mode-equivalent *ESS*, *SES*, and *SSE* processes.

To confirm the magnitude of the calculated barriers, we recorded the temperature dependent 25.2 MHz ^{13}C {^1H} NMR spectra[19] of 1[20] in 4:1 CF_2Cl_2/CF_3Br. At -140 °C the singlet due to the methyl carbons (δ_{Me_4Si} 31.0 ppm at -70 °C) splits into two singlets in a ratio of ~2:1 (δ 32.3 and 26.4 ppm at -157 °C, respectively). The corresponding value of $\Delta G_c^{\ddagger}$, 6.1 $\pm$ 0.3 kcal/mol,[21] is in good agreement with the barrier of 6.8 kcal/mol calculated by the EFF method.[23] The observation of two resonance signals is in accord with our calculations which indicate that the (nonobserved) threshold mechanism (*SSS*) for this compound averages two of the three methyl environments at lower temperatures.[24]

The above analysis may be extended to any system of the type $t\text{-}Bu_3MX$. Thus, besides the obvious analogies to other silanes,[25] the observed coalescences in tri-*tert*-butylphosphines[26] might similarly be explained by a process involving correlated rotation.[27]

Further discussion is reserved for the detailed account of this work.

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(2) Correlated rotation of alkyl groups has been suggested and looked for. See, for example, (a) D. T. Dix, G. Fraenkel, H. A. Karnes, and M. S. Newman, *Tetrahedron Lett.*, 517 (1966); (b) H. Kwart and S. Alekman, *J. Am. Chem. Soc.*, **90**, 4482 (1968); (c) B. Nelander and S. Sunner, *ibid.*, **94**, 3576 (1972); (d) E. E. Burnell and P. Diehl, *Mol. Phys.*, **24**, 489 (1972), and *Org. Magn. Reson.*, **5**, 137 (1973); (e) J. E. Anderson, R. W. Franck, and W. L. Mandella, *J. Am. Chem. Soc.*, **94**, 4608 (1972); (f) R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 777 (1975), and D. S. Bomse and T. H. Morton, *ibid.*, 781 (1975); (g) S. Hoogasian, C. H. Bushweller, W. G. Anderson, and G. Kingsley, *J. Phys. Chem.*, **80**, 643 (1976); (h) C. Roussel, A. Lidén, M. Chanon, J. Metzger, and J. Sandström, *J. Am. Chem. Soc.*, **98**, 2847 (1976), A. Lidén, C. Roussel, T. Liljefors, M. Chanon, R. E. Carter, J. Metzger, and J. Sandström, *ibid.*, **98**, 2853 (1976); and T. Liljefors and J. Sandström, *Org. Magn. Reson.*, **9**, 276 (1977); (i) S. Brownstein, J. Dunogues, D. Lindsay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2073 (1977). In the case of hexamethylbenzene, geared rotation is indicated on the basis of computational and experimental evidence: (j) W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966); (k) J. Jonas, *J. Chem. Phys.*, **47**, 4884 (1967), especially footnote 13; (l) W. C. Hamilton, J. W. Edmonds, A. Tippe and J. J. Rush, *Discuss. Faraday Soc.*, **48**, 192 (1969).
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calculations[10] and by electron diffraction,[11] respectively. For $t\text{-}Bu_3P$, values for ϕ of ~36 and 46° have been found by CNDO/2 calculations[12a] and by electron diffraction,[12b] respectively. All of these stereochemically correspondent[13] structures represent examples of static gearing;[3] i.e., a methyl group on one *tert*-butyl group fits between the methyl "teeth" of an adjacent *tert*-butyl, resulting in a "geared", chiral (C_3) structure.
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(22) The computer program used was adapted from one developed by M. Saunders (see M. Saunders in "Magnetic Resonances in Biological Systems", A. Ehrenberg, B. G. Malmström, and T. Vänngard, Ed., Pergamon Press, New York, N.Y., 1967, p 85).
(23) A more meaningful comparison would be the one between calculated (EFF) activation energy and $\Delta H^{\ddagger}$. However, we refrain from reporting $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ components derived from line-shape analysis because of the high uncertainties in these values; cf. R. R. Shoup, E. D. Becker, and M. L. McNeel, *J. Phys. Chem.*, **76**, 71 (1972), and references therein.
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Chemically Modified Electrodes. 11.
Predictability of Formal Potentials of Covalently Immobilized Charge-Transfer Reagents

Sir:

This research in covalent anchoring of redox reagents to electrode surfaces[1] examines the correspondence between electrochemical properties of an immobilized reagent and its solution analogue. Good correspondence is desired for predictive design of electrocatalytic systems.[1b,2]

Predictability of the electrochemical step I and the chemical step II can be scrutinized separately. While developing a diverse chemistry useful for covalently immobilizing OX/RED couples, we have measured a sufficiently extensive series of
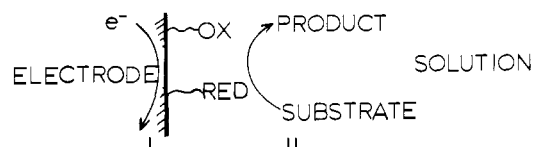
Table I. Comparison of Formal Potential^a $E^{\circ\prime}_{surf}$ of Redox Couples Immobilized on Chemically Modified Electrodes with Formal Potential^a of Solution Analogues^b

couple	electrode (supposed structure)	$E^{\circ\prime}_{surf}$ vs. SCE^c	$E^{\circ\prime}_{soln}$ vs. SCE
	Reductions^d		
R1	C (T(m-NH$_2$)PP)^e	$-1.08, -1.50^f$	$-1.05, -1.47^g$
R2	C (Fe^{III}T(p-NH$_2$)PP)^e	$-0.11, -1.17, -1.68$	$-0.13, -1.17, -1.65^h$
R3	C (Co^{III}T(m-NH$_2$)PP)^e	$+0.10, -0.86^i$	$+0.06, -0.85^j$
R4	C (Cu^{II}T(p-NH$_2$)PP)^e	$-1.19, -1.65$	$-1.20, -1.68^g$
R5	C (Zn^{II}T(p-NH$_2$)PP)^e	$-1.39, -1.75$	$-1.31, -1.72^g$
R6	C (Ni^{II}T(p-NH$_2$)PP)^e	$-1.21, -1.78$	$-1.18, -1.75^g$
R7	C (CONHCH$_2$-4-PyRu^{III}(NH$_3$)$_5$)	$+0.135^k$	$+0.044^k$
R8	RuO$_2$ (-OSi(CH$_2$)$_3$NHCO-4-(NO$_2$)Ph)	-0.89^l	-0.89^l
R9	RuO$_2$ (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCO-3-(NO$_2$)Ph)	-1.04^l	-0.96^l
R10	PtO (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCO-3,5-(NO$_2$)$_2$Ph)^m	$-0.77, -1.14^n$	$-0.72, -1.12^n$
R11	PtO (-OSi(CH$_2$)$_2$-4-(Py)Ru^{II}(bipy)$_2$Cl)	$-1.46, -1.68$	$-1.50, -1.72$
	Oxidations^o		
O1	RuO$_2$ (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCO(tetrathiafulvalene))^m	$+0.41, +0.77$	$+0.47, +0.83^p$
O2	PtO (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCOCpFeCp)^m	$+0.56$	$+0.52$
O3	PtO (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCOCpFeCpCOOH)^{m,q,r}	$+0.76$	$+0.69$
O4	PtO (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCH$_2$CpFeCp)^s	$+0.43$	$+0.37$
O5	RuO$_2$ (-OSi(CH$_2$)$_3$CONH-4-(Ph)CpFeCp)^t	$+0.44$	$+0.40$
O6	C (CONH-4-(phenyl)CpFeCp)^e	$+0.44$	$+0.42^u$
O7	RuO$_2$ (-OSi(CH$_2$)$_3$CONHCpFeCp)^t	$+0.34$	$+0.30$
O8	PtO (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCOCH$_2$PhCpFeCp)^m	$+0.43$	$+0.42$
O9	SnO$_2$ (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCO(N-p-anisylpyrazoline)^v	$+0.30$	$+0.29$
O10	PtO (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCO-4-(Py)Ru^{II}(bipy)$_2$(4-PyCOOH))^{m,r}	$+1.31$	$+1.32^w$
O11	PtO (-OSi(CH$_2$)$_2$-4-(Py)Ru^{II}(bipy)$_2$Cl)	$+0.75$	$+0.79$
O12	PtO (-OSi(CH$_2$)$_3$NH(CH$_2$)$_2$NHCO-4-(Py)Ru^{II}(bipy)$_2$Cl)	$+0.79$	$+0.82^w$

^{a} Average of cathodic and anodic cyclic voltammetric peak potentials. In all cases $i_{p,c}/i_{p,a} = 1.0$. Surface waves are stable over measurement period. Identifiable chemical nature of waves discussed elsewhere. ^{b} Solution analogues are corresponding tetraphenylporphyrin ($R1$) and metallotetraphenylporphyrins ($R2$–$R6$), butylamides of nitrobenzoic acids ($R8$–$R10$) and ferrocenecarboxylic acids ($O2$, $O3$), similarly ligated ruthenium complexes ($R7$, $R11$, $O10$, $O11$, $O12$), ester of tetrathiafulvalene ($O1$) and of $O8$, $(CH_3)_2NCH_2CpFeCp$ ($O4$), acetamide of 4-aminophenylferrocene ($O5$) and aminoferrocene ($O7$), and benzamide of 4-aminophenylferrocene ($O6$), all examined in same solvent/supporting electrolyte. ^{c} Estimated typical uncertainty ± 10 mV. ^{d} Except entry $R7$ (aqueous) and $R11$ (CH_3CN), all in Me$_2$SO solvent with Et$_4$NClO$_4$ electrolyte. ^{e} Tetra(aminophenyl)porphyrin amide coupled to glassy carbon[3] and metalated in situ with metal dichloride in DMF, except FeCl$_2$ was used in anhydrous THF ($O6$ similarly amide coupled). ^{f} Reference 5. ^{g} R. H. Felton and H. Linschitz, *J. Am. Chem. Soc.*, **88**, 1113 (1966). ^{h} L. A. Constant and D. G. Davis, *Anal. Chem.*, **47**, 2253 (1975). ^{i} Reference 5. ^{j} L. A. Truxillo and D. G. Davis, *Anal. Chem.*, **47**, 2260 (1975). ^{k} C. A. Koval and F. C. Anson, *ibid.*, **50**, 223 (1978). ^{l} Reference 1b. ^{m} Metal oxide electrode silanized with 3-(2-aminoethylamino)propyl-trimethoxysilane (en-silane)[1] and amide coupled to indicated carboxylic acid using dicyclohexylcarbodiimide. ^{n} Reference 1c. ^{o} All in CH_3CN solvent with Et$_4$NClO$_4$ electrolyte. ^{p} D. C. Green, *J. Chem. Soc., Chem. Commun.*, 101 (1977). ^{q} 1,1'-Ferrocenedicarboxylic acid. ^{r} Extent of mono- vs. difunctional coupling undetermined. ^{s} Metal oxide electrode silanized with en-silane and reacted with CpFeCpCH$_2$N(CH$_3$)$_3$$^+I^-$. ^{t} Metal oxide electrode silanized with 4-(methyldichlorosilyl)butyryl chloride and amide coupled to indicated amine. ^{u} Both this and $E^{\circ\prime}$ for ferrocene were experimentally ascertained to be 80–90 mV more positive than earlier data (W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn, and A. P. Sanders, *J. Am. Chem. Soc.*, **86**, 1376 (1964)) owing to difference in supporting electrolyte. ^{v} SnO$_2$ electrode reacted with en silane and then with a derivative of N-p-anisylpyrazoline (A. Diaz, *ibid.*, **99**, 5838 (1977)). ^{w} D. J. Salmon, Ph.D. Thesis, University of North Carolina, Chapel Hill, N.C., 1976.

formal potentials $E^{\circ\prime}$ so as to allow the first general test of the predictability of this important thermodynamic parameter. Table I compares formal potentials $E^{\circ\prime}$ of immobilized OX/RED couples[3] with their dissolved analogues. Table I includes a diversity in chemical structure and charge (neutral, cationic, anionic reactants), and the couples exhibit widely varying surface interaction effects as gauged from cyclic voltammetric peak widths[4] of immobilized OX/RED. Surface coverages (from cyclic voltammetric charges) are typically monolayer or less. Two couples ($O8$, $O11$) gave identical $E^{\circ\prime}_{surf}$ results at monolayer and multilayer coverages. For silanized metal oxides, $E^{\circ\prime}_{surf}$ appears to be independent of the metal oxide electrode substrate; couples $R10$, $O1$, $O3$, and $O5$ have been studied with two–three different oxide electrodes. Use of glassy carbon instead of metal oxide was similarly without effect ($O5$, $O6$). Adsorption control experiments were carried out electrochemically for all OX/RED couples listed (and ESCA controls for several), and results are consistent with covalent binding (rather than adsorption) of OX/RED to the electrode as planned in the surface synthesis and represented in Table I. Tag elements in immobilized OX/RED were ESCA detected (S 2p, Ru 3d$_{5/2}$, N 1s, Fe 2p$_{3/2}$, Co 2p$_{3/2}$). In several cases the expected surface elemental stoichiometry was quantitatively confirmed (e.g., N 1s/Fe 2p$_{3/2}$ in $O4$). The largest $E^{\circ\prime}_{surf} - E^{\circ\prime}_{soln}$ difference appearing in Table I is 90 mV ($R7$); the average difference of the 33 determinations is 36 mV, which is near the probable accuracy of the solution analogs.

The data of Table I demonstrate in a general way the moderate insensitivity of thermodynamic redox potentials to the act of OX/RED immobilization. This is desired for predictive electrocatalysis design. A variety of factors could promote $E^{\circ\prime}_{surf} - E^{\circ\prime}_{soln}$ divergence, and identification of them is worthwhile. First, reorganization of interfacial solvent composition and immobilized molecular stereochemistry could accompany electron-transfer reactions (for instance because of coulombic repulsion effects). Such reorganization can provoke initial–final state differences in OX and RED not mirrored in initial and final states of free OX and RED in solution. Second, asymmetry in the interaction parameters[4] between immobilized chemicals can shift $E^{\circ\prime}_{surf}$. Most of the listed immobilized redox couples require an interaction or chemical (structure/solvation) heterogeneity[5] factor for description of their cyclic voltammetric wave shape. Third, if the

planned structure of immobilized OX/RED is not achieved owing to synthetic misadventure during immobilization, substantial variation in $E^{\circ\prime}{}_{surf}$ could result.[6] Last, if immobilized OX or RED interact strongly (or differently) with the underlying electrode material, as in classical electrode adsorption,[7,8] or coherently with each other to form two-dimensional pseudocrystalline phases,[9] shifts in $E^{\circ\prime}{}_{surf}$ would result. Absence of large $E^{\circ\prime}{}_{surf} - E^{\circ\prime}{}_{soln}$ differences does not of course prove these effects absent, merely that in general they are of modest size.

Table I results show that immobilized OX/RED electrochemistry is thermodynamically predictable. The examples of Table I include also new immobilization schemes extrapolated from solution chemistry; this surface synthetic ability indirectly favors chemical reliability of step II. Thus, surface-bound aminosilane is employed as an amide former (e.g., *R*9, *O*1, *O*3) and also as a nucleophilic reagent (e.g., *O*4), just as one would expect from solution chemistry. Likewise, surface-bound pyridinesilane behaves as a ligand as expected (e.g., *R*11, *O*11, and immobilization of the important ruthenium bipyridyl system is achieved). The butyryl chloride silane is a new reagent which formed amides (e.g., *O*5, *O*7) with ease. Acid chloride functionalities on carbon bind amines (*R*1, *R*7, *O*6) in the expected manner. Preparation of a family of immobilized metallotetraphenylporphyrins (*R*2–*R*6) was possible using reaction conditions similar to solution metalations; *R*2 is a particularly interesting member of this family.

Unaddressed above is the important but separate question of step I and II kinetics, which must be understood before electrocatalytic design can be truly predictive. One qualitative example of designed electrocatalysis using a chemically modified electrode has appeared.[2]

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Nonbonded Interactions in Phenylcarbenium Ions

Sir:

The intriguing concept of nonbonded electronic interactions, as developed recently by Epiotis, provides an explanation for several cases of torsional isomerism where a more sterically crowded geometry is more stable than less crowded geometries.[1-7] In this communication we suggest that nonbonded interaction may also have a substantial influence on the distribution of electrons within a molecule, particularly in charged, conjugated systems.[8] Specifically, attractive and repulsive nonbonded interactions are discussed in relation to the distribution of charge in phenylcarbenium ions (benzyl cations) with the aim of providing an explanation for some unusual ^{13}C NMR chemical shifts.

The concept of nonbonded electronic interactions is based on orbital symmetry arguments and as such may be expressed in various ways. The simplest approach is to consider whether a possible interaction is aromatic, nonaromatic, or antiaromatic.[3,9] Nonbonded interactions of this type occur when two atoms (not formally bonded) approach closely enough for orbital overlap so that the overlap completes a continuous cycle of overlapping orbitals. With Hückel topology for the cyclic array of orbitals, attractive nonbonded interactions will be present if the cycle is aromatic, i.e., when $4N + 2$ electrons are in the cycle. Repulsive nonbonded interactions are expected for a cycle of $4N$ electrons.

In phenylcarbenium ions substituted at the carbenium center, nonbonded π-electron interactions can be considered for a 4-atom cycle of p orbitals that is completed by long-range overlap between the substituent and the syn ortho carbon, in analogy with cis-1,2-disubstituted ethylenes.[1,3-5] Considering only the two resonance structures that place charge in the ortho positions, it can be seen that, with the substituent contributing 2π electrons,[10] the 4-atom cycle contains 4π electrons and is thus antiaromatic when the charge is at the syn ortho carbon. Resonance structure **1** with repulsive, antiaromatic interactions

antiaromatic   nonaromatic
 1   **2**
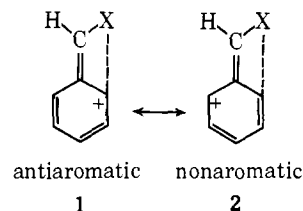
should contribute less to the resonance hybrid than structure **2** where such effects are absent; hence, less positive charge is expected to reside at the syn ortho carbon than the anti ortho carbon.

Chart I presents the ^{13}C NMR chemical shifts for ring carbons in some stable phenylcarbenium ions.[11] The ortho and para carbons are deshielded owing to positive charge, but there is a large difference between the ortho carbons in ions **3–5**. The difference is 12.9 ppm in **3**, 11.2 ppm in **4**, and 11.5 ppm in **5**. The syn ortho carbon is substantially shielded relative to the anti ortho carbon or the para carbon, consistent with the prediction of less positive charge due to repulsive nonbonded interactions. However, it is difficult to quantitatively assess this postulated effect in terms of π-electron densities, because the well known γ-substituent effect is probably operative also in shielding both ortho carbons. The shielding effect of a γ substituent is usually larger in a syn or gauche alignment relative to anti, but no other cases have been reported where the difference between syn and anti effects approaches the magnitude of 11–13 ppm.[12]

The data for ion **6** indicate that the shielding of the syn ortho carbons is not a constant effect of the nearby carbenium substituent. If the shielding effect were constant and additive, extrapolation from ions **3** and **5** would predict a difference of 1.4 ppm instead of the 6.5-ppm difference observed for the ortho carbons in ion **6**. A reasonable conclusion is that orbital interaction is more effective for fluorine than methyl, so that the repulsive interaction involving the fluorine atom dominates. The methyl repulsive interaction would shift charge from the