the mechanism requires the transfer of hydrogen from 5′-deoxyadenosine to substrate with the re-formation of the coenzyme Co–C bond. This step seems unlikely because the methyl group is normally considered inert. We would like to emphasize that, held close to the cobalt by the protein, this may not be so and the metal atom may be involved directly in the activation of the $C_5$′-methyl group.

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## An Investigation of the Trans Effect in Some Cobalt(III) Complexes by $^{19}F$ Nuclear Magnetic Resonance Spectroscopy

*Sir:*

Cis and trans effects in six-coordinate cobalt(III) complexes have been observed[1] mainly in studies of the thermodynamics and kinetics of replacement reactions. We have previously reported[2-4] investigations by $^1H$ nmr spectroscopy of the cis effect in corrinoids,[2] cobalt(III) dimethylglyoximates,[3] and cobalt(III) Schiffs base complexes.[4] However, $^1H$ chemical shifts are small and their interpretation is sometimes complicated[4] by "through-space" effects such as those due to the ring currents of aromatic ligands and the electric field associated with dipoles in the complex. $^{19}F$ chemical shifts, on the other hand, are larger and in meta- and para-substituted fluorobenzenes, for example, have been used[5-7] to investigate the $\sigma$- and $\pi$-donor properties of substituents, inasmuch as they can be separated. Thus the meta shift, $\Delta_m$, may be considered[6] a $\sigma$-electron effect parameter, while the difference between the para, $\Delta_p$, and meta shifts, $(\Delta_p - \Delta_m)$, has been termed[6] a $\pi$-electron-effect parameter. The availability[8] of aryl derivatives of cobalt(III) complexes of the type $m$-($p$-) $FC_6H_4Co(III)\{(DO)(DOH)pn\}X$ (1), where $\{(DO)(DOH)pn\}$ is diacetylmonoximeimino diacetylmonoximatoiminopropane-1,3 and X is an anionic ligand, has made possible an investigation of the trans effect and allows a comparison with a similar study[9] of cis and trans effects in square-planar *trans-m-* (*p*-) fluorophenylbis(triethylphosphine)platinum complexes.

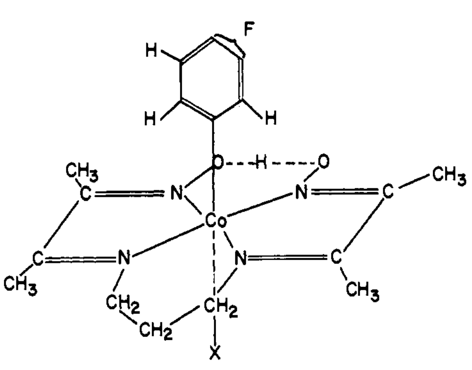

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**Table I.** $^{19}F$ Nmr Chemical Shifts[a] of *m*-Fluoroaryl–Cobalt(III)[b] and –Platinum(II) Complexes

|  | $m$-$FC_6H_4Co$-$\{(DO)(DOH)pn\}X$ |  | $m$-$FC_6H_4Pt$-$(P(C_2H_5)_3)_2X$[c] |  |
|---|---|---|---|---|
| X | In $CH_2Cl_2$ | In $(CH_3)_2SO$ | In $(CH_3)_2CO$ | In $C_6H_{12}$ |
| $CH_3$ | 3·05 | 3·05 | 3·93 | 4·26 |
| $m$-$FC_6H_4$ | 1·99 | 2·05 | 3·07 |  |
| OCN (or NCO) | *d* | 0·98 | 2·30 | 2·48 |
| Br | *d* | 0·68 | 1·97 | 2·34 |
| SCN (or NCS) | *d* | 0·52 | 1·75 | 1·90 |
| I | *d* | 0·50 | 1·56 | 2·00 |

[a] Relative to $C_6H_5F$. [b] The complexes were characterized by $^1H$ nmr spectroscopy and had satisfactory elemental analyses. [c] From ref 9. [d] Not sufficiently soluble.

**Table II.** $^{19}F$ Nmr Chemical Shifts[a] of *p*-Fluoroaryl–Cobalt(III)[b] and –Platinum(II) Complexes

|  | $p$-$FC_6H_4Co$-$\{(DO)(DOH)pn\}X$ |  |  | $p$-$FC_6H_4Pt(P(C_2H_5)_3)_2X$[c] |  |  |
|---|---|---|---|---|---|---|
| X | In $CH_2Cl_2$ | In $(CH_3)_2SO$ | $(\Delta_p - \Delta_m)$[d] | In $(CH_3)_2CO$ | In $C_6H_{12}$ | $(\Delta_p - \Delta_m)$[e] |
| $CH_3$ | 11·3 | 11·3 | 8·25 | 11·7 | 11·7 | 7·77 |
| $p$-$FC_6H_4$ | 10·4 | 10·6 |  | 10·8 | 10·8 |  |
| OCN (or NCO) | *f* | 9·72 | 8·74 | 10·1 | 10·2 | 7·80 |
| I | 9·46 | 9·73 | 9·23 | 9·54 | 9·70 | 7·98 |
| Br | 9·46 | 9·73 | 9·05 | 9·86 | 10·0 | 7·89 |
| SCN (or NCS) | *f* | 9·29 | 8·77 | 9·29 | 9·20 | 7·54 |

[a] Relative to $C_6H_5F$. [b] The complexes were characterized by $^1H$ nmr spectroscopy and had satisfactory elemental analyses. [c] From ref 9. [d] Data derived from measurements in $(CH_3)_2SO$. [e] Data derived from measurements in $(CH_3)_2CO$. [f] Not sufficiently soluble.

The $^{19}F$ chemical shifts $\Delta_m$ and $\Delta_p$ of the Co(III) complexes are given in Tables I and II, together with comparable data[9] for the Pt(II) complexes. Considered as substituents of fluorobenzene, both the Co(III) and the Pt(II) complexes behave as strong donors (relative to hydrogen) particularly when they are para substituents. The $\Delta_m$ values suggest that the Co(III) complexes are consistently poorer $\sigma$ donors (better $\sigma$ acceptors) than the Pt(II) complexes, but, most interestingly, the effect of the trans ligand X is qualitatively the same in both sets of complexes, with the resultant $\sigma$ donation (to the aryl ligand) decreasing in the order $CH_3 > m$-$FC_6H_4 >$ OCN(NCO)[10] > Br > SCN(NCS)[10] > I and shown in Figure 1a. The previous investigation[3] of the cis effect had concluded that the

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(10) We have not been able to obtain conclusive evidence of the nature of the ligand atom in the cyanato complexes. Preliminary studies indicate that thiocyanate coordinates mainly *via* sulfur.

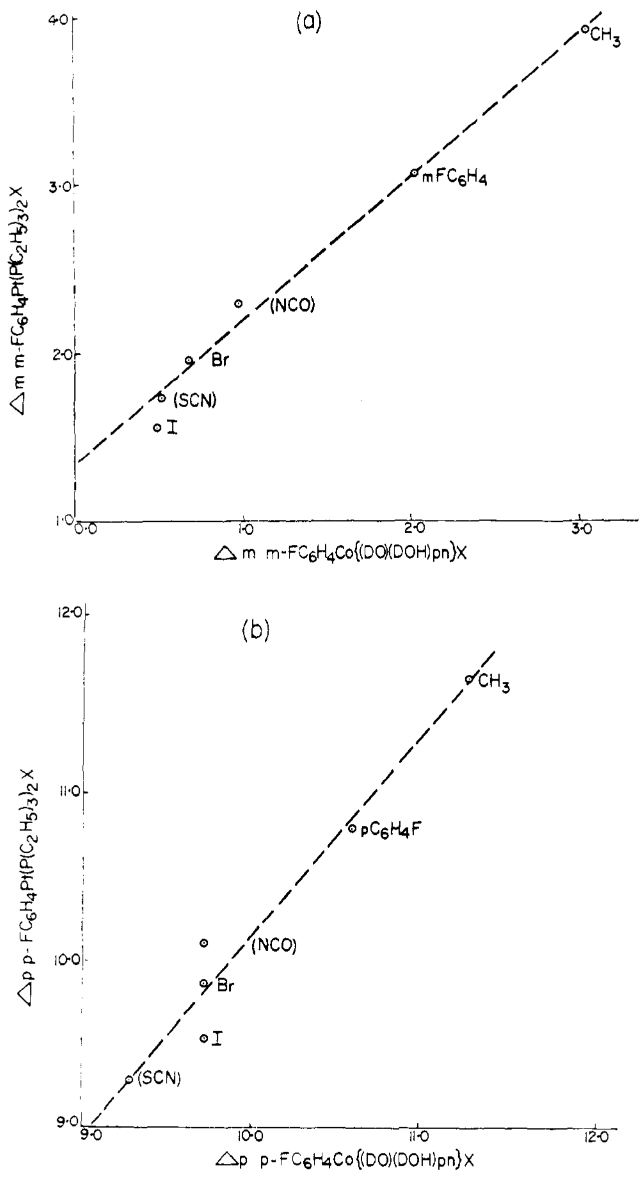

Figure 1. Plot of the $^{19}$F chemicals shifts (ppm) of (a) *m*-FC$_6$H$_4$Co-{(DO)(DOH)pn}X in (CH$_3$)$_2$SO *vs.* *m*-FC$_6$H$_4$Pt(P(C$_2$H$_5$)$_3$)X in (CH$_3$)$_2$CO and (b) *p*-FC$_6$H$_4$Co{(DO)(DOH)pn}X in (CH$_3$)$_2$SO *vs.* *p*-FC$_6$H$_4$Pt(P(C$_2$H$_5$)$_3$)$_2$X in (CH$_3$)$_2$CO.

$\sigma$-donor properties of the ligand were mainly responsible for the observed $^1$H chemical shifts. Differences between the Co(III) and Pt(II) complexes are more apparent in $\Delta_p$ values, since they include both $\sigma$ and $\pi$ interactions (Figure 1b). The $\pi$-electron-effect parameters, ($\Delta_p - \Delta_m$), Table II, imply that the Co(III) complexes are better $\pi$ donors (poorer $\pi$ acceptors) than the Pt(II) complexes and, interestingly, show a greater sensitivity to the trans ligand X. The donor properties of the metal complexes have different dependence on X: for Co(III), I > Br > SCN(NCS) > OCN(NCO) > CH$_3$; for Pt(II), I > Br > OCN(NCO) > CH$_3$ > SCN(NCS). The different orders may be accounted for if it is assumed that the thiocyanate ligand acts as a $\pi$ donor in the Co(III) complexes and a $\pi$ acceptor in the Pt(II) complexes.

These results suggest that $\sigma$-bonding effects in cobalt(III) and platinum(II) complexes are similar; that there is extensive $\pi$ interaction with aryl ligands coordinated in complexes of *both* metals which is modified by the trans ligand; and that the two metal ions are differently sensitive to the influence of the trans ligand X in as far as it affects the $\pi$ interaction with the aryl ligand.

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## Structure and Photochemical Reactivity of Excited States of Halopentaamminerhodium(III) Complexes[1]

*Sir:*

The photochemical behavior of rhodium(III)–ammine complexes is of interest both for its uniqueness and for its similarities to the behavior of other nd$^6$ complexes. For example, features which seem common to the photochemistries of nd$^6$ complexes (especially of cobalt, rhodium, and platinum) are wavelength-dependent product yields and oxidation–reduction reactions subsequent to the irradiation of charge transfer to metal bands.[2,3]

A feature of great potential significance in the photochemistry of rhodium(III) is the relatively high product yields which result from irradiation of ligand field absorption bands.[3–5] It is the purpose of this report to call attention to some unanticipated inferences which may be made based on the photochemical behavior which results from the ligand field excitation of Rh$^{III}$(NH$_3$)$_5$X (X = Cl, Br, I) complexes. It has been reported that ligand field excitation of Rh(NH$_3$)$_5$Cl$^{2+}$ and Rh(NH$_3$)$_5$I$^{2+}$ [3] results in predominantly (*i.e.*, >90%) halide or ammonia aquation, respectively (eq 1 and 2). We have now found that Rh(NH$_3$)$_5$Br$^{2+}$ exhibits intermediate behavior, *i.e.*, Br$^-$, NH$_4^+$, *trans*-Rh(NH$_3$)$_4$OH$_2$Br$^{2+}$, and Rh(NH$_3$)$_5$OH$_2^{3+}$ result from the irradiation of the ligand field absorption bands of this complex (see Table I).

$$H_2O + Rh^{III}(NH_3)_5X + h\nu(d-d) \left\{ \begin{array}{ll} \xrightarrow{\Phi_X} Rh(NH_3)_5OH_2^{3+} + X^- & (1) \\ \xrightarrow{\Phi_{NH_3}} \textit{trans}\text{-}Rh(NH_3)_4OH_2X + NH_4^+ & (2) \end{array} \right.$$

All three halopentaammine complexes of rhodium(III) quench the biacetyl phosphorescence but do not affect the fluorescence at room temperature. Stern–Volmer quenching plots are linear and consistent with similar studies of the sensitized photolysis of coordination complexes.[2,6,7] However, for these rhodium(III) com-

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[7] V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *ibid.*, **93**, 339 (1971).