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Notes

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Mononuclear Tungsten(VI) Calix[4]arene Complexes

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Calix[*n*]arenes[2] provide a unique polyphenoxo binding surface for transition-metal ions. In particular, metalation[3,4] of calix[*n*]arenes serves to shape the receptor cavity of the calix[*n*]arene via a significant molecular reorganization and to study the chemistry of a metal site bonded on a polyoxo surface. The later point is, however, very difficult to pursue, because very rarely the complexes so far reported and derived from the metalation of calix[*n*]arenes have the required characteristics for undergoing, among others, organometallic functionalization.

Our report deals with the introduction of a single tungsten(VI) over the oxo surface of calix[4]arene.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The syntheses of calix[4]arene, *p-tert*-butylcalix[4]arene, and $WOCl_4$ have been performed as reported in the literature. ^1H NMR spectra were recorded with a Brucker AC200 instrument.

Solid-State Structures of 4 and 5. Crystallographic data, atomic coordinates, and selected bond distances and angles are reported in Tables I–V.

Preparation of 1. A toluene (80 mL) suspension of $WOCl_4$ (1.23 g, 2.93 mmol) was reacted with calix[4]arene (1.00 g, 2.93 mmol). The suspension was refluxed for 12 h. The resulting solid extracted with CH_2Cl_2 gave red crystals (68%) of **1**. Anal. Calcd for [(calix[4]arene)WO]·1.5CH_2Cl_2, $C_{29.5}H_{23}Cl_3O_5W$: C, 47.39; H, 3.10. Found: C, 47.54; H, 2.95. ^1H NMR (CD_2Cl_2, 200 MHz, ppm): δ 7.17 (d, 8 H, Ph *m*-H, J_{HH} = 7.17 Hz), 6.79 (t, 4 H, Ph *p*-H, J_{HH} = 7.17 Hz), 4.63 (d, 4 H, CH_2, J_{HH} = 12.67 Hz); 3.38 (d, 4 H, CH_2, J_{HH} = 12.67 Hz).

Preparation of 2. A benzene (80 mL) orange-brown suspension of $WOCl_4$ (2.23 g, 6.52 mmol) was reacted with *p*-Bu^t-calix[4]arene (4.22 g, 6.52 mmol). The suspension was refluxed for 48 h and then filtered. The resulting brown solid was extracted with toluene, obtaining a yellow-brown crystalline solid (65%). Anal. Calcd for [(*p*-Bu^t-calix[4]arene)WO]·C_7H_8, $C_{51}H_{60}O_5W$: C, 65.38; H, 6.45. Found: C, 64.88, H, 6.44. ^1H NMR (CD_2Cl_2, 200 MHz, ppm): δ 7.17 (m, 16 H, Ph and toluene), 4.58 (d, 4 H, CH_2, J_{HH} = 12.79 Hz), 3.32 (d, 4 H, CH_2, J_{HH} = 12.79 Hz), 2.33 (s, 3 H, CH_3(tol)), 1.18 (m, 36 H, Bu^t).

Table I. Crystal Data for Complexes **4** and **5**

	4	**5**
formula	$C_{28}H_{20}O_5W\cdot 2C_2H_4O_2$	$C_{44}H_{52}Cl_2O_4W\cdot 3C_6H_6$
cryst system	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*n*
cell params at 295 K		
a/Å	14.671 (3)	18.127 (2)
b/Å	10.297 (2)	21.765 (2)
c/Å	20.607 (3)	14.729 (2)
β/deg	103.03 (1)	108.4 (1)
Z	4	4
no. of unique obsd data	2443	6619
intens measmt	*a*	*a*
struct refinement	*b*, *c*	*b*, *d*
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.026	0.037

[a] Intensities and background individual profiles were analyzed by the following: Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Struct. Crystallogr., Cryst. Chem.* **1974**, *A30*, 580. [b] Refinement was by blocked full-matrix least-squares first isotropically and then anisotropically for all non-hydrogen atoms. [c] Acetic acid molecule coordinated to W1 was refined with constrained geometry. [d] The benzene solvent molecules were refined as rigid hexagons.

Table II. Atomic Coordinates ($\times 10^4$) for Complex **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*
W	0	634.1 (2)	2500
O1	1174 (2)	924 (3)	3081 (1)
O2	559 (2)	928 (3)	1773 (1)
O3	0	−1015 (4)	2500
C1	1707 (3)	1979 (4)	3341 (2)
C2	1600 (3)	2509 (4)	3936 (2)
C3	2198 (3)	3513 (5)	4210 (2)
C4	2863 (3)	3980 (5)	3893 (3)
C5	2928 (3)	3466 (5)	3289 (2)
C6	2344 (3)	2472 (4)	2988 (2)
C7	2378 (3)	1989 (4)	2299 (2)
C8	1669 (3)	2621 (4)	1740 (2)
C9	1864 (3)	3786 (5)	1461 (2)
C10	1205 (4)	4405 (5)	973 (3)
C11	345 (4)	3840 (6)	740 (2)
C12	114 (3)	2657 (4)	991 (2)
C13	787 (3)	2077 (4)	1496 (2)
C14	839 (3)	2028 (5)	4271 (2)
O4	0	2951 (4)	2500
C21	0	4149 (6)	2500
O5[a]	666 (12)	4853 (18)	2893 (15)
C22[a]	−888 (17)	4854 (27)	2197 (24)
O6	3334 (3)	8314 (4)	5591 (2)
O7	3357 (3)	6385 (4)	5135 (2)
C31	3738 (4)	7250 (6)	5514 (3)
C32	4709 (5)	7112 (7)	5898 (3)

[a] The site occupation factor for the disordered O5 and C22 atoms is 0.5.

Preparation of 3. To a toluene (80 mL) violet suspension of $WOCl_4$ (1.23 g, 2.93 mmol) was added calix[4]arene (1.01 g, 2.93 mmol). The suspension was refluxed for 12 h and then filtered. A red solid was obtained (44%). Anal. Calcd for [(calix[4]arene)WO]·H_2O·0.25C_7H_8, $C_{29.5}H_{22}O_6W$: C, 53.98; H, 3.38. Found: C, 54.03; H, 3.74. ^1H NMR (CD_2Cl_2, 200 MHz, ppm): δ 7.17 (d, 8 H, Ph, J_{HH} = 7.54 Hz), 6.74 (d, 4 H, Ph, J_{HH} = 7.54 Hz), 4.66 (t, 4 H, CH_2, J_{HH} = 12.76 Hz), 3.88 (s, 2 H, H_2O), 3.37 (d, 4 H, CH_2, J_{HH} = 12.76 Hz).

Preparation of 4. To a toluene (80 mL) violet suspension of $WOCl_4$ (1.70 g 4.04 mmol) was added calix[4]arene (1.40 g, 4.09 mmol). The suspension was refluxed for 12 h and then filtered. A red solid was

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Table III. Fractional Atomic Coordinates ($\times 10^4$) for Complex **5**

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
W	4905.6 (1)	1739.2 (1)	−35.0 (2)	C30	1739 (7)	2302 (7)	2673 (10)
Cl1	3751 (1)	1812 (1)	−1289 (1)	C31	2873 (8)	2171 (9)	4040 (9)
Cl2	5530 (1)	1719 (1)	−1188 (1)	C32	2128 (11)	1289 (6)	3343 (14)
O1	4362 (2)	1763 (2)	829 (3)	C33	6262 (4)	3692 (4)	3905 (6)
O2	5039 (2)	2595 (2)	216 (3)	C34	6750 (8)	4242 (5)	3813 (8)
O3	5896 (2)	1678 (2)	867 (3)	C35	5674 (6)	3845 (8)	4378 (8)
O4	4880 (2)	879 (2)	118 (3)	C36	6859 (6)	3249 (6)	4576 (7)
C1	3867 (3)	1788 (3)	1337 (4)	C37	9161 (4)	1518 (3)	1803 (6)
C2	3584 (3)	1231 (3)	1564 (4)	C38	9514 (5)	1715 (6)	2811 (7)
C3	3108 (3)	1272 (3)	2151 (5)	C39	9452 (5)	880 (5)	1691 (9)
C4	2922 (3)	1834 (3)	2462 (4)	C40	9430 (5)	1933 (6)	1122 (9)
C5	3192 (3)	2369 (3)	2168 (5)	C41	5918 (5)	−440 (4)	3630 (5)
C6	3671 (3)	2358 (3)	1604 (4)	C1S	5304 (3)	1755 (4)	3786 (7)
C7	3952 (4)	2929 (3)	1226 (5)	C2S	5795 (3)	1650 (4)	3239 (7)
C8	4826 (3)	3026 (3)	1623 (5)	C3S	6590 (3)	1565 (4)	3688 (7)
C9	5136 (3)	3285 (3)	2511 (4)	C4S	6894 (3)	1586 (4)	4683 (7)
C10	5923 (4)	3379 (3)	2930 (5)	C5S	6403 (3)	1692 (4)	5230 (7)
C11	6408 (3)	3201 (3)	2417 (5)	C6S	5608 (3)	1776 (4)	4782 (7)
C12	6132 (3)	2946 (3)	1508 (5)	C7S	5725 (6)	4798 (6)	−641 (7)
C13	5333 (3)	2864 (3)	1105 (5)	C8S	5854 (6)	5430 (6)	−538 (7)
C14	6698 (4)	2787 (3)	969 (5)	C9S	6239 (6)	5677 (6)	361 (7)
C15	7102 (3)	2172 (3)	1187 (4)	C10S	6495 (6)	5293 (6)	1157 (7)
C16	7902 (4)	2117 (3)	1430 (5)	C11S	6366 (6)	4661 (6)	1054 (7)
C17	8272 (4)	1541 (3)	1525 (5)	C12S	5981 (6)	4414 (6)	155 (7)
C18	7807 (4)	1026 (3)	1336 (5)	C13S	2059 (6)	4173 (4)	3009 (10)
C19	6995 (3)	1055 (3)	1093 (4)	C14S	2084 (6)	4381 (4)	2124 (10)
C20	6666 (3)	1631 (3)	1050 (4)	C15S	2785 (6)	4584 (4)	2024 (10)
C21	6482 (4)	495 (3)	788 (5)	C16S	3460 (6)	4579 (4)	2810 (10)
C22	5898 (3)	374 (3)	1315 (4)	C17S	3435 (6)	4371 (4)	3696 (10)
C23	6135 (4)	51 (3)	2169 (5)	C18S	2735 (6)	4168 (4)	3796 (10)
C24	5638 (4)	−82 (3)	2690 (5)	C42A[a]	6440 (11)	−23 (10)	4398 (12)
C25	4883 (4)	119 (3)	2322 (5)	C43A[a]	6358 (11)	−1015 (9)	3516 (14)
C26	4602 (4)	444 (3)	1472 (5)	C44A[a]	5234 (12)	−730 (10)	3916 (15)
C27	5132 (4)	555 (3)	971 (4)	C42B[a]	5570 (15)	−1078 (13)	3502 (19)
C28	3760 (4)	649 (3)	1123 (5)	C43B[a]	5786 (15)	−82 (13)	4425 (17)
C29	2411 (4)	1886 (4)	3114 (6)	C44B[a]	6820 (17)	−649 (14)	3881 (21)

[a] The site occupation factors for the disordered methyl carbons are 0.5683 and 0.4317 for the A and B positions, respectively.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complex **4**

W–O3	1.698 (4)	W–O2	1.888 (3)
W–O1	1.887 (2)	W–O4	2.386 (4)
O2–W–O4	80.8 (1)	O1–W–O3	99.1 (1)
O1–W–O4	80.9 (1)	O1–W–O2′	88.2 (1)
O1–W–O2	88.9 (1)	W–O1–C1	136.9 (2)
O3–W–O4	180.0 (–)	W–O2–C13	130.7 (2)
O3–W–O2	99.2 (1)	W–O4–C21	180.0 (–)

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex **5**

W–Cl1	2.319 (2)	W–O2	1.899 (4)
W–Cl2	2.319 (2)	W–O3	1.871 (3)
W–O1	1.840 (4)	W–O4	1.871 (3)
O3–W–O4	84.2 (2)	Cl2–W–O1	177.0 (1)
O2–W–O4	162.9 (2)	Cl1–W–O4	96.5 (1)
O2–W–O3	84.1 (2)	Cl1–W–O3	173.3 (1)
O1–W–O4	84.7 (2)	Cl1–W–O2	96.6 (1)
O1–W–O4	96.6 (2)	Cl1–W–O1	90.2 (1)
O1–W–O2	84.3 (2)	Cl1–W–Cl2	86.8 (1)
Cl2–W–O4	96.0 (1)	W–O1–C1	171.1 (4)
Cl2–W–O3	86.4 (1)	W–O2–C13	126.0 (4)
Cl2–W–O2	95.7 (1)		

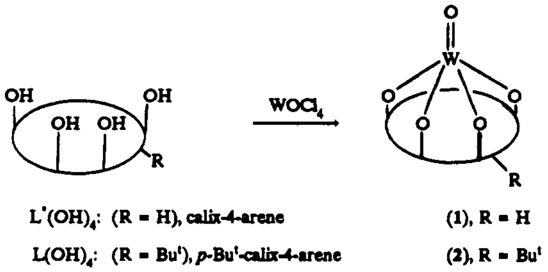
obtained, which was extracted with CH_3COOH, obtaining a gold-yellow solution. A yellow crystalline solid was obtained (77.6%). Anal. Calcd for [(calix[4]arene)WO]·$2CH_3COOH$, $C_{32}H_{28}O_9W$: C, 51.91; H, 3.81. Found: C, 51.19; H, 3.92. ^1H NMR (CD_2Cl_2, 200 MHz, ppm, 293 K): δ 7.17 (d, 8 H, Ph, J_{HH} = 7.6 Hz), 6.73 (t, 4 H, Ph, J_{HH} = 7.6 Hz), 4.66 (d, 4 H, CH_2, J_{HH} = 12.77 Hz), 3.38 (d, 4 H, CH_2, J_{HH} = 12.77 Hz), 2.06 (br, 6 H, CH_3COOH). ^1H NMR (CD_2Cl_2, 200 MHz, ppm, 200 K): δ 12.63 (br, 2 H, CH_3COOH), 7.17 (d, 8 H, Ph, J_{HH} = 7.6 Hz), 6.73 (t, 4 H, Ph, J_{HH} = 7.6 Hz), 4.55 (d, 4 H, CH_2, J_{HH} = 12.77 Hz), 3.38 (d, 4 H, CH_2, J_{HH} = 12.77 Hz), 2.06 (br, 6 H, CH_3COOH).

Preparation of 5. A benzene (100 mL) suspension of WCl_6 (9.24 g, 23.27 mmol) was reacted with *p*-Bu^t-calix[4]arene (15.00 g, 23.27 mmol). The violet suspension was stirred for 12 h, and then the violet-green solid was extracted with benzene during 2 days, obtaining a violet crystalline solid (77%). Anal. Calcd for [(*p*-Bu^t-calix[4]arene)-WCl_2]·$3C_6H_6$, $C_{62}H_{70}Cl_2O_4W$: C, 65.67; H, 6.22. Found: C, 65.60; H, 6.39. ^1H NMR (CD_2Cl_2, 200 MHz, ppm): δ 7.21 (s, 4 H, Ph), 6.92 (s, 4 H, Ph), 5.05 (d, 4 H, CH_2, J_{HH} = 13.80 Hz), 3.31 (d, 4 H, CH_2, J_{HH} = 13.80 Hz), 1.24 (s, 18 H, Bu^t), 0.74 (s, 18 H, Bu^t).

Reaction of 5 with $AlCl_3$ in CH_3COOH. A suspension of [(*p*-Bu^t-calix[4]arene)WCl_2]·$3C_6H_6$ (0.83 g, 0.73 mmol) in CH_3COOH was refluxed for 24 h in the presence of $AlCl_3$ and then filtered. Unreacted [(*p*-Bu^t-calix[4]arene)WCl_2]·$3C_6H_6$ was still observed, and from the yellow solution, kept standing at room temperature for 24 h, **4** separated as a yellow crystalline solid (40%). Anal. Calcd for [(calix[4]arene)-WO]·$2CH_3COOH$, $C_{32}H_{28}O_9W$: C, 51.91; H, 3.81. Found: C, 51.39; H, 3.82.

Results and Discussion

Reaction of *p-tert*-butylcalix[4]arene, [L(OH)$_4$], and calix[4]arene, [L*(OH)$_4$], with $WOCl_4$ in benzene or toluene, followed by an extraction with CH_2Cl_2 or toluene, gave crystalline tungstenyl [W=O] complexes **1** and **2**. Such complexes contain, usually, solvent of crystallization and clathration as reported in the experimental section.



(1)

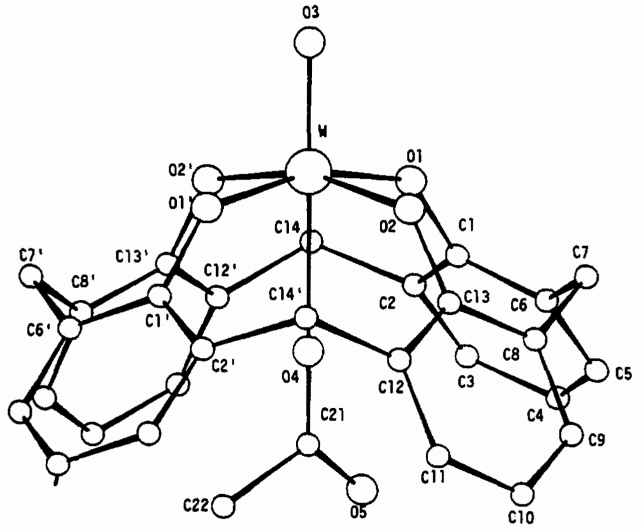


Figure 1. PLUTO drawing of complex **4**. Coordinates for primed atoms: $\bar{x}, y, {}^1/_2 - z$.

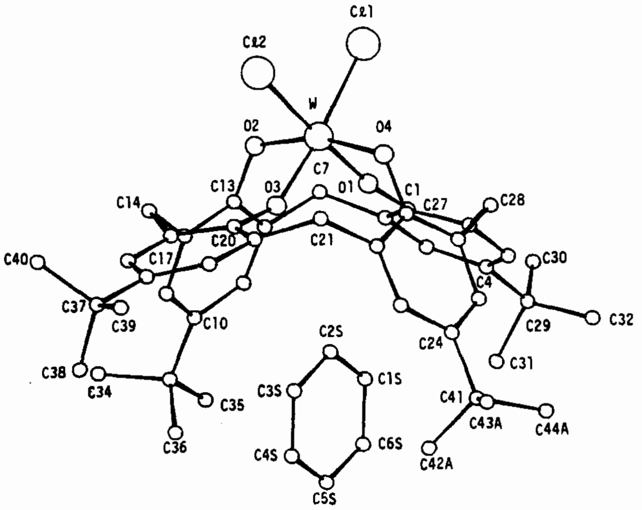
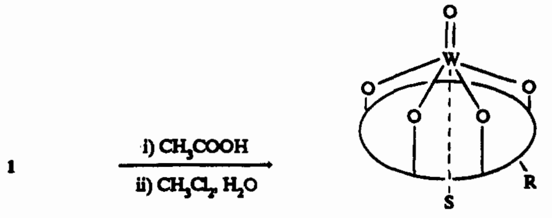


Figure 2. PLUTO drawing of complex **5**.

Complex **1** recrystallized either from acetic acid or from wet CH_2Cl_2 gave solvated forms **3** and **4** containing an hexacoordinate metal.



1 (2)

S = H_2O, **3**

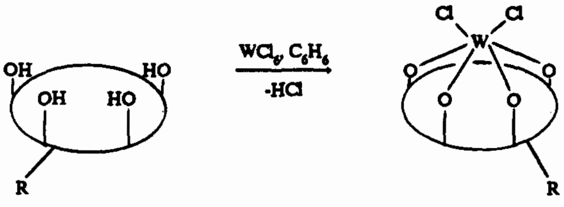
S = CH_3COOH, **4**

R = H

The structure of **4** containing an additional molecule of CH_3COOH of crystallization is shown in Figure 1 (vide infra).

Due to the rather unreactive character of [W═O],[5] we tried to introduce a more reactive functionality at the metal. The reaction of WCl_6 with *p-tert*-butylcalix[4]arene in benzene produces a high yield of **5**, whose structure is given in Figure 2.

By reaction of **5** in acetic acid in the presence of $AlCl_3$, dealkylation of the Bu^t-calix[4]arene was observed (eq 4), which



(3)

2 **5**

R = Bu^t R = Bu^t

(4)

5 **4**

R = Bu^t R = H

is a known reaction in calix[*n*]arene chemistry.[6] It was followed by the deoxygenation of CH_3COOH by a W(VI) halide[7] and led to the transformation of **5** to **4**. Complex **5** is a rather reactive species; its transformation into organometallic derivatives and the replacement by other donor ligands is currently being carried out in our laboratory.

Moving from **4** to **5**, a distortion is introduced into the calix[*n*]arene skeleton, since the two additional ligands at the metal are trans in **4** and cis in **5**. In order to emphasise such a distortion, we selected some parameters, like the following:

(i) The geometrical arrangement of the four oxygens, which are almost coplanar in **4**, define the equatorial coordination plane, while in **5** the equatorial best plane of the octahedron is defined by W,O1,O3,Cl1,Cl2 and O4 assume a trans arrangement. Therefore, we move from an almost spherical cone section of the ligand in **4** to an elliptical one in **5** elongated along the O1⋯O3 direction. Such a cavity ellipticity can be expressed by the distance between the two carbon atoms in the para position of the opposite phenyl rings of the calixarene. Those distances are C4⋯C4′ = 9.04 (1) Å and C10⋯C10′ = 7.88 (1) Å in complex **4** and C4⋯C17 = 10.24 (1) Å and C10⋯C24 = 7.55 (1) Å in complex **5**.

(ii) The dihedral angles between opposite phenyl rings varying with a rather wide range {83.2 (1)° [C1⋯C6 and C1′⋯C6′] and 59.2 (1)° [C8⋯C13 and C8′⋯C13′] in complex **4**; 126.1 (2)° [C1⋯C6 and C15⋯C20] and 49.0 (2)° [C8⋯C13 and C22⋯C27] in complex **5**} prove the dissymmetry in the calixarene conicity. Such differences in the opposite dihedral angles are expected to affect the ^1H NMR spectrum of the bridging methylene.[2] In both compounds at room temperature a single pair of doublets is observed, however, in agreement with a fluxional behavior in solution of the calix skeleton.

(iii) The dihedral angles between adjacent phenyl rings range from 63.9 (2) to 69.5 (2)° in **5** (mean value 65.8°), while they are very different in **4**, 107.3 (2)° for C1⋯C6 and C8⋯C13 and 69.0 (1)° for C8⋯C13 and C1′⋯C6′.

Both compounds **4** and **5** contain solvent of crystallization and guest molecules. Complex **4** crystallizes with two molecules of CH_3COOH, one of them bonding the metal (see Figure 1). The O4 oxygen lies on the 2-fold axis, O5 and C22 being disordered on two positions. The acetic acid in the lattice appears hydrogen-bonded in centrosymmetric dimers. Complex **5** crystallizes with three molecules of benzene, one of them as a guest in the calixarene cavity.

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Supplementary Material Available: For **4** and **5**, ORTEP projections of the complexes and their unit cells and complete listings of crystallographic data, fractional atomic coordinates for hydrogen atoms, anisotropic thermal parameters, and bond distances and angles (14 pages); listings of observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

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Oxidative Homolysis Reactions between Organochromium Macrocycles and Dihalide Radical Anions

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Many electron acceptors are able to oxidize organometals. In the case of organochromium(III) complexes such as $(H_2O)_5CrR^{2+}$ and $RCrL(H_2O)^{2+}$ (L = [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane), studies of the oxidation step have been examined as in eq 1 for the acceptors $Ru(bpy)_3{}^{3+}$, ^2E-$Cr(bpy)_3{}^{3+}$, Ni([14]aneN_4)$^{3+}$, and $IrCl_6{}^{2-}$.[2-4] Indeed, although I_2 is a very weak acceptor, reaction 1 for $RCrL(H_2O)^{2+}$ complexes produces enough $RCrL^{3+}$, and then by its homolysis, enough $R^\bullet$ is formed to initiate a chain sequence for the electrophilic cleavage of the chromium–carbon bond by iodine.[5] As a result of the reaction between $R^\bullet$ and I_2, $I^\bullet$ is formed and thus $I_2{}^{\bullet -}$. The form of the rate law for the reaction between I_2 and $RCrL(H_2O)^{2+}$ allowed us to infer that one of the chain-propagating steps was the oxidation of the organometal by $I_2{}^{\bullet -}$:

$$CrR^{2+} + A \rightarrow CrR^{3+} + A^- \qquad (1)$$

$$I_2{}^{\bullet -} + RCrL(H_2O)^{2+} \rightarrow 2I^- + RCrL(H_2O)^{3+} \qquad (2)$$

The study of the I_2 reaction did not give a value of this rate constant, because *k* for the chain reaction is a composite that contains also the rate constants for the initiation and termination steps.

We decided to investigate reaction 2 for several reasons. First, we wanted to confirm that such a reaction occurs rapidly enough for it to be a chain propagation step in the iodine reaction. Second, we wanted to use its rate constant, in conjunction with the observed constant for the chain reaction, to calculate the rate constant for other elementary steps in the chain. Third, by variation of the group R and by use of other $X_2{}^{\bullet -}$ radicals, we sought to learn more about the nature of the rate-determining step in the reaction. The point behind the use of the macrocycle is that, in donating considerable electron density to the metal, it assists oxidative pathways (for X_2 and $X_2{}^{\bullet -}$) and decreases solvolytic and homolytic decomposition pathways.

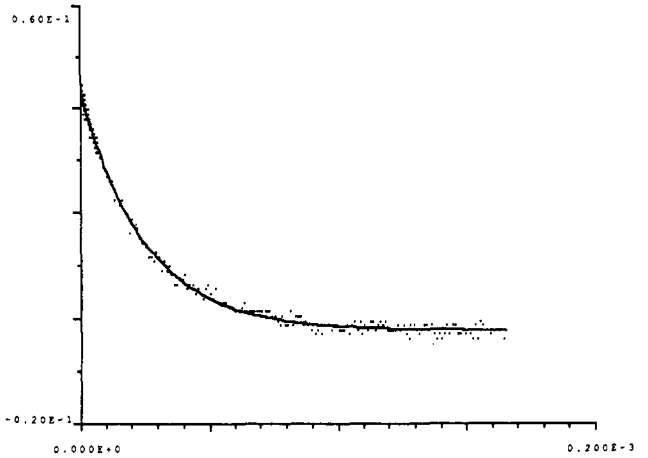

Figure 1. Kinetic trace showing the decay of $Br_2{}^{\bullet -}$ at 400 nm. The radical was generated by pulse radiolysis in N_2O-saturated solution. This is the reaction with 4-$CH_3C_6H_4CH_2Cr$([15]aneN_4)$(H_2O)^{2+}$ at 2.5 × 10^{-4} M. The solid curve was calculated from a nonlinear first-order fitting program. The vertical axis shows absorbance, and the horizontal time in seconds.

Experimental Section

The organochromium complexes were prepared[6,7] from the reaction of organic halide and $(H_2O)_2CrL^{2+}$ for the R groups 4-$BrC_6H_4CH_2$, 4-$CH_3C_6H_4CH_2$, $C_2H_5CH_2$, and $(CH_3)_2CH$. The complexes were separated and purified by ion-exchange chromatography, and their concentrations were determined spectrophotometrically.

The dihalide reagents $X_2{}^{\bullet -}$ (X = I, Br, SCN) were generated by pulse radiolysis of N_2O-saturated solutions of sodium halides or sodium thiocyanate. Hydrated electrons were converted to hydroxyl radicals by reaction with N_2O; the [H^+] was 10^{-4} M so this reaction occurred rather than H atom formation. The reaction of $HO^\bullet$ with X^- forms the desired $X_2{}^{\bullet -}$ species. Ionic strength was maintained with sodium perchlorate. The Argonne electron beam has a 15-MeV energy and a 4-ns pulse length. The reactions were followed by monitoring the disappearance of $X_2{}^{\bullet -}$ at 340, 370, 400, or 475 nm as required. The cell path was 1 or 2 cm as needed to detect $X_2{}^{\bullet -}$ yet minimize the background absorption of the organochromium complex.

The reactions were conducted so as to generate a small burst of $X_2{}^{\bullet -}$ in the presence of a much larger concentration of $RCrL(H_2O)^{2+}$. The disproportionation of the radical (eq 3) contributes to the signal, although

$$2X_2{}^{\bullet -} \rightarrow X^- + X_3{}^- \qquad (3)$$

it is a minor component. It contributed typically 5% at the start of a reaction and progressively less as it proceeded. The kinetic data conformed to first-order kinetics; the data were fit by a nonlinear least-squares equation. A typical kinetic trace, and the first-order fit, are shown in Figure 1.

Results and Discussion

The kinetic experiments had concentrations of the organochromium(III) complexes in the range 10^{-4}–10^{-3} M. The pseudo-first-order rate constants observed were between 9 × 10^3 and 8 × 10^4 s^{-1}. The rate constants were independent of the wavelength of observation. That such a fast decay occurs is consistent with a reaction between $RCrL(H_2O)^{2+}$ and $I_2{}^{\bullet -}$, as suggested from the data on the I_2 chain reaction.

The variation of k_{obs} with [$RCrL(H_2O)^{2+}$] is linear. These lines have small intercepts corresponding to eq 3 and slopes that are the bimolecular rate constants for the desired $X_2{}^{\bullet -}$ reactions. These values are summarized in Table I, along with the oxidation potentials of the $X_2{}^{\bullet -}$ radicals.[8-11] The two complexes whose re-

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