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P(III) Ligands in Homogeneous Catalysis : Good Deeds and Misdeeds

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P(III) LIGANDS IN HOMOGENEOUS CATALYSIS : GOOD DEEDS AND MISDEEDS

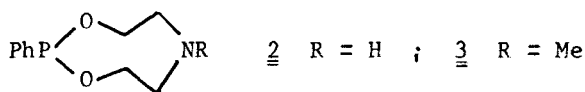
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INTRODUCTION

The use of P(III) compounds as ancillary ligands on transition metal species active in homogeneous catalysis often provides dramatic or subtle modifications of their activity and/or selectivity in the conversion of unsaturated substrates.¹ The versatile behaviour of P(III) ligands has been assessed to steric and electronic control on the co-ordination sphere of the metal centre.² This can be extended by the use of functionalized phosphanes.

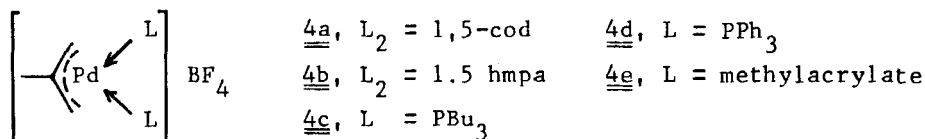
This paper will report some examples taken from our work on selective transformations of specific unsaturated substrates catalysed by tributylphosphane 1 and perhydro-1,3,6,2-dioxaphosphocines 2, 3.



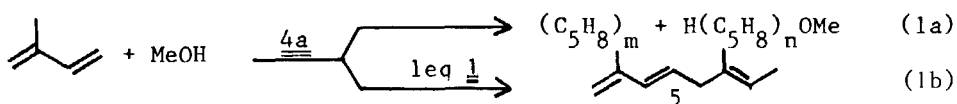
RESULTS AND DISCUSSION

Modification of cationic allylpalladium complex

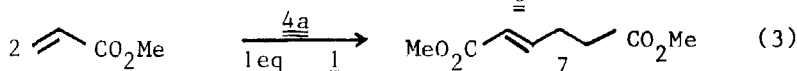
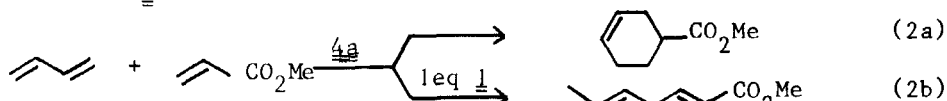
Reaction of butadiene with alcohols in the presence of 4a was



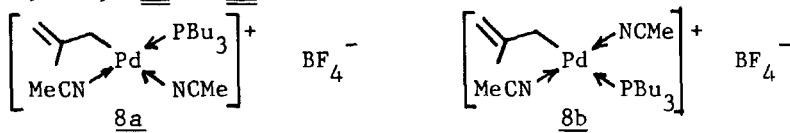
reported to produce higher telomers with a good selectivity for the telomerisation of four butadiene units with methanol.³ Extension of this reaction to isoprene led to the production of mixtures of oligomers and telomers, Eq (1a). However, addition of 1 eq 1 to 4a considerably affects the course of the reaction, Eq (1b), since the tail-to-head dimer 5 is obtained with high selectivity.



A similar behaviour is observed for the co-dimerisation of 1,3-dienes and acrylates and dimerisation of acrylates, Eqs (2), (3). Substitution of 1 with less basic phosphanes (PPh_3 , $\text{P}(\text{OPh})_3$) or excess 1 led to no reaction or to the Diels-Alder adduct.



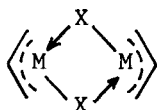
Model reactions and NMR studies indicate that the role of basic ligands is (i) to stabilize cationic hydridopalladium species, and (ii) to induce the η^3 -allyl \rightleftharpoons η^1 -allyl shift where 1,3-dienes are concerned. ^{31}P NMR monitoring of Eq (3) evidenced a singlet ($\delta 12.8\text{ppm}$) in the proton-decoupled mode and a doublet ($J_{\text{PH}} = 196 \text{ Hz}$) in the non-decoupled mode, which is assigned to trans- $[\text{Pd}(\text{H})(\text{PBu}_3)_2\text{L}]^+$. Reaction of 1 eq PPh_3 on 4a only leads to a 1:1 mixture of 4a and 4d (IR, ^1H and ^{31}P NMR). Addition of 1 eq 1 to 4a gives rise to two adducts: 4c and a complex containing the η^1 -2-methylallyl 8a or 8b



Modification of allyl-nickel and -palladium complexes

Ligands 2 and 3 reacted with η^3 -allyl complexes 9, 10 to give rise to various compounds whose structure, stability and reactivity

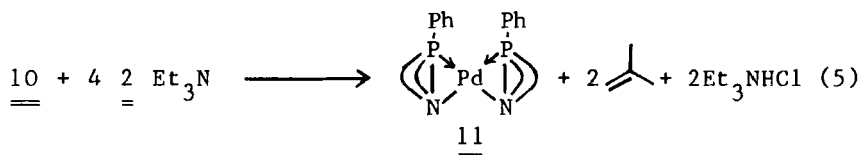
strongly depend on the nature of the metal and the nitrogen substituant, and the metal to ligand ratio. Stability trends are $\underline{2}$, $\underline{9} > \underline{2}$, $\underline{10}$ and $\underline{3}$, $\underline{10} > \underline{3}, \underline{9}$.



$\underline{9}$, M = Ni ; X = Br

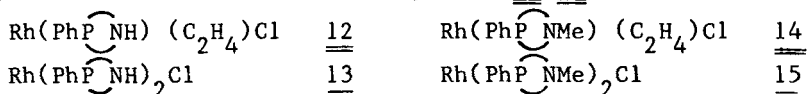
$\underline{10}$, M = Pd ; X = Cl

The occurrence of a $>NH$ moiety in $\underline{2}$ should be considered since lability of the N-H bond has been demonstrated for $\underline{2}$ -group VI metal complexes.⁵ In fact, reaction of $\underline{10}$ with 4eq $\underline{2}$ in the presence of Et_3N led to the formation of an unstable complex whose $^{31}P\{^1H\}$ NMR spectrum ($-20^\circ C$; multiplet centred at δ 14 ppm) could be assigned to $\underline{11}$, Eq (5). This reaction may explain the lack of catalytic activity for $\underline{2}$ - $\underline{9}$, $\underline{10}$ adducts in oligomerisation, co-oligomerisation and telomerisation reactions.⁶



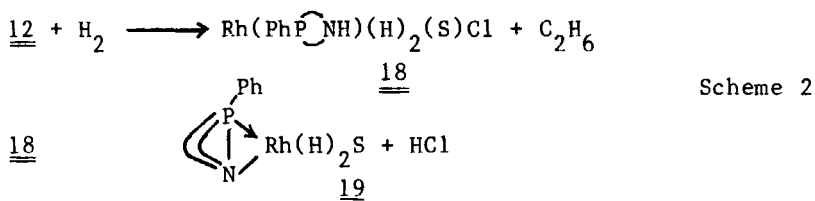
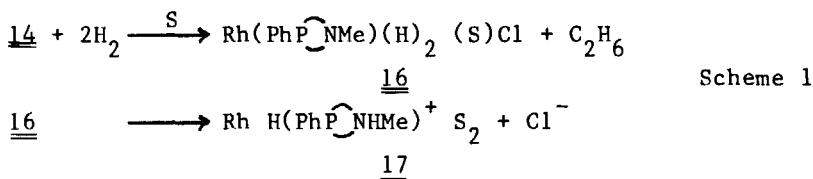
Modification of rhodium complexes

In the line of these observations, comparison of the behaviour of $\underline{2}$, $\underline{3}$ has been extended to rhodium complexes which were already known with $\underline{2}$.⁷ This comparison was carried out for the hydroformylation of hex-1-ene with complexes $\underline{12}$ - $\underline{15}$



Complex $\underline{14}$ is much more active than $\underline{12}$ and leads to a lower amount of hydrogenation products, but the n / iso ratio of C_7 aldehydes is smaller (1.5 vs 2.25). The hydrogenation and isomerisation capabilities of $\underline{14}$, $\underline{15}$ are higher than that of $\underline{12}$, $\underline{13}$. This may explain the low n / iso ratio observed for hydroformylation with $\underline{14}$. Hence, the nature of the substituant on the nitrogen donating atom of the bidentate ligands also modify the properties of the rhodium centre. This trend is confirmed by the effect of bases (Et_3N) and acids ($HClO_4$) used as "co-catalysts".

The amino arm of 2, 3 may act as a base in the case of 3, scheme 1, or may give rise to new complexes resulting from a deprotonation reaction, scheme 2, similar to that observed in Eq (5).



CONCLUSION

Drastic modifications of the activity and/or selectivity of a coordination complex can be achieved in homogeneous catalysis with trivial P(III) ligands. The use of rustic catalyst systems has obvious advantages. The increase in the complexity of P(III) ligands requires for their application sharper conditions that may restrict the development of new catalytic processes.⁸

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