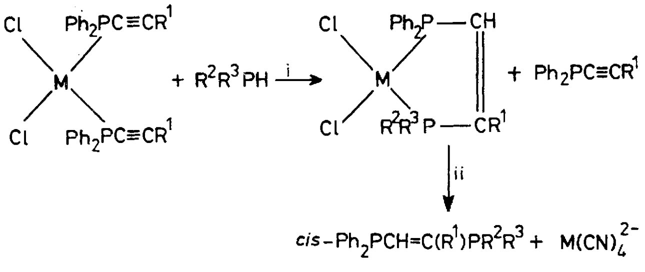
Stereospecific, Transition Metal-mediated Synthesis of Unsymmetrical *cis* Olefinic Diphosphines

By DAVID K. JOHNSON and ARTHUR J. CARTY*

(*Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada* N2L 3G1)

Summary Rigid, unsymmetrical *cis* olefinic diphosphines $Ph_2PCH{=}C(R^1)PR^2R^3$ can be synthesised in good yields by the stereospecific addition of secondary phosphines R^2R^3PH across the triple bond of a phosphorus co-ordinated phosphinoacetylene in *cis*-$MCl_2(Ph_2PC{\equiv}CR)_2$ ($M = Pd$ or Pt); a fundamental change in coupling through the metal atom is responsible for the sequence of $J\,^{31}P\text{–}^{31}P$ values (Ni>>Pd>Pt) in d^8 complexes of $Ph_2PCH{=}C(R^1)PR^2R^3$.

THE synthesis and co-ordination chemistry of rigid ditertiary phosphines have recently assumed renewed importance with the development of transition metal based asymmetric catalytic systems for the production of optically pure steroids and amino-acids.[1] We report a novel synthetic route (Scheme) to symmetrical or unsymmetrical, rigid



SCHEME. i, CH_2Cl_2. ii, Excess CN^-, H_2O–C_6H_6; in a typical experiment the platinum chloride complex (1 g) and KCN (12 g) were heated to reflux overnight in C_6H_6 (250 ml) and degassed water (120 ml). The organic layer was separated, dried over $MgSO_4$, filtered, and evaporated to give the diphosphine.

TABLE

Yields and ^{31}P n.m.r. parameters[a] for selected diphosphines and their complexes.[b]

	Compound	Yield/%	PPh_2		PR^2R^3		$\|J(P–P)\|$
			δ	$^1J(^{195}Pt–^{31}P)$	δ	$^1J(^{195}Pt–^{31}P)$	
(1)	*cis*-$Ph_2PCH{=}C(CF_3)PPh_2$	55	−26·3		−18·0		131
(2)	*cis*-$Ph_2PCH{=}C(Ph)PPh_2$	88	−28·1		−7·0		146
(3)	*cis*-$Ph_2PCH{=}C(Bu^t)PPh_2$	77	−32·2		−14·8		37
(4)	*cis*-$Ph_2PCH{=}C(CF_3)PEtPh$	70	−25·8		−25·8		c
(5)	*cis*-$Ph_2PCH{=}C(Ph)PEtPh$	92	−27·8		−21·1		146
(6)	*cis*-$Ph_2PCH{=}C(Bu^t)PEtPh$	61	−32·5		−15·8		45
(7)	*cis*-$Ph_2PCH{=}C(Bu^t)P(C_2H_4CN)_2$	90	−35·5		−25·0		18
(8)	$Cl_2Ni\{Ph_2PCH{=}C(Ph)PPh_2\}$	53	46·0		69·3		69
(9)	$Cl_2Ni\{Ph_2PCH{=}C(Bu^t)PPh_2\}$	49	43·8		72·1		71
(10)	$Cl_2Pd\{Ph_2PCH{=}C(CF_3)PPh_2\}$	61	56·6		73·6		21
(11)	$Cl_2Pd\{Ph_2PCH{=}C(Ph)PPh_2\}$	52	51·1		75·6		15
(12)	$Cl_2Pd\{Ph_2PCH{=}C(Ph)P(C_2H_4CN)_2\}$	80	53·6		81·7		13
(13)	$Cl_2Pt\{Ph_2PCH{=}C(Ph)PPh_2\}$	86	30·5	3552	53·1	3640	<2
(14)	$Cl_2Pt\{Ph_2PCH{=}C(Bu^t)PPh_2\}$	85	25·9	3425	53·2	3613	<2
(15)	$Cl_2Pt\{Ph_2PCH{=}C(Ph)PEtPh\}$	68	30·4	3640	55·5	3554	<2

[a] Shifts are in p.p.m. relative to external 85% H_3PO_4 (downfield +). *J* values are in Hz. [b] Yields of diphosphines are based on $Cl_2Pt\{Ph_2PCH{=}C(R)PR^2R^3\}$. [c] A_2 spectrum; *J*(P–P) was not observed.

olefinic diphosphines and their square-planar complexes which involves the stereospecific addition of a secondary phosphine across the triple bond of a co-ordinated phosphinoacetylene. A wide range of new, *cis* olefinic diphosphines with differing steric and electronic characteristics can be prepared. Furthermore, the method has potential for the introduction of chirality at phosphorus (*cf.* entries 4—6 and 15 in the Table) or at an olefinic substituent. Direct observation of $^{31}P–^{31}P$ coupling in the ^{31}P n.m.r. spectra of unsymmetrical complexes provides a valuable structural probe. Finally, the reactivity of the unco-ordinated acetylenic triple bond in phosphinoacetylene complexes, illustrated here for P–H additions, should be capable of further exploitation.

The easy room temperature addition† (Scheme) generates stereospecifically, in high yield, *cis*-diphosphines, in sharp contrast to the base catalysed, elevated temperature addition to 'free' $Ph_2PC{\equiv}CH$ which gives only unwanted *trans*-$Ph_2PCH{=}CHPPh_2$[2] which cannot behave as a chelating ligand. The new *cis* ligands $Ph_2PCH{=}C(R^1)PR^2R^3$ (Table) are colourless crystalline solids (*e.g.*, $R^1 = Bu^t$, $R^2 = Et$, $R^3 = Ph$; $R^1 = Bu^t$, $R^2 = R^3 = Ph$; $R^1 = R^2 = Ph$, $R^3 = Bu^t$; and $R^1 = CF_3$, $R^2 = R^3 = Ph$) or oils (*e.g.*, $R^1 = R^2 = R^3 = Ph$; $R^1 = CF_3$, $R^2 = Et$, $R^3 = Ph$; and $R^1 = CF_3$, $R^2 = R^3 = CH_2CH_2CN$) while the highly crystalline *cis* complexes are red (M = Ni), pale yellow (M = Pd), or colourless (M = Pt). The method of synthesis should be applicable to other d^8 phosphinoacetylene complexes or *cis*-bis(phosphinoacetylene) M^0 derivatives.

Data on *cis* $^{31}P–^{31}P$ coupling constants for nickel triad complexes are sparse and factors influencing *J*(P–P) are poorly understood.[3] The availability of a variety of diphosphines and isostructural, monometallic M^{II} complexes throughout the range of combinations of R^1, R^2, R^3, and M permitted by the synthetic method allowed a systematic study of *J*(P–P) magnitudes (Table). Within the free ligands ^3J(P–P) is, unexpectedly, determined largely by the olefinic substituent rather than the groups on phosphorus. The absolute magnitude of *J*(P–P) in $MCl_2\{Ph_2PCH{=}C(R^1)PR^2R^3\}$ decreases in sequence Ni>>Pd>Pt. Similar, but much less dramatic trends in *J*(P–P) have very recently been noted for $M(CO)_4L_2$ (M = Cr, Mo, or W).[4,5]

Consideration of the large ^3J(P–P) values in $Ph_2PCH{=}C(R^1)PR^2R^3$ ($R^1 = CF_3$ or Ph, $R^2 = R^3 = Ph$) and values in the corresponding Ni, Pd, and Pt complexes suggests a massive reduction in 'backbone' $^{31}P–^{31}P$ coupling on complexation. Furthermore, analysis of ^3J(P–P) in $Ph_2PCH{=}C(Bu^t)PPh_2$ (37 Hz) and its complexes [*J*(P–P) does not differ significantly from values for complexes of the other ligands] implies that 'backbone' contributions to *J*(P–P) are uniform. More importantly, since *J*(P–P) values are very similar for the series *cis*-$MCl_2\{Ph_2PCH{=}C(R^1)PR^2R^3\}$ and *cis*-$MCl_2(Ph_2PCH_2CH_2PMe_2)$[4] (73 ± 4 for M = Ni; 15 ± 5 for M = Pd; and < 2 for M = Pt), it is apparent that a fundamental change in coupling through the metal is responsible for the sequence of |*J*(P–P)| values Ni>>Pd>Pt. These results may have important ramifications for metal–phosphorus bonding in the nickel triad.

(*Received*, 24*th August*, 1977; *Com.* 899.)

---

† Additions were made at 195 K and reaction mixtures were allowed to warm up to room temperature.

[1] See, for example, T. P. Dang, and H. B. Kagan, *J. Amer. Chem. Soc.*, 1972, **94**, 6429; W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, *ibid.*, 1975, **97**, 2567; K. Achiwa, *ibid.*, 1976, **98**, 8265; W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J.C.S. Chem. Comm.*, 1972, 10; G. Gelbard, H. B. Kagan, and R. Sern, *Tetrahedron*, 1976, **32**, 233.

[2] R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, 1971, **93**, 4158.

[3] E. G. Finer and R. K. Harris, *Progr. NMR Spectroscopy*, 1970, **6**, 61.

[4] S. O. Grim, R. C. Barth, J. D. Mitchell, and J. Del Gaudio, *Inorg. Chem.*, 1977, **16**, 1776.

[5] R. B. King and J. C. Cloyd, Jr., *Inorg. Chem.*, 1975, **14**, 1550.