Oxygenation Studies. Part 8.[1] Catalytic Oxygenations of Arylphosphines at Platinum(0)†

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Experimental support for the view that trace protic species may play a key role in the catalytic co-oxygenation of arylphosphines at $[Pt(PPh_3)_3]$ under nominally aprotic conditions has been sought but not found. Marked reductions in the catalytic rates are observed when PPh_3 and $PMePh_2$ are oxidised in the presence of trace levels of moisture or alcohols. The inhibiting influence of Ph_2PO_2H and p-$MeC_6H_4SO_3H$ is even greater. Oxygen uptake for the oxygenation of $PMePh_2$, in benzene at 25 °C, is shown to follow the rate law below and is considered in terms of a general

$$\text{Rate } (O_2) = [Pt]_{tot}\,(15.41\,[\text{phosphine}]\,[O_2]^{-1} + 1\,290)^{-1}$$

scheme for the co-oxygenation of arylphosphines at Pt^0 in aprotic solvents. It is suggested that the 'oxygen insertion' step is best interpreted as intramolecular nucleophilic attack on two co-ordinated phosphines followed by breakdown of the resulting metallacycle by reductive elimination; a mechanism embracing features which may well occur in a range of co-oxygenations at Group 8 transition-metal centres.

Few of the many examples of catalytic co-oxygenation of arylphosphines (PR_3) at metal centres by molecular oxygen have received detailed mechanistic attention.[2-4] Halpern and co-workers[3] reported studies on one such oxygenation in benzene using $[Pt(PPh_3)_3]$ as the catalyst [reaction (1)]. In a later related study, using $PMePh_2$ and PMe_2Ph as substrates and ethanol–toluene (5:1) as solvent, they detected hydroperoxidic intermediates in the protic medium and suggested that these might also be involved in related catalytic processes under nominally aprotic conditions where such species would have to be formed from 'trace protic impurities'.[4] Such a key mechanistic role for trace impurities could have important implications for the mechanisms of the co-oxygenations of alkenes at rhodium centres[1,5] in which PPh_3 and terminal alkenes are co-oxygenated to PPh_3O and methyl ketones in anhydrous benzene at room temperature [reaction (2), R = alkyl]. A competing co-oxygenation which parallels reaction (1) also takes place but only in the presence of the alkene and, as in the case of Halpern's studies, related co-oxygenations of the alkenes in protic solvents[6] are thought to involve hydroperoxidic intermediates.[7] We have therefore sought direct evidence for the participation of protic species in reaction (1) and in the analogous reaction involving the stronger nucleophile $PMePh_2$. Our findings, and a discussion of the key oxygenative step, are reported in this paper.

$$2\,PPh_3 + O_2 \xrightarrow[C_6H_6]{[Pt(PPh_3)_3]} 2\,PPh_3O \qquad (1)$$

$$R\text{–}CH{=}CH_2 + PPh_3 + O_2 \xrightarrow[C_6H_6]{[RhCl(PPh_3)_3]} PPh_3O + RCOCH_3 \qquad (2)$$

Experimental

General.—A JEOL PFT 100 instrument was used to make ^{31}P n.m.r. measurements using H_3PO_4 as an external standard and either benzene–deuteriobenzene or toluene–deuteriotoluene as solvent.

Benzene was purified as previously described.[7] Ethanol was dried according to the method of Vogel.[8] Triphenylphosphine was recrystallised from ethanol under N_2 and dried at 50 °C (0.005 mmHg) before use; $PMePh_2$ (Fluka), PMe_2Ph (Fluka), and C_2D_5OD (Aldrich, Gold label) were used without purification. The complex $[Pt(PPh_3)_4]$ was prepared by the method of Malatesta and Cariello.[9]

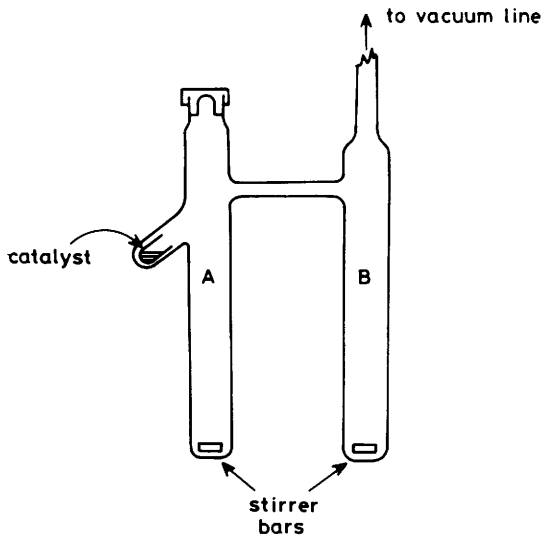


Figure 1. Vessel for preparation of anhydrous solutions

Catalytic Studies.—For runs in which moisture was rigorously excluded, PPh_3 (0.74 g, 2.81×10^{-3} mol) and a magnetic follower were placed in section A of the glass reaction vessel (Figure 1). The catalyst (0.015 g, 1.21×10^{-5} mol), in a 'Teflon' cup which could be moved magnetically, was placed in the side-arm. Lithium aluminium hydride (*ca.* 0.1 g) and a magnetic follower were placed in section B.

† *Non-S.I. unit employed:* mmHg ≈ 133 N m^{-2}.

A 'subaseal' septum was fitted to section A and section B was connected directly to a vacuum line.

Benzene (25 cm^3), degassed and dried over $LiAlH_4$, was sublimed into section B by standard techniques. The limb connecting the evacuated reaction vessel and the vacuum line was sealed using a natural gas–oxygen torch. The solvent was allowed to thaw then stirred with the $LiAlH_4$ for 5 min before being refrozen and sublimed into section A. The thawing, stirring, refreezing, and subliming procedure was repeated to return the solvent and any trace of moisture within the apparatus to section B. The procedure was repeated once more to transfer the benzene to section A and the limb connecting sections A and B sealed by use of a natural gas–oxygen torch. Oxygen was fed into section A *via* a gas control unit supplied by Petric Instrumentation (Shepperton) connected to section A by polypropylene tubing (3 mm outside diameter) and a hyperdermic needle through the 'subaseal' septum.

Section A was placed in a water-bath maintained at 25 ± 0.5 °C by a Gallenkamp water circulator and the solution was stirred by means of a submersible magnetic stirrer supplied by Rank Bros. (Bottisham). After the system had equilibrated (5 min), the catalyst was dropped into the phosphine solution and the gas uptake was monitored by the control unit.

The oxidations of $PMePh_2$ and PMe_2Ph were carried out in a similar manner except that the liquid substrates were introduced into the solvent prior to the catalyst *via* the septum, as were the alcohols. Solid additives were introduced into section A at the initial stage.

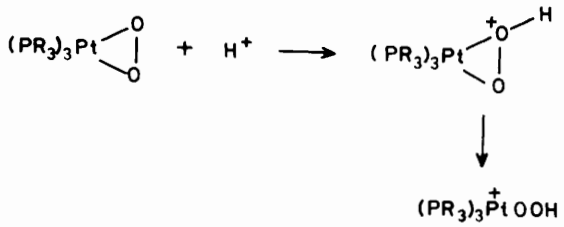
Results and Discussion

Studies on PPh_3 *Co-oxygenation.* Kinetic studies by Halpern[3] have shown that the co-oxygenation of PPh_3 is described by the reactions (3) and (4), in which k_1 and k_2 have

$$[Pt(PPh_3)_3] + O_2 \xrightarrow{k_1} [Pt(PPh_3)_2(O_2)] + PPh_3 \quad (3)$$

$$[Pt(PPh_3)_2(O_2)] + PPh_3 \xrightarrow{k_2} [Pt(PPh_3)_3(O_2)] \xrightarrow[\text{fast}]{2\ PPh_3} [Pt(PPh_3)_3] + 2\ PPh_3O \quad (4)$$

values of 2.6 $dm^3\ mol^{-1}\ s^{-1}$ and 0.15 $dm^3\ mol^{-1}\ s^{-1}$ respectively for benzene at 25 °C. The speculated intervention of a protic species is associated with the fast decomposition of $[Pt(PPh_3)_3(O_2)]$, the intermediate in reaction (4). Scheme 1 depicts the general case. Similar hydroperoxide formations appear to

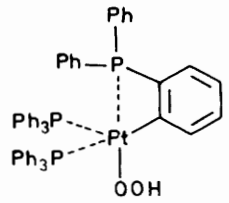


Scheme 1. R_3 = Ph_3, Me_2Ph, or $MePh_2$

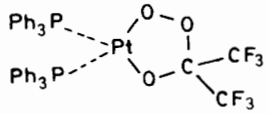
take place with *o*-dihydric phenols[10] and strong acids.[11] Rhodium analogues are also converted to hydroperoxidic species by weakly acidic β-diketones.[12]

In principle it should be possible to establish that a species is involved in the fast step of a reaction by lowering its concentration to such a level that the rate of that step becomes rate determining. We have therefore measured the rate of oxygenation under conditions designed to remove the last trace of adventitious moisture from the substrates and the reaction vessel. Four such runs gave initial rate values which were within 2% of calculated figures based on Halpern's rate constants,[3] whereas rates measured under conditions which did not rigorously exclude moisture were only 74.2 ± 3.0% of the calculated figures. Equally significant was the observation that the introduction of 0.018% of ethanol into the solvent decreased the rate of oxygenation by 35%. Ethanol levels of 0.18 and 12.0% reduced the rate by 74 and 89% respectively. The catalytic cycle was particularly sensitive to trace amounts of strong acid. Diphenylphosphinic acid at a concentration of 1×10^{-3} mol dm^{-3} reduced the observed rate by 56% and toluene-*p*-sulphonic acid at the same concentration virtually stopped the reaction.

In a second approach to this question we sought evidence for the participation of a hydroperoxidic species such as (**1**) generated intramolecularly by *ortho* metallation of co-ordinated PPh_3. Plausible mechanistic routes can be formulated in which



(**1**)



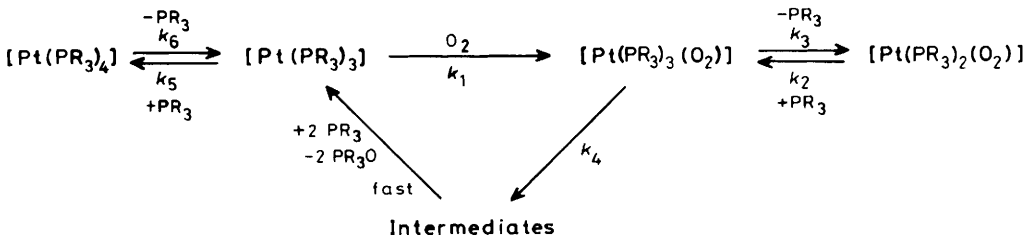
(**2**)

deuterium exchange of the hydroperoxidic proton would lead to *o*-deuteriated PPh_3O. Mass spectroscopic analysis of PPh_3O isolated from the catalytic reaction carried out in benzene containing 2% deuteriated ethyl alcohol showed a $M:M+1$ ratio consistent with very low incorporation of deuterium but this evidence was not substantiated by a more sensitive ^2H n.m.r. examination of the product.

These attempts to gain support for the role of hydroperoxidic intermediates in the co-oxygenation have therefore been unsuccessful. The studies show, in particular, that traces of protic species significantly inhibit the catalytic reaction and it is possible that they compete with O_2 for a co-ordination site on $[Pt(PPh_3)_3]$ [reaction (3)] or with PPh_3 for a co-ordination site on $[Pt(PPh_3)_2(O_2)]$ [reaction (4)]. The findings do not eliminate the possibility of a stronger association of a protic species with the co-ordinated oxygen as pictured in Scheme 1, but they provide no support for it.

It appears probable that the species $[Pt(PPh_3)_3(O_2)]$ [reaction (4)] is also an intermediate in reaction (3) and on this basis Scheme 2 provides a profile of the co-oxygenation. Assuming this common intermediary, the rate of loss of $[Pt(PPh_3)_2(O_2)]$ in reaction (4) is given by $k_2[k_4/(k_3 + k_4)]$-$[Pt(PPh_3)_2(O_2)][PPh_3]$, rather than $k_2[Pt(PPh_3)_2(O_2)]$-$[PPh_3]$, the term taken by Halpern.[3] The constant 'k_2' measured by Halpern would be composite and, in practice, correspond approximately to $k_4(k_2/k_3)$ since it is clear that $k_3 \gg k_4$. The significance of this kinetic detail would be particularly marked if protic species were associated with the oxygenative breakdown of $[Pt(PPh_3)_3(O_2)]$, *i.e.* if $k_4 = k_4'$-$[H^+]$, for deviations from the kinetic fit would occur unless the level of adventitious proton were constant. The excellence of the kinetic fit of Halpern's data therefore further suggests that a protic species is not involved in the mechanism.

Studies on $PMePh_2$ *and* PMe_2Ph *Co-oxygenation.*—In their study of the oxygenative mechanism in protic solvents Sen and Halpern[4] have shown that excess of the more basic phosphine, $PMePh_2$, effectively displaces PPh_3 from $[Pt(PPh_3)_2(O_2)]$ in ethanolic solution at −70 °C to give the five-co-ordinate



Scheme 2. R_3 = Ph_3, Me_2Ph, or $MePh_2$

$[Pt(PMePh_2)_3(O_2)]$. There is no oxygenative displacement of PPh_3 as the oxide. The tetrakis(phosphine) complex, $[Pt(PMePh_2)_4]$, is also obtained whereas in the PPh_3 series (in benzene) it is the tris(phosphine) complex which is thermodynamically the more stable over a wide range of phosphine concentrations.[3a] It was of interest to examine the extent to which this picture for $PMePh_2$ held in aprotic solutions. We have therefore studied the co-oxygenation of $PMePh_2$, in anhydrous benzene at 25 °C, over a range of substrate concentrations and investigated the effects of low concentrations of protic species on such co-oxygenations, using oxygen uptake measurements.

An initial rapid phase lasting some 40—50 min preceded the steady catalytic oxygenation, see Figure 2. The detection, by ^{31}P n.m.r. of both PPh_3O and PPh_3 at an early stage in the reaction clearly pointed to this first phase being associated with the rapid co-oxygenation of co-ordinated PPh_3 in a reaction which competed with its displacement by $PMePh_2$. The overall rate of co-oxygenation of $PMePh_2$ was markedly slower than that of PPh_3, being only 10% as fast at platinum, phosphine, and oxygen concentrations of 4.94×10^{-4}, 1.12×10^{-1}, and 6.04×10^{-3} mol dm^{-3} respectively.

Measurements of the linear oxygen uptake (nominally after 120 min) showed the rate to be first order in [Pt] between 2.6×10^{-4} and 1.01×10^{-3} mol dm^{-3}. The reaction showed limited sensitivity to phosphine and oxygen concentration changes. The rate of uptake increased slightly as $[PMePh_2]$ decreased from 2.24×10^{-1} to 5.6×10^{-2} mol dm^{-3} although at the lower end of this range there was a slow decline in catalytic performance throughout each run due, possibly, to some inhibition by the $PMePh_2O$ at the lower $[PMePh_2]$. A five-fold reduction in $[O_2]$, from 8.95×10^{-3} to 1.93×10^{-3} mol dm^{-3}, decreased the catalytic rate by 30%. The data from this part of the study are given in Table 1.

The rate term for the oxygen uptake under equilibrium conditions in the catalytic system depicted in Scheme 2 is given by equation (5) (cat = catalyst). However, the ^{31}P n.m.r. spectrum of the catalytic system in toluene at −50 °C shows that $[Pt(PMePh_2)_4]$ is the thermodynamically stable form of Pt^0 under aprotic as well as protic conditions.[3] Thus $k_5[PR_3] \gg k_6$. Furthermore, although we have not observed $[Pt(PMePh_2)_3(O_2)]$ or $[Pt(PMePh_2)_2(O_2)]$ under the conditions of our spectroscopic studies, the former is the more stable in ethanolic solutions[3] and must be expected to be more favoured in benzene, *i.e.* $[Pt(PMePh_2)_2(O_2)]$ makes an insignificant contribution to $[cat]_{tot}$ and $k_2[PR_3] \gg k_3$. On this basis equation (5) can be simplified and rearranged to give equation (6). A plot of $[cat]_{tot}/Rate(O_2)$ *vs.* $[PR_3]/[O_2]$ leads to

$$\frac{[cat]_{tot}}{Rate(O_2)} = \frac{k_5}{k_1k_6}\frac{[PR_3]}{[O_2]} + \frac{1}{k_4} \qquad (6)$$

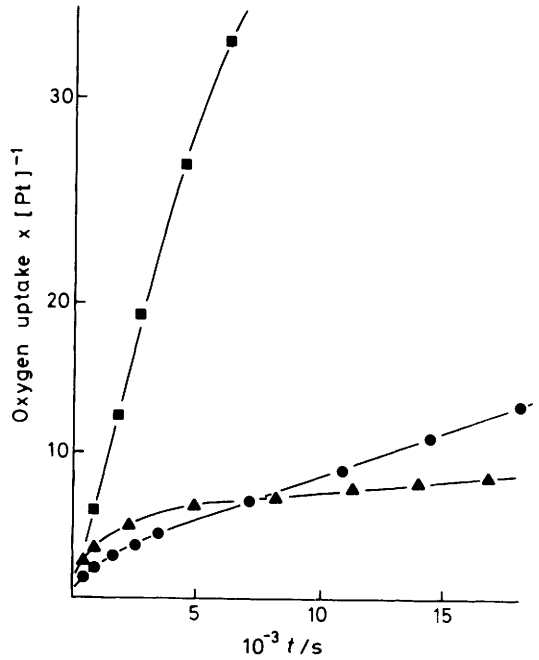


Figure 2. Oxygen uptake profiles for catalytic oxygenation of PPh_3 (■), $PMePh_2$ (●), and PMe_2Ph (▲) in anhydrous benzene at 25 °C; $[Pt] = 4.97 \times 10^{-4}$, $[PR_3] = 1.12 \times 10^{-1}$, and $[O_2] = 6.10 \times 10^{-3}$ mol dm^{-3}

values of 6.49×10^{-2} s^{-1} for $k_1(k_6/k_5)$ and 7.75×10^{-4} s^{-1} for k_4. The excellence of the data fit is shown by the final column in Table 1.

The findings for the oxygenation of $PMePh_2$ are therefore also consistent with a mechanism in which the rate of oxygen uptake shows a dependence on k_4. Again, if k_4 is a pseudo constant,

$$Rate(O_2) = \frac{k_1k_2k_4k_6[cat]_{tot}}{k_2k_4(k_5[PR_3] + k_6)[O_2]^{-1} + k_1k_6(k_2[PR_3] + k_3)[PR_3]^{-1}} \qquad (5)$$

embracing a concentration of catalytic proton, addition of proton would be expected to lead to an increase in the catalytic rate. No such rate enhancement was observed in the presence of t-butyl alcohol (3.0×10^{-3} mol dm^{-3}) or ethanol (3.4×10^{-3} mol dm^{-3}). The alcohols decreased the rate by 50 and 29% respectively. The stronger acids, diphenylphosphinic acid and toluene-*p*-sulphonic acid effectively inhibited the oxygenation at concentrations of 1.1×10^{-3} mol dm^{-3}.

Our examination of the analogous co-oxygenation of PMe_2Ph has been limited. As with $PMePh_2$, there was a rapid initial phase before slow steady catalytic oxygenation was observed. The initial phase is more marked than in the case of $PMePh_2$ suggesting that PPh_3 remains associated with the catalytic species for a longer period but under equivalent

Table 1. Variation of rate of oxygen uptake for the oxidation of $PMePh_2$ in benzene at 25 °C

Run	10^4 $[Pt]_{tot}$/mol dm^{-3}	10^3 $[O_2]$/mol dm^{-3}	10^1 $[PMePh_2]$/mol dm^3	10^6 R_e[a]/dm^3 mol^{-1} s^{-1}	10^6 R_c[b]/dm^3 mol^{-1} s^{-1}	R_e/R_c
1	10.02	6.048	1.12	0.641	0.636	1.008
2	4.77	8.954	1.12	0.314	0.322	0.976
3	5.11	6.013	2.24	0.271	0.274	0.989
4	4.99	6.032	1.12	0.317	0.317	1.000
5	4.85	6.055	1.12	0.308	0.308	1.000
6	4.75	6.020	1.12	0.305	0.301	1.012
7	4.93	6.032	0.56	0.321	0.344	0.933
8	4.79	3.854	1.12	0.275	0.276	0.998
9	4.83	1.930	1.12	0.222	0.221	1.004
10	2.59	6.045	1.12	0.167	0.164	1.016

[a] Experimental rate, based on duplicate runs. [b] Calculated rate, based on $[Pd](15.41[PMePh_2][O_2]^{-1} + 1\,290)^{-1}$.

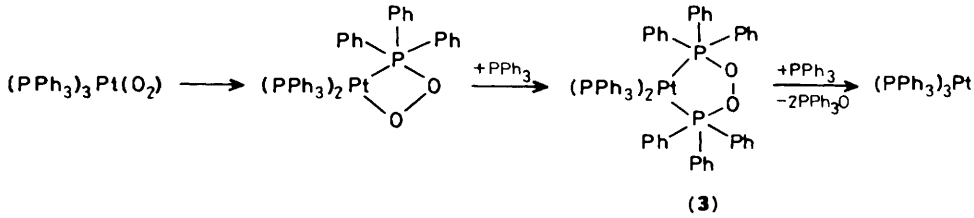
Table 2. Variation of rate of oxygen uptake with $[O_2]$ for the oxidation of PMe_2Ph in benzene at 25 °C[a]

10^4 $[Pt]_{tot}$/dm^3 mol^{-1}	10^3 $[O_2]$/dm^3 mol^{-1}	10^7 Rate[b]/dm^3 mol^{-1} s^{-1}
5.10	1.37	1.22
4.91	0.94	1.04
4.96	0.30	0.66

[a] $[PMe_2Ph] = 1.12 \times 10^{-1}$ mol dm^{-3}. [b] Based on duplicate runs.

in what is essentially a reductive elimination. We have recently proposed closely related mechanisms for the co-oxygenation of PPh_3 and cyclo-octene[16] and of cyclo-octa-1,5-diene[1] at peroxyrhodium centres and see no findings inconsistent with similar mechanistic pictures for the vast majority of co-oxygenations under aprotic conditions at mononuclear Group 8 transition-metal centres.[17]

It is apparent from these studies and those of Halpern[3,4] that a clear distinction must be made in the co-oxygenation of



(3)

Scheme 3.

conditions the steady catalytic oxygenation was only 33% that of the diarylphosphine, see Figure 2. The dependence of the catalytic rate on oxygen concentration was more marked than in the $PMePh_2$ cases, see Table 2.

The Oxygenation Step.—The studies described above support the view that the oxygen-atom transfer step in these reactions is an uncatalysed breakdown of $[Pt(PR_3)_3(O_2)]$ (R_3 = Ph_3, Me_2Ph, or $MePh_2$). A meaningful formulation for such a 'oxygen insertion' has presented earlier authors with some difficulties. However it is clear that the act of co-ordination makes a co-ordinating ligand more electrophilic and a co-ordinated ligand more nucleophilic. The co-ordinated dioxygen in peroxo complexes such as $[Pt(PPh_3)_2(O_2)]$ has been found to acquire the nucleophilic characteristics of peroxidic oxygen when acetone,[13] hexafluoroacetone,[14] or alkenes carrying electron-withdrawing substituents[15] co-ordinate to the metal centre. Peroxymetallacyclic complexes such as (2) are formed. It is suggested that when the co-ordinating ligand is a phosphine, as in the cases considered here, loss of electron density by donation to the metal converts the phosphorus from a nucleophilic centre into one which, by virtue of its empty *d* orbitals, can accept electrons from the peroxo oxygen to generate a four-membered metallacycle (see Scheme 3). Co-ordination of a second molecule of phosphine to the vacated co-ordination site and repetition of the process leads to the five-membered metallacycle (3). Breakdown of this species may require further co-ordination of phosphine before two phosphine oxides can be released and the metal returned to Pt^0 phosphines between reactions in protic media and in aprotic media. There are major mechanistic differences and the latter are markedly faster. These generalisations also appear to hold for co-oxygenations involving terminal alkenes at rhodium.[5,6] The relative rates of co-oxygenation of PMe_2Ph, $PMePh_2$, and PPh_3, under the conditions listed in Figure 2, are close to 1:3:10 respectively. These, of course, do not reflect the relative magnitudes of k_4 for each system. Our studies only isolate k_4 in the case of $PMePh_2$. There are, however, some pointers which suggest that the k_4 values follow the order of the observed rates. To enable $[Pt(PPh_3)_2(O_2)]$ to be isolated from solutions containing free phosphine,[18] a value for k_2/k_3 of a little more than unity, at most, might be anticipated indicating that k_4 for the PPh_3 oxidation should be 0.15 s^{-1} or larger, compared with 7.75×10^{-4} s^{-1} for $PMePh_2$. Furthermore, if the equilibrium and intermediate steps which govern the rate of co-oxygenation of PMe_2Ph are the same as those governing the co-oxygenation of $PMePh_2$, the limited data on $[O_2]$ dependence obtained for the former co-oxygenation suggest that k_4 for PMe_2Ph is 3×10^{-4} s^{-1}, *i.e.* 40% that for $PMePh_2$. Should this order for the relative rates of decomposition of $[Pt(PR_3)_3(O_2)]$ be confirmed, the electrophilicity of the co-ordinated phosphine and/or release of steric compression would be implicated as the principal factors responsible.

Acknowledgements

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