The bonding may be seen to be satisfactory by a simple valence-bond analysis in which the nine valence shell orbitals of each metal atom are divided into three sets. Three empty trigonally directed (hybrid) orbitals are used for σ bonds to the CO groups. Three more filled orbitals are used mainly for π donation to the CO groups. This leaves three half-filled trigonal orbitals directed approximately toward the neighboring three CO atoms. The entire set of 12 such orbitals and 12 electrons suffices to form six two-electron Co–Co bonds and six empty Co–Co antibonding orbitals. An equivalent MO formulation[9] in which the electronic configuration is $(A_1)^2(E)^2(T_2)^2(T_1{}^*)(T_2{}^*)$ or $(A_1)^2(T_2)^2(E)^2(T_1{}^*)(T_2{}^*)$ (where the asterisk denotes an antibonding orbital) has also been developed.[10]

To summmarize and extend into the realm of prediction (something which a pragmatically valid idea should be capable of) the foregoing ideas, the following specific statements are made.

(1) Two reasonable molecular structures containing bridges are possible and interconvertable by the mechanism suggested here. These are the only ones of the type in which there are only singly bridging CO groups (so-called "ketonic" bridges) and no more than one such bridge on any edge of the Co_4 tetrahedron.

(2) It is thus quite possible and indeed likely (though *not* certain) that both Smith and Corradini are correct—each for the phase with which he was dealing.[10a]

(3) There is considerable likelihood that if either or both of the rearrangement processes considered, *i.e.*, $A \rightleftharpoons B$, $A \rightleftharpoons C$, are sufficiently fast, all CO groups will appear nmr equivalent (using ^{13}C or ^{17}O) even though they are not in either of the structures B or C.[10–12]

(4) The opportunity for facile internal rearrangement is even greater than that implied by the $A \rightleftharpoons B$, $A \rightleftharpoons C$ paths. The close resemblance of the arrangement of the CO groups in structure A to the arrangement of the 12 vertices of a cuboctahedron leads to the following idea. The Co atoms can be thought of as instantaneously lying inside one set of four triangular faces of the cuboctahedron, leaving another unoccupied, tetrahedrally disposed set of triangular faces. There are then three twofold axes about which the Co_4 tetrahedron may rotate to bring it into the alternative orientation. Should such a process actually occur, it would constitute a case of valence tautomerism or steric nonrigidity quite as remarkable in its scale as that provided by Bullvalene.[13]

(5) While the structure of T_d symmetry which has no bridging groups has not been observed for $Co_4(CO)_{12}$, the general trend[14] toward lower stability of CO-bridged, M–M-bonded pairs of metal atoms as compared to unbridged pairs, as one goes from carbonyl-type compounds of the first transition series to their analogs in the second and third series, leads to a structural prediction, namely, that just possibly $Rh_4(CO)_{12}$, but much more probably $Ir_4(CO)_{12}$, may have structure A in the crystal, in solution, or in both.

Postscript.—In the discussion following the presentation of this material at the Middle Atlantic Regional Meeting of the American Chemical Society, Professor L. F. Dahl announced (a) that Dr. C. H. Wei and he have conclusively ascertained Corradini's structure for crystalline $Co_4(CO)_{12}$ by three-dimensional work, (b) that $Rh_4(CO)_{12}$ seems likely to have the same structure, but (c) that $Ir_4(CO)_{12}$ has structure A. It will be interesting to see how well the other predictions offered here stand up to experimental test.

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[9] F. A. Cotton, unpublished work.

[10] The possibility of $B \rightleftharpoons C$ interconversion which bypasses A and instead involves a structure with just the $Co^{(1)}$–$Co^{(2)}$ and $Co^{(2)}$–$Co^{(3)}$ bridges is relatively unattractive since (1) a sequential shifting seems less likely than a concerted shift and (2) this intermediate would appear to be much less stable than A.

[10a] NOTE ADDED IN PROOF.—The author has been informed by Professor R. K. Sheline, Department of Chemistry, Florida State University, that measurements of the Co^{59} nmr spectrum of $Co_4(CO)_{12}$ in *n*-hexane solution (H. Haas, Ph.D. Thesis, Florida State University, 1965) show two closely spaced absorptions in an intensity ratio of about 3:1. If the ratio is truly 3:1, this result is most naturally explained by postulating that Corradini's structure is present in solution. Assumptions as to the weakness or overlap of CO stretching bands must then be made. It would then also be necessary to assume that neither structure A nor structure C is stable enough to persist in appreciable concentration in solution. However, the suggested intramolecular exchange of CO environments *via* structure A remains valid.

[11] The exchange of CO with $Co_4(CO)_{12}$ has already been studied[12] in benzene at 25° with the conclusion that all CO groups in the molecule exchange at the same rate. Such a result is, of course, an obvious corollary to point 3. However, in view of the ideas presented here, the dissociative mechanism previously suggested[12] is considered unnecessary and unlikely.

[12] D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).

[13] W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); *Tetrahedron*, **19**, 715 (1963).

[14] To be discussed in detail in a future publication with G. Yagupsky, but certainly apparent to those familiar with the field.

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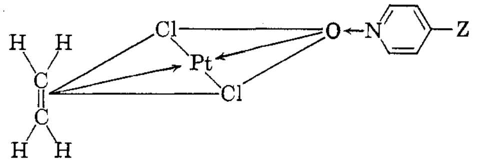
On the Interpretation of the Nuclear Magnetic Resonance Data of Kaplan and Orchin for Platinum–Olefin Complexes

Sir:

Kaplan and Orchin have recently shown[1] that in complexes of type I electron-withdrawing groups Z decrease the shielding of the ethylene protons. This is the result expected (as Kaplan and Orchin point out) from a decrease of platinum–ethylene back-bonding.



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A more surprising result is that electron-withdrawing groups increase the coupling between the Pt^{195} and the H^1 nuclei. Kaplan and Orchin rationalize this finding by postulating a variation in the Pt–C_2H_4 bond length. There is, we believe, a simpler explanation.

The π^* orbitals of C_2H_4, into which the metal do-

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[1] P. D. Kaplan and M. Orchin, *Inorg. Chem.*, **4**, 1393 (1965).

nates electrons, are odd under reflection in the plane between the two carbon atoms. This is a true symmetry plane of the molecule (at least in $[Pt(C_2H_4)(NH(CH_3)_2)Cl_2]$,[2] as well as in Zeise's salt itself).[3] It follows that the metal→ligand bond has no metal s-orbital character and therefore is not responsible for the Pt–H coupling. While hybrid orbitals with some metal s character may readily be drawn from the metal toward each lobe of the ligand π^* orbital, these hybrids are not true molecular orbitals, and the above symmetry arguments show that their contributions to the Pt–H coupling must exactly cancel.

It follows that the Pt–H coupling arises entirely from the ligand→metal σ bond. The nodal plane of that π orbital of the C_2H_4 fragment which is involved in this bond is not a symmetry plane of the molecule, and the bond can mix with the C–C σ bond. This is tantamount to saying that the carbon atoms can rehybridize in the same way (though doubtless not to the same extent) as in cyclopropane, if we regard the latter as derived from ethylene and a bent singlet carbene group. [Coupling could also arise from the carbon p orbitals in C–C π and C_2H_4–Pt σ bonds, if the hydrogen atoms are bent away from the metal and the C_2H_4 group is no longer coplanar, but in any case, such a loss of planarity would itself be a consequence of the rehybridization suggested here.]

The increase in Pt–H coupling with electron-withdrawing character of the group Z is then no longer surprising. An electron-withdrawing group Z will reduce the pyridine N-oxide→metal σ bonding and make the metal a better acceptor in the C_2H_4→metal σ bond. This leads directly to the observed increase in coupling, by increasing the Pt s character in this bond.[4] The large amount of coupling implies that the C_2H_4 fragment is appreciably rehybridized in all cases.

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[2] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Cryst.*, **13**, 149 (1960).

[3] J. A. Wunderlich and D. P. Mellor, *ibid.*, **7**, 130 (1954); **8**, 57 (1955).

[4] This does not imply a large change in the amount of carbon s character in this bond. Such a change would tend to cause the proton resonances to move upfield, contrary to observation, and Kaplan and Orchin[1] therefore reject this possibility. The present argument is that Pt–H coupling depends on both the C s character and the Pt s character in the C_2H_4→Pt σ bond. The first is large (since the coupling is large) but not necessarily sensitive to the group Z. The second is expected to be sensitive to Z, in such a way as to account for the observed changes in Pt–H coupling constant.

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