Cs+ the shift of $\bar{\nu}_{\max}$ is only -500 cm^{-1}.[10] In the same series in $PtCN_4^{2-}$, where the emission is thought to involve the orbitals ($6p_z$, $5d_{z^2}$), the variation is ~2000 cm^{-1} in the other direction. Since a major component of the proposed transition is the $5d_{z^2}$ orbital, one might expect considerably more variation than is seen.

It is disappointing that no clear choice is indicated for the assignment. However, one can examine the possibilities of a further assumption of the authors cited.[6e] In the cases where there is little or no structure evident in the absorption band they suggest that the transition can be correlated, through intermediate D_{2d} symmetry, to a low-lying ^3T_d state; this is the case for the weak red absorption. This would explain the observed similarity of the absorption and emission bands. Another point to be noted in this respect is that the absorption and emission do not overlap; that is, there is no obvious $\bar{\nu}_{0'-0}$ transition. While there are a number of possible conditions under which the intensity of this transition may be made very low, it is also consistent with a transition between two states of greatly differing geometry such as square planar to (distorted) tetrahedral.

The experimental evidence is then that the emission (a) has a band width similar to the nearest absorption, (b) does not clearly overlap the absorption, (c) is primarily polarized in the xy plane, and (d) is quite insensitive to z-axis perturbation. This behavior is consistent either with MTK alternative (A) with unique e_u vibration mixing or with emission from a low-lying T_d-like state.

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[10] A. Zanobi, Laurea Thesis, Istituto Chimico, Università di Roma, Oct 1969.

Correspondence

Phosphine Exchange in Carbonylchlorobis(dimethylphenylphosphine)-rhodium(I)

Sir:

Early in 1969 we described[1] the conditions that lead to nuclear magnetic resonance AX decoupling in A′AX systems. We showed specifically that the methyl proton magnetic resonance (pmr) in some planar methylphosphine complexes might appear as a singlet, a doublet (with varied splitting), or a complex multiplet, the "virtually coupled" triplet of trans planar complexes being a well-known example.

To summarize these results for an equilibrium such as that indicated by reaction 1 under nonparamagnetic conditions, where L = L*, a methylphosphine, B, is a

$$ML_2B_2 + L^* \rightleftarrows MLL^*B_2 + L \qquad (1)$$

nonmagnetic ligand, and M is a metal to which L and B are coordinated, the following pmr spectra of the methyl group may be expected.[2]

I. With[3] $[L] \ll [ML_2B_2]$ and very slow chemical exchange of L, the spectrum will appear as a doublet, $J_{PH} \approx 10$–14 Hz,[4] if $J_{PP'} \approx 0$ as in a cis planar complex. If $J_{PP'} \gg (J_{HP} - J_{HP'})$ as in a trans planar complex, then the pmr spectrum will appear as a triplet.[5]

II. With $[L] \ll [ML_2B_2]$, $J_{PP'}/J_{PH} > 5$, and $J_{PH}/J_{P'H}$ near unit magnitude,[6] the pmr spectrum will appear as a "triplet" under slow-exchange conditions, a "singlet" with intermediate exchange rates, and a "doublet" under conditions of fast chemical exchange of L.

III. With $[L] \approx [ML_2B_2]$, fast chemical exchange, and the coupling conditions for ML_2B_2 present in II, the pmr spectrum for the methyl group will be a doublet in which the coupling constant is related to the weighted average of the coupling constants for coordinated and uncoordinated phosphine. The chemical shift should also be an average value.[7] Since the sign of J_{PH} is positive for L and negative for ML_2B_2 in those cases studied,[4] a singlet will be produced at a ratio of free to coordinated phosphine near 3–5, depending on the specific value of J_{P-H} in coordinated and uncoordinated phosphine.

IV. With $[L] \gg [ML_2B_2]$ and fast chemical exchange, a narrow doublet typical of uncoordinated L will appear.

At the time of our[1] study we were unaware of any *single system* which clearly *displays* the *conditions set out in all four of the above*. The *trans*-$RhCl(CO)(P(CH_3)_2C_6H_5)_2$ complex studied by Deeming and Shaw[8] appears to fit these conditions so well that this correspondence is prompted. As reported (loosely quoted) by Deeming and Shaw, the complex (*ca.* 0.3 *M* in benzene) shows a 1:2:1 triplet pattern (conditions as in I) which is almost unaltered by the addition of 0.01 mol of $P(CH_3)_2C_6H_5$ (slow-exchange conditions of II). With 0.02–0.03 mol of added phosphine a singlet is obtained (intermediate exchange rate conditions of II) which on further addition broadens and starts to form a doublet until, with 0.08 mol of added phosphine, a well-defined 1:1 doublet

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[1] J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, **91**, 1941 (1969).

[2] The captions in Figures 2 and 3 of ref 1 were inadvertently interchanged.

[3] The brackets refer to the concentrations of the species.

[4] W. McFarlane, *Chem. Commun.*, 58 (1967).

[5] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); *Inorg. Chem.*, **5**, 701 (1966).

[6] A reasonable value for a *trans*-ML_2B_2 complex appears to be ~3.

[7] A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, 89 (1966).

[8] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 597 (1969).

is obtained (fast-exchange conditions of II). As more $P(CH_3)_2C_6H_5$ is added, the doublet separation decreases (conditions of III) until with 4.7 mol of added phosphine a singlet is obtained (as described in III). On further addition, about 12 mol of $P(CH_3)_2C_6H_5$, a narrow doublet is formed (conditions of IV) which on further addition of phosphine approaches the doublet separation of the free phosphine.

Deeming and Shaw correctly analyzed[9] the pmr spectrum of the rhodium complex under conditions as described in III and IV and assumed that to explain the results for ~0.08 mol of added phosphine "rapid ligand exchange will eliminate coupling with the Rh [^{103}Rh, $I = {}^1/_2$; 100% abundance but J_{Rh-H} only ~1 Hz in the complex], with other P nuclei . . . also effects due to strong phosphorus–phosphorus coupling across the rhodium atom." In other words, time averaging is assumed to have eliminated the anticipated splitting due to spin–spin coupling. It is on this latter point that these authors are incorrect. *Strong P–P coupling is required to obtain the observations of II.* This coupling decouples the phosphorus–hydrogen atom coupling.

Assuming that $J_{PP'} \approx 80$ (a reasonable value for trans planar phosphine complexes[10]), one estimates that the lifetime for phosphine exchange in $RhCl(CO)(P(CH_3)_2C_6H_5)_2$ is approximately 4×10^{-3} sec, under those conditions which produce the observed singlet at $[P(CH_3)_2C_6H_5] \approx 0.02–0.03\ M$. If equilibrium 1 exists, this number reflects a bimolecular rate constant of $\sim 2.5 \times 10^2\ M^{-1}\ sec^{-1}$. Thus the exchange rate appears to be similar to that for substitution in other planar group VIII complexes.[11,12]

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[9] These authors assumed the presence of a five-coordinate species in equilibrium with the four-coordinate rhodium complex and the free phosphine but that the concentration of this five-coordinate species is never significant. There is nothing in their data that requires formation of a five-coordinate species, except perhaps as a transition state, provided equilibrium 1 occurs.

[10] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, **6**, 1133 (1967).

[11] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 351.

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