

ORGANOMETALLIC REACTIONS OF PLATINUM INVOLVING METALLIC HYDRIDES*

George M. Whitesides, Robert H. Reamey, Robert L. Bratnard,
Alan N. Izumi, and Thomas J. McCarthy

*Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138*

INTRODUCTION

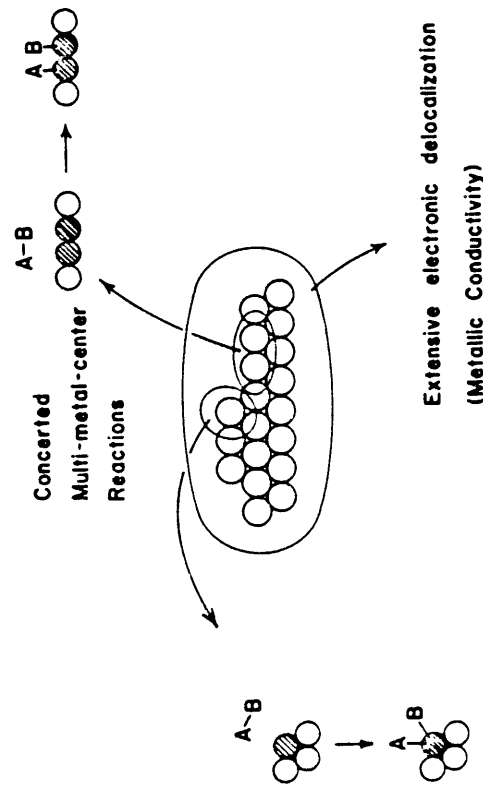
Hydroalkylmetal compounds are intermediates in a large number of reactions—both homogeneous and heterogeneous—that are catalyzed by transition metals. We have maintained a program for some years designed to examine the mechanisms of elementary reactions in which carbon-hydrogen bonds are broken by oxidative addition to platinum, and formed by reductive elimination from it. Our work has focused on platinum for two reasons. First, many soluble platinum organometallic compounds are stable and easily characterized, and thus suitable for detailed mechanistic study. Second, platinum is a useful heterogeneous catalyst, with catalytic activity in reforming and olefin hydrogenation.¹⁻⁴

One objective of our work is to compare the chemistry of homogeneous alkyls with that of metal surface alkyls. This work is intended to help clarify several central problems in current research in catalysis. Does the catalytic activity displayed by aggregated metals (either bulk metal or metal clusters) reflect special electronic features associated with this aggregation, or is heterogeneous catalysis by aggregated metals simply localized surface organometallic chemistry (FIGURE 1)? Do the arrays of adjacent metal centers in a heterogeneous catalyst participate in reactions in some cooperative way, or do these metal atoms act singly?

It will be difficult to resolve these questions fully. The approach we have taken to these problems lies in comparison of the reactivities of alkyl groups attached to single metal atoms in soluble organometallic compounds with those of alkyl groups attached to metal surfaces. We suggest that if the reactions observed for alkyl groups in soluble organometallic complexes closely resemble those of alkyl groups on metal surfaces, then we may be able to rationalize the heterogeneous catalytic reactions in terms of single-center or highly localized chemistry. If, on the other hand, the reactions observed for heterogeneous metal alkyls have no counterpart in soluble organometallic chemistry, then we must consider carefully the possibility that aggregated metals possess unique reactivity.

Carbon-hydrogen bond activation provides one reaction that may be used to explore this problem. This reaction occurs readily over a wide variety of metal clusters and bulk metals,^{1,2} but has been observed only infrequently for single metal atoms in soluble organometallic complexes.³⁻⁷ Why is there this difference?

* This work has been supported by the National Science Foundation, most recently by Grant CHE-82 05143, and by grants to the Harvard Materials Research Laboratory.



Surface Organometallics

FIGURE 1. Why are bulk metals (or metal clusters) catalytically active? Is catalysis by metals a single metal atom phenomenon, one requiring cooperating metal atoms, or one requiring extensive electronic delocalization over many centers?

RESULTS AND DISCUSSION

Mechanisms

Most of our work on the mechanisms of reactions of soluble organometallic compounds has been concerned with bis(trialkylphosphine)alkylplatinum(II) complexes. The techniques used to study the transformations of these compounds are an exceptional mixture of kinetics, isotopic labeling, and thermodynamics. All of these methods are straightforward in principle (although often demanding in practice), with the possible exception of the thermodynamics. Obtaining accurate kinetic data (on which the thermodynamic parameters rest) in organometallic systems may be difficult. Rates can be influenced by precipitation of zero-valent metals, by trace impurities, by air and water, and by the surfaces of reaction vessels. Further, the interpretation of the thermodynamic parameters—especially the activation entropy—requires caution. We will not review these methods and problems in this paper, and instead refer to the several published papers that contain details.⁸⁻¹⁵ Here we only summarize relevant results.

For most thermal decomposition reactions of complexes having the structure L_2PtR_2 , a critical step is an initial dissociation of a phosphine ligand (although occasional exceptions to this apparent requirement for initial dissociation are known). A representative scheme is that for the β -hydride elimination reaction observed in bis(tri-*n*-butylphosphine)diethylplatinum(II)⁸ and bis(triethylphosphine)diethylplatinum(II).⁹ A reaction mechanism for the latter is outlined in FIGURE 2. The coordinately unsaturated complex $LPtR_2$ appears to be the essential reactive species in this and many similar reactions. We suggest that the creation of a vacant coordination site on this four-coordinate soluble

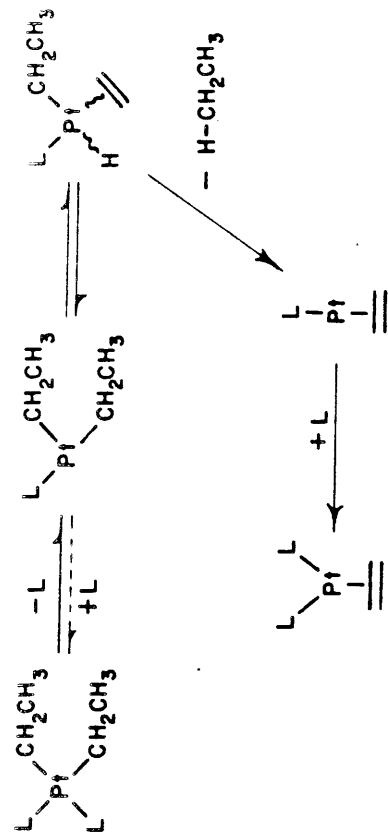


FIGURE 2. β -Hydride elimination. Mechanism of thermal decomposition of $(Et_3P)_2PtEt_2$.

platinum complex is analogous to the formation of a reactive site on the surface of a phosphine-poisoned heterogeneous catalyst. Once this vacant, reactive site has been formed, a number of subsequent reactions appear to occur rapidly.

Activation of β Carbon-Hydrogen Bonds

As a generalization, this type of C—H bond cleavage reaction is one that occurs most rapidly for those platinum complexes having accessible β carbon-hydrogen bonds. The β -hydride elimination reaction is, however, usually not the overall rate-limiting step: in some instances, the initial phosphine dissociation is rate limiting; in others, a subsequent reductive elimination of alkane with concomitant carbon-hydrogen bond formation seems to be slow. In certain cases, reductive elimination of alkane is not possible (as in the decomposition of complexes having the structure L_2PtClR) and olefin loss or, perhaps, β -hydride activation is the rate-limiting step.

Activation of γ Carbon-Hydrogen Bonds

This reaction has been of particular interest to us because it provides an intramolecular model for the reaction of greatest interest as a probe for comparisons of soluble and surface metal alkyls, that is, *intermolecular* activation of unactivated carbon-hydrogen bonds. The reaction is also of considerable interest as an important step in the many processes that form metallacycles by internal cyclometalation.¹⁶

The mechanism of a typical reaction—that of thermal decomposition of bis(triethylphosphine)lineopentylplatinum(II)—is shown in FIGURE 3. This reaction is very similar to that observed for β -hydride activation for L_2PtR_2 complexes: an initial dissociation of phosphine is followed by reversible γ carbon-hydrogen activation, and the overall rate-limiting step is reductive elimination of neopentane with concomitant carbon-hydrogen bond formation. We have studied this reaction

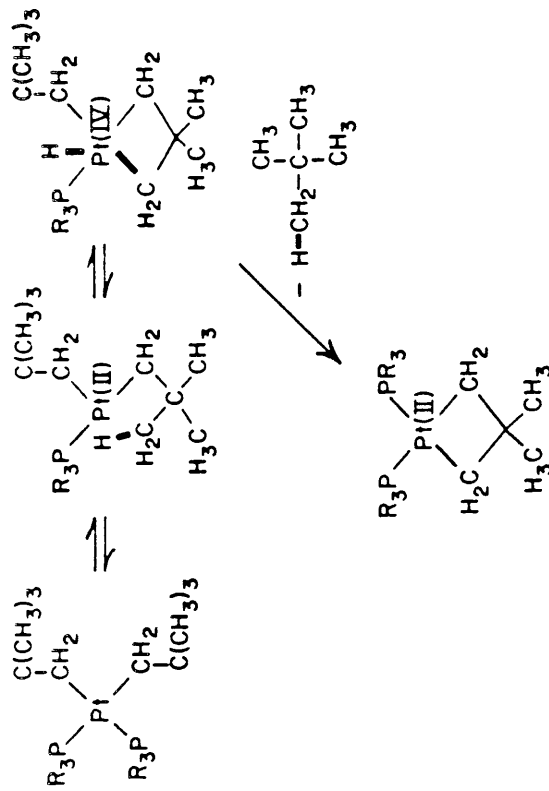


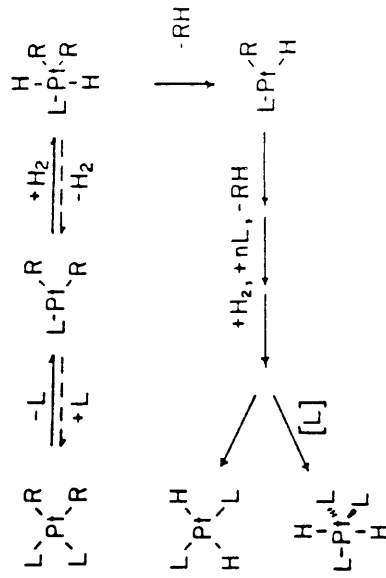
FIGURE 3. γ Carbon-hydrogen bond activation. Mechanism of thermal decomposition of $(Et_3P)_2Pt(CH_2C(CH_3)_3)_2$.

in considerable detail,¹⁰ trying to understand why it proceeds so readily while the corresponding intermolecular reaction proceeds unobservably slowly. Although this analysis is not yet complete, it is sufficiently advanced to exclude a number of possible reasons for the difference in the intra- and intermolecular reactions. Differences in bond energies are probably not dominant, since the bonds formed in both inter- and intramolecular reactions are similar. It is unlikely that electronic effects due to differences in bond angles are sufficient to explain the difference. There seems to be no particular stability associated with the formation of platinumacyclic rings.¹⁴ Hence, it seems probable that the intramolecular reaction proceeds in preference to the intermolecular reaction because of some combination of differences in reaction entropy and differences in the amount of intramolecular nonbonded steric strain. At present, the relative contribution of these two factors is not known. Probably both are significant.

Although the reason for the facility of the intramolecular activation reactions is not well understood, the qualitative fact that they occur readily is important. There is, thus, little question that an unactivated carbon-hydrogen bond will react readily with a platinum atom present in the ligand environment provided by one phosphine and two alkyl groups: adjacent or aggregated platinum centers are not required for reactivity toward unactivated C—H bonds.

Intermolecular Reactions

We have never observed authentic intermolecular activation of carbon-hydrogen bonds by oxidative addition of alkanes to the platinum(II) center in complexes of

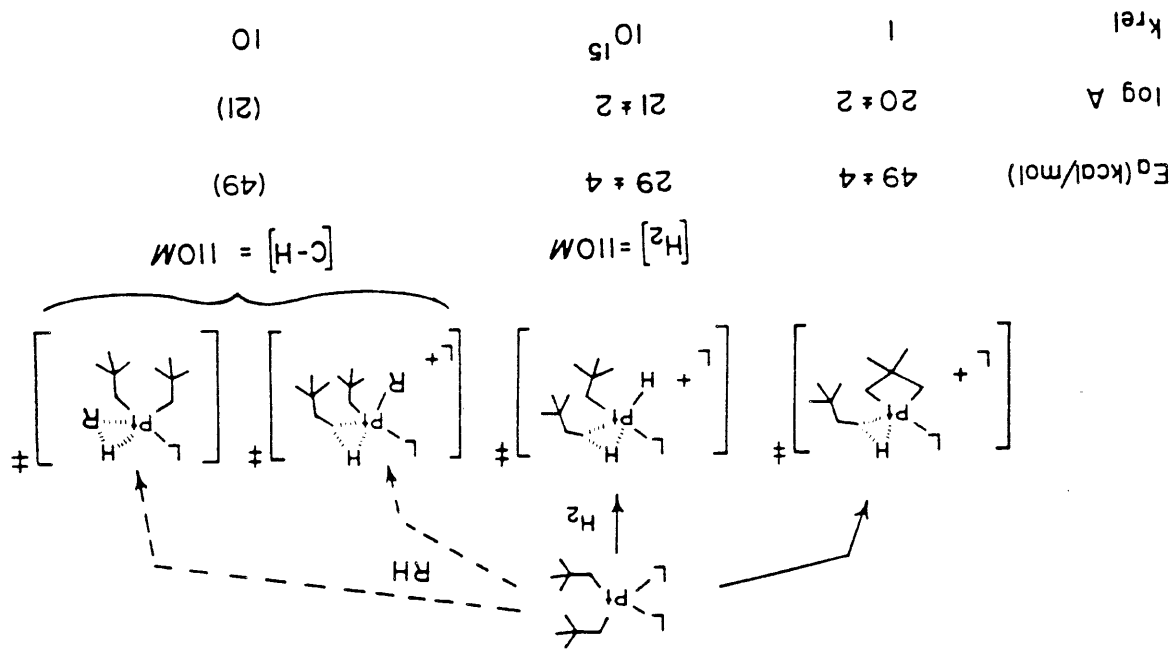
FIGURE 4. Mechanism of reaction of $(Et_3P)_2Pt(CH_2C(CH_3)_3)_2$ with H_2 .

structure L_2PR_2 , although recent work from a number of other research groups has provided examples of carbon-hydrogen bond activation by reaction with soluble metal centers in solution.⁵⁻⁷ The contrast between the homogeneous and heterogeneous reactivity of platinum toward carbon-hydrogen bonds is striking. Intermolecular reactions of dihydrogen with coordinatively unsaturated platinum centers is, however, a facile reaction, and occurs by a mechanism very similar to that of the intramolecular reaction that cleaves carbon-hydrogen bonds¹⁵ (FIGURE 4). Why does dihydrogen react so much more readily than compounds containing carbon-hydrogen bonds? By how much do the two reaction types differ in rate?

We have made a qualitative estimate for these rate differences by comparing thermodynamic parameters for intramolecular carbon-hydrogen activation and intermolecular hydrogen-hydrogen activation (FIGURE 5). Our estimate was calculated by assuming that intermolecular carbon-hydrogen bond activation of a solvent molecule (assumed to be cyclohexane) would proceed with the *activation energy* of the *intramolecular* reaction and the *activation entropy* of the *intermolecular* reaction with dihydrogen.[†] The result of this calculation is that intermolecular activation of carbon-hydrogen bonds of solvent would be expected to occur 10 times faster than intramolecular activation of carbon-hydrogen bonds. Thus expectation is not in accord with experiment, and is thus based on one or more incorrect premises. What are they? We do not presently know, and will not be certain until we have been able to examine and analyze authentic intermolecular carbon-hydrogen bond-cleaving reactions. We note, however, that the estimation summarized in FIGURE 5 explicitly neglects substantial differences between nonbonded interactions for addition of the carbon-hydrogen bond of cyclohexane to L_2PR_2 and those for addition of (the much smaller) H_2 . There may also be significant differences in the entropies of the transition states for these reactions, reflecting restrictions to bending or torsional motions.

[†] To facilitate comparison, concentration of H_2 was set equal to the concentration of C—H bonds in pure cyclohexane (110 M).

FIGURE 5. Comparisons of kinetic parameters for several organometallic reactions, and estimates of the relative rate of inter- and intramolecular reactions breaking carbon-hydrogen bonds.



Whatever the origin of the failure of the calculation summarized in FIGURE 5, several useful facts emerge from it. First, the relative rates of intra- and intermolecular cleavage of comparable carbon-hydrogen bonds by addition to an $LPtR_2$ fragment are probably not greatly different. Second, the slower rate of the intermolecular reaction is not due exclusively to the difference in entropy arising from the necessity of combining two particles into one: the effective concentration of C-H bonds in liquid hydrocarbon is very high. Third, the most probable (in our opinion) origin for the slowness of the intermolecular reaction is steric congestion in the transition state. This congestion might be reflected in either E_a (that is, in nonbonded steric strain) or in $\log A$ (restricted rotation and bending in a crowded transition state).

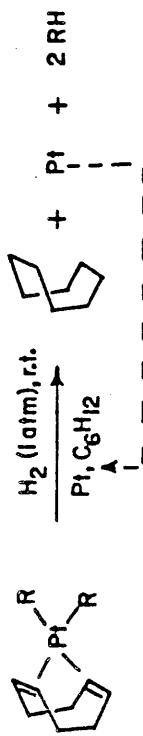
Heterogeneous Reactions

The original problem posed in this study was that of understanding why bulk platinum metal activates carbon-hydrogen bonds intermolecularly with considerable facility, while platinum ions in soluble complexes do not do so. We have suggested that there are three broad types of rationalizations for this difference.

1. The bulk metal has characteristic electronic features reflecting cooperative interactions between metals or extensive electronic delocalization that give it unique catalytic activity.
2. The bulk metal provides no more than an array of individual metal surface atoms, but these metal atoms are, by their nature, coordinatively unsaturated and hence highly reactive.
3. Catalysis involves some mechanism intermediate between 1 and 2, that is, localized surface organometallic chemistry, but organometallic chemistry requiring cooperation of several adjacent metal centers.

In order to distinguish between these possibilities, it is important to develop techniques for studying heterogeneous catalytic reactions over metals. There is general agreement that metal surface alkyls are intermediates in many of these catalytic systems, and considerable evidence concerning their structures (at least under certain circumstances). There is, however, little agreement concerning the factors that influence the rates of formation or transformation of these intermediates. For mechanistic studies in this area, we would like to be able to prepare alkyls on the surfaces of catalytically interesting transition metals by routes independent of those normally used in catalysis, and under circumstances in which carbon skeletons and isotopic labeling patterns are (at least initially) well defined. Ideally, we would like to be able to carry out these preparations under conditions similar to those encountered during heterogeneous catalytic reactions.

Our efforts in this area have so far centered on heterogeneous catalytic hydrogenation, rather than on carbon-hydrogen activation. The reason for this choice is pragmatic: we have developed a new type of experimental system that is applicable to studies of the mechanism of the former reaction, but not (yet) to that of the latter reaction. In this new approach, we examine the heterogeneous platinum-catalyzed reduction by dihydrogen of soluble (bisolefin)diethylplatinum(II)



Proposal:

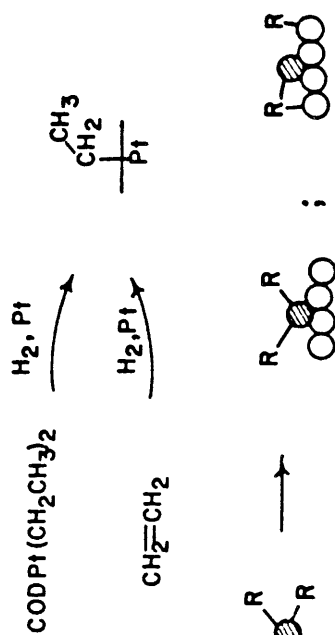


FIGURE 6. Heterogeneous platinum-catalyzed hydrogenation of $(COD)PtR_2$.

complexes (FIGURE 6).¹⁸ We believe that this reaction proceeds by initial adsorption of the organoplatinum compound on the catalyst surface, with concomitant dissociation into adsorbed diolefin and adsorbed "diethylplatinum." Once the alkyl group originally present in the dialkyl platinum moiety has been transferred to the platinum surface, we believe that it loses its memory of its origin, and becomes indistinguishable from corresponding alkyl groups formed by reaction of olefins with hydrogen on the metal surface. Evidence supporting the proposed reaction mechanism is summarized elsewhere.¹⁸ The essential features of this evidence are:

1. The kinetics of the platinum-catalyzed reduction of (cycloocta-1,5-diene)-dimethylplatinum(II) by dihydrogen are very similar to those for the reduction of typical olefins by dihydrogen using the same catalyst system.
2. Hydrogen interchange occurs between the olefin and the alkyl groups during reduction. This exchanging hydrogen can, in turn, exchange with deuterium present in deuterated solvents.[†] We infer that the exchanging hydrogen is present as mobile platinum surface hydride.
3. The platinum metal originally present in the soluble organoplatinum complex plates or precipitates on the surface of the catalyst. This process constantly renews the surface of the heterogeneous catalyst and effectively prevents its poisoning. The system is thus a particularly easy one to study kinetically.

[†] Methanol- d_4 or diethyl ether saturated with D_2O was used in these experiments, using procedures outlined in Reference 18.

4. The relative rates of certain diagnostic reactions (especially hydrogen-deuteration exchange between adsorbed alkyl groups and solvent and reductive elimination of alkyl groups from the surface to form alkanes) are the same for the catalytic reduction of ethylene and of (cyclooctadiene)diethylplatinum.

What have studies of this heterogeneous catalytic reaction involving homogeneous organometal complexes shown to date? Some of the chemistry of the alkyl groups transferred to the catalyst surface via soluble (diolefin)diethylplatinum complexes is similar to that of platinum alkyl complexes in solution, but other features of the chemistry of these species are quite different. Similarly, the catalytic reduction of the diolefin group originally present in the soluble organoplatinum complex is similar to that observed in separate heterogeneous hydrogenation of the diolefin, but here also there are significant differences in reactivity. We give one example of characteristic reactivity observed for the alkyl and diolefin moieties in the heterogeneous reduction of (diolefin)diethylplatinum(II) complexes.

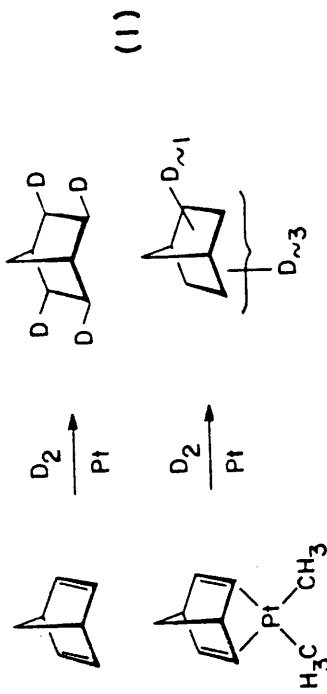
Relative Rates of α and β Carbon-Hydrogen Bond Activation in Soluble Complexes and on Surfaces

In solution, the relative rates of carbon-hydrogen bond activation are, in general, $\beta > \gamma > \alpha$ (α carbon-hydrogen bond activation is seldom observed for organoplatinum compounds in solution). On the platinum surface, the relative rates of these reactions can be inferred by determining the relative rates of deuterium transfer to cyclooctadiene from, e.g., $\text{Pt}(\text{CH}_2\text{CD}_3)_2$ and $\text{Pt}(\text{C}_2\text{H}_5)_2$. These results indicate qualitatively that the relative rates of C-H bond-cleavage reactions are $\alpha > \beta, \gamma$. This result is significant in that it suggests either a bridging alkylidene species **1** or a surface carbene **2** is readily formed on the surface.



Stereochemistry of Olefin Hydrogenation

Deuteration of norbornadiene over supported platinum yields almost entirely the *exo* deuterated product. Deuteration of (norbornadiene)dimethylplatinum yields a mixture of deuterated species, containing a significant quantity of *endo* deuterated material (the ratio of *endo*- to *exo*-deuterium is approximately 3:1 (Equation 1)). The *exo* stereochemistry observed for the deuteration of norbornadiene itself is consistent with initial adsorption of the olefin on its least hindered side. Rationalization of the stereochemistry of hydrogenation of (norbornadiene)dimethylplatinum is less clear because of the complexity of the product mixture formed. The result is consistent with (but does not demand) an



initial adsorption of NBdPtMe_2 at platinum, followed by transfer of the diolefin to the metal surface on its *endo* face and subsequent reduction at this face.

Exploration of this new catalytic heterogeneous reaction has just begun. It is, however, one that offers promise of a range of opportunities for the preparation and study of otherwise inaccessible platinum surface alkyls, especially those -phenyl , CF_3 , CH_3 that would be impossible to form from olefinic precursors by hydrogenation.

CONCLUSION

What do we conclude from these studies concerning the origin of the apparent difference in the ability of bulk platinum, and of individual soluble platinum atoms present in organometallic complexes of structure $\text{L}(\text{PR})_2$, to break carbon-hydrogen bonds? Our tentative conclusion is that, in fact, the intrinsic reactivity of platinum in these two different environments toward carbon-hydrogen bonds may not be very different. In solution, however, for reasons that are not yet entirely clear, intramolecular carbon-hydrogen bond activation involving the alkyl platinum moieties or the phosphines, or some other reaction involving the phosphines, is sufficiently rapid that it essentially precludes intermolecular carbon-hydrogen bond activation. If it were possible to suppress this (these) intramolecular reaction, it should then be possible to observe intermolecular carbon-hydrogen activation. The technical key to further progress in this area thus seems to be the design and synthesis of phosphines and alkyl ligands that are capable of maintaining the platinum (or other transition metal) centers in soluble, reactive form, but are themselves unreactive in cyclometalation, intramolecular carbon-hydrogen activation, or other reactions.

SUMMARY

This paper discusses mechanisms of a number of elementary reactions of organoplatinum compounds in solution, with particular emphasis on reactions that activate carbon-hydrogen bonds. It also summarizes a new reaction—the platinum-catalyzed heterogeneous hydrogenation of soluble (diolefin)diethylplatinum(II) compounds—which provides a bridge between the chemistry of soluble and surface platinum alkyls.

ACKNOWLEDGMENTS

A number of individuals other than those listed as coauthors have made important contributions to this work. The names of these individuals will be found in the references listed in the text.

REFERENCES

1. WEBB, G. 1978. *In Catalysis* 2: 145-175. The Chemical Society, London, England.
2. KUZNETSOV, B. N., Y. I. YERMAKOV, M. BOUDART & J. P. COLLIMAN. 1978. *J. Mol. Catal.* 4: 49-55.
3. CSICSERY, S. M. 1979. *Adv. Catal.* 28: 293-321.
4. VASSILIEV, Y. B., V. S. BAGOTZKY, O. A. KHAZOVA, V. V. CHERNY & A. M. MERFITSKY. 1979. *J. Electroanal. Chem.* 98: 253-272.
5. JANOWICZ, A. H. & R. G. BERGMAN. 1982. *J. Am. Chem. Soc.* 104: 352-354.
6. CRABTREE, R. H., M. F. MELLEA, J. M. MIHELIC & J. M. QUIRK. 1982. *J. Am. Chem. Soc.* 104: 107-113.
7. HOYANO, J. K. & W. A. G. GRAHAM. 1982. *J. Am. Chem. Soc.* 104: 3723-3725.
8. WHITESIDES, G. M., J. F. GAASCH & E. R. STEDRONSKY. 1972. *J. Am. Chem. Soc.* 94: 5258-5270.
9. MCCARTHY, T. J., R. G. NUZZO & G. M. WHITESIDES. 1981. *J. Am. Chem. Soc.* 103: 3396-3403.
10. FOLEY, P. R., DICOSIMO & G. M. WHITESIDES. 1980. *J. Am. Chem. Soc.* 102: 6713-6725.
11. NUZZO, R. G., T. J. MCCARTHY & G. M. WHITESIDES. 1981. *J. Am. Chem. Soc.* 103: 3404-3410.
12. IBERS, J. C., R. DICOSIMO & G. M. WHITESIDES. 1982. *Organometallics* 1: 13-20.
13. DICOSIMO, R. & G. M. WHITESIDES. 1982. *J. Am. Chem. Soc.* 104: 3601-3607.
14. DICOSIMO, R., S. S. MOORE, A. F. SOWINSKI & G. M. WHITESIDES. 1982. *J. Am. Chem. Soc.* 104: 124-133.
15. REAMEY, R. H. & G. M. WHITESIDES. *J. Am. Chem. Soc.* (Submitted)
16. WEBSTER, D. E. 1977. *Adv. Organomet. Chem.* 15: 147-188.
17. PARSHALL, G. W. 1975. *Acc. Chem. Res.* 8: 113-121.
18. MCCARTHY, T. J., Y.-S. SHIH & G. M. WHITESIDES. 1981. *Proc. Nat. Acad. Sci. USA* 78: 4649-4651.

IRIDIUM HYDRIDES WITH DI(TERTIARY PHOSPHINE) BRIDGES AND CHELATES*

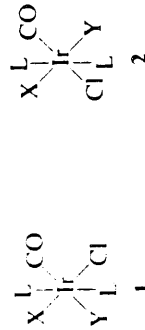
Richard Eisenberg and Barbara J. Fisher

Department of Chemistry
University of Rochester
Rochester, New York 14627

INTRODUCTION

The activation of substrate is an essential step in catalysis, and generally involves a weakening or breaking of bonds within the substrate. The effectiveness of transition metal complexes as catalysts is closely related to their ability to perform this process. Substrate activation is often accomplished by donation of electron density from filled metal d orbitals into vacant antibonding orbitals of the substrate, thus perturbing its electronic structure, and resulting in an oxidative addition reaction if a substrate bond is cleaved. Complexes of electron-rich metals are particularly effective in activating substrates in this manner, and within this genre, no set of complexes has been more vigorously studied over the past two decades than those of Rh(I) and Ir(I). Complexes of these d⁸ ions possess a rich oxidative addition chemistry, and are active as catalysts for a variety of reactions including hydrogenations, hydroformylation, and carbonylations (see Reference 1 for examples).

While complexes of Ir(I) are often not as catalytically active as analogous Rh(I) systems, the electron richness of Ir(I) frequently yields more stable substrate adducts and oxidative addition products (see Reference 2 and references therein). In this context, Vaska's complex, IrCl(CO)(PPh₃)₂, is especially notable, undergoing reactions with numerous substrates including H₂, HX (X = Cl, Br, or I), MeI, BzBr, RCOX, and R₃SiH among others.³⁻⁵ In this reaction chemistry and that of closely related analogues, the phosphine ligands L generally maintain their *trans* disposition and yield stable adducts having Structures 1 or 2 depending on the substrate XY and the mechanism of adduct formation.



In this paper, we describe our studies on iridium complexes containing di(tertiary phosphine) ligands. These ligand systems may either chelate a single metal center or bridge two Ir ions. The former leads to a *cis* stereochemistry of phosphine donors different from that observed in most adducts of Vaska's complex

* This research was supported in part by the National Science Foundation and by the Office of Naval Research.