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Preliminary communication

Simple and conjugated phosphorus ylides as ligands in zero-valent metal complexes

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The exceptionally low ionization energies of phosphorus ylides, $R_3P{=}CHR'$, as revealed by photoelectron spectroscopy[**] and the high degree of localization of the π-electrons at the ylidic carbon[***], caused us to examine their characteristics as ligands in low valent metal complexes. We report below the thermal and photochemical preparation of some Group VI penta- and tetracarbonyl complexes of simple and conjugated *P*-triphenylphosphorus ylides.

All the reactions were carried out under highly purified nitrogen. The ylides were prepared by the usual salt method with butyllithium[2], as well as salt free in liquid ammonia[3] and in boiling THF[4].

When equimolar amounts of ylide and $M(CO)_6$ (M = Cr, Mo, W) are refluxed in petroleum ether (b.p. 50–60°), the corresponding pentacarbonyl is formed. It also can be prepared under UV irradiation in different solvents at about 10° (6–60 h), the progress of the reaction being monitored by measuring the amount of carbon monoxide evolved according to eqn. (1).

$$Ph_3P{=}CHR + M(CO)_6 \rightarrow M(CO)_5(Ph_3P{=}CHR) + CO \qquad (1)$$

I, R = Ph
II, R = $CH{=}CH_2$
III, R = $CH{=}CHCH_3$
IV, R = CH=CHPh

V, M = Cr; R = Ph
VI, M = Mo; R = Ph
VII, M = W; R = Ph
VIII, M = Mo; R = $CH{=}CH_2$
IX, M = Cr; R = $CH{=}CHCH_3$
X, M = Mo; R = $CH{=}CHCH_3$
XI, M = Mo; R = CH=CHPh

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[**] $(CH_3)_3P{=}CH_2$, IE_1 6.87 eV; $(CH_3)_3P{=}CHC_6H_5$, IE_1, 6.60 eV. Details on the PE spectra of *P*-trimethyl phosphorus ylides will be published jointly with H. Schmidbaur.

[***] From CNDO/2 calculations: $c_{p_z}(C_\alpha)$ = 0.7913 in $(CH_3)_3P{=}CH_2$ (ref. 1).

Refluxing the reagents at higher temperature (*e.g.* light petroleum ether (b.p. 80–100°), benzene) sometimes results in the formation of bis-ylide-metal-tetracarbonyls. See eqn. (2).

$$2\,Ph_3P{=}CHPh + M(CO)_6 \rightarrow M(CO)_4(Ph_3P{=}CHPh)_2 + 2\,CO \qquad (2)$$

XII, M = Mo
XIII, M = W

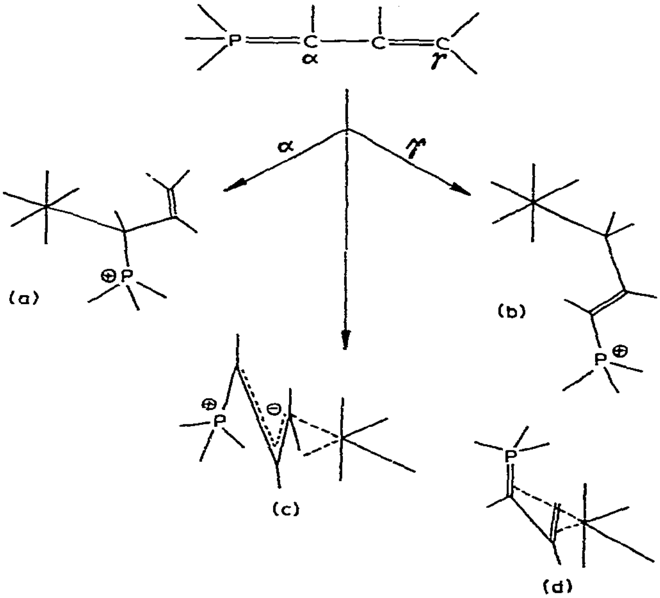
Some certain ylides, however, form tetracarbonyls having a different composition. On theoretical grounds and in the light of previous experimental studies on the coordination chemistry of heterobutadienes[5], we were especially interested in the behavior of β,γ-unsaturated ylides, and expected them to react as bidentate ligands. Triphenylphosphine-allylidene II and the methallylidene XIV were found to give the mono-ylide tetracarbonyls on prolonged irradiation.

$$Ph_3P{=}CH{-}CR{=}CH_2 + Mo(CO)_6 \xrightarrow{-2CO} (Ph_3P{=}CH{-}CR{=}CH_2)Mo(CO)_4 \qquad (3)$$

II, R = H
XIV, R = CH_3

XV, R = H
XVI, R = CH_3

In all isolated complexes the ylide is stabilized towards oxidation and hydrolysis. The complexes are only slightly soluble in nonpolar solvents, while the mother liquids



invariably contain small amounts of colorless phosphine pentacarbonyls, resulting from a ligand rearrangement[6].

Table 1 indicates the conditions used for preparations and also lists the metal carbonyl stretching frequencies used to characterize the products.

Satisfactory C, H, P analyses were obtained for most complexes after extraction of excess ylide and high vacuum–low temperature sublimation of excess carbonyl.

TABLE 1

PREPARATION CONDITIONS AND CO STRETCHING FREQUENCIES[a] OF *P*-YLIDE METAL CARBONYLS

Complex	*ν(CO) (cm^{-1}) in "C_{4v}"*				*Preparation conditions*		
	A_1^1	B_1	E	A_1^2	$h\nu$	T	*solvent*
V	2051	1970	1908	1862	+		petroleum ether
VI	2062	1969	1936/ 1917	1881	+	+	petroleum ether
VII	2060	1962	1918/ 1908	1869	+		petroleum ether
VIII	2061	1974	1929	1892		+	benzene
IX	2060		1930	1875	+		THF
X	2062	1971	1919/ 1905	1852	+		petroleum ether
XI	2060	1970	1925/ 1911	1887	+		petroleum ether
	ν(CO) (cm^{-1}) in "C_{2v}"						
	A_1^1	B_1	A_1^2	B_2			
XII	2012	1880	1847	1796		+	petroleum ether
XIII	2009	[b]		1795	+		petroleum ether
XV	2008	1902	1868	1830	+	–	petroleum ether
XVI	2008	1897	1872	1837	+		petroleum ether

[a] In nujol. [b] Several bands at 1895, 1865, 1840, 1818.

Simple ylides act as donor ligands[7] by changing the hybridisation at the α-carbon, approximately from $sp^2 \rightarrow sp^3$ (ref. 8). The strong dependence of the donor properties of ylides on steric requirements is shown by comparison with the corresponding phosphorus imine and oxide complexes[7,9]. In the conjugated, non-aromatic ylides II, III, IV, XIV there may be the choice between α- and γ-coordination (a or b). Donor properties are no longer a simple function of MO energies and MO coefficients and obviously the nature of the substituents becomes the decisive factor. This is consistent with the occurrence of *E*-splitting in several pentacarbonyls, and the ease of formation of XV and XVI, for which the phosphonium-substituted allylic-anion formulation (c) seems on steric grounds more likely than the *cis*-structure (d) (Scheme 1).

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