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ansa-Chromocene Complexes. 1. Synthesis and Characterization of Cr(II) Carbonyl and *tert*-Butyl Isocyanide Complexes

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ansa-Calcocene compounds are effective reagents for the synthesis of *ansa*-chromocene complexes from $CrCl_2$ in the presence of a trapping ligand such as carbon monoxide or an isonitrile. A variety of *ansa*-chromocene carbonyl and *tert*-butyl isocyanide complexes have been prepared in this manner in high yields. The X-ray crystal structure of one of these complexes, [*trans*-1,2-(3,4-$(CH_3O)_2C_6H_3)_2C_2H_2\{\eta^5$-$C_5H_4\}_2$]CrCO, is described. Electrochemical studies on these complexes show that the isonitrile derivatives are more easily oxidized than the carbonyl derivatives. Preliminary examination of the reactivity of these complexes indicates that the nature of the substitution along the ethanediyl *ansa*-bridge influences the relative stabilities of the carbonyl complexes to oxidation in air, the ease with which the carbonyl ligands undergo substitution with *tert*-butyl isocyanide, and the relative sensitivities of the *tert*-butyl isocyanide adducts to photodecomposition. The *ansa*-bridge substitution also appears to influence the ability of the complexes to undergo structural changes, such as ring slippage, as revealed in their cyclic voltammograms.

Introduction

Bent-sandwich dicyclopentadienyl complexes of the early transition metals from groups 3−6, with the exception of chromium, have exhibited a rich and varied chemistry that continues to be useful for homogeneous catalysis, organic synthesis, and the elucidation of organometallic reaction mechanisms. The chemistry of bent-sandwich chromocene has eluded chemists largely due to the reluctance of 16e$^-$ Cp_2Cr to coordinate ligands such as CO,[1] which cause it to adopt a bent-sandwich geometry, and the propensity of chromocene toward cyclopentadienyl ring loss.[2a−d] No bona fide bent chromocene derivative had been characterized until 1982, when Brintzinger and co-workers reported the synthesis, X-ray crystal structure, and chemical properties of *ansa*-$Me_4C_2(C_5H_4)_2CrCO$.[3] The presence of an interannular tetramethylethano bridge is crucial to the stability of this species, which, unlike the parent complex, Cp_2CrCO, retains its coordinated carbonyl in the absence of a CO overpressure. Brintzinger and co-workers showed in an EHMO study that the instability of the parent chromocene complex to CO loss is mainly due to the d-electron repulsion associated with undergoing a multiplicity change from paramagnetic Cp_2Cr to diamagnetic Cp_2CrCO.[4] Simpson et al. interpreted calculations at the STO-3G level as indicating that the enhanced stability of the *ansa*-chromocene carbonyl complex is attributable to both the raising of the frontier orbital energies and the elimination of ring−ring repulsive forces due to enforced bending of the rings.[5] One can surmise from these studies that the greater stability of the *ansa*-chromocene carbonyl complex relative to Cp_2CO is associated with the lower stability of the 16e$^-$ *ansa*-chromocene fragment relative to Cp_2Cr, since the *ansa*-bridge prevents the chromocene from assuming a parallel ring geometry, hence preventing relaxation to a more stable triplet state. This explanation is confirmed by recent density functional calculations by Green and Jardine.[6] The effect of the *ansa*-bridge on the redox properties of the metal center[7] is consistent with the calculated effects of ring bending on the energies of the frontier orbitals.[4−6,8] The bridge also increases the tendency of the chromocene to undergo ring slippage.[9]

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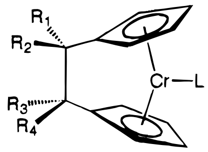
Thus, enforcing a bent-sandwich geometry about the metal in an *ansa*-metallocene complex appears to be an ideal approach for stabilizing bent-sandwich chromocene derivatives and finally exploring their reaction chemistry. Besides filling a gap in the reaction chemistry of early transition metal bent metallocenes, we anticipate using these complexes to develop new examples of homogeneous catalysis and to model the chemistry of poorly understood chromium-based ethylene polymerization catalysts such as the Union Carbide catalyst[10] and the Phillips catalyst,[11] for which relatively few homogeneous model systems currently exist.[12a−i]

Results and Discussion

Synthesis and Physical Properties of *ansa*-Chromocene(II) Carbonyl and Isocyanide Complexes. The need for a higher-yielding, more convenient synthetic route to *ansa*-chromocene starting materials required us to improve upon their synthesis. We found Edelmann's *ansa*-calcocene complex, $Me_4C_2(C_5H_4)_2Ca(THF)_2$,[13] to be a more convenient source of the ligand framework than the di-Grignard $(CH_3)_4C_2[\eta^5\text{-}C_5H_4]_2Mg_2Cl_2\cdot 4THF$[14] and demonstrated the synthesis of $Me_4C_2(C_5H_4)_2CrL$ (L = CO (**2a**), CNtBu (**2b**)) by reacting the *ansa*-calcocene with $CrCl_2$ in the presence of the trapping ligand.[15] One remaining annoyance was the presence of a persistent, inseparable impurity in our *ansa*-calcocene syntheses, 1,1′-diisopropylcalcocene, which not only reduced our yields of the *ansa*-chromocene derivatives but also produced the paramagnetic 1,1′-diisopropylchromocene as an impurity in our preparations of **2a** and **2b**. To eliminate this problem, we replaced 6,6′-dimethylfulvene with 6-phenylfulvene as a substrate for reductive coupling by activated calcium. The resulting 70:30 mixture of *trans*- and *cis*-$Ph_2C_2H_2(C_5H_4)_2Ca(THF)_2$ is obtained cleanly, in high yields, and the *trans* and *cis* isomers are readily separable by recrystallization.[16] We have described the use of this new *ansa*-calcocene reagent to prepare the corresponding *ansa*-ferrocene and *ansa*-zirconocene complexes. Now we report the use of this reagent and related diphenylethanediyl-bridged calcocenes in the synthesis of diamagnetic *ansa*-metallocene complexes of Cr(II). The synthesis and characterization of the new complexes **3a**,**b**, and **4a**,**b** (Figure 1), including cyclovoltammetric measurements on complexes **2a**,**b**, **3a**,**b**, and **4a**,**b**, are described, along with an X-ray crystal structure of **4a**.



2a: L = CO; $R_1=R_2=R_3=R_4=Me$
2b: L = *t*-BuNC; $R_1=R_2=R_3=R_4=Me$
3a: L = CO; $R_1=R_4=Ph$; $R_2=R_3=H$ (racemate)
3b: L = *t*-BuNC; $R_1=R_4=Ph$; $R_2=R_3=H$ (racemate)
4a: L = CO; $R_1=R_4=3,4\text{-}(MeO)_2C_6H_3$; $R_2=R_3=H$ (racemate)
4b: L = *t*-BuNC; $R_1=R_4=3,4\text{-}(MeO)_2C_6H_3$; $R_2=R_3=H$ (racemate)

Figure 1.

The *ansa*-chromocene carbonyl and isocyanide derivatives are prepared in the manner described previously[15] by combining the *ansa*-calcocene reagent with $CrCl_2$ in tetrahydrofuran at −78 °C in the presence of either an equivalent of *tert*-butyl isocyanide or an atmosphere of carbon monoxide and allowing the reaction mixture to warm gradually to room temperature. After removal of the THF, the product is extracted away from the $CaCl_2$ with petroleum ether, hexane, or toluene. These solutions are then cooled at −78 °C to precipitate the diamagnetic reaction products as red-brown powders in relatively good yields (67−87%). Characteristic of the ^1H NMR spectra of these complexes dissolved in C_6D_6 are four distinct pseudotriplets in the 3−5 ppm region for the protons on the cyclopentadienyl rings. A sharp, single resonance belonging to the benzylic protons of the diphenylethanediyl bridge is found among the cyclopentadienyl resonances at ca. 4 ppm. An (H,C)-HETCOR analysis was necessary to make definitive ^1H and ^{13}C assignments for complexes **4a**,**b**.

The ν(CO) IR absorptions for complexes **3a** (1882 cm^{-1}) and **4a** (1888 cm^{-1}) are substantially lower in frequency than the values reported for **2a** (1905 cm^{-1}) and parent $(C_5H_5)_2CrCO$ (1900 cm^{-1}), reflecting a greater degree of π-back-bonding between the chromium center and the carbonyl adducts in **3a** and **4a**. Although there are no substantial differences among the electrochemical oxidation potentials of the carbonyl complexes (vide infra), **3a** and **4a** are slightly more stable in air than **2a**. Whereas solid **2a** turns from red-brown to dark green instantaneously upon exposure to air, a similar color change for **3a** and **4a** occurs more gradually. Oddly, however, **3a** and **4a** undergo carbonyl ligand substitution with *tert*-butyl isocyanide more readily than **2a**. Whereas complexes **3b** and **4b** are formed over a matter of hours upon exposing C_6D_6 solutions of **3a** or **4a** to an equivalent of *tert*-butyl isocyanide, **2a** does not undergo this substitution to form **2b** until photolyzed with a medium-pressure mercury lamp. These differences in ligand substitution activity may be associated with the relative tendencies of the complexes to undergo ring slippage, as reflected in the differing cyclovoltammetric behavior of the complexes (vide infra). This raises the question of whether an associative or dissociative mechanism of ligand substitution is operating in these different cases. The possibility of an associative mechanism involving ring slippage is supported by the finding by van Raaij and Brintzinger that both Cp_2CrCO and **2a** undergo ring slippage to coordinate a second

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carbonyl ligand and that for **2a** this ring slippage is greatly accelerated by small amounts of oxidants.[9] Ring slippage by the complexes Cp^*_2CrCO[17] and $Me_2Si(C_5Me4)_2CrCO$[18] to accommodate a second carbonyl ligand has also been observed. Nevertheless, Ernst has demonstrated that 18-electron half-open chromocene carbonyl complexes undergo CO exchange predominantly by a dissociative mechanism.[19] Therefore, the possibility of a dissociative mechanism must also be considered, and kinetic investigations of ligand substitution in these systems are forthcoming.

All of the *tert*-butyl isocyanide adducts (**2b**, **3b**, and **4b**) undergo ligand exchange with CO in the presence of an atmosphere of carbon monoxide. They undergo decomposition in the presence of excess *tert*-butyl isocyanide, presumably due to displacement of the metallocene framework from the chromium by the isocyanide ligands since similar behavior has been observed with chromocene[2] and with half-open chromocene.[20]

The ν(CN) IR absorptions for the *tert*-butyl isocyanide adducts, **2b**, **3b**, and **4b**, are 1835, 1841, and 1843 cm^{-1}, respectively. The *tert*-butyl isocyanide complexes **3b** and **4b** are considerably more air-sensitive than their carbonyl analogues, smoldering upon contact with the air. All of the *tert*-butyl isocyanide complexes are photolytically sensitive, particularly **4b**, which must be stored in the absence of light. Complexes **2b** and **3b** are moderately stable in the presence of light; however, they eliminate isobutene upon photolysis with a medium-pressure mercury lamp to form a black, benzene-soluble paramagnetic material, the identity of which has not yet been determined. We are currently investigating the details of this C−N bond cleavage reaction.

X-ray Crystal Structure of 1,2-*trans*-Bis(3,4-dimethoxyphenyl)ethanochromocene Carbonyl. We have used the Edelmann methodology[13] to prepare a variety of *ansa*-calcocene compounds from their respective fulvenes, including 6,6-diphenylfulvene, 6-methyl-6-phenylfulvene,[21] 1-(*E*)-benzylidene-4,7-dimethylindene,[16] and 6,6-(3,4-dimethoxyphenyl)fulvene. The latter fulvene is coupled by activated calcium in either tetrahydrofuran or dimethoxyethane to form the *ansa*-calcocene species 1,2-$(3,4\text{-}(MeO)_2C_6H_3)_2C_2H_2\{C_5H_4\}_2\text{-}CaL'_2$ (**1**: $L'_2 = (THF)_2$ or dimethoxyethane) as an approximately 60:40 mixture of *trans*:*cis* isomers. The *trans* isomer is easily isolated from the mixture in 55% overall yield by crystallization. An X-ray crystal structure of the corresponding chromocene carbonyl complex, **4a**, has also been obtained from crystals that were grown from a solution composed of a 3:1:1 mixture of methylene chloride, dimethoxyethane, and hexane. Figure 2 shows an ORTEP drawing of the molecular structure of **4a**. Crystal data collection and refinement parameters are given in Table 1.

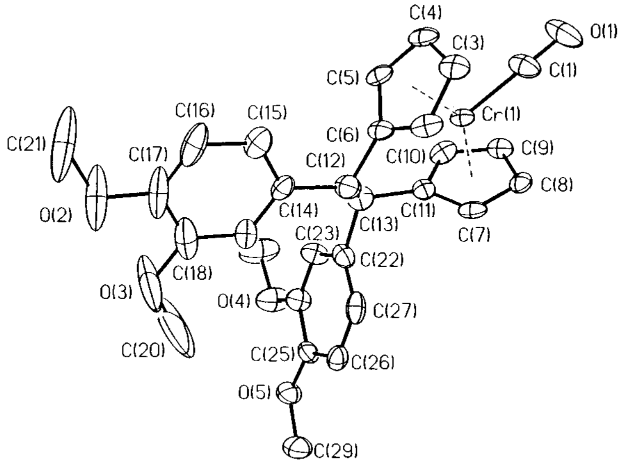

Figure 2. ORTEP drawing of the molecular structure of $[trans\text{-}1,2\text{-}(3,4\text{-}(CH_3O)_2C_6H_3)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2]CrCO$ (**4a**). Thermal ellipsoids are plotted at 30% probability. Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for 4a

formula	$C_{29}H_{28}CrO_5$
mol wt	508.51
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	31.4156(3)
b (Å)	7.7228(2)
c (Å)	20.6960(3)
α (deg)	90
β (deg)	105.4791(3)
γ (deg)	90
V (Å^3)	4839.06(14)
Z	8
T (K)	173(2)
λ (Å)	0.70173 (Mo Kα)
ρ_{calcd} (g/cm^3)	1.396
μ (mm^{-1})	0.511
F_{000}	2128
cryst size (mm)	0.40 × 0.30 × 0.10
θ range (deg)	2.12−25.00
hkl limits	−36/37;−9/9;−24/23
no. reflns collected	9025
no. indep reflns	4185 ($R_{int} = 0.0373$)
no. data/restraints/params	4185/0/316
GOF	1.785
$R(F_o)$	0.0762 ($F > 2\sigma(F)$)
$wR(F_o^2)$	0.2385
largest diff peak/hole e Å^{-3}	1.420/−0.514

Table 2. Comparison of Selected Bond Lengths and Angles from the X-ray Crystal Structures of 2a[a] and 4a[b]

	2a	4a
centroid−Cr−centroid	143.3(5)	143.4(5)
Cr−CO	1.85(1)	1.848(6)
CrC−O	1.16(1)	1.171(7)
C−C (ethano bridge)	1.60(1)	1.519(7)
ring plane 1−ring plane 2	38.5(5)	39.8(2)
nonbonded ipso C(Cp1)- - -C(Cp2)	2.61	2.61
av Cr−Cent	1.78(1)	1.792(1)

[a] Reference 3. [b] This reference.

The molecular structure of **4a** is almost identical to that of **2a**, whose structure was determined by Brintzinger and co-workers.[3] Selected distances and angles for **4a** are listed in Table 2 along with some corresponding values for **2a**. Although the ethanediyl bridge of **4a**, with a C(12)−C(13) distance of 1.519(7) Å, is slightly shorter than the ethanediyl bridge in **2a**, which has a C−C distance of 1.60(1) Å, this has little effect on the pitch of the cyclopentadienyl rings on the chromium, as can be seen from the similar centroid−Cr−centroid

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Table 3. Cyclic Voltammetric Data for the Cr(II/III) Redox Couple of Chromocene and the *ansa*-Chromocene Complexes 2a,b−4a,b

complex	L	ΔE_p, mV	$(E_a + E_c)/2$, mV	i_a/i_c
Cp_2Cr		94	−1103	1.0
2a	CO	68	−948	1.1
2b	CN-*t*-Bu	68	−1154	1.0
3a	CO	72	−882	1.0
3b	CN-*t*-Bu	68	−1238	1.0
4a	CO	84	−967	1.1
4b	CN-*t*-Bu	83	−1278	0.90

angles, the similar nonbonding distances between the bridged ring carbons, and the similar angles between the cyclopentadienyl ring planes. The Cr−centroid distances of the two complexes are also within a standard deviation of each other. The difference in metal-to-carbonyl π-back-bonding for the two complexes, indicated by the substantial difference between their carbonyl stretching frequencies (vide supra), is barely evident from the M−CO and C−O bond lengths in the two structures. The aryl ring planes adopt a nearly perpendicular relative orientation, with a twist angle of 81.9°, probably to minimize steric interactions between the methoxy groups on opposite rings.

Electrochemical Measurements on 2a,b, 3a,b, and 4a,b. We hope to use the electrochemical behavior of the *ansa*-chromocene complexes as a guide in exploring the reactivity of these systems. Much of the interesting chemistry exhibited by the heavier tungstenocene and molybdenocene congeners involves the metals in their formally +4 oxidation states;[2c,d,22a−d] thus, we are interested in accessing this formal oxidation state in our *ansa*-chromocene systems. Brintzinger and co-workers have already demonstrated that the interannular bridge has a pronounced effect on the redox properties of **2a** as compared with the parent chromocene carbonyl complex.[7] Whereas Cp_2CrCO readily loses CO upon one-electron oxidation in the presence of a CO atmosphere, **2a** retains its CO upon one-electron oxidation in the presence of an atmosphere of CO and experiences only partial CO loss during the course of the sweep in the absence of a CO overpressure. Other differences between **2a** and parent chromocene include the presence of a III/IV couple for **2a** that was not observed for parent chromocene and an electron-transfer-catalyzed ring slippage for **2a** that is also not observed for the parent complex.[9]

We have examined the cyclic voltammetric behavior of **2a**, **2b**, **3a**, **3b**, **4a**, and **4b**. We reexamined parent chromocene[23] and **2a**[7] in order to be able to compare their values with our compounds under identical experimental conditions. All potentials were referenced to the ferrocene/ferrocinium couple and are listed in Table 3. All of the complexes exhibit a quasi-reversible oxidation to the CrL^+ cations. Representative cyclic voltammograms of **3a** and **3b** are shown in Figure 3. The most striking result from these measurements is the difference in the redox potentials of the isocyanide adducts versus the carbonyl adducts, the former being substantially more negative than the latter. Due to the greater σ-donating ability of the *tert*-butyl isocyanide ligand relative to carbon monoxide,[24] complexes **2b**, **3b**, and **4b** are more easily oxidized than their carbonyl analogues. Thus, there is a greater effect of these ligands on the energies of the HOMOs of the chromocene complexes than initially assumed by van Raaij et al.[7] We are currently performing theoretical calculations on model chromocene isonitrile complexes in order to understand these differences. More subtle, but still noticeable, is the influence of the substitution at the ethylene bridge on the redox properties of these *ansa*-chromocenes. The trends are not identical for the carbonyl versus the isocyanide complexes, but, overall, the complexes with the 3,4-dimethoxyphenyl groups on the bridge (**4a** and **4b**) are more easily oxidized.

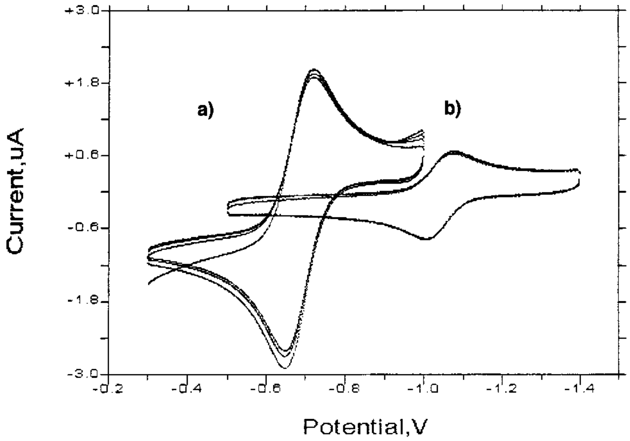

Figure 3. Cyclic voltammograms of Cr(II/III) couples for (a) **3a** and (b) **3b**.

The cyclic voltammograms of each compound were also examined over a wider potential range to determine the availability of other oxidation states to these complexes. In Figure 4 are shown the cyclic voltammograms for **2b** and **3b** between +800 and −2500 mV. We attribute the weak chemically irreversible cathodic peak at approximately −2200 mV to the one-electron reduction of the neutral complex to the monoanion. This peak appears in approximately the same region for all of the other complexes. A similar peak was found by van Raaij et al. for **2a**. Both **2b** and **3b** exhibit a chemically irreversible anodic peak at ca. +200 mV, which we attribute to oxidation of the monocations to the dications. A conjugate peak for reduction of the cation is barely perceptible for **3b** and simply not present for **2b**. There are additional peaks in the cyclic voltammogram for **3b** that are not observed for **2b**. As can been seen in Figure 4b, complex **3b** has a weak anodic peak at −199 mV and a weak cathodic peak at −1459 mV. Similar peaks at −680 and −1600 mV, respectively, are observed for **4b**. One explanation for the anodic peak at −199 mV is the formation of a ring-slipped 17e$^-$ solvent adduct of the monocation, $[Ph_2C_2H_2\{\eta^3\text{-}C_5H_4\}\{\eta^5\text{-}C_5H_4\}]\text{-}Cr(THF)(CN\text{-}t\text{-}Bu)]^+$, which would be easier to oxidize. The cathodic peak at −1459 could, similarly, be due to

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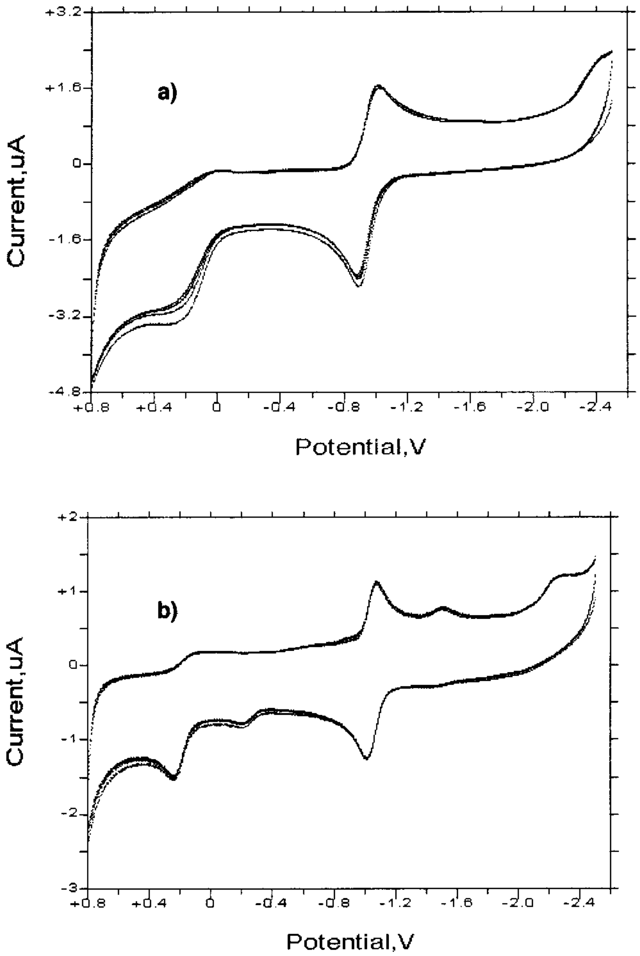

Figure 4. Cyclic voltammograms of (a) **2b** and (b) **3b** over wider potential ranges.

reduction of a ring-slipped 16e$^-$ form of the neutral complex, which would occur at a less negative potential than the neutral 18e$^-$ species. In any case, these additional peaks reflect structural changes in **3b** and **4b**, which are not exhibited by **2b**.

Conclusions

In summary, we have found a synthetically versatile and reliable method for the synthesis of 18e$^-$ *ansa*-chromocene carbonyl and isonitrile complexes in sufficient quantities to allow us to explore their reactivity. The *ansa*-calcocenes can also be used to prepare 17e$^-$ *ansa*-chromocene halide complexes from the Cr(III) starting materials $CrCl_3$ and $CrBr_3$. These complexes will be discussed in a future publication.

Electrochemical studies show that the redox potentials of the *ansa*-chromocene complexes are strongly influenced by the nature of the 2e$^-$-donating ligand L. Changing the substituents on the ethanediyl bridge has a comparatively small influence on the potential of the Cr(II/III) couple, yet it appears to affect the tendency of the complexes to undergo structural changes, possibly ring slippage, which produce additional oxidation/reduction peaks in the cyclic voltammograms.

Effects from the substitution at the bridge are also seen in the lower CO stretching frequencies of **3a** and **4a** relative to **2a** and the greater stability of the former two complexes in the presence of air. Differences in the reactivity of the *tert*-butyl isocyanide adducts of the different *ansa*-chromocenes are also observed in that **4b** readily loses its isocyanide ligand in the presence of light, whereas **2b** and **3b** undergo C−N bond cleavage to eliminate isobutene under photolyzing conditions.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques, and all reaction and NMR solvents were dried as described elsewhere. HPLC grade tetrahydrofuran (Fisher) for the electrochemical measurements was used as received. Pyrrolidine (Aldrich) and tetrabutylammonium hexafluorophosphate (Aldrich) were also used as received. Calcium granules were activated beforehand in the manner described by Edelmann and stored in a nitrogen-filled glovebox. The preparation of [*trans*-1,2-$(C_6H_5)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]Ca-$(THF)_2$ has been previously described.[16] NMR spectra were recorded on an IBM NR-300 (300 MHz ^{1}H, 75 MHz ^{13}C), an IBM NR-200 (200 MHz ^{1}H, 50 MHz ^{13}C), and an Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C). Elemental analyses were determined by Desert Analytics (Tuscon, AZ).

Preparation of 6-(3,4-Dimethoxyphenyl)fulvene. The fulvene synthesis follows the method described by Stone and Little.[25] Pyrrolidine (30 mL, 0.3611 mol) catalyzes a reaction between cyclopentadiene (39.76 g, 0.6015 mol) and 3,4-dimethoxybenzaldehyde (40 g, 0.2407 mol) in 200 mL of methanol to afford the fulvene, which is obtained as a red, air-stable solid (mp 71.3−71.5 °C) after crystallization in petroleum ether (yield 39.03 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14−7.10 (m, 3H, $C_6H_3(OCH_3)_2$), 6.84 (d, 1H, $^4J_{HH}$ = 8.5 Hz, fulvenyl−H_6), 6.66−6.67 (m, 1H, C_5H_4), 6.60−6.62 (m, 1H, C_5H_4), 6.42−6.43 (m, 1H, C_5H_4), 6.25−6.27 (m, 1H, C_5H_4), 3.79 (s, 6H, CH_3O). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.7, 149.4, 130.2, 120.2, 113.5, 111.5, ($C_6H_3(OCH_3)_2$), 143.9, 139.0, 135.5, 130.3, 127.8, 125.2 (fulvene), 56.3, 56.4 ($C_6H_3(OCH_3)_2$). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.61; H, 6.46.

Preparation of [*trans*-1,2-$(3,4\text{-}(CH_3O)_2C_6H_3)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]Ca(DME) (1). Calcium granules (0.80 g, 20 mmol) that had been preactivated with $HgCl_2$ were suspended in 150 mL of dry dimethoxyethane, and 6-(3,4-dimethoxyphenyl)fulvene (8.00 g, 37.3 mmol) was added gradually as the reaction was stirred at room temperature. The reaction mixture was stirred for 2 days, over which time the red color of the fulvene had disappeared completely and a white precipitate had formed. The dimethoxyethane was removed under vaccum, and the residue was redissolved in methylene chloride and filtered to remove any unreacted calcium. The resulting clear, colorless filtrate was dried under vacuum, leaving a white foam, which contained a 60:40 mixture of the *trans*:*cis* isomers of the calcocene. Upon dissolution of the foam in dimethoxyethane and cooling at −78 °C, the *trans* isomer precipitated selectively (yield 3.56 g, 55%). ^{1}H NMR (200 MHz, DMSO-d_6): δ 6.89 (s, 2H, aryl−H), 6.79, 6.60 (2d, 4H, $^3J_{HH}$ = 8.1 Hz, aryl−H), 5.85 (m, 2H, C_5H_4), 5.53 (m, 4H, C_5H_4), 5.33 (m, 2H, C_5H_4), 4.51 (s, 2H, $(aryl)_2C_2H_2$), 3.64, 3.59 (2s, 12H, $(C_6H_3(OCH_3)_2)$), 3.42 (s, 4H, $CH_3O(CH_2)_2OCH_3$), 3.23 (s, 6H, $CH_3O(CH_2)_2OCH_3$). ^{13}C NMR (50 MHz, DMSO-d_6): 148.6, 146.7, 141.7, 121.0, 113.4, 112.1 ($C_6H_3(OCH_3)_2$)), 128.7, 108.2, 106.6, 104.3, 102.4 (C_5H_4), 72.0 ($CH_3O(CH_2)_2OCH_3$), 58.9 ($CH_3O(CH_2)_2OCH_3$), 54.5, 54.7 ($C_6H_3(OCH_3)_2$). Anal. Calcd for $C_{32}H_{38}CaO_6$: C, 68.79; H, 6.86. Found: C, 68.68; H, 6.62.

Preparation of [*trans*-1,2-$(C_6H_5)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]CrCO (3a). An atmosphere of carbon monoxide was added to a suspension of [*trans*-1,2-$(C_6H_5)C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]Ca$(THF)_2$ (0.8 g, 1.6 mmol) and $CrCl_2$ (0.2 g, 1.6 mmol) in 50 mL of THF

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[25] Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

cooled at −78 °C. The reaction mixture was allowed to warm gradually to room temperature and stirred for 12 h, affording a dark red solution. All volatiles were removed under vacuum, and the product was extracted from the $CaCl_2$ with hexane. Concentration of the hexane solution and cooling to −78 °C precipitated **3a** as a brown powder (yield: 0.42 g, 67.5%). ^1H NMR (200 MHz, C_6D_6): δ 7.03 (m, 10H, aryl), 4.73, 4.31, 3.83, 3.45 (4m, 8H, C_5H_4), 3.83 (s, 2H, [$(aryl)_2C_2H_2$]). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 141.3, 128.9, 128.3, 126.4 (C_6H_5), 76.9, 77.7, 77.9, 78.6 (C_5H_4), 51.2 [$(aryl)_2C_2H_2$]. IR (KBr plates, Nujol mull, cm^{-1}): 1882 (ν(CO)). Anal. Calcd for $C_{25}H_{20}CrO$: C, 77.30; H, 5.19. Found: C, 77.69, H, 5.28.

Preparation of [*trans*-1,2-$(C_6H_5)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]CrCN-*t*-Bu (3b). *tert*-Butyl isocyanide (0.15 mL. 1.32 mmol) was condensed at −78 °C into a round-bottomed flask containing [*trans*-1,2-$(C_6H_5)C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]Ca$(THF)_2$ (0.65 g, 1.32 mmol) and $CrCl_2$ (0.16 g, 1.32 mmol) in 100 mL of THF. The reaction mixture was allowed to warm gradually to room temperature and stirred overnight. The volatiles were removed under vacuum, the desired product was extracted from the $CaCl_2$ with petroleum ether, and the petroleum ether solution was concentrated and cooled to −78 °C to precipitate **3b** as a brown powder (yield: 0.51 g, 87%). ^1H NMR (200 MHz, C_6D_6): δ 7.07 (m, 10H, aryl), 4.97, 4.56, 4.15, 3.71 (4m, 8H, C_5H_4), 3.90 (s, 2H, [$(aryl)_2C_2H_2$]), 1.34 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 141.5, 127.3, 127.1, 125.3 (aryl), 80.5, 77.5, 76.3, 75.8 (C_5H_4), 53.5 ($(aryl)_2C_2H_2$), 29.5 ($NC(CH_3)_3$). IR (KBr plates, Nujol mull, cm^{-1}): 1841 (ν(CN)). Anal. Calcd For $C_{29}H_{22}CrN$: C, 78.52; H, 6.58; N, 3.15. Found: C, 78.03, H, 6.73, N, 3.40.

Preparation of [*trans*-1,2-$(3,4\text{-}(CH_3O)_2C_6H_3)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]CrCO (4a). Tetrahydrofuran (100 mL) was added to a flask containing **1** (2.50 g, 4.47 mmol) and $CrCl_2$ (0.55 g, 4.47 mmol) at −78 °C. An atmosphere of carbon monoxide was introduced to the reaction vessel, and the reaction was allowed to warm gradually to room temperature with stirring. After stirring for 12 h, the red reaction mixture was filtered to remove most of the $CaCl_2$ byproduct, and the filtrate was dried under vacuum, leaving a red-brown solid. The solid was redissolved in toluene, and the solution was filtered again to remove any insolubles. The toluene solution was concentrated and cooled at −78 °C. Addition of petroleum ether to the solution precipitated **4a** as a brown-red powder (yield: 1.85 g, 81%). ^1H NMR (200 MHz, C_6D_6): δ 6.80, 6.55 (2d, 4H, aryl, $^3J_{HH} = 7.8$ Hz, aryl), 6.68 (s, 2H, aryl-*H*), 4.92, 4.42, 3.99, 3.52 (4m, 8H, C_5H_4), 3.90 (s, 2H, [$(aryl)_2C_2H_2$]), 3.38 (overlapping singlets, 12H, m- and p-OCH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 148.2, 147.5, 133.9, 118.6, 111.2, 110.6 ($C_6H_3(OCH_3)_2$), 100.2, 76.2, 76.0, 75.4,75.0 (C_5H_4), 53.0 [$(aryl)_2C_2H_2$], 54.0, 54.1 ($C_6H_3(OCH_3)_2$). IR (KBr plates, Nujol mull, cm^{-1}): 1888 (ν(CO)). Anal. Calcd for $C_{29}H_{28}O_5Cr$: C, 68.50; H, 5.56. Found: C, 68.44, H, 5.35.

Preparation of [*trans*-1,2-$(3,4\text{-}(CH_3O)C_6H_3)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]CrCN-*t*-Bu (4b). *tert*-Butyl isocyanide (0.101 mL. 0.895 mmol) was condensed at −78 °C into a round-bottomed flask containing **1** (0.500 g, 0.895 mmol) and $CrCl_2$ (0.110 g, 0.895 mmol) in 100 mL of THF. The mixture was allowed to warm gradually to room temperature and after stirring for 12 h afforded a red-brown solution. All manipulations after removing the volatiles under reduced pressure are performed with the reaction vessel wrapped in aluminum foil in order to exclude light. The desired reaction product was extracted from the $CaCl_2$ with toluene. Concentration of the toluene solution and addition of petroleum ether afforded **4b** as a red-brown solid (yield: 0.382 g, 77%). ^1H NMR (200 MHz, C_6D_6): 6.87, 6.55 (2d, 4H, $^3J_{HH} = 8.2$ Hz, aryl−*H*), 6.74 (s, 2H, aryl−*H*), 3.94 (s, 2H, [$(aryl)_2C_2H_2$]), 4.23, 4.65, 5.11, 3.79 (4m, 8H, C_5H_4), 3.37, 3.38 (2s, 6H, ($C_6H_3(OCH_3)_2$), 1.33 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (50.3 MHz, C_6D_6): 148.9, 148.1, 135.2, 119.4, 111.6, 112.2 ($C_6H_3(OCH_3)_2$), 99.5, 81.0, 77.9, 76.8, 76.2, (C_5H_4), 54.1 ($C_6H_3(OCH_3)_2$), 54.0 [$(aryl)_2C_2H_2$], 30.2 ($NC(CH_3)_3$). IR (KBr plates, Nujol Mull, cm^{-1}): 1843 (ν(C≡N)). Anal. Calcd for $C_{33}H_{37}NO_4Cr$: C, 70.32; H, 6.62; N, 2.49. Found: C, 69.24; H, 6.59; N, 2.30. Due to the extreme sensitivity of the compound to photolysis, the carbon value is unavoidably low.

Crystallographic Structure Determination. The single-crystal X-ray diffraction experiment for **4a** was performed on a Siemens P4/CCD diffractometer. The systematic absences suggested the space groups *C*2/*c* and *Cc* for **2**. The E-statistics suggested the centrosymmetric option for the structure. The structure was solved by the Patterson function, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms were treated as ideal contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Cyclic Voltammetry. Measurements were performed on a BAS CV50 Voltammetric Analyzer in a nitrogen-filled glovebox. Potentials were measured, without IR compensation, against a reference electrode consisting of a silver wire immersed in a solution of $AgNO_3$ (0.01 M) and $[NBu_4][PF_6]$ (0.1 M) in acetonitrile, using a glassy carbon working electrode and a platinum wire as the auxiliary electrode. Measurements were performed on THF solutions of the sample chromocene compound (<1 mM) containing 0.3 M $[NBu_4][PF_6]$ electrolyte. All potentials are referenced to the ferrocene (II/III) couple ($E_p \approx 200$ mV), which was measured separately and prior to each sample measurement. The ferrocene reference potential and the chromocene potentials listed in Table 2 represent an average of five sweeps. In these cases the sweeps were limited to the Cr(II/III) and Fe(II/III) windows. Sweep rates of 100 mV/s were used starting from the more positive potential. Wider sweeps of each of the chromocene complexes were also performed to get a broader view of the redox profile of these complexes. In these cases the starting potentials were varied to examine for effects due to the decomposition of highly reduced or highly oxidized chromium species.

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Supporting Information Available: Details of the structure determinations for **4a** including ORTEP drawing, listings of atomic coordinates, thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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