A reply to the Note of Poilblanc and Bigorgne, concerning assignments of CO fundamentals in $M(CO)_{6-n}L_n$ molecules

Poilblanc and Bigorgne[1] have recently raised two problems on both of which a few further remarks appear justified.

(*1*) *The assignment in trans-$ML_3(CO)_3$ molecules*. It is true that some of my previous conclusions[2] in this respect are incorrect, but this is *solely* and *precisely* because they were based upon the *erroneous data* published by Poilblanc and Bigorgne[3]. There is no fault in the logic used in the attempt to interpret the erroneous data.

Leaving aside the curious fact that they now make no attempt to explain the presence of the band at 1909 cm^{-1} in the spectrum of *trans*-$Mo(CO)_3[P(OC_2H_5)_3]_3$, I accept their suggestion that the genuine bands are those at 1988, 1890, and 1883 cm^{-1}. With these frequencies we reason as follows. The 1988 band must be due to the A_1^2 mode. Using only the criterion of whether the force constants are reasonable, the other two bands could be assigned either 1890 (A_1^1), 1883 (B_1) or the reverse, since, the sets of force constants obtained are equally acceptable. They are, respectively, $k_1 = 14.61$, $k_2 = 15.04$, $k_1 = 0.36$, and $k_1 = 14.52$, $k_2 = 15.12$, $k_1 = 0.35$. However, on the basis of the kind of intensity considerations explained by Orgel[4], it seems safe to say that the first one is correct. Thus, given correct experimental data, I reach exactly the same conclusion as Poilblanc and Bigorgne.

Moreover, now that we know from the new data that the A_1^1 and B_1 modes in the $P(OC_2H_5)_3$ complex are very close together, there is no longer any reason to question the assignment in the $P(C_2H_5)_3$ compound which places both the A_1^1 and B_1 frequencies at $\sim$ 1846 cm^{-1}. Indeed, the possibility that the 1887 cm^{-1} band *could* belong to this molecule would now appear highly unlikely. It is therefore gratifying that Poilblanc and Bigorgne have now succeeded in recording the spectrum of well-purified samples and find that the band at 1887 cm^{-1} which was shown in their earlier paper but not assigned or otherwise explained, is indeed due to a contaminant in the earlier samples.

The assertion that I "found questionable" the assignments made by Poilblanc and Bigorgne for *trans*-$Mo(CO)_3[P(OC_6H_5)_3]_3$ is not accurate, perhaps because of readily understandable linguistic difficulties. I merely observed that an interchange in the assignment of the two low energy bands could not be ruled out on the basis of the force constants. The use of an intensity argument, once again, to resolve such an ambiguity seems sound and I accept their assignment as the more probable one.

It could be said that the fact that the original assignment of Poilblanc and Bigorgne[3] for *trans*-$Mo(CO)_3[P(OC_2H_5)_3]_3$, using the set of frequencies 1988, 1909, 1883 cm^{-1}, was consistent with the intensities but clearly unacceptable by reason of the force constants, as I pointed out, while, at the same time, the assignment I proposed gave acceptable force constants but unlikely relative intensities could have been taken as a signal that the experimental data were in some way incorrect. Because the data of Poilblanc and Bigorgne[3] were so often obtained from measurements on a *mélange réactionnel*, where there was much overlapping of bands, I tended to place little reliance in the intensity criteria, and therefore failed to put forward such an argument.

(This statement is *not* intended as a criticism of the experimental competence of Poilblanc and Bigorgne. On the contrary, knowing from experience the formidable experimental difficulties they faced, their work arouses my admiration.)

In summary, with the new data reported above by Poilblanc and Bigorgne, they and I agree entirely on the assignments in the *trans*-M(CO)$_3$L$_3$ molecules.

(2) *The spectra of diamine- and triamine-substituted species.* The idea of Poilblanc and Bigorgne to use methyl-substituted en and dien to improve solubility is ingenious and admirable; but it is not the answer to all difficulties regarding solvent effects for several reasons. First, it is not completely effective in rendering all compounds soluble in non-polar, non-H-bonding solvents. For their Mo(CO)$_3$dien analog they were still forced to use a polar solvent (in which their data differ insignificantly from those obtained by Kraihanzel and Cotton[5] in a different polar solvent); they then apply an empirical correction, of uncertain accuracy, to obtain frequencies they believe applicable for the hypothetical hydrocarbon solution of this compound.

Second, and more important, is that if one wishes to compare data, either in the form of frequencies as Poilblanc and Bigorgne do or in the form of derived force constants as we have done, it is important that solvent effects be *uniform* for all compounds compared. The best kind of uniformity would of course be that in which there is a virtual absence of solvent effects due to the non-polar nature of the solvent used in *every* case. However, there are a number of interesting compounds, for example, those containing alcohols and ethers which are prepared photochemically[6], which cannot be isolated* and then examined in hydrocarbon solvents since they are formed only in the corresponding alcohol or ether. Thus, it can certainly be argued that for the certain purposes, particularly to compare data for an extensive list of compounds, not *all* of which can be measured in non-polar solvents, the fact that *some* can be is not particularly helpful. In other words, there are times when it is preferable to have extensive comparisons using data which are all from polar solvents, rather than limited comparisons using data all from non-polar solvents, *and vice versa*. Each type of study has its place and purpose. It was with the former type that Ref. 2 was concerned.

(3) If one is to insist that the use of data from non-polar solvents is *de rigueur* one should also insist on taking account of anharmonicity, since the latter might cause shifts comparable to solvent effect shifts. It does not seem to me to be logical to emphasize only one of these two things.

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* Attempts were made at M.I.T. to isolate the compounds measured *in situ* in this paper (Ref. 6) but without success or any indication that they are stable enough to do so.