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Double metallation of a molecular tweezers with chromium and visible light-induced metal transfer into the cavity[☆]

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Abstract

cis,exo-2-Phenyl-3-(2-*E*-phenylethenyl)norbornane reacts with $Cr(CO)_6$ to give mainly a bis-arene tricarbonylchromium complex. Under the influence of visible light, the latter undergoes conversion from externally to internally arene-bonded chromium carbonyl, with carbonyl displacement by the double bond, to form an η^6,η^2 metal-coordinated complex. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chromium carbonyl; Molecular tweezers; Visible light; X-ray diffraction

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1. Introduction

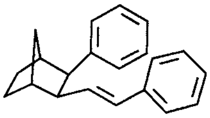
Rigid ligands offering coordination sites for transition metals inside a cavity have proved to be of great interest for many reactions [1]. For example, many insertion processes, especially those involved in polymerisation of unsaturated substrates, can take advantage of the favourable steric arrangement of the migratory group and of the substrate undergoing insertion. Recent examples of metals hosted in cavities containing aromatic groups are offered by zirconium complexes with bis-arene ligands [2] and niobium complexes with tetraphenylborate [3]. Our recent work [4] had enabled us to synthesize rigid molecular tweezers such as *cis,exo*-2-phenyl-3-(2-*E*-phenylethenyl)norbornane **1** (Fig. 1).

We wondered whether a metal could be hosted in the cavity of **1**. One of the most successful ways to coordinate metals to arene systems consists of the reaction of hexacarbonylchromium or naphthalene tricarbonylchromium with the appropriate arene compound and to this end we set out to study the reaction of **1** with carbonylchromium species.

2. Results and discussion

Our attempts to prepare tricarbonylchromium derivatives of **1** led us to obtain the bis-arene tricarbonylchromium compound **2** as the predominant product (Fig. 2).

Complex **2** was obtained in 77% yield as a yellow microcrystalline powder by reaction of 2-phenyl-3-(2-*E*-



1

Fig. 1. The molecular tweezers *cis,exo*-2-phenyl-3-(2-*E*-phenylethenyl)norbornane **1**.

[☆] Dedicated to Professor Alberto Ceccon in recognition of his outstanding contribution to organometallic chemistry

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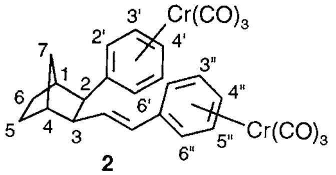


2

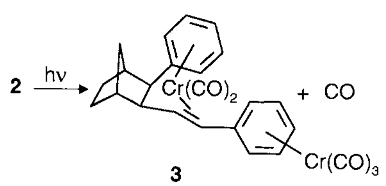
Fig. 2. Bis-arene tricarbonylchromium compound **2**.

phenylethenyl)norbornane with $Cr(CO)_6$ in a 1:4 molar ratio at reflux for 24 h in di-*n*-butyl ether containing ca. 10% of tetrahydrofuran (THF) [5]. An excess of $Cr(CO)_6$ was needed to obtain the predominant formation of compound **2**, which was isolated by flash chromatography together with two minor products (14 and 8% yield), which were shown to be monoarenetricarbonylchromium isomers by mass spectrometry and not further investigated. Compound **2** was characterized by ^{1}H-NMR, IR and MS. Assignment of the structure is based on decoupling, COSY and NOESY spectra. The phenyl and phenylethenyl groups display great rigidity due to hindered rotation. Among the many cross signals observed in the NOESY spectra particularly indicative are those of H2′ with both H1 and H7*syn*. These dipolar interactions clearly indicate that the aromatic proton H2′ is directed towards the side of the bridge of the norbornyl unit, while H6′ points to the lower part of the norbornyl ring, as suggested by the dipolar interaction with H2. In the same way the vinyl proton bonded to the norbornyl group shows nOe only with H7*syn*, while the other vinyl proton (=C*H*Ph) gives an intense cross peak with H3.

We then wondered whether the desired encapsulated chromium species containing a $Cr(CO)_2$ unit inside the cavity of the organic ligand could be obtained. It is well-known that olefins can replace a carbon monoxide ligand to form complexes of type arene-(olefin)dicarbonylchromium [6]. In particular, alkenylarene tricarbonylchromium compounds containing the double bond separated from the aromatic ring by two or three atoms or CH_2 groups have proved to readily undergo intramolecular cyclization by UV irradiation to form stable chelate alkenylarene dicarbonylchromium complexes [7].

We have found that photolysis of **2** dissolved in benzene/cyclohexane (2:1) in a closed vessel with a common 150 watt Philips bulb at room temperature under nitrogen gives the arene chelate complex **3** in 90% yield according to Eq. (1).

(1)



3

Thus it appears that the carbon–carbon double bond of the phenylethenyl group is placed in such a favourable position to allow the displacement of a carbon monoxide molecule even by irradiation with visible light. During the irradiation, the colour of the solution changes from yellow to red and within 18 h the compound precipitates out in red prismatic crystals suitable for X-ray crystallographic analysis. The structure of the complex is shown in Fig. 3. The crystal data and selected bonding parameters are reported in Tables 1 and 2.

The norbornene moiety shows normal geometry and its bond distances and angles do not deviate significantly from the expected values. As previously observed in similar complexes [8], the C–C aromatic distances are larger than the values observed in uncomplexed rings [average C3···C8 = 1.411(3), C18···C23 = 1.406(7) versus 1.388 Å]. The B–Cr–C_{carb} angles (B is the centroid of the aromatic rings) range from 123.7(2) to 127.6(3)° while the mean C=O, Cr–C_{carb} and Cr–C_{Ph} are 1.158(3), 1.840(4) and 2.226(4) Å, respectively. The Cr1–B and Cr2–B distances [1.720(4) and 1.720(5) Å] and the Cr–B–C_{Ph} angles near to 90° establish the practically planar η^6-coordination of the benzene ligands which are quasi-perpendicular to each other being 75.7° the dihedral angle between their mean planes.

The coordinations of chromium atoms, which assume staggered conformations, are of ‘three-legged piano-stool’ type and while the Cr1 coordinates the centroid of the C3–C8 aromatic ring, two carbonyl carbons and the C16=C17 double bond, the Cr2 coordinates the centroid of the C18–C23 aromatic ring and three carbonyl carbons. The molecules are joined in the crystal by normal Van der Waals interactions.

Complex **3** is rather stable and remains intact even in the presence of carbon monoxide. In conclusion, we

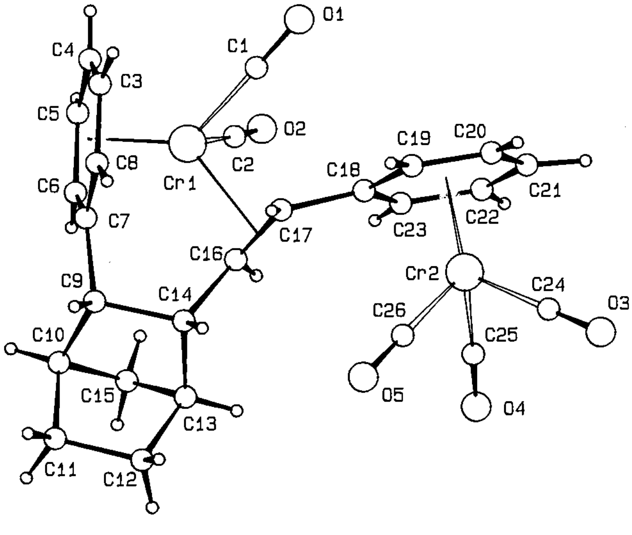


Fig. 3. Projection of complex **3** with arbitrary numbering scheme.

Table 1
Crystallographic data and experimental information for complex **3**

Formula	$C_{26}H_{22}O_5Cr_2$
Formula weight	518.45
Colour	Red
Shape	Prism
Dimensions (mm)	0.11 × 0.16 × 0.19
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell constants:	
a (Å)	11.277(3)
b (Å)	12.331(3)
c (Å)	9.544(2)
α (°)	101.25(2)
β (°)	106.73(2)
γ (°)	112.47(2)
Cell volume (Å^3)	1102.48(6)
Formula units	2
D_{calc} (g cm^{-3})	1.56
μ_{calc} (cm^{-1})	5.20
No. of reflections	30
θ range (°)	10.8–19.4
Temperature	Room
Diffractometer	Philips PW1100
Radiation, wavelength (Å)	Mo–K$_\alpha$, 0.71069
Standard reflection, step	One, every 100
Decay of standard	None
Reflections measured	5317
Reflections. observed [$I > 2\sigma(I)$]	3687
θ range (°)	3–28
Indices range: h, k, l	−14/13, −16/15, 0/12
No. of refined parameters	303
R	0.051
R_w	0.060
Weights	$w = 1.0/(\sigma^2 F0 + 0.0164F^2)$
$\Delta\rho_{min/max}$	−0.19/0.26
Min/max absorb. corr. factors	0.90/1.31

have found a very facile way to insert a $Cr(CO)_2$ group into a cavity of a molecular tweezers. Work is in progress to exploit the possibility of obtaining complexes of various transition metals, which might be interesting for catalytic reactions.

3. Experimental

All reactions were performed under a dinitrogen atmosphere using standard Schlenk techniques. The ligand was prepared as reported in reference [4]. Reagents were commercial grade and were used as obtained. Tetrahydrofuran (THF), di-*n*-butyl ether, benzene and cyclohexane were freshly distilled from sodium benzophenone ketyl prior to use. ^{1}H-NMR spectra were recorded on a Bruker AMX-400 spectrometer and were referenced using the residual proton solvent resonance relative to tetramethylsilane. The assignments of the proton resonances were obtained by decoupling, COSY and NOESY spectra. IR spectra were run on an FT/IR Nicolet 5PC instrument. Positive-ion FAB mass spectra were obtained with a Finnigan 1020 spectrometer using 3-nitrobenzyl alcohol matrix.

3.1. Synthesis of complex **2**

A Schlenk-type flask, equipped with a magnetic stirring bar, was charged with 537 mg (2.44 mmol) of $Cr(CO)_6$, 166 mg (0.61 mmol) of 2-phenyl-3-(2-*E*-phenylethenyl)norbornane and 10 ml of di-*n*-butyl ether and 1 ml of THF. This solution was heated at reflux with constant stirring; after 24 h the resulting yellow solution was slowly cooled to room temperature and the solvent removed under vacuum. The crude was flash chromatographed over a 3 × 40 cm silica gel column. Elution with hexane/ethyl acetate 9:1 as eluent yielded 255 mg (77%) of **2**, along with 35 and 20 mg of two compounds with $R_f = 0.37$ and 0.23 in 14 and 8% yield, respectively. The latter turned out to be monoarene tricarbonylchromium species on the basis of their mass spectra (compound with $R_f = 0.37$: M$^+$ 410

Table 2
Atomic fractional coordinates (× 10^4) and U_{eq} (× 10^4 Å^2) for non-hydrogen atoms of complex **3**

Atom	x/a	y/b	z/c	U_{eq}
CR1	196(1)	7558(1)	3629(1)	256(2)
CR2	−3152(1)	6761(1)	−2158(1)	273(3)
O1	−2519(4)	7429(4)	3634(5)	605(19)
O2	−1310(5)	4752(3)	2426(5)	754(24)
O3	−4746(4)	7248(4)	−4857(4)	673(21)
O4	−2398(4)	5249(4)	−4265(5)	723(25)
O5	−574(4)	8937(3)	−1822(5)	622(18)
C1	−1480(4)	7481(4)	3612(5)	361(18)
C2	−737(5)	5838(4)	2842(5)	413(22)
C3	1201(5)	9148(5)	5841(5)	433(24)
C4	1087(6)	8060(6)	6195(6)	495(24)
C5	1631(5)	7335(5)	5581(5)	446(24)
C6	2324(5)	7700(4)	4604(5)	364(20)
C7	2449(4)	8790(4)	4247(4)	290(16)
C8	1906(4)	9529(4)	4885(5)	365(19)
C9	3003(4)	9138(4)	3056(5)	288(17)
C10	3990(4)	8632(4)	2701(5)	368(21)
C11	4715(5)	9438(5)	1863(6)	436(23)
C12	3509(5)	9042(5)	289(6)	396(21)
C13	2254(4)	7987(4)	370(5)	324(17)
C14	1734(4)	8573(4)	1458(4)	259(16)
C15	2988(5)	7399(4)	1357(6)	381(21)
C16	360(4)	7582(4)	1393(4)	249(15)
C17	−703(4)	7914(4)	1439(5)	277(15)
C18	−2205(4)	7104(4)	403(5)	295(17)
C19	−3104(5)	7666(6)	109(6)	400(24)
C20	−4488(5)	6987(6)	−942(6)	476(28)
C21	−5045(5)	5699(6)	−1761(6)	495(23)
C22	−4207(5)	5124(5)	−1500(5)	418(22)
C23	−2779(5)	5820(4)	−435(5)	323(18)
C24	−4138(4)	7049(4)	−3824(5)	396(19)
C25	−2712(4)	5814(4)	−3470(5)	414(22)
C26	−1582(4)	8108(4)	−1941(5)	364(17)

(23) *m*/*e* 326 (100, −3CO); compound with $R_f = 0.23$: M$^+$ 410 (24) *m*/*e* 326 (100, −3CO)).

3.2. Spectral data for **2**

^{1}H-NMR (C_6D_6, 400 MHz, 298 K; ′ refers to the protons of the phenyl ring and ″ to the aromatic protons of the phenylethenyl moiety): δ 5.46 (1H, d, *J* = 15.5 Hz, =C*H*Ph), 5.13 (1H, dd, *J* = 15.5, 10.2 Hz, C*H*=CHPh), 5.02 (1H, td, *J* = 6.4, 1.2 Hz, H5′), 4.75 (1H, td, *J* = 6.4, 1.2 Hz, H3′), 4.63 (1H, d with further couplings, *J* = 6.6 Hz, H2′), 4.58 (1H, tt, *J* = 6.3, 1.0 Hz, H4′), 4.56–4.49 (2H, m, H6′, H4″), 4.49–4.44 (2H, m, H2″, H5″), 4.38 (1H, d with further couplings, *J* = 6.5 Hz, H6″), 4.34 (1H, tt, *J* = 6.1, 1.0 Hz, H3″), 2.42 (1H, d with further couplings, *J* = 9.3 Hz, H2), 2.36 (1H, br s, H1), 2.15 (1H, dd with further couplings, *J* = 10.0, 9.6 Hz, H3), 1.97 (1H, br s, H4), 1.60–1.42 (2H, m, H5*exo*, H6*exo*), 1.42–1.32 (2H, m, H6*endo*, H7*syn*), 1.20–1.12 (1H, m, H5*endo*), 1.06 (1H, d quintets, *J* = 10.3, 1.4 Hz, H7*anti*). IR ($CHCl_3$, cm^{-1}): 1968.6, 1896.3 with a right shoulder. MS: M$^+$ 546 (4) *m*/*e* 462 (31, −3CO), 326 (100, −3CO, −Cr(CO)$_3$).

3.3. Synthesis of complex **3**

In a Schlenk-type flask 159 mg (0.29 mmol) of **2** were dissolved in 6 ml benzene and 3 ml cyclohexane and the resulting yellow solution was irradiated for 18 h at room temperature using a 150 watt Philips bulb. The colour gradually passed from yellow to red and after the reported time 121 mg (90%) of **3** separated from the solution as red crystals. IR (Nujol mull, cm^{-1}): 1954.1, 1915.6, 1899.0, 1853.0, 1840.3. MS: *m*/*e* 462(10, −2CO), 410 (20, −2CO, −Cr), 326 (100, −2CO, −Cr, −3CO).

3.4. X-Ray structure determination

X-ray analysis was performed with a Siemens AED diffractometer with the crystal sealed in a Lindemann tube under dinitrogen. The crystal data and pertinent details of the experimental conditions are summarized in Table 1. The Lorentz and polarisation effects were corrected during the data reduction procedure [9]. The absorption correction was performed with the method of Walker and Stuart [10] with program DIFABS [11]. The structure was solved by direct methods with SIR97 [12] and refined by anisotropic full-matrix least-squares [13]. All hydrogen atoms were located in a ΔF map and refined isotropically.

The atomic coordinates of the heavy atoms are in Table 2. The conformation of the molecule with the respective labelling scheme is in Fig. 3. Table 3 reports the selected geometrical parameters of the molecule.

Table 3
Selected bond distances (Å) and bond angles (°)

Bond lengths			
CR1–C1	1.851(5)	CR2–C22	2.230(6)
CR1–C2	1.840(4)	CR2–C23	2.224(6)
CR1–C3	2.212(5)	CR2–C24	1.842(5)
CR1–C4	2.215(5)	CR2–C25	1.846(6)
CR1–C5	2.229(6)	CR2–C26	1.828(4)
CR1–C6	2.233(6)	O1–C1	1.155(7)
CR1–C7	2.224(4)	O2–C2	1.163(5)
CR1–C8	2.239(4)	O3–C24	1.156(7)
CR1–C16	2.199(4)	O4–C25	1.150(8)
CR1–C17	2.251(5)	O5–C26	1.158(6)
CR2–C18	2.246(5)	C14–C16	1.538(6)
CR2–C19	2.208(6)	C16–C17	1.416(8)
CR2–C20	2.213(7)	C17–C18	1.484(5)
CR2–C21	2.222(6)		
Bond angles			
CR1–C1–O1	178.4(4)	C24–CR2–C26	87.7(2)
CR1–C2–O2	176.4(4)	C24–CR2–C25	89.8(2)
CR1–C3–C8	72.6(2)	CR2–C24–O3	179.0(4)
C14–C16–C17	118.8(4)	CR2–C24–O3	179.0(4)
C2–CR1–C1	86.7(2)	CR2–C25–O4	178.0(4)
C25–CR2–C26	86.3(2)	CR2–C26–O5	177.9(4)

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