together with a parameter k_{rel} indicating the relative outer-sphere reactivity. The order for k_{rel} parallels the rates of dissolution of metal oxide films by these reagents and suggests that of these common reductants, only $Cr(edta)^{2-}$ is more potent than $V(pic)_3^-$.

The self-exchange rate for $V(pic)_3^{0/-}$ of 3.1×10^6 M^{-1} s^{-1} is 8 orders of magnitude larger than the value for $V(H_2O)_6^{3+/2+}$.[42] This may imply that the structural rearrangement associated with the electron-transfer process is smaller for $V(pic)_3^{0/-}$ than for $V(H_2O)_6^{3+/2+}$. It is noteworthy that the estimate for the $V(bpy)_3^{3+/2+}$ exchange is 10^7 M^{-1} s^{-1}.[9]

Acknowledgment. This paper is published by permission of the CEGB. The authors wish to thank SERC for a CASE studentship (to A.M.L.) and for financial support, which was also provided by the CEGB and the Universities of Glasgow and Notre Dame. Purchase of equipment was supported by an Atlantic Richfield Grant from the Research Corp. This work was carried out in part at the University of Glasgow.

Registry No. $V(pic)_3^-$, 76298-57-2; $Co(edta)^-$, 87698-06-4; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(en)_3^{3+}$, 14878-41-2; $Co(sep)^{3+}$, 72496-77-6.

---

[42] Krishnamurty, K. V.; Wahl, A. C. *J. Am. Chem. Soc.* **1958**, *80*, 5921-5924.

Contribution from the Institut für Anorganische und Angewandte Chemie,
Universität Hamburg, D-2000 Hamburg 13, Germany

Oligo(phosphine) Ligands. 7.[1] Free-Radical-Catalyzed Synthesis of Some Completely Alkylated Oligo(tertiary phosphines) Containing Trimethylene Linkages

MARTIN ANTBERG, CONSTANZE PRENGEL, and LUTZ DAHLENBURG*

Received December 2, 1983

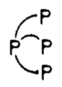
Novel alkylated tri- and tetradentate phosphine ligands containing trimethylene connecting chains between the donor atoms have been prepared through free-radical addition of P–H functionalized alkylphosphines to allylphosphines. Thus, the permethylated tris(phosphine) $MeP(CH_2CH_2CH_2PMe_2)_2$ has been obtained in high yield by irradiating a mixture of $MeP(CH_2CH{=}CH_2)_2$ and excess Me_2PH at $\lambda > 300$ nm in the presence of catalytic amounts of azo-2,2′-bis(isobutyronitrile). The terminally ethylated homologue $MeP(CH_2CH_2CH_2PEt_2)_2$ has been synthesized similarly from $MeP(CH_2CH{=}CH_2)_2$ and Et_2PH. Radical-initiated addition of Me_2PH to $t\text{-}BuP(CH_2CH{=}CH_2)_2$ has been applied as an efficient method of synthesis for the tridentate $t\text{-}BuP(CH_2CH_2CH_2PMe_2)_2$. Futhermore, the completely aliphatic tripod tetrakis(tertiary phosphines) $P(CH_2CH_2CH_2PR_2)_3$ (R = Me, Et) have been made accessible by coupling Me_2PH and Et_2PH, respectively, onto triallylphosphine. The NMR (^1H, ^{31}P, ^{13}C) and mass spectra of these new oligo(phosphine) ligands are described.

Introduction

Oligo(phosphines) containing flexible trimethylene linkages are valuable chelating ligands for the platinum metal ions. This has mainly been demonstrated by Meek and his coworkers in a series of papers dating back to the early 1970s.[2] One straightforward route to this class of compounds involves coupling reactions between (3-chloropropyl)phosphines $R_2P(CH_2)_3Cl$ and phosphide nucleophiles, e.g. $R_2P(CH_2)_3P(R)Li$, or between chlorophosphines $R_{3-n}PCl_n$ (n = 1–3) and $R_2P(CH_2)_3MgCl$ Grignard reagents.[3-6] However, the range of application of this method is limited by the stability of the 3-chloropropyl key compounds, which appear to be available only with bulky substituents such as phenyl or cyclohexyl on phosphorus.

Various efforts have therefore been made to develop more variable methods of synthesis from which three major strategies have begun to emerge: (1) base-assisted coupling of vinyl and allyl (and 3-chloropropyl) phosphine units onto trimethylene-linked secondary–tertiary bis(phosphines) within the coordination sphere of a d^8 transition-metal ion;[7] (2) radical-catalyzed P–H addition to allyl derivatives of P(V), viz. $H_2C{=}CHCH_2P(O)(O\text{-}i\text{-}Pr)_{2-n}Me_n$ (n = 0, 1), followed by $LiAlH_4$ reduction;[8] (3) free-radical addition of P–H functionalized mono- and bis(phosphines) to an appropriate allylphosphine $H_2C{=}CHCH_2PR_2$.[9,10] With allyl alcohol, allyl ethers, and allylamines as reactants, the latter method has been used recently also by Meek's group for the synthesis of a variety of C_3-linked phosphine ligands containing mixed P,O and P,N donor sets.[4]

In this report we demonstrate how the radical-chain addition of P–H groups across the double bonds of allylphosphines containing two or three $H_2C{=}CHCH_2-$ functions can conveniently be exploited for the high-yield synthesis of the hitherto unknown P⌒P⌒P and



compounds $MeP(CH_2CH_2CH_2PMe_2)_2$, $MeP(CH_2CH_2CH_2PEt_2)_2$, $t\text{-}BuP(CH_2CH_2CH_2PMe_2)_2$, $P(CH_2CH_2CH_2PMe_2)_3$, and $P(CH_2CH_2CH_2PEt_2)_3$. Due to their completely aliphatic character, these flexible tris(tertiary phosphine) and tripod tetrakis(tertiary phosphine) ligands should be particularly suitable for the preparation of low-valent transition-metal complexes, which then should exhibit increased basicity and, hence, reactivity at the central atom.

Experimental Section

General Procedures and Instrumentation. All manipulations were carried out under nitrogen atmosphere with standard Schlenk tech-

---

[1] Part 6: Dahlenburg, L.; Prengel, C. *Organometallics* **1984**, *3*, 934.

[2] (a) Nappier, T. E.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194. For reviews see: (b) Mason, R.; Meek, D. W. *Angew. Chem.* **1978**, *90*, 195; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183. (c) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266.

[3] Grim, S. O.; Barth, R. C. *J. Organomet. Chem.* **1975**, *94*, 327.

[4] Uriarte, R.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79.

[5] Arpac, E.; Dahlenburg, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 146.

[6] McAuliffe, C. A.; Levason, W. "Phosphine, Arsine, and Stibine Complexes of the Transition Elements"; Elsevier: Amsterdam, 1979; p 23.

[7] (a) Waid, R. D.; Meek, D. W. *Organometallics* **1983**, *2*, 932. (b) Waid, R. D.; Meek, D. W. *Inorg. Chem.* **1984**, *23*, 778.

[8] (a) Baacke, M.; Stelzer, O.; Wray, V. *Chem. Ber.* **1980**, *113*, 1356. (b) Baacke, M.; Hietkamp, S.; Morton, S.; Stelzer, O. *Chem. Ber.* **1981**, *114*, 2568.

[9] Arpac, E.; Dahlenburg, L. *Angew. Chem.* **1982**, *94*, 929; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 931; *Angew. Chem., Suppl.* **1982**, 1950.

[10] (a) Diel, B. N.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700. (b) Diel, B. N.; Norman, A. D. *Phosphorus Sulfur* **1982**, *12*, 227.

0020-1669/84/1323-4170$01.50/0

niques. *Caution*! Phosphines are toxic compounds with an obnoxious odor. All procedures must therefore be carried out in an efficient fume hood. Effluent vapor should be passed through NaOCl traps before venting them into the hood exhaust.

The photolysis experiments were done by externally irradiating the reactants contained in 150-mL Duran Schlenk tubes. The irradiation source was a quartz-jacketed water-cooled high-pressure mercury lamp (Philips HPK 125 W; $\lambda > 300$ nm[11]).

Solvents were dried according to recommended methods and were distilled under nitrogen prior to use.

Proton NMR spectra were recorded in C_6D_6 at 80 MHz on a Bruker WP 80 spectrometer. ^{31}P NMR spectra were collected in toluene on a Bruker WH 90 instrument operating at 36.44 MHz. ^{13}C NMR data were obtained in C_6D_6 either at 20.15 MHz (Bruker WP 80) or at 22.63 MHz (Bruker WH 90). Chemical shifts are reported in ppm relative to external Me_4Si (^1H, ^{13}C) or H_3PO_4 standards (downfield positive). Mass spectra were taken at 70 eV on a Varian CH 7 spectrometer.

Starting Materials. Allyl chloride was obtained from Riedel de Haen (Seelze) and was distilled under nitrogen before use. Tri-*n*-butylphosphine was purchased from Merck-Schuchardt (Darmstadt) and was used without further purification. Methyldichlorophosphine was supplied by Hoechst (Frankfurt) and was employed as obtained. *t*-$BuPCl_2$,[12] $Me_2P(S)P(S)Me_2$,[13] and $Et_2P(S)P(S)Et_2$[14] were synthesized according to published procedures. The desulfuration of $Me_2P(S)P(S)Me_2$ by tri-*n*-butylphosphine in the presence of water[15] was found to be the method of choice for the shorttime synthesis of dimethylphosphine in quantities up to 20 g. Consequently, diethylphosphine was prepared by an analogous route:

Et_2PH.

$$2Et_2P(S)P(S)Et_2 + 4n\text{-}Bu_3P + 2H_2O \rightarrow 3Et_2PH + 4n\text{-}Bu_3PS + Et_2P(O)OH \quad (1)$$

A 250-mL, round-bottomed Schlenk flask was charged with a mixture of 25.7 g (0.106 mol) of $Et_2P(S)P(S)Et_2$, 43.0 g (0.213 mol) of *n*-Bu_3P, and 1.9 g (0.106 mol) of water. The flask was fitted with a 20-cm Vigreux column connected to a compact distillation head and an ice-cooled receiver, and the temperature was raised slowly to ca. 170 °C (oil bath) when the reaction mixture became homogeneous. Within 3 h, the temperature was further raised to 230 °C to distill 9 g (63%) of diethylphosphine, which was collected at 55–65 °C (lit.[14] bp 83–85 °C). The distillate appeared to contain minor amounts of water, as indicated by its slight turbidity. However, the product could be used in the two syntheses described below without additional purification.

The identity of the material thus obtained was confirmed by ^{13}C and ^1H NMR spectroscopy; an "attached proton test" (APT) pulse sequence with $\tau = 8$ ms[16] revealed the CH_2 and CH_3 carbons at δ 13.6 and 12.8 as doublets of opposite amplitudes with $J(PC) = 10$ Hz each; the proton NMR spectrum showed the P–H moiety at δ 3.00 as a double quintet characterized by $^1J(PH) = 191.0$ Hz (lit.[17] $J = 190$ Hz) and $^3J(HH) = 6.1$ Hz (complex PEt_2 multiplet at $1.5 > \delta > 0.7$ (10 H) not analyzed.

Diallylmethyl- and diallyl-*t*-butylphosphine are known in the literature,[8b,18] but no preparative details have so far been reported. We obtained these organophosphines as follows:

$MeP(CH_2CH{=}CH_2)_2$.

$$MePCl_2 + 2H_2C{=}CHCH_2MgCl \xrightarrow{THF} MeP(CH_2CH{=}CH_2)_2 + 2MgCl_2 \quad (2)$$

A 27-g (0.23 mol) sample of $MePCl_2$ dissolved in 100 mL of THF was added dropwise to a stirred solution of 0.6 mol of the allyl Grignard reagent in 300 mL of THF. After the addition was complete, the mixture was refluxed for 1 h. Subsequently, a 200-mL portion of the solvent was removed by distillation, 200 mL of a deoxygenated, saturated aqueous solution of ammonium chloride was added, and the mixture was shaken vigorously with 200 mL of diethyl ether. The organic layer was separated, and the aqueous solution was extracted with three 80-mL portions of Et_2O. The combined organic fractions were dried over Na_2SO_4 and then distilled to give 19 g (65%) of $MeP(CH_2CH{=}CH_2)_2$ as a colorless liquid, bp 152 °C (760 mm).

^1H NMR: $\delta(PCH_3) = 0.78$ (3 H, d, $^2J(PH) = 4.1$ Hz), $\delta(PCH_2) = 1.9$–2.1 (4 H, m), $\delta(CH{=}CH_2) = 4.7$–5.0 (4 H, m), $\delta(CH{=}CH_2) = 5.4$–6.0 (2 H, m). ^{13}C NMR: $\delta(PCH_3) = 9.8$ (d, $^1J(PC) = 19$ Hz), $\delta(PCH_2) = 33.8$ (d, $^1J(PC) = 16$ Hz), $\delta(CH{=}CH_2) = 116.3$ (d, $^3J(PC) = 9$ Hz), $\delta(CH{=}CH_2) = 133.6$ (d, $^2J(PC) = 6$ Hz).

***t*-$BuP(CH_2CH{=}CH_2)_2$.**

$$t\text{-}BuPCl_2 + 2H_2C{=}CHCH_2MgCl \xrightarrow{THF} t\text{-}BuP(CH_2CH{=}CH_2)_2 + 2MgCl_2 \quad (3)$$

This phosphine was obtained from 0.6 mol of $H_2C{=}CHCH_2MgCl$ (in 500 mL of THF) and 35 g (0.22 mol) of *t*-$BuPCl_2$ (in 200 mL of THF). The yield was 30 g (80%) of *t*-$BuP(CH_2CH{=}CH_2)_2$ distilling at 42–45 °C (0.5 mm).

^1H NMR: $\delta(CH_3) = 0.94$ (9 H, d, $^3J(PH) = 11.2$ Hz), $\delta(PCH_2) = 2.1$ (4 H, d (br), $^3J(HH) \simeq 7$ Hz), $\delta(CH{=}CH_2) = 4.8$–5.1 (4 H, m), $\delta(CH{=}CH_2) = 5.5$–6.1 (2 H, m). ^{31}P NMR: δ −5.9 (lit.[18] δ −6.0).

Triallylphosphine[19] was also prepared with the $H_2C{=}CHCH_2MgCl$/THF Grignard reagent. Yields were up to 75%.

^1H NMR: $\delta(PCH_2) = 2.07$ (6 H, dd, $^2J(PH) < 1$ Hz, $^3J(HH) = 7.5$ Hz), $\delta(CH{=}CH_2) = 4.1$–5.0 (6 H, m), $\delta(CH{=}CH_2) = 5.4$–6.0 (3 H, m). ^{13}C NMR: $\delta(PCH_2) = 30.7$ (d, $^1J(PC) = 19$ Hz), $\delta(CH{=}CH_2) = 116.8$ (d, $^3J(PC) = 7$ Hz), $\delta(CH{=}CH_2) = 133.8$ (d, $^2J(PC) = 6$ Hz). ^{31}P NMR: δ −33.5 (lit.[20] δ −34.3).

Tridentate Phosphine Ligands. $MeP(CH_2CH_2CH_2PMe_2)_2$.

$$MeP(CH_2CH{=}CH_2)_2 + 2HPMe_2 \xrightarrow{UV\ (AIBN)} MeP(CH_2CH_2CH_2PMe_2)_2 \quad (4)$$

A 150-mL Duran Schlenk tube was charged with 9.6 g (0.075 mol) of $MeP(CH_2CH{=}CH_2)_2$, 19.8 g (0.319 mol) of Me_2PH, and 100 mg of AIBN [azo-2,2′-bis(isobutyronitrile)]. A reflux condenser cooled to −35 °C by means of a cryostat was attached to the reaction vessel, and the mixture was irradiated from the outside for 48 h with constant stirring. Excess dimethylphosphine was then removed under reduced pressure at room temperature, and the product was freed from any remaining volatile materials by heating to 50 °C under a dynamic vacuum. The yield was 16.6 g (88%) of colorless, liquid $MeP(CH_2CH_2CH_2PMe_2)_2$ identified by the NMR and mass spectral data reported below.

$MeP(CH_2CH_2CH_2PEt_2)_2$.

$$MeP(CH_2CH{=}CH_2)_2 + 2HPEt_2 \xrightarrow{UV\ (AIBN)} MeP(CH_2CH_2CH_2PEt_2)_2 \quad (5)$$

A Duran Schlenk flask containing 5.8 g (0.045 mol) of $MeP(CH_2CH{=}CH_2)_2$, 9.0 g (0.100 mol) of Et_2PH, and 100 mg of AIBN was irradiated for 46 h with stirring. Any volatile components were then removed from the resulting mixture at 25–50 °C in vacuo to give 13.8 g (99%) of a colorless oil, which was characterized as the desired tris(phosphine) on the basis of its spectral properties (vide infra).

The ligand was also characterized in the form of the five-coordinate ruthenium complex $RuCl_2[MeP(CH_2CH_2CH_2PEt_2)_2]$, which gave a satisfactory elemental analysis.[21] Anal. Calcd: C, 37.51; H, 7.34; Cl, 14.76; P, 19.34. Found: C, 37.5; H, 7.3; Cl, 13.9; P, 18.5.

***t*-$BuP(CH_2CH_2CH_2PMe_2)_2$.**

$$t\text{-}BuP(CH_2CH{=}CH_2)_2 + 2HPMe_2 \xrightarrow{UV\ (AIBN)} t\text{-}BuP(CH_2CH_2CH_2PMe_2)_2 \quad (6)$$

A mixture of 11.4 g (0.067 mol) of *t*-$BuP(CH_2CH{=}CH_2)_2$, 15.0 g (0.242 mol) of Me_2PH, and 0.10 g of AIBN was irradiated for 48

---

(11) Duran borosilicate glassware transmits only slight irradiation below 350 nm and is virtually impervious below 300 nm.

(12) Fild, M.; Stelzer, O.; Schmutzler, R. *Inorg. Synth.* **1973**, *14*, 4.

(13) Butter, S. A.; Chatt, J. *Inorg. Synth.* **1974**, *15*, 185.

(14) Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 704.

(15) Trenkle, A.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 642.

(16) Patt, L. S.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.

(17) Moedritzer, K.; Maier, L.; Groenweghe, L. C. D. *J. Chem. Eng. Data* **1962**, *7*, 307.

(18) Grim, S. O.; Yankowsky, A. W.; Bruno, S. A.; Baily, W. J.; Davidoff, E. F.; Marks, T. J. *J. Chem. Eng. Data* **1970**, *15*, 497.

(19) Jones, W. J.; Davies, W. C.; Bowden, S. T.; Edwards, C.; Davis, V. E.; Thomas, L. H. *J. Chem. Soc.* **1947**, 1446.

(20) Fluck, E.; Lorenz, J. *Z. Naturforsch., B: Chem., Biochem., Biophys., Biol.* **1967**, *22B*, 1095.

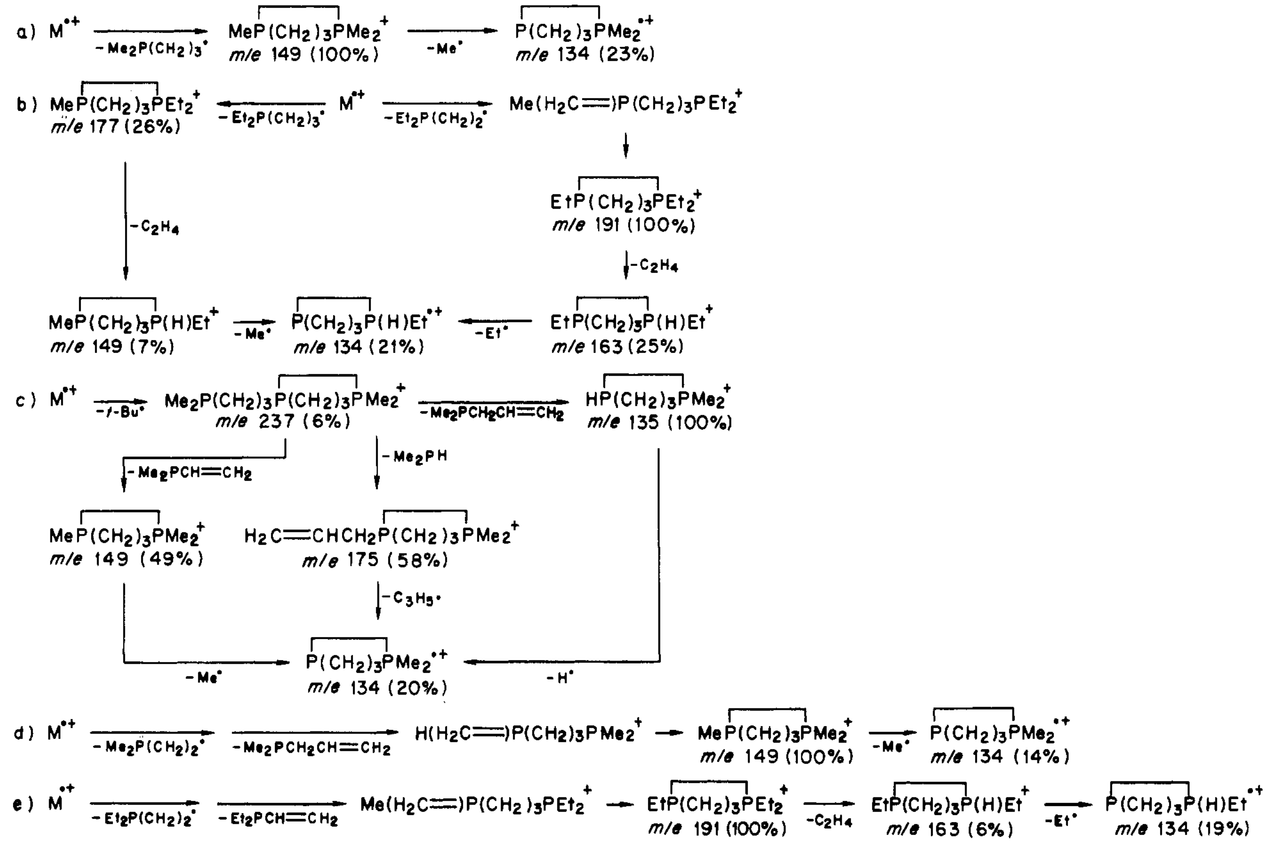
(21) Antberg, M. Diplomarbeit, Universität Hamburg, 1983.

Table I. NMR Data of the $RP(CH_2CH_2CH_2PR'_2)_2$ and $P(CH_2CH_2CH_2PR_2)_3$ Compounds[a]

	δ				
	$MeP[(CH_2)_3PMe_2]_2$	$MeP[(CH_2)_3PEt_2]_2$	t-$BuP[(CH_2)_3PMe_2]_2$	$P[(CH_2)_3PMe_2]_3$	$P[(CH_2)_3PEt_2]_3$
			^1H NMR		
PCH_3	0.80 (15 H, d (2.7)	0.8–1.5 (overlapping multiplet)	0.81 (12 H, d (2.5))	0.80 (18 H, d (2.6))	0.9–1.4 (overlapping multiplet)
PCH_2CH_3					
$CH_2CH_2CH_2$	1.2–1.6 (12 H, m)		1.3–1.5 (12 H, m)	1.3–1.6 (18 H, m)	
$PC(CH_3)_3$			0.92 (9 H, d (11.2))		
			^{31}P NMR		
P_c[e] obsd	−44.7	−44.9	−5.8	−34.4	−34.7
calcd[b]	−43	−43	+1	−33	−33
P_t obsd	−54.3	−25.1	−54.3	−54.2	−25.1
calcd[b]	−53	−25	−53	−53	−25
			^{13}C NMR		
PCH_3	12.0 (d (18))	12.2 (d (18))			
$P(CH_3)_2$	14.5 (d (15))		14.6 (d (15))	14.8 (d (16))	
$P\mathit{C}(CH_3)_2$			27.9 (d (13))[c]		
$PC(\mathit{C}H_3)_3$			27.9 (d (13))[c]		
$P(\mathit{C}H_2CH_3)_2$		19.4 (d (13))			19.6 (d (14))
$P(CH_2\mathit{C}H_3)_2$		10.0 (d (13))			10.0 (d (14))
$P_c\mathit{C}H_2CH_2CH_2P_t$	32.0 (t′ (12))	28.8 (dd′ (13))	26.6 (t′ (10))[d]	29.6 (dd′ (13))	28.9 (dd′ (13))[d]
$P_cCH_2\mathit{C}H_2CH_2P_t$	22.5 (t′ (14))	22.8 (t′ (14))	24.5 (dd′ (17))[d]	22.8 (t′ (14))	23.1 (t′ (15))
$P_cCH_2CH_2\mathit{C}H_2P_t$	34.4 (t′ (11))	32.8 (t′ (10))	34.5 (t′ (12))	34.6 (t′ (11)	29.8 (dd′ (13))[d]

[a] Values of J(PH) or J(PC), in Hz, in parentheses; d = doublet, m = multiplet, dd′ = pseudodoublet of doublets [X part of an ABX spin system (A, B = ^{31}P; X = ^{13}C)], t′ = ABX pseudotriplet. For the ABX multiplets the splittings $N/2$ are given [$N = |J(P_cC) + J(P_tC)|$]. [b] Shift values were calculated from Grim's alkyl group contributions.[30] [c] Assignment on the basis of an APT ^{13}C NMR experiment; cf. Figure 1. [d] Assignment uncertain. [e] Key to subscripts: c, central; t, terminal.

Scheme I. Important Mass Spectral Fragmentation Pathways for (a) $MeP[(CH_2)_3PMe_2]_2$, (b) $MeP[(CH_2)_3PEt_2]_2$, (c) t-$BuP[(CH_2)_3PMe_2]_2$, (d) $P[(CH_2)_3PMe_2]_3$, and (e) $P[(CH_2)_3PEt_2]_3$ (Fragment Ion Structures Tentative)



h. The resulting product was worked up as described above, yielding 18.7 g (95%) of a colorless, oily liquid. This material was readily identified as the expected tridentate ligand by NMR (Table I) and mass spectroscopy (Scheme I).

For further characterization of the compound, the four-coordinate rhodium complex $RhCl[t\text{-}BuP(CH_2CH_2CH_2PMe_2)_2]$ was isolated.[22] The combustion analysis of this derivative gave the following results. Anal. Calcd: C, 38.86; H, 7.69; P, 21.47. Found: C, 39.7; H, 7.7; P, 20.7.

Tripod Tetradentate Phosphine Ligands. $P(CH_2CH_2CH_2PMe_2)_3$.

$$P(CH_2CH{=}CH_2)_3 + 3HPMe_2 \xrightarrow{\text{UV (AIBN)}} P(CH_2CH_2CH_2PMe_2)_3 \quad (7)$$

This material was obtained by irradiating 13.2 g (0.086 mol) of $P(CH_2CH{=}CH_2)_3$, 22.6 g (0.365 mol) of Me_2PH, and 100 mg of AIBN for 64 h. Subsequent removal of excess Me_2PH in vacuo yielded

---

(22) Prengel, C. Dissertation (in progress), Universität Hamburg, 1983.

29.1 g (>99%) of the PP_3 compound as a colorless oil.

The identity of the tetrakis(phosphine) was derived from the spectral data given below as well as from the characterization of a series of iron, ruthenium, and osmium complexes $MX_2[P(CH_2CH_2CH_2PMe_2)_3]$.[21] The analysis obtained for the Ru(II) compound $RuCl_2[P(CH_2CH_2CH_2PMe_2)_3]$, which has also been investigated by X-ray diffraction,[23] is given. Anal. Calcd: C, 35.17; H, 7.08; Cl, 13.84. Found: C, 35.0; H, 7.4; Cl, 13.4.

$P(CH_2CH_2CH_2PEt_2)_3$.

$$P(CH_2CH{=}CH_2)_3 + 2HPEt_2 \xrightarrow{\text{UV (AIBN)}} P(CH_2CH_2CH_2PEt_2)_3 \tag{8}$$

A Schlenk tube containing 8.2 g (0.053 mol) of $P(CH_2CH{=}CH_2)_3$, 21.9 g (0.243 mol) of Et_2PH, and 0.10 g of AIBN was irradiated for 64 h at room temperature. Any volatile materials were then removed by warming the product under a dynamic vacuum to 50 °C. The yield of colorless, oily $P(CH_2CH_2CH_2PEt_2)_3$ was 21.3 g (95%). Composition and purity of the phosphine were checked by NMR and mass spectroscopy (vide infra).

The elemental analysis of an osmium complex of this oligophosphine, viz. $OsCl_2[P(CH_2CH_2CH_2PEt_2)_3]$, gave the following results.[23] Anal. Calcd: C, 36.79; H, 7.06 Cl, 10.34. Found: C, 37.5; H, 7.0; Cl, 10.4.

Results and Discussion

Method of Synthesis. The UV/AIBN-initiated[24] anti-Markovnikov addition of dimethyl- and diethylphosphine across the carbon–carbon double bonds of allylphosphines $R_nP(CH_2CH{=}CH_2)_{3-n}$ (R = Me, *t*-Bu; n = 0, 1) has been found to be an attractive method for the preparation of some completely alkylated trimethylene-linked tris- and tetrakis(phosphines) (cf. eq 4–8).

Formation of byproducts due to competing side-reactions or rearrangement processes as observed by Meek[4,7b,25] and ourselves[9] for some AIBN-assisted phosphine/allylphosphine coupling reactions carried out at 100–110 °C did not occur in any of the room-temperature photolysis experiments described above.[26] We note, however, the failure of an attempt to synthesize $t\text{-}BuP(CH_2CH_2CH_2PBu\text{-}t_2)_2$ from $t\text{-}BuP(CH_2CH{=}CH_2)_2$ and $t\text{-}Bu_2PH$: short-time irradiation resulted in incomplete conversion of the reactants; prolonged photolysis lead to a nonseparable mixture of unidentified products.[22] On the other hand, Meek's phenylated $PhP(CH_2CH_2CH_2PPh_2)_2$ ligand[2a,4,5] was also obtained in an almost quantitative yield by irradiating a mixture of $PhP(CH_2CH{=}CH_2)_2$ and excess Ph_2PH for 22 h although we found it difficult to completely remove the relatively high-boiling diphenylphosphine from the product.[22]

The preparative value of the free-radical-catalyzed phosphine/allylphosphine addition reactions may particularly be exemplified by the high-yield synthesis of the two methylated oligophosphines $MeP(CH_2CH_2CH_2PMe_2)_2$ and $P(CH_2CH_2CH_2PMe_2)_3$. Whereas phosphine ligands and their transition-metal complexes have generally been studied in more detail than the corresponding arsine compounds, the reverse is true for the $Me_nP(CH_2CH_2CH_2PMe_2)_{3-n}/Me_nAs(CH_2CH_2CH_2AsMe_2)_{3-n}$ homologues with n = 0 or 1. In these cases, the arsines $MeAs(CH_2CH_2CH_2AsMe_2)_2$ and $As(CH_2CH_2CH_2AsMe_2)_3$ are readily available via the easily prepared building block $ClMgCH_2CH_2CH_2AsMe_2$ and have consequently been known for more than 20 years.[28] In contrast, a Grignard intermediate $ClMgCH_2CH_2CH_2PMe_2$ does not seem to be accessible, and neither $MeP(CH_2CH_2CH_2PMe_2)_2$ nor $P(CH_2CH_2CH_2PMe_2)_3$ has been mentioned before although there have been at least three reports on the hybrid ligands $E(CH_2CH_2CH_2AsMe_2)_3$ (E = P, Sb, Bi).[29-31]

^1H NMR Spectra. Proton spectra have been used to check the completeness of the $>PH/H_2C{=}CHCH_2-$ addition, which is indicated by the absence of any resonances in the olefinic ranges $4.1 < \delta < 5.1$ and $5.4 < \delta < 6.1$.

The methyl signals of the phosphines containing Me_2P- groups are simple doublets (Table I) irrespective of whether the methyl groups are enantiotopic or diastereotopic.[32] Thus, the hydrogens of the pairwise diastereotopic terminal CH_3- substituents of $MeP(CH_2CH_2CH_2PMe_2)_2$ and $t\text{-}BuP(CH_2CH_2CH_2PMe_2)_2$ are not sufficiently different for their nonequivalence to be detected at 80 MHz. Within experimental error, their shifts and splittings match those of the protons attached to the mutually enantiotopic methyl groups of the tripod ligand $P(CH_2CH_2CH_2PMe_2)_3$. These results are similar to those previously obtained by King and Cloyd from the 60- and 100-MHz spectra of the homologous ethylene-bridged oligo(phosphines) $MeP(CH_2CH_2PMe_2)_2$ and $P(CH_2CH_2PMe_2)_3$.[27]

^{31}P NMR Spectra. As expected, the new phosphines were found to display ^{31}P singlets occurring fairly upfield from the H_3PO_4 standard (Table I). Compared to the ^{31}P shifts of King's compounds $MeP(CH_2CH_2PMe_2)_2$ [$\delta(PMe) = -34.3$, $\delta(PMe_2) = -48.6$][27] and $P(CH_2CH_2PMe_2)_3$ [$\delta(P) = -19.6$, $\delta(PMe_2) = -48.0$],[27] the signals of the respective central and terminal ^{31}P nuclei of the two C_3-linked phosphines $MeP(CH_2CH_2CH_2PMe_2)_2$ and $P(CH_2CH_2CH_2PMe_2)_3$ are shifted to higher field by, approximately, −15 (P), −10 (PMe), and −6 (PMe_2) ppm. This finding is thought to reflect a decrease in the effective steric bulk of the $P(CH_2)_nP$ units when an ethylene is exchanged for a trimethylene connecting chain.[9]

---

[23] Antberg, M. Dissertation (in progress), Universität Hamburg, 1983.

[24] The reviewers asked us to comment on the specific purpose of the added AIBN radical initiator and to clarify whether the addition reactions described in this paper were actually brought about by photolysis or whether irradiation served only to decompose the added AIBN into free radicals. The anti-Markovnikov addition of P-H bonds to $(H_2C{=}CHCH_2)_{3-n}PR_n$ molecules will in fact occur when the reactants are irradiated in the absence of AIBN. This is shown (1) by the results of Diel and Norman[10b] who obtained $H_2P(CH_2)_3PHCH_2CH{=}CH_2$ from the gas-phase photolysis of $H_2C{=}CHCH_2PH_2$ and (2) by observations of our own according to which $P(CH_2CH_2CH_2PMe_2)_3$ is also formed in approximately quantitative yields when the $P(CH_2CH{=}CH_2)_3/HPMe_2$ photolysis is carried out without adding AIBN.[23] However, these findings do not unequivocally demonstrate the photochemical initiation of the P–H bond-addition reactions since trace amounts of impurities forming free radicals upon irradiation cannot be excluded. Moreover, in view of the comparatively long wavelength of the radiation employed (phosphines will absorb in the 200–220-nm region!), such *adventitious* radical sources, e.g. allyl chloride from the phosphine preparations, are indeed likely promoters of "UV-initiated" P–H addition reactions.[10b] AIBN was therefore added in each case so as to maintain a *defined* free-radical source during irradiation.

[25] DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011.

[26] There is, for example, no evidence of β-allyl attack, i.e. formation of $Me_2P(CH_2)_3PMeCH_2CH(PMe_2)CH_3$ or related compounds: oligophosphines containing ethylene connecting chains between the donor atoms will give rise to ^{31}P NMR spectra exhibiting PP couplings of ca. 20 Hz,[27] which have not been detected for any of the new phosphines discussed herein. Although no elemental analyses were done, the yields of the metal complexes prepared for additional characterization of the new PP_2 and PP_3 ligands (cf. Experimental Section) appeared to be quantitative enough (up to 80%) to ensure that the reactant oligo(phosphine) was indeed only the one in question.

[27] King, R. B.; Cloyd, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 53.

[28] (a) Barclay, G. A.; Barnard, A. K. *J. Chem. Soc.* **1961**, 4296. (b) Barclay, G. A.; Nyholm, R. S.; Parish, R. V. *J. Chem. Soc.* **1961**, 4433.

[29] Benner, G. S.; Hatfield, W. E.; Meek, D. W. *Inorg. Chem.* **1964**, *3*, 1544.

[30] McAuliffe, C. A.; Meek, D. W. *Inorg. Chim. Acta* **1971**, *5*, 270.

[31] Reference 6, p 26.

[32] One of the reviewers argued that the terminal methyl groups of, e.g., $MeP(CH_2CH_2CH_2PMe_2)_2$ were enantiotopic rather than diastereotopic. However, since phosphines are normally configurationally stable on the NMR time scale up to 200 °C,[33] the bridging phosphorus atom of a $RP(CH_2CH_2CH_2PMe_2)_2$ molecule should constitute a stable tetrahedral center. Hence, there is no molecular symmetry plane bisecting the Me–P–Me angles of the prochiral Me_2P moieties, the paired methyl groups thus becoming diastereotopic.[34] On the other hand, there are three molecular symmetry planes bisecting the Me–P–Me angles of the $P(CH_2CH_2CH_2PMe_2)_3$ molecule, which renders the methyl substituents of this compound enantiotopic.[34]

[33] Lambert, J. B. *Top. Stereochem.* **1971**, *6*, 19.

[34] Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307.

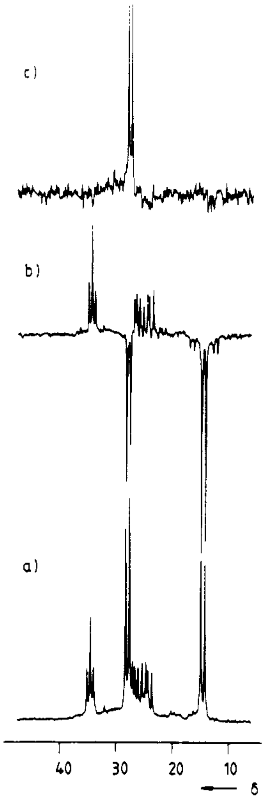


Figure 1. Identification of the resonance of the quaternary carbon C_q of t-BuP($CH_2CH_2CH_2PMe_2$)$_2$ using the attached proton test (APT) pulse sequence:[16] (a) 20.15-MHz $^{13}C\{^1H\}$ NMR spectrum; (b) APT experiment (pulse width 45°, relaxation delay 2 s, τ = 8 ms) showing the CH_3 signals with inverted amplitudes (note the decrease in intensity of the doublet at δ 27.9 superimposed by the (positive) signal of C_q); (c) APT pulse sequence (τ = 4 ms) solely displaying the C_q doublet.

Note that apart from δ(t-BuP) the $\delta(^{31}P)$ values are predictable with a high degree of confidence using Grim's alkyl group contributions to ^{31}P chemical shifts.[35]

^{13}C NMR Spectra. ^{13}C NMR shifts and carbon-phosphorus coupling constants of bis- and tris(phosphines) containing -$CH_2CH_2CH_2$-backbones have previously been reported by McAuliffe, Hill, and Dyer[36] as well as by ourselves.[5,9] Thus, the ^{13}C spectra of the compounds described herein were readily assigned by comparison with the data from the cited papers; cf. Table I.

Similar to the methyl and ethyl carbon resonances of the phosphines studied earlier,[5,9,36] the CH_3 and CH_2 carbons of the alkyl substituents attached to the terminal phosphorus atoms gave rise to doublets well upfield from the trimethylene region. Within the C_3 linkages the signals of the central carbons occurred at higher field than those of the ^{13}C nuclei directly linked to phosphorus although there remained some ambiguity concerning the assignment of the respective CH_2 resonances in the spectrum of t-BuP($CH_2CH_2CH_2PMe_2$)$_2$. Most of the trimethylene ^{13}C multiplets exhibited the ABX pseudotriplet splitting frequently found for P_ACCCP_B moieties;[5,9,36] in some cases a four-line spectral pattern was observed, indicating a somewhat more pronounced difference between ^1J(PC), ^2J(PC), and ^3J(PC) than is usual.[5,9,36-38]

A rather curious situation was met with the quaternary carbon atom of t-BuP($CH_2CH_2CH_2PMe_2$)$_2$, which could not be identified from the routine $^{13}C\{^1H\}$ spectrum. However, an attached proton test experiment[16] did unambiguously reveal the resonance of this unique carbon as a doublet precisely coincident with the signal originating from the adjecent methyl ^{13}C nuclei (Figure 1).

Mass Spectra. The major mass spectral fragmentation pathways are shown in Scheme I.

$R_2P(CH_2)_3\cdot$, $R_2P(CH_2)_2\cdot$, and t-$C_4H_9\cdot$ radicals are readily lost from the parent ions, which have not been observed for any of the alkylated oligo(phosphines) described in this paper. The stability of the $R_2P(CH_2)_3PR^+$ fragments generated according to the scheme is ascribed to the formation of heterocyclic onium ions containing P-alkylated five-membered ring structures of the 1,2-diphospholane type. As reported earlier,[5,9] facile generation of stable $R^2\overline{P(CH_2)_3P}R^+$ fragment ions is also a common feature of the mass spectra of trimethylene-bridged tris(phosphines) bearing phenyl groups at the donor atoms. The smooth formation of the 1,2-diphospholane system from $P(CH_2)_3P$ precursors is further demonstrated by an observation of Issleib and Thorausch[39] who reported the facile elimination of dihydrogen from the lithio derivative of 1,3-propanediylbis(phosphine) according to $H_2P(CH_2)_3P(Li)H \rightarrow H\overline{P(CH_2)_3P}PLi + H_2$.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Bonn) for financial support of this research (Grant Da 123/4-1) and to Hoechst AG (Frankfurt) for a generous gift of $MePCl_2$. Thanks are also expressed to Dr. E. Haupt for carrying out the APT NMR experiments and to Prof. W. A. König and his group for taking the mass spectra.

---

(35) Grim, S. O.; McFarlane, W.; Davidoff, E. F. *J. Org. Chem.* **1967**, *32*, 781.
(36) Briggs, J. C.; McAuliffe, C. A.; Hill, W. E.; Minahan, D. M. A.; Dyer, G. *J. Chem. Soc., Perkin Trans. 2* **1982**, 321.
(37) Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30.
(38) King, R. B.; Cloyd, J. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 938.
(39) Issleib, K.; Thorausch, P. *Phosphorus and Sulfur* **1978**, *4*, 137.

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Trifluoramine Oxide with Nitric Oxide: A Facile in Situ Source of Nitrosyl Fluoride

SCOTT A. KINKEAD and JEAN'NE M. SHREEVE*

Received March 19, 1984

Trifluoramine oxide (NF_3O) has been found to react rapidly with nitric oxide to give nitrosyl fluoride (FNO). A free-radical reaction involving the known difluoronitryl ($F_2NO\cdot$) radical is proposed as a plausible mechanism. This reaction has been used as an in situ source of nitrosyl fluoride to synthesize the previously unknown nitroso compounds $R_f(CF_3)CFNO$ (R_f = n-C_5H_{11}, SF_5, OC_2F_5).

Nitrosyl fluoride, first synthesized by Ruff in 1905 from AgF_2 and NOCl,[1] has been prepared by a variety of methods, including the reaction of fluoride ion with nitrosyl salts[2-4] or N_2O_4[5] and the direct reaction of nitric oxide with F_2.[6] In

0020-1669/84/1323-4174$01.50/0