

Electrochemical Oxidation of Rhenium Alkyl Complexes of the Type $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{R}]$: Implications for the Mechanism of Hydride Abstraction by $\text{Ph}_3\text{C}^+\text{PF}_6^-$

Marianna F. Asaro,^{1a} Gerardo S. Bodner,^{1b} John A. Gladysz,^{* 1b,2b} Stephen R. Cooper,^{* 1a} and N. John Cooper^{* 1a,2a}

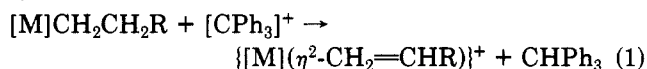
Departments of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and University of Utah, Salt City, Utah 84112

Received September 14, 1984

Electrochemical oxidation of 12 rhenium alkyls of the type $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{R}]$ has been examined as part of an investigation into the possibility that hydride abstraction from these substrates by $\text{Ph}_3\text{C}^+\text{PF}_6^-$ involves an electron-transfer mechanism. Cyclic voltammograms of each complex exhibit a single oxidation between +300 and +500 mV (vs. SCE) that is partially reversible chemically. Substituent effects for this oxidation suggest that the complexes fall into two categories which have different base potentials while potentials within each group follow the expected inductive trends. Controlled potential coulometry establishes that exhaustive oxidation of both types is a two-electron process, but differences in the observed ΔE_p values suggest that type I and type II complexes are undergoing ECE and EEC processes, respectively. This is confirmed by comparison of the current functions observed for oxidation of the complexes. Most of the complexes are slightly harder to oxidize in CH_2Cl_2 than the trityl radical, implying that it would not be feasible to trap thermally any odd-electron intermediates formed during hydride abstraction from these substrates. No correlation is observed between the potentials at which the complexes oxidize and the selectivity for α - or β -hydride abstraction from type I complexes.

Introduction

The triphenylmethyl cation (commonly known as tritylium) is extensively used as a hydride abstraction reagent in both organic and inorganic chemistry, and it has been known for some time that this reagent reacts with transition-metal alkyls to form alkene complexes and triphenylmethane (eq 1).³ The β -regioselectivity of this reaction has been confirmed by labeling studies³⁻⁵ and has been used as the basis for regio- and stereoselective olefin synthesis.⁶



Until recently, the only case in which hydride abstraction from an alkyl complex gave a product other than an alkene complex involved a benzocyclobutenyl complex of iron that lost an α -hydride ion to give a benzocyclobutenylidene complex.⁴ In 1980, however, some of us reported selective α -hydride abstraction from a simple alkyl complex, $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{CH}_2\text{CH}_3]$, to give the corresponding alkylidene complex $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{=CHCH}_3]^+$.⁷ β -Abstraction appeared to be a reasonable alternative reaction with this substrate (indeed, $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{=CH}_2)]^+$ has been subsequently prepared by an independent route and shown to be stable under the reaction conditions⁸), and we suggested that the electron-transfer capabilities of the tritylium cation might be responsible for the observed α -selectivity.⁷ This possibility has received circumstantial support from

the discovery that hydride abstraction from the tungstenocene dialkyls $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{R})(\text{CH}_2\text{R}')]]$ ($\text{R} = \text{R}' = \text{H}, \text{CH}_3$; $\text{R} = \text{H}, \text{R}' = \text{CH}_3$), the only other class of transition-metal alkyls reported to date to undergo α -selective hydride abstraction, occurs exclusively by an electron-transfer mechanism.⁹ Attempts at both Utah and Harvard to establish directly whether the reactions of $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{R}]$ complexes with Ph_3C^+ involve a similar electron-transfer mechanism have, however, been unsuccessful: both groups have obtained preliminary EPR evidence for the formation of Re centered radicals in the course of such reactions, but in neither laboratory has it been possible to characterize the species formed nor to demonstrate their involvement in the hydride abstractions.

Subsequent work at Utah has established that the regioselectivity of hydride abstraction from $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{R}]$ alkyls is more complex than was at first apparent and that abstraction can occur from α , β , or α and β positions depending on the nature of the alkyl.¹⁰ This result raises the possibility of dual mechanisms for abstraction from these substrates, and led us to examine the electrochemical properties of a representative sample of the rhenium alkyls with the aim of establishing the mechanism or mechanisms operating and the origins of the observed selectivities. This paper reports the results of these investigations, which address three questions: the thermodynamic favorability of electron transfer from the rhenium alkyls to the tritylium cation; the feasibility of trapping or of independently preparing the $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{R}]^+$ cations, which are intermediates in the putative electron-transfer mechanism for hydride abstraction; and finally the possible existence of a correlation

(1) (a) Harvard University. (b) University of Utah.
 (2) (a) Fellow of the Alfred P. Sloan Foundation (1982-1985). (b) Fellow of the Alfred P. Sloan Foundation (1980-1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980-1985).
 (3) Green, M. L. H.; Nagy, P. L. *J. Organomet. Chem.* **1963**, *1*, 58.
 (4) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430.
 (5) Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V.; Sanders, A. *J. Organomet. Chem.* **1974**, *65*, C57.
 (6) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291.
 (7) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299.
 (8) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

(9) (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.; Jernakoff, P.; Miller, G. A.; Cooper, N. J. *Pure Appl. Chem.* **1984**, *56*, 25.
 (10) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.
 (11) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
 (12) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

Table I. Cyclic Voltammetric Data for Oxidation of $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{R}]$ Complexes in CH_2Cl_2

complex	R	H ⁻ abstractn selectivity ^{10,11}	scan rate, mV s ⁻¹	ΔE_p , mV	$(E_a + E_c)/2$, mV	peak current ratio i_a/i_c	current functn $i_a/\nu^{1/2}C_0$, A L s ^{1/2} V ^{-1/2} mol ⁻¹
Type I							
1 ¹¹	CH ₃	α	500	130	380	2.98	0.075
2 ¹⁰	CH ₂ CH ₃	α	10	66	362	1.50	0.090
3 ¹⁰	CH ₂ CH ₂ CH ₃	α	10	61	368	1.29	0.142
4 ¹⁰	CH ₂ CH ₂ Ph	α (63%), β (18%)	10	61	418	1.31	0.082
5 ¹⁰	CH ₂ CH(CH ₃) ₂	β	10	58	369	1.31	0.133
6 ¹⁰	CH ₂ C(CH ₃) ₃	α	10	61	365	1.10	0.109
7 ¹⁰	CH(CH ₃) ₂	β	10	62	300	1.47	0.134
8 ¹⁰	CH(CH ₃)(CH ₂ Ph)	β^{26}	10	62	345	1.15	0.163
9 ¹²	CH ₂ Ph	α	10	74	472	1.20	0.232
Type II							
10 ¹²	CH(CH ₃)Ph (<i>RS,SR</i>)	β	5	41	350	1.24	0.333
			50	78	353	1.05	0.306
11 ¹²	CH(CH ₂ Ph)Ph (<i>SS,RR</i>)	β^{26}	5	42	376	1.08	0.365
			50	76	375	1.01	0.347
12 ¹²	CH(CH ₂ CH ₃)Ph (<i>RS,SR</i>)	β^{26}	5	42	339	1.18	0.379
			50	74	334	1.01	0.320

^a Complex 6 gives neither an alkylidene nor an alkene complex when treated with Ph_3CPF_6 .¹⁰

between the ease of oxidation of, and the regioselectivity for abstraction from, the various rhenium alkyls.

Experimental Section

The rhenium alkyls were prepared by literature methods as indicated in Table I, and the purity of complexes was confirmed by ¹H NMR spectroscopy. Methylene chloride and acetonitrile were distilled from CaH₂ before use, except in the case of experiments involving Ph_3CPF_6 in acetonitrile. It was found necessary in these cases to distill the CH₃CN from CaH₂ and then from P₂O₅ and finally redistill from CaH₂. Cyclic voltammetry in CH₂Cl₂ was performed on solutions that contained 0.5 M tetra-*n*-butylammonium perchlorate (TBAP), prepared by a literature procedure,¹³ as the supporting electrolyte. Cyclic voltammetry in CH₃CN was carried out on solutions that contained 0.1 M tetraethylammonium perchlorate (TEAP), prepared by a literature procedure,¹³ as the supporting electrolyte. The voltammograms reported are for solutions which were 1.0×10^{-3} M in substrate, except as noted in tables.

Electrochemical experiments were performed under N₂ with a Princeton Applied Research Model 173 potentiostat, 175 programmer, 179 coulometer, and RE 0074 X-Y recorder. All potentials were recorded relative to a saturated calomel electrode (SCE) and are uncorrected for junction potentials. Reference electrodes were checked periodically relative to a 1.0×10^{-3} M solution of ferrocene in acetonitrile containing 0.10 M LiClO₄, which was found to have a potential of 350 mV (cf. 350 mV¹⁴). Cyclic voltammograms were recorded at 3 ± 2 °C, as maintained by an ice bath. Cyclic voltammograms were recorded with a platinum disk electrode and a platinum gauze auxiliary electrode. A platinum mesh basket was used for coulometric determinations.

Results

Since hydride abstraction from rhenium alkyls of the type $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{R}]$ is typically carried out in CH₂Cl₂, the electrochemical behavior of the complexes was examined primarily in this solvent to facilitate comparison between the electrochemical data and the selectivities observed for hydride abstraction.

Cyclic voltammograms of each of a representative selection of the alkyls exhibit, between the solvent limits (ca. -1.5 and 1.5 V), a single oxidation between +300 and +500 mV (Table I). At slow scan rates the oxidations are, with

Table II. Dependence of the Voltammetric Data in CH₂Cl₂ for Oxidation of a Typical Type I Complex, $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{CH}_2\text{CH}_3]$ (2), on Scan Rate^a

scan rate, mV/s	ΔE_p , mV	i_a/i_c	$(E_a + E_c)/2$, mV
10	66	1.50	362
20	72	1.45	364
50	77	1.38	364
100	89	1.33	363
200	106	1.32	362
500	127	1.24	365

^a The solvent contained 0.50 M TBAP as supporting electrolyte, and the scan range was 0.0–0.6 V.

one exception, partially reversible chemically with i_a/i_c varying from 1 to 1.5. A plot of i_a against the square root of the scan speed (ν) was linear for all complexes across a range of 10–200 mV s⁻¹ (correlation coefficient > 0.99) as expected for a diffusion-controlled electrode process.¹⁵

The separation of the anodic and cathodic waves (ΔE_p) increased with increasing scan speed for all complexes, but, with the use of slow rates (≤ 20 mV s⁻¹) and the highly soluble supporting electrolyte tetrabutylammonium perchlorate (0.5 M), ΔE_p for complexes 2 to 9 approached 55 mV, the value anticipated for a one-electron Nernstian couple at 3 °C (ref 15, p 229). The dependence of ΔE_p on the scan rate for a typical complex is illustrated by the data in Table II for the ethyl complex 2.

Several lines of evidence suggest that the scan rate dependence of ΔE_p derives from uncompensated resistance (a consequence of the low dielectric constant of the CH₂Cl₂) rather than kinetic effects such as slow electron transfer.¹⁶ First, the scan rate dependence of ΔE_p varies with the concentration of supporting electrolyte; second, and more importantly, well-behaved couples such as ferrocene/ferrocenium exhibit similar $\Delta E_p - \nu$ dependence under the same conditions.

In contrast to complexes 2–9, complexes 10–12 have ΔE_p values below 55 mV under many conditions, as discussed in more detail below. This difference in behavior is one of several indications that complexes 2–9, together with

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

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

(15) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980.

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

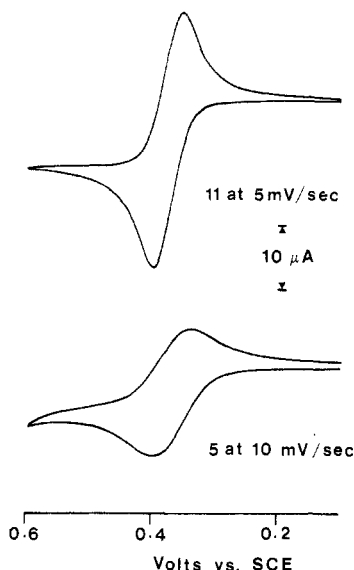


Figure 1. Cyclic voltammograms in CH_2Cl_2 of typical type I and II complexes (0.0010 M with 0.5 M TBAP): 5, $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{CH}_2\text{CH}(\text{CH}_3)_2]$; 11, $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{CH}(\text{CH}_2\text{Ph})\text{Ph}]$ (*RR*,*SS*).

1, form a subset of the complexes (grouped together as type I in Table I) with similar electrochemical behavior differing from that of complexes 10–12 (grouped together as type II in Table I). This classification will be used to simplify the presentation of results throughout the remainder of this paper. Cyclic voltammograms of typical type I and II complexes are illustrated in Figure 1.

The Initial Electrochemical Process for Type I Complexes and the Effect of Substituents. The approach of ΔE_p to 55 mV for complexes 2–9 would suggest that these compounds undergo one-electron oxidations to give the radical cations $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{R}]^+$, which can be reduced to the starting compounds. The departure of the peak current ratio from unity indicates that the cations undergo rapid subsequent reactions (such as solvolysis or decomposition) as shown by the decrease in the peak current ratio with increase in scan rate (illustrated again by the data for 2 in Table II). These data also establish that the average of the anodic and cathodic peak potentials, unlike ΔE_p or i_a/i_c , is insensitive to scan rate and that this average can therefore be taken to approximate the formal potential, E_f , for the $2/2^+$ couple despite the lack of rigorous reversibility in the system. The same conclusion holds for complexes 3–12.

The variation in the potentials of the n/n^+ couples for complexes 2–9 can be readily rationalized in terms of the substituent effects anticipated by analogy with organic electrochemistry.¹⁷ Thus, comparison of the ethyl complex 2 with the isopropyl complex 7 shows that addition of an α -methyl group (an electron-donating group) makes the complex easier to oxidize (by ca. 60 mV). Such effects fall off rapidly with chain length, and comparison of 2 with 3 and 3 with 5 and 6 shows that addition of β -methyl groups has no noticeable effect on the ease of oxidation of the complexes.

The effect of a β -phenyl group also follows qualitatively from its negative inductive effect, and comparison of E_f for 2 with E_f for 4 and of E_f for 7 with E_f for 8 would suggest that a β -phenyl makes the rhenium ca. 40–60 mV harder to oxidize. Excluding the data for the methyl complex 1 (see below) the effect of an α -phenyl group is

hard to quantify, but comparison of E_f for the benzyl complex 9 with that for the ethyl complex 2 would suggest that it is qualitatively similar to that of a β -phenyl group: replacement of an α -methyl group with a phenyl makes 9 ca. 110 mV harder to oxidize.

The behavior of the methyl complex 1 fits qualitatively into the pattern of substituent effects for the other type I complexes; at 380 mV complex 1 is, for example, ca. 20 mV harder to oxidize than the ethyl complex. The relative instability of 1^+ , however ($i_a/i_c \gg 1$ even at a scan rate of 500 mV s^{-1}), leaves E_f undefined for this couple.

Substituent Effects and Type II Behavior. At first sight correlations between substituent effects and $(E_a + E_c)/2$ at 5 mV s^{-1} for complexes 10–12 (Table I) appear to break down. For example, comparison of the potentials for 2 and 10 would suggest that an α -phenyl substituent has little effect on the ease of oxidation of the rhenium center, while comparison of 4 with 11 and of 3 with 12 would suggest that the α -phenyl in both 11 and 12 actually makes the complexes easier to oxidize. However, a comparison of the potentials of 10, 11, and 12 with each other indicates that substituent effects within this group are again similar to those observed in organic electrochemistry. Thus comparison of the data for 10 with those for 11 reveals a positive shift (of ca. 25 mV) following addition of a β -phenyl group, while addition of a methyl group, even in the β -position (10 and 12), produces an observable (ca. 10 mV) shift in the expected direction to a more negative potential.

These differences in substituent effects constitute a major difference between type I and II complexes, and it would appear that the two types have different base potentials while potentials within each group follow the expected inductive trends. The difference in base potential suggests that the electrochemical processes occurring in the two types of complex differ significantly, as confirmed by further examination of the electrochemical properties of the complexes.

The Origin of Type I and Type II Behavior: ECE vs. EEC Processes. In the case of the type II complexes the peak to peak separation at slow scan speeds is significantly less than the 55 mV expected for a Nernstian one-electron couple, suggesting that the complexes may be undergoing two- rather than one-electron oxidations. While the negative shift of the potential for two-electron oxidation would suggest that the second electron is easier to remove than the first, the ΔE_p observed for 10, 11, and 12 is larger than the theoretical value of ca. 28 mV expected in this case (ref 15, p 229). The large ΔE_p is probably, however, again due to uncompensated resistance in the solution. The greater Faradaic current for a two-electron process makes uncompensated resistance a greater problem than in the one-electron case and causes the marked observed dependence on scan rate (Table I). Consistent with this explanation, ΔE_p for 10, for example, decreases to 31 mV at 5 mV s^{-1} in a medium with higher conductivity (CH_3CN with TEAP as supporting electrolyte—see Table III).

Controlled potential coulometry (CPC) provides the most obvious and direct way to confirm that the type II complexes undergo two-electron oxidations. Controlled potential coulometry in CH_2Cl_2 at a potential slightly beyond the CV oxidation (Table IV) does in fact confirm that complete oxidation of 10 is a two-electron process. Cyclic voltammetry of the solution after oxidation, however, shows that the ultimate products of the CV and CPC experiments differ. The CPC results therefore indicate that a two-electron process is followed by solvolysis or

(17) Zuman, P. "Substituent Effects in Organic Polarography"; Plenum Press: New York, 1967.

Table III. Cyclic Voltammetric Data for Oxidation of $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{R}]$ Complexes in Acetonitrile

complex	R	scan rate, mV s^{-1}	ΔE_p , mV	$(E_c + E_a)/2$, mV	i_a/i_c
1	CH_3	500	132	331	2.86
2	CH_2CH_3	10	59	294	1.36
3	$\text{CH}_2\text{CH}_2\text{CH}_3$	10	59	294	1.30
4	$\text{CH}_2\text{CH}_2\text{Ph}$	10	60	337	1.40
10 ^a	$\text{CH}(\text{CH}_3)\text{Ph}$	10	37	262	1.20
10 ^a	$\text{CH}(\text{CH}_3)\text{Ph}$	5	31	262	1.22

^a The limited solubility of this complex restricted voltammetric studies in CH_3CN to solutions that were 7.1×10^{-4} M in 10 and 7.2×10^{-2} M in TEAP.

Table IV. Results of Controlled Potential Coulometry on $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})\text{R}]$ Complexes in CH_2Cl_2

complex	R	T , $^\circ\text{C}$	potential, mV	no. of electrons removed in oxidatn (SD ^a)
3	$\text{CH}_2\text{CH}_2\text{CH}_3$	4	450-550	2.00 (0.12)
4	$\text{CH}_2\text{CH}_2\text{Ph}$	5	500-600	1.89 (0.18)
10	$\text{CH}(\text{CH}_3)\text{Ph}$	3	450-550	2.00 (0.14)

^a Each result is the average of at least seven determinations on aliquots of a standard solution of the complex.

decomposition (EEE process), in accord with the deviations from unity of the peak current ratios of the type II complexes.

Controlled potential coulometry was also used to investigate the number of electrons being transferred during oxidation of type I molecules, and the results for two typical type I molecules are shown in Table IV. Surprisingly, CPC again establishes the occurrence of an overall two-electron process. Since, however, the solution after oxidation was shown by CV to contain a mixture of products, none of which reduced to starting material, the significance of the CPC data is unclear. This could once again indicate that an EEC process is occurring, but an alternative explanation is that an initial one-electron oxidation is followed by formation of a solvolysis or decomposition product that undergoes further oxidation. Such an ECE process would be consistent with the potentials of the two classes and with the ΔE_p data. Unfortunately, however, attempts to confirm the one-electron oxidation stoichiometry for type I complexes by use of thin layer CV¹⁸ were thwarted by the high resistivity of CH_2Cl_2 solutions.

A third approach to the determination of the number of electrons (n) involved in a voltametric experiment does not suffer from the ambiguities caused by subsequent solvolysis or decomposition. The peak current i_p is given by (ref 15, eq 6.2.18)

$$i_p = 0.4463n^{3/2}FAC_0(F/RT)^{1/2}\nu^{1/2}D_0^{1/2} \quad (2)$$

where A is the area of the electrode, D_0 is the diffusion constant for the electroactive species, C_0 is its concentration, and ν is the scan rate. For a given electrode the expression $i_p/\nu^{1/2}C_0$ (sometimes called the current function: ref 15, p 219) should therefore depend only on $n^{3/2}$ and $D_0^{1/2}$ (the diffusion constants for the rhenium complexes should all be similar in the same solvent). The current function for a two-electron process should accordingly be

Table V. Cyclic Voltammetric Data for Reduction of Ph_3CPF_6 at 23 $^\circ\text{C}$

solv	concn, M	scan rate, mV	ΔE_p , mV	$(E_c + E_a)/2$, mV	peak current ratio i_a/i_c
CH_2Cl_2	0.0010	10	74	331	0.82
CH_3CN	0.0011	50	70	261	0.96

approximately 2.8 times that for a one-electron process. Current functions based on the anodic currents i_a are included in Table I.

Inspection of Table I shows that, despite some scatter as a result of varying cation stability, the current functions are distinctly different for the two types of complexes. The average current function for 10-12 is 2.90 times the average for 1-9, in excellent agreement with the ratio anticipated from eq 2. With the possible exception of the benzyl complex 9, which has a rather high current function for a Type I complex, it is reasonable to conclude that type I and type II complexes indeed undergo, respectively, one- and two-electron initial oxidations, corresponding to overall ECE and EEC processes.

In principle, distortions in the CV waves resulting from uncompensated resistance could also cause the observed differences in the current functions of type I and II complexes. This possibility can be ruled out, however, by examination of complexes 10, 11, and 12 at a higher scan speed (50 mV s^{-1}), at which ΔE_p for these complexes is comparable to that of the type I complexes (Table I). Current functions measured under these conditions, although slightly smaller than those at 5 mV s^{-1} , still differ distinctly from those of type I complexes.

Electrochemistry of the Tritylium Cation. Reduction of the tritylium cation to the tritylium radical has been studied by polarography in acetonitrile²⁰ and benzonitrile.²¹ To permit direct comparison with the rhenium alkyls, however, we also examined this reduction by CV in CH_2Cl_2 and CH_3CN (Table V). The reduction is only partially reversible chemically in both solvents, with peak current ratios slightly less than unity, and, even at the optimal scan rates reported, the peak separations are significantly larger than the value of 59 mV expected for a one-electron Nernstian couple. The deviations from reversibility probably result from dimerization of the electrogenerated radical,²² but, although the lack of reversibility implies that the potentials in Table V lack rigorous thermodynamic significance, the small size of the deviations allows the use of the $(E_a + E_c)/2$ values for comparative purposes.

Discussion

Most of the rhenium complexes $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{R}]$ are slightly harder to oxidize in CH_2Cl_2 than the tritylium radical, which implies that the equilibrium constant for electron transfer from rhenium to the tritylium cation is small for these complexes (the only exception is the rhenium isopropyl 7, the most easily oxidized substrate). The relative unfavorability of electron transfer does not rule out its involvement in some or all of the hydride transfers, but for most of the substrates such a mechanism would then require that electron transfer be followed by hydrogen atom abstraction from a small steady-state concentration of a rhenium radical. It is interesting to note that $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)\text{R}]$ complexes

(18) Cushing, J. P.; Hubbard, A. T. *J. Electroanal. Chem.* **1969**, *23*, 183. This electrode gave satisfactory results for $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ in 1 F HCl.¹⁹

(19) Hubbard, A. T.; Anson, F. C. *Anal. Chem.* **1966**, *38*, 58, as corrected by: Hubbard, A. T.; Anson, F. C. *Electroanal. Chemistry* **1970**, *4*, 129.

(20) Volz, H.; Lotsch, W. *Tetrahedron Lett.* **1969**, 2275.

(21) Kothe, G.; Sümermann, W.; Baumgärtel, H.; Zimmermann, H. *Tetrahedron Lett.* **1969**, 2185.

(22) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

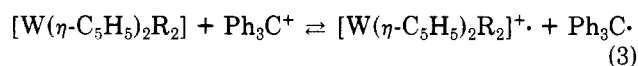
are much easier to oxidize than $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{CH}_3]$, a model for the classic $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{R}]$ substrates for which β -hydride abstraction has been established by labelling studies.³⁻⁵ The methyl complex exhibits an irreversible anodic wave at 880 mV in CH_3CN ,²³ and comparison with Table V suggests that the driving force for electron transfer from alkyls of this type to the tritylium cation would be so unfavorable that an electron-transfer mechanism for hydride abstraction would be improbable in the iron system.

As outlined above, the electrochemical behavior of the rhenium complexes can be interpreted in terms of ECE (type I) and EEC (type II) processes, and within each class the potentials at which the complexes oxidize can be readily rationalized in terms of inductive changes within the substituents. The difference in base potentials for oxidation of the two types of complex is a natural consequence of the occurrence of different electrochemical processes, but the underlying differences in electronic or molecular structure that distinguish the classes are unclear. It is tempting to speculate that the α -phenyl group in type II complexes facilitates two-electron oxidation by allowing the alkyl to become an η^3 -benzyl ligand, but this suggestion would require that unidentified steric or electronic factors prevent similar η^3 -benzyl coordination in the case of the parent benzyl complex 9.

The determination that the electrochemical behavior of the type I complexes involves initial one electron oxidation was particularly important, because only if the oxidation were one electron could significance be attached to a comparison of the potentials with the selectivity observed for hydride abstraction (Table I). Observation of a correlation (such as a threshold potential below which α -abstraction predominated over β -abstraction) might have provided evidence for competing electron-transfer and non-electron-transfer mechanisms, but examination of the data in Table I shows that no such correlation exists for the type I complexes. In the absence of any such correlation, the present study provides no evidence for or against the occurrence or selectivity of electron-transfer pathways in this system. At most it may be concluded that if electron-transfer pathways occur, then selectivity must be at least partly determined by other factors such as steric

constraints on the approach to the substrate of intermediate tritylium radical. The importance of steric factors is particularly strongly suggested by the reversal in selectivity from β to α between the branched alkyl complex 5 and the unbranched alkyl complexes 2 and 3 (despite the similar potentials for oxidation of all three complexes) and by the β -selectivity observed for hydride abstraction from the isopropyl complex 7 (the most easily oxidized complex in the table).

The present electrochemical studies establish that it is impossible in the rhenium system to carry out thermal trapping studies of the sort that demonstrated the involvement of electron-transfer pathways in hydride abstraction from tungstenocene dialkyls.⁹ Trapping is possible in the tungsten system first because the tungstenocene dialkyls are easy to oxidize (ca. -400 mV;²⁴ the equilibrium in eq 3 lies far to the right) and second because



the tungsten-centered radicals are sufficiently stable to be readily isolated and purified.^{9b,c,25} Neither of these conditions holds for the rhenium system: the analogous equilibria lie to the left and the rhenium-centered radicals decompose rapidly (on the time scale of the controlled potential coulometry: ca. 5 min) to give as yet unidentified species. We conclude that redox properties are not the sole factor determining the regiochemistry of hydride abstraction from rhenium alkyls.

Acknowledgment. We thank Peter Haaland at Harvard for early electrochemical studies that laid the foundations for this work and the National Science Foundation (N.J.C.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (N.J.C. and S.R.C.), and the Department of Energy (J.A.G.) for generous financial support.

Registry No. 1, 71763-18-3; 2, 74540-90-2; 3, 74540-91-3; 4, 85926-75-6; 5, 85926-73-4; 6, 85926-74-5; 7, 85956-36-1; 8, 95586-03-1; 9, 71763-28-5; 10, 82374-39-8; 11, 82374-41-2; 12, 82374-40-1.

(23) Magnuson, R. H.; Zulu, S.; T'sai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887.

(24) Asaro, M. F.; Cooper, N. J., manuscript in preparation.

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

(26) Bodner, G. S.; Gladysz, J. A., unpublished results.