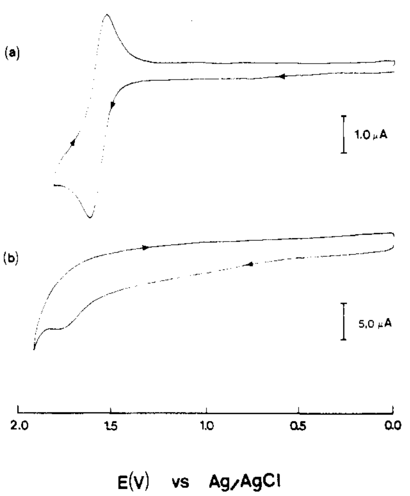

Figure 9. (a) Cyclic voltammogram at 20 °C for oxidation of 5.0×10^{-4} M $[Cu([14]aneN_4)]^{2+}$ in acetonitrile (0.1 M Bu_4NClO_4) at a platinum electrode (scan rate = 100 mV s^{-1}). (b) Cyclic voltammogram at 20 °C for oxidation of 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in acetonitrile (0.1 M Bu_4NClO_4) at a platinum electrode (scan rate = 200 mV s^{-1}).

both are chemically irreversible at all scan rates (20–500 mV s^{-1}) and temperatures (20 to −70 °C) examined. Furthermore, copper stripping peaks are observed even after the first reduction process in both coordinating and noncoordinating solvents. A chemically reversible one-electron oxidation is observed under voltammetric conditions in all solvents examined (Table V and Figure 9), confirming previous data in acetonitrile.[23a] Apparently, the macrocyclic ligand in $[Cu[14]aneN_4]^{2+}$ stabilizes higher oxidation states. $[Cu[14]aneN_4]^{3+}$ is unstable on longer time scale controlled-potential electrolysis experiments,[23a] giving rise to a multielectron oxidation process.[41] By contrast, $[Cu(N_4)MeIm]^{2+}$ is irreversibly oxidized even on the voltammetric time scale (20 °C, scan rate 500 mV s^{-1}, Table V, Figure 9). That is, factors that stabilize high-oxidation-state copper complexes seem to destabilize the lower oxidation states. Electrochemical oxidation[42] of the mercury(II) complex $[Hg[14]aneN_4](BF_4)_2$ at low temperature is consistent with the formation of a mercury(III) complex. Conversely, reduction of $[Hg[14]aneN_4]^{2+}$ produces elemental mercury without evidence for a zerovalent formally mercury(0) complex. A combination of an unsaturated macrocycle, the correct charge, and reduction in an inert solvent in the absence of moisture and oxygen are factors that appear to be required to stabilize formally zero oxidation state copper macrocyclic complexes. Data imply that it is not necessary to block the fifth or sixth coordination sites by a ligand such as MeIm. This role (if required) can be fulfilled by the solvent or anion of the electrolyte.

Acknowledgment. The award of a Gordon Fellowship by Deakin University and leave provided by Alexandria University to M.A.K. enabled this investigation to be undertaken at Deakin University. Financial support from the Australian Research Grants Scheme and technical support from D. L. Luscombe are also gratefully acknowledged. Suggestions for some of the mechanisms contained in this paper were provided by a reviewer, whose contribution is also highly appreciated.

Registry No. $[Cu(N_4)MeIm](PF_6)_2$, 84667-54-9; $[Hg(MeIm)_6](ClO_4)_2$, 106251-96-1; $Cu(ClO_4)_2$, 13770-18-8; $[Cu([14]aneN_4)](ClO_4)_2$, 71170-98-4; MeIm, 616-47-7; $Co(C_5H_5)_2$, 1277-43-6; $[Cu(N_4)]^0$, 106251-97-2; $[Cu(N_4)]^+$, 80502-51-8; Pt, 7440-06-4; Hg, 7439-97-6; Au, 7440-57-5; C, 7440-44-0; CH_2Cl_2, 75-09-2; CH_3COCH_3, 67-64-1; CH_3CN, 75-05-8.

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Contribution from the Department of Chemistry,
University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Two-Electron Reduction of (η^6-Naphthalene)tricarbonylchromium. Haptotropic Rearrangement to the (η^4-Naphthalene)tricarbonylchromium Dianion

Reuben D. Rieke,* William P. Henry, and Jon S. Arney

Received August 28, 1986

The electrochemical and chemical reduction of (η^6-naphthalene)tricarbonylchromium is a two-electron ECE reduction. The chemical step is a haptotropic rearrangement, which leads ultimately to the (η^4-naphthalene)tricarbonylchromium dianion. The dianion displays some unusual ^{13}C NMR features that provide strong support for the proposed "slip-fold" mechanism. Reaction of the dianion with a proton source produces a (η^5-cyclohexadienyl)tricarbonylchromium anion species, which can be oxidized to the original naphthalene complex. Molecular orbital arguments support the "slip-fold" mechanism. Finally, complete electrochemical reductive properties of the naphthalene complex are presented.

Introduction

Considerable interest has been shown in recent years concerning the generation of anions of (arene)tricarbonylchromium complexes. Methods used include proton abstraction (eq 1),[1-15] nucleophilic addition (eq 2),[16-24] and direct electrochemical reduction (eq 3).[25-36]

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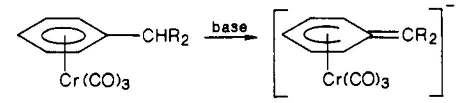

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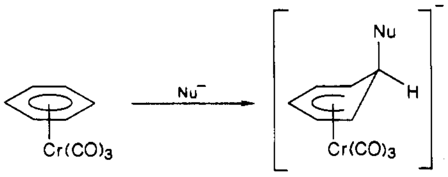

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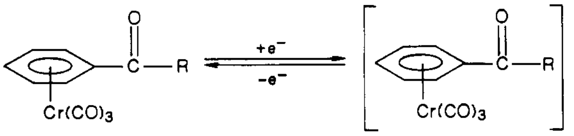

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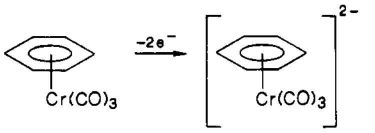

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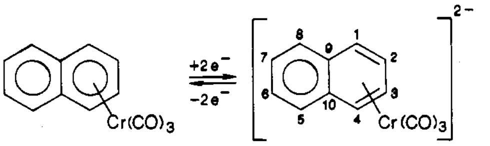

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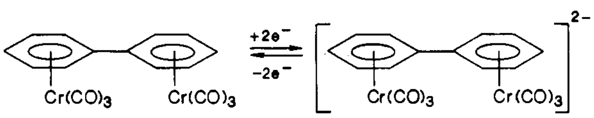
I



(3d)

Table I. ^{13}C NMR Data for I, IV, and Naphthalene

species	δ ($^1J_{C-H}$, Hz)^a					
	$C_{1,4}$	$C_{2,3}$	$C_{5,8}$	$C_{6,7}$	$C_{9,10}$	C_{CO}
I^b	88.7	90.4	126.8	126.7	103.7	228.3
I	91.6	93.2	128.3	127.9		
IV	56.2 (d, 149)	84.0 (d, 160)	*c*	*c*	151.3 (s)	247.0 (s)
naph	127.1	125.0	127.1	125.0	132.9	

^{a}All data obtained in THF-d_8 unless otherwise noted; Me_4Si was used as the reference. ^{b}Obtained in $CDCl_3$. ^{c}Assignment between $C_{5,8}$ and $C_{6,7}$ was not possible; values obtained for these two resonances were 114.5 (d, 154) and 117.6 (d, 159).

Table II. ^1H NMR Data for I, IV, and Naphthalene^a

species	δ				ref
	$H_{1,4}$	$H_{2,3}$	$H_{5,8}$	$H_{6,7}$	
I	6.09	5.48	7.53	7.37	61
IV	2.00	5.23	5.6–5.7		*b*
naph	7.38	7.76	7.38	7.76	*b*

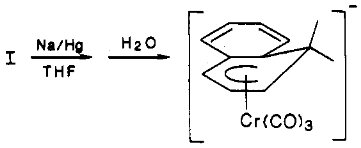
$^a Me_4Si$ was used as reference. ^{b}This work.

Table III. ^1H NMR Data for Various η^4-Diene and η^4-Arene Complexes^a

species	δ				ref
	$H_{1,4}$	$H_{2,3}$	$H_{5,8}$	$H_{6,7}$	
(anth)$Fe(CO)_3$	3.70	6.20			57
$TaH(\eta^4$-naph)$(dmpe)_2$	1.51	4.47	6.51	6.39	40
$TaCH_3(\eta^4$-naph)$(dmpe)_2$	1.51	3.94	6.58	6.46	40
(1,3-chd)$Fe(CO)_3$	3.28	5.30			44
(btd)$Fe(CO)_3$	1.46	4.89			44
(1,3-chd)$Mn(CO)_3$	2.15	4.50			50

$^a Me_4Si$ was used as reference. Abbreviations: anth, anthracene; naph, naphthalene; chd, cyclohexadiene; btd, butadiene; dmpe, 1,2-bis(dimethylphosphino)ethane.

We suggested earlier that the electrochemical reduction of (η^6-naphthalene)tricarbonylchromium (I) proceeded via an ECE two-electron process in which the $Cr(CO)_3$ group went from η^6 bonding to η^4 bonding in the chemical step of the ECE mechanism.[25] This would maintain the 18-electron nature of the dianion metal complex, and the species would be isoelectronic with a (η^4-butadiene)$Fe(CO)_3$ complex. In a later communication, we reported on the protonation of the dianion of I to yield the (η^5-cyclohexadienyl)tricarbonylchromium II.[33]



II

In this paper, we wish to report on the spectroscopic (^{13}C NMR, ^1H NMR, and IR) characterization of the dianion formed upon electrochemical or chemical reduction of I. The spectroscopic studies fully support the η^4 character of the $Cr(CO)_3$ group in the dianion. The proposed "slip-fold" distortion that has been suggested for other arene complexes[37–41] leads to some unique

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Table IV. ^{13}C NMR Data for Various Diene Complexes[a]

species	δ ($^1J_{C-H}$, Hz)				ref	solvent
	$C_{1,4}$	$C_{2,3}$	$C_{5,6}$	C_{CO}		
1,3-chd	126.3	124.9	22.7		44	CD_3COCD_3
(1,3-chd)$Fe(CO)_3$	61.1 (d, 158)	84.3 (d, 173)	26.8 (t, 130)	213.7 (s)	44	CD_3COCD_3
1,3-btd	117.5 (t)	137.7 (d)			42	$CDCl_3$
(1,3-btd)$Fe(CO)_3$	40.4 (t, 160)	85.2 (d, 169)		211.3	42	$CDCl_3$

[a] Me_4Si was used as reference; abbreviations are given in Table III.

Table V. ^{13}C NMR Differences between Complexed and Uncomplexed Arenes and Butadienes[a]

species	$\Delta\delta$[b]		
	$C_{1,4}$	$C_{2,3}$	$C_{5,6}$
(bze)$Cr(CO)_3$	30	30	30
I	35.5	31.8	29.2
IV	70.9	41.0	−18.4
(1,3-chd)$Fe(CO)_3$	65.2	40.6	−4.1
(1,3-btd)$Fe(CO)_3$	77.1	52.5	

[a] See Table III for abbreviations; bze = benzene. [b] $\Delta\delta = \delta_{uncomplexed} - \delta_{complexed}$.

NMR properties. Finally, complete electrochemical properties of the neutral complex are presented. The electrochemical reductive properties parallel the chemical reductions of I. Moreover, the follow-up chemistry of the resulting dianion with a proton source is identical for both the electrochemically and the chemically generated dianions.

Chemical Reductions

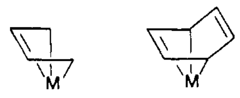
Results and Discussion. Table I lists the ^{13}C NMR data for the dianion of I with sodium as the counterion. Table II contains the ^1H NMR data. These results were obtained by reducing I in THF-d_8 with sodium amalgam (1%) and then transferring the resulting solution to an NMR tube, all under argon.

In both the ^{13}C and ^1H NMR spectra, the equivalence of carbons and protons on opposite halves of the ring suggests a plane of symmetry perpendicular to the ring. $Cr(CO)_3$ is therefore most likely bound symmetrically to the naphthalene ligand. Low-temperature NMR studies were not possible due to solubility problems. Only one resonance occurs for the carbons of the coordinated carbon monoxides, demonstrating that the $Cr(CO)_3$ moiety is rotating rapidly with respect to the time frame of the NMR experiment at room temperature.

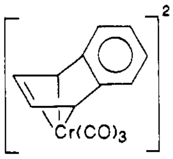
As can be seen from the ^1H NMR data for the model η^4-diene and η^4-arene complexes (Table III), the shifts of the proton resonances vary dramatically from complex to complex. Even the variation between the 1,3-cyclohexadiene and butadiene iron complexes is large. The one feature that appears consistently in all complexes is the difference in shifts between the 1,4-protons and the 2,3-protons. In all cases, the difference is in the range of 2–3.5 ppm. While the difference between the two upfield resonances of the dianion of I (Table II) is in this range, it cannot be considered unequivocal proof of an (η^4-naphthalene)tricarbonylchromium species.

The ^{13}C NMR data (Table I) are much more definitive. Carbon resonances appear at 56.2 and 84.0 ppm in the dianion and are assigned to carbons 1–4. The high-field signal is assigned to 1,4-carbon atoms, while the resonance at 84.0 ppm is assigned to the 2,3-carbon atoms. These assignments are based on the very similar resonances of the isoelectronic (butadiene)tricarbonyliron complexes (Tables IV and V). It is of interest to note that the one-bond coupling constants, $^1J_{C-H}$, of the dianion of I and the iron complexes are also very similar. The smaller coupling constants for carbon atoms 1 and 4 (149 Hz) relative to those of atoms 2 and 3 (160 Hz) are consistent with the rehybridization of atoms 1 and 4 with more σ-bond character in the carbon–chromium bond.

It is generally agreed that (η^4-diene)tricarbonyliron complexes are best described as having a significant contribution of resonance structure III.[42–46] This resonance form is invoked because of a dramatic shortening of the C_2–C_3 bond lengths with respect to a C–C single bond. Conversely, the C_1–C_2 and C_3–C_4 bonds are longer than would be expected for a double bond. In some instances, the former bond is shorter than the latter ones. It appears that the dianion of (naphthalene)tricarbonylchromium is best described by invoking a significant contribution of resonance structure IV.



III



IV

A significant result regarding the ^{13}C NMR data of the dianion of I is the chemical shift changes of carbons 9 and 10. This resonance is readily assigned because of the absence of $^1J_{C-H}$ coupling. In the neutral complex, the signal appears at 103.7 ppm, while in the dianion, it shifts to a surprisingly low value of 151.3 ppm. This downfield shift upon the addition of two electrons at first appears totally inconsistent. However, this result provides substantial proof of our proposed "slip-fold" mechanism upon reduction. Frank Kohler[62] had proposed several years ago that the hapticity of indenyl metal complexes could be determined by the ^{13}C chemical shifts of the five-membered ring carbon atoms

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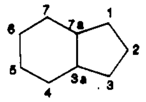
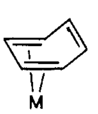
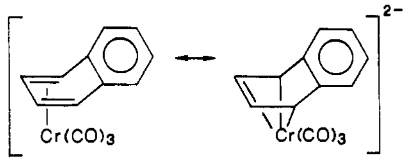
compared with those of indene; for η^3-indenyl ligands C_{1-3} are shielded while $C_{3a,7a}$ are not.



Recently Baker and Tulip[63] have reexamined this question and expanded on this concept. They calculated more quantitative comparisons relative to the indenyl sodium, $\delta_C = \delta_C(\eta\text{-indenyl}) - \delta_C(\text{indenyl sodium})$ for a variety of d^6 and d^8 complexes. They found that the δ_C values correlated well with the hapticity of the indenyl ligand and with distortion or bonding of the six-membered ring. The range of values found were $\delta_{C_{3a,7a}} = -20$ to -40 for planar η^5-indenyl, -10 to -20 for distorted η^5-indenyl, and $+5$ to $+30$ for η^3-indenyl ligands. In both the η^5 complexes and the η^3 complexes downfield shifts were noted upon folding up of the six-membered ring. Our results are totally consistent with this picture, and the dianion of I merely represents the first naphthalene complex to display this "slip-fold" bonding. The large downfield shift would suggest considerable bending, and efforts are under way to grow crystals and determine the structure of the dianion of I. It is also of interest to note that several benzene complexes have been shown to exhibit this "slip-fold" η^4-arene bonding (V).[37-41] Accordingly, we feel the best representation for the bonding in the dianion of I is a combination of resonance structures VI and VII.

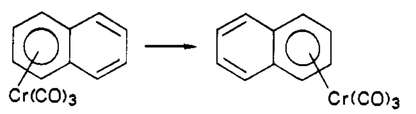


V

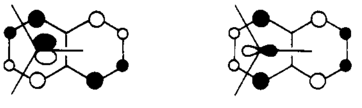


VI VII

Molecular Orbital Considerations. The proposed "slip-fold" haptotropic rearrangement is totally consistent with and is supported by the molecular orbital treatments of Albright and Hoffmann for the (naphthalene)tricarbonylchromium complex.[47,48,64-67] They examined a number of haptotropic rearrangements where an ML_n unit changes its connectivity or hapticity to some ligand with multi-coordination-site possibilities. In the case of (naphthalene)tricarbonylchromium, they examined the rearrangement of the $Cr(CO)_3$ group from one ring to the other by various possible routes.

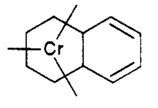


Their calculations indicated that any movement of the $Cr(CO)_3$ unit toward the 9,10-carbon atoms leads to a rapid increase of energy. On the other hand, there is a rather low energy barrier for movement toward the 2,3-carbon atoms. In fact, the ground state they calculated had the $Cr(CO)_3$ unit shifted 0.12 Å away from η^6 toward the C_2–C_3 bond. This also is in the direction and in the range of magnitudes that are experimentally found for complexes of this sort. The same situation holds for the dianion. Orbital interaction diagrams have been presented for I.[47,48] There are two major differences we have to consider in comparison to the neutral complex. First and most important, there are two extra electrons, which are added to the antibonding molecular orbital. This orbital is composed primarily of the naphthalene antibonding orbital $2\pi_s$ and the metal orbital $2e_s$. The two most important orbitals then in determination of energy changes upon movement of the $Cr(CO)_3$ unit are the HOMO ($2\pi_s + 2e_s$) and the next highest occupied MO ($2\pi_a + 2e_a$). In both cases, it can be seen that movement of the $Cr(CO)_3$ unit toward the 2,3-carbon atoms will lead to increased overlap and less antibonding interaction with the 5,8-carbon atoms. This can be readily seen from a bottom view of these two dominant bonding orbitals.

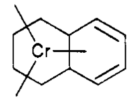


$2\pi_a + 2e_a$ $2\pi_s + 2e_s$

The second point to note is that in the neutral complex conformation VIII is the most stable conformation; however, in the dianion, conformation IX is the most stable. Theoretical arguments for this consideration have been presented elsewhere by Albright.[47,48,64,65,66]



VIII

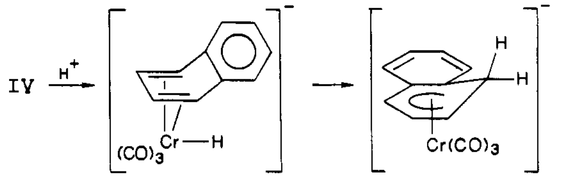


IX

In summary, qualitative molecular orbital arguments are totally consistent with and support the proposed movement of the Cr-$(CO)_3$ unit toward the 2,3-carbon atoms.

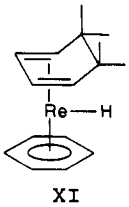
Reaction of Dianion with Protons. Reaction of the dianion of I with a proton source produces the (η^5-cyclohexadienyl)tricarbonylchromium species II.[32] Identification of this product was accomplished by using ^{13}C NMR, ^1H NMR, and IR analysis. All NMR data agreed with those of previously isolated (η^5-cyclohexadienyl)metal complexes. The IR bands in the CO stretching region also agreed with those of compounds of this nature. If a KBr pellet IR spectrum was taken, an abnormally low CH stretch was observed, which is characteristic of this type of complex.

It was shown that attack of the proton upon the dianion of I occurs in an endo manner. This conclusion is based on the ^1H NMR data of the species formed when D_2O is added to the dianion. It was observed that the resonance that was still present in the NMR spectrum of the deuteriated species showed a very small coupling with the proton on the carbon next to it. From previous reports of η^5-cyclohexadienyl complexes, it was known that the coupling between the exo proton on the methylene and the adjacent proton was small, while the endo proton coupled to a much greater extent. Also, the low CH stretch in the IR spectrum is still present for the deuteriated species, suggesting that the exo proton is still present. This reaction most probably goes by a metal–ligand shift of a hydride where the proton initially attacks the metal atom (eq 4). Recently, an example of a (diene)metal hydride similar to X was reported[49] (XI). Closely related is the (η^3-arene)tricarbonylmanganese hydride (XII) formed from the addition of a proton to the (η^4-diene)tricarbonylmanganese anion.[50,51] In this species, the hydride is bridging between the metal and one of the carbons on the ring.

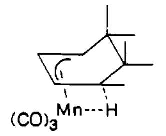


(4)

X II



XI



XII

It should be pointed out that it is not necessary to invoke a fully formed chromium hydride. Instead, protonation could occur as

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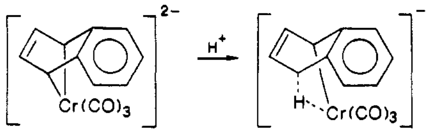
(63) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.
(64) Albright, T. A. *Tetrahedron* **1982**, *38*, 1339.
(65) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092.
(66) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1591.
(67) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

Table VI. IR Data in the CO Stretching Region

species	counterion, ion pairing[a]	ν_{CO}, cm^{-1}	ref
I		1960 (s), 1890 (s, bd)	*b*
IV	Na^+, tight	1895, 1835, 1800, 1730	*b*
IV	Bu_4N^+, ss	1818, 1702, 1680	*b*
II	Na^+, tight	1895, 1800, 1745	*b*
II	Bu_4N^+, ss	1895, 1800, 1745	*b*
$Cr(CO)_6$		1975	52
$Cr(CO)_5^{2-}$	Na^+, tight	1819, 1768	52
$Cr(CO)_5^{2-}$	Na^+, ss	1760, 1722	52
$CpCr(CO)_3^-$	Na^+, tight	1897, 1793, 1743	53
$CpCr(CO)_3^-$	Na^+, ss	1895, 1778	53

[a] Abbreviations: "tight" = tight ion pair; "ss" = solvent-separated ion pair. [b] This work.

shown below and involve an agostic proton that migrates to the α position, yielding the final product:

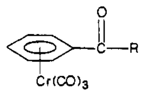
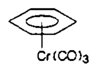
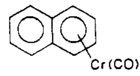
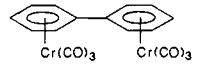


Infrared data for the carbonyl stretch for all the species involved in the reaction sequence is given in Table VI. These data include the IR data from the electrochemical generation of IV and II, where the counterion is the tetrabutylammonium cation. Included in this table for comparison are the data for the various reduced species generated from $Cr(CO)_6$. Also included are the data for (cyclopentadienyl)tricarbonylchromium anions.

The significance of ion-pairing effects becomes evident by an examination of Table VI. In the dianion, as is the case in $Cr(CO)_5^{2-}$, the ion-pairing effects cause a significant increase in the wavenumbers for the CO stretch for the tight-ion-pair species in THF as opposed to that for the nontightly paired species (large counterion or in HMPA solution).[52,53] However, when the $Cr(CO)_3$ is bound to an anionic ring (cyclopentadienyl or cyclohexadienyl), the ion-pairing effects are not as great, as exemplified by the $CpCr(CO)_3$ anion. It should be pointed out that the increase in number of IR-active bands from 2 for I to 3 for VI is consistent with the reduced local symmetry of VI.

IV is a member of the rather exclusive class of η^4-arene complexes.[37-41,54-57] Of these complexes, only two were formed under nonreducing conditions.[38,57] It may therefore be quite general that the reduction of η^6-arene complexes with a electron source, either chemical or electrochemical, will result in an η^4-arene complex. These complexes are very likely intermediates in some catalytic processes,[37,58] so that their study is of interest.

Table VII. Classification of (Arene)tricarbonylchromium Complexes according to Their Reductive Electrochemical Behavior

class	type of complex	reductive behavior	comment	ref
1		1e, rev	mainly redn of ligand	8, 11–15
2		2e, irrev	product oxidizes 1.8 V anodic of redn $E_{1/2}$	8, 10
3		2e, rev		8
4		2e, rev	reduces by 1e/$Cr(CO)_3$	9

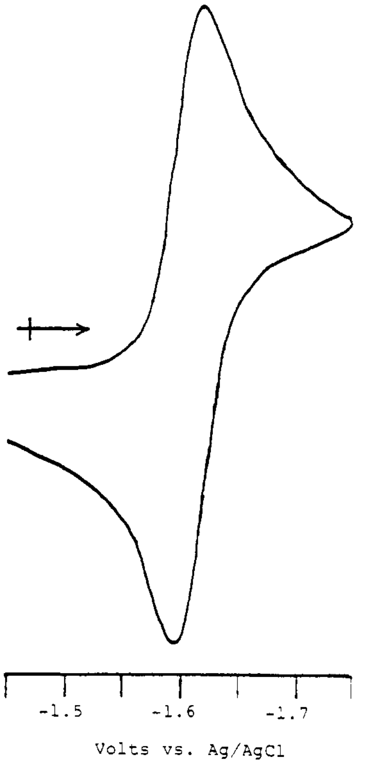


Figure 1. Cyclic voltammogram of I in propylene carbonate (0.25 M TEAP) on a HMDE at 200 mV/s.

Electrochemical Results

Introduction. (Arene)tricarbonylchromium complexes have received much attention in recent years concerned with their electrochemical behavior.[25-32,68-75] Both oxidative[68-75] and reductive[25-32] studies have appeared. The complexes can be classified according to their reductive electrochemical behavior into one of four classes (see Table VII). While this paper will deal with class 3, it is felt that the only difference between class 2 and class 3 may be the rate of the follow-up reactions with a proton source.

Results and Discussion. Three nonaqueous solvents were employed in this study. They were propylene carbonate (PC, with 0.25 M TEAP), acetonitrile (AN, with 0.1 M TEAP), and tetrahydrofuran (THF, with 0.2 M TBAP). While dc, pulse, and differential pulse polarographic measurements and slow cyclic voltammograms were obtained in all three solvents, propylene carbonate was the solvent of choice for the accumulation of kinetic data. This was due to its ease of purification and high dielectric constant, which minimized problems due to *iR* drop across the cell.

We only report the polarographic data for PC and AN for the reduction of I. The data obtained in THF are consistent with that obtained in the other two solvents, but adsorption and *iR* effects preclude any meaningful information. However, THF was the solvent of choice for the exhaustive reduction of I.

Polarography yielded an $E_{1/2}$ value of −1.62 V vs. the Ag/AgCl reference electrode in both PC and AN. The $E_{1/4-3/4}$ value was 30 mV in both solvents. The diffusion coefficient was 6.0. This value is twice that obtained for anthroquinone, which is known

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(68) Rieke, R. D.; Milligan, S. N.; Tucker, I.; Dowler, K. A.; Willeford, B. R. *J. Organomet. Chem.* **1981**, *218*, C25.

(69) Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938.

(70) Milligan, S. N.; Tucker, I.; Rieke, R. D. *Inorg. Chem.* **1983**, *22*, 987.

(71) Peterleitner, M. G.; Tolstays, M. V.; Krivyku, V. V.; Denisovitch, L. I.; Rybinskaya, M. I. *J. Organomet. Chem.* **1983**, *254*, 313.

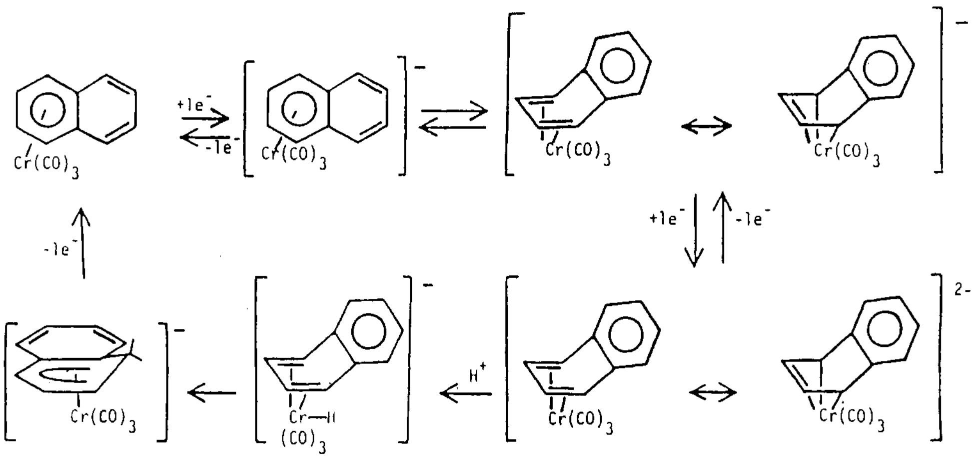
(72) Degrand, C.; Besancon, J.; Radecki-Sudre, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *160*, 199.

(73) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1743.

(74) Doysee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819 and references therein.

(75) Finke, R. G.; Voegell, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347.

Scheme I. Mechanism for the Reduction of I



to reduce by one electron in a reversible fashion. Thus, all polarographic data suggested a two-electron process. This was conclusively demonstrated by carrying out coulometric investigations in both PC and THF, which showed that the process was a two-electron reduction.

Figure 1 shows a cyclic voltammogram for I obtained on a hanging mercury drop electrode (HMDE) in propylene carbonate (0.25 M TEAP). At scan rates as low as 0.01 V/s, the ratio of peak currents (i_{pa}/i_{pc}) is unity.[76] It is therefore apparent that on the time frame of cyclic voltammetry the anion is quite stable.

The peak separation ($\Delta E_p = E_{pa} - E_{pc}$) for CV's obtained at scan rates below 0.100 V/s is 30 mV, which is expected for a two-electron reversible process.[77,78] However, if the scan rate is increased above this value, the ΔE_p value increases rapidly, suggesting a quasi-reversible electrochemical reduction. The current function behavior further supports the quasi-reversible reduction process. As one increases the scan rate beyond 10 mV/s, the current function rapidly falls off. In the range of 700–800 mV/s, the current function levels off at a value of half the 10 mV/s value. At the higher sweep rates, we are presumably beginning to exceed the kinetics of the chemical or isomerization step. Accordingly, we are beginning to see a one-electron reduction and a resulting decrease in the current function to a one-electron process.

Figure 2 shows the CV obtained in PC after exhaustive reduction of I. In PC, the dianion is not stable but reacts to form a species that is oxidizable at −0.397 V, regenerating I.[79] In rigorously dry THF, on the other hand, the dianion is stable for hours. It is possible to obtain an IR spectrum for the dianion, which has CO bands at 1818, 1702, and 1680 cm^{-1}. This is the same species generated by chemical reduction of I.

However, if a proton source is added to the THF solution of I prior to electrolysis, the reduction at −1.62 V becomes totally irreversible. A cyclic voltammetric analysis results in a new oxidation wave at −0.45 V (strong adsorption). This wave is similar in position to the oxidation wave observed in PC. IR analysis of this solution in the CO region results in bands at 1895, 1800, and 1745 cm^{-1}. We interpret these results as suggesting that, in propylene carbonate, the dianion reacts with a proton source, forming II. Compound II is also formed when I is reduced in the presence of a proton source in THF.

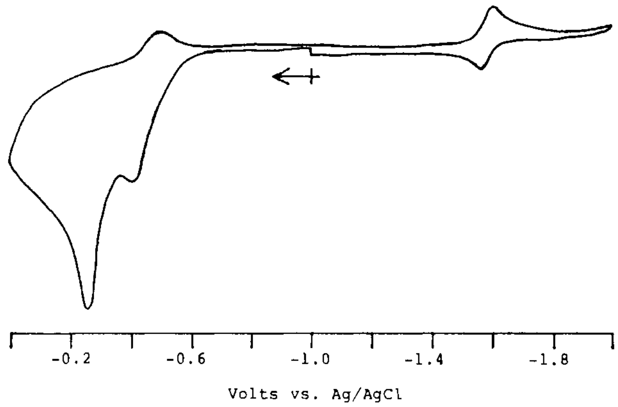


Figure 2. Cyclic voltammogram obtained after exhaustive reduction of I in propylene carbonate (0.25 M TEAP) on a HMDE at 200 mV/s.

To substantiate that the oxidation peaks at approximately −0.397 and −0.242 V were the product from protonation of the dianion, a proton source was added to a propylene carbonate solution of I and CV's were run. It was found that the reduction process became totally irreversible and that oxidation peaks at −0.440 and −0.270 V were observed. This material proved to be identical in all respects to II that was generated by reacting the dianion of I with a proton source. Finally, bulk electrochemical oxidation of II regenerated I in near-quantitative fashion. Thin-layer electrochemical experiments indicate that the reoxidation process is a one-electron oxidation.

Cyclic voltammetric behavior as observed for the reduction of I (ΔE_p increasing and $i_p/v^{1/2}$ decreasing with increasing v) is characteristic of a slow heterogeneous rate constant (k^0).[78] It is possible to estimate k^0 from the cyclic voltammetric data or, more specifically, from the peak separation. This was done by employing the equation of Nicholson (eq 5).[78] From ΔE_p, ψ is obtained from

$$\psi = k^0(D_O/D_R)^{\alpha/2}/(D_O \pi v n F/RT)^{1/2} \qquad (5)$$

the working curve constructed from Nicholson's data.[96] If the diffusion constant is known, then k_0 can be calculated from eq 5 for each scan rate. The diffusion coefficient (D_O) was calculated for I from the I_d value by employing the known capillary constants for our capillary, yielding a value of 1.7×10^{-7} cm^2/s. If the assumptions are made that $\alpha = 0.5$ and $D_O = D_R$, k^0 is estimated to be 2.3×10^{-2} cm/s.

Low k^0 values in organic and organometallic chemistry have been explained in terms of geometric isomerization concurrent with electron transfer.[80] Examples include the reduction of COT,[81-89] ferrocene,[90,91] nickelocene,[92] and other π-bonded sys-

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(76) While the same behavior occurs on a platinum-button electrode for CV analysis, the platinum becomes coated upon reducing I. This is manifested by a decrease in the peak current upon subsequent scans. For this reason, no CV data on platinum will be reported.

(77) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(78) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(79) While it appears that both oxidation peaks correspond to an overall two-electron oxidation, I can be regenerated if a potential just anodic of the first peak is used for the reoxidation. In this way, I can be regenerated upon a one-electron oxidation, where initially it was a two-electron reduction. From these resutls, it can be deduced that the second oxidation process is probably resulting from the H• that would be released from II when I is formed.

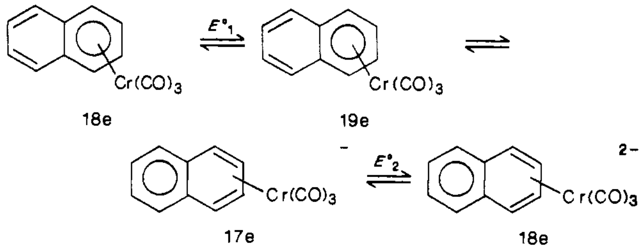
(80) Evans, D. H.; O'Connell, K. M. *Electroanal. Chem.* **1984**, *14*, 392.

(81) Huebert, B. J.; Smith, D. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *31*, 333.

(82) Allendoerfer, R. D.; Rieger, P. H. *J. Am. Chem. Soc.* **1965**, *87*, 2336.

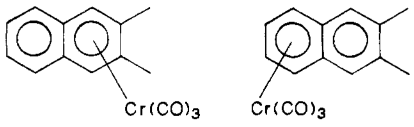
tems.[75,93] In the π-bound organometallic systems, the geometric isomerization has often been suggested to be "ring slippage", where the metal bonds to less carbons in the reduced species than in the starting complex. It should be pointed out that this argument is not unequivocal. Recent studies have reported examples where slow heterogeneous rate constants are, in fact, not associated with structural changes.[98] However, for the present study, the NMR data clearly show that at some point in the reduction of I there is definitely a structural isomerization.

While the value of k^0 is only an estimate and no attempt has been made to determine effects of size of the cation of the electrolyte, ion-pairing effects, or double-layer corrections, this value does indicate a relatively slow heterogeneous electron-transfer rate, which is consistent with the observed cyclic voltammetric behavior. However, until further studies are carried out, it is impossible to indicate whether bond reorganization occurs with the initial electron transfer or if it occurs only after the first electron has been transferred to I. Accordingly, the proposed ECE scheme shown below is consistent with all the observed data:



The product of the isomerization is a 17-electron species and is expected to be readily reduced to the stable 18-electron dianion. This explanation is consistent with the experimental observation that E°_2 must be positive of E°_1. In a recent study[97] involving rhodium and iridium complexes that underwent an $\eta^6 \rightarrow \eta^4$ isomerization upon a two-electron reduction, the authors proposed that the isomerization occurred after the second electron had been transferred. However, in the rhodium case, there were clearly two separate one-electron waves. In the iridium case there were large variations in CV shapes and ΔE_p values depending on electrode material and solvents. While our proposed ECE mechanism is far from unequivocal, it is consistent with the electrochemical data, which suggest that E_2 is positive of E_1, which would be the case if the process were ECE.

In order to determine the effects of alkyl substituents, the reductive properties of the tricarbonylchromium complexes of 2,3-dimethylnaphthalene (XIII) and tetralin (XIV) were determined. For both compounds two isomers are possible. In the case of 2,3-dimethylnaphthalene, the isomers were isolated and studied by themselves and as a mixture. For tetralin the mixture of isomers was examined. For XIII and XIV, the electrochemical properties were identical for both compounds as well as for both isomers. Both compounds gave clean dc, pulse, and differential pulse polarographic results as well as cyclic voltammetric results. For both XIII and XIV, a single reduction wave at −1.68 V vs. the Ag/AgCl reference was obtained. When mixtures of the two isomers were examined for both XIII and XIV, there was no hint of two separate waves in the cyclic voltammetric waves or differential pulse polarograms. Peak separations at slow scan rates (100 mV/s or less) were 30 mV, which is identical with the results obtained for the naphthalene complex itself. Computer simulations of differential pulse polarograms suggest that for two successive $n = 2$ electrochemical processes a difference of as little as $\Delta E_{1/2} = 40$ mV would be readily detected.[94,95] Accordingly, the reduction potentials of the two isomers for XIII and XIV must be very close to identical. This result is rather unexpected, particularly if the folding upon reduction is at all extensive. In the dianion, the $-Cr(CO)_3$ unit would be essentially bound to a butadiene unit and it would be expected that a 2,3-dimethylbutadiene ligand would be substantially different from an unsubstituted butadiene ligand. This result would suggest that the HOMO of the dianion is primarily weighted on the metal and carbonyls or that the folding is not extensive.



XIII

In order to determine if we were simply looking at some averaged fluxional process, the two isomers of XIII were separated by sublimation under reduced pressure and each isomer was exhaustively reduced electrochemically and then reoxidized. The isomers were isolated and totally characterized. The analysis showed that only the original isomers were recovered. This clearly demonstrates that no haptotropic rearrangement between the two rings has occurred during the reduction process.

Finally, the overall reduction process followed by reaction with a proton source and ultimately reoxidation to regenerate the original starting complex is given in Scheme I. It is of interest to note that throughout this process no CO's are lost during reduction, reaction with a proton source, or subsequent oxidation. It should be pointed out that the one-electron oxidation of II to generate I should also yield H_2 as a second product. We did not attempt to identify this product.

Conclusions

Chemical or electrochemical reduction of the (η^6-naphthalene)tricarbonylchromium complex is an overall two-electron process to give a stable dianion under anhydrous conditions. The reduction is suggested to be an ECE process in which the chemical step represents a haptotropic rearrangement, and finally upon addition of the second electron an (η^4-naphthalene)tricarbonylchromium dianion complex is formed. The "slip-fold" mechanism is supported by the ^{13}C NMR data, which show an unusual downfield shift of almost 50 ppm for the 9,10-carbon atoms. The "slip-fold" mechanism is also consistent with molecular orbital calculations already published. Protonation of the dianion yields an unusual (η^5-cyclohexadienyl)tricarbonylchromium anion. The protonation of the α position of the naphthalene ring in the dianion complex was demonstrated to occur in an endo manner, suggesting involvement of the chromium atom. Finally oxidation of II regenerates I. Remarkably no CO's are lost throughout this process.

Experimental Section

The cells and equipment used for routine polarographic and cyclic voltammetric analysis as well as bulk reductions and oxidations have been described previously.[25,95] Fast-scan CV data were obtained by employing a cell with a Luggin probe configuration to minimize iR drop across the cell. The cell was placed in a Faraday cage to minimize spurious noise.

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Data were acquired with a Nicolet lab computer. All electrochemistry was done under an atmosphere of purified argon.

THF was distilled immediately prior to use from sodium benzophenone. Propylene carbonate was vacuum-distilled by employing a commercial spinning-band distillation apparatus. Supporting electrolytes were purchased from Eastman Chemicals and dried in vacuo at 100 °C for at least 1 h immediately prior to use.

NMR data were obtained on a Varian XL-200 or Nicolet 360-MHz instrument. IR data were obtained on a Perkin-Elmer 283 spectrometer. THF was distilled from sodium benzophenone immediately prior to use. THF-d_8 was pot-to-pot distilled from sodium or P_2O_5 after at least five freeze-pump-thaw cycles to remove any O_2. Dioxane was freshly distilled from Na/K alloy immediately prior to use. All work was done under argon (dried and deoxygenated) with use of standard manifold techniques.

Preparation of I, XIII, and XIV. Naphthalene (9.44 g, 0.072 mol) and hexacarbonylchromium (8.80 g, 0.040 mol) were refluxed in a 36-mL mixture of dioxane/THF (6/1 by volume) for 6 days. The reaction was then filtered and the solvent removed under reduced pressure. Purification was accomplished by column chromatography on silica gel, employing hexane/diethyl ether as eluent. ^{1}H NMR and IR bands and melting points all agreed with literature values.[59-61,95]

Preparation of IV. I (0.264 g, 1.0 mmol) was dissolved in 1.0 mL of THF or THF-d_8, depending on the purpose of the experiment. This solution was then added to the Na/Hg amalgam prepared by adding 0.1 g of Na to 1 mL of Hg with stirring. The amalgam was prepared in the reaction flask. This mixture was allowed to react until the IR spectrum of I disappeared (approximately 0.25 h). The solution was filtered and used.

Preparation of II. (a) The sodium salt of II can be prepared by adding an equimolar amount of H_2O to the solution of IV as prepared above. Filtration, followed by removal of the solvent under vacuum, yields a purple solid, which has been characterized as II.

(b) II with tetraethylammonium as the counterion can be prepared by adding tetraethylammonium chloride to the solution prior to filtration. If this mixture is stirred for 2 h and then worked up as in (a), the Et_4N^+ salt of II is obtained.

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Contribution from the Chemistry Department,
The Ohio State University, Columbus, Ohio 43210

Inclusion Complexes Involving a Novel Ligand Superstructure: Dioxygen Adducts and Other Derivatives of Retro-Bridged Cyclidene Iron, Cobalt, and Nickel Complexes

James H. Cameron, Masaaki Kojima, Bohdan Korybut-Daszkiewicz, Bradley K. Coltrain, Thomas J. Meade, Nathaniel W. Alcock,[†] and Daryle H. Busch*

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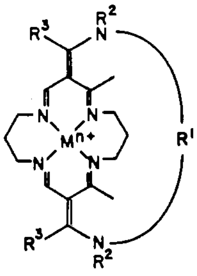
New iron(II) and cobalt(II) dioxygen carriers have been synthesized with a novel family of *retro-bridged* lacunar cyclidene ligands (structure V) by consecutive template reactions. NMR and ESR spectroscopy, electrochemistry, and equilibrium studies have been applied to the characterization of the new dioxygen carriers. The cobalt complexes unambiguously demonstrate steric control of dioxygen affinity while the iron(II) complexes exhibit both greater dioxygen affinities than previously reported iron(II) lacunar cyclidene complexes and surprisingly moderate sensitivity toward autoxidation. By combining the new retro-bridge with the previously known bridging reaction, both lacunar (structure VI) and vaulted (structure VII) *doubly bridged* cyclidene complexes of nickel(II) have been prepared. The X-ray crystal structure determination of $[Ni\{(CH_2)_8(CH_2pipz)_2(3,6\text{-dur})[16]cyclidene\}](PF_6)_2 \cdot CH_3CN$ is reported and the results applied to the understanding of the chemistry of the unusual compound: orthorhombic, space group $Pna2_1$; cell parameters $a = 18.863$ (4) Å, $b = 19.822$ (3) Å, $c = 13.761$ Å, $Z = 4$.

Introduction

Inclusion chemistry is among the most promising contemporaneous areas for applying molecular design to the investigation of chemical relationships involving the association of independent chemical entities. The classic case of metal coordination templates was addressed long ago by one of us,[1] while Cram has clearly delineated the host-guest relationships for the case where a guest is included within the cylindrical cavity of a macrocyclic host.[2] Lehn and others have considered more complex mixed cyclic structures designed to include two or more guests or more than one functional moiety in a single guest.[3] There is a parallel between this molecular design and the so-called compartmental ligands, defined by Fenton,[4] which coordinate two, or more, metal ions in well-defined coordination sites. The first such ligand was probably that reported by Travis and Busch.[5] Subsequently, we have departed from these single-function host or ligand molecules and designed ligands having sites for accommodating two or three different classes of included species.[6-9]

Lacunar cyclidene complexes (structure I) were designed to provide new families of dioxygen carriers.[10] The ligands are bicyclic structures in which one cycle accommodates the metal ion (cobalt(II) or iron(II)) while the second ring provides a



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* To whom correspondence should be addressed.

[†] Department of Chemistry, University of Warwick, Coventry CV4 7AL, England.

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