Alkyl Group Transfer from Rhodium(I) to Electrophilic Reagents; Inducement by a Tertiary Phosphine

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Although the compound $RhMe(CO)\{MeC(CH_2PPh_2)_3\}$ (1) is normally inert to methyl iodide, chlorotrimethyltin and acetone, it reacts in the presence of trimethylphosphine with (a) methyl iodide to form the cationic complex $[Rh(CO)(PMe_3)\{MeC(CH_2PPh_2)_3\}]^+$ (2), methane, and ethylene but not ethane, (b) chlorotrimethyltin to form (2) and tetramethyltin, and (c) acetone to form (2) and t-butoxide; the role of the trimethylphosphine seems to involve substituting one arm of the triphosphine, thus rendering the Rh–Me moiety more reactive towards electrophilic reagents.

Rhodium(I) complexes are often susceptible to attack by electrophilic reagents, yielding organorhodium(III) products on treatment with, for instance, alkyl halides,[1] *i.e.*, reaction (1), where R = alkyl, X = halide, L = CO, tertiary phosphine.

$$RhXL_3 + RX \rightarrow RhRX_2L_3 \qquad (1)$$

In several cases, addition of iodide ion is known to accelerate such oxidative addition processes, apparently by co-ordination of the iodide to the rhodium to give anionic rhodium(I) species of enhanced nucleophilicity and hence greater reactivity.[2] We now report the similar use of tertiary phosphines to enhance the reactivity of the rhodium(I) compound RhMe(CO)(triphos) (**1**)[3] [triphos = the tridentate ligand $MeC(CH_2PPh_2)_3$] to electrophilic substrates as diverse as methyl iodide, chlorotrimethyltin, and acetone.

As in earlier work, which has shown that the five-co-ordinated complexes RhCl(CO)(triphos) and $[Rh(CO)_2(triphos)]^+$ react very slowly with methyl iodide,[3] we have found that a solution of (**1**) in tetrahydrofuran (THF) is inert to an equimolar amount of methyl iodide. Further, although (**1**) does react smoothly with carbon monoxide and t-butyl isonitrile to form the acetyl complexes Rh(MeCO)L(triphos) (L = CO, Bu^tNC),[3] a solution of (**1**) in THF is essentially unaffected by a twenty-fold excess of trimethylphosphine, neither acyl nor substitution products being evident by i.r. spectroscopy.

Interestingly, therefore, the addition of one molar equivalent of PMe_3 to the solution of (**1**) and methyl iodide (1 : 1) in THF was found to result in the immediate and quantitative conversion of (**1**) [ν(CO) 1895 cm^{-1}] to the known cationic complex[3] $[Rh(CO)(PMe_3)(triphos)]^+$ [(**2**), ν(CO) 1922 cm^{-1}]. ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of the product in CD_2Cl_2 confirmed this identification, while g.c. analysis of the organic products indicated the presence of methane and ethylene (2 : 1 ratio) but not ethane.

$$[Rh(CO)(PMe_3)(triphos)]^+$$

(**2**)

The methylrhodium compound (**1**) is also inert to excess of chlorotrimethyltin in THF, and thus it was interesting to find that addition of PMe$_3$ to a solution of (**1**) and chlorotrimethyltin [PMe$_3$: (**1**) : Me$_3$SnCl = 1 : 1 : 2] in THF resulted in the rapid and quantitative formation of [Rh(CO)(PMe$_3$)(triphos)]$^+$ (**2**) and tetramethyltin. The presence of (**2**) was confirmed by i.r., ^{1}H n.m.r., and ^{31}P{^{1}H} n.m.r. spectroscopy, while the presence of Me$_4$Sn was confirmed by ^{1}H n.m.r. spectroscopy (δ 0.05) and, when formed utilizing [^{2}H$_3$]-(**1**) by ^{2}H n.m.r. spectroscopy (δ −0.13).

As (**1**) is stable in acetone, it was very surprising to find that addition of one molar equivalent of PMe$_3$ to a suspension of (**1**) in acetone resulted in about 40% conversion of (**1**) to (**2**). Addition of a further five equivalents of PMe$_3$ resulted in complete dissolution of the suspension of (**1**) and quantitative conversion of (**1**) and (**2**) (by i.r. spectroscopy). Subsequent removal of the solvent, extraction into D$_2$O and analysis of the ^{1}H and ^{13}C{^{1}H} n.m.r. spectra of the extract revealed the presence of t-butyl alcohol (^{1}H: δ 1.14; ^{13}C: δ 30.5, 70.6). The formation of the latter, in which [^{2}H$_3$]-t-butoxide was prepared utilizing [^{2}H$_3$]-(**1**) was also confirmed by ^{2}H n.m.r. spectroscopy.

Since a common feature of these novel reactions is the combination of (**1**) and PMe$_3$ to form (**2**), possible reactions between the former two compounds were investigated more extensively. While an i.r. study suggested that a solution of (**1**) in THF is essentially unaffected by the presence of large excesses of PMe$_3$, a ^{31}P{^{1}H} n.m.r. spectrum of a solution of PMe$_3$ and (**1**) (ratio 20 : 1) in THF–C$_6$D$_6$ (4 : 1) exhibited resonances at δ −25 (singlet) and δ −58 (br. $\nu_{\frac{1}{2}} \approx 500$ Hz) (ratio ≈ 1 : 6). The former is in the region of free triphos, and suggests significant deco-ordination of that ligand. The latter is in the region of free PMe$_3$, but the excessive line width suggests rapid exchange between free and co-ordinated ligand. It thus seems that (**1**) reacts with PMe$_3$ to form low equilibrium concentrations of an intermediate in which PMe$_3$ has substituted one or more arms of the triphos ligand, *i.e.*, reaction (2). Indeed, ^{31}P{^{1}H} n.m.r. spectroscopy at 190 K revealed a set of resonances assignable to (**3**).

$$\underset{(\mathbf{1})}{\text{RhMe(CO)(triphos)}} + \text{PMe}_3 \rightarrow \underset{(\mathbf{3})}{\text{RhMe(CO)(PMe}_3\text{)(}\eta^2\text{-triphos)}} \quad (2)$$

In view of the small size and better electron-donating properties of PMe$_3$ relative to a -CH$_2$PPh$_2$ group of triphos, it is to be expected, on both steric and electronic grounds, that (**3**) would be more susceptible to oxidative addition processes than is (**1**). Thus (**3**) could react with methyl iodide as in equation (3).

$$\underset{(\mathbf{3})}{\text{RhMe(CO)(PMe}_3\text{)(}\eta^2\text{-triphos)}} + \text{MeI} \rightarrow \underset{(\mathbf{4})}{[\text{RhMe}_2\text{(CO)(PMe}_3\text{)(}\eta^2\text{-triphos)]I}} \quad (3)$$

While reductive elimination of ethane from (**4**) would be expected,^{4} this does not occur. Instead, methane and ethylene (2 : 1) are formed in a process which remains obscure, although we note possible precedents in the thermal decomposition of FeMe$_2$(dpe)$_2$^{5a} (dpe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and in the oxidatively induced disproportionation of the methyl group of η^5-C$_5$H$_5$Re(NO)(PPh$_3$)Me.^{5b} A better understanding of this chemistry must await further experimentation, but we find that PMe$_3$ induces similar reactions of RhPh(CO)(triphos)^3 with methyl iodide and methylene chloride, and of (**1**) with ethyl chloride, ethyl iodide, and methylene chloride. We also find that other ligands, notably PEt$_3$, PBu$^n_3$, PMe$_2$Ph, and PMePh$_2$, induce similar albeit slower reactions of (**1**) with CH$_2$Cl$_2$, but that the bulky PPh$_3$ and the relatively non-nucleophilic CO and Bu^{t}NC do not (see above). A variety of types of organic products are formed in the alkyl halide reactions, depending *inter alia* on the nature and relative concentration of the alkyl halide.

The PMe$_3$-induced reaction of chlorotrimethyltin with (**1**) may also involve an oxidative addition step, as in equation (3), followed by reductive elimination of SnMe$_4$. The same type of reaction was induced by PEt$_3$ and PMe$_2$Ph, but not by CO or PPh$_3$. Carbon monoxide induces only the rapid formation of the acetyl compound Rh(COMe)(CO)(triphos),^{3} while the bulky phosphine is unreactive. Similar chemistry also appears to proceed with RhPh(CO)(triphos),^{3} which forms (**2**) on treatment with PMe$_3$ and Me$_3$SnCl, and with reactions of (**1**) and RhPh(CO)(triphos) with Ph$_3$SnCl and PMe$_3$, which also result in the formation of (**2**).

The phosphine-induced reaction sequence of (**1**) with acetone, however, presumably does not involve an oxidative addition process. Instead, we note what appears to be a resemblance to the chemistry of polar alkyl metal complexes such as organotitanium compounds,^{6} which are known to transfer carbanions to ketones. As this type of reactivity appears to be hitherto unknown for alkyl compounds of the platinum metals, which generally contain relatively non-polar metal–carbon σ bonds, the role of the PMe$_3$ is presumably to render the Rh–Me moiety more electron-rich and hence more nucleophilic. Again, the reaction appears to be general, as (**1**) has been found to react with both acetophenone and benzophenone to form (**2**).

In summary, partial substitution of the tridentate ligand of RhMe(CO)(triphos) (**1**) by PMe$_3$ results in the formation of a highly reactive intermediate, possibly RhMe(CO)(PMe$_3$)(η^2-triphos). The latter, more electron-rich and sterically less encumbered than (**1**), undergoes facile oxidative addition–reductive elimination processes and transfers its methyl group, as a carbanion, to ketones.

We thank the Natural Sciences and Engineering Research Council for financial assistance (operating grant to M. C. B. and graduate scholarships to G. G. J.), and Johnson-Matthey and Inco for loans of rhodium salts.

Received, 10th February 1989; Com. 9/00660E

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