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OPENING OF PHOSPHIRANE-TUNGSTEN-COMPLEXES BY NUCLEOPHILES

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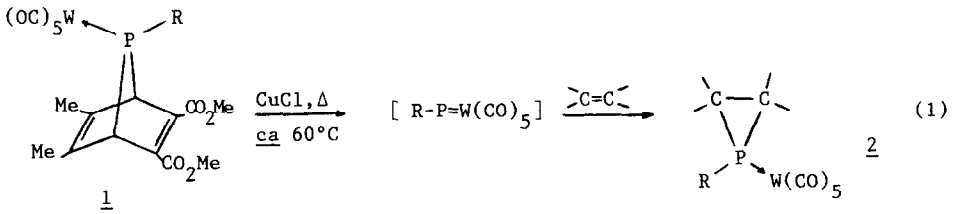
Abstract: The reactions of two phosphirane P-$W(CO)_5$ complexes with nitrogen, oxygen, phosphorus and sulphur nucleophiles have been studied. Except when the nucleophile is too bulky, the initial attack takes place at phosphorus. In this case, two main reaction paths have been observed : the first one is a ring opening giving a carbanion which may be protonated, or which can react with the $W(CO)_5$ group to yield a cyclic Fischer carbene complex. In the second reaction path, the whole carbon-carbon unit of the three-membered ring is lost and the final products formally result from the addition of the nucleophile onto the phosphinidene unit [RP→$W(CO)_5$]. Nitrogen and oxygen nucleophiles tend to follow the first path, whereas phosphorus and sulphur nucleophiles tend to follow the second one.

In spite of its early discovery by Wagner in 1963[1], the phosphirane ring has mainly been studied from a structural and spectroscopic standpoint until now[2]. Recently, several new syntheses of this ring have been devised with some emphasis on its stabilization by bulky substituents [3-8] or, in some cases, by complexation [9-10]. Nevertheless, a thorough investigation of the chemical reactivity of this heterocycle is still lacking today. This gap is undoubtedly due to the low stability and, hence, to the rather erratic reactivity of this highly strained system. An early study on the metalation of the P-H bond of the parent phosphirane showed that it was possible to observe a clean reactivity provided that the phosphorus atom was coordinated to a $Mo(CO)_5$ unit [11]. This observation led us to envisage a systematic study of the chemistry of the phosphirane ring in the coordination sphere of a metal.
This idea was all the more tempting since we had previously devised a very general and versatile synthesis of the phosphirane P-$W(CO)_5$ complexes [12]. (eq.1)

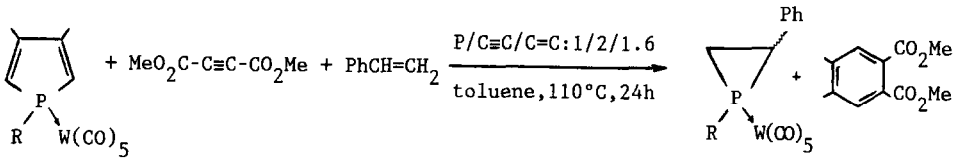


1 2 (1)

Our first results are reported hereafter.

RESULTS AND DISCUSSION

In order to facilitate our subsequent work, we first decided to simplify the synthesis of the phosphirane complexes such as 2. Since the 7-phosphanorbornadiene precursors (1) are prepared from phosphole complexes [13], we tried to perform the direct conversion of phosphole into phosphirane complexes. We were indeed able to obtain directly the phosphirane complexes 5 and 6 from the readily available phosphole complexes 3 and 4 [14]. (eq.2)



3 R=Ph
4 R=Me

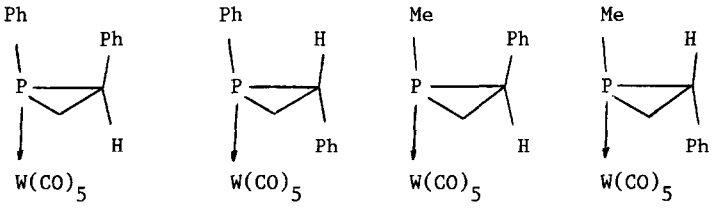
5 a,b R=Ph, 80%
6 a,b R=Me, 64% (2)

The two phosphirane complexes were both obtained as mixtures of two isomers as indicated by the ^{31}P NMR spectra (in toluene) :

5a : $\delta^{31}P$ -156.5 ppm ; 5b : $\delta^{31}P$ -151.1 ppm ; ratio 5a / 5b ca 3.6

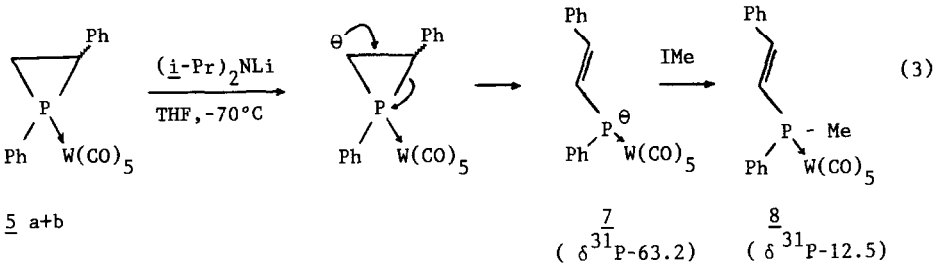
6a : $\delta^{31}P$ -177.1 ppm ; 6b : $\delta^{31}P$ -164.5 ppm ; ratio 6a / 6b ca 1.2

Since the time when our first paper was published [12], we carried out the X-ray crystal structure analysis of a 1,2,3-triphenylphosphirane P-$W(CO)_5$ complex [15]. This work demonstrated that the ^2J (H-P) coupling constant within the ring is high (ca 8 Hz) when H is trans to W, contrary to what we expected, and low (ca 1 Hz) when H is cis to W. On this basis, we assign the following stereochemistries to these isomers (the structure of 5b is deduced from the structure of 5a since it has been impossible to isolate it in the pure state):



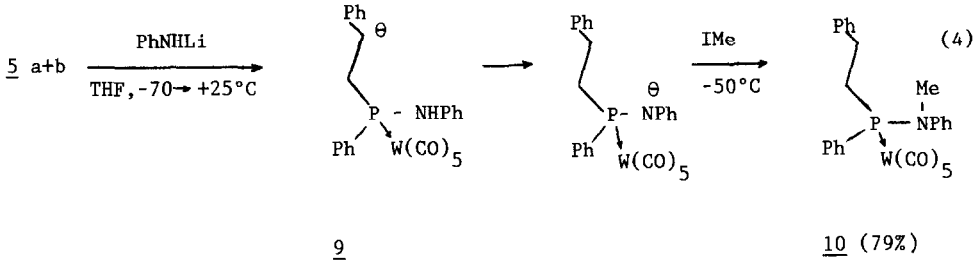
5a ^2J(H-P)∿ OHz 5b 6a ^2J(H-P)∿ OHz 6b ^2J(H-P)∿7.8 Hz

All the subsequent work was performed with the mixtures 5 a+b and 6 a+b. According to the preliminary indications of the literature[2], it appeared that the reactivity of the phosphirane ring toward electrophiles is low and that it tends to polymerize in the presence of strong Lewis acids. On the contrary, a clean opening was observed in a particular case with a nucleophile such as methylenetrimethylphosphorane[16]. Thus, we decided to start our investigations with a systematic study of the reactivity of our complexes toward nucleophiles. With nitrogen nucleophiles, we observed three types of reactions. When using a very strong base such as $(i\text{-Pr})_2NLi$, a CH_2 α-proton is abstracted and the carbanion thus obtained rearranges to give the corresponding open-chain phosphanion 7 (eq.3).



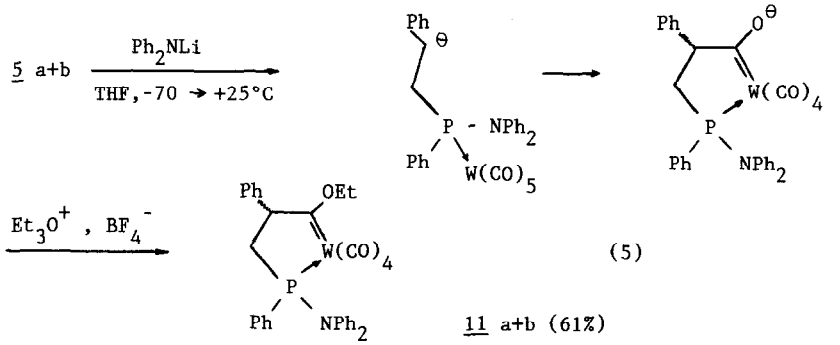
(3)

A similar ring opening was observed by Quast in the reaction between R_2NLi and 1,2,3-tris (tert-butyl)phosphirane oxide[17]. With a weaker and less hindered base such as PhNHLi, the attack takes place at phosphorus (eq.4).



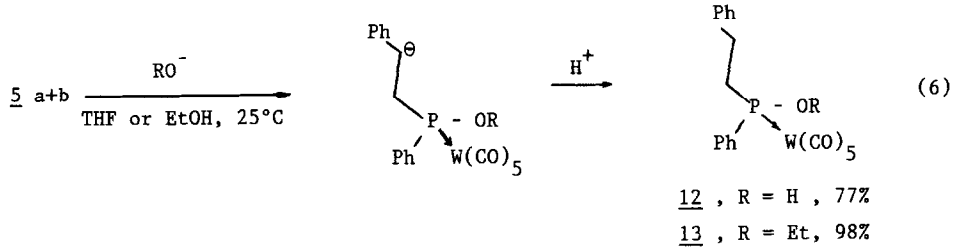
(4)

If the nitrogen nucleophile has no N-H bond, then, of course, the transient carbanion resulting from the initial ring-opening cannot undergo a protonation as in the case of 9. In that case, the attack of a cis $W(CO)_5$ carbonyl group is observed to give a carbene complex (eq.5)



(5)

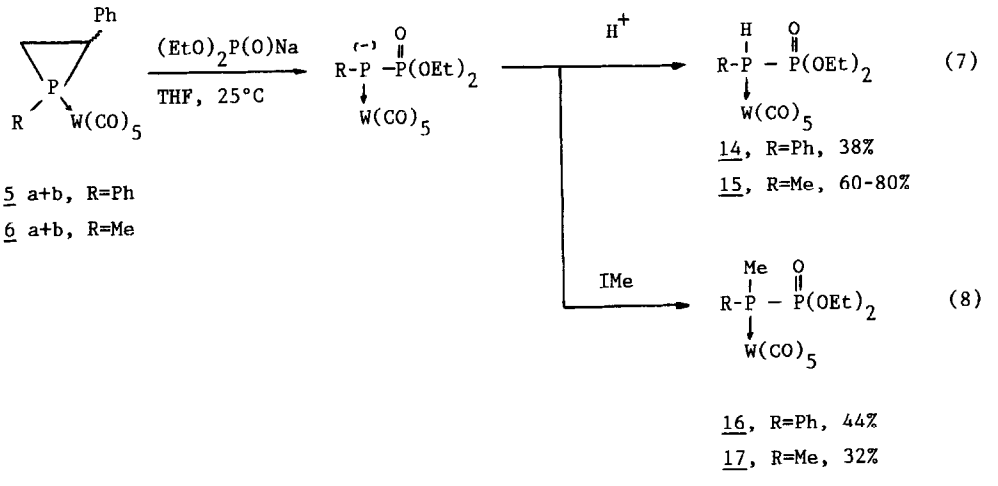
On the ^{13}C NMR spectrum of 11, a characteristic carbenic resonance appears at 336.7 ppm. The story is far more simple with oxygen nucleophiles. In the two cases that we studied, we observed a ring opening similar to that depicted in equation 4 (eq.6).



12 , R = H , 77%
13 , R = Et, 98%

(6)

It must be noted however that the reaction with EtO^- was run in ethanol so that the transient carbanion could not escape protonation. In aprotic media, a cyclisation to give a carbene complex similar to 11 might have taken place instead. The behaviour of phosphorus nucleophiles is again completely different. In all cases, a loss of styrene was observed (eq.7-9).



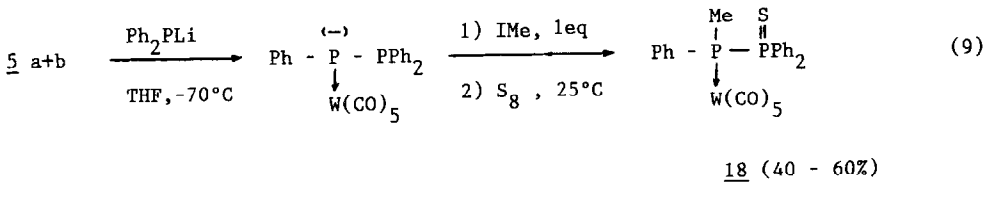
5 a+b, R=Ph
6 a+b, R=Me

14, R=Ph, 38%
15, R=Me, 60-80%

16, R=Ph, 44%
17, R=Me, 32%

(7)

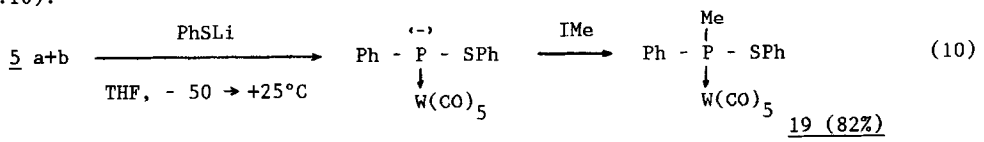
(8)



18 (40 - 60%)

(9)

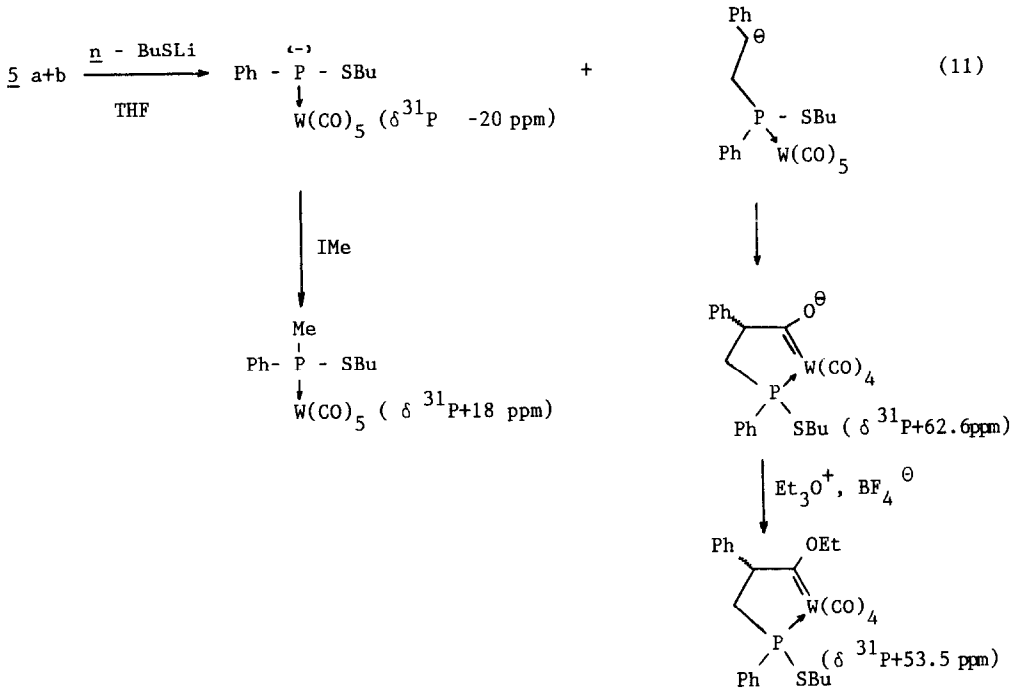
Finally, the behaviour of sulphur nucleophiles appears to be intermediate between those of nitrogen and phosphorus nucleophiles. With PhS^- , the loss of styrene exclusively takes place (eq.10).



19 (82%)

(10)

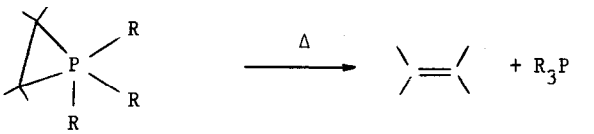
On the contrary with n-BuS$^-$, the loss of styrene and the opening of the ring simultaneously occur (eq.11).



(11)

In that case, the reaction was followed by ^{31}P NMR spectroscopy but the products were not fully characterized.

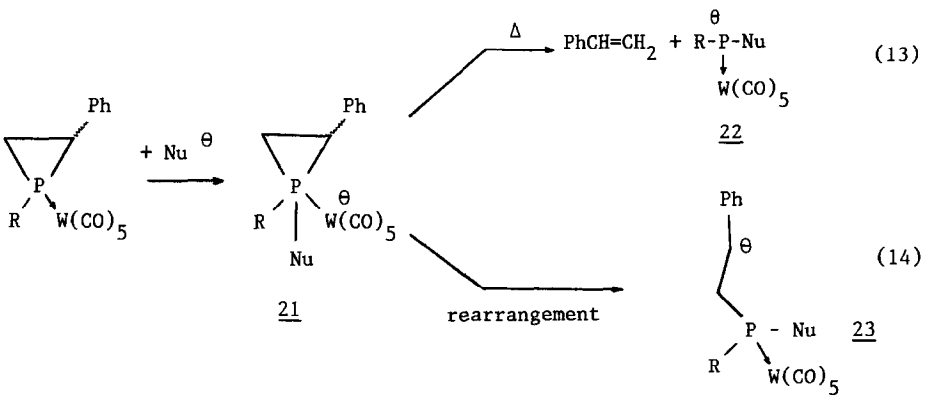
If we exclude the particular case of the CH_2 metalation depicted in equation 3, it is possible to rationalize all the results that we have observed on the basis of a unique mechanism. Denney[18] has demonstrated that phosphoranes including a phosphirane ring such as 20 can exist and that their stability is very dependent on the nature of the R substituents. Oxygen substituents stabilize the structure much more efficiently than sulphur substituents. The easy thermal decomposition of these phosphoranes yields the corresponding olefin and a tricoordinated phosphorus species (eq.12).



(12)

20

On this basis, we propose the following general scheme :



If the stability of the intermediate phosphorane 21 is too low, it rapidly decomposes to give styrene and the phosphido anion 22 (eq.13). If, on the contrary, the phosphorane is stable enough, the rearrangement giving the carbanion 23 (eq.14) can take place. Apparently, in line with the results of Denney, electronegative substituents such as R_2N and RO stabilize 21 more efficiently than less electronegative substituents such as R_2P, $R_2P(O)$ and RS.

EXPERIMENTAL SECTION

^{31}P NMR spectra : Brucker WP 80 at 32.435 MHz ; ^{1}H NMR : Brucker AC 200 SY at 200.132 MHz ; ^{13}C NMR : Brucker AC 200 SY at 50.323 MHz. IR spectra : Perkin Elmer Model 297. Mass spectra : Shimadzu GC MS QP 1000. Elemental analyses were performed by Service de Microanalyse du CNRS (Gif sur Yvette). Chromatographic separations were carried out on silica gel columns (70-230 mesh Riedel de Haën).

Synthesis of phosphirane $W(CO)_5$ complexes (5,6) General procedure :

(Phosphole) pentacarbonyltungsten complexes (3,4) (20 mmol), dimethyl acetylenedicarboxylate (4.9 ml, 40 mmol) and styrene (3.7 ml, 32 mmol) were heated at 112°C in toluene (13 ml) for 24 h. The solvent was removed by evaporation. The residue was chromatographed with hexane.

5 a,b : Yield 80%. See ref. 12.

6 a,b : Yield 64% ; 6a : m.p. 62°C ; ^{1}H NMR (C_6D_6) δ 0.35 (d, ^{2}J(H-P)=6.9 Hz, PMe), 0.9 (m, 2H, CH_2), 2.42 (t, ^{2}J(H-H)=9.5 Hz, PCHPh), 6.7-7 (m, Ph) ; ^{13}C NMR (C_6D_6) δ 10.94 (d, ^{1}J(C-P) =15.1 Hz, PMe), 13.19 (d, ^{1}J(C-P)=10.1 Hz, PCH_2), 27.82 (d, ^{1}J(C-P)=14.6 Hz, PCHPh), 196.13 (d, ^{2}J(C-P)=8.6 Hz, cis CO), 198.24 (d, ^{2}J(C-P)= 30.2 Hz, trans CO) ppm ; IR (decalin) ν (CO) 2070 (m), 1945 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e (relative intensity) 474 (M,42), 342 (M-CO-$PhCHCH_2$, 100). Anal. calcd. for $C_{14}H_{11}O_5PW$: C, 35.47 ; H, 2.34. Found : C, 35.48 ; H, 2.76

6b : m.p. < 50°C ; ^{1}H NMR (C_6D_6) δ 0.71 (d, ^{2}J(H-P)=6.9 Hz, PMe), 0.84 (m, 1H), 1.19 (m,1H), 2.07 (m, ^{2}J(H-P)=7.8 Hz, PCHPh), 7.0 (m, Ph) ; ^{13}C NMR (C_6D_6) δ13.76 (d, ^{1}J(C-P)=12.6 Hz,PMe), 18.09 (d, ^{2}J(C-P)=13.6 Hz, PCH_2), 27.64 (d, ^{1}J(C-P)=15.1 Hz, PCHPh), 195.44 (d, ^{2}J(C-P)=8.1 Hz, cis CO), 197.91 (d, ^{2}J(C-P)=30.7 Hz, trans CO) ; IR (decalin) ν(CO) 2070 (m), 1950 (sh), 1940 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 474 (M, 30), 342 (M-CO-$PhCHCH_2$, 100) ; Anal Found : C, 35.66 ; H, 2.43.

Ring opening with nitrogen nucleophiles. General procedure for reactions (3), (4) and (5) :

n-Butyllithium (1.3 mmol - hexane solution) was added at -78°C to a stirred solution of the amine (1.1 mmol) in THF. After a few minutes, phosphirane complex 5 (1 mmol) was added. The mixture was stirred at -78°C for about 30 min and then allowed to warm to room temperature. Iodomethane (1.1 mmol) (reactions (3) and (4) or $Et_3O^+BF_4^-$ (1.1 mmol) (reaction (5)) were added at room temperature. Chromatographic purifications of the final products were performed with hexane or hexane/CH_2Cl_2 mixtures as eluent.

8 : Yield 97% ; oil ; ^{1}H NMR (C_6D_6) δ 1.54 (d, ^{2}J(H-P)=7.1 Hz, PCH_3), 6.35 (ABX, ^{3}J(H-H)=17.1 Hz, ^{2}J(H-P)=14.9 Hz, PCH), 6.9-7.4 (m) ; ^{13}C NMR (C_6D_6) δ18.69 (d, ^{1}J(C-P)=30.7 Hz, PCH_3), 125.16 (d, ^{1}J(C-P)=41.8 Hz, P-CH), 144.74 (d, ^{2}J(C-P)=9.1 Hz, CHPh), 197.40 (d, ^{2}J(C-P)=6.0 Hz, cis CO), 199.78 (d, ^{2}J(C-P)=19.6 Hz, trans CO) ppm ; IR (decalin)ν (CO) 2070 (m), 1940 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 550 (M, 17), 410 (M-5CO, 100) ; Anal. Calcd for $C_{20}H_{15}O_5PW$: C, 43.66 ; H, 2.75. Found : C, 43.94 ; H, 2.87.

10 : Yield 79% ; m.p. 134°C ; ^{31}P NMR (C_6D_6) δ 65.4 (^{1}J(P-W)=266 Hz) ; ^{1}H NMR (C_6D_6) δ2.2-2.5 (m), 2.5-2.8 (m), 2.68 (d,^{3}J(H-P)=7.7 Hz, NMe), 3.0-3.3 (m), 6.8-7.3 (m) ; ^{13}C NMR (C_6D_6) δ 31.04 (s, CH_2Ph), 36.69 (d, ^{1}J(C-P)=27.2 Hz, PCH_2), 40.87 (s, NMe), 197.21 (d, ^{2}J(C-P)=7.0 Hz, cis CO), 199.26 (d, ^{2}J(C-P)=23.15 Hz, trans CO) ppm ; IR (decalin) ν(CO) 2075 (m), 1940 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 643 (M,16), 453 (M-3CO-PhNMe, 100) ; Anal. Calcd for $C_{26}H_{22}NO_5PW$: C, 48.54 ; H, 3.45 ; N, 2.18. Found : C, 48,49 ; H, 3.30 ; N, 2.13.

11 a,b : Yield 61% - 11 b : minor isomer ; ^{31}P NMR (C_6D_6)δ 83.9 ppm.

11 a : m.p; 149°C ; ^{31}P NMR (C_6D_6)δ 86.2 (^{1}J(P-W)=263.7 Hz) ; ^{1}H NMR (C_6D_6)δ 0.88 (t, ^{3}J(H-H)= 7.2 Hz, CH_3), 2.3 (m, 1H), 2.7 (m, 1H), 3.1 (m, 1H), 4.63 (q, OCH_2), 6.7-7 (m, Ph), 8.0 (m,2H, Ph) ; ^{13}C NMR (C_6D_6) δ 14.24 (s, CH_3), 44.98 (d, ^{1}J(C-P)=26.2 Hz, PCH_2), 71.71 (d, ^{2}J(C-P)= 12.1 Hz, CHPh), 80.53 (s, OCH_2), 201.93 (d, ^{2}J(C-P)=7.6 Hz, CO cis to P and carbene, 202.37 (d, ^{2}J(C-P)=6.0 Hz, CO cis to P and carbene), 209.21 (d, ^{2}J(C-P)=32.2 Hz, CO trans to P), 216.65 (d, ^{2}J(C-P)=7.1 Hz, CO cis to P and trans to carbene), 336.69 (C=W) ppm ; IR (decalin) ν(CO) 2020 (s), 1935 (s), 1918 (vs), 1895 (s) cm^{-1} ; Mass spectrum (^{184}W) m/e 733 (M, 5), 649 (M-3CO, 8), 621 (M-4CO, 7), 276 ($PhPNPh_2$, 100) ; Anal. Calcd for $C_{33}H_{28}O_5NPW$: C, 54.04 ; H, 3.85 ; N, 1.91. Found : C, 54.08 ; H, 3.78 ; N, 2.07.

Ring opening with oxygen nucleophiles

Hydrolysis of complex 5 a.b. Complex 5 a,b (1 mmol) was hydrolyzed in THF/H_2O with KOH at room temperature. After 1h, THF was evaporated, the residue extracted with ether and purified by chromatography with hexane/ether (80:20).

12 : Yield 77% ; oil ; ^{31}P NMR (C_6D_6) δ99.4 (^1J(P-W)=268.6 Hz) ; ^1H NMR (C_6D_6) δ2.0-2.8 (m, 4H), 2.98 (1H, POH), 6.8-7.3 (m, Ph) ; ^{13}C NMR (C_6D_6) δ 29.69 (s, CH_2Ph), 42.1 (d, ^1J(C-P)= 23.7 Hz, PCH_2), 196.82 (d, ^2J(C-P)=7.5 Hz, cis CO), 199.62 (d, ^2J(C-P)=23.1 Hz, trans CO) ppm ; IR (decalin) ν(CO) 2065 (m), 1960 (sh), 1940 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 544 (M, 20), 414 (M-5CO, 100).

Reaction of 5 a,b with sodium ethoxide. Complex 5 a,b (1 mmol) was added at room temperature to an excess (1:2.5) of sodium ethoxide in ethanol. After 1h the reaction mixture was hydrolyzed with acetic acid. Evaporation of the solvent, extraction with ether and chromatography with hexane gave pure 13 as a colorless solid.

13 : Yield 98% ; m.p.< 50°C ; ^{31}P NMR (hexane) δ 121.8 (^1J(P-W)=275.9 Hz) ; ^1H NMR (C_6D_6) δ 0.95 (t, ^3J(H-H)=6.9 Hz, Me), 2.3-2.9 (m, 4H), 3.34 (m, ^3J(H-P)=7.0 Hz, OCH_2), 6.9-7.4 (m, Ph) ; ^{13}C NMR (C_6D_6) δ 16.16 (d, ^3J(C-P)=7.5 Hz, CH_3), 29.94 (s, CH_2Ph), 39.25 (d, ^1J(C-P)=22.6 Hz, PCH_2), 63.33 (d, ^2J(C-P)=5.0 Hz, OCH_2), 197.75 (d, ^2J(C-P)=7.5 Hz, cis CO), 199.55 (d, ^2J(C-P) =24.2 Hz, trans CO) ppm ; IR (decalin) ν (CO) 2070 (m), 1950 (s), 1940 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 583 (M+1, 19), 499 (M+1-3CO, 100), 442 (M-5CO, 94) ; Anal. Calcd. for $C_{21}H_{19}O_6PW$: C, 43.32 ; H, 3.29. Found : C, 43.25 ; H, 3.22.

Ring opening with phosphorus nucleophiles

Reaction of 5 a,b with sodium diethylphosphite. Diethylphosphite (1.1 mmol) was added slowly at room temperature to 120 mg of Na H (1.3 mmol) in THF. After the H_2 evolution had ceased complex 5 a,b (1 mmol) was added. The mixture was stirred at room temperature for 24h. The anion was then trapped :

a) by adding aqueous hydrocloric acid at 0°C (pH∿6) to give 14

b) by adding an excess ICH_3 at 0°C to give 16

After extraction of the reaction mixture with ether the final product was purified by chromatography with hexane/ether (60:40).

14 : Yield 38% ; m.p. 55°C ; ^{31}P NMR (hexane/ether) δ 20.4 (AB, ^1J(P-P)=83.0 Hz, $P(O)(OEt)_2$), -52.1 (AB, ^1J(P-W)=225 Hz) ; ^1H NMR (C_6D_6) δ6.73 (t, ^3J(H-H)=7.1 Hz, CH_3), 6.74 (t, ^3J(H-H) =7.1 Hz, CH_3), 3.7 (m, 4H, CH_2), 5.55 (d, ^1J(H-P)=340.0 Hz, PH), 6.9 (m, 3H, Ph), 7.5 (m, 2H, Ph) ppm ; IR (decalin) ν (CO) 2070 (m), 1950 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 570 (M, 10), 430 (M-5CO, 60), 338 (WPPh HOEt, 100) ; Anal. Calcd. for $C_{15}H_{16}O_8P_2W$: C, 31.60 ; H, 2.83. Found : C, 31.43 ; H, 2.83.

16 : Yield 70% ; m.p.< 50°C ; ^{31}P NMR (hexane/ether) δ 23.5 (AB, ^1J(P-P)=78.1 Hz, $P(O)(OEt)_2$), -27.7 (AB, ^1J(P-W)=234 Hz) ; ^1H NMR (C_6D_6) δ0.83 (t, ^3J(H-H)=7.1 Hz, CH_3), 0.90 (t, ^3J(H-H)= 7.1 Hz, CH_3), 1.83 (dd, ^2J(H-P)=13.6 Hz, ^3J(H-P)=6.8 Hz, PMe), 3.7 (m, 4H, CH_2), 6.9 (m, 3H, Ph), 7.6 (m, 2H, Ph) ; IR (decalin) ν (CO) 2070 (m), 1950 (sh), 1940 (vs) ; mass spectrum

(^{184}W) m/e 556 (M-CO, 10), 444 (M-5CO, 36), 352 (WPPh Me OEt, 100).

Reaction of 6 a,b with sodium diethylphosphite. Diethylphosphite (1.1 mmol) was added slowly at room temperature to 120 mg of Na H (1.3 mmol -60% dispersion in mineral oil) in THF. After the H_2 evolution had ceased, 1 mmol of complex 6 a,b was added. The mixture was stirred at room temperature for 2h ; the anion was then trapped :

a) by adding aqueous hydrocloric acid at 0°C (pH ∿6) to give 15

b) by adding at 0°C an excess ICH_3 to give 17

After hydrolysis, evaporation of THF and extraction with ether, the final product was purified by chromatography with hexane/ether (60:40).

15 : Yield 60% ; oil ; ^{31}P NMR (hexane/ether) δ 22.4 (AB, ^1J(P-P)=100.1 Hz, $P(O)(OEt)_2$), -84.9 (AB, ^1J(P-W)=225 Hz) ; ^1H NMR (C_6D_6) δ 0.95 (t, ^3J(H-H)=7.0 Hz, CH_3), 0.96 (t, ^3J(H-H)=7.0 Hz, CH_3), 1.26 (m, 3H, PMe), 3.41 (m, 4H, OCH_2), 4.26 (m, ^1J(H-P)=333.9 Hz, ^3J(H-H)=6.9 Hz, ^2J(H-P) =2.0 Hz, PH) ppm. IR (decalin) ν(CO) 2070 (m), 1945 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 508 (M, 32), 452 (M-2CO, 72), 368 (M-5CO, 100). Anal. Calcd. for $C_{10}H_{14}O_8P_2W$: C, 23.64 ; H, 2.78. Found : C, 23.90 ; H, 2.72.

17 : Yield 32% ; m.p. 51°C ; ^{31}P NMR (hexane/ether) δ 25.7 (AB, ^1J(P-P)=87.9 Hz, $P(O)(OEt)_2$), -43.0 (AB, ^1J(P-W)=229 Hz) ; ^1H NMR (C_6D_6) δ 0.96 (t, ^3J(H-H)=7.1 Hz, CH_3), 1.35 (dd, ^2J(H-P)= 13.9 Hz, ^3J(H-P)=7.2 Hz, PMe), 3.85 (m, 4H, OCH_2) ppm ; IR (decalin) ν (CO) 2065 (m), 1950 (sh), 1940 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 522 (M, 9), 410 (M-5CO, 100). Anal. Calcd. for $C_{11}H_{16}O_8P_2W$: C, 25.31 ; H, 3.09. Found : C, 25.23 ; H, 3.26.

Reaction of 5 a,b with lithium diphenylphosphide. nBuLi (1,2 mmol) (1.6 M solution in hexane) was added at -70°C to a solution of diphenylphosphine (1.1 mmol) in THF. After about 10 minutes, phosphirane complex 5 a,b (1 mmol) was added and allowed to react for 30 min. at -70°C. Iodomethane (1 mmol) was then added, and the reaction mixture warmed to room temperature. Sulphur (1.1 mmol) was then added and the reaction was monitored by ^{31}P NMR. Careful colum chromatography with hexane/ether (98:2) and crystallization are necessary to purify 18 from minor side products.

18 : Yield 60% ; m.p. 97°C ; ^{31}P NMR (THF) δ 47.7 (AB, ^1J(P-P)=129 Hz, $P(S)Ph_2$), 3.0 (AB, ^1J (P-W)=244 Hz) ; ^1H NMR (C_6D_6) δ 1.98 (dd, ^2J(H-P)=11.6 Hz, ^3J(H-P)=5.2 Hz, PMe), 6.8-8.4 (m,Ph) ppm ; IR (decalin) ν(CO) 2070 (m), 1950 (vs), 1940 (vs) cm^{-1} ; mass spectrum (^{184}W) m/e 636 (M-CO, 25), 524 (M-5CO, 100) ; Anal. Calcd. for $C_{24}H_{18}O_5P_2SW$: C, 43.40 ; H, 2.73. Found : C, 43.38 ; H, 3.15.

Ring opening with sulphur nucleophiles

Reaction of 5 a,b with lithium phenylsulfide. Thiophenol (1.2 mmol) was allowed to react with n-BuLi (1.3 mmol) in THF at -70°C. Phosphirane complex 5 a,b (1 mmol) was then added and allowed to react at room temperature for about 1h. Iodomethane (1.1 mmol) was added at 0°C. After hydrolysis, the solvent was removed. Extraction and chromatography with hexane gave pure 19.

19 : Yield 82% ; m.p. 102°C ; ^{31}P NMR (CH_2Cl_2) δ 23.7 (^{1}J(P-W)=247 Hz) ; ^{1}H NMR (C_6D_6) δ1.62 (d, ^{2}J(H-P)=5.3 Hz, PMe), 6.6-7.3 (m, Ph) ppm ; IR (decalin) ν(CO) 2070 (m), 1940 (vs) cm^{-1}; mass spectrum (^{184}W) m/e 556 (M, 17), 416 (M-5CO, 100) ; Anal. Calcd. for $C_{18}H_{13}O_5PSW$: C, 38.87 ; H, 2.36. Found : C, 39.08 ; H, 2.37.

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