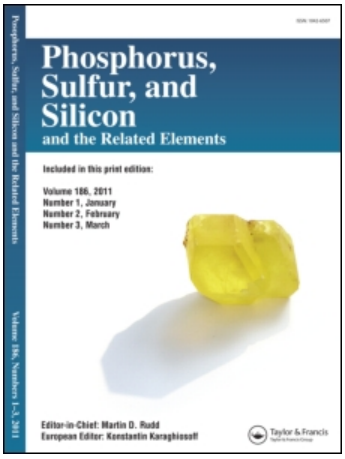

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THE ROLE OF PHOSPHORUS LIGANDS IN THE REVERSIBLE ACTIVATION OF SMALL MOLECULES BY METAL COMPLEXES

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Abstract The influence of $(aryl)_3P$ and $(alkyl)_3P$ ligands on the reversibility of oxidative addition reactions of metal complexes is discussed and illustrated by the reactivity of $[Ir(C\ell)(CO)(R_3P)_2]$ (R = alkyl or aryl).

INTRODUCTION

Since the reports in early 1960's of an unusual reactivity of a triphenylphosphine complex, $[Ir(C\ell)(CO)(Ph_3P)_2]$,[1-3] many important advances have been made in the activation of small molecules and homogeneous catalysis by tertiary phosphine complexes of transition metals.[4-9] There remain, however, some subtle questions regarding the role of phosphorus ligands in the reversibility of these processes. In this note we offer some thoughts on this subject by examining some previously reported data.

REACTIONS OF $[Ir(C\ell)(CO)(Ph_3P)_2]$ WITH SMALL MOLECULES

Our model compound is known to react with a large number and variety of species, XY, by either cleaving the X-Y bond (X-Ir-Y), commonly called *oxidative addition reactions*, or leaving it intact (Ir-XY) but with accompanying reduction of the bond order. Some examples are given in Eq. (1).

$$[Ir(C\ell)(CO)(Ph_3P)_2] + XY \rightleftharpoons [(XY)Ir(C\ell)(CO)(Ph_3P)_2] \qquad (1)$$

X-Y bond cleaved: H_2, $HC\ell$, H_2S, HCN, $C\ell_2$, CH_3I, etc.
X-Y bond intact: O_2, CO, CO_2, C_2H_2, C_2H_4, SO_2, etc.

Most of these reactions, especially in the second category, are readily reversible, and for some systems kinetic, thermodynamic, mechanistic and structural data have been obtained, including the analyses of

electronic and steric effects of the ligands.[10-12] The roles of the reacting molecule (XY)[4] and the activator complex[5] have been examined, and it has been concluded that the addition reactions are best interpreted as generalized acid (XY)-base (metal complex) interactions, but that the roles of the two reactants may be reversed when the addendum (XY) exhibits basic or amphoteric properties relative to the metal complex.[4,5]

WHAT DETERMINES THE REVERSIBILITY?

This question has been answered in terms of the acid-base concept referred to above, but the influence of the phosphine ligands on the reversibility does not seem to have been fully elucidated. To this end, some previously reported data[10] are briefly analyzed.

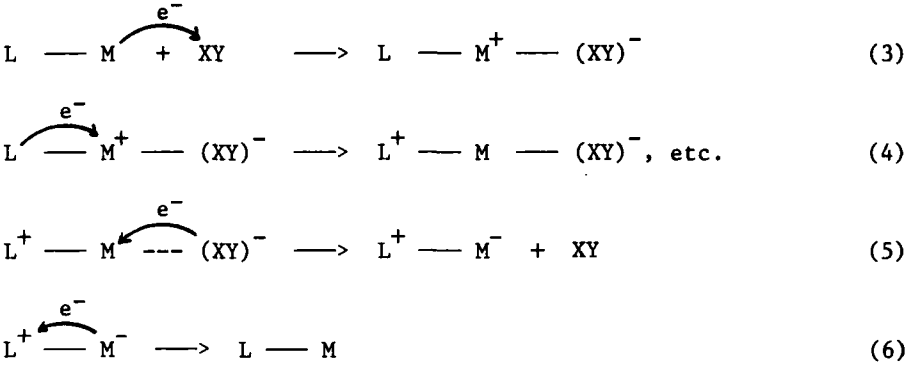
For the reversible activation of molecular oxygen, Eq. (2),

$$[Ir(C\ell)(CO)(R_3P)_2] + O_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [(O_2)Ir(C\ell)(CO)(R_3P)_2] \qquad (2)$$

the following observations emerge when the reaction rates are compared for complexes with $(aryl)_3P$ and $(alkyl)_3P$ ligands, and correlated with the "latent basicity" of $[Ir(C\ell)(CO)(R_3P)_2]$. The latter is a function of R in R_3P, and is reflected by the ν_{CO} in the complex. While the rates of oxygenation (k_2) generally increase, as expected, with increasing basicity of R_3P (except in cases of significant steric differences), the reverse reaction (k_{-1}) does not appear to be a sole function of base strength of the complex. Instead, the deoxygenation is more facile for complexes with $(aryl)_3P$ than with $(alkyl)_3P$ ligands of comparable basicities (ν_{CO}). For example, the complexes with $(\underline{p}\text{-}CH_3OC_6H_4)_3P$ and $(C_2H_5)_3P$ show nearly identical ν_{CO}'s (1947 and 1948 cm^{-1}) in the starting materials (Eq. 2), and their oxygenations (k_2) do occur at comparable rates, but the deoxygenation (k_{-1}) is about eight times faster for the $(aryl)_3P$ complex.

These results — and similar ones with other R_3P ligands — suggest a special role for arylphosphines in promoting the rates of the reverse reactions of the type shown in Eq. (1,2). This role appears to derive from an electron delocalization process involving the phenyl rings in the Ph_3P-Metal-PPh_3 units. That is, such units seem to

approach extended π-systems which engage in suppressing an accumulation of excess charge on the metal atom during the reversible reaction, in accordance with Pauling electroneutrality principle. This view is schematically depicted in Eq. (3-6) for a reversible one-electron oxidative addition reaction, where M = metal center, L = ligands participating in electron delocalization (e.g., Ph_3P), XY = acidic or oxidant molecule (cf. Eq. 1).



$$L - M + XY \longrightarrow L - M^+ - (XY)^- \quad (3)$$

$$L - M^+ - (XY)^- \longrightarrow L^+ - M - (XY)^-, \text{ etc.} \quad (4)$$

$$L^+ - M - (XY)^- \longrightarrow L^+ - M^- + XY \quad (5)$$

$$L^+ - M^- \longrightarrow L - M \quad (6)$$

Eq. (3) and (5) refer to oxidative addition and reductive elimination, respectively, while Eq. (4) and (6) (and analogous processes) represent redistribution of charges. Thus, according to this notion, the reactions of complexes with mobile π-electron systems should — other things being equal or nearly so — proceed at higher reverse rates than those less capable of charge delocalization, e.g., $(aryl)_3P$ > $(alkyl)_3P$. That a delocalization of electrons in the metal-ligand assemblies seems to be a general requirement for facile reversibility is further suggested by other examples, such as metalloporphyrins with their extended π-systems (e.g., reversible oxygenation of hemoglobin), and by metallic surfaces (reversible chemisorption and heterogeneous catalysis) which can be viewed as exhibiting "infinite" delocalization networks.

CONCLUDING REMARKS

It should be recalled that triphenylphosphine has played an historic role in the development of modern coordination chemistry in its various manifestations.[13] The stabilization of a zerovalent metal complex by Malatesta, $[Pt(Ph_3P)_4]$, the outstanding activity of Wilkinson's catalyst, $[Rh(C\ell)(Ph_3P)_3]$, and the versatility of our model compound,

$[Ir(C\ell)(CO)(Ph_3P)_2]$, all appear to derive, in part, from the electron delocalization mechanism proposed above. The corresponding $(alkyl)_3P$ complexes are either unknown or elusive, or much inferior in these particular respects, i.e., as far as the stabilization of low oxidation states and catalytic activity are concerned.

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