inappropriate as an internal standard for some systems due to overlapping waves. In these cases other compounds such as cobaltocene ($E° = -0.918$ V vs. NHE)[12] or any of a variety of aromatic compounds, comprising a virtual continuum of reduction potentials, can be substituted.[13] Potentials can still be related to $E^f(Fc^+/Fc)$ through a second experiment.

Employing a redox couple as an internal standard in electrochemical experiments can be compared to the use of internal standards in nuclear magnetic resonance spectroscopy. For example, in proton NMR spectroscopy tetramethylsilane is commonly used to reference chemical shifts of other protons but is sometimes replaced by chloroform or other materials to avoid overlapping signals. As with NMR standards, an ideal electrochemical internal standard should not interact with other species in solution. Ferrocene adequately fills this criterion.

Use of ferrocene as an internal standard demands the observation of reversible electrochemistry for the Fc^+/Fc couple. Reversible behavior has been observed in a wide variety of solvents with the following limitations: (a) in water and alcohols the instability of the ferrocenium ion causes reduction potentials measured by potentiometry to differ from values measured by faster techniques; (b) cyclic voltammetry at slow scan rates (10–50 mV s^{-1}) results in reversible behavior, while faster scan rates (>1 V s^{-1}) reveal quasi-reversible behavior.[14–16]

Cyclic voltammetric peak separations, ΔE_p, serve as one criterion for electrochemical reversibility. For example, a one-electron process ($n = 1$) is expected to have $\Delta E_p = 59$ mV. High solution resistance, especially in nonaqueous solvents, can result in large peak separations, complicating wave shape analysis.[17,18] State of the art electrochemical instrumentation provides a capability for compensating for IR drop in an attempt to overcome solution resistance contributions to the shapes of cyclic voltammetric waves. Unfortunately some instrumentation permits overcompensation, sometimes resulting in meaningless results. For example, we have been able to obtain peak separations of 40–50 mV for both the Fc^+/Fc and $Ru(acac)_3/Ru(acac)_3^-$ couples by using instrumental IR compensation. In practice we do not use instrumental IR compensation, but simply compare ΔE_p for the couple of interest with that of the Fc^+/Fc couple under the same conditions. It should be emphasized that, while wave shape comparisons may be useful, reproducibility of reduction potential measurements is the key advantage of the ferrocene referencing system.

Thermodynamic Significance. The notion of ferrocene as an internal reference couple stems in part from attempts by others to compare redox potentials obtained in different solvents. The potential scale in water is established by assigning the potential of the hydrogen half-reaction as zero. Since the activity of the proton is not necessarily the same in all solvents, a similar convention establishes a different scale in each solvent. The problems associated with measuring and comparing reduction potentials on the same scale in a wide variety of solvents has received considerable attention through attempts to estimate free energies of transfer of single ions, ΔG_{tr}.[19]

These estimates require the use of an extrathermodynamic assumption. One such assumption is that the activity of a univalent, large, symmetrical ion, with the charge deeply buried, is the same as the activity of an uncharged molecule of the same size and structure in all solvents. Strehlow proposed that Fc^+/Fc fits the requirements and as such is a solvent-independent redox couple.[12] Thus $E°$ (Fc^+/Fc) in any solvent is assumed to be the same as measured in water, i.e., 0.400 V vs. NHE, and potentials vs. the Fc^+/Fc couple are directly comparable between solvents. Alternatively, tabulations of $\Delta G_{tr}(Ag^+)$ based on other assumptions[14,20] can be used to calculate the potential of Ag/Ag^+ reference electrodes (Pleskov electrodes) vs. NHE in water.[21]

It is not obvious which of the extrathermodynamic assumptions used to interrelate electrochemical potentials measured in various solvents is more valid, and we do not presume in principle to favor any one assumption over another. In practice, reproducibility of potentials vs. the Ag/Ag^+ Pleskov electrode are adversely affected by the insolubility of silver salts in some solvents like dichloromethane,[3] by reactions of Ag^+ with some solvents such as acetone and *N*,*N*-dimethylformamide,[3] or by trace impurities such as water which interact strongly with Ag^+.[14] Likewise, reference electrodes containing known concentrations of Fc and Fc^+ are unstable due to decomposition of ferrocenium ion.[14,15] Instead, we prefer the *internal* use of ferrocene because it is convenient, is reproducible, provides a basis for judging electrochemical reversibility, and allows for a quantitative comparison of reduction potentials measured in various solvents.

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(13) Bauer, D.; Beck, J. P. *Bull. Soc. Chim. Fr.* **1973**, 1252–1259.

(14) Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 1148–1158.

(15) Diggle, J. W.; Parker, A. J. *Electrochim. Acta* **1973**, *18*, 975–979.

(16) Delahay, P. *J. Am. Chem. Soc.* **1953**, *75*, 1430–1435.

(17) Adams, R. N. "Electrochemistry at Solid Electrodes"; Marcel Dekker: New York, 1969; pp 143–162.

(18) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 667–671, 1351–1355.

(19) For example see: (a) Popovych, O. "Treatise on Analytical Chemistry", 2nd ed.; Kolthoff, I. M., Elving, P. J., Eds.; Wiley: New York, 1978; Vol. 1, pp 711–771; (b) Popovych, O. *CRC Crit. Rev. Anal. Chem.* **1970**, *1*, 73–117; (c) Bauer, D.; Breant, M. *Electroanal. Chem.* **1976**, *8*, 282–348; (d) Strehlow, H. "Chemistry of Non-Aqueous Solvents"; Lagowski, J. J., Ed.; Academic Press: New York, 1966; pp 129–171.

(20) Cox, B. G.; Hedwig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem.* **1974**, *27*, 477–501. Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Phys. Chem.* **1972**, *76*, 2024–2034.

(21) $E_{NHE}(Ag^+, S) = E°_{NHE}(Ag^+, H_2O) + \{\Delta G_{tr}(Ag^+, H_2O \rightarrow S) + RT \ln [a_{Ag^+}]\}/nF$ where $E°_{NHE}(Ag^+, H_2O) = 0.799$ V and S is the solvent of interest.[15]

(22) Contribution No. 6139.

Transferability of Ligand Field Parameters and Nonlinear Ligation in Chromium(III) Complexes

Sir:

In a previous paper[1] we have demonstrated that transferable ligand field parameters of an additive field quite satisfactorily could account for our experimental spectral results for a series of *trans*-tetraammine- and tetrakis(pyridine)chromium(III) complexes. We used the angular overlap model to describe the chromium(III)–pyridine bond and obtained a negative $\Delta'_{\pi py}$ for pyridine.

This latter result has acted as an impetus for a recent paper in this journal by Smith[2] in which this result is questioned, partly by reviewing our paper in a fashion which we find unsatisfactory. The present paper is an attempt to clarify and extend certain points in our previous paper and also to discuss

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(1) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399.

(2) Smith, D. W. *Inorg. Chem.* **1978**, *17*, 3153.

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Table I. Angular Overlap Model Parameter Estimates (μm^{-1}) for Some *trans*-[ML_4A_2] Complexes, Assuming Linear Ligation (Cf. Eq 1)[a]

complex	$\Delta_{\sigma L} - \Delta_{\pi L}$	$\Delta_{\sigma A} - \Delta_{\pi L}$	$\Delta_{\pi A} - \Delta_{\pi L}$
trans-[$Ni(py)_4Cl_2$][b]	1.17	0.66	−0.02
trans-[$Ni(Et_2en)_2Cl_2$][c]	1.19	0.51	−0.11
trans-[$Ni(py)_4Br_2$][b]	1.15	0.53	−0.06
trans-[$Ni(Et_2en)_2Br_2$][c]	1.18	0.36	−0.26
trans-[$Cr(py)_4Cl_2$]$^+$[d]	1.95	1.84	0.41
trans-[$Cr(NH_3)_4Cl_2$]$^+$[d]	2.11	1.60	0.29
trans-[$Cr(py)_4Br_2$]$^+$[d]	1.94	1.72	0.44
trans-[$Cr(NH_3)_4Br_2$]$^+$[d]	2.17	1.51	0.36

[a] Et_2en = *N,N'*-diethyl-1,2-ethanediamine. [b] Reference 4. [c] Reference 5. [d] Reference 1.

Table II. Angular Overlap Model Parameters (μm^{-1}) for Some *trans*-[CrN_4F_2]$^+$ Chromophores, Based upon Room-Temperature Solution Spectra (Treated as in Ref 1)

N_4[a]	$\Delta_{\sigma N} - \Delta_{\pi N}$	$\Delta_{\sigma F} - \Delta_{\pi N}$	$\Delta_{\pi F} - \Delta_{\pi N}$	Δ_F
$(chxn)_2$	2.169	2.25	0.68	1.57
$(en)_2$	2.166	2.29	0.71	1.58
$(tn)_2$	2.164	2.23	0.69	1.54
$(NH_3)_4$	2.084	2.23	0.70	1.53
$(CH_3NH_2)_4$	2.080	2.27	0.71	1.56
$(CH_3CH_2NH_2)_4$	2.069	2.27	0.72	1.55
$(CH_3CH_2CH_2NH_2)_4$	2.055	2.28	0.73	1.55

[a] chxn = (*R*,*R*)-trans-1,2-cyclohexanediamine, en = 1,2-ethanediamine, tn = 1,3-propanediamine.

both the experiments cited by Smith and some new more rigorous data from the point of view of our earlier article.

The main reason for the paper by Smith is said to be that our results, in particular the negative π parameter for pyridine, were "inconsistent with the apparent behavior of pyridine in [$M(py)_4A_2$] (M = Fe(II), Co(II), Ni(II); A = Cl^-, Br^-, NCS^-)" for which "the d–d spectra of the nickel complexes suggest that $\Delta_{\pi py}$ is positive". We cannot see this inconsistency for the nickel complexes as will be explained in this letter, and we also do not find it logical to cite the magnetic work[3] on the cobalt and iron complexes in support of a positive $\Delta_{\pi py}$ because these data did not allow a value for this parameter to be estimated unambiguously.

For a complex of the type *trans*-[ML_4A_2] coordinated with linearly ligating ligands, the three empirical parameters of the nonadditive field and three linear combinations of the four parameters of the additive field are related by eq 1.[1]

$$\Delta(d) = \tfrac{1}{3}(\Delta_{\sigma A} - \Delta_{\pi L}) - \tfrac{1}{3}(\Delta_{\pi A} - \Delta_{\pi L}) + \tfrac{2}{3}(\Delta_{\sigma L} - \Delta_{\pi L}) \equiv \tfrac{1}{3}\Delta'_{\sigma A} - \tfrac{1}{3}\Delta'_{\pi A} + \tfrac{2}{3}\Delta'_{\sigma L} \quad (1a)$$

$$\Delta(e) = -\tfrac{2}{3}(\Delta_{\sigma A} - \Delta_{\pi L}) + \tfrac{2}{3}(\Delta_{\sigma L} - \Delta_{\pi L}) \equiv -\tfrac{2}{3}\Delta'_{\sigma A} + \tfrac{2}{3}\Delta'_{\sigma L} \quad (1b)$$

$$\Delta(t_2) = -\tfrac{1}{2}(\Delta_{\pi A} - \Delta_{\pi L}) \equiv -\tfrac{1}{2}\Delta'_{\pi A} \quad (1c)$$

In Table I the results for [$Ni(py)_4A_2$] cited[4] by Smith have been tabulated by using eq 1. Literature data for some nickel(II) complexes[5] of a saturated amine ligand and some of our own data[1] for the chromium(III) complexes are also included in the table.

The trends in the variation of the halide parameters[6] on going from pyridine to amine complexes are seen to be essentially the same for the nickel(II) and for the chromium(III) complexes. The fact that the value for ($\Delta_{\pi A} - \Delta_{\pi py}$) is negative for the nickel(II) pyridine complexes is probably the basis for Smith's conclusion that $\Delta_{\pi py}$ is positive. However, this can only be based upon the preconceived notion that $\Delta_{\pi A}$ cannot be negative even though ($\Delta_{\pi A} - \Delta_{\pi N}$) in the nickel(II) amine complexes, not cited by Smith, is even more negative.[7]

In our earlier paper we demonstrated that the single ligand parameter transferability assumption was inconsistent with pyridine as a linearly ligating ligand. Of these two alternatives Smith chooses to question the transferability assumption with reference to angular overlap model parameter estimates for a number of *trans*-(tetraamine)bis(fluorido)chromium(III) complexes taken from a variety of literature sources[1,8,9] including such different experimental conditions as solution spectra at room temperature and diffuse reflectance spectra at liquid-nitrogen temperature. Most of these complexes were originally prepared and measured in this laboratory, and parameter estimates were available to us when we wrote our paper. Few of these complexes have, however, geometries which are easily handled by using the angular overlap model in a rigorous fashion. $\Delta'_{\sigma F}$ and $\Delta'_{\pi F}$ parameters estimated on the basis of an assumed effective D_{4h} symmetry were, however, found to be very close to the values estimated for *trans*-(tetraammine)bis(fluorido)chromium(III), as shown in Table II.

It is well-known that the band positions of fluorido complexes are particularly dependent upon the chemical environment,[10] and it is, therefore, significant that the $\Delta_{\sigma F}$ and $\Delta_{\pi F}$ parameters, derived on the basis of our present data, show a much smaller variation (less than 10%) than that exhibited by Smith's collection of data which led him to reject the transferability assumption.

When the pyridine ligand in the *trans*-tetrakis(pyridine)chromium(III) complexes is not considered linearly ligating,

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(3) Gerloch, M.; McMeeking, R. F.; White, A. M. *J. Chem. Soc., Dalton Trans.* **1975**, 2443, 2452; *Ibid.* **1976**, 655.

(4) Schreiner, A. F.; Hamm, D. J. *Inorg. Chem.* **1973**, *12*, 2037.

(5) Lever, A. B. P.; London, G.; McCarthy, P. J. *Can. J. Chem.* **1977**, *55*, 3172.

(6) The increase in Δ values on going from water to ethanediamine is 35% for Ni(II) and 26% for Cr(III), while the same numbers are 1.7% on going from pyridine to *N,N'*-Et_2en with Ni(II) and 8.2% on going from pyridine to ethanediamine with Cr(III). The comparatively large value of Δ_{py} for Ni(II) as compared with that for Cr(III) is evidence that $\Delta_{\pi py}$ is relatively more negative for Ni(II) than for Cr(III).

(7) The problem of the molecular orbital interpretation of the angular overlap model parameters is perhaps of some chemical interest. It is satisfactory that the σ parmeters are always found to be large and positive since they essentially represent the σ-antibonding energy caused by the interaction between metal d orbitals and filled ligand σ orbitals. The π parameters are usually found to be quite small. They contain positive (antibonding) and negative (bonding) contributions which cannot be experimentally separated. $\Delta'_{\pi X}$ (X = Cl, Br) are positive for chromium(III) and negative for nickel(II) but very small in both cases. It is clear that the empty d orbitals on Cl^- and Br^- will give a negative contribution for both metal ions and most likely a larger one for nickel(II). However, at best these bonding parameters refer to bonding involving the d electrons, and it is most probable that the angular overlap model does not warrant a discussion based upon so small parameter variations.

(8) Barton, T. J.; Slade, R. C. *J. Chem. Soc., Dalton Trans.* **1975**, 650.

(9) Glerup, J.; Josephsen, J.; Michelsen, K.; Pedersen, E.; Schäffer, C. E. *Acta Chem. Scand.* **1970**, *24*, 247.

(10) Glerup, J.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1408.

(11) It is seen that this new model does not allow the determination of $\Delta'_{\pi py}$ without further assumptions. Smith therefore invokes the molecular orbital point of view of the angular overlap model according to which the empirical parmeters are proportional to squared overlap integrals, which in principle can be calculated from Hartree–Fock functions. With an assumed (+1) oxidation state of the central metal ion and without ligand s orbitals participating in the overlap, he then calculated $\alpha \equiv [d\Delta_\sigma(R)/dR]_{R=R_0}/[d\Delta_\pi(R)/dR]_{R=R_0} = 1.75$ (F^-, R_0 = 1.95 Å), 1.91 (Cl^-, R_0 = 2.35 Å), and 2.03 (Br^-, R_0 = 2.50 Å), a result which Smith justifies with reference to his collection of (tetraamine)bis(fluorido)chromium(III) data. From an average α value of 1.9 in combination with the numerical results of eq 4, $[\varkappa_\sigma]_{\Psi=45} \approx 0.21\ \mu m^{-1}$, $[\varkappa_\pi]_{\Psi=45} \approx 0.11\ \mu m^{-1}$, and $[\Delta'_{\pi py}]_{\Psi=45} \approx 0.06\ \mu m^{-1}$ are obtained.

eq 1 is modified[1] to eq 2, where Ψ is the angle between the

$$\Delta(\mathrm{d}) = \tfrac{1}{3}\Delta'_{\sigma\mathrm{A}} - \tfrac{1}{3}\Delta'_{\pi\mathrm{A}} + \tfrac{2}{3}\Delta'_{\sigma\mathrm{py}} - \tfrac{2}{3}\Delta'_{\pi\mathrm{py}} \qquad (2a)$$

$$\Delta(\mathrm{e}) = -\tfrac{2}{3}\Delta'_{\sigma\mathrm{A}} + \tfrac{2}{3}\Delta'_{\sigma\mathrm{py}} \qquad (2b)$$

$$\Delta(\mathrm{t}_2) = -\tfrac{1}{2}\Delta'_{\pi\mathrm{A}} + \tfrac{1}{2}\Delta'_{\pi\mathrm{py}} - \tfrac{3}{2}(\cos 2\Psi)\Delta_{\pi\mathrm{py}} \qquad (2c)$$

assumed fourfold axis of the complex and the normal to the planar pyridine ligand. The transferability assumption alone allows the estimation of $\Delta'_{\sigma\mathrm{py}}$ and $\Delta'_{\pi\mathrm{py}}$ from eq 1, 2a, and 2b. This estimation is independent of Ψ, cf. Table III in our previous paper, a point which apparently has not been appreciated by Smith. However, with an assumed value for $\Delta_{\pi\mathrm{NH}_3}$ in our case taken as 0, Ψ may be determined[12] from eq 2c.

If we similarly treat the nickel(II) data in Table I under the assumption that the halogen ligand parameters are transferable from the amine to the pyridine complexes (i.e., using eq 1, 2a, and 2b), we obtain $\Delta'_{\sigma\mathrm{py}} \approx 1.02\ \mu\mathrm{m}^{-1}$ and $\Delta'_{\pi\mathrm{py}} \approx -0.18\ \mu\mathrm{m}^{-1}$ for the chlorido complexes and 0.98 and −0.15 $\mu\mathrm{m}^{-1}$ for the bromido complexes. It is seen that $\Delta'_{\pi\mathrm{py}}$ is relatively larger, compared to $\Delta'_{\sigma\mathrm{py}}$, for nickel(II) than for chromium(III), which is in agreement with the conclusion drawn from other types of evidence (cf. ref 7). If eq 2c is further used and $\Delta_{\pi\mathrm{N}}$ is taken as zero, Ψ is calculated to be ~40 and ~48°, respectively.

Smith's rejection of the transferability asumption forces him arbitrarily to assume $\Psi = 45°$ in order to carry out further calculations. This of course can only be justified by determinations of structures in solution, but if this idea is followed, $\Delta'_{\sigma\mathrm{py}}$, $\Delta'_{\pi\mathrm{py}}$, and $(\cos 2\Psi)\Delta_{\pi\mathrm{py}}$ of eq 2 may be transformed into pyridine parameters and differences in σ and π parameters for the trans ligands in ammine and pyridine complexes, which may be defined as eq 3.

$$\varkappa_{\lambda\mathrm{A}} \equiv \Delta'_{\lambda\mathrm{A}}(\mathrm{py}) - \Delta'_{\lambda\mathrm{A}}(\mathrm{NH}_3) \qquad \lambda = \sigma, \pi \qquad (3)$$

The transformation to the four parameters of this new model[11] is given in eq 4. The numbers are calculated by

$$[\Delta'_{\sigma\mathrm{py}} - \Delta'_{\pi\mathrm{py}}]_{\Psi=45} = [\Delta'_{\sigma\mathrm{py}} - \Delta'_{\pi\mathrm{py}} + (\cos 2\Psi)\Delta_{\pi\mathrm{py}}] \approx 1.904\ \mu\mathrm{m}^{-1} \qquad (4a)$$

$$[\varkappa_{\sigma} - \Delta'_{\pi\mathrm{py}}]_{\Psi=45} = [-\Delta'_{\pi\mathrm{py}} + (\cos 2\Psi)\Delta_{\pi\mathrm{py}}] \approx 0.15\ \mu\mathrm{m}^{-1} \qquad (4b)$$

$$[\varkappa_{\pi} - \Delta'_{\pi\mathrm{py}}]_{\Psi=45} = [-\Delta'_{\pi\mathrm{py}} + (3\cos 2\Psi)\Delta_{\pi\mathrm{py}}] \approx 0.05\ \mu\mathrm{m}^{-1} \qquad (4c)$$

means of Table IV, ref 1, which the statistical analysis made us accept as a fair representation of the original experiments, an analysis which has apparently not been questioned (with $\varkappa_{\lambda\mathrm{A}}$ independent of A).

In view of the demonstrated mathematical equivalence between these two chemically different models, we see no reason, in the absence of conclusive experiments, not to prefer the simpler alternative which allows extraction of single ligand parameters that are not dependent upon the remaining coordination sphere. It is of course true that such parameters, although rigorously derived, can rarely reproduce the experimental data within the measuring accuracy. We nevertheless find them useful for a semiquantitative description of the spectrochemical behavior of a large class of coordination compounds. As a consequence of this point of view, the $\Delta'_{\pi\mathrm{py}}$ parameter in Cr(III) complexes is negative, and this value is independent of any assumptions of a particular pyridine ligand rotational orientation.

Registry No. *trans*-$[\mathrm{Cr(chxn)_2F_2}]^+$, 46935-55-1; *trans*-$[\mathrm{Cr(en)_2F_2}]^+$, 24407-74-7; *trans*-$[\mathrm{Cr(tn)_2F_2}]^+$, 42476-30-2; *trans*-$[\mathrm{Cr(NH_3)_4F_2}]^+$, 31253-66-4; *trans*-$[\mathrm{Cr(CH_3NH_2)_4F_2}]^+$, 73697-80-0; *trans*-$[\mathrm{Cr(CH_3CH_2NH_2)_4F_2}]^+$, 73697-81-1; *trans*-$[\mathrm{Cr(CH_3CH_2CH_2NH_2)_4F_2}]^+$, 73697-82-2.

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[12] Assuming Ψ to be the same for a series of complexes, we found[1] a value of 37.8 ± 1.1. In a recent paper[13] it was pointed out that a symmetrical participation of the pyridine ligands in π bonding with t_{2g} orbitals gives an essentially symmetry-based value of $\Psi = 35.26$.

(13) Laier, T.; Schäffer, C. E.; Springborg, J. *Acta Chem. Scand.*, in press.

Stereospecificity of Hydride Additions to Rings in Organometallics

Sir:

Addition of nucleophiles to (tropylium)$\mathrm{M(CO)_3}$ cations (M = Cr or Mo) was suggested by Pauson to occur normally by addition to the ring rather than attack at the metal.[1] Subsequent studies on analogous compounds have been interpreted in terms of attack exo to the metal atom,[2] and today there seems to be a general consensus that nucleophile addition to a ring π-bonded to a metal will occur stereospecifically from an exo direction. In attempting to prepare $[\mathrm{C_7H_6DMo(CO)_3}]^+$ we have found that the reaction is far from stereospecific and in some cases only moderately stereoselective. Furthermore, upon examination of the previous literature we have discovered some interesting cases of misinterpretation or potential misinterpretation of data which might serve as a caveat to current workers in this field.

The stereochemistry of addition of hydride or deuteride to metal-bound rings has had a rather confused history. In 1959 Green, Pratt, and Wilkinson suggested endo additions on the basis of reasonable assumptions regarding unusual C–H stretching bands in $\mathrm{(C_5H_5)(C_5H_5X)Co}$ complexes.[3] These complexes show a relatively intense IR absorption at ~2750 cm^{-1}, which was originally assumed to be a C–H stretch lowered by interaction with the metal. A weaker band at 2780 cm^{-1} observed in a number of $\mathrm{(C_5H_5)(C_5H_6)M}$ compounds also failed to appear in $\mathrm{(C_5H_5)(C_5H_5X)Co}$, as well as in similar arene–iron complexes, e.g., $\mathrm{(C_6H_6)(C_5H_5X)Fe}$. The absence of low-frequency bands was thus taken as evidence that the H on the substituted carbon was exo.

In 1964 Churchill and Mason[4] established that the substituents in compounds for which the low-frequency vibration had "disappeared" actually occupied the exo position and the H was in the endo position. Consequently, it appeared that the anomalous C–H stretch should be associated with the exo H. This was finally demonstrated by Bird and Churchill[5] in the examination of $\mathrm{(C_6Me_6H)Re(CO)_3}$ obtained by hydride attack on (hexamethylbenzene)rhenium tricarbonyl cation.[6] This is one of relatively few complexes which has no endo H and shows the broad, low-frequency (2790-cm^{-1}) stretch. Thus, predominantly on the weight of the evidence of this study, the presence of a low-frequency C–H stretch in the IR

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(1) Munro, J. D.; Pauson, P. L. *J. Chem. Soc.* **1961**, 3475.
(2) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2387.
(3) Green, M. L. H.; Pratt, L.; Wilkinson, C. *J. Chem. Soc.* **1959**, 3753.
(4) Churchill, M. R.; Mason, R. *Proc. R. Soc. London, Ser. A* **1964**, 279, 191.
(5) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 777.
(6) Winkhaus, G.; Singer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1963**, *18B*, 418.

0020-1669/80/1319-2857$01.00/0