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Complexes with Two (Arene)chromium Tricarbonyl Moieties Separated by Rigid Spacers: Preparation, X-ray Structures, and Oxidative Voltammetry

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Chromium tricarbonyl complexes with arenes bonded to rigid polynorbornyl-type spacers [**1**], [**2**], and [**3**] (structures are given in the text) have been prepared. The dinuclear complexes, e.g., [**1**][Cr(CO)$_3$]$_2$, which is the bis(chromium tricarbonyl) derivative of ligand [**1**], all adopt an exo,exo configuration. The structures of [**1**][Cr(CO)$_3$], [**1**][Cr(CO)$_3$]$_2$, and [**3**][Cr(CO)$_3$]$_2$·(CH$_3$)$_2$CO were determined by X-ray crystallography: for [**1**][Cr(CO)$_3$], $C_{18}H_{12}CrO_3$, triclinic, $P\bar{1}$, a = 8.143 (3) Å, b = 8.356 (4) Å, c = 11.116 (6) Å, α = 75.76 (4)°, β = 78.06 (3)°, γ = 87.06°, V = 717.8 Å^3, Z = 2, ($R(F)$ = 3.40%; for [**1**][Cr(CO)$_3$]$_2$, $C_{21}H_{12}Cr_2O_6$, orthorhombic, $P2_12_12_1$, a = 8.090 (1) Å, b = 10.568 (2) Å, c = 22.336 (3) Å, V = 1909.9 (5) Å^3, Z = 4, $R(F)$ = 4.47%; for [**3**][Cr(CO)$_3$]$_2$·(CH$_3$)$_2$CO, $C_{32}H_{28}Cr_2O_6 \cdot C_3H_6O$, orthrohombic $Pnma$, a = 23.807 (10) Å, b = 10.568 (5) Å, c = 12.409 (5) Å, V = 3121 (2) Å^3, Z = 4, $R(F)$ = 5.38%. Oxidations of the new complexes were studied by cyclic voltammetry and controlled-potential coulometry and through reaction with tris(*p*-bromophenyl)ammoniumyl ion. Each dinuclear complex oxidizes by two electrons to a dication: in a single process for the complex of [**3**], within a single oxidation wave for that of [**2**], and in two resolved one-electron steps for [**1**][Cr(CO)$_3$]$_2$. The $E°$ separation of 140 mV for the last compound is large, considering that the two metals are separated by 6.48 Å. The interaction between the two redox sites is ascribed to efficient through-bond coupling through the bicyclic spacer. Some characterization of the cation radicals was accomplished by low-temperature IR and ESR studies.

Introduction

Compounds **1**–**3** possess arene functionalities separated by rigid polynorbornyl-type spacers having bridge lengths of two, four, and six bonds, respectively.[1] These systems


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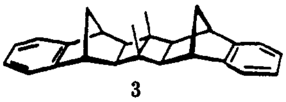
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are members of a more general class of molecules in which two chromophores or redox sites are fused at the ends of polynorbornyl spacers of variable length. Such molecules have been of considerable use in exploring the distance dependence of long-range intramolecular electron-transfer dynamics.[2] An important outcome of these studies has been the finding that the polynorbornyl spacer greatly facilitates intramolecular electron transfer by way of through-bond coupling mechanisms.[2,3] In this respect, we felt that metal π complexes of **1**–**3** would be worthy of synthesis on the grounds that any long-range electronic coupling between the benzene rings that may be present in such complexes could be manifested in their one-electron or multielectron redox processes.

Photoelectron and electron transmission spectroscopic studies on the free ligands **1** and **2**, together with data on the corresponding dienes, revealed the presence of substantial interactions between the π and π^* orbitals of the two aromatic rings, resulting from through-bond interactions.[4] For example, the π,π and π^*,π^* splitting energies in the four-bond system **2** are about 0.5 eV, which is quite substantial, considering that the two benzene groups have an edge-to-edge separation of ca. 7 Å.[4c,d]

Moieties such as Cr(CO)$_3$,[5] Fe(η^5-C$_5$R$_5$)$^+$,[6] and Ru(η^6-C$_6$R$_6$)$^{2+}$[7] are convenient electrochemical labels when π-bonded to arenes. In this paper we offer results on the preparation of dinuclear Cr(CO)$_3$ complexes of ligands **1**–**3**. The mononuclear complex of **1** was also prepared. Three of the complexes, namely [**1**][Cr(CO)$_3$], [**1**][Cr(CO)$_3$]$_2$, and [**3**][Cr(CO)$_3$]$_2$, were characterized by X-ray crystallography, and the one- or two-electron oxidation of each complex has been studied by cyclic voltammetry (CV). IR and ESR spectra of the oxidation products of [**1**][Cr(CO)$_3$]$_2$ have been obtained.

Experimental Section

All procedures were conducted under an atmosphere of N$_2$, using standard Schlenk techniques or a Vacuum Atmospheres

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(1) The IUPAC names of these systems are given in the Experimental Section.

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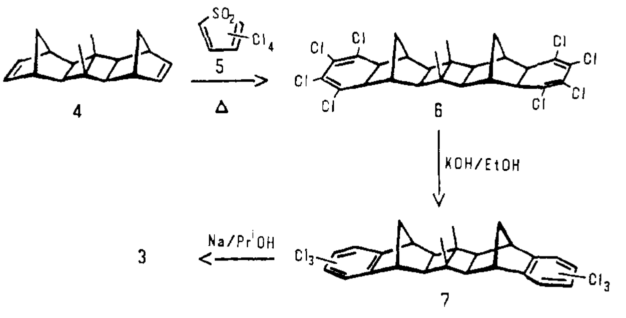
Scheme I



drybox. Electrochemical procedures and purification of reagents are as previously described.[8] The solvent/electrolyte system was $\mathrm{CH_2Cl_2}$/0.1 M $[\mathrm{Bu_4N}][\mathrm{PF_6}]$. Potentials are reported vs the ferrocene/ferrocenium (Fc) reference couple (+0.46 V vs SCE), as recommended by IUPAC.[9] The experimental reference electrode was calibrated with an internal standard at the finish of each experiment. The average of the anodic and cathodic peak potentials is reported as $E_{1/2}$ rather than as $E°$ since waves for two complexes, namely $[\mathbf{2}][\mathrm{Cr(CO)_3}]_2$ and $[\mathbf{3}][\mathrm{Cr(CO)_3}]_2$, are composites of two separate processes.

IR spectra were recorded on a Nicolet Model 6000 FTIR at 2-cm^{-1} resolution using the low-temperature apparatus previously described.[10] The one-electron oxidant $[(p\text{-}\mathrm{BrC_6H_4})_3\mathrm{N}][\mathrm{PF_6}]$ was prepared by $\mathrm{Ag^+}$ oxidation of the neutral amine.[11] The chromium complexes were prepared at the University of Vermont. Their mass spectra were obtained on a Finnigan Model MAT 4500 system by either chemical ionization (with methane) or electron-impact ionization. In each case, a molecular ion peak was observed. NMR spectra were recorded on a Bruker 270-MHz instrument. ESR studies utilized a modified Varian E-4 instrument with the sample at 77 K.

Preparation of Ligands. The syntheses of 9,10-dihydro-9,10-methanoanthracene (1) and (5α,5aβ,6α,11α,11aβ,12α)-5,5a,6,11,11a,12-hexahydro-5,12:6,11-dimethanonaphthacene (2) have been previously reported.[12]

(5α,5aβ,5bα,5cβ,6α,11α,11aβ,11bα,11cβ,12α)-5,5a,5c,6,11,11a,11c,12-Octahydro-5,12:6,11-dimethano-5b,11b-dimethylnaphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (3). This compound was synthesized from the known[13] diene 4, according to Scheme I. A mixture of 3 (2.0 g, 8.4 mmol) and tetrachlorothiophene 1,1-dioxide (5)[14] (4.5 g, 17.7 mmol) in toluene (15 mL) was refluxed for 3 h. The solvent was removed under reduced pressure. The residue was dissolved in chloroform, and excess ethanol was added to the resulting solution. The precipitated bis adduct 6 was collected (5.1 g, 99%) and used immediately without further purification.

A suspension of 6 (5.1 g, 8.2 mmol) in ethanolic KOH (1.2 g of KOH in 120 mL of EtOH) was refluxed for 18 h. The solvent was removed and the residue dissolved in $\mathrm{CH_2Cl_2}$ (250 mL). The solution was washed successively with water (2 × 100 mL) and brine (100 mL) and then dried over $\mathrm{Na_2SO_4}$. Evaporation gave 7 (4.4 g, 98%), which was not purified further.

The hexachloro compound 7 (4.4 g, 8.1 mmol) was dechlorinated by treatment with sodium shot (11 g, 0.49 mol) in a refluxing mixture of THF (150 mL) and propan-2-ol (300 mL) for 18 h. The cooled reaction mixture was extracted with dichloromethane (3 × 100 mL). The combined extracts were successively washed with water (3 × 100 mL) and brine (100 mL) and then dried ($\mathrm{Na_2SO_4}$). Evaporation gave a light yellow solid (2.7 g), which was purified by column chromatography (silica gel, light petroleum ether–EtOAc, 70:30) to give 3 (2.5 g, 92%), mp 266–267 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.01 (s, 6 H, 2 Me), 1.65 (dm, J = 9.3 Hz, 2 H), 1.85 (d, J = 9.3 Hz, 2 H), 1.88 (s, 4 H), 3.28 (br s, 4 H), 3.28 (br s, 4 H), 7.03–7.05 (m, 4 H, arom), 7.13–7.14 (m, 4 H, arom). A satisfactory C, H analysis was obtained.

Preparation of Chromium Complexes. The complexes were prepared by the basic procedure outlined in detail below for $[\mathbf{1}][\mathrm{Cr(CO)_3}]_2$. Further details are available.[15] No attempts were made to maximize yields.

$[\mathbf{1}][\mathbf{Cr(CO)_3}]_2$. A 100-mg (0.53-mmol) amount of 1 and 640 mg (2.9 mmol) of $\mathrm{Cr(CO)_6}$ (Strem Chemicals) were refluxed for 11 h in 22 mL of dry 9:1 butyl ether–THF. The dark solution was evaporated, and excess $\mathrm{Cr(CO)_6}$ was removed through sublimation. The residue was dissolved in THF and the solution filtered. Addition of pentane resulted in precipitation of a yellow product, yield 110 mg (50%). IR ($\mathrm{CH_2Cl_2}$): ν_{CO} at 1976, 1960, 1893 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 4.42 (q, 4 H), 4.11 (q, 4 H), 2.69 (s, 2 H), 1.99 (s, 2 H). MS (EI): m/e calcd 328.02, found 328.

Crystals for X-ray analysis were grown from a saturated solution of the complex in 1:3 THF–hexanes at 248 K.

$[\mathbf{1}][\mathbf{Cr(CO)_3}]$. A 100-mg (0.53-mmol) amount of 1 and 115 mg (0.52 mmol) of $\mathrm{Cr(CO)_6}$ refluxed as above for 7 h gave a yellow oil, which was chromatographed under $\mathrm{N_2}$ on silica gel (dried in vaicuo at 373 K). Elution with 1:1 $\mathrm{CH_2Cl_2}$–hexanes and subsequent evaporation gave a warm-hexanes-soluble residue which afforded yellow needles in 2 days at 248 K: yield 65 mg (38%). IR ($\mathrm{CH_2Cl_2}$): ν_{CO} at 1963, 1885 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.29 (q, 2 H), 6.99 (q, 2 H), 5.57 (q, 2 H), 5.17 (q, 2 H), 4.08 (s, 2 H), 2.71 (d, 1 H), 2.32 (d, 1 H). MS (CI, methane): m/e calc 463.94, found 464.

$[\mathbf{2}][\mathbf{Cr(CO)_3}]_2$. A 200-mg (0.77-mmol) amount of 2 and 1360 mg (6.2 mmol) of $\mathrm{Cr(CO)_6}$ refluxed for 18 h in 22 mL of dry 9:1 butyl ether–THF, followed by evaporation and redissolution in THF, gave a yellow solution. Partial evaporation and addition of hexanes crystallized the complex at 248 K overnight: yield 200 mg (48%). IR ($\mathrm{CH_2Cl_2}$): ν_{CO} at 1961 and 1883 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 5.39 (q, 4 H), 5.16 (q, 4 H), 3.07 (s, 4 H), 2.27 (d, 2 H), 1.85 (d, 2 H), 1.76 (s, 2 H). MS (CI, methane): m/e calcd 529.99, found 530.

$[\mathbf{3}][\mathbf{Cr(CO)_3}]_2$. An 85-mg (0.25-mmol) amount of 3 and 700 mg (3.2 mmol) of $\mathrm{Cr(CO)_6}$ were refluxed for 7 h in 10 mL of dry 9:1 butyl ether–THF. The evaporated residue (see preparation of $[\mathbf{1}][\mathrm{Cr(CO)_3}]_2$) was dissolved in THF, this solution was filtered and evaporated, and the residue was washed with hexanes and recrystallized from acetone–hexanes at 263 K or from ethyl acetate–hexanes by liquid–liquid diffusion: yield 20% of vacuum-dried crystals. IR ($\mathrm{CH_2Cl_2}$): ν_{CO} at 1960 and 1883 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 5.43 (q, 4 H), 5.18 (q, 4 H), 3.03 (s, 4 H), 1.98 (s, 4 H), 1.77 (d, 2 H), 1.60 (d, 2 H), 0.93 (s, 6 H). MS (EI): m/e calcd 610.05, found 610.

X-ray-quality crystals were grown from a saturated 1:1 acetone–hexanes solution left 5 days at 248 K.

Crystallographic Structure Determinations of $[\mathbf{1}][\mathbf{Cr(CO)_3}]$, $[\mathbf{1}][\mathbf{Cr(CO)_3}]_2$, and $[\mathbf{3}][\mathbf{Cr(CO)_3}]_2\cdot\mathbf{(CH_3)_2CO}$. Crystallographic data are consolidated in Table I. Crystals were mounted on glass fibers, and the unit cells were determined from the angular settings of 25 high-angle reflections. The space group for $[\mathbf{1}][\mathrm{Cr(CO)_3}]$ was initially assigned to the centrosymmetric alternative, $P\bar{1}$, and the well-behaved refinement process in this space group suggested that the initial assignment was correct. Similarly, the space group for $[\mathbf{3}][\mathrm{Cr(CO)_3}]$, *Pnma*, was determined to be centrosymmetric. For $[\mathbf{1}][\mathrm{Cr(CO)_3}]$, the space group was uniquely assigned from systematic absences in the reflection data. The upper limit on 2θ for the data collections was determined by a 5% observed data criterion. The data were corrected for a small linear decay in check reflection intensities and for minor absorption effects by empirical (ψ-scan) methods.

In all cases, the structures were solved from Patterson syntheses and completed from difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. Atomic coordinates are given in Tables II–IV (supplementary material). All com-

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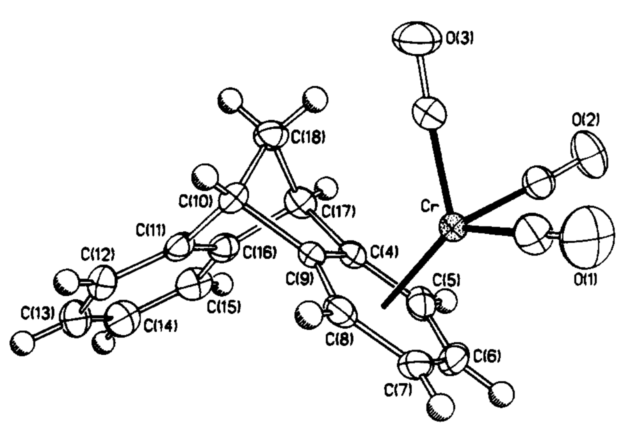


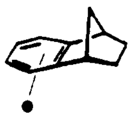
Figure 1. ORTEP diagram of [1][Cr(CO)$_3$].

putations used programs contained in the SHELXTL (5.1) program library (G. Sheldrick, Nicolet (Siemens) XRD Corp., Madison, WI).

Results and Discussion

Preparation and Structures of Complexes. The desired mono- or dinuclear complexes were prepared in a straightforward fashion by refluxing the ligand in 9:1 *n*-butyl ether–THF[16] with either an equimolar amount of Cr(CO)$_6$ (mononuclear complex) or excess Cr(CO)$_6$ (dinuclear complexes). Air-stable golden crystalline products were obtained in all cases in moderate yields. The proton NMR spectra of the new compounds were interpreted in terms of the metal moieties bonding always in an exo position (structure A).[17] Whereas both exo and endo (structure B) isomers have been widely reported for mononuclear Cr(CO)$_3$ complexes of arenes bonded to bicyclic systems,[18-20] most previously reported *di*nuclear complexes have an exo,endo (or trans) configuration (structure C).[21,22] Thus, the exo,exo (or cis) configuration (structure D) implied by NMR results for the present dinuclear complexes was sufficiently unusual to warrant crystallographic studies. We note that exo bonding is also favored in mono-


A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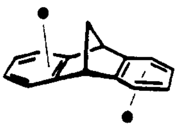
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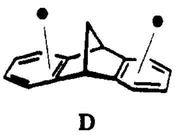
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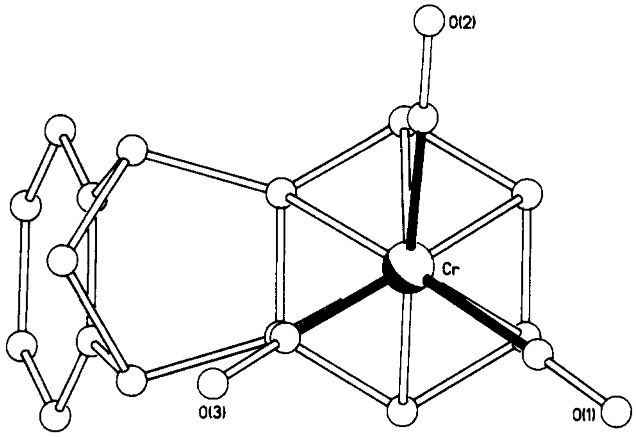

Figure 2. View of [1][Cr(CO)$_3$] perpendicular to the Cr–arene axis, showing the nearly eclisped chromium tricarbonyl group.

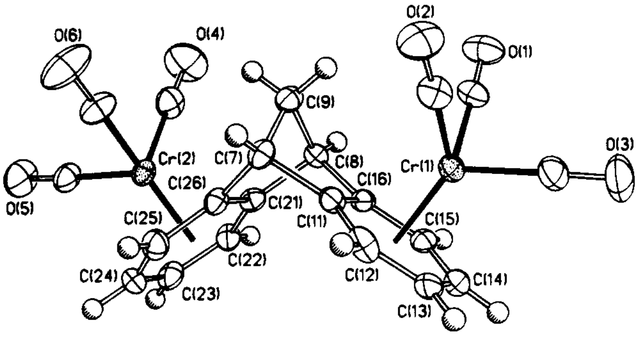

Figure 3. ORTEP diagram of [1][Cr(CO)$_3$]$_2$.

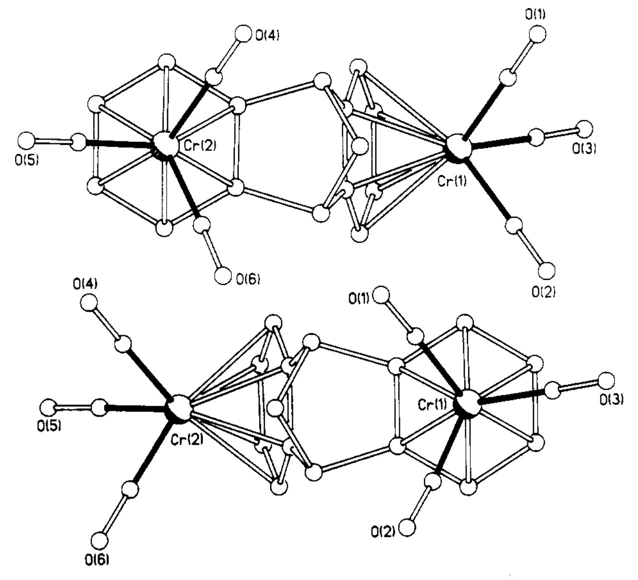

Figure 4. View of [1][Cr(CO)$_3$]$_2$ perpendicular to one Cr–arene axis, showing the staggered conformations of Cr(CO)$_3$ groups.

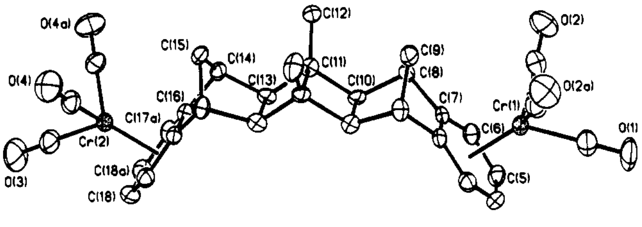

Figure 5. ORTEP diagram of [3][Cr(CO)$_3$]$_2$.

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Table I. Crystallographic Data for $C_{18}H_{12}CrO_3$, $C_{21}H_{12}Cr_2O_6$, and $C_{32}H_{28}Cr_2O_6$

	(a) Crystal Parameters		
formula	$C_{18}H_{12}CrO_3$	$C_{21}H_{12}Cr_2O_6$	$C_{32}H_{28}Cr_2O_6 \cdot C_3H_6O$
fw	328.27	464.32	670.59
cryst syst	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$	*Pnma*
a, Å	8.148 (3)	8.090 (1)	23.807 (10)
b, Å	8.356 (4)	10.568 (2)	10.568 (5)
c, Å	11.116 (6)	22.336 (3)	12.409 (5)
α, deg	75.76 (4)		
β, deg	78.06 (3)		
γ, deg	87.06 93)		
V, Å^3	717.8 (6)	1909.9 (5)	3121 (2)
Z	2	4	4
cryst dimens, mm	0.06 × 0.14 × 0.32	0.15 × 0.21 × 0.42	0.38 × 0.39 × 0.41
cryst color	yellow	yellow	yellow
D(calc), g cm^3	1.519	1.615	1.427
μ(Mo Kα), cm^{-1}	7.85	11.45	7.14
temp, K	297	297	297
	(b) Data Collection		
diffractometer		Nicolet R3m	
monochromator		graphite	
radiation		Mo Kα (λ = 0.71073 Å)	
2θ scan range, deg	4–45	4–54	4–45
data collected (*hkl*)	±9,±9,+13	+11,+14,+29	+26,+12,+14
no. of rflns collected	1993	2280	2361
no. of indpt rflns	1873	2256	2174
R(merg), %	0.022		
no. of indpt obs rflns $F_o \geq n\sigma(F_o)$	1520 (*n* = 5)	1736 (*n* = 4)	1468 (*n* = 4)
std rflns	3 stds/197 rflns	3 stds/197 rflns	3 stds/197 rflns
var in stds	<1	~3	~3
	(c) Refinement		
R(*F*), %	3.40	4.47	5.38
R(w*F*), %	3.75	4.77	5.77
Δ/σ(max)	0.061	0.069	0.028
$\Delta(\rho)$, e Å^{-3}	0.22	0.62	0.42
N_o/N_v	7.64	6.63	6.99
GOF	1.157	1.216	1.592

Table V. Selected Bond Distances and Angles for [1][Cr(CO)$_3$]

(a) Bond Distances (Å)			
Cr–CNT	1.741 (3)	C(1)–O(1)	1.150 (5)
Cr–C(1)	1.838 (4)	C(2)–O(2)	1.163 (5)
Cr–C(2)	1.830 (4)	C(3)–O(3)	1.144 (5)
Cr–C(3)	1.837 (4)		
(b) Bond Angles (deg)			
CNT–Cr–C(1)	125.6 (2)	C(1)–Cr–C(2)	89.5 (2)
CNT–Cr–C(2)	125.9 (2)	C(1)–Cr–C(3)	85.2 (2)
CNT–Cr–C(3)	129.4 (2)	C(2)–Cr–C(3)	88.0 (2)
Cr–C(1)–O(1)	178.2 (4)	C(9)–C(10)–C(11)	104.4 (3)
Cr–C(2)–O(2)	178.9 (3)	C(4)–C(17)–C(16)	104.8 (2)
Cr–C(3)–O(3)	177.0 (3)	C(10)–C(18)–C(17)	94.3 (3)

Table VI. Selected Bond Distances and Angles for [1][Cr(CO)$_3$]$_2$

(a) Bond Distances (Å)			
CNT(1)–Cr(1)	1.729 (6)	C(1)–O(1)	1.142 (8)
CNT(2)–Cr(2)	1.723 (6)	C(2)–O(2)	1.140 (9)
Cr(1)–C(1)	1.843 (6)	C(3)–O(3)	1.157 (10)
Cr(1)–C(2)	1.854 (7)	C(4)–O(4)	1.140 (9)
Cr(1)–C(3)	1.841 (7)	C(5)–O(5)	1.150 (9)
Cr(2)–C(4)	1.846 (7)	C(6)–O(6)	1.151 (8)
Cr(2)–C(5)	1.859 (6)		
Cr(2)–C(6)	1.832 (6)		
(b) Bond Angles (deg)			
CNT(1)–Cr(1)–C(1)	125.7 (3)	C(4)–Cr(2)–C(5)	88.5 (3)
CNT(1)–Cr(1)–C(2)	126.0 (3)	C(4)–Cr(2)–C(6)	88.1 (3)
CNT(1)–Cr(1)–C(3)	126.4 (3)	C(5)–Cr(2)–C(6)	87.9 (3)
CNT(2)–Cr(2)–C(4)	127.3 (3)	Cr(1)–C(1)–O(1)	178.0 (6)
CNT(2)–Cr(2)–C(5)	127.1 (3)	Cr(1)–C(2)–O(2)	175.8 (6)
CNT(2)–Cr(2)–C(6)	125.2 93)	Cr(1)–C(3)–O(3)	178.4 (7)
C(1)–Cr(1)–C(2)	89.4 (3)	Cr(2)–C(4)–O(4)	179.2 (10)
C(1)–Cr(1)–C(3)	88.7 (3)	Cr(2)–C(5)–O(5)	177.4 (7)
C(2)–Cr(1)–C(3)	90.6 (3)	Cr(2)–C(6)–O(6)	178.2 (8)
		C(11)–C(7)–C(26)	103.4 (5)
		C(16)–C(8)–C(21)	102.1 (5)
		C(7)–C(9)–C(8)	95.1 (5)

and dinuclear complexes of (pentamethylcyclopentadienyl)ruthenium cation with the related bicyclic ligand triptycene.[23] In complexes of a rigid bridge with cyclopentadienyl end groups, both exo,exo and exo,endo diiron complexes have been isolated.[24]

Three compounds were structurally characterized in the solid state, namely [1][Cr(CO)$_3$], [1][Cr(CO)$_3$]$_2$, and [**3**][Cr(CO)$_3$]$_2$. Each crystallized as independent, well-separated molecules. [**3**][Cr(CO)$_3$]$_2$ cocrystallized with a molecule of acetone. The chromium environment in all complexes is the anticipated three-legged piano-stool arrangement, and in all cases the Cr(CO)$_3$ moiety is situated in an exo position, so that only structures of types A and D were observed.

Selected bond distances and angles are given in Tables V–VII, respectively, for [1][Cr(CO)$_3$], [1][Cr(CO)$_3$]$_2$, and [**3**][Cr(CO)$_3$]$_2$. The metal–metal distances are of interest. Separations of 6.48 and 11.46 Å are observed for the complexes [1][Cr(CO)$_3$]$_2$ and [**3**][Cr(CO)$_3$]$_2$, respectively.

Figures 1 and 2 contain views of [1][Cr(CO)$_3$], Figures 3 and 4 of [1][Cr(CO)$_3$]$_2$, and Figures 5 and 6 of [**3**][Cr(CO)$_3$]$_2$. The most striking difference among these structures is the nearly eclipsed conformation found in [1][Cr(CO)$_3$], compared to the staggered conformation of the four other Cr(CO)$_3$ moieties in [1][Cr(CO)$_3$]$_2$ and

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Table VII. Selected Bond Distances and Angles for $[3][Cr(CO)_3]_2$

(a) Bond Distances (Å)			
CNT(1)–Cr(1)	1.720 (7)	C(1)–O(1)	1.155 (12)
CNT(2)–Cr(2)	1.717 (6)	C(2)–O(2)	1.152 (9)
Cr(1)–C(1)	1.833 (10)	C(3)–O(3)	1.163 (13)
Cr(1)–C(2)	1.843 (7)	C(4)–O(4)	1.162 (9)
Cr(2)–Cr(3)	1.814 (10)		
Cr(2)–C(4)	1.814 (7)		
(b) Bond Angles (deg)			
CNT(1)–Cr(1)–C(1)	126.9	Cr(1)–C(1)–O(1)	180.0 (9)
CNT(1)–Cr(1)–C(2)	125.0	Cr(1)–C(2)–O(2)	177.7 (6)
CNT(2)–Cr(2)–C(3)	123.2	Cr(2)–C(3)–O(3)	178.3 (9)
CNT(2)–Cr(2)–C(4)	126.9	Cr(2)–C(4)–O(4)	177.7 (6)
C(1)–Cr(1)–C(2)	89.3 (3)		
C(2)–Cr(1)–C(2a)	89.7 (4)		
C(3)–Cr(2)–C(4)	90.9 (3)		
C(4)–Cr(2)–C(4a)	86.6 (4)		

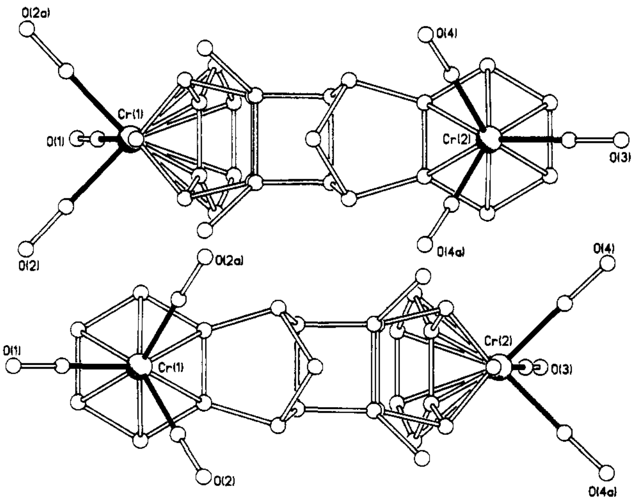
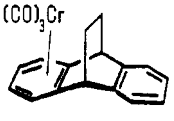


Figure 6. View of $[3][Cr(CO)_3]_2$ showing staggered $Cr(CO)_3$ groups.

$[3][Cr(CO)_3]_2$. In a mononuclear complex closely related to $[1][Cr(CO)_3]$, namely (dibenzobicyclo[2.2.2]octadiene)$[Cr(CO)_3]$ (8), both exo and endo isomers were isolated and structurally characterized.[20] Oddly, in the exo isomer, which crystallizes with two crystallographically independent molecules, both of the possible staggered conformations are seen (either the ortho-disubstituted C–C bond and those related to it by 120° are bisected by the projection of the Cr–C–O legs or the set rotated by 60° is bisected), whereas in $[1][Cr(CO)_3]_2$ and $[3][Cr(CO)_3]_2$ only the latter is seen. Given the variety of conformations seen in the set of the four aforementioned compounds and the lack of clear trends in the conformations of a wider range of ortho-disubstituted arene compounds, it may be concluded that conformations are determined substantially by intermolecular (packing) forces, despite theoretical studies claiming intramolecular control.[25] The very low, 1–2 kcal mol^{-1} barrier to rotation is comparable to lattice energy terms for polar interactions.



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In the mononuclear complexes $[1][Cr(CO)_3]$ and, for comparison, 8, the dihedral angles relating the arene planes to those of the bicyclodiene ligand reveal minor steric effects. In $[1][Cr(CO)_3]$, the angle between C(4,5,6,7,8,9) and C(10,9,4,17) is 5.7°, whereas the comparable angle on the uncomplexed side is 1.2°. In the comparable dinuclear complex $[1][Cr(CO)_3]_2$ the same angles are equal and intemediate at 3.7°.

Table VIII. Electrochemical Results for (arene)$Cr(CO)_3$ Complexes in CH_2Cl_2/0.1 M $[Bu_4N][PF_6]$[a]

complex	$E_{1/2}$, V	n	$i/Cv^{1/2}$,[b] μA mM^{-1} $V^{-1/2}$ $s^{1/2}$	$t_{1/2}$,[c] s (n^+)
$(C_6H_6)Cr(CO)_3$[5]	ca. +0.4	1		ca. 5 (+)
$[1][Cr(CO)_3]$	+0.37	1	20.6	5 (+)
$[1][Cr(CO)_3]_2$	+0.37	1	21.8	0.1 (+)
$[1][Cr(CO)_3]_2$	+0.51	1		0.02 (2+)
$[2][Cr(CO)_3]_2$	+0.37	2	41.5	2 (+, 2+)[d]
$[3][Cr(CO)_3]_2$	+0.29	2		>10[e]

[a] Potentials are given vs the Fc/Fc^+ couple. [b] Current function at Pt-bead electrode, proportional to n (number of electrons transferred). [c] Half-life of oxidized species (n+) at ambient temperature, computed from i_c/i_a values using the method of Nicholson (*Anal. Chem.* **1966**, *38*, 1406) and assuming first-order decomposition. Value for $(C_6H_6)Cr(CO)_3^+$ estimated from CV of Figure 2 in ref 5. [d] One two-electron wave. The species undergoing decomposition (+ or 2+) is unknown. [e] Chemically reversible with CV scan rates ≥0.05 V s^{-1}.

The central dihedral angle, formed by the folding at the bridgehead carbon atoms, is compressed slightly by the addition of a second $Cr(CO)_3$ group: in $[1][Cr(CO)_3]$, 111.2°; in $[1][Cr(CO)_3]_2$, 109.2°. As expected from ring-strain arguments, this dihedral angle is affected by the number of methylene groups in the bridge; when the number is increased to two, as in 8, the angle increases to 122°. The smaller the dihedral angle, the less the interaction between two exo,exo $Cr(CO)_3$ groups, but the greater the interaction were the groups to be endo. Undoubtedly, this accounts for our inability to isolate a mononuclear endo-substituted bicycloheptadiene complex. In $[3][Cr(CO)_3]_2$, these effects are nearly identical with those seen in $[1][Cr(CO)_3]_2$. The dihedral angles differ by less than what could be attributed to packing forces.

Oxidative Voltammetry. The new complexes were studied by cyclic voltammetry (CV) in CH_2Cl_2/0.1 M $[Bu_4N][PF_6]$ in order to minimize decomposition of the one-electron-oxidation products.[26] Voltammetry of the mononuclear complex $[1][Cr(CO)_3]$ was unremarkable. Its diffusion-controled one-electron Nernstian oxidation wave (eq 1) at $E_{1/2}$ ($\sim E°$) = +0.37 V vs Fc is typical of (η^6-arene)$Cr(CO)_3$ complexes.[27]

$$[1][Cr(CO)_3] \rightleftharpoons [1][Cr(CO)_3]^+ + e^- \tag{1}$$

Some deviation from chemical reversibility was noted at ambient temperatures (i_c/i_a = 0.78 with v = 0.10 V s^{-1}), but the couple was chemically reversible at the slowest scan rates at 272 K. An irreversible second oxidation at E_p = +1.13 V (v = 0.1 V s^{-1}) was noted. Pertinent electrochemical parameters are collected in Table VIII.

The monooxidized dinuclear complex $[1][Cr(CO)_3]_2^+$ was *less* stable than was $[1][Cr(CO)_3]^+$. Scan rates above 1 V s^{-1} were necessary to see chemical reversibility for the couple $[1][Cr(CO)_3]_2^{0/+}$ (eq 2). When scan rates were sufficiently fast to outrun the cation decomposition process, the anodic current function $i_{pa}/Cv^{1/2}$, which is proportional to the number of electrons transfered (n), matched that of $[1][Cr(CO)_3]^{0/+}$. A half-life of ca. 0.1 s was calculated for $[1][Cr(CO)_3]_2^+$ at 298 K, compared to $t_{1/2}$

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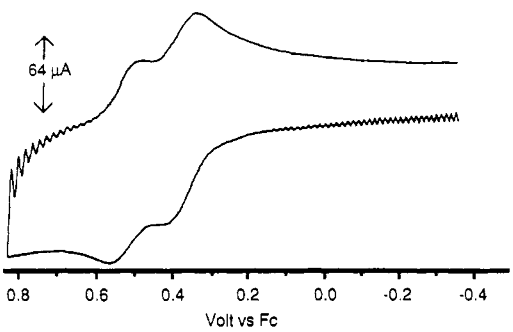


Figure 7. Anodic CV scan of 0.4 mM $[1][Cr(CO)_3]_2$ in CH_2Cl_2 (ambient temperature, scan rate 75 V/s, Pt electrode). The ringing pattern is a consequence of the potentiostat being close to instability owing to the use of positive feedback methodology.

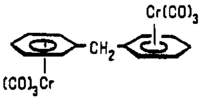
= 0.7 s for $[1][Cr(CO)_3]^+$ (Table VIII). The dication of the dinuclear system was quite unstable, demonstrating chemical reversibility only with $v > 20$ V s^{-1} ($t_{1/2} = 0.025$ s). Moderately fast-scan voltammetry (Figure 7) allowed evaluation of the two 1e$^-$ reactions of eqs 2 and 3 as $E_{1/2}{}^1$

$$[1][Cr(CO)_3]_2 \rightleftharpoons [1][Cr(CO)_3]_2{}^+ + e^- \quad E_{1/2}{}^1 \qquad (2)$$

$$[1][Cr(CO)_3]_2{}^+ \rightleftharpoons [1][Cr(CO)_3]_2{}^{2+} + e^- \quad E_{1/2}{}^2 \qquad (3)$$

= +0.37 V and $E_{1/2}{}^2$ = +0.51 V. The decomposition products of the cation(s) were of little interest, owing to the number of previous studies of the decomposition mechanism of Cr(I) and Cr(II) species derived from (arene)$Cr(CO)_3$ complexes.[26-28]

The $\Delta E_{1/2}$ value ($=E_{1/2}{}^2 - E_{1/2}{}^1$) of 140 mV for the processes $[1][Cr(CO)_3]_2{}^{0/+/2+}$ is quite large, given that the two metals are held ca. 6.5 Å apart, separated by a spacer having two saturated C–C bonds between the arenes. For comparison, note that (diphenylmethane)$[Cr(CO)_3]_2$[29] (**9**)



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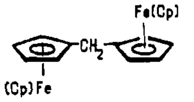

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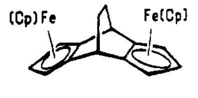

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has a $\Delta E_{1/2}$ value of ca. 45 mV, close to the value of 36 mV expected for two noninteracting redox centers.[30,31] The origin of the increase in $\Delta E_{1/2}$ for $[1][Cr(CO)_3]_2$ is discussed below. It is of interest to note that ferrocenyl groups separated by one or more saturated carbons tend to have $\Delta E_{1/2}$ values larger than those exhibited by separated (arene)$Cr(CO)_3$ groups. Specifically, the $\Delta E_{1/2}$ values for biferrocene (direct linkage of two ferrocenyl groups), **10** (one CH_2, two C–C bonds), and **11** (two C–C bonds, analogue of $[1][Cr(CO)_3]_2$) are 350,[32] 170,[33] and 160 mV,[24] respectively.

Complexes $[2][Cr(CO)_3]_2$ and $[3][Cr(CO)_3]_2$ were each oxidized in a *single* oxidation wave of apparent two-electron height, with $E_{1/2}$(app) = +0.37 and +0.29 V, respectively. The current function for $[2][Cr(CO)_3]_2$ of 41.5 ± 1.5 μA mM^{-1} V$^{-1/2}$ s$^{1/2}$ was approximately twice that of the one-electron processes $[1][Cr(CO)_3]^{0/+}$ and $[1][Cr(CO)_3]_2{}^{0/+}$ (20.6 and 21.8 μA M^{-1} V$^{-1/2}$ s$^{1/2}$, respectively). From the i_c/i_a value for $[2][Cr(CO)_3]_2$ at slower sweep rates (e.g., 0.70 at v = 200 mV s^{-1}) an apparent rate constant for decomposition of the oxidized form was obtained as 0.29 s^{-1} ($t_{1/2}$ = 2.4 s, Table VIII), similar to that of the mononuclear cation $[1][Cr(CO)_3]^+$. Since the oxidation of $[2][Cr(CO)_3]_2$ occurs in a two-electron wave, however, it is not clear whether the decomposition of $[2][Cr(CO)_3]_2{}^{n+}$ occurs through the monocation (n = 1), the dication (n = 2), or both species.

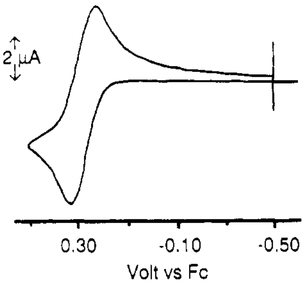

Figure 8. CV scan of 0.4 mM $[3][Cr(CO)_3]_2$ in CH_2Cl_2 (ambient temperature, scan rate 0.2 V/s, Pt electrode).

There is some evidence that the $E_{1/2}$ values of the two oxidation processes of $[2][Cr(CO)_3]_2$ are sufficiently different to broaden the CV wave. One-electron Nernstian waves under our measurement conditions generally displayed ΔE_p values of 70–75 mV and δE_p ($=E_p - E_{p/2}$) values of 55–60 mV with v = 0.2 V s^{-1}. However, the corresponding values for $[2][Cr(CO)_3]_2{}^{0/2+}$ were 110 and 77 mV, respectively, too large to arise from resistive distortions. These parameters suggest a $\Delta E_{1/2}$ value of ca. 50 mV for $[2][Cr(CO)_3]_2{}^{0/+/2+}$. Hence, there may be a small but finite Coulombic interaction between the metal redox centers even though they are separated by ca. 9 Å, since two noninteracting redox centers should only have $\Delta E_{1/2}$ = 35.2 mV.[30] This possibility will be pursued with analogues which may give more stable cations and less ambiguous answers.

Electrodic studies on $[3][Cr(CO)_3]_2$ were restricted owing to the tendency of the dication to partially passivate the electrode after each scan. Only one voltammetric wave was observed in the pertinent potential range, and it had the shape and diagnostics of a chemically reversible, nearly Nernstian, n = 1e$^-$ process ($E_{1/2}$ = +0.29 V, Figure 8). In a dinuclear system such as $[3][Cr(CO)_3]_2$, this behavior is interpreted as consistent with *independent* one-electron redox centers separated by ca. $\Delta E_{1/2}$ = 36 mV, the probability-determined value.

Spectral Characterization of Oxidation Products of $[1][Cr(CO)_3]_m$ (m = 1, 2). IR spectra of monooxidized species are often helpful in diagnosing mixed-valency classifications of dinuclear systems. In previous studies of the oxidation of (diarene)$Cr_2(CO)_4(PR_3)_2$ complexes, ν_{CO}(sym) has proved a convenient diagnostic, shifting ca. 100 cm^{-1} to higher frequency for the carbonyls bonded to a fully positive Cr atom.[29,34,35] The same predictions are made for analogous $Cr(CO)_3$ complexes, but their 17e$^-$ cations are generally less stable than those of the corresponding phosphine-substituted complexes. Consequently, oxidations of $[1][Cr(CO)_3]$ and $[1][Cr(CO)_3]_2$ were performed at subambient temperatures to facilitate moni-

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Table IX. ESR Results for $17e^-$ Mono- and Dinuclear Chromium Tricarbonyl Complexes at 77 K in 1:1 CH_2Cl_2–$C_2H_4Cl_2$

radical	*g* values
$(C_6Me_6)Cr(CO)_3^+$	2.126, 2.035, 1.991
$[1][Cr(CO)_3]^+$	2.131, 2.038, 1.994
$[1][Cr(CO)_3]_2^+$	2.126, 2.035, 1.995
$[2][Cr(CO)_3]_2^+$	2.128, 2.088, 1.993

toring of their primary oxidation products.

Oxidation of a 2 mM solution of $[1][Cr(CO)_3]$ (ν_{CO} 1958, 1880 cm^{-1}) by a slight excess of $(p\text{-}BrC_6H_4)_3N^+$ at 203 K was investigated as a reference system. The expected bands for $[1][Cr(CO)_3]^+$ were observed at ν_{CO} 2067, 2000 cm^{-1} together with minor contributions from the starting material, indicating incomplete oxidation and/or regeneration of the starting material. Back-reduction of $\{[1][Cr(CO)_3]\}^+$ with Cp_2Fe regenerated the spectrum of $[1][Cr(CO)_3]$.

Chemical oxidation of the dinuclear complex $[1][Cr(CO)_3]_2$ is complicated by the possible presence of both mono- and dicationic products as well as *mononuclear* decomposition products. The latter was eliminated as an important factor by a control experiment.[36]

$(p\text{-}BrC_6H_4)_3N^+$ oxidation of $[1][Cr(CO)_3]_2$ at 198 K gave oxidation products less stable than those of the mononuclear analogue $[1][Cr(CO)_3]$, as expected from CV results (Table VIII). With an approximately 3:1 excess of oxidant, strong CO bands were observed (Figure 9) at 2068 and 1995 cm^{-1}, typical of a localized positive charge. Back-reduction of the deep red solution by ferrocene regenerated the original bands (ν_{CO} = 1971, 1957, 1886 cm^{-1}). The spectral quality and reaction stoichiometry in successive additions of oxidant were sufficiently poor that we could not confidently assign contributions to mono- and dioxidized species. At no point, however, were spectra observed with carbonyl frequencies shifted drastically from either $[1][Cr(CO)_3]_2$ or a Cr(I) site. We conclude therefore that the monocation $\{[1][Cr(CO)_3]_2\}^+$ has trapped valence and categorize this system as class II mixed valent[37] on the basis of the IR and CV results.

ESR spectra of the dinuclear monocations were also consistent with localized spin on one metal site, in that the *g*-value parameters were very similar to that of the mononuclear Cr(I) species (hexamethylbenzene)$Cr(CO)_3^+$ (Table IX).

Conclusions

All three of the new dinuclear complexes display weak coupling, at best, of the redox centers. This is not unexpected for compounds in which two $Cr(CO)_2L$ moieties are separated by a bridging diarene. The HOMO's of these complexes, if similar to those of the mononuclear reference compounds (arene)$Cr(CO)_2L$, have little arene character.[38,39] On this basis the metal centers are likely to show coupling only through space or through the σ framework of the bridging ligand. If one eliminates the former because of the large M–M distance (>6 Å), through-bond coupling is seen as mainly responsible for any interaction between the redox sites. As manifested by the $\Delta E_{1/2}$ values, this interaction decreases in the expected fashion as the number of σ-bonds in the bridging ligand increases from two ([1]) to four ([2]) to six ([3]).

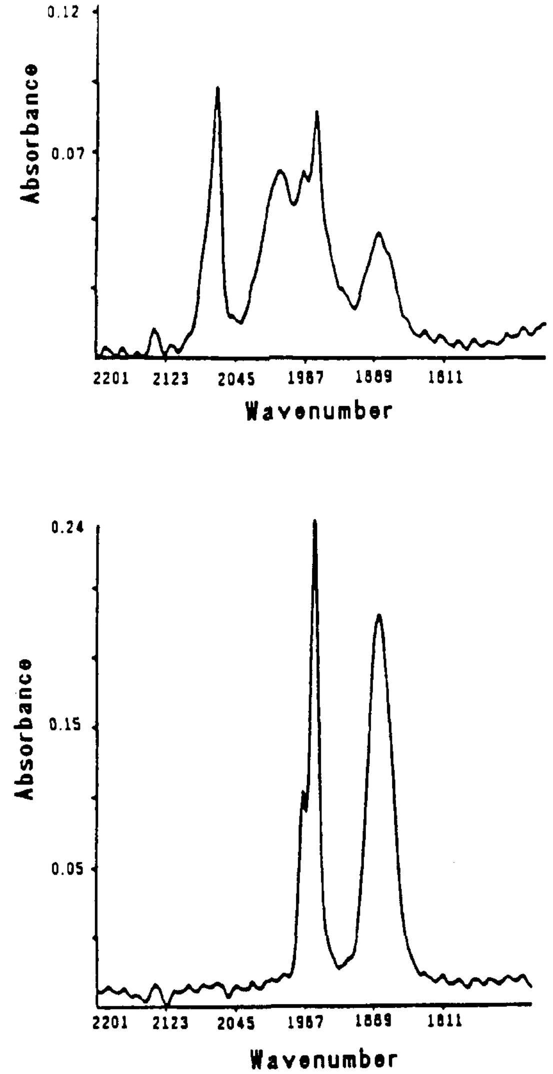

Figure 9. IR spectra in CH_2Cl_2 at 203 K: (top) approximately monooxidized $[1][Cr(CO)_3]_2$ from reaction of neutral complex with $(p\text{-}BrC_6H_4)_3N^+$ at 198 K; (bottom) back-reduced solution after treatment with Cp_2Fe, showing regeneration of the original neutral complex.

It is of interest to compare the $\Delta E_{1/2}$ value of $[1][Cr(CO)_3]_2$ to those measured for certain other dinuclear Cr compounds. The value of 140 mV is substantially larger than that of **9**, which also has two C–C bonds separating the electroactive sites.[29] The larger value of $\Delta E_{1/2}$ for $[1][Cr(CO)_3]_2$ is believed to arise from the all-trans arrangement of the σ bonds of the bridging system, which may lead to more efficient charge transmission or to hyperconjugative interactions between the metal orbitals and those of the central CH–CH_2–CH bridge of the ligand.[40] Given the apparent low percentage of arene character in the HOMO's of (arene)$Cr(CO)_3$ funtionalities,[39] charge transmission may involve other filled orbitals of lower energy.

One of the interesting features of through-bond interactions is that they drop off slowly compared to through-

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[36] Partial demetalization of a dinuclear monocation through $[1][Cr(CO)_3]_2^+ \rightarrow [1][Cr(CO)_3]^+$ produces a possible spectral interference with CO bands easily confused with those of a nondelocalized dinuclear monocation.[29,34] Approximately one-electron oxidation of $[1][Cr(CO)_3]_2$ by $(p\text{-}BrC_6H_4)_3N^+$ at 198 K for 3 min gave a deep red solution which was back-reduced with ferrocene, followed by evaporation and extraction with diethyl ether. ^1H NMR of this extract gave 85% $[1][Cr(CO)_3]_2$ and 15% $[1][Cr(CO)_3]$, establishing that demetalation is only a minor complication. IR results gave similar estimates (for details see ref 15).

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space interactions. Our present data are ambiguous on the question of whether the $\Delta E_{1/2}$ value for the four-bond Cr_2 system is larger than the statistically predicted value, since the conditions for chemical reversibility of the (arene)-$Cr(CO)_3$ groups place limits on the voltammetric accuracy. Future work will hopefully be able to answer this question. The present results and those of ref 24 show that polynorbornyl spacers have promise for the investigation of relatively weak metal–metal interactions.

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Supplementary Material Available: Tables II–IV, listing atomic coordinates, isotropic and anisotropic thermal parameters, bond angles, bond lengths, and H atom positions for the three crystallographic determinations (17 pages). Ordering information is given on any current masthead page.

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Novel Disilylation of a Dinitrogen Ligand in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$. Synthesis and Reactivity of *mer*-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$[1]

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When treated with a mixture of $ClMe_2SiCH_2CH_2SiMe_2Cl$ and excess NaI in benzene, *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ afforded a novel disilylhydrazido(2−) complex *mer*-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$ (**1**). Reactions of **1** with CO, $CH_2{=}CH_2$, and nitriles gave a series of neutral disilylhydrazido(2−) complexes $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2(L)]$ (**3**, L = CO; **4**, L = $CH_2{=}CH_2$; **5a**, L = MeCN; **5b**, L = EtCN; **5c**, L = *p*-MeC_6H_4CN; **5d**, L = *p*-$MeCOC_6H_4CN$), whereas treatment of **1** with *t*-BuNC afforded a cationic complex *mer*-$[WI(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3(t\text{-}BuNC)]I$ (**6a**) as a major product together with a neutral complex $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2(t\text{-}BuNC)]$ (**6b**). Furthermore, when **1** was allowed to react with CH_2X_2, paramagnetic disilylhydrazido(2−) complexes $[WX_3(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2]$ (**7a**, X = Cl; **7b**, X = I) were formed. The molecular structures of **1**, **5d**, and **7a** were determined by the X-ray analyses. Crystal data: **1**, monoclinic $P2_1/n$, $a = 14.378$ (4) Å, $b = 25.657$ (4) Å, $c = 10.601$ (2) Å, $\beta = 95.58$ (2)°, $Z = 4$, and $R = 0.057$ for 7760 reflections; **5d**, monoclinic $P2_1/a$, $a = 20.423$ (6) Å, $b = 12.488$ (4) Å, $c = 16.150$ (4) Å, $\beta = 105.09$ (2)°, $Z = 4$, and $R = 0.067$ for 3649 reflections; **7a**, orthorhombic $P2_12_12_1$, $a = 24.778$ (4) Å, $b = 12.593$ (2) Å, $c = 10.024$ (2) Å, $Z = 4$, and $R = 0.055$ for 2882 reflections.

Introduction

We have previously reported that dinitrogen complexes $[M(N_2)_2(\mathbf{P})_4]$ (M = Mo, W; $\mathbf{P}$ = PMe_2Ph, $^1/_2$ dpe; dpe = $Ph_2PCH_2CH_2PPh_2$) react with Me_3SiX (X = I, CF_3SO_3) to give silyldiazenido complexes *trans*-$[MX(NNSiMe_3)(\mathbf{P})_4]$, which demonstrates the first clarified example of the Si–N bond formation at the coordinated dinitrogen (eq 1).[2]

$$[M(N_2)_2(\mathbf{P})_4] + Me_3SiX \rightarrow trans\text{-}[MX(NNSiMe_3)(\mathbf{P})_4] \quad (1)$$

$$M = Mo, W; \mathbf{P} = PMe_2Ph, \tfrac{1}{2}\ dpe; X = I, CF_3SO_3$$

Importantly, this finding has led to the development of the novel catalytic N_2-fixing system promoted by these dinitrogen complexes, in which molecular nitrogen is converted into silylamines under mild conditions (eq 2).[3]

$$Me_3SiCl + Na + N_2 \xrightarrow[\text{THF, 30 °C, 4 h}]{cis\text{-}[Mo(N_2)_2(PMe_2Ph)_4]} N(SiMe_3)_3 + HN(SiMe_3)_2 \quad (2)$$

This has prompted us to study more extensively the silylation reactions of coordinated dinitrogen, which has subsequently revealed that a variety of silyldiazenido complexes such as *trans*-$[WI(NNSiR_3)(PMe_2Ph)_4]$ (R_3 = Me_nPh_{3-n} (n = 0–3), Et_3, $Me_2(OMe)$, $Me(OMe)_2$)[4] and $[M(NNSiR_3)(\mathbf{P})_4](\mu\text{-}OC)[Co(CO)_3]$ (R_3 = $PhMe_2$, Ph_2Me)[5] can be readily prepared by the reactions of these dinitrogen complexes with R_3SiCl/NaI and $R_3SiCo(CO)_4$, respectively.

In relevance to the formation of $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ in the catalytic reaction shown in eq 2, disilylation or trisilylation of the coordinated dinitrogen is of particular interest. However, in spite of the exploitation of various reactions forming silylated dinitrogen complexes, all the

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