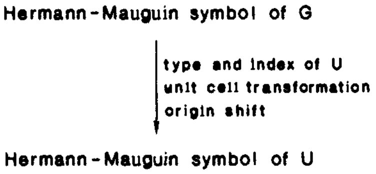
MnP-type structure and the ideal axial ratio of 1.633.

A 28k-point set for the hexagonal structure and a 27k-point set for the orthorhombic phases were used in the irreducible wedge[61] of the Brillouin zone for the density of states calculations.

Appendix II

The symmetry relation between crystal structures can be made more transparent by the use of maximal subgroup–minimal supergroup relations.[12-14] The maximal nonisomorphic subgroups U of a space group G are divided into two types: (I) t = "translationsgleich" (lattice-equivalent) and (II) k = "klassengleich" (class equivalent). In case I the subgroup U contains all translations of G and its crystal class is of lower symmetry than that of G. In case II G and U have the same crystal class but belong to different space group types. Thus U has lost translational symmetry, i.e., the primitive cell of U is larger than that of G. The index of a subgroup U (i.e., t3 or k2) is the number of cosets of U in G. The general formulation of the symmetry relations is given in the form



---

(61) Pack, J. D.; Monkhorst, J. J. *Phys. Rev.* **1977**, *B16*, 1748.

Electrochemical Evidence for a Three-Center, Three-Electron Agostic Interaction in Tungstenocene Dialkyl Cations and Estimation of the Magnitude of the Interaction

Marianne F. Asaro, Stephen R. Cooper, and N. John Cooper*

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received August 26, 1985*

Abstract: The role of three-electron agostic interactions in the chemistry of d^1 tungstenocene alkyl complexes has been explored electrochemically. Cyclic voltammograms in acetonitrile of the dialkyls $[W(\eta\text{-}C_5H_5)_2RR']$ ($R = R' = CH_3$, CH_2CH_3, or $CH_2C(CH_3)_3$; $R = CH_3$, $R' = CH_2CH_3$, $CH(CH_3)_2$, or Ph; $R = CH_2CH_3$, $R' = CH_2Ph$), of the alkyl and aryl halides $[W(\eta\text{-}C_5H_5)_2RX]$ ($R = CH_3$, X = Cl or I; $R = CH_2CH_3$, X = Cl or I; $R = CH(CH_3)_2$, X = Cl; $R = CH_2C(CH_3)_3$, X = Cl; R = Ph, X = Cl, Br, or I), and of $[W(\eta\text{-}C_5H_5)_2(CH_3)(OCH_3)]$ exhibit a reversible one-electron oxidation between −450 and +125 mV vs. SCE. The substituent effects are additive and result from a combination of inductive effects and π-effects involving donation into the partially occupied frontier orbital of the metal. Methoxide is the strongest π-donor, and only $[W(\eta\text{-}C_5H_5)_2(CH_3)(OCH_3)]$ has a low potential, reversible second oxidation. The donor interactions of the halides (Cl > Br > I) reverse the usual electronegativity trend, probably because of unusually good d-p π-overlap. The π-donor effects of the alkyl ligands suggest a stabilizing three-electron agostic interaction in the cations, controlled by steric repulsion between the alkyls and the cyclopentadienyl ligands. Partitioning the substituent effects in branched alkyls into inductive and agostic components suggests that agostic interactions with methyl and ethyl ligands stabilize the d^1 metal center by up to 2.7 and 0.7 kcal mol^{-1}, respectively.

We have recently demonstrated that hydrogen atom abstraction from the paramagnetic tungstenocene dialkyl cations $[W(\eta\text{-}C_5H_5)_2RR']^+$ ($R = R' = CH_3$ or CH_2CH_3; $R = CH_3$, $R' = CH_2CH_3$) is an α-selective process, giving rise to highly reactive intermediate cationic alkylidene complexes.[1] We have also speculated that this α-selectivity reflects ground-state delocalization of unpaired electron density from the metal center on to an α-C–H bond, possibly via overlap of the α-C–H bond with the half-filled frontier orbital of the 17-electron bent metallocene moiety;[1b-d] such a three-center, three-electron interaction is reminiscent of the three-center, two-electron interactions involving overlap of vacant transition-metal orbitals with α- or β-C–H bonds for which the term agostic was recently coined.[2]

Agostic interactions can significantly stabilize diamagnetic, electronically unsaturated complexes, and the importance of such interactions in the reaction chemistry of transition-metal alkyls has been underlined by two recent reports of "alkene hydrides" with β-agostic ground states[3] and by the observation that β-agostic interactions may play a crucial role in Ziegler–Natta polymerization of alkenes by stabilizing the coordinatively unsaturated alkyl intermediates.[4] The only fully established example of an analogous three-center, three-electron interaction in a paramagnetic transition-metal complex, however, is in an early structural study[5] which established that the interaction between an allylic C–H bond and the metal in the 16-electron cyclooctenyl cation $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]^+$ was partially retained in the neutral 17-electron complex $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]$.

Since the paramagnetic tungstenocene dialkyl cations may provide unusual examples of three-electron agostic interactions and since such interactions may also play a significant role in the chemistry of the complexes, we have investigated the cations by using the physical techniques previously reported to provide evidence for agostic interactions.[2] We have been unable so far, however, to structually characterize any of the cations,[6] the

---

* Fellow of the Alfred P. Sloan Foundation, 1982–1985.

(1) (a) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648. (b) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (c) Hayes, J. C.; Cooper, N. J. *Organometallic Compounds: Synthesis, Structure, and Theory*; Texas A & M University Press: College Station, 1983; p 353. (d) Hayes, J. C.; Jernakoff, P.; Miller, G. A.; Cooper, N. J. *Pure Appl. Chem.* **1984**, *56*, 25.

(2) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(3) (a) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 691. (b) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326.

(4) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443.

(5) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 7496.

0002-7863/86/1508-5187$01.50/0

paramagnetism of the complexes has ruled out examination by ^1H or ^{13}C NMR spectroscopy, and the IR spectrum of the archetypal tungstenocene dialkyl cation, $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]PF_6$, exhibits none of the low energy C–H stretching absorptions reported for some molecules containing four-electron agostic interactions.[2]

Since more established approaches had been unsuccessful, we recently turned to an electrochemical investigation of the oxidation (eq 1) of the neutral tungstenocene dialkyls (and some related complexes): early results had indicated that the potentials required

$$[W(\eta\text{-}C_5H_5)_2RR'] \xrightarrow{-e^-} [W(\eta\text{-}C_5H_5)_2RR']^+ \qquad (1)$$

did not have a simple dependence on the inductive effects of the alkyl ligands, and we felt that the patterns in the oxidation potentials might provide alternative evidence for π-interactions between the metal atom and the alkyl ligands in the cationic tungstenocene system. The present paper presents the results of that investigation, which not only indicate that agostic interactions do indeed occur in tungstenocene dialkyl cations but which also allow us to estimate the magnitude of the interactions for some simple alkyl groups. The results incidentally establish that electrochemistry can provide an effective and sensitive alternative to conventional probes of bonding interactions in transition-metal alkyls.

Experimental Section

General. All manipulations were conducted under a nitrogen or argon atmosphere by using standard Schlenk-tube techniques or a Vacuum atmospheres Dri-lab glovebox. Glassware was oven dried or flamed under vacuum before use. Spectrophotometric grade dimethylformamide (DMF) was used without further purification. Diethyl ether was freshly distilled from sodium benzophenone ketyl, pentane from $LiAlH_4$, and acetonitrile from CaH_2. Ferrocene was doubly sublimed. Isopropylmagnesium bromide was prepared from fractionally distilled isopropyl bromide in diethyl ether and was titrated with absolute ethanol and 1,10-phenanthroline as indicator. ^1H NMR spectra were recorded on a Bruker WM-300-WB at 300 MHz. IR spectra were obtained as KBr pellets on a Perkin-Elmer 683 spectrometer, and mass spectra were recorded with a Kratos MS-9 spectrometer. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Electrochemistry. Cyclic voltammetry was performed at ambient temperature (22 ± 2 °C) on CH_3CN solutions containing 0.10 M tetraethylammonium perchlorate (TEAP)[18] as the supporting electrolyte. All the solutions for which voltammograms are reported were 1.0×10^{-3} M in both substrate and internal standard, except as noted in Table I. Electrochemical experiments were performed under acetonitrile saturated N_2 with a Princeton Applied Research Model 173 potentiometer, Model 175 programmer, and Model 179 coulometer. Cyclic voltammograms were recorded with a Pt disk working electrode and a Pt gauze auxiliary electrode. A Pt mesh basket was used for coulometry. All voltammograms were recorded by using a saturated calomel reference electrode (SCE; checked periodically relative to a 1.0×10^{-3} M solution of ferrocene in acetonitrile containing 0.10 M $LiClO_4$, for which the ferrocenium/ferrocene reduction potential was 350 mV in agreement with the literature[19]). All the potentials in Table I were then calibrated using the indicated internal standards to minimize the effects of changes in junction potentials introduced by variations in the salt bridges and other experimental details.[20] The choice of standard was dictated by the potential range of the particular couple. Many of the couples were examined on a number of occasions, and internal calibration allowed the potentials to be reproduced to within ±5 mV. The presence of a standard did not observably affect the electrochemical behavior of any of the complexes. Under the experimental conditions the internal ferrocene standard exhibited a reversible oxidation with $(E_a + E_c)/2 = 376$ mV vs. SCE and $i_a/i_c = 1.00$ at 50 mV s^{-1}. The slight difference between this potential and that observed for the external ferrocenium/ferrocene electrode presumably reflects changes in junction potentials with changes in the supporting electrolyte.

Table I. Cyclic Voltammetric Data for Oxidation of $[W(\eta\text{-}C_5H_5)_2RR']$ and $[W(\eta\text{-}C_5H_5)_2RX]$ Complexes in CH_3CN[a]

complex	R	R′	ΔE_p, mV	$(E_a + E_c)/2$	i_a/i_c
1[7]	CH_3	CH_3	64	−448[b]	1.01
2[c]	CH_3	$CH(CH_3)_2$	64	−442[b]	0.95
3[1b]	CH_3	CH_2CH_3	61	−415[b]	1.02
4[8]	CH_3	OCH_3	62	−402[d]	0.96
5[9]	CH_2CH_3	CH_2CH_3	60	−383[b]	0.96
6[10]	$CH_2C(CH_3)_3$	$CH_2C(CH_3)_3$	61	−323[b]	0.97
7	CH_2CH_3	CH_2Ph	64	−286[b]	1.04
8[11]	CH_3	Ph	63	−273[b]	0.98
9[12]	$CH(CH_3)_2$	Cl	64	−111[e]	0.95
10[13]	CH_3	Cl	64	−97[e]	0.95
11[14]	CH_2CH_3	Cl	62	−68[e]	0.95
12[14]	$CH_2C(CH_3)_3$	Cl	64	−19[e]	0.99
13[f,15]	CH_3	I	63	−31[e]	0.97
14[16]	CH_2CH_3	I	63	+1[e]	0.98
15[17]	Ph	Cl	64	+72[e]	1.02
16[17]	Ph	Br	64	+104[e]	0.98
17[17]	Ph	I	64	+123[e]	1.05

[a] Potentials are reported relative to SCE and were determined using the internal standards indicated. Scans were recorded at 20 mV s^{-1} and were begun at potentials a minimum of 250 mV more negative than the oxidation peak. Switching potentials were a minimum of 300 mV more positive than the reduction peak. [b] $[Fe(\eta\text{-}C_5H_5)_2]$ as internal reference. [c] ^1H NMR indicated 90% chemical purity for this compound. [d] $[W(\eta\text{-}C_5H_5)_2(CH_2CH_3)Cl]$ as internal reference. [e] $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ as internal reference. [f] In situ solvolysis (see text) reduced the concentration of $[(\eta\text{-}C_5H_5)_2W(CH_3)I]$ to 0.00095 M for this scan.

Preparation of Substrates. Substrates were prepared as indicated in Table I or as described below and were checked for purity by ^1H NMR.

$[W(\eta\text{-}C_5H_5)_2(CH_2CH_3)(CH_2Ph)]$ (7). A solution of $NaBH_4$ (0.74 g, 19.7 mmol) in DMF (10 mL) was added to a slurry of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)(CH_2Ph)][Br]$[21] (0.604 g, 1.2 mmol) in 20 mL of DMF. A further 60 mL of DMF was added to the orange solution and the mixture left for 2 h with occasional swirling. The orange–amber solution was diluted with 90 mL of diethyl ether, and 90 mL of water was added with vigorous shaking and occasional dipping into liquid nitrogen to control the reaction. The aqueous phase was removed and the orange ethereal phase washed with water (2 × 90 mL) to remove excess DMF. The solvent was removed under reduced pressure to leave an orange solid, which was extracted with 125 mL of pentane in three portions. The solvent was removed from the filtered solution and the resulting orange solid dried under vacuum for 13 h. The material obtained in this way (0.364 g, ca. 0.84 mmol ≡ 70%) was shown (^1H NMR) to be principally (95%) $[W(\eta\text{-}C_5H_5)_2(CH_2CH_3)(CH_2Ph)]$, which could be obtained as analytically pure orange needles in 52% overall yield by recrystallization from warm pentane. Anal. Calcd for $C_{19}H_{22}W$: C, 52.55; H, 5.11. Found: C, 52.23; H, 5.00. Mass spectrum: parent ion with the W isotope pattern at m/e 434, with fragments corresponding to loss of ethyl, benzyl, and both ethyl and benzyl groups. ^1H NMR (acetone-d_6): δ 7.04–7.10 (m, 2 H, $m\text{-}C_6H_5$), 6.97–7.00 (m, 2 H, $o\text{-}C_6H_5$), 6.78–6.84 (t of t, J = 7.14, 1.35 Hz, 1 H, $p\text{-}C_6H_5$), 4.54 (s, 10 H, C_5H_5), 1.74 (s, (satellites $J_{W\text{-}H}$ = 8.31 Hz), 2 H, CH_2Ph), 1.38 (t, J = 7.38 Hz (satellites $J_{W\text{-}H}$ = 3.79 Hz), 3 H, CH_3), 0.38 (q, J = 7.38 Hz (satellites $J_{W\text{-}H}$ = 5.89 Hz), 2 H, CH_2).

---

(6) Although a number of salts, including $[W(\eta\text{-}C_5H_5)_2(CH_2CH_3)_2]^+$ with PF_6^-, BF_4^-, and tosylate counterions and $[W(\eta\text{-}C_5H_5)_2(CH_2CH_3)(CH_3)]^+$ with BF_4^- and tosylate counterions, could be obtained in crystalline form, none gave crystals which were amenable to X-ray diffraction studies.

(7) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

(8) Farrugia, L.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1975**, 416.

(9) Hayes, J. C. Ph.D. Dissertation, Harvard University, 1983.

(10) Diversi, P.; Ingrosso, G.; Lucherini, A.; Porzio, W.; Zocchi, M. *J. Chem. Soc., Dalton Trans.* **1983**, 967.

(11) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026.

(12) McNally, J.; Cooper, N. J., unpublished results.

(13) Jernakoff, P.; Cooper, N. J., unpublished results.

(14) Miller, G. A.; Cooper, N. J., unpublished results.

(15) (a) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. (b) A more convenient preparation of this complex from $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ will be described shortly.

(16) Hayes, J. C.; Miller, G. A.; Cooper, N. J., unpublished results.

(17) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc. A* **1971**, 1508.

(18) Sawyer, D. T.; Roberts, J.L. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974; p 212.

(19) Nelson, I. V.; Iwamoto, R. T. *Anal. Chem.* **1963**, *35*, 867.

(20) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527.

(21) Benfield, F. W. S.; Cooper, N. J.; Green, M. L. H. *J. Organomet. Chem.* **1974**, *76*, 49.

Table II. Dependence of the Voltammetric Data for Oxidation of $[(\eta\text{-}C_5H_5)_2W(CH_3)(Ph)]$ (**8**) in CH_3CN with 0.10 M TEAP on Scan Rate[a]

scan rate, mV/s	ΔE_p, mV	i_a/i_c	$i_a + i_c$, μA	$(E_a + E_c)/2$, mV
10	64	0.96	38.2	-273
20	63	0.98	52.8	-273
50	70	0.99	79.9	-273
100	73	1.02	111.4	-275
200	80	1.05	153.9	-276
500	89	1.04	238.2	-278

[a] Scan range = -650 to +750 mV.

$[W(\eta\text{-}C_5H_5)_2(CH(CH_3)_2)(CH_3)]$ (**2**). A 2.40 M solution of isopropylmagnesium bromide (0.80 mL, 1.92 mmol) was syringed into a magnetically stirred slurry of dark-green $[W(\eta\text{-}C_5H_5)_2(CH_3)(I)]$[15] (0.196 g, 0.43 mmol) in 40 mL of diethyl ether. The resulting dark-green solution lightened over 13 h, at which point additional Grignard was added (0.40 mL, 0.96 mmol) and the volume reduced by one-half. The reaction was judged to be complete after a further 3 h, as evidenced by the orange color of the slightly cloudy solution.[22] Ether was removed under vacuum and the orange oil quenched with cold (5 °C) absolute ethanol. Ethanol was removed and the remaining orange and white solid dried under vacuum for 3 h. Extraction with 35 mL of pentane in three portions gave a solution from which a yellow solid and an orange oil were obtained by solvent removal under reduced pressure. The mixture was then reextracted with 50 mL of pentane in three portions at -78 °C (to reduce the amount of the less soluble $[W(\eta\text{-}C_5H_5)_2H_2]$ in the sample). Pentane was removed under vacuum to give an oily orange solid (ca. 0.055 g, 0.15 mmol ≡ 34%) shown to be about 85% $[W(\eta\text{-}C_5H_5)_2(CH(CH_3)_2)(CH_3)]$ (^1H NMR (benzene-d_6): δ 4.08 (s, 10 H, C_5H_5), 1.57–1.69 (m, 1 H, CH), 1.50 (d, J = 6.4 Hz, 6 H, $(CH_3)_2$, 0.45 (s, (satellites J_{W-H} = 6.21 Hz), 3 H, CH_3)) contaminated with 4% $[W(\eta\text{-}C_5H_5)_2H_2]$, ca. 5% $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$, and ca. 6% unidentified $[W(\eta\text{-}C_5H_5)_2X_2]$ complex. Attempts to further purify the product by sublimation, recrystallization, or column chromatography were unsuccessful, but combustion analysis was consistent with the bulk of the material being $[W(\eta\text{-}C_5H_5)_2(CH(CH_3)_2)(CH_3)]$ (Anal. Calcd for $C_{14}H_{20}W$: C, 45.18; H, 5.42. Found: C, 44.73; H, 5.65), and the ^1H NMR identification was strongly supported by mass spectral data: the spectrum contains a parent ion peak exhibiting the tungsten isotope pattern at m/e 372 together with peaks assigned to fragments formed by loss of methyl, isopropyl, and both methyl and isopropyl groups. The sample used for electrochemical measurements was shown by ^1H NMR to be 90% $[W(\eta\text{-}C_5H_5)_2(CH(CH_3)_2)(CH_3)]$, 4% $[W(\eta\text{-}C_5H_5)_2H_2]$, 1% $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$, and 5% of the unidentified $[W(\eta\text{-}C_5H_5)_2X_2]$ complex.

Results

The cyclic voltammograms of the tungstenocene derivatives were recorded in acetonitrile between the solvent limits (ca. -1.5 and 1.5 V); all the complexes exhibited an oxidation between -450 and +125 mV which was chemically reversible at scan rates between 10 and 500 mV/s, with i_a/i_c within the range 0.95–1.05. The positions of these oxidations are reported in order of increasing potential in Table I. A plot of i_a against the square root of the scan speed was linear for all the oxidations across a range of 10–500 mV s^{-1} (square of the correlation constant > 0.995), as expected for a diffusion-controlled electrode process.[23]

The average of the anodic and cathodic peak potentials was independent of the scan rate for all these oxidations, while the separation of the anodic and cathodic waves (ΔE_p) decreased with decreasing scan speed (v) until a limiting value between 60 and 64 mV, close to the value of 59 mV anticipated for a one-electron Nernstian couple at 25 °C (ref 23, p 229), was reached at $v \leq$ 20 mV/s. The dependence of ΔE_p on the scan rate is illustrated by the data in Table II for a typical complex, the methyl phenyl complex **8**. The ferrocene internal standard exhibits similar behavior under these conditions, suggesting that the $\Delta E_p - v$ dependence results from uncompensated resistance in the organic solvent system rather than kinetic effects such as slow electron transfer.[24] This interpretation is confirmed by the linear relationship between ΔE_p and the peak to peak current $i_a + i_c$ (R^2 = 0.995). Extrapolation to zero peak to peak current leads to a corrected ΔE_p of 59.5 mV, in good agreement with theory. The cyclic voltammogram of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ at 20 mV s^{-1}, which is typical of those observed for all the complexes, is illustrated in Figure 1.

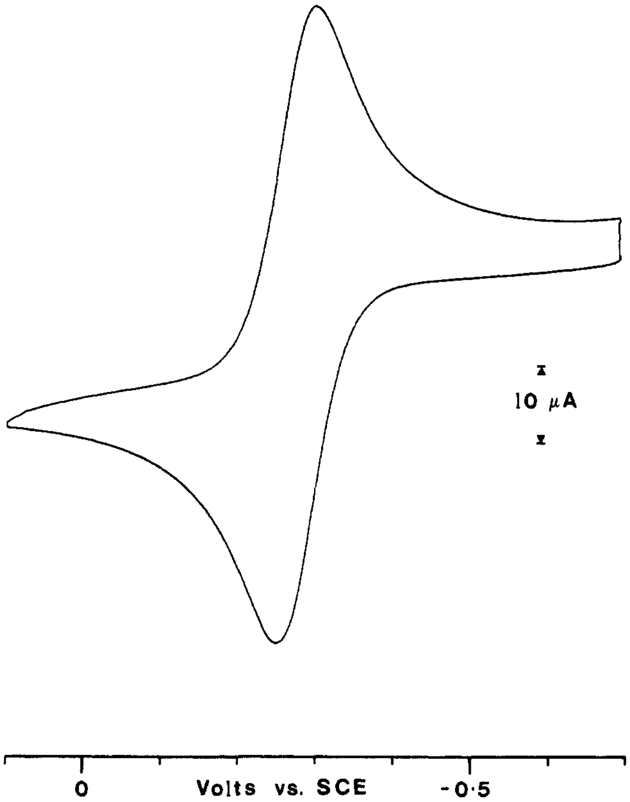


Figure 1. Cyclic voltammogram of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ at 20 mV s^{-1} in CH_3CN with 0.10 M TEAP.

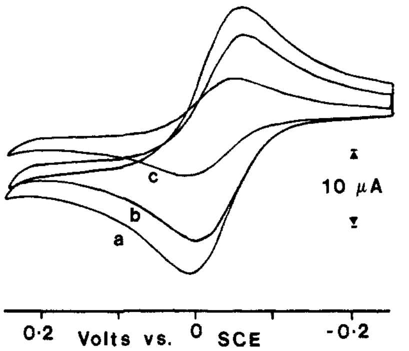


Figure 2. Successive cyclic voltammograms of an initially 0.001 M solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)I]$ at 20 mV s^{-1} in CH_3CN after (a) 0, (b) 11.6, and (c) 89.8 min.

The one-electron character of the oxidation, established in several cases by the isolation and characterization of the 17-electron products,[1,6,9,11,14,25] was confirmed by controlled potential coulometry in acetonitrile with $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ as the substrate. The oxidation was performed at potentials 30–105 mV more positive than the corresponding CV oxidation and was shown to involve the transfer of an average of 0.96 electrons (five determinations, SD 0.05).

In addition to the first oxidation some of the tungstenocene dialkyls and alkyl–aryls exhibit a second, irreversible oxidation between +700 and +900 mV vs. SCE. A second oxidation was

---

[22] Heating to 35 °C at any point during the reaction accelerates the rate of disappearance of green $[W(\eta\text{-}C_5H_5)_2(CH_3)(I)]$ but results in $[W(\eta\text{-}C_5H_5)_2H_2]$ becoming the predominant product.

[23] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

[24] Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

[25] Cooper, N. J.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1557.

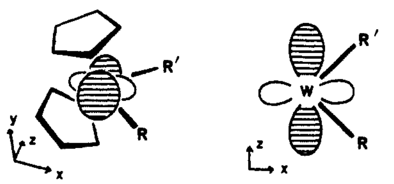


Figure 3. Perspective and plan views of the $1a_1$ frontier orbital, which contains the nonbonding electrons, of $[W(\eta\text{-}C_5H_5)_2RR']$ complexes.[28]

also observed for $[W(\eta\text{-}C_5H_5)_2(CH_3)(OCH_3)]$ at a somewhat lower potential of 431 mV, but in this case the second oxidation is reversible, with $\Delta E_p = 62$ mV and $i_a/i_c = 0.97$ at 20 mV/s. The oxidation presumably corresponds to formation of a stable dication $[W(\eta\text{-}C_5H_5)_2(CH_3)(OCH_3)]^{2+}$, and scanning through the second oxidation does not alter the reversibility of the first.

Solvolysis of the Iodo Alkyl and Aryl Complexes. Although i_a/i_c for the iodo alkyl and aryl complexes **13**, **14**, and **17** did not depart significantly from unity, the heights of their oxidation and reduction waves did diminish during electrochemical experiments, as illustrated by he cyclic voltammograms in Figure 2 of the iodo methyl complex **13**, suggesting that the complexes slowly decompose or solvolyse. This behavior was investigated in detail for **13**, for which it was observed that decomposition was accompanied by the appearance of a new chemically reversible oxidation wave at 502 mV ($[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ as internal reference), with $\Delta E_p = 65$ mV and $i_a/i_c = 1.04$ at 20 mV/s. Independent cyclic voltammograms of a fully characterized sample of $[W(\eta\text{-}C_5H_5)_2(CH_3)(NCCH_3)][PF_6]$ (**18**)[9] indicated that the new oxidation could be reasonably assigned to one-electron oxidation of **18**, suggesting that **13** solvolyses as shown in eq 2.

$$[W(\eta\text{-}C_5H_5)_2(CH_3)I] + CH_3CN \rightarrow [W(\eta\text{-}C_5H_5)_2(CH_3)(CH_3CN)]^+ + I^- \quad (2)$$

The facility of this solvolysis was confirmed by monitoring a sample of **13** in CD_3CN over a period of 5 h by ^1H NMR. This experiment confirmed the formation of **18** and indicated, as expected, first-order kinetics ($r^2 = 0.999$ for data recorded over more than three half-lives) with $k = 1.4 \times 10^{-4}$ s^{-1} ($t_{1/2} = 85$ min). The kinetics of solvolysis are very similar under electrochemical conditions, as determined by taking the peak current i_p in each of a series of voltammograms as a measure of the concentration C of the unreacted **13** (ref 23, eq 6.2.18). These data confirmed the first-order kinetics over four half-lives ($r^2 = 0.996$) and gave $k = 1.5 \times 10^{-4}$ s^{-1}, corresponding to $t_{1/2} = 75$ min.

An analogous solvolysis was observed by Kotz et al. during electrochemical studies of the tungstenocene dihalides[26] in which they observed that the rate of the reaction varied as I > Br ≫ Cl. A similar pattern seems to hold in the case of the tungstenocene alkyl halides, since none of the chlorides or bromides examined solvolysed during a typical electrochemical run (ca. 1 h).

Discussion

One-electron oxidation of the $[W(\eta\text{-}C_5H_5)_2R_2]$, $[W(\eta\text{-}C_5H_5)_2RR']$, and $[W(\eta\text{-}C_5H_5)_2RX]$ complexes examined was electrochemically reversible whether or not the corresponding radical cation had been previously isolated. Many of the uncharacterized cations are isolable, and some have been independently prepared in our laboratories in the course of other investigations and will be reported later.

Electronic Structures of the $[W(\eta\text{-}C_5H_2)_2X_2]$ Complexes and of the Corresponding Cations. The tungstenocene dialkyls and the other complexes studied are all d^2 bent metallocene derivatives of the type $[M(\eta\text{-}C_5H_5)_2X_2]$. The molecular and electronic structures of such complexes of early transition metals have been extensively studied: the ligands form an approximately tetrahedral array about the metal atom, and the "Alcock"[27] frontier orbital which contains the nonbonding electrons is essentially metal derived and is located within the mirror plane between the cyclopentadienyl ligands (in an eclipsed conformation) and perpendicular to the plane bisecting the XMX angle as illustrated in Figure 3.[28] Oxidation of the d^2 complexes involves removal of one of these nonbonding electrons.

Influence of Substituents on the Ease of Oxidation of the Tungstenocene Derivatives. (a) Phenyl and Halide Dependence and the Importance of π-Effects. In a previous study of the oxidation of the rhenium alkyls $[Re(\eta\text{-}C_5H_5)(PPh_3)(NO)R]$, we observed substituent effects that paralleled organic inductive effects.[29] Replacement of a hydrogen on an α-carbon by CH_3, for example, makes the complexes easier to oxidize by ca. 60 mV, while replacement of a hydrogen on a β-carbon with a phenyl group makes the complexes 40–60 mV harder to oxidize.

It is apparent from Table I that a similar correlation holds for some tungstenocene ligand replacements. Replacement of a methyl ligand with a phenyl group, for example, shifts the potentials to higher values since the methyl ligand is better able to stabilize the cation. The shifts are also essentially independent of the other ligand: the methyl–phenyl **8**, the phenyl–iodide **17**, and the phenyl–chloride **15** are 175, 154, and 169 mV harder to oxidize, respectively, than the dimethyl complex **1**, the methyl–iodide **13**, and the methyl–chloride **10**.

The effect of replacing an alkyl with a halide is similarly both additive and consistent with inductive destabilization of the cation by the halide: the methyl–chloride **10**, the ethyl–chloride **11**, and the phenyl–chloride **15** are 351, 347, and 345 mV harder to oxidize, respectively, than the R–methyl analogues **1**, **3**, and **8**.

Surprisingly, however, the potential shifts produced by different halides do not correlate with their electronegativities: replacement of a methyl ligand by an iodide renders the methyl–iodide **13**, the ethyl–iodide **14**, and the phenyl–iodide **17** harder to oxidize the corresponding R–methyl complexes **1**, **3**, and **8**, but the magnitude of the shifts, at 417, 416, and 396 mV, respectively, are larger than in the chloride case rather than smaller. Since the sole bromide complex examined (**16**) experiences an intermediate shift (377 mV harder to oxidize than **8**), the ease of oxidation of the monohalides seems to vary as Cl > Br > I. A similar halide dependence has been noted previously without comment for oxidation of the tungstenocene dihalides.[26]

Substituent effects in organic chemistry must often be interpreted in terms of interacting inductive and resonance effects, and the unusual pattern of potential changes in the present system must originate in a similar duality. In a metal-centered system, π-donor and π-acceptor effects are the most obvious potential secondary effects, and it has been previously established by structural,[28c,f] photoelectron,[28j] EPR,[30] and theoretical[28g,i,l] studies that there is significant π-interaction between halide ligands and the Alcock orbital in d^0, d^1, and d^2 bent metallocene complexes of the type $[M(\eta\text{-}C_5H_5)_2X_2]$; in the most closely related case the EPR of $[W(\eta\text{-}C_5H_5)_2Br_2]^+$ establishes that there is significant delocalization of unpaired electron density on to the ^{79}Br and ^{81}Br.[30]

π-Interaction lowers the energy of the ligand donor orbital and raises the energy of the Alcock orbital by a slightly smaller amount and, relative to otherwise identical species lacking such π-interaction, will therefore stabilize a d^1 $[W(\eta\text{-}C_5H_5)_2RX]^+$ cation and

---

(26) Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68.

(27) Alcock, N. W. *J. Chem. Soc. A* **1967**, 2001.

(28) (a) Green, J. C.; Green, M. L. H.; Prout, C. K. *J. Chem. Soc., Chem. Comm.* **1972**, 421. (b) Green, M. L. H. *Pure Appl. Chem.* **1972**, *30*, 373. (c) Prout, C. K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B.* **1974**, *B30*, 2290. (d) Petersen, J. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1974**, *96*, 2248. (e) Petersen, J. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416. (f) Petersen, J. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422. (g) Petersen, J. F.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433. (h) Green, J. C.; Jackson, S. E.; Higginson, B. *J. Chem. Soc., Dalton Trans.* **1975**, 403. (i) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (j) Clark, J. P.; Green, J. C. *J. Less Common Met.* **1977**, *54*, 63. (k) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragala, I. L.; Ciliberto, E.; Coleman, A. W. *J. Electron. Spectrosc. Relat. Phenom.* **1980**, *18*, 61. (l) Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639.

(29) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, S. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020.

(30) Lindsell, W. E. *J. Chem. Soc., Dalton Trans.* **1975**, 2548.

slightly destabilize a d^2 neutral complex in which both orbitals are occupied. Both changes will make it easier to oxidize the neutral complex, and the sequence in the potentials for oxidation can thus be attributed to increased π-donation from the earlier halides which stabilizes the $[W(\eta\text{-}C_5H_5)_2RX]^+$ cations more than they are destabilized by the corresponding increase in the halide σ-acceptor abilities, i.e., the π-donor abilities of the halides vary as Cl > Br > I and this dominates the ease of oxidation of the tungstenocene monohalides.

Since the halide dependence reverses the normal halide electronegativity trend the system must be unusually sensitive to the dominant π-donor effects, and this can be rationalized in terms of the location and extension of the metal orbital. Figure 3 shows that this orbital has the correct symmetry to overlap with the halogen p-orbitals, and could have excellent d–p π-overlap. This suggestion is supported by recent SCF–Xα–SW calculations on the titanocene dihalides, which indicate that there is significant metal–halide π-interaction in the complexes and suggest that the energy of the Alcock orbital decreases in the sequence F > Cl > Br > I as a consequence of a parallel decrease in the π-interaction.[28l] A similar decrease in π-interaction in the tungstenocene derivatives would account very satisfactorily for the halide dependence observed by ourselves and by Kotz and Dias.[26]

(b) Effect of an Alkoxide Ligand. One of the more surprising patterns in the potentials in Table I is that the methoxy–methyl complex **4** is as easy to oxidize as a tungstenocene dialkyl, indicating that the metal center in **4** is much more electron rich than would be anticipated on the basis of σ_I for methoxide (about half that for chloride[31]). It would seem that methoxide has an unusual π-donor effect which is even more marked than that of chloride: consistent with this, **4** is the only complex examined which undergoes a reversible second oxidation, and this second oxidation occurs at a potential only 308 mV above the first oxidation of the phenyl–iodide **17**.

(c) Alkyl Dependence and Evidence for Agostic Effects. The most surprising substituent effects on the oxidation of the tungstenocene derivatives are those induced by modification of the alkyl ligands. For example, the dimethyl complex **1** is the most easily oxidized at −448 mV, while the diethyl complex **5** is harder to oxidize rather than easier as anticipated on inductive grounds. The 65-mV shift corresponds to an average shift of 32.5 mV for ethyl for methyl ligand replacement, and the effect of alkyl ligand modification, like other ligand exchanges, is additive: the potential for oxidizing the ethyl–methyl complex **3** is 33 mV above that for the dimethyl complex, in excellent agreement with the average ethyl for methyl shift between **1** and **5**.

This contrainductive potential shift suggests that alkyl ligands influence the oxidation of the metal by a secondary mechanism analogous to the π-donor interactions of the halide ligands. The most obvious potential secondary interaction with an alkyl ligand is an agostic interaction between an α-C–H bond and the half-filled Alcock orbital which could significantly stabilize the 17-electron cations. We have previously proposed such an interaction to account for the α-selectivity of hydrogen atom abstraction from the radical cations derived from **1**, **3**, and **5**, and the ability of this agostic hypothesis to account for such seemingly disparate aspects of the chemistry of the tungstenocene dialkyls makes it particularly attractive. The feasibility of such an interaction in this system is supported by the previous evidence from ^{1}H NMR[32] and PES[33] studies for metal–alkyl π-interaction in closely related high-spin d^2 vanadocene monoalkyls.

To account for the contrainductive effect of ethyl for methyl replacement, the hydrogens of a methyl ligand must have a stronger agostic interaction with a cationic d^1 tungstenocene center than do the hydrogens of an ethyl ligand. Loss of agostic stabilization might then be larger than the gain in inductive stabilization from addition of a methyl group on the α-carbon. The electrochemical argument once again has an interesting parallel with the reactivity of the complexes: we have previously demonstrated that hydrogen atom abstraction from the radical cation $[W(\eta\text{-}C_5H_5)_2(CH_3)(CH_2CH_3)]^+$ is methyl selective and have suggested that this reflects greater delocalization of unpaired electron density from the metal center on to the α-C–H bond of the methyl group.[1b–d] A stronger agostic interaction would provide a straightforward and attractive mechanism for precisely such a delocalization.

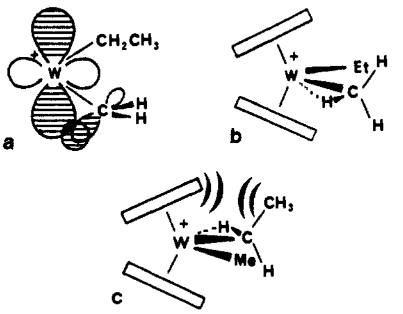


Figure 4. Possible steric origin of preference for agostic interaction with the methyl ligand in $[W(\eta\text{-}C_5H_5)_2(CH_3)(CH_2CH_3)]^+$: (a) overlap involved in agostic interaction between C–H bond and metal frontier orbital; (b) conformation required to allow such an interaction with the methyl ligand; (c) conformation required to allow such an interaction with the ethyl ligand.

Preferential agostic interaction with a methyl ligand can be rationalized stereochemically. The disposition of the Alcock orbital implies that agostic interaction with an ethyl α-hydrogen would enforce an unfavorable orientation in which the CH_3 of the ethyl group would be held close to a cyclopentadienyl ligand, and an agostic interaction involving the ethyl group may therefore be less stabilizing than one involving the methyl group (Figure 4).

The argument for steric control of a stabilizing agostic interaction is strengthened by its ability to provide a straightforward interpretation of the potentials required to oxidize two other tungstenocene dialkyls. Although the dineopentyl complex **6** is formally derived from the dimethyl by substitution of α-hydrogens by electron-donating *tert*-butyl groups, the effect is to make the metal center 125 mV harder to oxidize. This observation suggests that the reduction in agostic stabilization of the cation associated with *tert*-butyl substitution of one methyl group is greater than the corresponding inductive stabilization by an amount equivalent to a 62.5-mV shift. Such a large reduction in agostic stabilization is consistent with the anticipated formidable steric interaction between the *tert*-butyl group and the cyclopentadienyl ligands in the agostic orientation.

The final, and perhaps most convincing, case is that of the isopropyl–methyl complex **2**, formally derived from the ethyl–methyl complex **3** by methyl substitution of a second hydrogen on the α-carbon. This complex does not continue the trend to higher oxidation potentials observed when **3** is formed by formal methyl substitution of an α-hydrogen in the parent dimethyl complex **1**: the isopropyl–methyl complex is instead easier to oxidize than **3**, presumably because the second methyl substituent stabilizes the cation inductively, while there is little further loss of agostic stabilization. Comparison of the potentials at which **1** and **2** are oxidized shows that replacement of a methyl ligand with an isopropyl ligand shifts the potential by only 6 mV.

The critical assumption that substituents on the α-carbon will have an unfavorable interaction with the cyclopentadienyl ring in the agostic conformation is supported by molecular models and, more importantly, the structures of some closely related complexes. The agostic conformation of the alkyl group in a $[W(\eta\text{-}C_5H_5)_2(CHRR')R'']^+$ dialkyl cation should be very similar to the conformation of the alkylidene ligand in the $[W(\eta\text{-}C_5H_5)_2(CRR')R'']^+$ complex which would be formed by hydrogen abstraction from the dialkyl cation, since the π-interactions use the same metal orbital.[28i] The most closely related tungsten alkylidene complex known has yet to be structurally characterized,[34] but the structures

---

(31) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975.

(32) Köhler, F. H.; Hofmann, P.; Prössdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 6359.

(33) Green, J. C.; Payne, M. P.; Teuben, J. H. *Organometallics* **1983**, *2*, 203.

of three isoelectronic tantalum complexes unambiguously support the steric arguments above: the methylidene ligand in [Ta(η-$C_5H_5)_2(CH_2)CH_3$] adopts the electronically optimal perpendicular orientation,[35] while the benzylidene ligand in [Ta(η-$C_5H_5)_2$-($CHC_6H_5)CH_2C_6H_5$] is tipped 5.7° out of this plane[36] and the neopentylidene ligand in [Ta(η-$C_5H_5)_2\{CHC(CH_3)_3\}Cl$] is 10.3° out of the plane.[37] The steric distortions of the tantalum complexes are smaller than those suggested for the tungstenocene dialkyl cations, but this would be predicted by the larger magnitude of the opposing π-bond (ca. 20 kcal mol^{-1} [38]). The severity of the steric problems is emphasized by the NMR parameters for [Ta(η-$C_5H_5)_2(CHCH_3)CH_3$]: although there is a metal–carbon π-interaction of >20.5 kcal mol^{-1} in this molecule, the single methyl substituent on the α-carbon is sufficient to force a rotation of ±5° out of the perpendicular plane.[38]

Estimation of the Magnitude of the Three-Electron Agostic Interactions. The additivity of the substituent effects for oxidation of the tungstenocene derivatives suggested that it might be possible to partition the potential shifts into σ- and π-components and hence estimate the magnitude of the agostic interactions of the alkyl ligands. This partitioning has proved feasible for tungstenocene dialkyls containing simple and branched alkyl ligands.

The conclusions above concerning the effect of replacing a methyl ligand with other alkyls can be summarized in eq 3–5 (corresponding to replacement by ethyl, neopentyl, and isopropyl ligands, respectively) in which the potential shifts produced by

$$A_e + I_m - A_m = 32.5 \qquad (3)$$

$$A_{np} + I_{tb} - A_m = 62.5 \qquad (4)$$

$$A_{ip} + 2I_m - A_m = 6 \qquad (5)$$

agostic interactions with methyl, ethyl, isopropyl, and neopentyl ligands are represented by A_m, A_e, A_{ip}, and A_{np} and the potential shifts associated with the inductive effects of methyl and *tert*-butyl substituents on the α-carbon are represented by I_m and I_{tb}.[39]

Evaluation of the components of these equations requires chemically reasonable assumptions about the relative magnitudes of the terms. The qualitative considerations above indicate that A_m, I_m, and I_{tb} are major factors, while A_e, A_{ip}, and A_{np} are smaller in magnitude. They further suggest that a methyl substituent on the α-carbon is sufficiently bulky to markedly reduce agostic interaction of an α-C–H bond with the cationic metal center: since the *tert*-butyl group of a neopentyl ligand is much bulkier, steric interactions will probably make the agostic orientation almost inaccessible, and we can assume that A_{np} is negligible. Similarly, the bulk of the isopropyl ligand means that A_{ip} must be much less than A_e and although it is less obviously negligible, we will also initally assume $A_{ip} = 0$. With these simplifications eq 4 and 5 reduce to eq 6 and 7.

$$I_{tb} - A_m = 62.5 \qquad (6)$$

$$2I_m - A_m = 6 \qquad (7)$$

Our earlier work on the oxidation of rhenium alkyls of the type [Re(η-C_5H_5)(PPh_3)(NO)R][29] suggests one further simplification. In the rhenium system the inductive effects by which changes in the alkyl ligands influence oxidation at the metal fall off rapidly with distance, and alkyl branching at the β-carbon has no observable effect so that the complexes with R = CH_2CH_3, $CH_2CH_2CH_3$, and $CH_2C(CH_3)_3$ oxidize at the same potential. If inductive effects fall off similarly in the tungstenocene system, we can assume that $I_{tb} = I_m$, in which case eq 6 becomes eq 8.

$$I_m - A_m = 62.5 \qquad (8)$$

Subtracting eq 8 from eq 7, we get eq 9.

$$I_m = -56.5 \qquad (9)$$

Whence A_m = −119 mV (≡2.7 kcal mol^{-1}), and by substitution in eq 3, A_e = −30 mV (≡0.7 kcal mol^{-1}).

We can now reexamine the validity of some of the simplifying assumptions made above. One is the assumption that steric interaction will completely prevent the agostic interaction of an isopropyl ligand with the d^1 metal center: given that the potential shift ascribed to agostic stabilization is reduced from −119 mV for a methyl ligand to −30 mV for an ethyl ligand, this assumption does not seem unreasonable and any error introduced will be small.

The assumption that alkyl branching at the β-carbon will have negligible inductive effects is also reasonable in light of the results obtained, since the inductive effect of a methyl group on an α-carbon is only 56 mV. It is also reassuring to note that this is similar to the 60-mV magnitude of the analogous inductive effect in the rhenium alkyls:[29] similar inductive effects would be anticipated in the two systems since inductive effects are primarily ion–dipole interactions and the W–C bond length should be similar to that of the Re–C bond.

Additivity of the Substituent Effects. Partitioning the substituent effects into σ- and π-components depends on the additivity indicated by some of the comparisons above. Additivity would be anticipated a priori for inductive effects but not necessarily for π-effects, and its applicability in the present system indicates that the perturbation of the metal frontier orbital by one π-interaction is small enough that it does not significantly influence the second π-interaction. Their small magnitude makes this a particularly reasonable conclusion for the agostic interactions, but we might expect some breakdowns when complexes contain the more strongly π-donating halide ligands. In practice, the additivity of, for example, ethyl for methyl replacement, carries over surprisingly well to the alkyl halides, and the chloro– and iodo–ethyl complexes **11** and **14** are 29 and 32 mV harder to oxidize, respectively, than the corresponding methyl complexes. It is only with the more strongly π-donating chloride ligand that the value differs from that of 32.5 mV in the dialkyl series, and it is not surprising that the two most serious breakdowns in additivity in the data in Table I also involve chloride complexes. Isopropyl for methyl replacement induces a potential shift of −14 mV in the monochloride series (compare **9** and **10**) instead of +6 mV as in the dialkyl series, and neopentyl for methyl replacement induces a potential shift of +78 mV in the monochloride series (compare **12** and **10**) instead of +62.5 mV as in the dialkyl series.

Conclusion

This investigation establishes that the potentials at which tungstenocene dialkyls, alkyl- and aryl–halides, and alkyl–alkoxides are oxidized are controlled by a combination of inductive and π-donor effects. Methoxide is the strongest π-donor of the ligands examined, while the π-donor abilities of the halides vary as Cl > Br > I and reverse the normal electronegativity trend for these ligands. The alkyl ligands have the weakest π-donor effects, although these are still sufficiently strong to cause potential shifts which run counter to those anticipated on inductive grounds.

The ligand dependence of the alkyl π-effects can be interpreted in terms of steric control of a three-electron agostic interaction in the cations, consistent with the structures of related complexes. This hypothesis allows the substituent effects for some branched alkyls to be partitioned into inductive and π-interaction components and leads to estimates of 2.7 and 0.7 kcal mol^{-1}, respectively, for the agostic stabilization from interaction of methyl and ethyl ligands with the half-filled frontier orbital of cationic tungstenocene alkyls. These effects are small and may not correspond to a marked distortion of the alkyl ligand like that observed for three-center, two-electron agostic interactions,[2] but the parallel between their magnitudes and the previously reported selectivities

---

[34] Miller, G. A.; Cooper, N.J. *J. Am. Chem. Soc.* **1985**, *107*, 709.

[35] Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578.

[36] Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

[37] Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957.

[38] Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.

[39] It should be noted that no additional information is available from potential comparisons other than those considered above because of the additivity of substituent effects. Thus, comparisons of the potential for oxidation of the bis neopentyl **6** with that for oxidation of the ethyl–methyl **3** or the diethyl **5** would only "add in" the effect of replacing a methyl ligand with an ethyl ligand, an effect which has already been analyzed by direct comparison of the potentials for oxidation of **3**, **5**, and the dimethyl **1**. Similar arguments can be advanced in the case of the isopropyl–methyl complex **2**.

for hydrogen atom abstraction from some of the complexes suggest that they are chemically significant.

Acknowledgment. We thank the National Science Foundation (Grant CHE-83-08078 to N.J.C.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (S.R.C.), for financial support. We also thank Peter Haaland and Jeffrey C. Hayes for preliminary experiments.

Registry No. **1**, 39333-53-4; **2**, 102977-65-1; **3**, 82917-94-0; **4**, 57175-17-4; **5**, 102977-66-2; **6**, 86949-29-3; **7**, 102977-67-3; **8**, 89710-99-6; **9**, 102977-68-4; **10**, 102977-69-5; **11**, 102977-70-8; **12**, 102977-71-9; **13**, 71531-99-2; **14**, 102977-72-0; **15**, 11084-56-3; **16**, 11084-55-2; **17**, 11133-01-0; $[W(\eta\text{-}C_5H_5)_2(C_2H_4)(CH_2Ph)][Br]$, 102977-73-1.

Experimental Probes of the Electronic Matrix Element Contributions to Bimolecular Reactions. The Electronic Energy Transfer Reactions of (^{2}E)-Chromium(III)–Polypyridyl Complexes with Transition-Metal Acceptors[1]

John F. Endicott,* R. Tamilarasan, and George R. Brubaker

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received August 9, 1985*

Abstract: The rates have been determined for quenching of (^{2}E)Cr(polypyridyl = PP)$_3^{3+}$ donors by a few dozen cobalt(III) complexes. The quenching rates for the cobalt(III) acceptors have been found to be as much as three orders of magnitude slower than the diffusion limit but independent of the donor–acceptor energy gap. This and other evidence indicates that the rates of these reactions are limited by electronic rather than by Franck–Condon factors. In accord with this interpretation the rates decrease with increasing donor and acceptor separation (r_{DA}). The distance dependence is compatible with expectation for energy transfer mediated by an exchange mechanism with k_q proportional to $\exp(-2\alpha r_{DA})$ and $\alpha = 5.5 \pm 0.5$ nm^{-1}. The rates also respond to charge-transfer perturbations, with the rates increasing as the energy of the perturbing charge-transfer excited (CT) states decreases. This effect can be interpreted either (a) in terms of the superexchange contribution to the donor–acceptor interaction energy or (b) as the result of polarizabion of the donor and acceptor wave functions by CT-induced dipole moments. Either interpretation results in an inverse dependence (of k_q or α, respectively) on the energy of the perturbing CT state. The correlations of experimental data suggest that low-energy CT states of the donor and acceptor tend to interfere.

The fundamental factors governing reactivity patterns of bimolecular energy transfer reactions in solution are in a general way common to many classes of important chemical and physical interactions. For example there have been several explicit comparisons of energy and electron transfer reaction dynamics[2-6] and the role of donor–acceptor exchange interactions is important in many aspects of spectroscopy.[7] Much of the recent interest in energy transfer reactions arises from the perception that many of these reactions are relatively sensitive to the purely electronic factors[2-6,8-11] which make significant contributions to chemical reactivity, but which are often obscured by much larger nuclear (or Franck–Condon) factors in other chemical reactions.[12-16]

The migration of electronic excitation energy between donor and acceptor centers is itself a fundamental concern in either understanding or in manipulating the behavior of reactive electronic excited states.[6,8-10,17-19] Those energy-transfer reactions in which the individual electronic transitions are dipole allowed have attracted the most attention and are well-understood theoretically.[8-10,17,20,21] In contrast, those reactions in which both of the individual electronic transitions are dipole forbidden have received less experimental or theoretical attention. However, the

---

(1) Partial support of this research by the National Science Foundation (Grant GP 80-05497) is gratefully acknowledged.

(2) (a) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152. (b) Balzani, V.; Indelli, M. T.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *84*, 852. (c) Maestri, M.; Sandrini, D. *Ibid.* **1981**, *85*, 2050. (d) Gandolfi, M. T.; Maestri, M.; Sandrini, D. Balzani, V. *Inorg. Chem.* **1983**, *22*, 3435.

(3) (a) Wilkinson, F.; Tsiamis, C. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1681. (b) Wilkinson, F.; Tsiamis, C. *J. Phys. Chem.* **1981**, *85*, 4153. (c) Wilkinson, F.; Tsiamis, C. *J. Am. Chem. Soc.* **1983**, *105*, 767.

(4) (a) Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777. (b) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

(5) (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *5*, 183. (b) Potasek, M. J.; Hopfield, J. J. *Ibid.* **1977**, *74*, 229. (c) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584.

(6) Soules, T. F.; Duke, C. B. *Phys. Rev. B: Solid State* **1971**, *B1*, 262.

(7) For example, see: Adrian, F. J. *J. Chem. Phys.* **1972**, *57*, 5107.

(8) Watts, R. K. In *Optical Properties of Ions in Solids*; DiBartolo, B., Pacheco, D., Eds.; Plenum: New York, 1975; p 307.

(9) Orbach, R. In *Optical Properties of Ions in Solids*; DiBartolo, B., Pacheco, D., Eds.; Plenum: New York, 1975; p 355.

(10) Powell, R. C.; Blasse, G. *Structure Bonding* (*Berlin*) **1980**, *42*, 43.

(11) Meares, C. F.; Yeh, S. M.; Stryer, L. *J. Am. Chem. Soc.* **1981**, *103*, 1607.

(12) (a) Sutin, N.; Brunschwig, B. S. *ACS Symp. Ser.* **1982**, *198*, 105. (b) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275. (c) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(13) (a) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141. (b) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754.

(14) Sutin, N.; Newton, M. D. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(15) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

(16) (a) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1726. (b) Isied, S. S.; Vassilian, A. *Ibid.* **1984**, *106*, 1732.

(17) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970. (b) Yardley, J. T. *Introduction to Molecular Energy Transfer*; Academic Press: New York, 1970.

(18) Balzani, V. Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.

(19) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966.

(20) Förster, T. *Ann. Phys.* (*Liepzig*) **1948**, *2*, 55.

(21) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.