reported, g_{iso} for a related isoelectronic Mn(0) complex, bis(1,3-butadiene)carbonylmanganese(0), has been reported to be 2.018.[13] A similar value for $Mn(CO)_5$ would be consistent with the observed CIDNP effects.

Further support for the proposed mechanism is provided by the following observations. (1) When $DMn(CO)_5$ was reacted with $C_6H_5C(CH_3){=}CH_2$, the formation of products was accompanied by isotopic exchange, reflected in the accumulation of $HMn(CO)_5$ and a decrease in the intensity of the CH_3 signal of the unreacted $C_6H_5C(CH_3){=}CH_2$, resulting from deuterium incorporation. This exchange is in accord with the requirement of reversibility of step 3 of the proposed mechanism. The extent of the observed exchange suggests that $k_{-3}/k_3' \gtrsim 1$. (2) The rate constant for the reaction of $DMn(CO)_5$ with $C_6H_5C(CH_3){=}CH_2$ was found to be larger than that for $HMn(CO)_5$ ($k_H'/k_D' \sim 0.4$ at 65 °C). In view of the very low initial frequency of the Mn-H bond ($\sim 1800\ cm^{-1}$) relative to that of the C-H bond ($\sim 3000\ cm^{-1}$), such an inverse isotope effect is not unexpected and has indeed been anticipated.[14] Similar inverse isotope effects also have been observed recently in related reactions of $HCo(CO)_4$[15] and $HMn(CO)_5$[16] with arenes.

Qualitatively similar CIDNP effects were observed for the corresponding reaction of $HMn(CO)_5$ with styrene, although the NMR spectra in this case were considerably more complex and have not yet been interpreted in detail. In the case of the reaction of styrene, the NMR spectra did reveal the transient formation in low concentrations of the organometallic coupling product, $C_6H_5CH(CH_3)Mn(CO)_5$. It remains to be established whether this species is associated with the principal reaction pathway or with a minor path.

Finally, we note that although CIDNP effects have been reported for a variety of reactions involving organometallic and coordination compounds, the mechanistic interpretations of these have been incomplete, particularly with respect to the role of the metal species.[17,18] We believe this to be the first definitive demonstration of a CIDNP effect to arise from a reaction in which one of the geminate radical pair is an inorganic metal-centered complex.

Acknowledgments. We are grateful to Dr. G. L. Closs of the University of Chicago and to Drs. J. W. Rathke and H. M. Feder of the Argonne National Laboratory for valuable discussions and advice. Support through a research grant from the National Science Foundation also is gratefully acknowledged.

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Role of Transition Metal-Dioxygen Complexes in Catalytic Oxidation. Catalysis of the Oxidation of Phosphines by Dioxygen Adducts of Platinum

Sir:

The chemistry of dioxygen adducts of transition metals has been the subject of intensive research in recent years[1] from several standpoints including the *possible* roles of such adducts in catalytic oxidation.[2-6] Several examples have been reported of the catalytic oxidation of organic substrates in the presence of metal-dioxygen adducts or of metal complexes which may form such adducts, but the mechanistic features of these systems have not been elucidated and at least in some cases it appears that free-radical, rather than "molecular", mechanisms are operative.[3,4,7] We report here the detailed elucidation of the mechanism of one class of reactions involving intermediate metal-dioxygen adducts, namely the oxidation of tertiary phosphines catalyzed by platinum(0) phosphine complexes.[8-10]

We have previously demonstrated that the catalysis of the oxidation of PPh_3 to Ph_3PO by $Pt(PPh_3)_3$ proceeds through the following reaction sequence in which the dioxygen adduct $Pt(PPh_3)_2(O_2)$ is an intermediate.[9,10]

$$Pt(PPh_3)_3 + O_2 \rightarrow Pt(PPh_3)_2(O_2) + PPh_3 \qquad (1)$$

$$\underline{Pt(PPh_3)_2(O_2) + 3PPh_3 \rightarrow Pt(PPh_3)_3 + 2Ph_3PO} \qquad (2)$$

$$2PPh_3 + O_2 \xrightarrow{Pt(PPh_3)_3} 2Ph_3PO \qquad (3)$$

The second-order rate law, $k_1[Pt(PPh_3)_3)_3][O_2]$, found for reaction 1[9,10] is consistent with the expected simple bimolecular displacement mechanism. On the other hand, the second-order rate law found for reaction 2, i.e., $k_2[Pt(PPh_3)_2(O_2)][PPh_3]$, clearly demonstrates that this reaction is a multistep process in which only *one* PPh_3 molecule reacts with $Pt(PPh_3)_2(O_2)$ in the initial rate-determining step, i.e.,

$$Pt(PPh_3)_2(O_2) \xrightarrow[k_2]{PPh_3} [\text{intermediate(s)}] \xrightarrow[\text{fast}]{2PPh_3} Pt(PPh_3)_3 + 2Ph_3PO \qquad (4)$$

Various mechanistic schemes for the reaction sequence 4 have been proposed, all involving transfer of *coordinated* oxygen either to coordinated or free phosphines.[9-13] However, these suggestions have not thus far been tested since, unfortunately, the intermediate stages in the reaction sequence 4 could not be detected and characterized, apparently because all subsequent steps are fast relative to the initial one (k_2). As detailed below, we have now successfully accomplished this by invoking the following approaches: (i) using the more reactive phosphines $PMePh_2$ and PMe_2Ph, in place of PPh_3, to increase the rate of the first step (k_2) relative to the subsequent stages and thereby achieving the accumulation of higher steady-state concentrations of the reaction intermediates; (ii) lowering the temperature to increase the lifetime of the reaction intermediates and thus to permit their detection; and (iii)

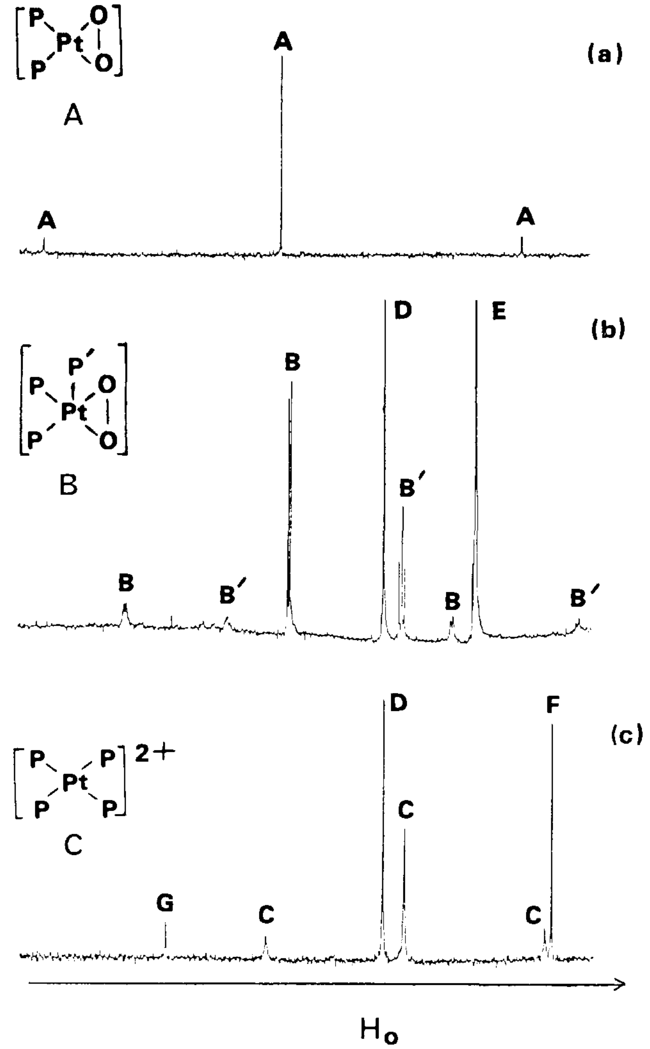


Figure 1. ^{31}P NMR spectra: (a) $[Pt(PPh_3)_2(O_2)]$; (b) $[Pt(PPh_3)_2(O_2)]$ + excess $PMePh_2$; (c) $[Pt(PPh_3)_2(O_2)]$ + excess PMe_2Ph (see text for details); A, $[Pt(PPh_3)_2O_2]$; B, $[Pt(PMePh_2)_3(O_2)]$; C, $[Pt(PMe_2Ph)_4]^{2+}$; D, PPh_3; E, $PMePh_2$; F, PMe_2Ph; G, Me_2PhPO.

Table I. ^{31}P NMR Parameters[a]

Species[b]	δ	$J_{^{195}Pt-P}$, Hz	J_{P-P}, Hz
$[Pt(PPh_3)_2(O_2)]$	16.4	4059	
$[Pt(PMePh_2)_3(O_2)]$	13.2 (d, 2 P)	2740	22
	−12.7 (t, 1 P)	2930	
$[Pt(PMe_2Ph)_4]^{2+}$	−14.1	2342	
$[Pt(PMePh_2)_4]$	−15.8	3807	
$[Pt(PMe_2Ph)_4]$	−34.9	3809	

[a] Chemical shifts (δ) measured at ca. −70 °C and reported with respect to 85% H_3PO_4 at 40 °C. Spectra were measured with a Bruker HFX-90 spectrometer. [b] Chemical shifts of uncoordinated phosphines and phosphine oxides follow: PPh_3 (−9.0); $PMePh_2$ (−29.0); PMe_2Ph (−48.0); $MePh_2PO$ (32.8); Me_2PhPO (41).

using ^{31}P NMR and polarography to identify and characterize the actual species in solution at various stages of the reaction. The following observations go a long way toward establishing the mechanistic features of reaction 2 and of corresponding reactions involving other phosphines.

(1) The addition of an excess of $PMePh_2$ to a $\sim 2 \times 10^{-2}$ M solution of $Pt(PPh_3)_2(O_2)$ in ethanol at −60 °C resulted in the quantitative displacement of PPh_3 and the formation of a new dioxygen adduct of the composition $Pt(PMePh_2)_3(O_2)$ according to eq 5.[14] The ^{31}P NMR spectrum of $Pt(PMePh_2)_3(O_2)$ (Figure 1, Table I) is consistent (although not uniquely so) with the structure depicted in Figure 1. The same species could also be generated (eq 6) by passing O_2 through a solution of $Pt(PMePh_2)_4$. These observations tend to support our original suggestion that the first step in the reaction sequence 4 is the coordination of an additional PPh_3 ligand to the Pt atom and that the first intermediate in this sequence (which cannot be detected for PPh_3 but is detectable for $PMePh_2$) is $Pt(PR_3)_3(O_2)$.[9] Warming the solution containing $Pt(PMePh_2)_3(O_2)$ and excess $PMePh_2$ to −20 °C resulted in the formation of $MePh_2PO$ and $Pt(PMePh_2)_4$ (eq 7).[15]

$$Pt(PPh_3)_2(O_2) + 3PMePh_2 \rightarrow Pt(PMePh_2)_3(O_2) + 2PPh_3 \quad (5)$$

$$Pt(PMePh_2)_4 + O_2 \rightarrow Pt(PMePh_2)_3(O_2) + PMePh_2 \quad (6)$$

$$Pt(PMePh_2)_3(O_2) + 3PMePh_2 \rightarrow Pt(PMePh_2)_4 + 2MePh_2PO \quad (7)$$

(2) The addition of an excess of the still smaller and more basic phosphine, PMe_2Ph, to an ethanol-toluene (5:1) solution of $Pt(PPh_3)_2(O_2)$ at −78 °C resulted in quantitative displacement of both the PPh_3 and O_2^{2-} ligands with the formation of $Pt(PMe_2Ph)_4^{2+}$ according to eq 8. The ^{31}P NMR spectrum of $Pt(PMe_2Ph)_4^{2+}$ (Figure 1, Table I) agreed with that of the same species prepared analogously from $Pt(PPh_3)_2Cl_2$ (eq 9) and of a solution of the independently synthesized salt, $[Pt(PMe_2Ph)_4](BF_4)_2$. The formation of hydrogen peroxide in reaction 8 was confirmed polarographically, the characteristic irreversible reduction wave at −1.10 V (vs. Ag/AgCl) of the resulting solution being identical in position and shape with that of a standard ethanol solution of H_2O_2 of the same concentration (2×10^{-2} M). The solution resulting from eq 8, containing a mixture of $[Pt(PMe_2Ph)_4]^{2+}$, PPh_3, excess PMe_2Ph, and H_2O_2 (or HO_2^-), *but only a trace of phosphine oxide*, was stable for many hours at −78 °C. The parallel between reactions 8 and 9 is consistent with the usual formulation of $Pt(PPh_3)_2(O_2)$ as a peroxide complex of platinum(II).

$$Pt(PPh_3)_2(O_2) + 4PMe_2Ph + EtOH \rightarrow Pt(PMe_2Ph)_4^{2+} + 2PPh_3 + HO_2^- + EtO^- \quad (8)$$

$$Pt(PPh_3)_2Cl_2 + 4PMe_2Ph \rightarrow Pt(PMe_2Ph)_4^{2+} + 2PPh_3 + 2Cl^- \quad (9)$$

(3) On warming the solution from reaction 8 to −40 °C, quantitative reduction of the peroxide by the excess PMe_2Ph occurred, according to eq 10, while the $Pt(PMe_2Ph)_4^{2+}$ was unaffected. The disappearance of the peroxide was confirmed polarographically and the quantitative formation of Me_2PhPO demonstrated by ^{31}P NMR.[15] The persistence of $Pt(PMe_2Ph)_4^{2+}$ was confirmed both polarographically and by ^{31}P NMR.

$$HO_2^- + PMe_2Ph \rightarrow Me_2PhPO + OH^- \quad (10)$$

(4) On further warming of the above solution from −40 to 25 °C, quantitative reduction of the $Pt(PMe_2Ph)_4^{2+}$ by the excess PMe_2Ph occurred according to eq 11, with the formation of $Pt(PMe_2Ph)_4$ and Me_2PhPO (both identified and determined by ^{31}P NMR). This reaction requires the presence of at least a stoichiometric amount of OH^- (formed in reaction 10), as demonstrated in corresponding experiments on synthetic solutions of $Pt(PMe_2Ph)_4^{2+}$ prepared from $Pt(PMe_2Ph)_2Cl_2$ by reaction 9 or by dissolving $[Pt(PMe_2Ph)_4](BF_4)_2$ in ethanol.

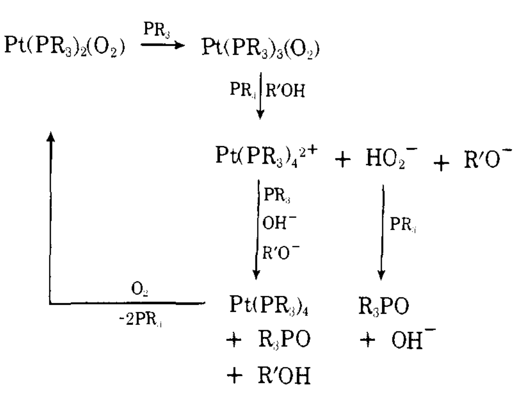
$$Pt(PMe_2Ph)_4^{2+} + PMe_2Ph + OH^- + EtO^- \rightarrow Pt(PMe_2Ph)_4 + Me_2PhPO + EtOH \quad (11)$$

Combination of the sequence of *demonstrated* steps 8, 10, and 11 yields the overall reaction 12 which is the "PMe_2Ph analogue" of reaction 2.

$$Pt(PPh_3)_2(O_2) + 6PMe_2Ph \rightarrow Pt(PMe_2Ph)_4 + 2Me_2PhPO + 2PPh_3 \quad (12)$$

These results strongly suggest the detailed mechanism 13 for the $Pt(PR_3)_n(O_2)$-catalyzed oxidation of phosphines.[16]

Although the various steps and intermediates in this scheme (13) have been demonstrated for the modified systems involving $PMePh_2$ and PMe_2Ph, the modification is sufficiently modest that it seems reasonable to extrapolate the mechanism also to the $Pt(PPh_3)_3$-catalyzed oxidation of PPh_3, as well as to the catalytic oxidation of phosphines by other metal complexes (e.g., $Rh(PPh_3)_3Cl$[5] and $Ru(NCS)(CO)(NO)(PPh_3)_2$[12]) which also form O_2 adducts. Furthermore, although the scheme (13) as depicted (and as demonstrated) uses protons derived from the solvent to generate the OH^- and HO_2^- intermediates, the steady-state concentrations of these intermediates, required to sustain a catalytic cycle, are sufficiently low that the same mechanism (using trace protic impurities) may also be invoked in nominally "aprotic" solvents such as benzene in which the catalytic reaction can occur.[8-10]



(13)

It is noteworthy that, in contrast to earlier suggestions,[9-13] the mechanism encompassed by scheme 13 does not involve direct oxygen transfer from the metal–dioxygen adduct to the substrate. Instead the role of the "substrate" (i.e., phosphine) is to effect the displacement of coordinated peroxide by nucleophilic attack on the metal. Not surprisingly, substrates such as olefins are not sufficiently strong nucleophiles to accomplish this and are not readily oxidized by O_2 adducts such as $Pt(PPh_3)_2O_2$. On the other hand, other *strong* nucleophiles such as carbanions are expected to exhibit reactions similar to phosphines and indeed steps analogous to 8 and 10 have been demonstrated for the reaction of LiBu with $Pt(PPh_3)_2(O_2)$, *even in an aprotic solvent.*[17]

The mechanistic conclusions derived from these studies suggest that the scope for oxidation of substrates via O_2 adducts such as $Pt(PR_3)_2(O_2)$ is rather limited. The effective oxidants in this system are really platinum(II) and free peroxide. Only strongly nucleophilic substrates such as phosphines are likely to effect the displacement of peroxide from the O_2 adduct and such substrates are almost certain to be themselves oxidized readily by the displaced peroxide. On the other hand, the reactivity patterns of platinum(II) complexes as oxidants (which we are presently investigating) are such that reduction by other substrates (for example reduction by olefins through Wacker-type mechanisms) may well compete with reduction by phosphines. Thus, *co-oxidation* of phosphines and other substrates may be possible through mechanisms related to those of scheme 13. The recently reported co-oxidation of olefins and PPh_3, catalyzed by $Rh(PPh_3)_3Cl$ under conditions where the latter forms O_2 adducts, may be an example of such a process.[5]

Acknowledgment. Support of this research through a grant from the National Science Foundation is gratefully acknowledged.

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(16) Our proposed mechanism predicts that in the presence of added excess H_2O, 50% of the oxygen in the product Me_2PhPO should be derived from the H_2O and the other 50% from the O_2. The results of preliminary experiments using ^{18}O-labeled H_2O are at least qualitatively consistent with this.
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Received August 8, 1977

Asymmetric Reduction. Reduction of Acetylenic Ketones with Chiral Hydride Agent

Sir:

The production of optically active synthetic intermediates from achiral starting materials via asymmetric induction has been of increasing interest in recent years.[1] One of the most widely studied aspects of this field has been the synthesis of chiral carbinols from the reduction of achiral ketones with chiral hydride agents.[1-5] Thus far, however, this area has been of more theoretical than practical interest since only aryl ketones have been reduced in high enantiomeric ratios (ranging from 85:15 to 93:7). Indeed there has not yet been to our knowledge an example of an asymmetric reduction of an aliphatic ketone to give enantiomeric ratios of greater than 70:30. We now wish to disclose our finding that the reduction of acetylenic ketones (Scheme I) with the complex formed from

Scheme I