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Two New Syntheses of the "Phospha-Wittig" Reagents

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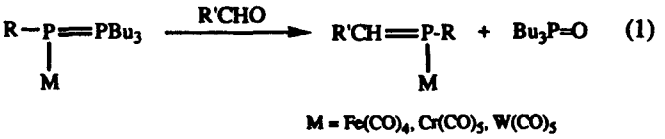
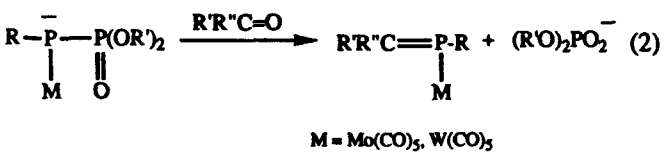
ABSTRACT

The secondary phosphorylphosphane complexes used in the synthesis of phosphaalkene complexes from carbonyl compounds by the so-called "phospha-Wittig" reaction can be obtained by two routes. In the first one, a primary lithiophosphine complex is condensed with a chlorophosphite. The resulting P–P compound is oxidized at the free phosphorus by 3-chloroperbenzoic acid. In the second one, bis(phosphoryl)phosphane complexes are allowed to react with sodium methylate in methanol or with water. One of the two P–P bonds of the starting product is thus cleaved to give the "phospha-Wittig" reagent. Both routes give better yields and are less sensitive to steric hindrance than the previously described method.

INTRODUCTION

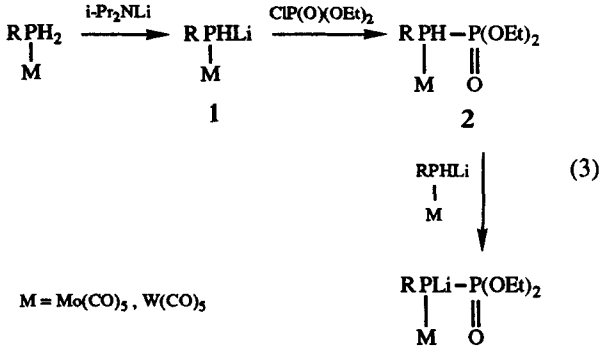
In recently published work [1–4], we have shown that it is possible to transpose the well-known Wittig and Horner-Emmons syntheses of alkenes to get phosphaalkene complexes from carbonyl compounds (Equations 1 and 2). In these schemes, the transition metal complexing group is used to stabilize both the starting "phospha-Wittig" reagents and the final phosphaalkenes. Without it, it becomes necessary to use bulky or electron-withdrawing substituents at the phosphinidene phosphorus and the "phospha-Wittig" reactions do not work properly anymore. Of the two variations, the second one is more efficient since both ketones and aldehydes can be used. However, the yields and generality of the presently available synthesis of secondary phosphorylphosphane complexes [4] are not fully satisfactory. We report here on two alternative syntheses of these species that proceed with better yields and greater generality.





RESULTS AND DISCUSSION

The current process relies on the phosphorylation of primary lithiophosphine complexes (Equation 3). Since the PH proton of **2** is very acidic, **2** is able to react with **1** so that two equivalents of lithium amide are necessary to perform the synthesis of the "phospha-Wittig" reagent. This excess of metalating agent



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This paper is dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

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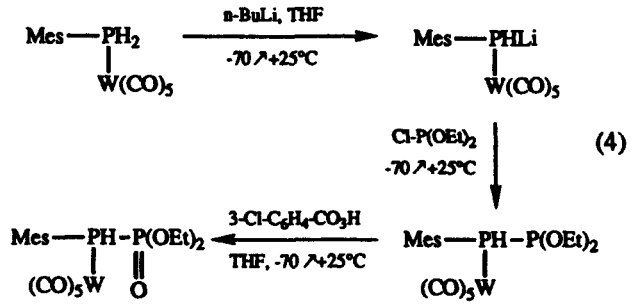
necessitates the use of an amide in order to prevent side-reactions of *n*BuLi with the metal carbonyl groups or with the chlorophosphate. We thought that it would be possible to improve the approach if the acidity of the PH proton of the final product was reduced. We thus decided to replace the chlorophosphate by a chlorophosphite and to perform the oxidation of the uncomplexed phosphorus after the building of the P–P bond. This new route is depicted in Equation 4.

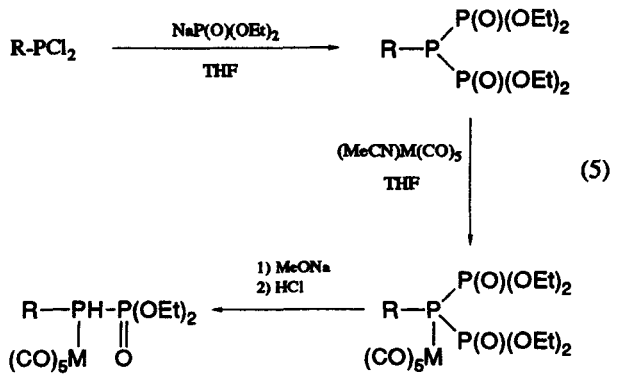


4 (overall yield 82%) **3**

(Mes = 2,4,6-$Me_3C_6H_2$)

The formation of the intermediate P–P compound **3** is monitored by ^{31}P NMR spectroscopy: $\delta^{31}P$ +181.9 and −62.0, ^1J(P–P) = 293 Hz. The overall yield is excellent. The former procedure (Equation 3) does not work properly with the mesityl substituent, perhaps for steric reasons.

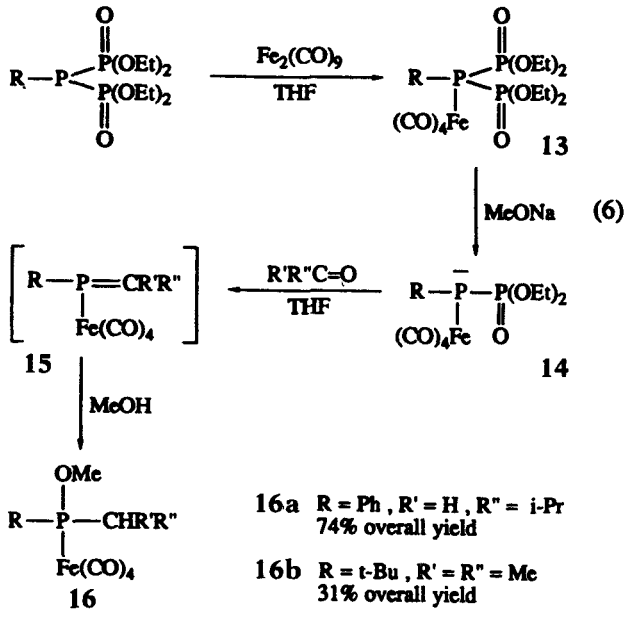
We also wanted to avoid the use of primary phosphine complexes. A solution to this problem was found via the use of bis(phosphoryl)phosphane complexes. Bis and tris(phosphoryl)phosphanes have been well known since the work of Fluck, Schmidpeter, and Weber [5–9]. Molybdenum and tungsten carbonyl complexes of these species are also known [10]. We found that it is possible to cleave selectively one phosphoryl–phosphorus bond in these complexes by using sodium methylate [11]. The synthesis of the phospha-Wittig reagents by this route is depicted in Equation 5.



5 R = Me, M = Mo, 52% overall yield
6 Me, W, 70%
7 Ph, Mo, 36%
8 Ph, W, 40%
9 t-Bu, W, 41%
10 Ph, W, 37%
11 BuO, W, 32%
12 W, 44%

As shown in the Equation, this method has considerable generality. It is relatively insensitive to steric hindrance (**9**) and it works with alkenyl substituents as well (**10** and **11**). In some cases, it is sufficient to use water to perform the cleavage of the P–P bond (**10** and **12**). The use of **10** for the synthesis of 2-phosphadiene complexes is reported elsewhere [12].

Having in hand an adequate synthesis of phosphorylphosphane molybdenum and tungsten carbonyl complexes, we tried to extend the method to other complexing groups. The inexpensive tetracarbonyliron derivatives were an obvious choice. The attempted transposition demonstrated that both the "phospha-Wittig" reagents and the phosphaalkene complexes were far less stable with $Fe(CO)_4$ than with $Mo(CO)_5$ or $W(CO)_5$ as the stabilizing moieties. Nevertheless, we were able to generate in situ both the reagents and the phosphaalkene complexes and to trap them with methanol (Equation 6). The versatility of this type of chemistry is once more illustrated.



EXPERIMENTAL

All reactions were performed under argon. Chromatographic separations were performed on a silica gel column (70-230 mesh, Merck). NMR spectra

were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C and on a Bruker WP 80 SY spectrometer operating at 32.43 MHz for ^{31}P. Chemical shifts are given in positive values downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct inlet method. Infrared spectra were recorded with a Perkin-Elmer Model 297 spectrometer.

[*Mesityl(diethylphosphoryl)phosphane*]$W(CO)_5$ *Complex* **4**

(Mesitylphosphine) $W(CO)_5$ complex was prepared as usual from mesitylphosphine [13] and $W(CO)_5(CH_3CN)$ in THF at 50°C and purified by chromatography with hexane as eluent.

*n*BuLi (2.7 mL, 4.3 mmol) was added at −78°C to a solution of (mesitylphosphine) $W(CO)_5$ (1.9 g, 4 mmol) in THF. After a few minutes diethylchlorophosphite (0.62 mL, 4.4 mmol) was added and the reaction mixture was then warmed to room temperature. The formation of complex **3** was monitored by ^{31}P NMR spectroscopy. Oxidation of complex **3** was performed by adding a solution of *m*-chloroperbenzoic acid (0.9 g, 80% acid, 4.4 mmol) in THF at −78°C.

Complex **4** was purified by column chromatography. By use of hexane/ether (80:20), small amounts of side-products were eluted; the final product was then eluted with hexane/ether (50:50). Yield 2.0 g (82%). Colorless solid ^{31}P NMR (C_6D_6) δ −86.45 (*AX*, $^1J(P-P)$ = 63.5 Hz, $^1J(^{31}P-^{183}W)$ = 215 Hz, PH), 18.46 (*AX*, P(O) $(OEt)_2$); ^1H NMR (C_6D_6) δ 0.80 (t, $^3J(H-H)$ = 7.0 Hz, CH_2CH_3), 0.99 (t, $^3J(H-H)$ = 7.0 Hz, CH_2CH_3), 1.98 (s, CH_3), 2.12 (s, CH_3), 2.75 (s, CH_3), 3.5–4 (m, 4H, CH_2), 6.43 (dd, $^1J(H-P)$ = 337.5 Hz, $^2J(H-P)$ = 6.1 Hz, PH), 6.54–6.62 (2H, CH(Mes)); IR (decalin) ν (CO) 2065 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) m/z 612 (M, 9%), 528 (M–3CO, 30%), 472 (M–5CO, 21%), 380 (100).

Synthesis of the (Bis(diethylphosphoryl)phosphane) M(CO)$_5$ Complexes

The starting dichlorophosphanes are either commercially available or prepared by literature methods [14].

A solution of dichlorophosphane (20 mmol) in THF was added slowly at 0°C to a sodium diethylphosphite (40 mmol) solution in THF. The reaction mixture was warmed to room temperature and the bis(diethylphosphoryl)phosphane was characterized by ^{31}P NMR spectroscopy. The reaction was almost quantitative in each case. A solution of (acetonitrile)$M(CO)_5$ complex (20 mmol) [4] in THF was reacted directly with the crude bis(diethylphosphoryl)phosphane at 40°C for several hours (at room temperature for molybdenum complexes). The extent of complexation was checked by ^{31}P NMR spectroscopy. The final product was characterized by ^{31}P NMR spectroscopy (see Table 1).

Synthesis of the (Diethylphosphorylphosphane)M(CO)$_5$ Complexes **5, 6, 7, 8, 9, 11**

The corresponding [bis(diethylphosphoryl)phosphane]$M(CO)_5$ complex (20 mmol) was reacted, without further purification, at 0°C with sodium methoxide (10 mL, 2M solution in MeOH). When the addition was complete, the reaction mixture was left at 0°C for about 10 minutes, then hydrolyzed with aqueous hydrochloric acid (pH < 7).

After extraction with hexane, the final product was purified either by crystallization or by column chromatography (hexane–ether mixtures; $R_f \sim 0.5$ in ether).

5: yield 4.4 g (52% from $MePCl_2$); colorless oil; ^1H NMR (C_6D_6) δ 0.97 (t, $^3J(H-H)$ = 7.0 Hz, CH_2CH_3), 0.98 (t, $^3J(H-H)$ = 7.0 Hz, CH_2CH_3), 1.13 (dt, $^2J(H-P)$ = 14.9 Hz, $^3J(H-P) \sim {}^3J(H-H)$ = 7.0 Hz, PCH_3), 3.99 (dq, $^1J(H-P)$ = 320.9 Hz, PH), 3.84 (m, 4H, OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 6.46 (d, $^1J(C-P)$ = 21.1 Hz, PCH_3), 16.29, 16.39 (s, CH_2CH_3), 63.13 (d, $^2J(C-P)$ = 7.5 Hz, OCH_2CH_3), 63.28 (d, $^2J(C-P)$ = 7.5 Hz, OCH_2CH_3), 204.86 (d, $^2J(C-P)$ = 8.6 Hz, cis CO), 209.11 (d, $^2J(C-P)$ = 24.7 Hz, trans CO); IR (decalin) ν (CO) 2080 (m), 1950 (vs) cm^{-1}; mass spectrum (^{98}Mo) m/z 422 (M, 7%), 394 (M–CO, 19%), 366 (M–2CO, 14%), 338 (M–3CO, 29%), 310 (M–4CO, 100%.

Spectroscopic data for complexes **6**, **7**, **8**, and **9** have already been reported (ref. [4], [15]).

11: yield 3.8 g (32% from BuO–CH=CH–PCl_2); colorless oil; ^1H NMR (C_6D_6) δ 0.74 (t, $^3J(H-H)$ = 7.2 Hz, 3H, CH_3 (Bu)), 1.0–1.4 (m, 10H, $2OCH_2CH_3$ + $2CH_2$ (Bu)), 3.36 (m, 2H, OCH_2 (Bu)), 3.94 (m, 4H, OCH_2CH_3), 4.95 (m, 1H, $^3J(H-H)$ = 13.0 Hz, $^3J(H-H)$ = 5.5 Hz, $^2J(H-P)$ = 11.5 Hz, $^3J(H-P)$ = 4.0 Hz, PCH=CH–O), 5.19 (ddd, $^1J(H-P)$ = 342.1 Hz, $^3J(H-H)$ = 5.5 Hz, $^3J(H-P)$ = 3.4 Hz, PH), 6.91 (td, $^3J(H-H) \sim {}^3J(H-P)$ = 13.1 Hz, $^4J(H-P)$ = 3.8 Hz, PCH=CH–O); ^{13}C NMR (C_6D_6) δ 13.47 (s, CH_3), 16.13, 16.22 (s, OCH_2CH_3), 18.85 (s, CH_2), 30.79 (s, CH_2), 63.17, 63.32 (OCH_2CH_3), 70.37 (s, OCH_2 (Bu)), 83.31 (d, $^1J(C-P)$ = 47.2 Hz, PCH=CH–O), 163.18 (dd, $^2J(C-P)$ = 24.2 Hz, $^3J(C-P)$ = 10.6 Hz, PCH=CH–O), 195.68 (d, $^2J(C-P)$ = 5.7 Hz, cis CO), 198.03 (d, $^2J(C-P)$ = 23.7 Hz, trans CO); IR (CCl_4) ν (CO) 2070 (m), 1930 (vs) cm^{-1}; mass spectrum (^{184}W) m/z 592 (M, 27%), 564 (M–CO, 20%), 480 (M–4CO, 67%), 452 (M–5CO, 100%).

Synthesis of the (Diethylphosphorylphosphane)M(CO)$_5$ Complexes **10** *and* **12**

The corresponding [bis(diethylphosphoryl)phosphane]$M(CO)_5$ complex was hydrolyzed with water

TABLE 1 ^{31}P NMR data for the bis(Diethylphosphoryl)phosphanes (a), Their $M(CO)_5$ Complexes (b) and the (Diethylphosphorylphosphane) $M(CO)_5$ Complexes (**5–12**).

R	*M*		δP_A	δP_B	$^1J(P-P)$	$^1J(H-P)$	*ref.*
Me		a	−85.0	31.5	175.8		
	W	b	−46.5	20.1	72.7		
	Mo	**5**	−64.4	23.5	70.8	320.9	
	W	**6**	−84.9	22.4	100.1	333.9	[14]
Ph		a	−61.8	26.8	156.3		
	Mo	b	−4.5	20.3	48.8		
	W	b	−22.6	18.9	70.8		
	Mo	**7**	−33.4	22.7	58.6	328.7	[4]
	W	**8**	−52.1	20.4	83.0	340.0	[14]
tBu		a	−36.0	27.9	208.3		
	W	b	10.5	22.0	31.7		
	W	**9**	−20.2	22.5	51.3	320.9	[4]
PhCH=CH		a	−68.0	27.5	151.4		
	W	b	−29.6	19.1	78.1		
	W	**10**	−66.1	18.5	97.5	340.9	
BuOCH=CH		a	−75.1	28.5	146.5		
	W	b	−40.3	18.8	87.9		
	W	**11**	−74.2	21.3	102.5	342.1	
2-thienyl		a	−79.6	25.4	141.6		
	W	b	−41.4	17.3	85.5		
	W	**12**	−73.3	19.0	100.1	346.7	

(5 mL) at room temperature (16 h). After extraction with ether, complexes **10** and **12** were purified by column chromatography with hexane/ether (70:30) as eluent.

10: yield 4.4 g (37% from $PhCH{=}CH{-}PCl_2$); colorless oil; ^1H NMR (C_6D_6) δ 0.95 (t, ^3J(H–H) = 7.0 Hz, CH_2CH_3), 1.01 (t, ^3J(H–H) = 7.0 Hz, CH_2CH_3), 3.9 (m, 4H, OCH_2CH_3), 5.30 (dd, ^1J(H–P) = 340.9 Hz, ^3J(H–H) = 5.7 Hz, PH), 6.50 (tt, ^3J(H–H) ~ ^2J(H–P) ~ 16.2 Hz, ^3J(H–H) ~ ^3J(H–P) ~ 5.7 Hz, PCH=CH–P); ^{13}C NMR (C_6D_6) δ 16.26, 16.36 (CH_2CH_3), 63.90, 63.99 (CH_2CH_3), 111.62 (d, ^1J(C–P) = 39.0 Hz, PCH=CHPh), 150.51 (t, ^2J(C–P) ~ ^3J(C–P) = 10.9 Hz, PCH=CHPh); IR (decalin) ν (CO) 2075 (m), 1950 (vs) cm^{-1}; mass spectrum (^{184}W) m/z 596 (M, 13%), 568 (M–CO, 17%), 512 (M–3CO, 20%), 456 (M–5CO, 100%).

12: yield 5.1 g (44% from dichlorothienylphosphane); colorless oil; ^1H NMR (C_6D_6) δ 0.87 (t, ^3J(H–H) = 7.0 Hz, CH_2CH_3), 0.96 (t, ^3J(H–H) = 7.0 Hz, CH_2CH_3), 3.8 (m, 4H, CH_2CH_3), 5.80 (dd, ^1J(H–P) = 346.7 Hz, ^2J(H–P) = 2.8 Hz, PH), 6.70, 7.00, 7.50 (m, 3H, thienyl); mass spectrum (^{184}W) m/z 576 (M, 17%), 548 (M–CO, 13%), 492 (M–3CO, 43%), 436 (M–5CO, 100%).

Synthesis and Trapping Reactions of the (Phosphaalkene)Fe(CO)$_4$ Complexes **15**

The corresponding bis(diethylphosphoryl)phosphane (10 mmol of crude product–see above) was reacted with $Fe_2(CO)_9$ (3.6 g, 10 mmol) in THF at 40°C for 45 min. After evaporation, extraction with hexane, filtration, and evaporation, about 8 mmoles of crude (bis(diethylphosphorylphosphane))$Fe(CO)_4$ complex **13** were obtained [**13b**: R = *t*Bu; ^{31}P NMR (THF) δ 20.7 (AX_2, ^1J(AX) = 46.4 Hz, $P(O)(OEt)_2$), 54.74 (AX_2, tBuP) ppm; paramagnetic side products prevented the recording of well-resolved ^{31}P NMR spectra for **13a** (R = Ph) and **13c** (R = Me)].

Complex **13** was dissolved in THF and NaOMe (4 mL, 2M solution in methanol) was added at 0°C. The anion **14** was formed instantaneously [**14a**: R = Ph, ^{31}P NMR (THF) δ −45.17 (*AB*, ^1J(AB) = 402.8 Hz, Ph P(−)), 58.77 (*AB*, $P(O)(OEt)_2$) ppm; **14b**: R = *t*Bu, ^{31}P NMR (THF) δ −25.0 (*AX*, ^1J(AX) = 424.8 Hz, *t*Bu P(−)), 58.0 (*AX*, $P(O)(OEt)_2$) ppm]. The carbonyl compound (acetone or isobutyraldehyde—40 mmol and 10 mmol respectively) was then added and the reaction was followed by ^{31}P NMR spectroscopy.

Complex **16a** was obtained instantaneously; complex **16b** was obtained after 2 h heating at 40°C. The final product was purified by column chromatography with hexane/ether (98:2) as eluent.

16a: yellow solid; mp <50°C (hexane); ^{31}P NMR (hexane) δ 181.7; ^1H NMR (C_6D_6) δ 0.80 (d, ^3J(H–H) = 6.6 Hz, 3H, $CHCH_3$), 0.87 (d, ^3J(H–H) = 6.6 Hz, 3H, $CHCH_3$), 1.6–1.9 (m, 2H, PCH_2), 2.2 (m, 1H, $CHMe_2$), 3.18 (d, ^3J(H–P) = 13.7 Hz, OCH_3), 7.0–7.6 (m, Ph); ^{13}C NMR (C_6D_6) δ 24.0 (d, J(C–P) = 5.2 Hz), 25.02 (d, J(C–P) = 12.6 Hz), 25.30 (s), 49.34 (d, ^1J(C–

P) = 39.2 Hz, PCH_2), 53.33 (d, ^2J(C–P) = 4.0 Hz, OCH_3), 213.57 (d, ^2J(C–P) = 20.0 Hz, $Fe(CO)_4$); IR (CCl_4) ν (CO) 2070 (m), 1920 (vs) cm^{-1}; mass spectrum m/z 364 (M, 10%), 336 (M–CO, 30%), 280 (M–4CO, 100%).

16b: yellow oil; ^{31}P NMR (C_6D_6) δ 211.2; ^1H NMR (C_6D_6) δ 1.0 (unresolved m, 15H, CH_3), 2.2 (m, 1H, $CHMe_2$), 3.30 (d, ^3J(H–P) = 11.5 Hz, OCH_3); ^{13}C NMR (C_6D_6) δ 18.21 (s, $CHCH_3$), 19.67 (s, $CHCH_3$), 26.50 (s, CMe_3), 33.77 (d, ^1J(C–P) = 23.9 Hz, $CHMe_2$), 41.83 (d, ^1J(C–P) = 30.5 Hz, CMe_3), 56.06 (s, OCH_3), 214.27 (d, ^2J(C–P) = 17.6 Hz, $Fe(CO)_4$); IR (decalin) ν (CO) 2040 (m), 1945 (vs), 1930 (vs) cm^{-1}; mass spectrum m/z 330 (M, 13%), 302 (M–CO, 23%), 246 (M–3CO, 65%), 218 (M–4CO, 100%).

REFERENCES AND NOTES

[1] P. Le Floch, A. Marinetti, L. Ricard, F. Mathey, *J. Am. Chem. Soc., 112,* 1990, 2407.

[2] P. Le Floch, F. Mathey, *Synlett,* 1990, 171.

[3] A. Marinetti, F. Mathey, *Angew. Chem., Int. Ed. Engl., 27,* 1988, 1382.

[4] A. Marinetti, S. Bauer, L. Ricard, F. Mathey, *Organometallics, 9,* 1990, 793.

[5] E. Fluck, H. Binder, *Inorg. Nucl. Chem. Letters, 3,* 1967, 307; E. Fluck, H. Binder: in A. H. Cowley (ed.), *Compounds Containing Phosphorus-Phosphorus Bonds* Hutchinson and Ross, Stroudsburg, PA, p. 134 (1973); D. Weber, E. Fluck, *Z. Naturforsch, 30b,* 1975, 60.

[6] D. Weber, G. Heckmann, E. Fluck, *Z. Naturforsch, 31b,* 1976, 81.

[7] A. Schmidpeter, S. Lochschmidt, G. Burget, W. S. Sheldrick, *Phosphorus & Sulfur, 18,* 1983, 23.

[8] D. Weber, K. Peters, H. G. von Schnering, E. Fluck, *Z. Naturforsch, 38b,* 1983, 208.

[9] A. Schmidpeter, *Nova Acta Leopoldina, 59,* 1985, 69.

[10] D. Weber, E. Fluck, H. G. von Schnering, K. Peters, *Z. Naturforsch, 37b,* 1982, 594.

[11] Selective cleavage of a phosphorylphosphane by an amine has been reported: see ref. [6].

[12] A. Marinetti, S. Bauer, L. Ricard, F. Mathey, *J. Chem. Soc., Dalton Trans.,* in press.

[13] G. Becker, *Z. Anorg. Allg. Chem., 443,* 1978, 42.

[14] Y. A. Levin, V. S. Galeev, E. K. Trutneva, *Zh. Obshch. Khim., 37,* 1967, 1783; M. Bentov, L. David, *J. Chem. Soc.,* 1964, 4750; S. V. Fridland, A. I. Efremov, *Zh. Obshch. Khim., 48,* 1978, 285.

[15] A. Marinetti, F. Mathey, *Tetrahedron, 45,* 1989, 3061.