Dialkylaminophosphines

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Reduction of Cx_2NPCl_2 (Cx = cyclohexyl) with $LiAlH_4$ gives Cx_2NPH_2 as an isolable air-sensitive liquid which can be converted into the relatively stable metal carbonyl complexes $Cx_2NPH_2M(CO)_5$ (M = Cr and W) and $Cx_2NPH_2Fe(CO)_4$; the 2,2,6,6-tetramethylpiperidino derivative $\overline{CMe_2[CH_2]_3CMe_2N}PH_2$ is also isolable and the di-isopropylamino derivative $Pr^i{}_2NPH_2$ has been detected in solution by ^{31}P n.m.r. spectroscopy.

Recent work from our laboratory[1] has indicated that bis(dialkylamino)phosphines, $(R_2N)_2PH$, can be isolated if the R_2N groups are sufficiently bulky. For example, the bis(di-isopropylamino) derivative, $(Pr^i{}_2N)_2PH$, is a relatively stable, albeit highly air-sensitive compound which is a useful ligand for transition metal carbonyls.[2] We have now also found that a similar principle can be used to provide the first isolable dialkylaminophosphines, R_2NPH_2, containing hydrocarbon R groups. In this case, however, a much larger R_2N group is needed to provide an isolable compound, relative to the $(R_2N)_2PH$ derivatives, since only one R_2N group is available in an R_2NPH_2 derivative for steric shielding of the phosphorus atom. The only R_2NPH_2 derivatives which have been reported previously are the silylamino derivatives $(Me_3Si)_2NPH_2$ [3] and $(Bu^tMe_2Si)_2NPH_2$.[4]

Our most extensive work to date has been with the dicyclohexylamino derivative Cx_2NPH_2 (Cx = cyclohexyl). In a typical preparation equimolar amounts of Cx_2NPCl_2 and

Table 1. Spectroscopic data on the PH_2 groups in dialkylaminophosphines and their metal carbonyl complexes.[a]

Compound	N.m.r. data ^1H δ(PH_2)	 ^{31}P δ(PH_2)[b]	 ^1J(P–H), Hz	I.r. data[c] ν(PH), cm^{-1}
$Pr^i_2NPH_2$		−82.9	196	
$\overline{CMe_2[CH_2]_3CMe_2N}PH_2$	4.51[d]	−86.6	202	2280m, 2210w
Cx_2NPH_2	4.75[d]	−72.3	200	2230sh, 2200m
$Cx_2NPH_2Cr(CO)_5$	6.40[e]	+6.2	330	2360w, 2250vw
$Cx_2NPH_2W(CO)_5$	5.38[d]	−47.6	341	2320vw
$Cx_2NPH_2Fe(CO)_4$	6.73[e]	+14.6	372	2330vw, 2250vw

[a] ^1H and ^{31}P chemical shifts are reported in p.p.m. *downfield* from internal Me_4Si and external 85% H_3PO_4, respectively. [b] Tetrahydrofuran solution. [c] Hexane solution. [d] C_6D_6 solution. [e] $CDCl_3$ solution.

$LiAlH_4$ were mixed in tetrahydrofuran (thf) at −78 °C. The resulting solution was then stirred overnight at room temperature. At this point the ^{31}P n.m.r. spectrum indicated complete conversion into Cx_2NPH_2. The product was isolated (after removal of solvent, extraction with dry pentane) in a 65—80% yield as a very air-sensitive colourless liquid, characterized by its i.r. and n.m.r. spectra (Table 1).

Since Cx_2NPH_2 could not be purified by vacuum distillation (which causes decomposition with the liberation of free Cx_2NH), it was characterized by conversion into its metal carbonyl complexes. These are relatively insensitive to air oxidation and are sufficiently thermally stable to be purified by vacuum sublimation. In a typical such experiment a solution of (thf)$W(CO)_5$, prepared by photolysis of 23.4 mmol of $W(CO)_6$ in thf (400 ml), was stirred (2 days) with Cx_2NPH_2 (23.3 mmol). The residue from the reaction (after removal of solvent *in vacuo*, extraction with hexane) was treated to remove $W(CO)_6$ and a small amount of Cx_2NH and then sublimed at 130 °C/0.005 mm Hg to give a 27% yield of pale yellow $Cx_2NPH_2W(CO)_5$ (m.p. 117 °C). A similar procedure was used to prepare light yellow $Cx_2NPH_2Cr(CO)_5$ (m.p. 109—110 °C), but failed to give the corresponding molybdenum derivative. The iron compound, $Cx_2NPH_2Fe(CO)_4$, a brown liquid freezing above −78 °C, was obtained by reaction of Cx_2NPH_2 with $Fe_2(CO)_9$ in thf. The metal carbonyl complexes were characterized by elemental analyses (C, H, N) and infrared spectra in the ν(CO) region.

A similar $LiAlH_4$ reduction of the 2,2,6,6-tetramethylpiperidino derivative, $\overline{CMe_2[CH_2]_3CMe_2N}PCl_2$, gave the corresponding R_2NPH_2 derivative. Reduction of $Pr^i_2NPCl_2$ with $LiAlH_4$ in thf at −78 °C gave a solution, shown (^{31}P n.m.r.) to contain $Pr^i_2NPH_2$. However, attempted isolation led to complete decomposition into a brown non-volatile sparingly soluble solid. Reduction of the 2,6-dimethylpiperidino derivative $\overline{CHMe[CH_2]_3CHMeN}PCl_2$ with $LiAlH_4$ under similar conditions failed to give any evidence (n.m.r.) for the formation of an R_2NPH_2 derivative in solution. These experiments indicate the need for a relatively large R_2N group in order to obtain an isolable R_2NPH_2 derivative. In addition, they indicate that the di-isopropylamino group, which gives an isolable and relatively stable $(R_2N)_2PH$ derivative,[1] is not sufficiently large to give an isolable R_2NPH_2 derivative.

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