effects have been discussed in detail previously.[9f]

Conclusion

We have presented the first ab initio HF study of CH_3 migration in tetracarbonylmethylcobalt(I) and dicarbonylcyclopentadienylmethyliron(II). Optimized geometries for important structures on the potential energy surfaces were obtained at the PRDDO level. Energetics were evaluated with large basis set ab initio calculations. At the ab initio level we found activation barriers of 21 kcal/mol for the cobalt system and 16 kcal/mol for the iron system. These values compare well with experimental estimates. The ΔE's for the overall carbonylation reactions were calculated to be -6 and -11 kcal/mol for the cobalt and iron systems, respectively. We examined the potential energy surfaces in order to estimate the transition-state structures, and we found that the transition states were less acyl-like than in the corresponding manganese system. We compared our results with recent HFS calculations on the cobalt system and found that, in general, our energetics are similar. However, our calculated structure for the intermediate (3) differs dramatically from that found previously. Our structure possesses geometrical parameters typical of normal η^1-bound acyl groups,[32-34] while the HFS study found a structure that in fact is very similar to our calculated *transition*-state structure. In contrast to EHT results, we found the structure of the intermediate in the iron system (9) to be quasi-trigonal planar rather than pyramidal. Finally, substituent effects were considered, and our calculations showed that replacing the methyl group with a trifluoromethyl group significantly increases the activation barrier in both systems, while replacing the methyl substituent with an ethyl group slightly reduces the activation barrier.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant No. Y-743), the University of Texas Center for High Performance Computing, and the Texas Advanced Technology Program for their support of this work.

Supplementary Material Available: Cartesian coordinates and total energies of structures 1-14 (13 pages). Ordering information is given on any current masthead page.

Metal-π Complexes of Benzene Derivatives. 37.[1] Redox Behavior of the Sandwich Complexes $C_{12}H_{12}M$ ($C_{12}H_{12}$ = C_6H_6 + C_6H_6, C_5H_5 + C_7H_7; M = V, Cr). A Comparative Study[†]

Christoph Elschenbroich,* Edgar Bilger, and Bernhard Metz

Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, D-3550 Marburg, Germany

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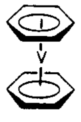
The prototypical sandwich complexes $(\eta^6\text{-}C_6H_6)_2V$ (1), $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)V$ (2), $(\eta^6\text{-}C_6H_6)_2Cr$ (3), and $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Cr$ (4) have been subjected to a cyclovoltammetric study in order to gain insight into the factors that govern the redox processes $C_{12}H_{12}M^{0/-}$ and $C_{12}H_{12}M^{0/+}$. Subsequent oxidation of the cations has also been studied. It is shown that, at constant complex charge, oxidation of the M d^6 species is easier than that of the M d^5 species, and symmetrical complexes (ligands C_6H_6 + C_6H_6) are oxidized preferentially to their unsymmetrical counterparts (ligands C_5H_5 + C_7H_7). The large anodic shift of $E_{1/2}(2^{0/+})$ relative to $E_{1/2}(1^{0/+})$ compared to the small shift of $E_{1/2}(4^{0/+})$ relative to $E_{1/2}(3^{0/+})$ is rationalized on the basis of unequal spin states for 2^+ and 1^+ as opposed to equal spin states for 4^+ and 3^+. The potentials $E_{1/2}$-$(C_{12}H_{12}M^{0/+})$ display an excellent linear correlation with the ionization potentials IP_1 (photoelectron spectroscopy). They also parallel the magnitudes of the appearance potentials (mass spectrometry).

Introduction

Among the four sandwich complexes of general composition $C_{12}H_{12}M$ [$(\eta^6\text{-}C_6H_6)_2V$ (1), $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)V$ (2), $(\eta^6\text{-}C_6H_6)_2Cr$ (3), and $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Cr$ (4)], the redox properties of (cyclopentadienyl)(cycloheptatrienyl)vanadium (2) stand out. This already manifests itself in the rates at which these materials undergo air oxidation, compound 2 being by far the easiest one to handle. In fact, whereas the symmetrical complex 1 in solution is oxidized by air instantaneously, its unsymmetrical counterpart 2 begins to deposit a brown precipitate only after a few minutes and in the solid state is stable in air at room temperature for extended periods of time.[2]



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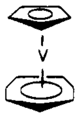

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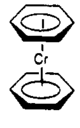

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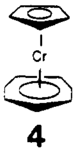

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This gradation, in particular the contrast between the two isoelectronic complexes 1 and 2, called for an inspection of the ionization potentials for the species $C_{12}H_{12}M$. In this paper, we put data obtained from different methods (cyclic voltammetry (CV), photoelectron spectroscopy (PS), mass spectrometry (MS)) in perspective and offer a rationale for the peculiar behavior of 2, which

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[†] Presented at the 200th National Meeting of the American Chemical Society, Symposium on Organometallic Electrochemistry, Washington, D.C., Aug 1990.

(1) Elschenbroich, Ch.; Heck, J.; Massa, W.; Birkhahn, M. *Chem. Ber.* **1990**, *123*, 2321.

(2) King, R. B.; Stone, F. G. A. *J. Am. Chem. Soc.* **1959**, *81*, 5263.

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Table I. Cyclic Voltammetric Data for Various Redox Processes of the Complexes $(C_{12}H_{12})M$ (M = Cr, V)[a]

		$E_{1/2}(0/-)/V^b$	$\Delta E_p/mV^b$	r^c	$E_{1/2}(0/+)/V^b$	$\Delta E_p/mV^b$	r^c	E_{pa}/V^d	E_{pa}/V^d
Bz_2V	1	−2.71 r	74	0.93	−0.35 r	66	1.00	0.24	0.46
CpVTr	2	−2.55 r[e]	66	1.00	+0.26 r[e]	64	0.93	1.03	
Bz_2Cr	3	<−3.1			−0.72 r	87	0.95	0.97	
CpCrTr	4	−2.89[d]			−0.61 r	56	0.83	1.59	

[a] In DME/$(n\text{-}Bu)_4NClO_4$ (0.1 M) at glassy carbon vs SCE, T = −35 °C, υ = 50 mV s^{-1}. Abbreviations: Cp, cyclopentadienyl; Bz, benzene; Tr, tropylium; r, reversible. [b] $E_{1/2} = {}^1/_2(E_{pa} + E_{pc})$; $\Delta E_p = E_{pa} - E_{pc}$. [c] $r = i_{pa}/i_{pc}$. For the couples $(C_{12}H_{12})M^{0/+}$, good linear correlation of i_p with $\upsilon^{1/2}$ is observed (correlation coefficient = 0.98–1.00). In the case of 1 and $2^{0/-}$, this correlation is inferior due to the proximity to the cathodic border of the solvent/electrolyte. [d] Peak potential of an irreversible wave. [e] One-electron process as demonstrated by CV, employing $3^{0/+}$ as an internal standard.

Table II. Electron Configurations and Ionization (IP_1), Half-Wave ($E_{1/2}$), and Appearance (AP) Potentials for the Sandwich Complexes $(C_{12}H_{12})M$ and $(C_{12}H_{12})M^+$, Respectively (M = V, Cr)

				IP_1/eV^a	ΔIP_1	$E_{1/2}/V$ (T, °C)	$\Delta E_{1/2}$	e/V^c
Bz_2V	1	$e_{2g}{}^4a_{1g}{}^1$	$^2A_1$	5.95		−0.35 (−35), −0.30 (+20)		6.26
	1^+	$e_{2g}{}^3a_{1g}{}^1$	$^3E_2{}^d$					
					0.45 (2, 1)		0.61 (2, 1)	
CpVTr	2	$e_2{}^4a_1{}^1$	$^2A_1$	6.40		+0.26 (−35), +0.32 (+20)		7.24
	2^+	$e_2{}^4$	$^1A_1{}^e$					
Bz_2Cr	3	$e_{2g}{}^4a_{1g}{}^2$	$^1A_1$	5.40		−0.72 (−35), −0.68 (+25)		5.91
	3^+	$e_{2g}{}^4a_{1g}{}^1$	$^2A_1$					
					0.20 (4, 3)		0.11 (4, 3)	5.96
CpCrTr	4	$e_2{}^4a_1{}^2$	$^1A_1$	5.60		−0.61 (−35), −0.55 (+25)		
	4^+	$e_2{}^4a_1{}^1$	$^2A_1$					

[a] First ionization potentials from photoelectron spectra ref 18. [b] Half-wave potentials from cyclic voltammetry, this work. [c] Appearance potentials from mass spectrometry, ref 19. [d] Reference 25. [e] 2^+ is diamagnetic.[24]

also takes into account disparate changes in magnetic properties for the oxidation $C_{12}H_{12}M^0 \rightarrow C_{12}H_{12}M^+$. Additionally, cyclovoltammetric studies concerning the couples $1^{0/-}$–$4^{0/-}$ as well as further oxidation of the cations 1^+–4^+ will be addressed. Some of the redox processes discussed in the present paper have been the subject of previous electrochemical study;[3] they were reinvestigated here in order to secure a consistent set of electrochemical data for the series 1–4 obtained under identical experimental conditions.

Results and Discussion

Redox Couple $(C_{12}H_{12})M^{0/-}$. Electrochemical potentials related to various oxidation states of the species of $C_{12}H_{12}M$ are presented in Table I. Photoelectron and mass spectrometric data alluded to in the discussion are collected in Table II.

Whereas for M = V, transfer of an electron to $(C_{12}H_{12})M$ completes the valence shell to an inert gas configuration, reduction for M = Cr formally leads to a 19-valence-electron (VE) species. Therefore, the anions 1^- and 2^- should be accessible by electrochemical reduction, albeit at fairly negative potentials, while electrochemical generation of the radical anions 3^- and 4^- should pose difficulties. This is borne out by cyclovoltammetry at low temperature in that both vanadium complexes show reversible reduction waves at $E_{1/2}(1^{0/-})$ = −2.71 V and $E_{1/2}(2^{0/-})$ = −2.55 V, respectively (Figure 1). As predicted from competitive reduction experiments of 1 in the presence of naphthalene, biphenyl, or benzene,[4] the potential for the couple $1^{0/-}$ closely resembles that of biphenyl$^{0/-}$ ($E_{1/2} \approx -2.7 \pm 0.1$ V, depending on the medium[5]). Recently, the bis(benzene)vanadium anion 1^- has even been isolated as its potassium salt.[6b] The anodic shift of the potential $E_{1/2}(2^{0/-})$ relative to $E_{1/2}(1^{0/-})$ reflects the higher electron-accepting properties of the ligand combination $C_5H_5 + C_7H_7$ com-

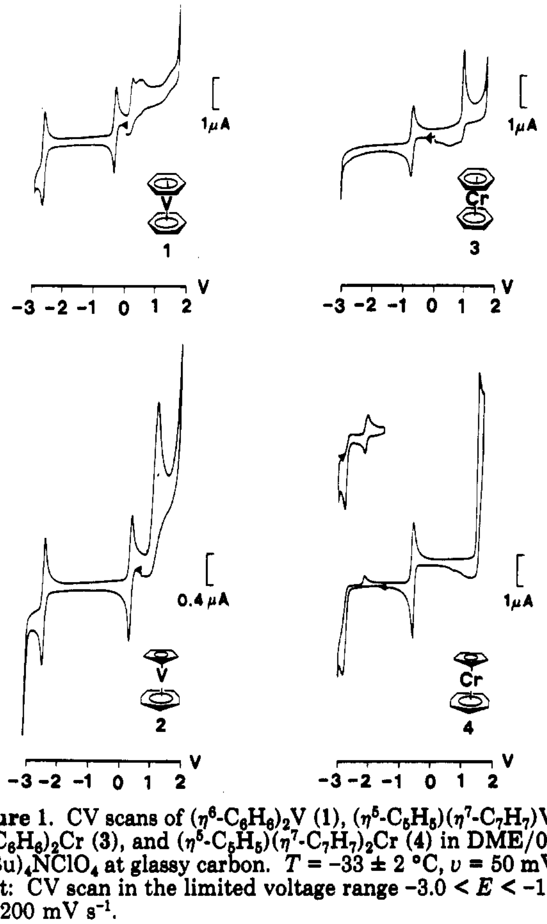

Figure 1. CV scans of $(\eta^6\text{-}C_6H_6)_2V$ (1), $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)V$ (2), $(\eta^6\text{-}C_6H_6)_2Cr$ (3), and $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)_2Cr$ (4) in DME/0.1 M $(n\text{-}Bu)_4NClO_4$ at glassy carbon. $T = -33 \pm 2$ °C, υ = 50 mV s^{-1}. Inset: CV scan in the limited voltage range $-3.0 < E < -1.5$ V, υ = 200 mV s^{-1}.

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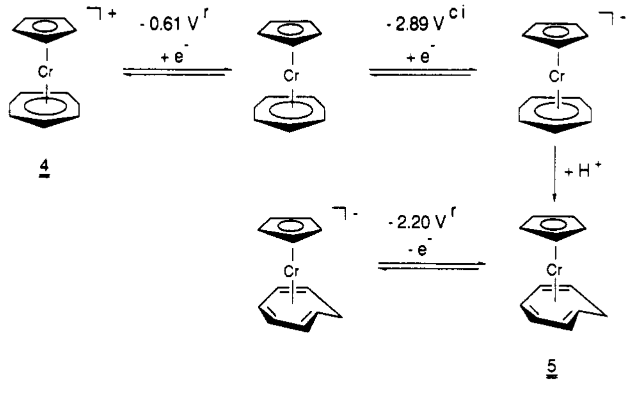
(3) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1 for leading references.

(4) Elschenbroich, Ch.; Gerson, F. *J. Am. Chem. Soc.* **1975**, *97*, 3556.

(5) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; p 178. Breant, M.; Georges, J. *Anal. Chim. Acta*, **1977**, *90*, 111. Yur'eva, L. P.; Nekrasov, L. N.; Pergudova, S. M.; Korotov, A. P.; Vykldotseva, L. N.; Zaitseva, N. N.; Shevelev, Yn. A. *J. Organomet. Chem.* **1982**, *238*, 197.

(6) (a) Fochi, G.; Braga, D.; Sabatina, P. *Organometallics* **1988**, *7*, 565. (b) Focchi, G.; Runjuan, X.; Colligiani, A. *J. Chem. Soc., Dalton Trans.* **1990**, 2551.

Scheme I



pared to C_6H_6 + C_6H_6 as will be discussed in the following section.

The reduction of the 18-VE complexes **3** and **4** requires considerably more negative potentials than that of the 17-VE species **1** and **2**.[7] Whereas $E_{1/2}(3^{0/-})$ is inaccessible in the electrochemical window provided by the medium $(n\text{-Bu})_4NClO_4$/DME, reduction of **4** is observed at its negative border, a cathodic peak being detected at $E_{pc} \approx -2.90$ V. This reduction is chemically irreversible since upon repetitive cycling a new, reversible wave grows at $E_{1/2} = -2.11$ V (Figure 1). As proved by comparison with an authentic sample, this redox process involves the complex (η^6-cycloheptatriene)(η^5-cyclopentadienyl)chromium(I) (**5**), formed by protonation of 4^-. Presumably, it is the $(n\text{-Bu})_4N^+$ cation of the supporting electrolyte that acts as the source of protons. The overall ECE process is depicted in Scheme I.

The radical anions 3^- and 4^- had been obtained previously by means of alkali-metal reduction in aprotic media. In line with the exceedingly negative potential for the reduction of free benzene, $E_{1/2}(C_6H_6^{0/-}) = -3.42$ V,[8] chemical reduction of complex **3** requires forcing conditions,[9] 3^- persisting only at low temperature. The unsymmetrical radical anion 4^-, on the other hand, is easily generated at room temperature and, under exclusion of air, is stable indefinitely. According to EPR analysis,[10] the unpaired electron in 4^- occupies an orbital with dominant π-ligand character that correlates with the LUMO e_{2u} of **3**.[11] Therefore, the facile formation and high stability of 4^- reflect an increase in electron-acceptor character for $C_5H_5 + C_7H_7$ relative to $C_6H_6 + C_6H_6$. As noted above, this property also causes the reduction of **2** to occur at more anodic potential than that of **1** since the process involves transfer of an electron to the HOMO a_{1g} (V $3d_{z^2}$), which should be lower in energy for **2**, compared to **1**, due to the somewhat more extensive metal–ligand charge transfer in **2**. The relative electron affinities of cyclic π perimeters C_nH_n as a function of ring size have been discussed by Fischer,[12] who, based on experimental ionization energies, derived values for the Coulomb integrals of the various C_nH_n π orbitals. Inspection of these estimates reveals that the sum of the Coulomb integrals ($a_1 + e_1 + e_2$) is considerably more negative for the combination $C_5H_5 + C_7H_7$ (≈−85 eV), compared to $C_6H_6 + C_6H_6$ (≈−74 eV), the former being dominated by the low energy of the C_7H_7 π orbitals. The energies of the C_7H_7 and metal e_2 orbitals are more compatible than is the case for the smaller rings. Hence, for C_7H_7, the metal–ligand interaction is thought to be particularly strong.[13]

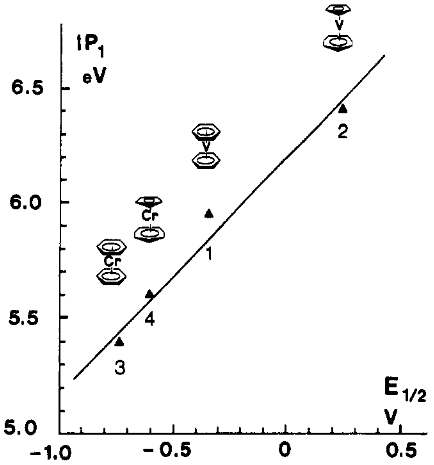


Figure 2. Plot of first ionization potentials IP_1 (photoelectron spectroscopy) vs redox potentials $E_{1/2}$ (cyclic voltammetry) ($IP_1 = 0.99E_{1/2} + 6.20$, $r = 0.995$, data from Table II).

Redox Couple $(C_{12}H_{12})M^{0/+}$. Cyclovoltammetric traces for the complexes **1**–**4** are also displayed in Figure 1, and the respective data are found in Table I. As amply demonstrated before, bis(η^6-benzene)chromium(0) (**3**) undergoes reversible one-electron oxidation to the radical cation 3^{+}.[14-16] This also applies to (η^7-cycloheptatrienyl)(η^5-cyclopentadienyl)chromium (**4**).[17] In the medium chosen for the present investigation, the half-wave potential, $E_{1/2}$, for the unsymmetrical complex **4** displays an anodic shift of +0.11 V relative to symmetrical **3**. A shift in the same direction but of much larger magnitude (+0.61 V) is observed if the cyclovoltammograms for the vanadium analogues **1** and **2**[7a] are compared. In order to underpin this spectacular increase, independent experimental evidence was searched for. In fact, the first ionization potentials, IP_1, derived from photoelectron spectra (PS) of the neutral complexes **1**–**4**,[18] parallel the CV values of $E_{1/2}$ in that the electron binding energy is conspicuously larger for **2** as compared to **1**, **3**, and **4**. The mass spectrometric appearance potentials for the molecular ions[19] point in the same direction (Table II).

As depicted in Figure 2, there is an excellent linear correlation between IP_1 and $E_{1/2}$ that is described by the equation $IP_1 = 0.99E_{1/2} + 6.20$ eV, the correlation coefficient being 0.995. This equation agrees very well with the relationship between ionization and electrode poten-

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[7] In previous investigations, due to limitations imposed by the solvent/electrolyte system, electrochemical reduction of **4** was not detected. (a) Gulick, W. M., Jr.; Geske, D. H. *Inorg. Chem.* **1967**, *6*, 1320. (b) Koelle, U.; Holzinger, W.; Müller, J. *Z. Naturforsch.* **1979**, *34b*, 759.

[8] Mortensen, J.; Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 84.

[9] Elschenbroich, Ch.; Bilger, E.; Koch, J.; Weber, J. *J. Am. Chem. Soc.* **1984**, *106*, 4297.

[10] Elschenbroich, Ch.; Gerson, F.; Stohler, F. *J. Am. Chem. Soc.* **1973**, *95*, 6956.

[11] Weber, J.; Geoffroy, M.; Goursot, A.; Pénigault, E. *J. Am. Chem. Soc.* **1978**, *100*, 3995.

[12] Fischer, R. D. *Theor. Chim. Acta* **1963**, *1*, 418.

[13] (a) Warren, K. D. *Struct. Bonding (Berlin)* **1976**, *27*, 45, p 151f. (b) Clack, D. W.; Warren, K. D. *Theor. Chim. Acta* **1977**, *46*, 313.

[14] Treichel, P. M.; Essenmacher, G. P.; Efner, H. F.; Klabunde, K. J. *Inorg. Chim. Acta* **1981**, *48*, 41.

[15] Yur'eva, L. P.; Peregudova, S. M.; Nekrasov, L. N.; Korotkov, A. P.; Zaitseva, N. N.; Zakurin, N. V.; Vasil'kov, A. Y. *J. Organomet. Chem.* **1981**, *219*, 43.

[16] Ito, N.; Saji, T.; Suga, K.; Aoyagui, S. *J. Organomet. Chem.* **1982**, *229*, 43.

[17] Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471.

[18] (a) Evans, S.; Green, J. C.; Jackson, S. E.; Higginson, B. *J. Chem. Soc., Dalton Trans.* **1974**, 304. (b) Cloke, F. G. N.; Dix, A. N.; Green, J. C.; Perutz, R. N.; Seddon, E. A. *Organometallics* **1983**, *2*, 1150.

[19] Müller, J.; Göser, P. *J. Organomet. Chem.* **1968**, *12*, 163.

tials, $IP_1 = \Delta E° + 6.36$ eV, which was derived by Parker for alternant aromatic hydrocarbons[20] and empirical correlations including a wide variety of organic substrates.[21] The quality of the correlation of IP_1 with $E_{1/2}$ for 1–4 is not all that surprising in view of the fact that the redox couples $C_{12}H_{12}M(d^6,d^5)$ and $C_{12}H_{12}M(d^5,d^4)$, respectively, involve changes in the occupation of a virtually nonbonding orbital a_{1g} (M $3d_{z^2}$) or a weakly bonding orbital e_{2g} (dominated by M $3d_{x^2-y^2,xy}$) so that the molecular dimensions change only marginally during oxidation/reduction.[22a] Accordingly, $(\Delta G°)_{solv}$, the change in solvation during the process $C_{12}H_{12}M \rightarrow C_{12}H_{12}M^+$, should be virtually identical for 1–4 and therefore be contained in the constant term of the linear correlation.

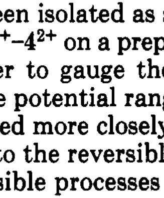
Since the gradation shown in Figure 2, rather than being influenced by medium (solvation) effects, mirrors the electronic structures of 1–4, a qualitative rationale for the sequence IP_1, $E_{1/2}$ 3 < 4 < 1 < 2 may be given and an explanation offered for the at first sight surprisingly anodic position of the data of 2:

(1) Ionization of the chromium d^6 complexes 3 and 4 (configuration $e_2{}^4a_1{}^2$) is easier than that of the vanadium d^5 complexes 1 and 2 (configuration $e_2{}^4a_1{}^1$). This may be traced to the fact that, in the case of 3 and 4, an electron is removed from the doubly occupied HOMO a_1, thereby decreasing Coulomb repulsion, whereas for 1 and 2 this HOMO is singly occupied and the electron is bound more tightly. In the case of 1, the frozen orbital approximation (Koopmans' theorem) actually fails, a phenomenon frequently encountered for sandwich complexes.[22b] Instead, in the electronically relaxed state of 1, the configuration $...e_2{}^3a_1{}^1$ pertains, which, being orbitally degenerate, exhibits stabilization by the exchange energy.

(2) Ionization of the symmetrical complexes 3 and 1, respectively, is easier than that of their unsymmetrical counterparts 4 and 2. This is certainly a consequence of the more pronounced π-acceptor character of the combination $C_7H_7 + C_5H_5$ compared to $C_6H_6 + C_6H_6$ (vide supra), which leads to a slightly larger positive partial charge on the central metal atom of the unsymmetrical complexes. Such a conclusion had been drawn previously from the electron binding energies E_B(Cr) in X-ray photoelectron spectra.[23]

(3) On proceeding from the symmetrical to the unsymmetrical ligand combination, the positive shift in IP_1 and $E_{1/2}$ for the ionization $C_{12}H_{12}M \rightarrow C_{12}H_{12}M^+$ is more than twice as large for M = V compared to M = Cr. A clue to the origin of this disparity can be derived from the observation that whereas 2–4 ionize from the HOMO a_1, 1 ionizes from the sub-HOMO e_2 with the result that 3^+ and 4^+ have identical spin states while those of 1^+ and 2^+ differ (Table I). Apparently, ionization of symmetrical 1 from the HOMO a_1 would lead to an excited configuration $e_{2g}{}^4$, which relaxes to the ground configuration $e_{2g}{}^3a_{1g}{}^1$ with an attendant gain in exchange energy and a decrease in electron repulsion. The latter effects favor ionization of the vanadium complex 1 and move the values for IP_1 and $E_{1/2}$ in the proximity of those for the chromium complexes 3 and 4. Contrarily, in the case of the unsymmetrical vanadium complex 2, due to the lower energy of the e_2 orbitals, the configuration $e_2{}^4$ represents the ground state. By way of conclusion, it may then be stated that rather than regarding the ionization of 2 as occurring at a surprisingly positive potential, that of 1 is effected at an anomalously negative value.

Redox Couple $C_{12}H_{12}M^{+/2+}$. Whereas the cations 1^+–4^+ have been isolated as stable salts, generation of the dications 1^{2+}–4^{2+} on a preparative scale has not been reported. In order to gauge the lifetimes of these dications, the positive potential range in the cyclovoltammograms was examined more closely. Bis(benzene)vanadium (1) in addition to the reversible wave for the couple $1^{0/+}$ features irreversible processes at E_{pa} = +0.35 V and E_{pa} = +0.64 V, which probably reflect the oxidations $1^{+/2+}$ and a consecutive process of unknown nature (Figure 1). Cyclopentadienylcycloheptatrienylvanadium cation (2^+) undergoes further irreversible oxidation at $E_{pa} \approx 1.10$ V. The anodic peak current suggests two close lying one-electron oxidations. 3 is that $C_{12}H_{12}M$ species which has been studied most extensively with regard to the existence of higher oxidation states. CV of the parent complex 3 in DME revealed that the reversible oxidation of $3^{0/+}$ is followed by a second oxidation step at E_{pa} = 1.14 V, which is irreversible even at low temperature (−45 °C). Reversibility can, however, be achieved by peripheral substitution of 3, which provides for kinetic stabilization of the dication. At −45 °C, bis(η^6-hexamethylbenzene)chromium (6) shows two reversible waves, $E_{1/2}(6^{0/+}) = -0.94$ V and $E_{1/2}(6^{+/2+}) = +0.45$ V,[26] and the second oxidation of (η^{12}-[2.2]paracyclophane)chromium (7) is reversible even at room temperature, $E_{1/2}(7^{0/+}) = -0.74$ V and $E_{1/2}(7^{+/2+}) = 1.24$ V.[27] Cycling the voltage at varying rates offers the opportunity to estimate the lifetime of the electrochemically generated dications in the medium DME/(n-Bu)$_4$NClO$_4$. In this way, at −40 °C, lifetimes of the order of seconds (3^{2+}), minutes (6^{2+}), and hours (7^{2+}) were derived.[28] Finally, the unsymmetrical cation (cyclopentadienyl)(cycloheptatrienyl)chromium(I) (4^+) un-



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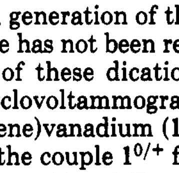

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[20] Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 5656.

[21] (a) Dewar, M. J. S.; Hashmall, J. A.; Trinajstic, N. *J. Am. Chem. Soc.* **1970**, *92*, 5555. (b) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916. (c) Nelson, S. F.; Peacock, V.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 5269. (d) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308.

[22] (a) Molecular dimensions of sandwich complexes and their cations, *d*(M–C): [$(C_6H_6)_2Cr$, 214 pm] Keulen, E.; Jellinek, F.; *J. Organomet. Chem.* **1966**, *5*, 490. [$(C_6H_6)_2Cr^+I^-$, 213 pm] Morosin, B. *Acta Crystallogr. Ser. B* **1974**, *30*, 838 (ionization from $a_{1g}{}^2$). [$(C_5H_5)_2Fe$ 203 pm] Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Ser. B* **1979**, *35*, 1068, 2020. [$(C_5H_5)_2Fe^+As_4Cl_{10}O_2^-$, 206 pm] Churchill, M. R.; Landers, A. G.; Rheingold, A. L. *Inorg. Chem.* **1981**, *20*, 849 (ionization from $e_{2g}{}^4$). (b) Coutiére, M.-M.; Demuynck, J.; Veillard, A. *Theor. Chim. Acta* **1972**, *27*, 281.

[23] Binder, H.; Elschenbroich, Ch. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 659.

[24] (a) Müller, J.; Göser, P.; Laubereau, P. *J. Organomet. Chem.* **1968**, *14*, 7. (b) Connelly, N. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3, p 687f.

[25] (a) Fischer, E. O.; Joos, G.; Meer, W. *Z. Naturforsch.* **1958**, *B13*, 456. (b) Calderazzo, F.; Cini, R. *J. Chem. Soc.* **1965**, 818.

[26] Bilger, E. Dissertation, Marburg, 1984. The couple $6^{+/2+}$ has also been studied by other workers: Markle, R. J.; Lagowski, J. J. *Organometallics* **1986**, *5*, 595.

[27] Elschenbroich, Ch.; Zenneck, U. Unpublished observation.

[28] The term "lifetime" is used here in the sense that it defines the shortest interval between anodic and cathodic scans that still leads to a clearly detectable cathodic peak. The observation of a reduction wave for a chemically unstable primary oxidation product (intermediate) on the reverse scan is sufficient to estimate the lifetime of the intermediate to about a factor of 5; see: Parker, V. D. *Adv. Phys. Org. Chem.* **1983**, *19*, 131.

dergoes further oxidation only at the very positive potential $E_{pa}(4^{+/2+})$ = 1.59 V near the anodic border of the electrochemical window (≈+1.75 V in TBAP/DME, Figure 1).

This oxidative stability of 4^+ could have been predicted from the aforementioned data since for this ion the factors that lead to anodic shifts of $E_{1/2}$ operate in unison. Explicitly, the very anodic potential $E_{pa}(4^{+/2+})$ may be rationalized by the facts that ionization occurs from a $C_{12}H_{12}M^+$ cation, the ligand combination in *unsymmetrical* and the redox orbital is *singly occupied*, no assistance to ionization being furnished by a release of pairing energy.

Experimental Section

Materials. $(\eta^6\text{-}C_6H_6)_2V$ (**1**),[29] $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)V$ (**2**),[2] $(\eta^6\text{-}C_6H_6)_2Cr$ (**3**),[30] and $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Cr$ (**4**)[31] were synthesized as previously reported. Dimethoxyethane (DME) was purified by refluxation and distillation from potassium benzophenone. The supporting electrolyte $(n\text{-}Bu)_4NClO_4$ was recrystallized three times from DME and dried in vacuo at 110 °C.

Apparatus. Cyclic voltammetry was performed with electrochemical equipment from AMEL (Milano) consisting of a Model 552 potentiostat, Model 568 function generator, Model 563 multipurpose unit, Nicolet Model 3091 storage oscilloscope, and Kipp and Zonen Model BD 90 x/y recorder. The electrochemical cell was operated under an atmosphere of argon, with glassy carbon, platinum rod, and saturated calomel (SCE) serving as working, counter, and reference electrodes, respectively. For temperature control, the cell was immersed in a thermostated cooling bath.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the donors of the Fonds der Chemischen Industrie for the support of this work.

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[29] Fischer, E. O.; Reckziegel, A. *Chem. Ber.* **1961**, *94*, 2204.

[30] Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1955**, *10b*, 665.

[31] Fischer, E. O.; Breitschaft, S. *Chem. Ber.* **1966**, *99*, 2905.

Characterization of the Heterobimetallic μ-(η^1-C:η^2-O,O′) Carbon Dioxide Complexes $(\eta^5\text{-}C_5H_5)(CO)_2MCO_2M'(Cl)(\eta^5\text{-}C_5H_5)_2$ (M = Fe, Ru; M′ = Ti, Zr)

Jose C. Vites, Bryan D. Steffey, Mary E. Giuseppetti-Dery, and Alan R. Cutler*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

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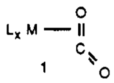
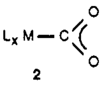
Heterobimetallic CO_2 adducts $Cp(CO)_2MC(O)OM'(Cl)Cp_2$ [M = Ru, M′ = Zr (**9a**), Ti (**9b**); M = Fe, M′ = Zr (**10a**), Ti (**10b**)] were prepared by treating the metallocarboxylates $CpM(CO)_2CO_2^-Na^+$ (M = Ru, Fe) with the appropriate zirconocene and titanocene dichloride at low temperatures. The metallocarboxylates $CpM(CO)_2CO_2^-Na^+$ are available from the reaction of a cold $CpM(CO)_2^-Na^+$ (−78 °C) solution with 1 equiv of CO_2, and $CpRu(CO)_2^-Na^+$ is prepared by sonication of Rp_2/sodium metal in tetrahydrofuran (THF). The solution stability of these bimetallocarboxylates, decreasing in the order RuZr (**9a**) ≫ FeZr (**10a**) > RuTi (**9b**) > FeTi (**10b**), determines how readily that they are isolated and characterized. The heterobimetallic CO_2 adduct **9a** is available analytically pure; IR, ^1H, and ^{13}C NMR spectral data are complete for **10a**, and IR spectral data for all four bimetallocarboxylates, as well as for the isotopomer $Cp(CO)_2Ru^{13}C(O)OZr(Cl)Cp_2$ (**9a-^{13}C**), are consistent with similar μ-(η^1-C:η^2-O,O′) carboxylate structures. All four bimetallic CO_2 adducts decompose in benzene solution to give similar products, $Cp_2M_2(CO)_4$ and μ-oxo $(Cp(Cl)M')_2O$; **10a**, **9b**, and **10b** decompose at or below room temperature, and **9a** slowly degrades above 40 °C. Protonating **9a** and **10a** with HBF_4 also deoxygenates the ligated CO_2 and affords $CpM(CO)_3^+BF_4^-$ (M = Ru, Fe) and $[Cp_2(Cl)Zr]_2O$ in moderate yields.

Introduction

Although numerous organotransition-metal carbon dioxide complexes **1** and **2** are known,[1] none undergo hydride transfer or net hydrogenation at the ligated CO_2. Bimetallic CO_2 complexes, represented by μ-(η^1-C:η^2-O,O′) **3** and μ-(η^1-C:η^1-O) **4** structures, potentially could facilitate CO_2 activation and reduction if the appropriate electron-rich (ML_x) and oxophilic ($M'L_y$) metal centers are paired. Relatively little is known, however, concerning the reactivity of ligated carbon dioxide.



1



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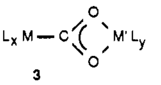

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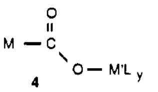

4

Several examples documenting reactions between mononuclear CO_2 complexes **1**/**2** and electrophiles have been reported. Anionic metallocarboxylates **2**[2,3] bind alkali- or

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[1] (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661; *Carbon Dioxide Activation by Metal Complexes*; VCH Publishers: Weinheim, Federal Republic of Germany, 1988. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988. (d) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (e) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984**, *6*, 291. (f) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (g) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (h) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel Publishers: Boston, MA, 1983, p 169. (i) Ito, T.; Yamamoto, A. In *Organic and BioOrganic Chemistry of Carbon Dioxide*, Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (j) Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, F. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 50.4.

[2] Recent selected examples include the following. (a) $FpCO_2^-Li^+$, Na^+, or K^+ [Fp = $Cp(CO)_2Fe$]: Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794; *Organometallics* **1985**, *4*, 1467. See also ref. 3. (b) $Cp(PPh_3)(CO)FeCO_2^-Li^+$ or K^+: Gibson, D. H.; Ong, T.-S. *J. Am. Chem. Soc.* **1987**, *109*, 7191. (c) $Cp(PPh_3)(NO)ReCO_2^-Li^+$ or K^+: Senn, D. R.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Inorg. Chem.* **1987**, *26*, 2737. (d) $Cp(NO)(CO)ReCO_2^-Na^+$ or Et_3NH^+: Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. (e) $Cp(N_2Ar)(CO)ReCO_2^-Li^+$, Na^+, or Ca^{2+}: Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478. (f) $(CO)_5WCO_2^{2-}(Li^+)_2$: Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

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