Electron Paramagnetic Resonance Studies on Some Group VIII Transition Metal Complexes

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Electron paramagnetic resonance (EPR) is a technique which has come into common usage to obtain structural and electronic information about transition metal complexes.[1] This technique has been utilized to obtain structural information about a series of five coordinate cobalt(II) trisphosphine complexes and their dioxygen adducts,[2] and to determine the nature of bonding of various bases to a rhodium dimer-nitroxide spin label complex.

A series of five coordinate cobalt(II) trisphosphine complexes ($Co(PR_3)_3L_2$, where R_3 = Me_3, Me_2Ph, $MePh_2$ and L = Br, CN) and their dioxygen adducts were investigated using EPR to enhance the understanding of oxygen binding to cobalt(II) complexes and to explain the formation of an unusual cobalt dimer discovered by Halpern and co-workers[3] which possesses dioxygen bound to cobalt in a ring-bonding mode, I.

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The $Co(PR_3)_3Br_2$ complexes with $g_{\parallel}$ ~2.4 and $g_{\perp}$ ~2.08 and broad unresolved hyperfine of the $g_{\parallel}$ signal are assigned a trigonal bipyramidal geometry with two phosphine ligands in axial positions and one phosphine and two bromide ligands in equitorial positions. This assignment is supported by an x-ray crystal structure of $Co(PF_2Ph)_3Br_2$.[4] The $Co(PR_3)_3(CN)_2$ complexes with g_1 ~2.18, g_2 ~2.14 and g_z ~2.01 and extensive hyperfine splitting in all regions due to cobalt (I = 7/2) and phosphorus (I = 1/2) are assigned a square pyramidal geometry with one axial phosphine and two cyanides and two phosphines in trans positions in the basal plane.

The dibromide complexes do not react with oxygen. Oxygen does react with the dicyano complexes by replacing the axial phosphine to form a five coordinate cobalt(II) dioxygen complex. This was the first time a five coordinate cobalt(II) dioxygen complex in which there are no chelating ligands was reported.[2] This unusual complex also appears to be the intermediate which leads to the formation of Halpern's[3] cobalt dimer with the ring-bonded oxygen.

There is an ongoing controversy in the literature about the ability of dirhodium tetracarboxylate dimers to undergo π as well as σ interaction with bases binding to the two axial sites.[5-10] In an effort to clarify this controversy the Q-band EPR spectra of the nitroxide spin label 2,2,6,6-tetramethylpiperidinyl-1-oxy (TMPNO) bound to one rhodium of dirhodium tetraperfluorobutyrate ($Rh_2(pfb)_4$) with the addition of σ and π bonding bases to the second rhodium was investigated.

Upon addition of TMPNO to $Rh_2(pfb)_4$ the g value of TMPNO increases 0.0105 from 2.0047 to 2.0152. This same effect was first observed with $Rh_2(O_2CCF_3)_4$[11] and is the largest g shift (Δg) yet reported for a bound nitroxide. Binding various bases (B) to the second rhodium atom causes a decrease in Δg of the bound TMPNO indicating a decreased Rh-TMPNO bond strength. The values of Δg range from 0.0083 for ethyl acetate, a weak base, to 0.0025 for piperidine, a strong base. Thus as the B-Rh bond strengthens the Rh-TMPNO bond weakens. To quantify this effect the E and C equation was utilized.[12]

$$-\Delta H = E_A E_B + C_A C_B$$

The E_A and C_A numbers for $Rh_2(pfb)_4$ had previously been determined[9] as well as the E_B and C_B numbers for the bases studied.[12] Thus the heats of formation, $-\Delta H$, due to the σ only interactions between $Rh_2(pfb)_4$ and bases were determined and a linear relationship was found between $-\Delta H$ and Δg for most of the bases. However, some bases, most notably acetonitrile and pyridine, were found to deviate substantially from this correlation in a manner which indicates π bonding must also be present. These results are in good agreement with previously published thermodynamic results.[5,6,9]

References

1. "Electron Spin Resonance," Vol. 1, London Chemical Society, John Wright and Son, Ltd., Bristol, England, 1971/72.
2. R. S. Drago, J. R. Stahlbush, D. J. Kitko and J. Breese, J. Am. Chem. Soc., 102, 1884 (1980).
3. J. Halpern, B. L. Goodall, G. P. Khare, H. S. Lim and J. J. Pluth, J. Am. Chem. Soc., 97, 2302 (1975).
4. O. Stelzer, W. S. Sheldrich and J. Subramanian, J. Chem. Soc., Dalton Trans., 966 (1977).
5. R. S. Drago, S. P. Tanner, R. M. Richman and J. R. Long, J. Am. Chem. Soc., 101, 2897 (1979).
6. R. S. Drago, J. R. Long and R. Cosmano, Inorg. Chem., 20, 2920 (1981).
7. G. G. Christoph, J. Halpern, G. P. Khare, Y. B. Koh and C. Romanowski, Inorg. Chem., 20, 3029 (1981).
8. B. E. Bursten and F. A. Cotton, Inorg. Chem., 20, 3042 (1981).
9. R. S. Drago, J. R. Long and R. Cosmano, Inorg. Chem., 21, 2196 (198
10. R. S. Drago, Inorg. Chem., 21, 1697 (1982).

11. R. M. Richman, T. C. Kuechler, S. P. Tanner and R. S. Drago, J. Am. Chem. Soc., 99, 1055 (1977).

12. R. S. Drago, Struct. Bonding, 15, 73 (1973).