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Molybdenum complexes containing substituted cyclopenta[*l*]phenanthrenyl ligand

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ABSTRACT

The synthesis of new cyclopenta[*l*]phenanthrenyl complexes $[(\eta^5\text{-}C_{17}H_{10}Me)(\eta^3\text{-}C_3H_5)Mo(CO)_2]$ and $[(\eta^5\text{-}C_{17}H_9(COOMe)N(CH_2)_4)(\eta^3\text{-}C_3H_5)Mo(CO)_2]$ is described. Although these compounds are structural analogues their reactivity is different. Protonation of $[(\eta^5\text{-}C_{17}H_{10}Me)(\eta^3\text{-}C_3H_5)Mo(CO)_2]$ gives a stable ionic compound $[(\eta^5\text{-}C_{17}H_{10}Me)Mo(CO)_2(NCMe)_2][BF_4]$ while its analogue containing both tertiary amino and carboxylic ester groups $[(\eta^5\text{-}C_{17}H_9(COOMe)N(CH_2)_4)(\eta^3\text{-}C_3H_5)Mo(CO)_2]$ decomposes under the same conditions. $[(\eta^5\text{-}C_{17}H_{10}Me)Mo(CO)_2(NCMe)_2][BF_4]$ reacts with cyclopentadiene to give a stable η^4-complex $[(\eta^4\text{-}C_5H_6)(\eta^5\text{-}C_{17}H_{10}Me)Mo(CO)_2][BF_4]$ that was successfully oxidized to the Mo(IV) dicationic compound $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{17}H_{10}Me)Mo(CO)_2][Br][BF_4]$.

1. Introduction

There is currently considerable interest in the π-allyl complexes $[Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ (Cp′ = substituted Cp; Cp = $\eta^5\text{-}C_5H_5$). They serve as effective precursors for the synthesis of molybdenocenes substituted in one cyclopentadienyl ring $[CpCp'MoL_2]^{n+}$ [1–5]. Protonation of $[Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ with HBF_4 followed by cyclopentadiene coordination and oxidation gives dicationic complexes $[CpCp'Mo(CO)_2]^{2+}$ [1,2].

Several routes have been developed for the synthesis of $[CpMo(\eta^3\text{-}C_3H_5)(CO)_2]$. The original one is based on photochemical decarbonylation of σ-allyl compound $[CpMo(\eta^1\text{-}C_3H_5)(CO)_3]$ [6]. The indenyl analogues $[CpMo(\eta^1\text{-}C_3H_5)(CO)_3]$ (Cp′ = $\eta^5\text{-}C_9H_7$, $\eta^5\text{-}C_9Me_7$) undergo η^1–η^3 allyl ligand rearrangement spontaneously without necessity of UV irradiation [7,8]. A more convenient route giving $[CpMo(\eta^3\text{-}C_3H_5)(CO)_2]$ starts from the allyl complex $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2X]$ (X = Cl or Br) and the lithium cyclopentadienide. It gives the product in 70–80% yield [1,9] and was extended for compounds with indenyl ($\eta^5\text{-}C_9H_7$) [10], fluorenyl ($\eta^5\text{-}C_{13}H_9$) [1], dibenzo[*c*,*g*]fluorenyl ($\eta^5\text{-}C_{21}H_{13}$) [11] and cyclopentadienyl ligands substituted with trimethylsilyl groups ($\eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$) [2,12] and carboxylic ester function ($\eta^5\text{-}C_5H_4COOMe$) [2]. An alternative route avoiding LiCp and low temperature procedures was developed for unsubstituted cyclopentadienyl complex $[CpMo(\eta^3\text{-}C_3H_5)(CO)_2]$. It is available through reaction of $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ with an excess cyclopentadiene and NEt_3 [1]. Amino acid derivatives were synthesized using another synthetic strategy. Lithiation of $[CpMo(\eta^3\text{-}C_3H_5)(CO)_2]$ followed by a treatment with CO_2 gives after water work up a compound with a carboxylic acid group in the cyclopentadienyl ring $[(\eta^5\text{-}C_5H_4COOH)Mo(\eta^3\text{-}C_3H_5)(CO)_2]$. This compound serves as the effective precursor for a variety of amino acid substituted cyclopentadienyl molybdenum compounds [13].

The aim of this work is to describe synthesis and reactivity of new molybdenum complexes containing a substituted cyclopenta[*l*]phenanthrenyl (dibenzo[*e*,*g*]indenyl) ligand.

2. Results and discussion

2.1. Synthesis of the substituted cyclopenta[*l*]phenanthrenes

Cyclopenta[*l*]phenanthrenes **3** and **6** were prepared according to Scheme 1. Synthesis of starting ketones **2** and **4** was done using a modified protocol [14]. Hydroxy-derivative **1** is available through condensation of 9,10-phenanthrenequinone and methyl acetoacetate as was previously described for the ethyl ester analogue (**1a**) [15]. The reaction of the compound **1** with hydriodic acid produces compound **2** in high yield (90%). Here described methyl ester (**2**) seems to be more stable toward acid hydrolysis than the ethyl analogue (**2a**) because **1a** gives a product of decarboxylation **4** under the same conditions [15]. The synthesis of the ketone **4** was optimized. It is given by a reaction of compound **2** with trifluoroacetic acid (tfa) in high yield (86%).

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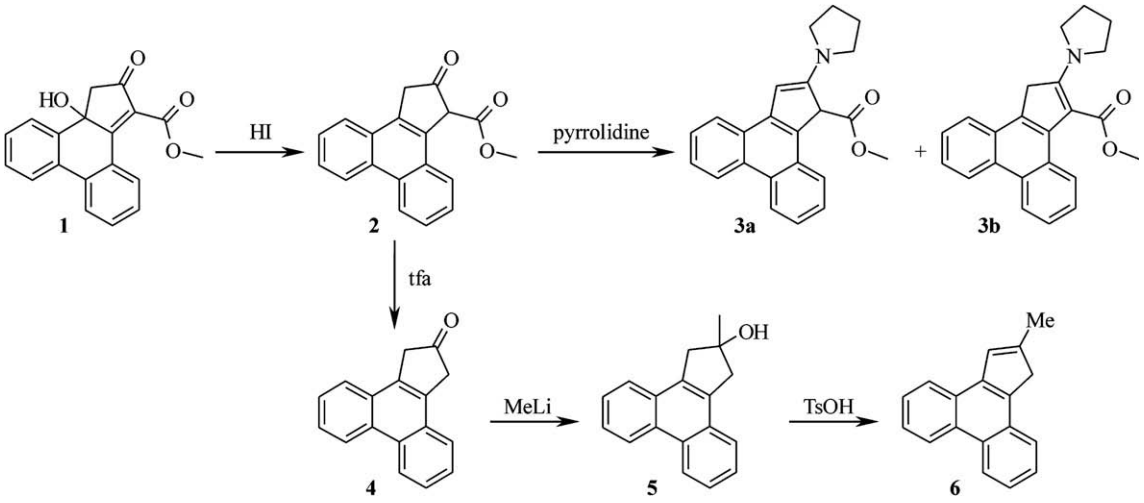


Scheme 1. Synthesis of substituted cyclopenta[*l*]phenanthrenes **3** and **6**.

Condensation of compound **2** with pyrrolidine gives cyclopenta[*l*]phenanthrene substituted with both methoxycarbonyl and tert amino functions (**3**). 2-Methyl-1*H*-cyclopenta[*l*]phenanthrene (**6**) was prepared from compound **4** in line with the previously described procedure [16].

2.2. Characterization of compounds *2–4*

Synthesis of compound **2** and its acid hydrolysis were followed by NMR and infrared spectroscopy. Appearance of the compound **2** is evident from two very strong bands of CO stretching that were found in the infrared spectrum at 1765 and 1720 cm^{-1}. They were assigned to ν_{CO}(CO) and ν_{CO}(COOMe), respectively. Compound **2** gives a characteristic phenanthrene pattern in the ^1H NMR spectrum (8.70–7.59 ppm), signals of CH (4.75 ppm), CH_2 (3.91 ppm) and CH_3 group (3.70 ppm). Molecular structure of compound **2** determined by X-ray crystallography is shown in Fig. 1.

Ketone **4** shows only one band in the C=O stretching region at 1746 cm^{-1}. The obtained NMR data are in agreement with those reported previously [17].

The NMR spectroscopic measurements prove that $CDCl_3$ solution of cyclopenta[*l*]phenanthrene **3** consists of isomers **3a** and **3b**, see Scheme 1. Their molar ratio was found to be 3:1. The ^1H NMR spectrum of **3** gives two series of signals at 8.71–6.63 ppm that were assigned to the phenanthrene protons. Multiplets of the pyrrolidine CH_2 groups were observed at 3.49–3.29 ppm and 2.06–1.97 ppm. Protons of the methoxycarbonyl group appear at 3.64 ppm (**3a**) and 3.95 ppm (**3b**). Integral intensity of the cyclopentadiene protons was used for the assignment of the isomers. Isomer **3a** gives two singlets of the cyclopentadiene CH groups that were observed at 5.79 and 4.84 ppm while **3a** gives one singlet of the CH_2 group at 3.65 ppm. Infrared spectrum of **3** shows one very strong band of CO stretching at 1721 cm^{-1}. It proves the presence of the ester group in the molecule. Fig. 2 shows the molecular structure of isomer **3a** that was determined by X-ray diffraction analysis.

2.3. Synthesis and characterization of cyclopenta[l]phenanthrenyl molybdenum compounds *7* and *8*

Lithium salts of substituted cyclopenta[*l*]phenanthrenes (**3-Li**, **6-Li**), prepared by treatment of **3** and **6** with one equivalent of *n*-BuLi, react with $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ to give η^5-complexes **7** and **8**, respectively (see Scheme 2). The complex **7** contains substituted cyclopenta[*l*]phenanthrenyl and η^3-allyl ligand as is evident from NMR spectra. Signals of the allyl protons were found at 2.86 (*meso*) 2.86 (*syn*), 0.99 (*syn*), 0.88 (*anti*) and 0.54 (*anti*). An infrared spectrum shows the carbonyl stretching in the

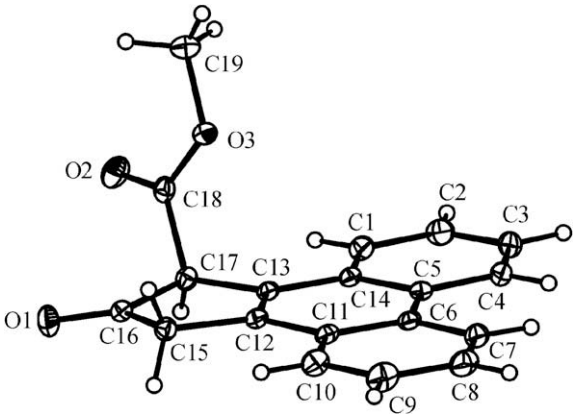


Fig. 1. ORTEP drawing of the compound **2** (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å): C16–O1 = 1.202(2), C18–O2 = 1.202(2), C18–O3 = 1.334(2), C19–O3 = 1.444(2).

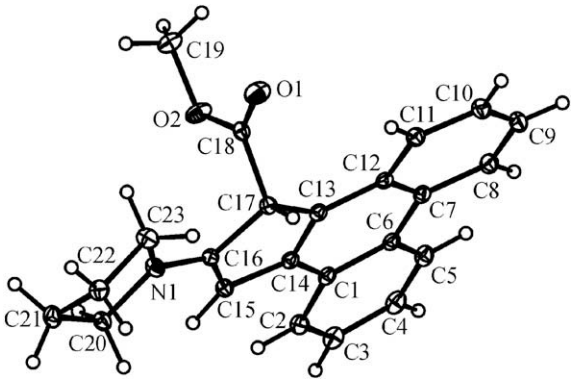
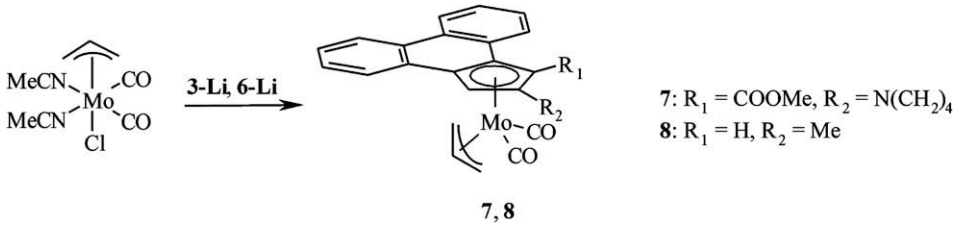


Fig. 2. ORTEP drawing of the compound **3a** (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and bond angles (°): C18–O1 = 1.203(2), C18–O2 = 1.329(2), C19–O2 = 1.446(2), C16–N1 = 1.348(2), C20–N1 = 1.467(2), C23–N1 = 1.463(2), C16–N1–C20 = 121.44(12), C16–N1–C23 = 125.17(14), C20–N1–C23 = 112.26(12).



Scheme 2. Synthesis of allyl molybdenum(II) complexes **7** and **8**.

range typical for [Cp′Mo(η^3-C_3H_5)$(CO)_2$] complexes (ν_a(CO) = 1936 cm^{-1}, ν_a(CO) = 1866 cm^{-1}). The presence of the ester group is evident from the C=O stretching band that was observed at 1712 cm^{-1}.

The ^{1}H NMR spectrum of compound **8** proves the presence of two conformers generated by the orientation of the η^3-coordinated allyl ligand relative to the Cp′. At room temperature, the molar ratio between *endo* (**8a**) and *exo* (**8b**) conformer was found to be 3.7:1. The η^5-bonded 2-methyl cyclopenta[*l*]phenanthrenyl gives a characteristic pattern in the ^{1}H NMR spectrum. It shows three multiplets of the phenanthrene protons at ~8.4, 7.7 and 7.5 ppm, singlet of the cyclopentadienyl part at ~6.3 ppm and singlet of the methyl group at ~2.5 ppm. The infrared spectrum of the compound **8** proves the presence of two carbonyl groups in the molecule. The bands of the very strong intensity, which were assigned to CO stretching, were observed at 1936 cm^{-1} (ν_a(CO)) and 1833 cm^{-1} (ν_s(CO)).

Structures of the complexes **7** and **8** were determined by X-ray crystallography (Figs. 3 and 4). Both molecules have the pseudotetrahedral coordination around molybdenum atom with η^3-allyl, η^5-bonded substituted cyclopenta[*l*]phenanthrenyl and two carbonyl ligands. The allyl ligand of the compound **7** is in *exo* orientation. Bond lengths Mo–C(allyl) are 2.353(2), 2.221(2) and 2.312(2) Å. In compound **8**, the allyl ligand has positional disorder. It was refined in *exo* and *endo* orientation with 50% occupancy. The distance between molybdenum atom and centroid of the η^5-bonded cyclopenta[*l*]phenanthrenyl is 2.0382(8) Å for compound **7** and 2.0273(10) Å for compound **8**. The Mo–C(Cp) distances vary between 2.312(2) and 2.454(2) Å. The cyclopenta[*l*]phenanthrenyl framework in compounds **7** and **8** is not planar but slightly arced.

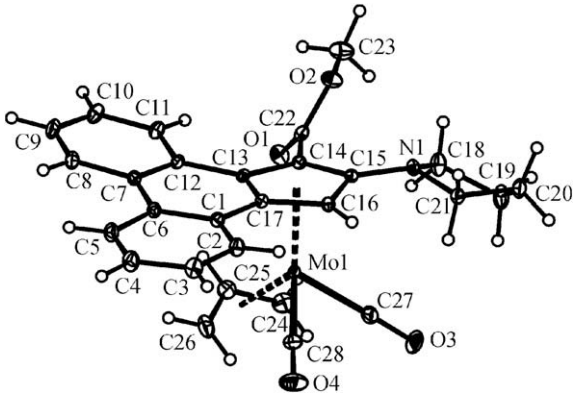


Fig. 3. ORTEP drawing of the compound **7** (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and bond angles (°): Mo1–C27 = 1.942(2), Mo1–C28 = 1.944(2), Mo1–C24 = 2.353(2), Mo1–C25 = 2.221(2), Mo1–C26 = 2.312(2), Mo1–C13 = 2.3809(17), Mo1–C14 = 2.3993(16), Mo1–C15 = 2.4539(18), Mo1–C16 = 2.3118(19), Mo1–C17 = 2.3287(18), C27–O3 = 1.157(3), C28–O4 = 1.160(3), C22–O1 = 1.202(2), C22–O2 = 1.338(2), C23–O2 = 1.456(3), C15–N1 = 1.369(2), C18–N1 = 1.467(3), C21–N1 = 1.465(3), C27–Mo1–C28 = 78.27(10), C15–N1–C18 = 122.85(16), C15–N1–C21 = 117.90(16), C18–N1–C21 = 110.75(16).

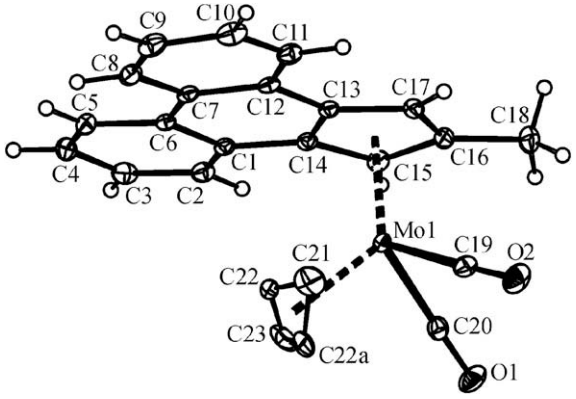


Fig. 4. ORTEP drawing of the compound **8** (ellipsoids: 30% probability). Numbering of all non-hydrogen atoms is shown. Selected bond lengths (Å) and bond angles (°): Mo1–C19 = 1.949(2), Mo1–C20 = 1.949(2), Mo1–C21 = 2.322(2), Mo1–C22 = 2.183(4), Mo1–C22a = 2.362(4), Mo1–C23 = 2.335(2), Mo1–C13 = 2.4150(19), Mo1–C14 = 2.4240(19), Mo1–C15 = 2.331(2), Mo1–C16 = 2.312(2), Mo1–C17 = 2.322(2), C19–O2 = 1.158(3), C20–O1 = 1.158(3), C19–Mo1–C20 = 79.38(9).

The interplanar angles between two external six-membered rings are 9.14(10)° for compound **7** and 6.92(10)° for compound **8**. This is consistent with structures of other η^5-cyclopenta[*l*]phenanthrenyl compounds, in which the polycyclic ligand is also slightly curved: [(η^5-$C_{17}H_{10}$Me)$TiCl_3$] [18], [(η^5-$C_{17}H_8Me_3$)Y(CH_2SiMe_3)$_2$(THF)] [19], [(η^5-$C_{17}H_8Me_3$)Y($CCSiMe_3$)(THF)]$_2$[(μ_2-$CCSiMe_3$)$_2$]·THF [19] and [(η^5-$C_{17}H_{10}$Ph)Ru$(CO)_2$Cl] [20].

The tert amino substituent in compound **7** shows almost trigonal planar nitrogen atom. The sum of the angles at nitrogen atom is 351.5°. This is only slightly smaller than the corresponding value found in the free cyclopenta[*l*]phenanthrene **3a** (358.9°). The bond lengths N–C(sp^2) in both compounds are also almost identical (**7**: 1.369(2) Å; **3a**: 1.348(2) Å). In compounds **7**, the methoxycarbonyl substituent is not coplanar with the five-membered ring. The interplanar angle between COO group and five-membered ring is 59.5(2)°. It contrasts with other molybdenum compounds that have the COR group coplanar with the cyclopentadienyl ring: [Cp′Mo(η^3-C_3H_5)$(CO)_2$] (Cp′ = η^5-C_5H_4COOMe [2]; η^5-C_5H_4COMe [21]; η^5-C_5H_4CO-Phe-OMe [13]).

2.4. Reactivity of cyclopenta[l]phenanthrenyl molybdenum compounds 7 and 8

The attempted protonation of allyl compounds **7** and **8** was successful only in case of compound **8**. Reaction with HBF_4 in presence of acetonitrile gives ionic complex **9** in high yield. Protonation of compounds **7** does not give any tractable product probably owing to preference in protonation of the amino-group that gives unstable products.

NMR spectra of compound **9** prove coordination of two acetonitriles. Signals of their protons are shifted to higher field (1.80 ppm) compared to free acetonitrile (1.94 ppm). This is

apparently the effect of the benzene rings because the analogous cyclopentadienyl compounds show shifting to the lower field ($\delta \sim 2.2$ ppm) [2,22]. Compound **9** has an infrared spectrum with the pattern characteristic of the complexes of the type $[Cp'Mo(CO)_2(NCMe)_2]^+$. It has two medium intensity bands in the region of CN stretching (at 2317 and 2284 cm^{-1}), two bands of very strong intensity in the region of the terminal carbonyl ligands (at 1982 and 1889 cm^{-1}) and a broad band of very strong intensity at 1060 cm^{-1} that was assigned to B–F stretching. The compound **9** was characterized by positive-ion ESI mass spectroscopy. It gives peaks of $[Cp'Mo(CO)_2(NCMe)_2]^+$ ($m/z = 465$) and $[Cp'Mo(CO)_2(NCMe)]^+$ ($m/z = 424$).

The compound **9** reacts with cyclopentadiene giving η^4-diene complex **10** (Scheme 3). Coordination of the cyclopentadiene was evidenced by NMR spectroscopy. The ^1H NMR spectrum shows the typical pattern for the η^4-coordinated cyclopentadiene with two triplets at 5.29 and 4.30 ppm ($^3J(^1H,^1H) = 2.5$ Hz) and two doublets at 4.30 and 3.49 ppm ($^2J(^1H,^1H) = 14.5$ Hz). The vibrations of the carbonyl ligands were found in the infrared spectra at 2025 and 1948 cm^{-1}.

Dicationic molybdenum(IV) compound **11** was obtained through oxidation of compound **10** by Br_2. The ^1H NMR spectrum shows the singlet of the η^5-bonded cyclopentadienyl ring at 6.09 ppm in addition to 2-methyl cyclopenta[*l*]phenanthrenyl pattern that was described above. Compound **11** gives the infrared spectrum with bands of the CO stretching at 2110 and 2060 cm^{-1}. Positive-ion ESI mass spectrum of the compound **11** shows two peaks with pattern characteristic for dications. They were assigned to $[CpCp'Mo(CO)_2]^{2+}$ ($m/z = 224$) and $[CpCp'Mo]^{2+}$ ($m/z = 196$).

3. Conclusions

Synthesis of amino-functionalized cyclopentadienes [23,24] and indenes [23–26] through reaction of the cyclopentenone (indanone) with secondary amines and their use for synthesis of the transition metal complexes [22–26] was the subject of several studies. However this is the first example of applying this method to the synthesis of the cyclopentadienyl-based framework containing both tertiary amino and carboxylic ester groups.

For this purpose, we have optimized the synthesis of methoxycarbonyl-substituted ketone **2** and used it for the assembly of substituted cyclopenta[*l*]phenanthrene **3**. It was found that lithium salt **3-Li** reacts with $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ to give stable η^5-complex $[(\eta^5\text{-}C_{17}H_9(COOMe)N(CH_2)_4)(\eta^3\text{-}C_3H_5)Mo(CO)_2]$ (**7**). Its analogue without the functional groups $[(\eta^5\text{-}C_{17}H_{10}Me)(\eta^3\text{-}C_3H_5)Mo(CO)_2]$ (**8**) was prepared using a similar procedure. Both molybdenum(II) compounds were isolated and characterized by spectroscopic methods and X-ray crystallography.

Although compounds **7** and **8** are structural analogues their reactivity is very different. Protonation of **8** with HBF_4 gives cation $[(\eta^5\text{-}C_{17}H_{10}Me)Mo(CO)_2(NCMe)_2]^+$ (**9**) while compound **7** decomposes under the same conditions. The unusual reactivity of the compound **7** is not presently understood and a more detailed study of the amino-group effect is currently under way.

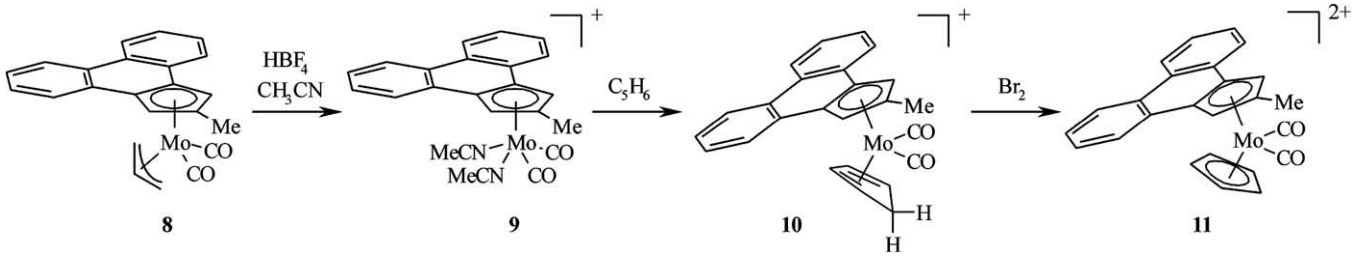
Within this study it was proven that compound **9** is an appropriate building block for the assembly of the CpCp′Mo moiety since its reaction with cyclopentadiene followed by oxidation produced the modified metallocene derivative $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{17}H_{10}Me)Mo(CO)_2]^{2+}$ (**11**). Such highly functionalized molybdenocenes may be of use in biomedical applications where the simplest, non-functionalized Cp_2MoX_2 complexes have already revealed some interesting antitumor activity.

4. Experimental

All operations were performed under nitrogen using conventional Schlenk-line techniques. The solvents were purified and dried by standard methods [27]. $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ [10], 3a-hydroxy-2-oxo-3,3a-dihydro-2H-cyclopenta[*l*]phenanthrene-1-carboxylic acid methyl ester (**1**) [15] and 2-methyl-1H-cyclopenta[*l*]phenanthrene (**6**) [16] were prepared according to literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured in $CDCl_3$ and CD_3CN solutions on Bruker Avance 400 spectrometer at room temperature. Chemical shifts are given in ppm relative to TMS. The infrared spectra were recorded in the 4000–440 cm^{-1} region (step 2 cm^{-1}) on a Mattson 7000 FT-IR spectrometer using KBr pellets. Positive and negative-ion electrospray ionization (ESI) mass spectra were recorded on API-ION TRAP (PO 03 MS). Samples were measured in MeCN solution. The molybdenum containing ions had a clearly visible metal isotope pattern, arising from the distribution: ^{92}Mo 14.84%, ^{94}Mo 9.25%, ^{95}Mo 15.92%, ^{96}Mo 16.68%, ^{97}Mo 9.55%, ^{98}Mo 24.13%, ^{100}Mo 9.63%.[37] Spectra obtained were computer simulated (WSearch32 2005).

4.1. Synthesis of 2-oxo-2,3-dihydro-1H-cyclopenta[l]phenanthrene-1-carboxylic acid methyl ester (2)

Compound **1** (18.6 g; 61 mmol) was suspended in 30 ml of HI (55% aqueous solution) and heated at 120 °C for 1 h. The resulting brown solid was removed by filtration and washed with water. The product was boiled with 10% aqueous solution of $NaHSO_3$. The crude product was filtered, washed with water and Soxhlet extracted with acetone. After first three extraction cycles the brown solution was replaced with pure solvent. Yield: 15.8 g (54 mmol; 90%). Anal. Calc. for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.56; H, 5.22%. ^1H NMR ($CDCl_3$; 400 MHz): 8.70 (d, $^3J(^1H,^1H) = 8.0$ Hz, 2H, $C_{14}H_8$), 7.74–7.59 (m, 6H, $C_{14}H_8$), 4.75 (s, 1H, *CH*COOMe), 3.91 (AX_2, 2H, CH_2), 3.70 (s, 3H, $COOCH_3$). ^{13}C NMR ($CDCl_3$; 101 MHz): 207.3 (*C*O), 168.5 (*C*OOMe), 134.5, 131.6, 130.8, 130.6, 128.6, 128.5 ($6 \times C_{ipso}$, $C_{14}H_8$), 127.7, 127.6, 127.5, 127.1, 125.6, 124.8, 123.7, 123.6 ($8 \times C$, $C_{14}H_8$), 60.7 ($COOCH_3$), 53.2 (*C*HCOOMe), 43.1 (CH_2). FTIR (KBr, cm^{-1}): 1765 vs [ν(CO) of C=O], 1720 vs [ν(CO) of COOMe]. The crystals suitable for X-ray analysis were obtained upon slow evaporation of CH_2Cl_2 solution.



Scheme 3. Assembly of the CpCp′Mo moiety via η^4-C_5H_6 intermediate.

4.2. Synthesis of 2-pyrrolidin-1-yl-H-cyclopenta[l]phenanthrene-1-carboxylic acid methyl ester (**3**)

Compound **2** (2.7 g; 9.3 mmol) was suspended in methanol (50 ml) and treated with an excess of pyrrolidine (3 ml). The mixture was refluxed for 5 min and filtered after cooling at room temperature. The yellow solid was washed with acetone. The crude product was extracted using acetone in Soxhlet extractor. Crystals suitable for X-ray analysis were obtained upon slow evaporation of acetone solution. Yield: 2.04 g; 5.9 mmol; 64%. Anal. Calc. for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.39; H, 6.25; N, 4.11%. ^{1}H NMR ($CDCl_3$; 400 MHz): 3:1 mixture **3a** and **3b**, 8.71 (d, $^3J(^1H,^1H)$ = 8.2 Hz, 1H of **b**, $C_{14}H_8$), 8.67 (d, $^3J(^1H,^1H)$ = 7.7 Hz, 1H of **a**, $C_{14}H_8$), 8.62 (d, 1H of **a** and 1H of **b**, $C_{14}H_8$), 8.06–8.00 (m, 1H of **a** and 1H of **b**, $C_{14}H_8$), 7.90 (d, $^3J(^1H,^1H)$ = 7.9 Hz, 1H of **a**, $C_{14}H_8$), 7.75 (d, $^3J(^1H,^1H)$ = 8.0 Hz, 1H of **b**, $C_{14}H_8$), 6.63–6.35 (m, 4H of **a** and 4H of **b**, $C_{14}H_8$), 5.79 (s, 1H of **a**, C*H*), 4.84 (s, 1H of **a**, C*H*), 3.95 (s, 3H of **b**, COOCH_3), 3.65 (s, 2H of **b**, CH_2), 3.64 (s, 3H of **a**, COOCH_3), 3.49–3.29 (m, 4H of **a** and 4H of **b**, C_4H_8N), 2.06–1.97 (m, 4H of **a** and 4H of **b**, C_4H_8N). ^{13}C NMR ($CDCl_3$; 101 MHz): 171.9 (**a**, *C*OOMe), 170.5 (**b**, *C*OOMe), 156.5 (**b**, *C*–N), 155.0 (**a**, *C*–N), 144.5 (C_{ipso}, **a**, $C_{14}H_8$), 139.4 (C_{ipso}, **b**, $C_{14}H_8$), 131.1, 129.6 (2 × C_{ipso}, **a**, $C_{14}H_8$), 129.3 (C_{ipso}, **b**, $C_{14}H_8$), 127.3, 127.2 (**a**, $C_{14}H_8$), 127.1, 127.0, 126.8, 126.3 (**a**, $C_{14}H_8$), 126.1 (**a**, $C_{14}H_8$), 125.9, 125.5, 123.6 (**a**, $C_{14}H_8$), 123.5, 123.4, 123.3 (**a**, $C_{14}H_8$), 122.9 (**a**, $C_{14}H_8$), 122.6, 121.9 (**a**, $C_{14}H_8$), 101.2 (**b**, *C*=), 94.9 (**a**, *C*H=), 56.6 (**a**, *C*HCOO), 52.8 (**a**, COOCH_3), 51.6 (**b**, COOCH_3), 50.5 (2C, **b**, C_4H_8N), 49.3 (2C, **a**, C_4H_8N), 39.4 (**b**, CH_2), 25.9 (2C, **b**, C_4H_8N), 25.8 (2C, **a**, C_4H_8N). FTIR (KBr, cm^{-1}): 1721 vs [ν(CO)].

4.3. Synthesis of 1,3-dihydro-cyclopenta[l]phenanthren-2-one (**4**)

Compound **2** (5.2 g; 18 mmol) was suspended in a mixture tfa–water (4:1) and stirred under reflux for 6 h. The white precipitate of the product was obtained upon cooling to room temperature. It was filtered on glass frit, washed with water and vacuum dried. Yield: 3.6 g; 15 mmol; 86%. Anal. Calc. for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 88.07; H, 5.28%. NMR data are in agreement with those reported previously [17]. FTIR (KBr, cm^{-1}): 1746 vs [ν(CO)].

4.4. 2-Methyl-2,3-dihydro-1H-cyclopenta[l]phenanthren-2-ol (**5**)

Spectroscopic data are in agreement with those reported previously [16]. ^{13}C NMR ($CDCl_3$; 101 MHz): 135.3, 130.5, 130.1 (3 × $2C_{ipso}$, $C_{14}H_8$), 126.9, 126.1, 125.0, 123.4 (4 × 2C, $C_{14}H_8$), 79.6 (1C, *C*OHMe), 48.3 (2C, CH_2), 28.7 (1C, CH_3).

4.5. 2-Methyl-1H-cyclopenta[l]phenanthrene (**6**)

Spectroscopic data are in agreement with those reported previously [16]. ^{13}C NMR ($CDCl_3$; 101 MHz): 146.2, 140.4, 137.3, 130.4, 129.9, 128.5, 127.7 ($7C_{ipso}$), 126.9, 126.5, 125.7, 125.3, 124.8, 124.6, 123.8, 123.6, 123.5 (9C, *C*H), 43.1 (1C, CH_2), 17.2 (1C, CH_3).

4.6. Synthesis of [(η^5-$C_{17}H_9$(COOMe)N(CH_2)$_4$)(η^3-C_3H_5)Mo(CO)$_2$] (**7**)

Compound **3** (1.7 g, 5 mmol) was diluted with 30 ml of THF, cooled at 0 °C and treated dropwise with 3.1 ml of *n*-BuLi (1.6 mol l^{-1}). The reaction mixture was stirred overnight and added dropwise to the THF solution of [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] (1.55 g, 5 mmol) precooled to −80 °C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The solid residue was washed twice with hot hexane and then extracted with toluene. The yellow extract was evaporated to dryness *in vacuo*. Yield: 1.12 g (2.1 mmol, 42%). Anal. Calc. for $C_{28}H_{26}MoNO_4$: C, 62.69; H, 4.89; N, 2.61. Found: C, 62.99; H, 5.21; N, 2.67%. ^{1}H NMR ($CDCl_3$; 400 MHz): 8.49 (m, 1H, $C_{17}H_9$), 8.42 (d, $^3J(^1H,^1H)$ = 8.1 Hz, 1H, $C_{17}H_9$), 7.84 (d, $^3J(^1H,^1H)$ = 8.1 Hz, 1H, $C_{17}H_9$), 7.71 (m, 1H, $C_{17}H_9$), 7.51 (m, 4H, $C_{17}H_9$), 7.78 (s, 1H, $C_{17}H_9$), 3.98 (s, 3H, COOCH_3), 3.20 (m, 4H, C_4H_8N), 2.86 (m, 1H *meso* and 1H *syn*, C_3H_5), 2.00 (m, 4H, C_4H_8N), 0.99 (d, $^3J(^1H,^1H)$ = 6.0 Hz, 1H, *syn* of C_3H_5), 0.88 (d, $^3J(^1H,^1H)$ = 10.3 Hz, 1H, *anti* of C_3H_5), 0.54 (d, $^3J(^1H,^1H)$ = 10.3 Hz, 1H, *anti* of C_3H_5). FTIR (KBr, cm^{-1}): 1936 vs [ν_a(CO)], 1866 vs [ν_s(CO)], 1712 vs [ν(CO) of COOMe]. The crystals suitable for X-ray analysis were prepared by careful overlayering of the CH_2Cl_2 solution with Et_2O.

4.7. Synthesis of [(η^5-$C_{17}H_{10}$Me)(η^3-C_3H_5)Mo(CO)$_2$] (**8**)

The reaction was carried out as described for compound **7** but with 2-methyl-1H-cyclopenta[*l*]phenanthrene (**6**) (1.16 g, 5 mmol). The crude product was recrystallized from Et_2O and dried *in vacuo* giving yellow powder of compound **8**. Yield: 1.58 g (3.7 mmol, 74%). Anal. Calc. for $C_{23}H_{18}MoO_2$: C, 65.41; H, 4.30. Found: C, 65.55; H, 4.36%. ^{1}H NMR ($CDCl_3$; 400 MHz; 3.7:1 mixture **8a** (*exo*) and **8b** (*endo*)): 8.42 (m, 2H of **a** and 2H of **b**, $C_{17}H_{10}$), 7.72 (m, 2H of **a** and 2H of **b**, $C_{17}H_{10}$), 7.51 (m, 4H of **a** and 4H of **b**, $C_{17}H_{10}$), 6.25 (s, 2H of **a** and 2H of **b**, $C_{17}H_{10}$), 3.28 (m, 1H of **b**, *meso* of C_3H_5), 2.90 (d, $^3J(^1H,^1H)$ = 6.1 Hz, 2H of **b**, *syn* of C_3H_5), 2.46 (s, 3H of **a** and 2H of **b**, CH_3), 1.8 (d, $^3J(^1H,^1H)$ = 7.2 Hz, 2H of **a**, *syn* of C_3H_5), 1.09 (m, 1H of **a**, *meso* of C_3H_5), 0.77 (d, $^3J(^1H,^1H)$ = 10.9 Hz, 2H of **a**, *anti* of C_3H_5), −0.62 (d, $^3J(^1H,^1H)$ = 10.8 Hz, 2H of **b**, *anti* of C_3H_5). FTIR (KBr, cm^{-1}): 1936 vs [ν_a(CO)], 1833 vs [ν_s(CO)]. The crystals suitable for X-ray analysis were prepared upon slow evaporation of the CH_2Cl_2 solution.

4.8. Synthesis of [(η^5-$C_{17}H_{10}$Me)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**9**)

[(η^5-$C_{15}H_{10}$Me)(η^3-C_3H_5)Mo(CO)$_2$] (**8**) (1.40 g, 3.3 mmol) was partially dissolved in a mixture CH_2Cl_2/MeCN (1:10), cooled at 0 °C and treated with one equivalent of HBF_4·Et_2O. After 10 min the reaction mixture was warmed up to room temperature and stirred for additional 1 h. During that time the rest of the yellow solid has dissolved and the solution changed to dark red. The solvents were vacuum evaporated and the crude product was recrystallized from MeCN/Et_2O, washed with Et_2O and vacuum dried giving a red solid. Yield: 1.71 g (3.1 mmol, 94%). Anal. Calc. for $C_{24}H_{19}MoBF_4N_2O_2$: C, 52.32; H, 3.48; N, 5.09. Found: C, 52.46; H, 3.27; N, 5.18%. Positive-ion MS: *m/z* = 465 [M–BF_4]$^+$, 424 (100%) [M–BF_4–MeCN]$^+$. Negative-ion MS: *m/z* = 87 (100%). ^{1}H NMR ($CDCl_3$; 400 MHz): 8.63 (d, $^3J(^1H,^1H)$ = 8.2 Hz, 2H, $C_{17}H_{10}$), 7.89 (d, $^3J(^1H,^1H)$ = 7.8 Hz, 2H, $C_{17}H_{10}$), 7.75 (t, $^3J(^1H,^1H)$ = 7.7 Hz, 2H, $C_{17}H_{10}$), 7.65 (t, $^3J(^1H,^1H)$ = 7.5 Hz, 2H, $C_{17}H_{10}$), 6.27 (s, 2H, $C_{17}H_{10}$), 2.06 (s, 3H, CH_3), 1.80 (s, 6H, CH_3CN). ^{13}C NMR ($CDCl_3$; 101 MHz): 250.1 (2C, *C*O), 140.0 (2C, CH_3*C*N), 131.3 (2C_{ipso}, $C_{17}H_{10}$), 129.4 (2C, $C_{17}H_{10}$), 128.4 (2C, $C_{17}H_{10}$), 126.7 (2C_{ipso}, $C_{17}H_{10}$), 125.3 (2C, $C_{17}H_{10}$), 124.8 (2C, $C_{17}H_{10}$), 115.0 (2C_{ipso}, $C_{17}H_{10}$), 106.8 (C_{ipso}, $C_{17}H_{10}$), 80.0 (2C, $C_{17}H_{10}$), 15.5 (CH_3), 3.1 (2C, CH_3*C*N). FTIR (KBr, cm^{-1}): 2317 m [ν_a(CN)], 2284 m [ν_s(CN)], 1982 vs [ν_a(CO)], 1889 vs [ν_s(CO)], 1060 vs–br [ν_s(BF)].

4.9. Synthesis of [(η^4-C_5H_6)(η^5-$C_{17}H_{10}$Me)Mo(CO)$_2$][BF_4] (**10**)

The solution of compound **9** (1.50 g, 2.7 mmol) in CH_2Cl_2 was treated with an excess of freshly distilled cyclopentadiene (1 ml, 12 mmol). After stirring the reaction mixture for 16 h, the volatiles were evaporated in vacuo. The crude product was washed with ether and small amount of CH_2Cl_2. The yellow powder of compound **10** was obtained after recrystallization from CH_2Cl_2/hexane. Yield: 1.42 g (2.7 mmol, 97%). Anal. Calc. for $C_{25}H_{19}BF_4MoO_2$: C, 56.21; H, 3.59. Found: C, 56.45; H, 3.37%. ^{1}H NMR ($CDCl_3$;

Table 1
Crystallographic data for compounds **2**, **3a**, **7** and **8**.

	2	**3a**	**7**	**8**
Formula	$C_{19}H_{14}O_3$	$C_{23}H_{21}NO_2$	$C_{28}H_{25}MoNO_4$	$C_{23}H_{13}MoO_2$
Formula weight	290.30	343.41	535.43	422.31
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)
a (Å)	10.0410(6)	8.8477(7)	9.4628(3)	10.6513(6)
b (Å)	16.4183(8)	14.8554(12)	13.8899(4)	14.9502(9)
c (Å)	9.1010(4)	12.8897(11)	17.4635(6)	11.6555(6)
α (°)	–	–	–	–
β (°)	113.009(2)	92.755(5)	–	109.084(2)
γ (°)	–	–	–	–
V (Å^3)	1380.99(12)	1692.2(2)	2295.36(13)	1754.00(17)
Z	4	4	4	4
D_c (g cm^{-3})	1.396	1.348	1.549	1.599
μ(mm^{-1})	0.094	0.086	0.608	0.762
F (0 0 0)	608	728	1096	856
Crystal size (mm)	0.10 × 0.08 × 0.06	0.18 × 0.12 × 0.10	0.30 × 0.20 × 0.10	0.20 × 0.20 × 0.08
θ Range	2.53–25.00	2.68–29.69	1.87–33.00	2.44–24.99
Index ranges	$-11 \leqslant h \leqslant 10$	$-12 \leqslant h \leqslant 12$	$-14 \leqslant h \leqslant 12$	$-12 \leqslant h \leqslant 12$
	$-18 \leqslant k \leqslant 19$	$-19 \leqslant k \leqslant 20$	$-20 \leqslant k \leqslant 20$	$-17 \leqslant k \leqslant 17$
	$-10 \leqslant l \leqslant 10$	$-17 \leqslant l \leqslant 17$	$-25 \leqslant l \leqslant 24$	$-13 \leqslant l \leqslant 13$
Reflections collected	11 975	17 113	27 680	26 600
Independent reflections	2358 (R_{int} = 0.028)	4657 (R_{int} = 0.037)	7324 (R_{int} = 0.028)	3089 (R_{int} = 0.020)
Parameters	204	244	308	245
Final R indices [$I > 2\sigma(I)$][a,b]	R_1 = 0.0365, wR_2 = 0.1112	R_1 = 0.0545, wR_2 = 0.1448	R_1 = 0.0255, wR_2 = 0.0664	R_1 = 0.0205, wR_2 = 0.0571
Final R indices (all data)[a,b]	R_1 = 0.0499, wR_2 = 0.1267	R_1 = 0.0861, wR_2 = 0.1647	R_1 = 0.0280, wR_2 = 0.0734	R_1 = 0.0214, wR_2 = 0.0578
Largest difference in peak and hole (e Å^{-3})	0.216, −0.182	0.452, −0.269	0.413, −0.445	0.513, −0.395

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR_2 = \sqrt{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]}$.

400 MHz): 8.52 (m, 2H, $C_{17}H_{10}$), 8.14 (m, 2H, $C_{17}H_{10}$), 7.74 (m, 4H, $C_{17}H_{10}$), 6.63 (s, 2H, $C_{17}H_{10}$), 5.29 (t, $^3J(^1H,^1H)$ = 2.5 Hz, 2H, C_5H_6), 4.30 (t, $^3J(^1H,^1H)$ = 2.5 Hz, 2H, C_5H_6), 3.49 (d, $^2J(^1H,^1H)$ = 14.5 Hz, 2H, C_5H_6), 3.17 (d, $^2J(^1H,^1H)$ = 14.5 Hz, 2H, C_5H_6), 2.40 (s, 3H, CH_3). FTIR (KBr, cm^{-1}): 2025 vs [ν_a(CO)], 1948 vs [ν_s(CO)], 1049 vs–br [ν_s(BF)].

4.10. Synthesis of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{17}H_{10}Me)Mo(CO)_2][Br][BF_4]$ (**11**)

The solution of compound **10** (1.30 g, 2.4 mmol) in CH_2Cl_2 was cooled at −80 °C and treated with an excess of bromine. The solution was stirred for 10 min at 0 °C. During that time an orange precipitate was formed. Solvents and the excess of bromine were vacuum evaporated. Product was washed three times with CH_2Cl_2, twice with ether, recrystallized from MeCN/Et_2O and vacuum dried. Yield: 1.12 g (1.8 mmol, 75%). Anal. Calc. for $C_{25}H_{18}BBrF_4MoO_2$: C, 48.98; H, 2.96. Found: C, 48.74; H, 2.77%. Positive-ion MS: m/z = 224 $[M–Br–BF_4]^{2+}$, 196 (100%) $[M–Br–BF_4–2CO]^{2+}$. ^{1}H NMR (CD_3CN; 400 MHz): 8.81 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 2H, $C_{17}H_{10}$), 8.48 (d, $^3J(^1H,^1H)$ = 7.4 Hz, 2H, $C_{17}H_{10}$), 8.03 (t, $^3J(^1H,^1H)$ = 7.8 Hz, 2H, $C_{17}H_{10}$), 7.94 (t, $^3J(^1H,^1H)$ = 7.7 Hz, 2H, $C_{17}H_{10}$), 6.09 (s, 5H, C_5H_5), 5.68 (s, 2H, $C_{17}H_{10}$), 2.65 (s, 3H, CH_3). FTIR (KBr, cm^{-1}): 2110 vs [ν_a(CO)], 2060 vs [ν_s(CO)], 1067 vs–br [ν_s(BF)].

4.11. X-ray structure determination

The measurements were carried out on a BRUKER SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from an X-ray tube. Details of crystallographic data and refinement parameters are given in Table 1. Programs used: data collection, Smart (Bruker 2003); data reduction, Saint (Bruker version 6); absorption correction, SADABS version 2.10 (Bruker AXS 2001). Structure solution and refinement was done using SHELXTL (Bruker 2003). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. The non-hydrogen atoms were refined anisotropically. The allyl group in compound **8** was disordered and the central carbon atom C22 (and C22a) was refined with 50% occupancy.

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Appendix A. Supplementary material

CCDC 721845, 721846, 721847, 721848 contain the supplementary crystallographic data for **2**, **3a**, **7** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.043.

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