New Polyphosphorus Ligands: Addition Reactions of 1,1-Bisdiphenylphosphinoethene

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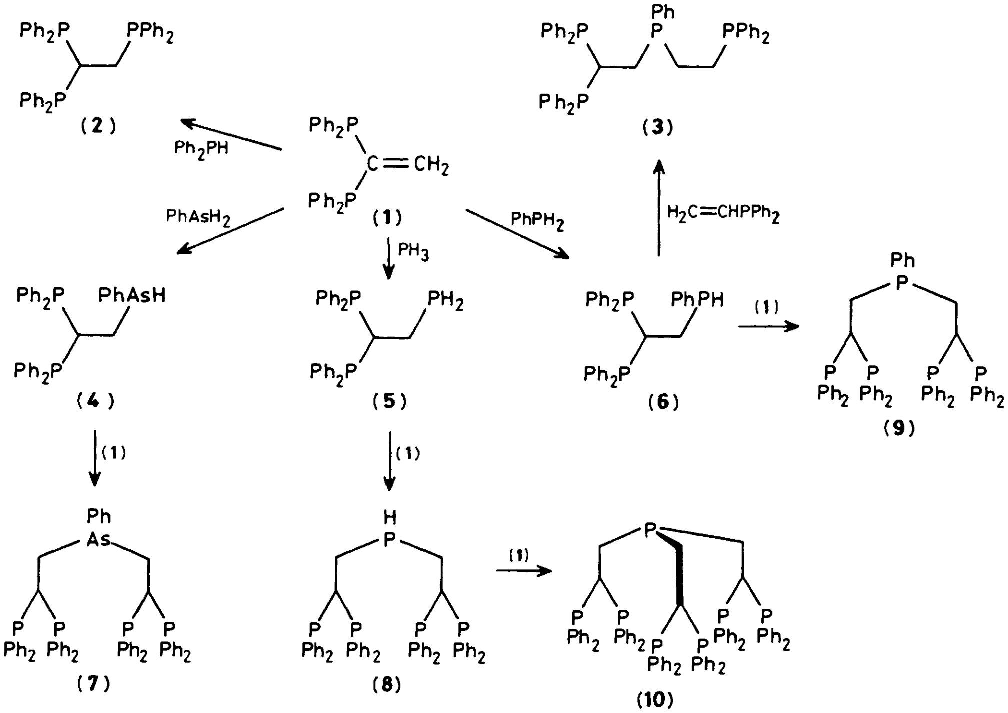
The reactivity of the double bond adjacent to the geminal diphenylphosphino groups of $(Ph_2P)_2C{=}CH_2$ facilitates the addition of species with one or more P–H bonds to provide a convenient high-yielding route to a range of new poly- and ambi-dentate ligands which can form a wide variety of different types of transition metal complex.

We have previously described[1] the synthesis of 1,1-bisdiphenylphosphinoethene (**1**), a versatile chelating ligand with a somewhat larger bite than bisdiphenylphosphinomethane, dppm,[2] and some of its transition metal complexes.[3] The presence of the double bond in (**1**) and its complexes provides the opportunity for a range of addition reactions not available to dppm, and we have used this feature to prepare 1,1,2-trisdiphenylphosphinoethane (**2**) and some of its deriva-

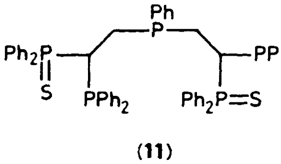


Scheme 1. Addition reactions of 1,1-bisdiphenylphosphinoethene (**1**). (Room temperature, in tetrahydrofuran, with Bu^tOK catalyst.)

Table 1. ^{31}P N.m.r. data for the ligands.

	Chemical shift, p.p.m.^{a}			Coupling constant/Hz		
Compound	P_A	P_B	P_C	$^2J(P_AP_B)$	$^3J(P_AP_C)$	$^3J(P_BP_C)$
(2)	−4.0	—	−19.6	b	24.4	—
(3)^c	−4.0	−4.0	−23.8	b	20.1	20.1
(6)	−3.9	−5.8	−54.8	112.3	15.9	17.1
(7)	−3.2	−4.6	—	96.3	—	—
(9)	−2.9	−4.8	−29.7	100.7	28.6	17.0
(10)	−2.7	—	−27.3	b	25.3	—

^{a} To high frequency of 85% H_3PO_4. P_A and P_B refer to geminal P atoms. ^{b} Not directly measurable from ^{31}P n.m.r. spectrum. ^{c} $\delta(P_D)$ −11.2 p.p.m.; $^3J(P_CP_D)$ 27.5 Hz. ^{d} In CH_2Cl_2, 10 mm tube.



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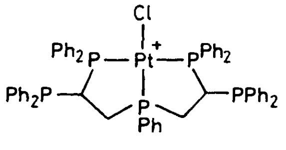

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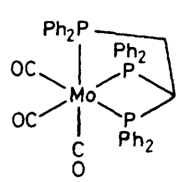

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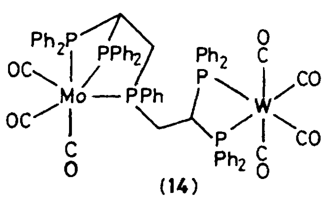

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tives.[4] We now report that this reaction is of wide scope owing to the enhanced reactivity of the double bond arising from the presence of the geminal diphenylphosphino groups even without any effect due to metal co-ordination,[5,6] and that it provides a straightforward high-yielding route to a range of potentially ambi- and poly-dentate ligands.

Typically, species with P–H bonds add to (**1**) in the presence of potassium t-butoxide[7] as shown in Scheme 1, which also illustrates corresponding reactions of some species with As–H bonds. The products were identified primarily from their characteristic ^{31}P n.m.r. spectra (multinuclear JEOL FX90Q operating at 36.2 MHz), and in addition compounds (**2**), (**3**), (**6**), (**7**), (**9**), and (**10**) have been obtained as air-stable white crystalline solids with sharp melting points and satisfactory elemental analyses.

In certain of these molecules the geminally related phosphorus atoms are rendered inequivalent by the presence of a chiral [(**4**) and (**6**)] or prochiral [(**7**)—(**9**)] centre at the other phosphorus or the arsenic atom, and this has important consequences for their n.m.r. spectra and their chemical behaviour. Thus different values of $\delta(^{31}P)$ and $^3J(^{31}P–^{31}P)$ occur (Table 1), and it is possible to measure $^2J(^{31}P–^{31}P)$ directly, values between 97 and 113 Hz being found. These may be compared with 125 Hz in dppm as determined by $^{13}C\{^{31}P\}$ multiple resonance experiments.[1] To a large extent the different values of the vicinal $^{31}P–^{31}P$ couplings probably reflect substantial imbalances in the conformational populations, and this is confirmed by the significant temperature dependences that we have found for these couplings. These conformational imbalances also have differential effects upon the reactivity of the phosphorus atoms, so that in reactions [*e.g.* with S_8 to give (**11**)] that can yield diastereoisomeric products these are *not obtained in the proportions to be expected on a simple statistical basis*. This observation has considerable bearing on the formation of metal complexes such as (**12**) by these ligands, and here too we find that the three isomers (arising from different relative orientations of the Ph_2P and Ph groups) are produced in apparently anomalous proportions.

As ligands, (**2**), (**5**), and (**6**) can co-ordinate in many different ways, and in particular resemble dppm and dppe in having the capability to form complexes with four- and five-membered chelate rings. In practice, direct reaction between the ligand and the metal-containing substrate tends to give complexes in which five-membered (presumably less strained) rings are favoured, but complexes with four-membered rings can be made indirectly although they tend to rearrange at elevated temperatures. It is also possible to make complexes such as (**13**) in which all three phosphorus atoms are co-ordinated to the same metal atom to give one four- and two five-membered chelate rings despite the considerable strain involved.

The possibilities for (**7**)—(**10**) are even more extensive, and we find that complexes such as (**12**) with two five-membered chelate rings and the remaining phosphorus atoms unco-ordinated are especially favoured. Further co-ordination to the *same* metal atom would involve very substantial strain, but we have made complexes in which the ligands have become pentadentate by bridging two metals as in (**14**).

We thank Dr. B. Wrackmeyer for gifts of phenylphosphine and phenylarsine, and the S.E.R.C. and the Sir John Cass's Foundation for support.

Received, 27th March 1986; Com. 403

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