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The Reactions of Lithium Dimethylphosphide with *cis* and *trans* 1,2-dichloroethylene

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Cis and *trans* 1,2-dichloroethylene react with $LiPPh_2$ [1] and $LiAsPh_2$ [2, 3] stereospecifically to form the corresponding vinylic diphosphines and diarsines in high yield. However *cis* 1,2-dichloroethylene and $NaAsMe_2$ produce 1,2-bis(dimethylarsino)ethylene, $Me_2AsCH = CHAsMe_2$, in approximately 30% with a *cis:trans* isomer ratio of *ca.* 1:10 [4, 5]. Here we report the corresponding reaction with lithium dimethylphosphide, and attempts to produce the new diphosphine ligand *cis*-1,2-bis(dimethylphosphino)ethylene. Carty *et al.* [6] have recently reported *in situ* syntheses of several *cis* diphosphinoethylenes by addition of secondary phosphines to metal-coordinated phosphinoacetylenes.

Results

The reaction of $LiPMe_2$ [7] in tetrahydrofuran with *trans* CHCl=CHCl produced 1,2-bis(dimethylphosphino)ethylene in 31% yield, as a colourless air-sensitive liquid. The ^1H nmr spectrum of the ligand (d_6 acetone) showed CH_3-P(t) 8.95 τ (~2 Hz), and a vinyl proton triplet 3.6 τ (15 Hz). The vinyl proton resonance was similar to that in *trans* $Ph_2PCH = CHPPh_2$ [3, 8], and identification of the product as the *trans* isomer was confirmed by its IR spectrum which had no absorbtion at *ca* 1560 cm^{-1} where *cis* disubstituted olefins absorb [1–3], and a strong absorbtion at 940–970 cm^{-1} assignable to the C–H deformation of a *trans* disubstituted olefin. The ligand gave a dimethiodide in which the CH_3-P resonance was a 'filled-in' doublet at 7.9 τ, and the vinyl protons appeared as a 1:2:1 triplet at 2.4 τ, $J_{P-H} = 20$ Hz.

Cis 1,2-CHCl = CHCl and $LiPMe_2$ produced a low yield of $Me_2PCH = CHPMe_2$ (16%) which had an identical ^1H nmr spectrum to the *trans* isomer and formed an identical methiodide. Careful fractionation of the products of this reaction failed to produce any evidence for the presence of *cis* $Me_2PCH = CHPMe_2$. Thus we conclude that the reaction of $LiPMe_2$ with either CHCl=CHCl isomer produces exclusively the *trans* $Me_2PCH = CHPMe_2$, rather than the much more desirable *cis* chelate. This result is consistent with an elimination–addition mechanism, with a phosphinoacetylene intermediate [8, 9].

Bennett *et al.* [4, 10, 11] found that *trans* $Me_2AsCH = CHAsMe_2$ was unaffected by UV irradiation, but that in the presence of Co^{II}, Ni^{II}, Pd^{II} or Pt^{II} halides, irradiation produced complexes of the *cis*-diarsine. Irradiation of *trans*-$Me_2PCH = CHPMe_2$ and sodium tetrachloropalladate(II) in ethanol (phosphine:Pd 2.2:1) for 16 hours produced no apparent change. Evaporation of the solvent, and treatment of the residue with aqueous sodium cyanide resulted in recovery of the *trans* $Me_2PCH = CHPMe_2$. Irradiation of the palladium complex in aqueous ethanol in the absence of free ligand resulted in decomposition.

The mechanism by which metal complexes of *trans* $Me_2AsCH = CHAsMe_2$ isomerise on irradiation is thought [4] to involve dissociation of one end of the *trans* bridging ligand, followed by excitation to a diradical. Rotation about the C–C bond is favoured by the stability of the chelated *cis* isomer produced. It may be in the present case that the very strong donor properties of the Me_2P group prevent (or at least greatly reduce the tendency to) dissociation from one metal, which must precede rotation to form the *cis* chelate.

Experimental

Physical measurements were made as described previously [7].

Trans 1,2-bis(dimethylphosphino)ethylene

All reactions were conducted under a dry nitrogen atmosphere. A solution of lithium dimethylphosphide (0.091 mol) was prepared as described [13] from lithium (2.9 g, 0.42 mol), phenyldimethylphosphine (17.9, 0.13 mol), ^tBuCl (8.4 g, 0.091 mol) in THF (250 cm^3). This was treated dropwise at room temperature with *trans*-1,2-dichloroethylene (4.4 g, 0.046 mol), and the mixture stirred for 2 hours. The resulting solution was hydrolysed with deoxygenated water, the organic layer separated, dried (Na_2SO_4) and distilled. Fractionation of the residue *in vacuo* gave the ligand, BP 68°/4 torr, 2.1 g, 31% (on $LiPMe_2$), ^1H nmr (τ) 8.95(t) (2 Hz) [6H], 3.6(t) (15 Hz) [H] (d_6-acetone).

Dimethiodide derivative: The ligand (0.2 cm^3) was added to iodomethane (5 cm^3) in acetone (10 cm^3), and the mixture gently warmed for 15 minutes. On cooling a cream powder was produced and this was dried *in vacuo.* fd C = 22.3%, H = 4.7%, $C_8H_{20}P_2I_2$

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req C = 22.25%, H = 4.7%, PM dec 250 °C. ^{1}H nmr 7.9(d) (15 Hz) [9H], 2.4(t) (20 Hz) [H] (d_6-dmso).

The Reaction of $LiPMe_2$ and Cis *CHCl=CHCl*

This was carried out as described for the *trans* isomer. Distillation gave 1.1 g 16% of $Me_2PCH = CHPMe_2$. ^{1}H nmr 8.95(t) (2 Hz) [6H], 3.6(t) (15 Hz) [H]. The methiodide dec 250 °C, fd C = 22.3%, H = 5.1%. ^{1}H nmr 7.9(d) (15 Hz) [9H], 2.4(t) (20 Hz) [H].

Attempted Isomerisation of trans-*$Me_2PCH = CHPMe_2$*

A filtered solution of sodium tetrachloropalladate [11] (0.55 g, 1.9 mmol) in ethanol (100 ml) was treated with *trans*-$Me_2PCH = CHPMe_2$ (0.61 g, 4.1 mmol). The reaction was carried out under nitrogen in an irradiation apparatus consisting of a 150 watt uv lamp surrounded by a water cooled quarz jacket. After 16 hours the mixture was rotary evaporated to dryness and a portion of the residue treated with sodium cyanide in d_6 dmso. The ^{1}H nmr showed signals assignable to *trans*-$Me_2PCH = CHPMe_2$ and no other vinyl signals were detected even at high sensitivity. Redissolving the residue in a water (50 ml)–ethanol (50 ml) mixture and further irradiation resulted in decomposition with a black deposit of palladium produced.

An essentially similar experiment was carried out using water (50 ml)–ethanol (50 ml) as an initial solvent for the uv irradiation but again the *trans*-ligand was regenerated with sodium cyanide.

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