (°)	2.09–24.97	3.04–27.47	4.60–66.94	1.61–25.97	2.10–24.97
Limiting indices	-11 ≤ h ≤ 11, -11 ≤ k ≤ 0, -21 ≤ l ≤ 21	-12 ≤ h ≤ 12; -12 ≤ k ≤ 12; -23 ≤ l ≤ 23	0 ≤ h ≤ 11, -13 ≤ k ≤ 11, -22 ≤ l ≤ 22	0 ≤ h ≤ 13, -19 ≤ k ≤ 0, -25 ≤ l ≤ 25	-11 ≤ h ≤ 11, 0 ≤ k ≤ 11, -21 ≤ l ≤ 21
Reflections collected/unique	6577/6191 [R _(int) = 0.0130]	29056/7795 [R _(int) = 0.0504]	6451/6064 [R _(int) = 0.0885]	7238/6861 [R _(int) = 0.1273]	6705/6110 [R _(int) = 0.0290]
Completeness to theta	99.4% (θ = 24.97)	98.7% (θ = 27.47)	96.1% (θ = 66.94)	100.0% (θ = 25.97)	98.5% (θ = 24.97)
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	6191/0/568	7795/0/585	6064/0/420	6861/0/407	6110/0/434
Goodness-of-fit on F ²	1.024	1.042	1.024	0.936	1.048
Final R indices [I > 2σ(I)]	R ₁ = 0.0458, wR ₂ = 0.1168	R ₁ = 0.0241, wR ₂ = 0.0537	R ₁ = 0.1050, wR ₂ = 0.2690	R ₁ = 0.0849, wR ₂ = 0.1985	R ₁ = 0.0636, wR ₂ = 0.1637
R indices (all data)	R ₁ = 0.0589, wR ₂ = 0.1234	R ₁ = 0.0265, wR ₂ = 0.0545	R ₁ = 0.1507, wR ₂ = 0.2949	R ₁ = 0.1787, wR ₂ = 0.2339	R ₁ = 0.0844, wR ₂ = 0.1773
Extinction coefficient	None	None	0.0026(5)	None	0.0010(13)
Absorption correction	Psi scan	Sortav	None	Difabs	Difabs
Largest differential peak and hole (e Å ⁻³)	1.952 and -0.454	1.047 and -1.904	1.381 and -1.312	1.985 and -2.295	2.033 and -0.834

solution formed almost immediately and gas evolution was observed. The mixture was stirred for 24 h and filtered. The solvent was evaporated to dryness leading to an orange solid in 92% yield (0.76 g). Anal. Calc. for $C_{40}H_{35}Cl_4W$: C, 57.10; H, 4.19. Found: C, 56.98; H, 4.31.

4.7. $[Mo(CpBz)(CO)_3Cl]$, **5**

$[Mo(CpBz)(CO)_3CH_3]$ (**3a**) (1.52 g, 2.14 mmol) in dichloromethane was added dropwise, at $-40\text{ }^\circ\text{C}$, to a solution of $PhI \cdot Cl_2$ (0.59 g, 2.14 mmol) in the same solvent. The colour of the reaction mixture turned dark red almost immediately and gas evolution was observed. The mixture was stirred overnight and solvent was then evaporated to dryness. The residue was extracted with hexane and the solution was filtered and evaporated to dryness. Crystals suitable for X-ray diffraction were grown from diethyl ether at $-20\text{ }^\circ\text{C}$. 1H NMR (C_6D_6 , 300 MHz): δ 6.88 (m, 15H, *m*- C_6H_5 + *p*- C_6H_5), 6.62 (m, 10H, *o*- C_6H_5), 3.72 (s, 10H CH_2Ph). ^{13}C NMR (C_6D_6): δ 227.4, 205.7 (CO), 139.4 (*i*- C_6H_5), 129.0 (*o*- C_6H_5), 128.3 (*m*- C_6H_5), 126.7 (*p*- C_6H_5), 113.2 (C_5Bz_5), 33.3 (CH_2). IR (KBr disc): $\nu(C\equiv O)$, cm^{-1} : 2032(s), 1963(s).

4.8. $[Mo(CpBz)Cl_4]$, **6**

$[Mo(\eta^5-C_5Bz_5)(CO)_3CH_3]$ (**3a**) (2.21 g, 3.10 mmol) in dichloromethane was added dropwise, at $-40\text{ }^\circ\text{C}$, to a solution of $PhI \cdot Cl_2$ (11.25 mmol) in the same solvent. The colour turned into red almost immediately and gas evolution was observed. The mixture was allowed to stir overnight. The solvent was removed under vacuum to give a red oil that was washed with cold hexane and left a dark-red powder (1.55 g, $\eta = 66\%$).

Anal. Calc. for $C_{40}H_{35}MoCl_4$: C, 63.76; H, 4.68. Found: C, 63.52; H, 4.79. EPR (C_6D_6): singlet with Mo satellites, $g = 1.976$, $\alpha_{Mo} = 38\text{ G}$.

5. X-ray diffraction experimental determination

Crystallographic and experimental details of crystal structure determinations for the five compounds are given in Table 3. Suitable crystals of complexes **2a**, **4** and **5** were mounted on a MACH3 Nonius diffractometer equipped with Mo radiation ($\lambda = 0.71069\text{ \AA}$). Data from compound **3** was collected on a TURBO CAD4 with a Cu rotating anode ($\lambda = 1.54180\text{ \AA}$). Data were collected at room temperature. For compound **2b**, data was collected at 120 K using a CCD with Mo radiation at the EPSRC, University of Southampton. Solution of all the molecular structures were made using direct methods program SIR97 [21] and SHELXL [22] and refinement, both included in the package of programs WINGX-Version 1.64.03b [23]. For all complexes all

non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions riding in the parent C atoms except for compound **2b** where they were located in the electron density map and refined. The poor crystal quality of compound **4** (seen in the R_{int} value obtained) prevented the refinement to lower R values. In compound **5** the Cl atom shows some disorder but no model gave a better R factor or better atomic displacement parameter, the residual electron density found in this complex reflects this disorder. Different absorption corrections were used in the crystal data and are referred in Table 3 [24,25]. Torsion angles, mean square planes and other geometrical parameters were calculated using PARST [26]. More experimental details are given in the Supplementary Material. Illustrations of the molecular structures were made with ORTEP 3 [27]. Data was deposited in CCDC under the deposit numbers CCDC 229976–229980 for compounds **2a**, **2b**, **3**, **4** and **5**, respectively.

Acknowledgements

We are grateful to Fundação para a Ciência e a Tecnologia, Portugal, that funded this work (POCTI/QUI/34400/2000 and SFRH/BPD/3590/2000).

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