

Preliminary communication

THE HYDROPALLADATION REACTION

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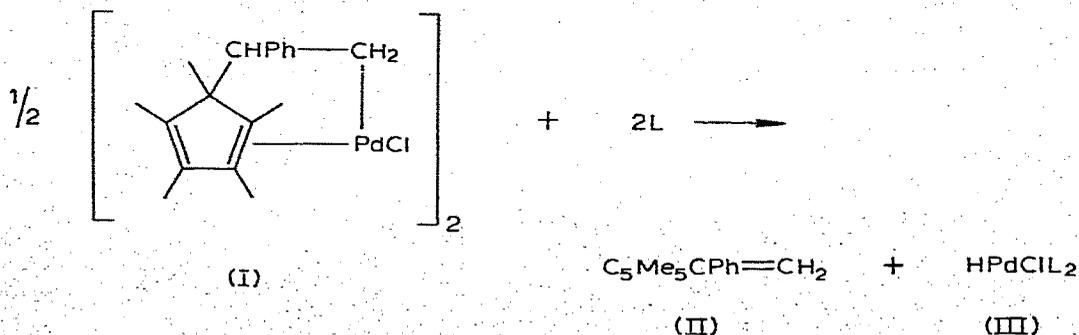
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Summary

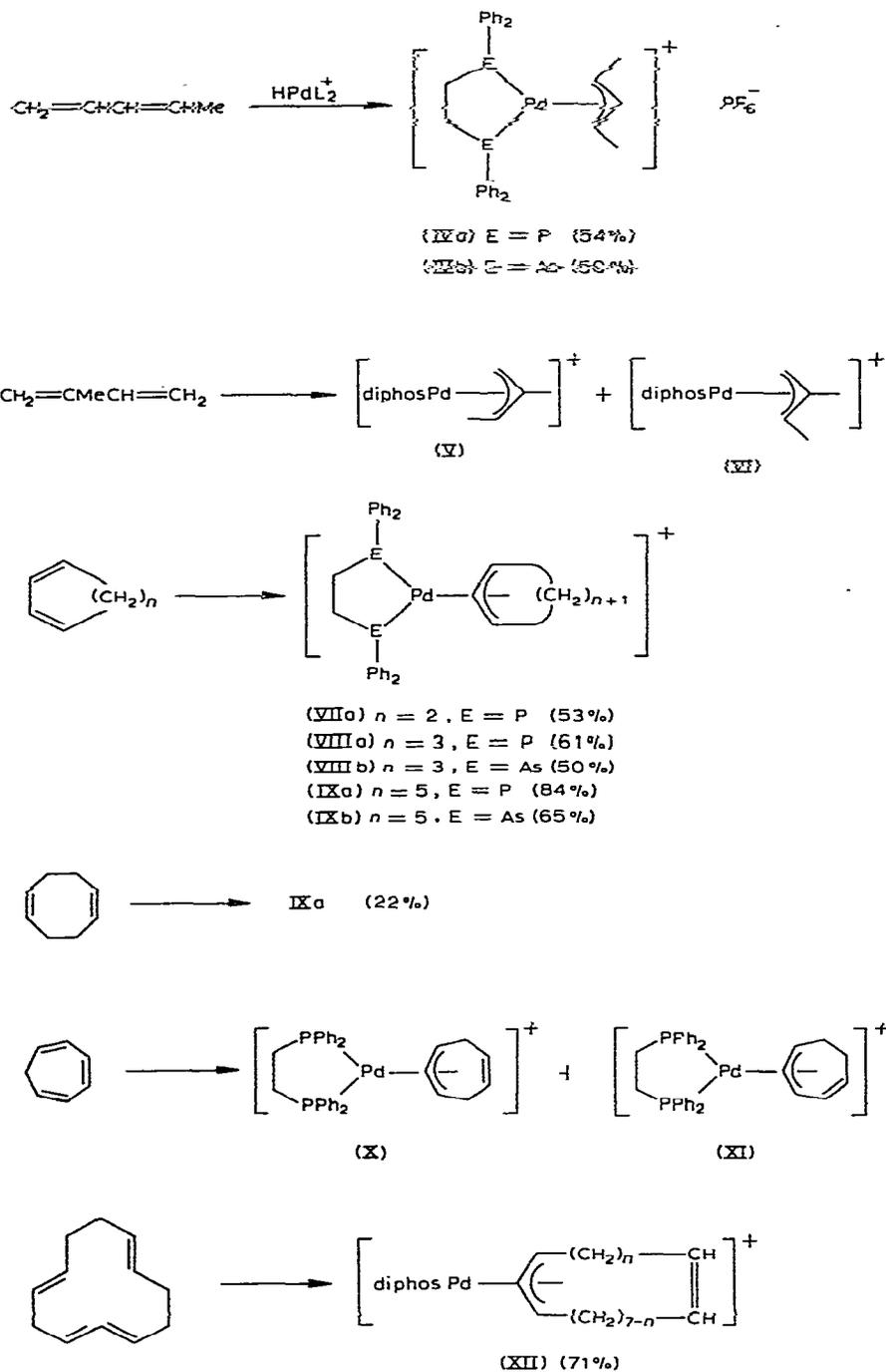
The addition of H—Pd (as $\text{HPd}[\text{Ph}_2\text{ECH}_2\text{CH}_2\text{EPh}_2]^+$, E = P or As) to a variety of 1,3-dienes gives cationic η^3 -allylic complexes; cycloocta-1,5-diene, cyclohepta-1,3,5-triene and cyclododeca-1,5,9-triene react similarly.

Although palladium hydrides have been widely implicated in a large number of catalytic and stoichiometric processes [1] there does not appear to have been any report of the direct addition of Pd—H to unsaturated organic molecules. One problem has always been the difficulty in generating an appropriate hydridopalladium compound.

We recently reported [2] that the σ, π -complex I reacted virtually quantitatively with triphenylphosphine in deacidified CDCl_3 to yield II and the hydride $\text{HPdCl}(\text{Ph}_3\text{P})_2$ (III, L = Ph_3P) which was moderately stable in CDCl_3 solution under argon at 25°C . Similar results have been obtained for L = tricyclohexylphosphine which gave the more stable *trans*- $\text{HPdCl}[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ [Pd—H τ 25.16 ppm; triplet, $J(\text{HP})$ 4.6 Hz]. Such reactions therefore represent a convenient in situ synthesis of palladium hydride complexes.



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Scheme 1

We describe here the reactions of the hydrides HPdL_2^{+*} , formed from I and the chelating ligands L_2 [$\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (diphos) or $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ (dae)] in the presence of AgPF_6 , with 1,3-dienes to give cationic η^3 -allylic complexes IV-IX. No formation of these allylic complexes was observed in the absence of AgPF_6 , the function of which is presumably to remove Cl^- and thereby create a vacant site *cis* to the hydride at which reaction can occur. The structures of the η^3 -allylic complexes were determined by microanalysis, ^1H , ^{13}C , and ^{31}P NMR spectroscopy and the results are summarised in Scheme 1.

It may be noted that isoprene gave the *anti*-1,2-dimethylallyl (V) as well as the *syn*-1,2-dimethylallyl complex (VI); this is similar to the observations of Tolman for additions to $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$ [3]. The cyclic dienes, cyclopentadiene, cyclohexa-1,3-diene and cycloocta-1,3-diene all gave the expected allylic complexes VII-IX (with yields increasing with increase in ring-size). The 1-3- η -cyclooctenyl complex was also obtained, though in poorer yield, from cycloocta-1,5-diene. This type of isomerisation is not uncommon [4].

An interesting reaction is that with cyclohepta-1,3,5-triene to give a mixture of the 1-3- η -cyclohepta-1,5-dienyl complex (X) and the 1-3- η -cyclohepta-1,4-dienyl complex (XI) (total yield 87%). The presence of both isomers was established from the ^1H -decoupled ^{31}P NMR spectrum which showed a singlet (δ 48.3, with respect to external 85% H_3PO_4) due to X, where the two phosphorus atoms are equivalent, as well as a double doublet [δ 45.7, 53.3; $J(\text{PP}')$ 43 Hz] due to XI which has two inequivalent phosphorus atoms. The ratio of X:XI was 3:7.

Cyclododeca-1,5,9-triene gave a single material XII with two inequivalent phosphorus atoms [δ 48.8, 49.4; $J(\text{PP}')$ 36 Hz], but no structure could be established for the ligand.

Reactions were also carried out with norbornadiene and but-2-yne; in both cases polymeric materials were obtained.

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References

- 1 See, for example, P.M. Maitlis, *The Organic Chemistry of Palladium*, Academic Press, New York, 1971, Vol. II, p. 127.
- 2 T. Hosokawa and P.M. Maitlis, *J. Amer. Chem. Soc.*, 95 (1973) 4924.
- 3 C.A. Tolman, *J. Amer. Chem. Soc.*, 92 (1970) 6785.
- 4 See, for example, K. Moseley, J.W. Kang and P.M. Maitlis, *Chem. Commun.*, (1969) 1155; H.B. Lee and P.M. Maitlis, *Chem. Commun.*, (1974) 601; H.B. Lee, K. Moseley, C. White and P.M. Maitlis, *J. Chem. Soc. Dalton*, (1975) in the press.

* Attempts to detect these species by NMR at low temperature were unsuccessful since reaction of I with L_2 only occurred at temperatures where further reaction was extremely rapid.