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 $\mathrm{t_{2g}}$ orbitals gives an essentially symmetry-based value of Ψ = 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 $\mathrm{cm^{-1}}$, which was originally assumed to be a C–H stretch lowered by interaction with the metal. A weaker band at 2780 $\mathrm{cm^{-1}}$ 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-$\mathrm{cm^{-1}}$) 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.

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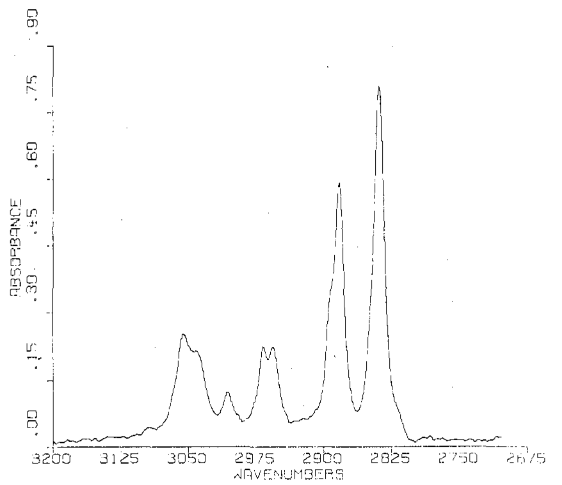

Figure 1. The C–H stretching region of $C_7H_8Mo(CO)_3$ in carbon tetrachloride. The spectrum was obtained with a FT infrared spectrometer.

is taken as physical proof of an exo H in complexes. Furthermore, the disappearance of this band is generally accepted as evidence for removal of an exo H.

Calderazzo appears to have considered the origins of this band most extensively.[7,8] As he points out, when one eliminates the possibility of BH impurities, the band is not really an "intense" band. That is, it is only strong relative to those of the aromatic C–H's, which may be lowered in intensity due to flattening of the ring on coordination. Furthermore, it is not all that low in frequency. The symmetric and antisymmetric C–H stretches in cycloheptatriene itself are at 2849 and 2967 cm^{-1}.[9] Thus the C–H oscillators should have a fundamental absorption at 2908 cm^{-1} split by 118 cm^{-1} from a stretch–stretch interaction. This interaction is an important feature because it demands that regardless of any difference in the $C–H_{exo}$ and $C–H_{endo}$ stretching force constants, two C–H bands will appear.

In $C_7H_8Mo(CO)_3$ two low-frequency C–H bands are observed[10] as shown in Figure 1 at 2838 and 2883 cm^{-1}, which may be assigned to the symmetric and antisymmetric methylene stretching modes. In this complex, the lower frequency band is not particularly broad and thus may not be directly related to those in the other complexes;[11] nevertheless, it disappears if the complex is prepared from the tropylium complex with BD_4^- or BD_3CN^-. However, if one accepts that coupling between the C–H vibrations occurs, *then this band must disappear regardless of which hydrogen is replaced by deuterium.* In the absence of an intrinsic difference in C–H stretching force constant for exo and endo H, one would expect a new band to appear approximtely halfway between the symmetric and antisymmetric bands of the CH_2 compound. Thus, in this case the disappearance of the band is not indicative of H_{exo} replacement by deuterium.

In $(C_7H_7D)Mo(CO)_3$, the C–H band appears at 2864 cm^{-1} and the bands at 2838 and 2883 cm^{-1} are reduced nearly to the base line. Only a single C–D stretching band is observed at 2118 cm^{-1}.[12] Nevertheless, the nature of the replacement is most readily followed by NMR. ^1H and ^2H NMR spectra are shown in Figure 2. The assignments follow those of earlier work[13] based on both shifts and coupling constants,[14,15] the best evidence being the magnitude of the coupling constants between the neighboring olefinic protons and the exo (δ 2.47, 2.6 Hz) and endo protons (δ 3.04, 8.7 Hz). On the basis of the structures of analogous compounds[4,5] one would anticipate an out-of-plane bending of the methylene which would result in a small dihedral angle between the endo protons and the vicinal olefin protons, whereas the exo proton would become nearly perpendicular to the plane of the olefinic protons. Thus, it is clear from the Karplus relationship[16,17] that the endo proton will be more strongly split by the vicinal protons.

The lack of specificity in the addition is clearly indicated by the deuterium NMR spectrum of the deuterated complex prepared from borodeuteride treatment of the (tropylium)-$Mo(CO)_3$ cation according to the procedure of Munro and Pauson.[1] In this case a ratio of endo to exo addition was found to be 28:72. When cyanoborodeutride was used, an even lower specificity was found, i.e., 40:60. Previous work has shown that intermolecular exchange of cycloheptatriene-d_1, which might be responsible for this observation, is extremely slow;[13] hence, intermolecular exchange can be ruled out as a mechanism for scrambling endo and exo D.

Thus, it appears that hydride additions may occur not just by the "normal" exo addition route but also by initial addition to the metal followed by migration to the ring. In view of the stable formyl complexes which are now well characterized,[18,19] one could also consider that the addition occurs partially or exclusively by attack at the carbonyl. The probability of multiple pathways is also suggested by the early observation that reduction of $[areneMn(CO)_3]^+$ cations also produces $C_6H_8Mn(CO)_3H$.[20] However, since hydrides could potentially be in equilibrium with formyls, a formyl may be an integral intermediate in moving the H from the metal to the ring.[21,22]

The probable existence of the tropylium metal hydride intermediate was cleverly demonstrated by the studies of hydrogen (or deuterium) migration in $(C_7H_7D)Mo(CO)_3$.[13] These studies were interpreted in terms of migration of the endo hydrogen (deuterium) to the metal, rotation of the seven-membered ring, and migration back to the ring. Thus, if a deuterium is exo in the methylene, it is scrambled to all of the olefinic sites by this process. However, an endo methylene deuterium would always return as an endo methylene deuterium. This can be seen in Figure 2C, where the deuterium intensity associated with the exo methylene is distributed over the ring after thermal rearrangement.

Although Roth and Grimme[13] suggested a symmetrical seven-membered ring in the hydride intermediate, it is more likely to be a fluxional η^5-C_7H_7 ring.[23] This rearrangement appears to occur by random addition of deuterium to the various positions of the ring.[24] Lamanna and Brookhart have

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(7) Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950.

(8) Calderazzo, F. *Inorg. Chem.* **1966**, *5*, 429.

(9) Evans, M. V.; Lord, R. C. *J. Am. Chem. Soc.* **1960**, *82*, 1876.

(10) Calderazzo, F.; Calvi, P. L. *Chim. Ind.* (*Milan*) **1962**, *44*, 1217.

(11) A broad, low-frequency band may indicate an exo H in some cases. The point made here is that assignments must be made with discretion.

(12) This complex is synthesized as a mixture of endo and exo D isomers (see below), and some C_7H_8 species is present owing to the impurity of the deuterating agents.

(13) Roth, W. R.; Grimme, W. *Tetrahedron Lett.* **1966**, 2347.

(14) Jensen, F. R.; Smith, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 956.

(15) Guenther, H; Wenzl, R. *Tetrahedron Lett.* **1966**, 787.

(16) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Elmsford, N.Y., 1966; Vol. 2, p 678.

(17) Schrock, R.; Osborn, J. *Inorg. Chem.* **1970**, *9*, 2339.

(18) Casey, C. P.; Andrews, M. A.; McAlister, R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

(19) Tam, W.; Wong, W. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

(20) Winkhaus, G. *Z. Anorg. Allg. Chem.* **1963**, *319*, 404.

(21) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544.

(22) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545.

(23) A fluxional η^5-cycloheptatrienyl ring is observed in $C_7H_7Mn(CO)_3$. See, e.g.: Whitesides, T. H.; Budnick, R. A. *Inorg. Chem.* **1976**, *15*, 874.

(24) Slight differences in intensities are observed in the deuterium olefin resonances. These may arise from a competitive rates for hydrogen migration and fluxional rearrangement or, more probably, from a combination of kinetic and equilibrium isotope effects.[25]

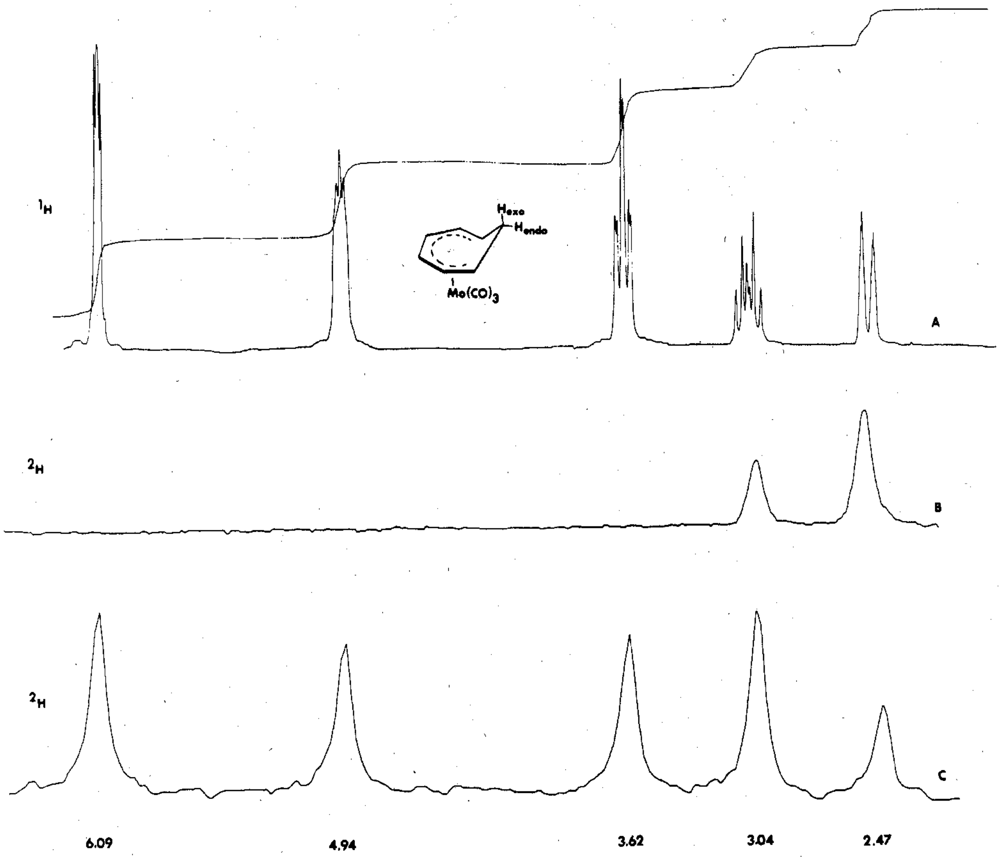

Figure 2. (A) A 270-MHz ^{1}H spectrum of $C_7H_8Mo(CO)_3$ in deuteriochloroform. (B) A 41.4-MHz $^2H\{^1H\}$ spectrum of $C_7H_7DMo(CO)_3$ in chloroform. This sample was prepared by treatment of $[C_7H_7Mo(CO)_3]PF_6$ with $NaBD_3CN$. (C) The ^{2}H spectrum of $C_7H_7DMo(CO)_3$ after being heated in octane for 1 h.

shown that a similar rearrangement apparently occurs in $C_6D_6HMn(CO)_3$ via an η^4-benzene intermediate.[26] This nonspecific migration contrasts with the interpretation of Pauson[27] of [1,5]-migrations in seven-membered rings attached to $Cu(CO)_3$. As Lamanna and Brookhart[26] suggest, however, the apparent specificity of the rearrangment probably arises from preferred geometries of the substituted intermediates.

The current interest in these metal-assisted rearrangments[2,26,27] suggests that many workers may be using a variety of physical methods to identify the isomers. It is clear from our work that NMR, particularly ^{2}H NMR, is the most reliable technique for following specificity and that low-frequency IR bands may be suspect.[28] A further caveat regarding intensity measurements in ^{1}H NMR is in order. We have found that the relaxation times of the endo and exo protons are significantly different and those in a CHD group are particularly long. Thus, the use of pulsed NMR spectrometers can often lead to erroneous measurements of relative intensities of H_{olefin} to H_{endo} to H_{exo}, if relaxation reagents or long pulse delays are not used.

Although we have considered only nucleophilic hydride addition, one might also note that protonations appear to occur by initial addition to the metal followed by migration to an endo position on the ring.[17,29,30]

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Registry No. $C_7H_8Mo(CO)_3$, 12125-77-8; $C_7H_7DMo(CO)_3$, 74244-62-5; $[C_7H_7Mo(CO)_3]PF_6$, 56253-18-0.

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[25] Faller, J. W.; Murray, H. M.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 2306.

[26] Brookhart, M.; Lamanna, W. Abstracts, IXth Organometallic Chemistry Conference, Dijon, Sept 1979, p C55; *J. Am. Chem. Soc.* **1980**, *102*, 3490.

[27] Foreman, M. I.; Knox, G. R.; Pauson, P. L.; Todd, K. H.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1141.

[28] The coupling of the vicinal H to the endo and exo methylene H(D) appears to provide the most reliable method of assignment. The upfield shift of H_{exo}, found in the $C_7H_8M(CO)_3$ complexes and attributed to ring currents,[29] may be reversed in some cases. That is, H_{endo} is at higher field in some rhodium complexes.[17,30]

[29] Winstein, S.; Kaesz, H. D.; Kreiter, C. G.; Friedrich, E. C. *J. Am. Chem. Soc.* **1965**, *87*, 3267.

[30] Brown, J. M.; Coles, D. G. *J. Organomet. Chem.* **1973**, *60*, C31.

A Comment on the Nature of "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$"

Sir:

Otsuka and co-workers have recently reported the preparation of compounds formulated as "$[Mo_2(N_2Ph)_3(S_2CNR_2)_4]$"[1] (R = Me or Et) by the reaction of $[MoO_2(S_2CNR_2)_2]$ with $PhNHNH_2$. As we have also studied this reaction and appeared to have isolated quite different prod-

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[1] A. Nakamura, M. Nakoyama, K. Sugihashi, and S. Otsuka, *Inorg. Chem.*, **18**, 394 (1979).