Pergamon

Tetrahedron Letters, Vol. 38, No. 15, pp. 2779-2782, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00469-3

Synthesis of [2-(Dimethylphosphino)ethyl]bis(trifluoromethyl)phosphine, $(CH_3)_2PCH_2CH_2P(CF_3)_2$

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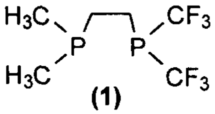
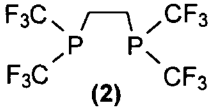
Abstract. The ethylene-bridged bisphosphine, [2-(dimethylphosphino)ethyl]bis(trifluoromethyl)phosphine, $[(CH_3)_2PCH_2CH_2P(CF_3)_2]$, was synthesised in four steps from the unsymmetrical bisphosphine $(CH_3)_2PCH_2CH_2PH_2$, using a new trifluoromethylation procedure employing CF_3Br and hexaethylphosphorus triamide. © 1997 Elsevier Science Ltd.

Bisphosphine ligands of the form $R_2PCH_2CH_2PR_2$ (R = alkyl and aryl) have been used extensively as ligands for organometallic complexes.[1-5] In recent years, there has been increasing interest in bisphosphine ligands containing fluorinated substituents ($R_2PCH_2CH_2PR_2$; R = perfluoroalkyl and perfluoroaryl).[6-9] Even from the limited number of studies so far, it is apparent that the incorporation of fluoroalkyl groups into bisphosphine ligands has a dramatic influence on the reactivity of organometallic complexes, compared to their non-fluorinated analogues.[10] The synthesis of unsymmetrical bisphosphines containing both fluorinated and non-fluorinated groups allows greater control over the properties of organometallic complexes incorporating these ligands.

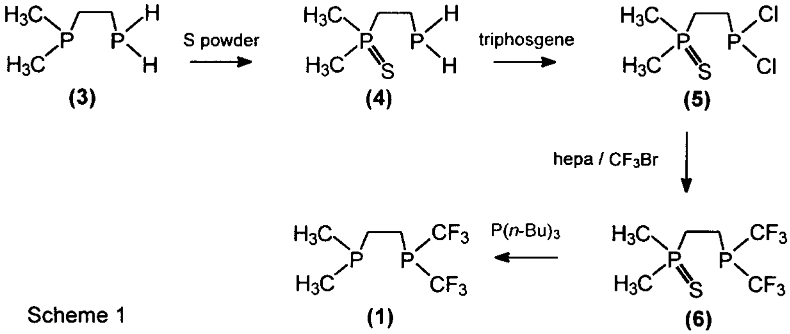
Few mixed bisphosphines of the form $R_2PCH_2CH_2PR'_2$ are known. Examples include $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$,[11] $H_2PCH_2CH_2P(CH_3)_2$,[12] $(C_6H_5)_2PCH_2CH_2P(CF_3)_2$[13] and $(C_6H_5)_2PCH_2CH_2P(C_6F_5)_2$.[14] In this paper we report the synthesis of a new unsymmetrical bisphosphine, $(CH_3)_2PCH_2CH_2P(CF_3)_2$, (**1**), containing phosphine donors with both alkyl and perfluoroalkyl substituents. In a previous paper,[15] we reported an improved synthesis of dfmpe, $(CF_3)_2PCH_2CH_2P(CF_3)_2$, (**2**), by trifluoromethylation of $Cl_2PCH_2CH_2PCl_2$ using CF_3Br and hexaethylphosphorus triamide (hepa). This basic approach for trifluoromethylation at phosphorus was employed for the synthesis of (**1**).


(1)


(2)

The synthesis of (2-(dimethylphosphino)ethyl)phosphine, $(CH_3)_2PCH_2CH_2PH_2$, (**3**),[12] provided a convenient starting point for the synthesis of $(CH_3)_2PCH_2CH_2P(CF_3)_2$. The dimethylphosphino group of (**3**) was protected by selective sulfurisation with sulfur powder at room temperature for 30 minutes to give $(CH_3)_2P(S)CH_2CH_2PH_2$, (**4**).[16] Sulfurisation at the tertiary centre is significantly faster than at the primary phosphine group and the unwanted doubly sulfurised product, $(CH_3)_2P(S)CH_2CH_2P(S)H_2$, was formed only if the sulfurisation was allowed to proceed for an extended time.

The primary phosphine terminus of (4) was converted to the dichloride by treatment with triphosgene $[(Cl_3CO)_2CO]$[17,18] to give $(CH_3)_2P(S)CH_2CH_2PCl_2$, (5), in good yield (70%).[19] Initial protection of the more reactive tertiary phosphine centre was essential to ensure chlorination only at the $-PH_2$ group. The alkylphosphine dichloride, (5), was treated with ten equivalents of trifluoromethyl bromide and four equivalents of hexaethylphosphorus triamide in dichloromethane at low temperature, to give $(CH_3)_2P(S)CH_2CH_2P(CF_3)_2$, (6), as an air-stable, white powder (Scheme 1).[20] Treatment of (6) with excess tri-*n*-butylphosphine at 200°C for 1 h effected desulfurisation to give the desired product, (1), which was isolated by distillation under high vacuum as a colourless, air-sensitive liquid.[21]



Scheme 1

All of the intermediate compounds in the synthesis of $(CH_3)_2PCH_2CH_2P(CF_3)_2$, (1), were fully characterised by multinuclear NMR spectroscopy. All compounds have characteristic ^{31}P NMR signatures which permit the progress of each step in the reaction sequence to be monitored conveniently. $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR data for the key intermediates in the synthetic sequence are listed in Table 1.

Table 1 $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR data of unsymmetrical bisphosphines

Compound	δ ^{31}P (ppm)[a]	$^3J_{P-P}$ (Hz)	δ ^{19}F (ppm)[d]
$(CH_3)_2PCH_2CH_2PH_2$ (3)	-49.7, -130.8[b]	15	-
$(CH_3)_2P(S)CH_2CH_2PH_2$ (4)	34.1, -129.7[b]	17	-
$(CH_3)_2P(S)CH_2CH_2PCl_2$ (5)	193.2, 36.2[b]	22	-
$(CH_3)_2P(S)CH_2CH_2P(CF_3)_2$ (6)	37.9, 1.6[c]	46	-50.8[e]
$(CH_3)_2PCH_2CH_2P(CF_3)_2$ (1)	2.1, -46.8[b]	38	-50.8[f]

a referenced to external neat trimethyl phosphite at δ 140.5 ppm; *b* C_6D_6 solution at 162.0 MHz; *c* $CDCl_3$ solution at 162.0 MHz; *d* referenced to external neat hexafluorobenzene at δ -163.0 ppm; *e* $CDCl_3$ solution at 376.4 MHz, $^2J_{P-F}$ = 70 Hz; *f* C_6D_6 solution at 376.4 MHz, $^2J_{P-F}$ = 67 Hz

The use of the P-Cl → P-CF$_3$ transformation in the synthesis of $(CH_3)_2PCH_2CH_2P(CF_3)_2$, **(1)**, demonstrates the applicability of the reagent combination hepa/CF$_3$Br to the synthesis of trifluoromethylated phosphines, increasing the range of substituents available to tune the electronic properties of phosphine ligands. An investigation of metal complexes of **(1)** is underway.

Acknowledgments. We gratefully acknowledge financial support from the Australian Research Council and the Australian Government for an Australian Postgraduate Research Award (MPW).

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was stirred for 30 min, filtered, and the ether was removed under reduced pressure to give $(CH_3)_2P(S)CH_2CH_2PH_2$, **(4)**, as a white powder (8.7 g, 88%). $^{31}P\{^1H\}$ NMR (C_6D_6) : δ 34.1 (1P, d, $(CH_3)_2\mathbf{P}(S)$-), -129.7 (1P, d, -$\mathbf{PH_2}$, $^3J_{P-P}$ = 17 Hz, $^1J_{P-H}$ = 192 Hz) ppm. ^1H NMR (C_6D_6) : δ 1.22 (6H, d, $(\mathbf{CH_3})_2P(S)$-, $^2J_{P-H}$ = 12.7 Hz), 1.70-1.52 (4H, m, -$P\mathbf{CH_2CH_2}P$-), 2.78 (2H, d, -$P\mathbf{H_2}$, $^1J_{P-H}$ = 192 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6) : δ 38.7 (1C, dd, $(CH_3)_2P(S)CH_2$-, $^1J_{C-P}$ = 49.2 Hz, $^2J_{C-P}$ = 4.2 Hz), 21.0 (2C, d, $(CH_3)_2P(S)$-, $^1J_{C-P}$ = 53.4 Hz), 7.7 (1C, dd, -CH_2PH_2, $^1J_{C-P}$ = 11.0 Hz, $^2J_{C-P}$ = 5.1 Hz) ppm. If the reaction mixture is left for an extended period (> 4 hrs) $(CH_3)_2P(S)CH_2CH_2P(S)H_2$ is the major product $^{31}P\{^1H\}$ NMR δ 38.0 (1P, d, $(CH_3)_2\mathbf{P}(S)$-, $^3J_{P-P}$ = 58 Hz), -12.2 (1P, d, -$\mathbf{P}(S)H_2$, $^1J_{P-H}$ = 453 Hz) ppm.

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19. A solution of triphosgene (2.6 g, 8.7 mmol) in toluene (50 ml) was added dropwise to a solution of $(CH_3)_2P(S)CH_2CH_2PH_2$, **(4)**, (2.0 g, 13 mmol) in toluene (100 ml). The reaction mixture was stirred for 4 h and the solvent was removed under reduced pressure. The residue was washed with hexane (2 × 10 ml) to give $(CH_3)_2P(S)CH_2CH_2PCl_2$, **(5)**, as a white powder (2.0 g, 70 %). $^{31}P\{^1H\}$ NMR (C_6D_6) : δ 193.2 (1P, d, -$\mathbf{P}Cl_2$), 36.2 (1P, d, $(CH_3)_2\mathbf{P}(S)$-), $^3J_{P-P}$ = 22 Hz) ppm. ^1H NMR (C_6D_6) : δ 2.54-2.43 (2H, m, -$\mathbf{CH_2}PCl_2$), 1.96-1.87 (2H, m, $(CH_3)_2P(S)\mathbf{CH_2}$-), 1.32 (6H, d, $(\mathbf{CH_3})_2P(S)$-, $^2J_{P-H}$ = 12.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6) : δ 35.4 (1C, dd, $(CH_3)_2P(S)CH_2$-, $^1J_{C-P}$ = 49 Hz, $^2J_{C-P}$ = 4 Hz), 27.8 (1C, dd, -CH_2PCl_2, $^1J_{C-P}$ = 51 Hz, $^2J_{C-P}$ = 10 Hz), 20.5 (2C, d, $(CH_3)_2P(S)$-, $^1J_{C-P}$ = 55 Hz) ppm.
20. Trifluoromethyl bromide (6.8 g, 46 mmol) was condensed into a flask and allowed to evaporate into a three-necked flask cooled to liquid nitrogen temperature and fitted with a dry-ice condenser. A solution of $(CH_3)_2P(S)CH_2CH_2PCl_2$, **(5)**, (0.80 g, 3.6 mmol) in dichloromethane (20 ml) was added and the reaction mixture was allowed to warm to -60°C. A solution of hexaethylphosphorus triamide (3.4 g, 14 mmol) in dichloromethane (20 ml) was added over a period of 1 h while the temperature was maintained between -60°C and -55°C. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. The crude reaction mixture was eluted through flash silica with dichloromethane, to give $(CH_3)_2P(S)CH_2CH_2P(CF_3)_2$, **(6)**, as a white, air-stable powder (0.19 g, 20%). $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 37.9 (1P, d, $(CH_3)_2\mathbf{P}(S)$-), $^3J_{P-P}$ = 46 Hz), 1.6 (1P, dsept, -$\mathbf{P}(CF_3)_2$, $^3J_{P-P}$ = 46 Hz, $^2J_{P-F}$ = 70 Hz) ppm. ^1H NMR ($CDCl_3$) : δ 2.45 (2H, m, -$\mathbf{CH_2}P(CF_3)_2$), 2.10 (2H, m, $(CH_3)_2P(S)\mathbf{CH_2}$-), 1.83 (6H, d, $(\mathbf{CH_3})_2P(S)$-, $^2J_{P-H}$ = 12.9 Hz) ppm. ^{19}F NMR ($CDCl_3$) : δ -50.8 (6F, d, -$P(\mathbf{CF_3})_2$, $^2J_{F-P}$ = 70 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 129.4 (2C, dq, -$P(\mathbf{CF_3})_2$, $^1J_{C-F}$ = 319 Hz, $^2J_{C-P}$ = 30 Hz), 29.7 (1C, dd, $(CH_3)_2P(S)CH_2$-, $^1J_{C-P}$ = 51 Hz, $^2J_{C-P}$ = 17 Hz), 21.5 (2C, d, $(CH_3)_2P(S)$-, $^1J_{C-P}$ = 55 Hz), 13.3 (1C, dd, -$CH_2P(CF_3)_2$, $^1J_{C-P}$ = 1 Hz, $^2J_{C-P}$ = 17 Hz) ppm.
    M.p. 58-60°C. Mass Spectrum (CI) *m/e* 221(100), 189(7), 171(55), 152(19), 93(40), 69(17).
21. NMR data for $(CH_3)_2PCH_2CH_2P(CF_3)_2$ **(1)** : $^{31}P\{^1H\}$ NMR (C_6D_6) : δ 2.1 (1P, dsep, $\mathbf{P}(CF_3)_2$, $^3J_{P-P}$ = 38 Hz, $^2J_{P-F}$ = 68 Hz), -46.8 (1P, d, $(CH_3)_2\mathbf{P}$-), $^3J_{P-P}$ = 38 Hz) ppm. ^1H NMR ($CDCl_3$) : δ 2.04 (2H, m, -$\mathbf{CH_2}P(CF_3)_2$), 1.33 (2H, m, $(CH_3)_2P\mathbf{CH_2}$-), 0.84 (6H, d, $(\mathbf{CH_3})_2P(S)$-, $^2J_{P-H}$ = 2.9 Hz) ppm. ^{19}F NMR ($CDCl_3$) : δ -50.8 (6F, d, -$P(\mathbf{CF_3})_2$, $^2J_{F-P}$ = 67 Hz) ppm.

(*Received in UK* 26 *February* 1997; *accepted* 7 *March* 1997)