metal–olefin bond was more important than the σ component in nickel(0)–, palladium(0)–, and platinum(0)–olefin complexes, was drawn from the observation[123] that replacing triphenylphosphine by the more strongly electron-donating tri-*p*-tolylphosphine increased the stabilities of the metal–olefin complexes $[(PR_3)_2M(C_2H_4)]$ (see Table XX).

C. Stability of Acetylene Complexes

Where directly comparable data are available, as in the case of silver(I) and iridium(I), acetylenes appear to form complexes that are slightly less stable than the corresponding olefin. Where the olefin can exist in two isomeric forms, the silver–alkyne complexes have a stability intermediate between the cis- and the trans-olefin stability. In the case of alkyl-substituted alkynes the stabilities of the silver(I) complexes show a similar susceptibility to the substituents as the olefin complexes do. These great similarities between the stabilities of olefin and acetylene complexes support a bonding scheme for acetylene complexes that is analogous to that described above (section IV) for olefin complexes.[16]

V. Application of Results

Probably the most important result to emerge from the study of the stabilities of metal–olefin complexes in solution is that the entropy change on complex formation is almost invariably negative. As a result the stability constants fall with increasing temperature. Thus if it is desired to isolate a metal–olefin complex, it will be best to use as low a temperature as possible, although this may necessitate waiting some time. When it is desired to use an olefin complex as an intermediate in a reaction in which an olefin is being treated with a reagent in the presence of a metal catalyst, then again as low a temperature should be used as is consistent with a reasonable rate in the subsequent reaction.

In many catalytic reactions a very stable metal–olefin complex is undesirable because its very stability inhibits the reaction. Thus, for example, the oxidative hydrolysis of ethylene to acetaldehyde can occur in the presence of either palladium(II) or platinum(II). However, platinum(II) forms a very stable olefin complex that requires boiling in water to effect the reaction, whereas palladium(II) olefin complexes react instantaneously with water[127] to yield carbonyl compounds. The accumulated thermodynamic data can be used to select a metal ion which gives a complex of suitable stability for a given reaction, although it is apparent that much more data are required than are currently available.

The thermodynamic data for metal–olefin systems can be used to consider the likely mechanisms of reactions involving metal–olefin complexes. However, great care must be exercised when using the data in this way because the data are thermodynamic in origin whereas the mechanism of a reaction is controlled by both kinetic and thermodynamic factors with the former often predominating. Thus it is possible to have two intermediates present, one in much lower concentration than the other, but because the former reacts much faster the actual mechanism of the reaction proceeds through this intermediate.

VI. Conclusions

It is apparent that a number of factors influence the stability of metal–olefin complexes. The present data are still rather limited for all metal ions except silver(I), and a full understanding of the factors involved in the interaction of metals and olefins will not be obtained until a great deal more data have been obtained for other metal ions. This is particularly true in view of the fact that the electronic influence of substituents in olefin complexes of silver(I), copper(I), and mercury(II) is apparently opposite to their influence in olefin complexes of the group VIII metals.

Acknowledgments. The author wishes to thank Professor W. Partenheimer for his many useful comments during the preparation of this review and Johnson, Matthey and Co., Ltd., for their generous support of the project of which this review forms a part.

---

[127] F. R. Hartley and J. L. Wagner, *J. Chem. Soc. A*, 2282 (1972).

ERRATUM

Volume 72, 1972

Synthetic Methods Involving Neighboring Group Interaction in Ortho-Substituted Nitrobenzene Derivatives. By P. N. Preston and G. Tennant

Page 677: Footnote 396 should read as follows: "A number of papers relevant to some of the sections of this review have appeared in the literature subsequent to the submission of the manuscript for publication. These have been summarized in an Appendix which appears following these pages . . ., etc."