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Synthesis of molybdenocene(IV) and tungstenocene(IV) tropolonato complexes: Its derivative containing calix[4]arene moiety

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Abstract

The cationic di-μ-hydroxo dinuclear complexes of molybdenocene and tungstenocene $[Cp_2M(\mu-OH)_2MCp_2]^+$ (Cp = η-C_5H_5; M = Mo or W) react with tropolone to afford corresponding tropolonato complexes $[Cp_2M(trop)]^+$ (trop = $C_7H_5O_2$). The products were investigated by IR, ^1H NMR, and ^{13}C NMR spectroscopy as well as by X-ray crystallography (M = W). The structure shows that the central metal is surrounded by a distorted tetrahedral array of the two centers of cyclopentadienyl ligands and the two oxygen atoms of tropolonato ligand. The reaction has been extended to the synthesis of calix[4]arene receptor functionalized at the 1,3-positions of the upper rim with two tropolonato-molybdenocene centers.
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1. Introduction

Tropolonato ligand ($C_7H_5O_2^-$, trop), which is known to form a series of chelate complexes with metal ions, is the seven-membered ring analogue of the benzenoid catecholato ligand [1]. Tropolonato complexes are also broadly similar to analogous β-diketonato complexes, although there are often very significant differences [2]. In comparison with catecholato or β-diketonato complexes relatively little information is available regarding the chemistry of the tropolonato complexes. In the course of our studies on the chemistry of metallocene derivatives of the group 6 transition metals, we decided to make molybdenocene and tungstenocene tropolonato complexes.

We have previously described the preparation of the cationic di-μ-hydroxo dinuclear complexes of molybdenocene and tungstenocene $[Cp_2M(\mu-OH)_2MCp_2]^+$ (Cp = η-C_5H_5; M = Mo (**1a**) or W (**1b**)) [3]. These complexes have exhib-

ited interesting reactivity patterns leading to new chemistry. For example, they reacted with tertiary phosphines in alcoholic solvents to yield novel alkoxo complexes $[Cp_2M(PR_3)(R'O)]^+$ [3b]. It occurred to us that these di-μ-hydroxo dinuclear complexes might be useful precursors for the molybdenocene and tungstenocene tropolonato complexes. Although there are many molybdenum and tungsten tropolonato complexes [4], none has been reported on complexes also containing a Cp ligand.

2. Results and discussion

2.1. Synthesis of molybdenocene(IV) and tungstenocene(IV) tropolonato complexes

The reactions of **1** with tropolone under argon in methanol at 50 °C for 5 h afforded the tropolonato complexes (M = Mo (**2a**), W (**2b**)) in almost quantitative yields (Scheme 1). The resulting complexes were not soluble in a non-polar solvent, such as benzene or toluene, but soluble in methanol and DMSO. They were found to be stable

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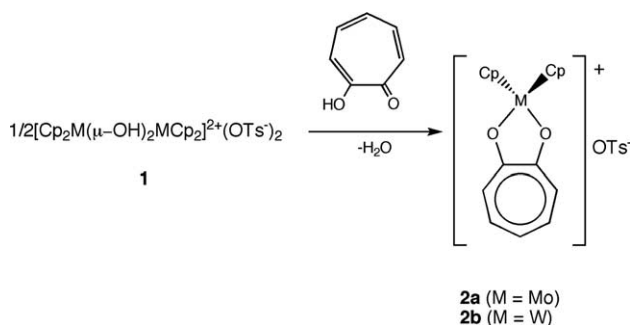
Scheme 1.

to air both in the solid state and in solution. In Table 1, selected spectroscopic data for the complexes **2a,b** are collected. The IR spectra of these complexes show a $\nu(C{=}O)$ stretch band at around 1340 cm^{-1}. In the ^{1}H NMR (CD$_3$OD) spectrum of **2a**, besides the singlet signal due to Cp protons at δ 5.89, doublet of doublets ($\delta = 7.67$, 2H, $J = 10.4$, 10.4 Hz, H-4,6), doublet ($\delta = 7.44$, 2H, $J = 10.4$ Hz, H-3,7), and doublet of doublets ($\delta = 7.37$, 1H, $J = 10.4$, 10.4 Hz, H-5) signals are, respectively, observed. The ^{13}C NMR spectrum of **2a** contains four signals assigned to the tropolonato carbons between 120 and 190 ppm together with the Cp carbon signal at

104.9 ppm. The spectrum of complex **2b** is almost identical to those of **2a**, supporting the analogous structure as **2a**.

The molecular structure of **2b** was fully confirmed by single-crystal X-ray analysis. Dark-red crystals suitable for X-ray analysis were obtained by recrystallization from acetone–hexane. The view of the molecular geometry of the cation is shown in Fig. 1. The more important bond lengths and bond angles are given in Table 2. A summary of the crystallographic data is given in Table 3 (see Section 3). The molecular structure is a neat and simple one; **2b** has geometry typical of bent metallocene. The tropolonato ligand exhibits an essentially planar seven-membered ring (mean deviation of the ring atom is 0.017 Å). The cyclopentadienyl rings lie above and below this plane. The structure can be compared with that of the parent tropolone [5] and complex **1b** [3b]. The C–C bond distances for trop ring average 1.395 Å, which is compatible with that of the parent tropolone (1.395 Å). The W–O bond lengths are nearly equivalent (2.076(3) and 2.092(3) Å). The internal ring angle is O2–W1–O1 = 74.7(1)°. The C–O bond lengths are found to average 1.304 Å, which is ca. 0.04 Å longer than the C=O double bond length in the parent tropolone but only slightly shorter than the C–OH single bond (1.333 Å).

The average C–C bond distance for the Cp rings in **2b** (1.396 Å) is comparable to the average C–C bond distance

Table 1
Selected spectroscopic data for [Cp$_2$M(trop)]$^+$ (M = Mo (**2a**) and W (**2b**))

Complexes	^{1}H NMR/ppm		^{13}C NMR/ppm
	δ (trop)	δ (Cp)	δ (trop)
2a	7.67 (dd, 2H, $J = 10.4$, 10.4, H-4,6)	5.89 (s, 10H)	186.5 (C-1,2)
	7.44 (d, 2H, $J = 10.4$, H-3,7)		141.2 (C-3,7)
	7.37 (dd, 1H, $J = 10.4$, 10.4, H-5)		132.5 (C-5)
			129.8 (C-4,6)
2b	7.74 (dd, 2H, $J = 10.4$, 10.4, H-4,6)	5.90 (s, 10H)	189.2 (C-1,2)
	7.57 (d, 2H, $J = 10.4$, H-3,7)		141.5 (C-3,7)
	7.45 (dd, 1H, $J = 10.4$, 10.4, H-5)		133.6 (C-5)
			129.7 (C-4,6)
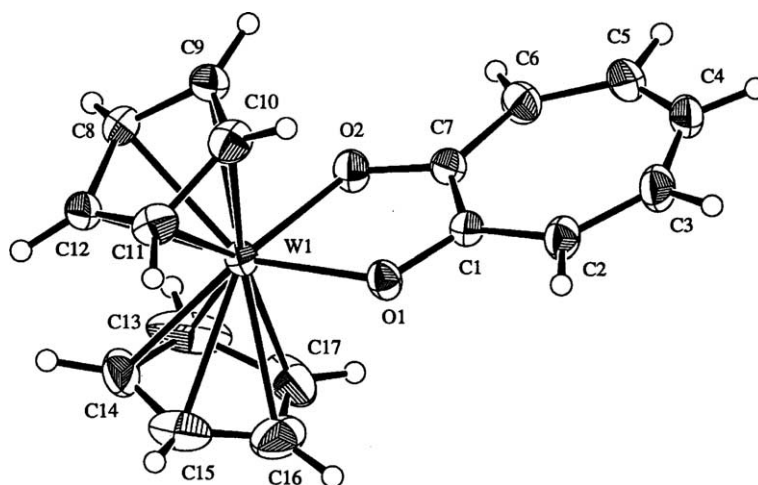
Fig. 1. Molecular structure of **2b**.

Table 2
Interatomic distances (Å) and angles (°) for **2b**

Distances			
W1–O1	2.076(3)	W1–O2	2.092(3)
W1–C8	2.268(4)	W1–C9	2.372(4)
W1–C10	2.374(4)	W1–C11	2.271(4)
W1–C12	2.249(4)	W1–C13	2.233(5)
W1–C14	2.272(5)	W1–C15	2.311(5)
W1–C16	2.353(5)	W1–C17	2.290(5)
O1–C1	1.301(4)	O2–C7	1.306(5)
C1–C2	1.402(5)	C1–C7	1.444(5)
C2–C3	1.374(6)	C3–C4	1.376(7)
C4–C5	1.383(8)	C5–C6	1.389(6)
C6–C7	1.399(5)	C8–C9	1.398(6)
C8–C12	1.424(6)	C9–C10	1.395(7)
C10–C11	1.420(7)	C11–C12	1.437(7)
C13–C14	1.43(1)	C13–C17	1.45(1)
C14–C15	1.357(9)	C15–C16	1.319(9)
Angles			
O1–W1–O2	74.7(1)	W1–O2–C7	117.7(2)
W1–O1–C1	118.3(2)	O2–C7–C1	114.4(3)
O1–C1–C2	118.5(4)	O1–C1–C7	114.7(3)
O2–C7–C6	118.2(4)	C5–C6–C7	129.1(5)
C3–C4–C5	127.7(4)	C2–C3–C4	130.4(4)
C2–C1–C7	126.8(3)	C1–C2–C3	129.0(4)
C4–C5–C6	129.3(4)	C1–C7–C6	127.4(4)

Table 3
Summary of crystal data for **2b**

|	
Empirical formula	$C_{25.50}H_{25}O_{5.50}SW$ (**2b** · 1/2acetone)
Formula weight	635.38
Temperature	23 °C
Crystal dimensions	0.40 × 0.32 × 0.20 mm
Crystal system	monoclinic
Space group	$C2/c$ (# 15)
Lattice type	C-centered
Lattice parameters	
a (Å)	15.15(1)
b (Å)	10.62(1)
c (Å)	30.68(1)
β (°)	106.34(5)
V (Å^3)	4739(7)
Z value	8
D_{calcd}	1.781 g/cm^3
$F(000)$	2496.00
μ(Mo Kα)	50.06 cm^{-1}
No. of reflections used for unit cell determination (2θ range)	14 (25.1–29.9°)
2θ max	55.0°
Scan rate	8.0°/min (in ω) (up to 9 scans)
No. of reflections measured	
Total	5941
Unique	5722 (R_{int} = 0.014)
No. observations ($I > 3.00\sigma(I)$)	4529
Residuals: R; Rw	0.024; 0.037
GOF	0.99

in **1b** (1.392 Å). The average metal–Cp ring carbon distances in **2b** is 2.299 Å, which is slightly shorter than the 2.326 Å found in **1b**. The internal C–C–C ring angles in **2b** range from 102.2° to 111.1°, which are compared favorably with the expected internal angle, 108°, for a planar pentagon.

At present, the structure of **2a** remains somewhat ambiguous, as no crystals suitable for X-ray diffraction are available. However the similarity of the ^{1}H and ^{13}C NMR spectra of **2a** and **2b**, along with the combustion analysis strongly suggests that **2a** and **2b** have similar structures.

2.2. Synthesis of a photosensitive calix[4]arene-based molybdenocene

It occurred to us that the cationic center of these complexes might interact with anions and neutral electron-rich molecules. We have envisioned that these complexes can be assembled to create new hybrid materials, when properly functionalized. Thus, we decided to incorporate the cationic component into a calix[4]arene framework. A number of calix[4]arenes carrying a wide variety of groups on the upper and lower rims have been prepared in the last decade. When appropriately modified they provide attractive platform to which to attach ligating moieties for transition metal centers [6]. The scope of calix[4]arenes chemistry is expected to be extended dramatically by incorporation of metallic centers into the peripheral sites [7,8].

The new calixarene-tropolonato–molybdenocene complex has been prepared according to Scheme 2. The molybdenocene-tropolonato groups are linked to the upper rim via photoactive azo spacers in order to change the properties of the resulting calixarene in response to light. Literature preparations were used to obtain the required de-*tert*-butylated calix[4]arene **3** [9]. The reaction of **3** with methyl *p*-toluenesulfonate in the presence of K$_2$CO$_3$ gave 1,3-dimethoxy-calix[4]arene **4** in 93% yield [10]. These methyl groups were used since their conformational influence on the calixarene was predictable [11]. Preparation of the tropolone-diazonium compound **5** was carried out by using the method of Nozoe [12]. Reaction of **4** with an excess of the diazonium salt, according to the method of Taniguchi and co-workers [13], gave **6** in 53% yield. The reaction of **6** with **1a** proceeded in similar fashion as tropolone and resulted in the formation of the desired
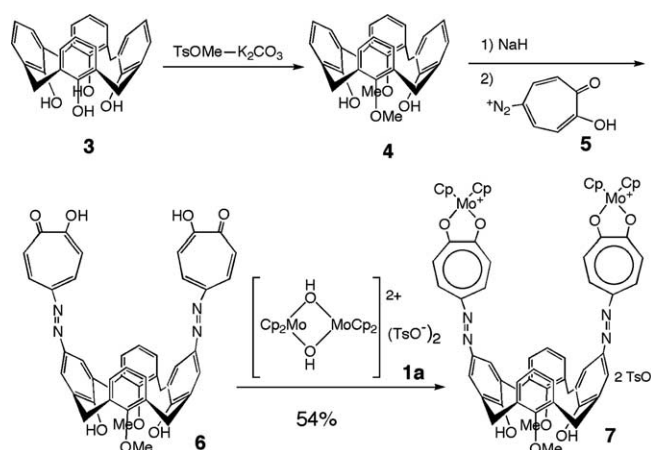
Scheme 2.

compound **7**. Resulting **7** exhibits marked air stability. ^{1}H NMR pattern for the ArC*H*$_2$Ar methylene protons of **7** showed the two pairs of doublets (δ 4.25 and 3.70, $J = 13.5$ Hz), indicating a cone conformation [14].

UV–Vis spectra of the free (compound **6**) and the metal complexed ligand (compound **7**) in pyridine are shown in Fig. 2.

The spectrum of **6** is characterized by the presence of one absorption maximum at around 420 nm; this value is closely similar to published data on 4-arylazo-1-naphthols [15] and *p*-nitrophenylazo-substituted calix[4]arenes [16], suggesting that **6** exists as the azo form. Complexation with cationic molybdenocene resulted in a large change in the absorption spectrum. The band at 420 nm decreased considerably and shifted to 470 nm; this shift can be attributed to the formation of the hydrazone form [15]. The present result is compatible with the study of Kishimoto and co-workers [17], who reported that, in tautomerism of 4-(4'-substituted-phenylazo)-1-naphthol [azo form vs. hydrazone form], the hydrazone form predominates with electron-withdrawing substituents. In addition to the band at 470 nm, a new peak at longer wavelength (720 nm) appeared. The remarkable red shift of the band of **7** can be ascribed to the lengthening of the conjugated system in the diimine form [17]. Thus, in pyridine the hydrazone form **7A** and the diimine form **7B** are in equilibrium (Scheme 3). In methanol, a sole band appeared at around 460 nm, ascribable to the hydrazone form **7A**; the longer wavelength absorption ($\sim$720 nm) due to the diimine form **7B** was virtually negligible. These results indicate that the equilibrium between **7A** and **7B** is strongly dependent on the property of media.
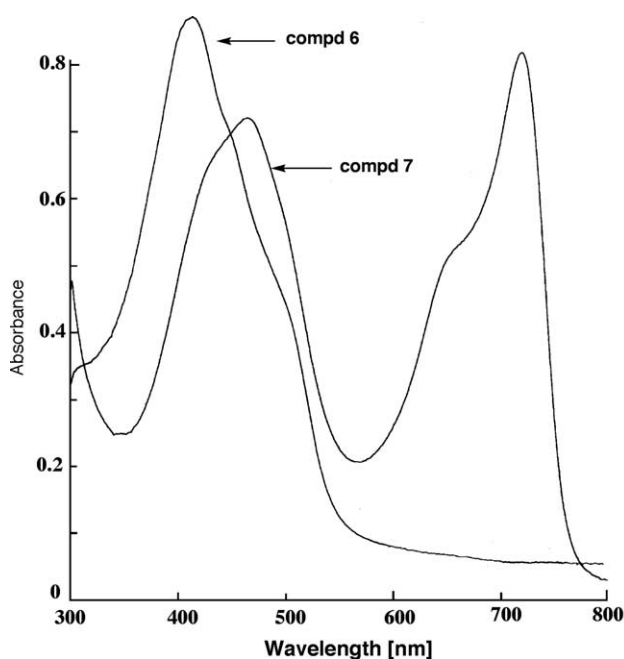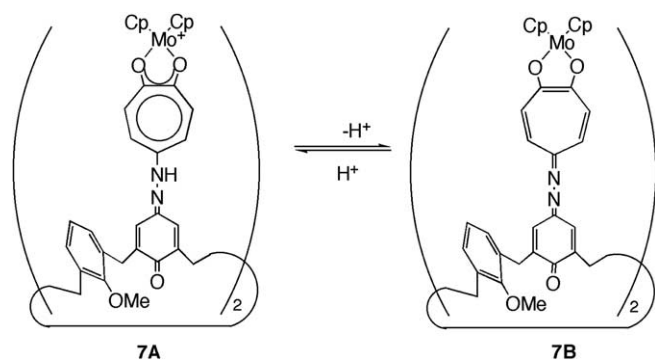

Scheme 3.

3. Experimental section

3.1. General procedures

Unless otherwise noted, all manipulations were conducted using standard Schlenk techniques under purified argon or nitrogen. Commercially available reagent grade chemicals were used as such without any further purification. All solvents were dried by standard methods and were stored under argon. The synthesis of **1** was presented in a previous paper [3b].

3.2. Synthesis of [Cp$_2$ M(trop)]$^+$ OTs$^-$ (M = Mo (**2a**), W (**2b**))

Tropolone (0.060 g, 0.49 mmol) was added to a slurry of **1a** (0.070 g, 0.085 mmol) in 5 mL of methanol. The resulting mixture was heated at 50 °C for 5 h to yield a dark-red solution. The solvent was removed in vacuo, and the residue was washed with hexane and ether. The crude product was extracted with acetone (20 mL) and then 20 mL of hexane was added. On standing at 0 °C, **2a** precipitated as dark-red crystals (96%). Anal. Calcd for C$_{24}$H$_{22}$O$_5$SMo: C, 55.60; H, 4.28. Found: C, 55.44; H, 4.29%. The tungsten complex **2b** could likewise be obtained as dark-red crystals (98%).

3.3. Synthesis of 6

To a cold suspension (ice bath temperature) of 5-amino tropolone (0.501 g, 3.65 mmol) in aqueous 1,4-dioxane (50%, 8 mL) was added dropwise sulfuric acid (0.6 mL), then a solution of NaNO$_2$ (0.327 g, 4.74 mmol) in water (1.2 mL) affording a solution of **5**. The reaction of **4** with NaH was carried out in a separate flask. **4** (0.403 g, 0.891 mmol) suspended in DMF (25 mL) was stirred at room temperature. NaH (60% oil, 0.399 g, 9.98 mmol) was added to the flask to dissolve **4**, forming a clear homogeneous solution. After cooling to 0 °C, to the resulting solution was added dropwise the aforementioned tropolone-diazonium solution (the temperature was held at 0 to 5 °C to avoid a side reaction). After addition was complete, the solution was allowed to warm to room

Fig. 2. Absorption spectra of **6** and **7** in pyridine (4×10^{-5} M).

temperature and was kept at this temperature for 2 h. The resulting mixture was adjusted to pH 3.0 by addition of dilute HCl and then heated with stirring at 60 °C for 30 min. Water (40 mL) was added and the resulting precipitate was repeatedly washed with water and methanol. The dried crude product was washed with CH_2Cl_2 and was reprecipitated with DMSO-methanol; yield: 0.355 g (53%). IR (KBr) 3211, 2933, 1709, 1615, 1557, 1469, 1350, 1297, 1262, 1210 cm^{-1}; ^{1}H NMR (DMSO-d_6, 20 °C) δ 8.04 (d, 4H, $J = 11.9$ Hz, COCHCH and COHCHCH in the tropolone), 7.84 (s, 4H, ArH in the azophenyl moiety), 7.37 (d, 4H, $J = 11.9$ Hz, COCHCH and COHCHCH in the tropolone), 7.11 (d, 4H, $J = 7.5$ Hz, ArH in the methoxyphenyl moiety), 6.82 (t, 2H,$J = 7.5$ Hz, ArH in the methoxyphenyl moiety), 4.24 (d, 4H, $J = 12.9$ Hz, ArCH_2Ar), 3.94 (s, 6H, OCH_3), 3.68 (d, 4H, $J = 12.9$ Hz, ArCH_2Ar).

3.4. Synthesis of 7

A suspension of **1a** (0.159 g, 0.192 mmol) and **6** (0.144 g, 0.192 mmol) in methanol (28 mL) was heated with stirring at 50 °C for 5 h. After filtration under argon and subsequent removal of the solvent under reduced pressure, the black residue was repeatedly washed with ether to yield **7** (0.160 g, 54%). IR (KBr) 3105, 2925, 1656, 1593, 1557, 1436, 1348, 1299, 1268, 1190 cm^{-1}; ^{1}H NMR (DMSO-d_6, 20 °C) δ 8.22 (d, 4H, $J = 12.2$ Hz, COCHCH in the tropolone), 7.88 (s, 4H, ArH in the azophenyl moiety), 7.56 (d, 4H, $J = 12.2$ Hz, COCHCH in the tropolone), 7.11 (d, 4H, $J = 7.4$ Hz, ArH in the methoxyphenyl moiety), 6.82 (t, 2H,$J = 7.4$ Hz, ArH in the methoxyphenyl moiety), 6.02 (s, 20H, Cp rings), 4.25 (d, 4H, $J = 13.5$ Hz, ArCH_2-Ar), 3.97 (s, 6H, OCH_3), 3.70 (d, 4H,$J = 13.5$ Hz, ArCH_2Ar). Resonances due to the TsO group's protons are omitted throughout. Both **6** and **7** are only soluble in polar solvents such as DMSO and pyridine. At present, no samples suitable for combustion analyses are available [18].

3.5. X-ray crystal structure analysis of 2b

A simple crystal of **2b** was grown from an acetone–hexane solution in a fridge, and was mounted on a glass fiber. All measurements were made on a Rigaku AFC-7R diffractometer by using Mo Kα radiation ($\lambda = 0.71069$ Å) with $\mu = 50.06$ cm^{-1} and $F(000) = 2496.00$ Å. The unit-cell parameters were obtained from a least-squares refinement using the setting angles of 14 carefully centered reflections in the range $25.1° \leqslant 2\theta \leqslant 29.9°$. The parameters used during the collection of diffraction data are given in Table 3. The structure was solved and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

CCDC reference number 270365. See http://www.rsc.org/suppdata/dt/b2/b209624m/ for crystallographic data in CIF or other electronic format.

3.6. UV–Visible spectral measurements

UV–Visible spectra were recorded at room temperature in a 1-cm quartz cell by using a JASCO V-550 spectrophotometer. Absolute pyridine was used as the solvent.

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