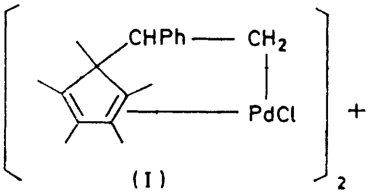
The Hydropalladation of Di- and Tri-olefins to give η^3-Allylic Palladium Complexes

By **Derek J. Mabbott** and **Peter M. Maitlis,*** Department of Chemistry, The University, Sheffield S3 7HF

Complexes of the type $[PdHL_2]^+$ [IIa; L_2 = 1,2-bis(diphenylphosphino)ethane and IIb; L_2 = 1,2-bis(diphenylarsino)-ethane], generated *in situ* by treatment of $[\{Pd(CH_2CHPhC_5Me_5)Cl\}_2]$ with $Ag[PF_6]$ and L_2, were treated with penta-1,3-diene, isoprene, cyclopentadiene, cyclohexa-1,3-diene, and cyclo-octa-1,3-diene to give the appropriate complexes of the type $[Pd(all)L_2][PF_6]$ (all = 1—3-η-allylic ligand) by addition of Pd–H to a double bond. Cyclo-octa-1,5-diene underwent isomerisation to give the same 1—3-η-cyclo-octenyl complex obtained from cyclo-octa-1,3-diene. Cycloheptatriene gave a mixture of two η^3-cycloheptadienyl complexes, while cyclododeca-1,5,9-triene gave an η^3-cyclododecadienyl complex. The complexes were characterised by ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy.

ALTHOUGH reactions of compounds containing Ni–H, Pt–H, Ni–C, Pd–C, and Pt–C bonds with olefins, dienes, and acetylenes to give insertion products are well-documented there has, with one exception, been no report of the reactions of species containing Pd–H with unsaturated organic molecules. Brooks and Glockling, who reported the first preparation of a palladium hydride complex, $[PdClH(PEt_3)_2]$,[1] noted that reaction did occur with phenylacetylene, butadiene, and acrylonitrile but were unable to characterise the products. In part this omission has certainly stemmed from the relative inaccessibility of palladium hydrides; however, such species have been widely implicated as intermediates in a large number of catalytic processes.[2]

One of us recently reported a convenient method for obtaining $[PdClH(PPh_3)_2]$ by reaction of the σ,π-complex (I) with triphenylphosphine;[3] a similar reaction also occurred with tricyclohexylphosphine (Pcy$_3$) to give the more stable $[PdClH(Pcy_3)_2]$.



(I)

$$+\ 4L \longrightarrow 2C_5Me_5CPh{=}CH_2 + 2[PdClHL_2]$$

When the hydridochloro-complexes $[PdClHL_2]$ were formed *in situ* in the presence of a diene (*e.g.* isoprene) no further reaction occurred. This is presumably due to the absence of an easily accessible co-ordination site on the metal at which reaction can occur. In order to create such a site and to ensure that the bonding diene and the hydride were mutually *cis* the reactions were carried out in the presence of silver hexafluorophosphate (to remove chloride) and with L_2 = bis(1,2-diphenylphosphino)-ethane (diphos) or bis(1,2-diphenylarsino)ethane (dae). This generated $[PdH(Ph_2PCH_2CH_2PPh_2)]^+$, (IIa), or $[PdH(Ph_2AsCH_2CH_2AsPh_2)]^+$, (IIb), *in situ* which then reacted with the diene or triene. A preliminary account of this work has been published,[4] and the observed reactions and products are summarised in the Scheme.

RESULTS AND DISCUSSION

Penta-1,3-*diene*.—Only a single compound, the η^3-1,3-dimethylallyl complex (IIIa), was isolated from reaction of penta-1,3-diene with (IIa). In order to simplify the n.m.r. spectra by removing coupling to phosphorus, the analogous dae complex (IIIb) from pentadiene and (IIb) was also prepared. The n.m.r. spectra of neither complex showed any evidence of isomer formation and, moreover, also allowed the conclusion to be drawn that addition of Pd–H had occurred to the terminal double bond.

The ^1H n.m.r. spectrum of (IIIb) (Table 1) showed that $J(H^1-H^2)$ = 12 Hz; by analogy with the *syn*,*syn*-η^3-1,3-dimethylallyltris(trimethyl phosphite)nickel cation where $J(H^1-H^2)$ = 11.5 Hz,[5] we therefore formulate (IIIb) with both methyls *syn*.

The ^1H spectrum of the diphos complex (IIIa) was similar but with added coupling to ^{31}P. In particular the methyl groups appeared here as a double triplet

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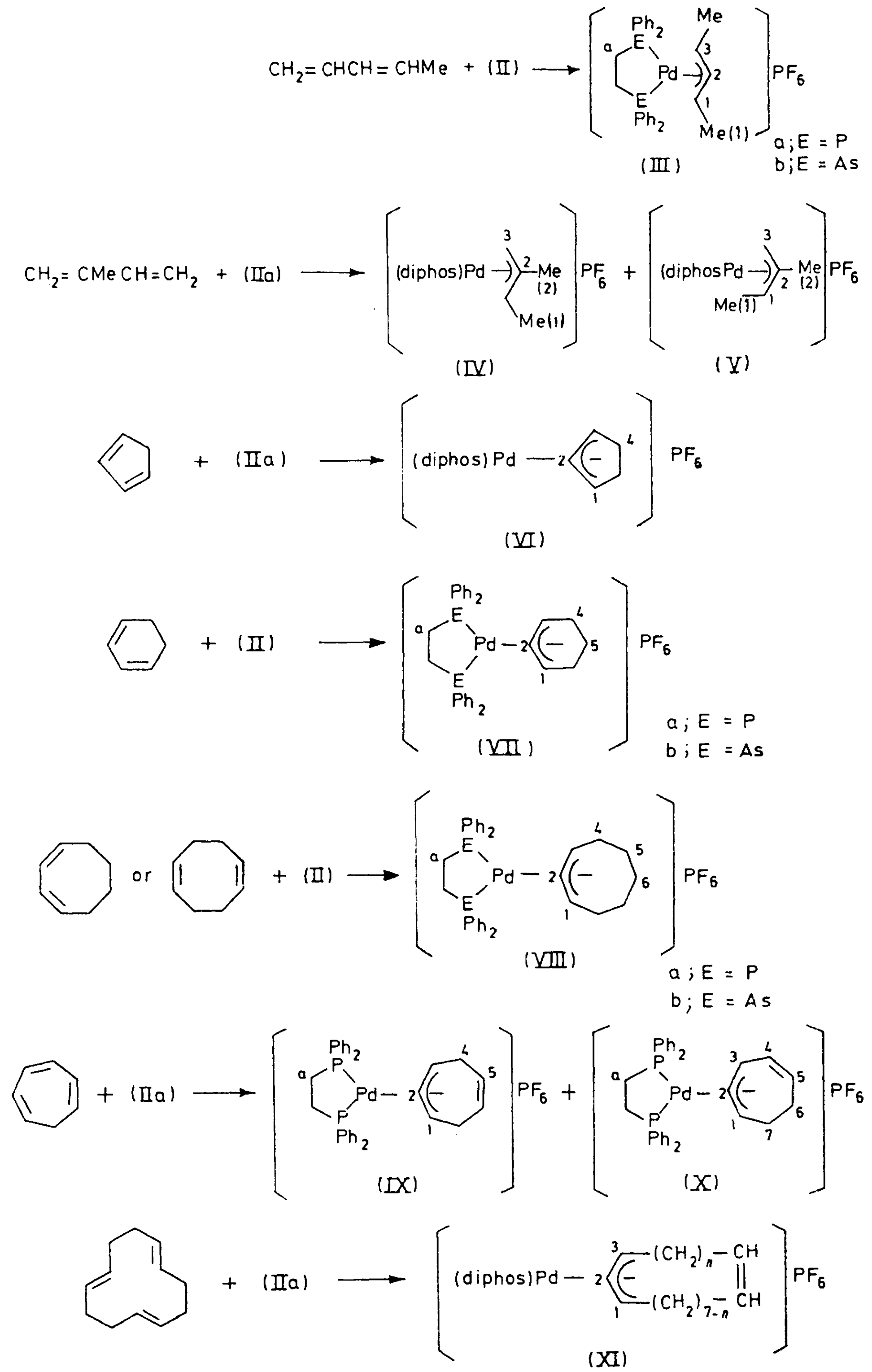
[1] E. H. Brooks and F. Glockling, *J. Chem. Soc.* (*A*), 1967, 1030.

[2] See, for example, P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. II, p. 127.

[3] T. Hosokawa and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1973, **95**, 4927.

[4] D. J. Mabbott and P. M. Maitlis, *J. Organometallic Chem.*, 1975, **102**, C34.

[5] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6785.



SCHEME

whereas in the dae complex (IIIb) only a doublet was observed, due to coupling to H^1. The observation of a triplet is probably a consequence of 'virtual coupling' where the protons of the methyl groups are coupled to both ^{31}P nuclei and are subject to their combined spin states.[6] The observed apparent coupling, J_{app}(H–P), of 10 Hz is then given by

$$J_{app}(\text{H–P}) = \tfrac{1}{2}|J(\text{H–P}^1) + J(\text{H–P}^2)| = \tfrac{1}{2}N\{\text{H–P}\}$$

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[6] D. E. Axelson and C. E. Holloway, *J.C.S. Chem. Comm.*, 1973, 455.

and the coupling is most conveniently expressed in terms of $N\{H-P\}$, in this case 20 Hz.

Similar triplets were found in the ^{13}C resonances of C(a) and C(1) in (IIIa), and again these coupling constants are most conveniently expressed in terms of the analogous quantity

$$N\{C-P\} = |J(C-P^1) + J(C-P^2)| = 2J_{app}(C-P)$$

The observed $N\{C-P\}$ are in good agreement with reported values for $[Pd(C_3H_5)(PR_3)_2]^+$.[6]

TABLE 1

N.m.r. spectra

Compound	^1H spectra (δ) [a]	$^{13}C\{H\}$ spectra (δ) [c] C(a) [d]	C(1)	C(2)	Other resonances
$[Pd(diphos)(\eta^3\text{-}1,3\text{-dimethylallyl})][PF_6]$ (IIIa)	1.61 (6 H, dt, J = 6,[b] $N\{PH\}$ = 20), 2.49 (4 H, m), 4.08 (2 H_{anti}, m), 5.64 (1 H, t, J = 12), 7.47 (20 H, Ph)	28.4{46}	85.9{34}	123.8(6) [e]	18.0[Me(1)]
$[Pd(dae)(\eta^3\text{-}1,3\text{-dimethylallyl})][PF_6]$ (IIIb)	1.78 (6 H, d, J = 6), 2.48 (4 H, m), 4.49 (2 H, dt, J = 6 and 12), 5.77 (1 H, t, J = 12), 7.47 (20 H, Ph)				
$[Pd(diphos)(\eta^3\text{-}1,2\text{-dimethylallyl})][PF_6]$ (IV)	1.51 (3 H, dt, J = 6, $N\{PH\}$ = 20), 1.84 (3 H, s,) 2.55 (4 H, m), 3.07 (1 H, m), 4.23 (1 H, q, J = 6), 4.44 (1 H_{syn}, m), 7.50 (20 H, Ph)	27.7{m}	87.5{m}	N.o.	67.1{m}[C(3)] 19.8[Me(1)] 15.0[Me(2)]
$[Pd(diphos)(1\text{—}3\text{-}\eta\text{-cyclopentenyl})][PF_6]$ (VI)	1.84 (4 H, m), 2.57 (4 H, m), 6.00 (1 H, t, J = 4), 6.17 (2 H, m), 7.45 (20 H, Ph)	27.4{46}	92.3{32}	116.3(7) [e]	30.0[C(4)]
$[Pd(diphos)(1\text{—}3\text{-}\eta\text{-cyclohexenyl})][PF_6]$ (VIIa)	1.20, 2,50 (10 H, bm), 5.84 (1 H, t, J = 7), 5.91 (2 H, m), 7.48 (20 H, Ph)	27.6{46}	86.9{35}	113.6(7) [e]	27.9[C(4)] 19.2[C(5)]
$[Pd(dae)(1\text{—}3\text{-}\eta\text{-cyclohexenyl})][PF_6]$ (VIIb)	1.46, 2.20 (6 H, bm), 2.58 (4 H, m), 5.76 (1 H, t, J = 6), 6.40 (2 H, bt, J = 6), 7.45 (20 H, Ph)	24.9	86.9	111.6	28.6[C(4)] 19.1[C(5)]
$[Pd(diphos)(1\text{—}3\text{-}\eta\text{-cyclo-octenyl})][PF_6]$ [c] (VIIIa)	1.46, 1.86 (10 H, bm), 2.62 (4 H, m), 5.43 (2 H, bt, J = 8), 5.63 (1 H, t, J = 8), 7.48 (20 H, Ph)	27.7{46}	86.6{37}	115.9(6) [e]	31.2[C(4)] 27.4[C(5)] 22.3[C(6)]
$[Pd(dae)(1\text{—}3\text{-}\eta\text{-cyclo-octenyl})][PF_6]$ (VIIIb)	1.58 (10 H, b), 2.57 (4 H, m), 5.60 (2 H, m, J = 8), 5.84 (1 H, t, J = 8), 7.45 (20 H, Ph)	25.1	86.4	113.9	31.8[C(4)] 27.3[C(5)] 23.0[C(6)]
$[Pd(diphos)(\eta^3\text{-cycloheptadienyl})][PF_6]$ (IX) + (X)	2.10 (4 H, b), 2.56 (4 H, b), 5.60 (5 H, b), 7.48 (20 H, Ph)	(IX) 27.8{46} (X) [f] 26.8(14) [e] 28.0(14)	86.4{37} 114.2(5, 18) [e]	113.0(6) [e] 118.8(6) [e]	33.6[C(4)] 126.8[C(5)] 88.5(6, 26)[C(3)] 35.5[C(6)]
$[Pd(diphos)(\eta^3\text{-cyclododecadienyl})][PF_6]$ (XI)	2.00 (18 H, b), 3.64 (2 H, b), 5.36 (3 H, b), 7.47 (20 H, Ph)	27.2{46}	86.4{12}		

[a] In $CDCl_3$ at 100 MHz except for (VIIIa) which was also measured at 220 MHz. [b] J in Hz. [c] Proton-decoupled ^{13}C spectra in $CDCl_3$ except for (IX) + (X) and (XI) which were measured in CD_2Cl_2. Numbers in parentheses are $N\{^{13}C-^{31}P\}$. Phenyl carbons have been omitted as they gave rise to very complex patterns in all cases. [d] C(a) is the CH_2 of diphos or dae. [e] $J(^{13}C-^{31}P)$. [f] Assigned by comparison with an authentic specimen by Dr. B. E. Mann. The molecule is fluxional.[10]

Isoprene.—The major component from reaction of isoprene with (IIa) was identified as the η^3-*syn*-1,2-dimethylallyl cation (IV) by comparison of its ^1H n.m.r. spectrum with the spectra of chloro(η^3-*syn*-1,2-dimethylallyl)(pentamethylcyclopentadienyl)-rhodium and -iridium,[7] as well as of the η^3-*syn*-1,2-dimethylallyltris(trimethyl phosphite)nickel cation.[5] In addition, the spectrum showed other very weak resonances due to another isomer, only the methyl resonances of which could clearly be distinguished at δ 1.89 (s) and 0.99 (m). The very high-field position of the latter is consistent with it being an *anti*-1-methyl and its multiplicity indicates that it must be directly coupled to a vicinal proton; hence these signals are assigned to the η^3-*anti*-1,2-dimethylallyl isomer, (V), present to the extent of *ca.* 10%.

The ^{31}P-{H} n.m.r. spectrum showed an AB pattern for the two most intense resonances (δ 48.4 and 49.4), indicating that the two phosphorus atoms in (IV) were inequivalent, as anticipated, with $J(P^1-P^2)$ = 32 Hz.

Cyclopentadiene and Cyclohexa-1,3-*diene.*—Both cyclopentadiene (from freshly cracked dicyclopentadiene) and cyclohexa-1,3-diene reacted very readily with (II) to give the η^3-cyclopentenyl- (VI) and η^3-cyclohexenyl- (VIIa or b) complexes respectively. The complexes were identified through their ^1H n.m.r. spectra; in particular, the triplet resonances in (VI) at δ 6.00 (J = 4 Hz), in (VIIa) at 5.84 (J = 7 Hz), and in (VIIb) at 5.76 (J = 6 Hz) arising from H^2 are characteristic for such ligands.[8] In these complexes H^1 (H^3) appear at *lower* field than H^2 whereas in the η^3-cyclohexenyl- and η^3-cyclopentenyl(pentamethylcyclopentadienyl)-rhodium and -iridium complexes of these ligands[8] the reverse occurs. The ^{13}C n.m.r. spectra of (VI), (VIIa), and (VIIb) are entirely consistent with the formulation.

Cyclo-octa-1,3- *and* -1,5-*diene.*—Both these dienes reacted with (IIa) to give the same complex which was identified as the 1—3-η-cyclo-octenyl complex (VIIIa). The dae complex (IIb) reacted with cyclo-octa-1,3-diene (1,3-cod) to give (VIIIb). Both these complexes were characterised by n.m.r. spectroscopy, in particular by the

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[7] H. B. Lee and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2316.

[8] H. B. Lee, K. Moseley, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2322.

typical[8] low field triplets ($J = 8$ Hz) at δ 5.63 (VIIIa) and 5.84 (VIIIb) in their ^{1}H spectra. The ^{13}C spectra were conclusive in formulating the complexes as 1—3-η- rather than 1:3,4-η- or 1:4,5-η-cyclo-octenyl since only the 1—3-η- would be expected to show the observed pattern and the observed number of resonances.

The observation that both 1,3-cod and 1,5-cod give the same 1—3-η-cyclo-octenyl complex is not surprising since palladium has long been known to be effective in double-bond isomerisation. This is, however, the first case in which a palladium hydride has clearly been implicated in such an isomerisation. The observed reaction is very reminiscent of the reaction of $[M_2Cl_3H(C_5Me_5)_2]$ (M = Rh or Ir) with 1,3-cod, 1,4-cod, or 1,5-cod in which again the isolated product was the 1—3-η-cyclo-octenyl-rhodium or -iridium complex.[8] A similar mechanism involving stepwise addition/elimination of Pd–H to a double-bond can readily be envisaged; and here too the 1—3-η-cyclo-octenyl is presumably the thermodynamically most stable isomer. The yield of (VIIIa) from 1,5-cod was much poorer (22%) than from 1,3-cod, though this may have been due to a competing reaction involving 1,5-cod and (I).[9]

TABLE 2

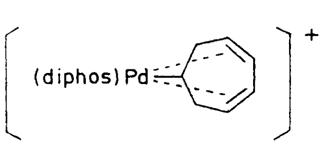
Analytical data (calculated values in parentheses) and yields

Compound		C (%)	H (%)	Yield (%)
$[Pd(diphos)(\eta^3\text{-}1,3\text{-dimethylallyl})][PF_6]$	(IIIa)	52.0 (51.8)	4.9 (4.6)	54
$[Pd(dae)(\eta^3\text{-}1,3\text{-dimethylallyl})][PF_6]$	(IIIb)	45.7 (46.2)	4.3 (4.1)	50
$[Pd(diphos)(\eta^3\text{-}1,2\text{-dimethylallyl})][PF_6]$	(IV) + (V)	51.7 (51.8)	4.8 (4.6)	72
$[Pd(diphos)(\eta^3\text{-cyclopentenyl})][PF_6]\cdot$acetone [a]	(VI)	52.9 (52.7)	4.6 (4.8)	53
$[Pd(diphos)(\eta^3\text{-cyclohexenyl})][PF_6]\cdot$acetone [a]	(VIIa)	53.4 (53.3)	5.2 (5.0)	61
$[Pd(dae)(\eta^3\text{-cyclohexenyl})][PF_6]$	(VIIb)	47.0 (46.9)	4.3 (4.0)	50
$[Pd(diphos)(\eta^3\text{-cyclo-octenyl})][PF_6]$	(VIIIa)	53.9 (53.8)	5.1 (4.9)	84
$[Pd(dae)(\eta^3\text{-cyclo-octenyl})][PF_6]$	(VIIIb)	48.5 (48.2)	4.6 (4.4)	65
$[Pd(diphos)(\eta^3\text{-cycloheptadienyl})][PF_6]$	(IX) + (X)	53.5 (53.3)	4.7 (4.5)	87
$[Pd(diphos)(\eta^3\text{-cyclododecadienyl})][PF_6]$	(XI)	55.9 (56.1)	5.3 (5.3)	71

[a] These complexes contained 1 molecule of acetone as confirmed by ^{1}H n.m.r. spectroscopy.

Cycloheptatriene.—The ^{1}H spectrum of the reaction product of (IIa) and cycloheptatriene could shed little light on the nature of the η-cycloheptadienyl ligand there. However, the ^{31}P-{H} spectrum showed a singlet (δ 48.3) arising from one species with equivalent phosphorus atoms and an AB pattern [δ 45.7, 53.3, $J(P^1\text{–}P^2) = 43$ Hz] arising from another species with inequivalent phosphorus atoms.

The compound which gave rise to the singlet ^{31}P resonance must be the symmetrical complex (IX). The other one could be the 1—3-η-isomer (X) or the σ,π-isomer (XIII), but only the formulation (X) is in agreement with the ^{13}C n.m.r. spectrum.[10] This structure is also to be expected since palladium has such a strong tendency to give 1—3-η-allylically bonded complexes.



(XIII)

trans,trans,trans-*Cyclododeca*-1,5,9-*triene* (*cdt*).—Reaction of cdt with (IIa) gave a crystalline material which appeared to be a single isomer. The ^{1}H n.m.r. spectrum showed only broad signals corresponding to three allylic protons (δ 5.36) and two olefinic protons (3.64), and the ^{13}C spectrum was not more informative. The ^{31}P-{H} spectrum showed an AB pattern [δ 48.8 and 49.4, $J(P^1\text{–}P^2) = 36$ Hz] indicating the two phosphorus atoms to be inequivalent and hence that the cyclododecadienyl ligand was asymmetrically bonded as expected. No further characterisation of the isomer present was possible.

Conclusion.—Pd–H [in the species (IIa) and (IIb) formed *in situ*] adds readily to a variety of di- and tri-olefins to give η^3-allylic complexes in high yields. Previous investigations of the reactions of M–H (M = Ni,[5] Rh, or Ir[8]) with acyclic conjugated dienes have shown that the reaction can take two different paths, with the diene adopting either an *s-cis*[5] or an *s-trans*[8] conformation. Evidence for the pathway of the Pd–H reactions reported here is limited, but our assignment of the *anti*-1,2-dimethylallyl to the minor isomer from reaction of (IIa) with isoprene suggests that the *s-cis* form of isoprene does react here. This may indeed be the major pathway as in the reactions of dienes with $[NiH\{P(OMe)_3\}_4]^+$ since Tolman[5] observed there that the *anti*-1-methyl isomer was kinetically favoured even though the *syn*-1-methyl isomer was the thermodynamically most stable final product. It was not possible to determine whether this is also the case in the work described here.

It may also be noted that the isolated yields of the cyclic η^3-allylic complexes from the 1,3-dienes and (IIa) increased with ring size (C_5 53%; C_6 61%; C_8 87%), and that the diphos complex (IIa) always gave higher yields than the dae complex (IIb).

Reaction of (IIa) with norbornadiene and but-2-yne gave polymeric materials which were not further characterised.

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[9] D. J. Mabbott, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1975, 521.

[10] B. E. Mann and P. M. Maitlis, unpublished results.

EXPERIMENTAL

Reactions were carried out under nitrogen. Complex (I) was prepared by the route described.[3] Yields and analytical data are collected in Table 2, and a typical reaction is described below. All the complexes were reasonably air-stable and did not decompose over long periods when kept below 0 °C.

[1,2-*Bis(diphenylphosphino)ethane*](1–3-η-*cyclo-octenyl)palladium Hexafluorophosphate* (VIIIa).—Silver hexafluorophosphate (0.13 g, 0.5 mmol) was added to a solution of the complex (I) (0.16 g, 0.21 mmol) in acetone (30 ml) at 20 °C; after the solution had been stirred for 5 min the precipitated silver chloride was filtered off to leave a yellow solution of $[\overline{\mathrm{Pd(CH_2CHPhC}}\mathrm{_5Me_5)(Me_2CO)_2][PF_6]}$. To this was added cyclo-octa-1,3-diene (1 ml) followed by 1,2-bis(diphenylphosphino)ethane (0.18 g, 0.45 mmol), whereupon the colour changed from yellow to green. The solution was stirred for 15 min and then evaporated to dryness on a rotary evaporator. The product was crystallised from acetone–diethyl ether (after purification with activated charcoal) to give colourless crystals of (VIIIa).

In separate experiments it was shown that cyclo-octa-1,3-diene did not react with (I) in the presence of $\mathrm{Ag[PF_6]}$.

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