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INSERTION OF TERMINAL ALKYNES INTO THE PHOSPHIRENE RING

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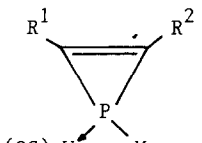
Summary :

In the presence of catalytic amounts of $Pd(PPh_3)_4$, terminal alkynes readily insert into the ring of phosphirene P-$W(CO)_5$complexes to give the corresponding phosphole complexes.

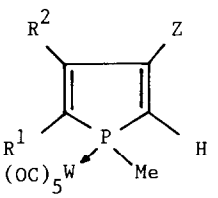
Whereas numerous insertion reactions have been described with silirenes [1] , only a few very peculiar examples of such reactions have been reported with phosphirenes [2] . In the silirene case, these insertions are often catalyzed by nickel or palladium salts [3] . Very recently, the intermediacy of four-membered metallasilacyclobutenes has been demonstrated in solution with nickel [4] . On the other hand, it has also been shown recently that 14-electron metallic species such as ML_2 (M=Pd, Pt, L=phosphine) readily insert into the phosphirene ring to give stable metallaphosphacyclobutene complexes[5] .

In view of all these data and taking into account the close parallelism between the chemistry of silirenes and phosphirenes [6] , we decided to investigate the possible application of Pd(0) as a catalyst for promoting various novel insertion reactions into the phosphirene ring. In so doing, we discovered that it was indeed possible to insert terminal alkynes into the ring of phosphirene complexes (eq.1).



1a-c

+ ZC≡CH (excess) $\xrightarrow[\text{toluene, }\Delta]{Pd(PPh_3)_4\ \ 1\%}$

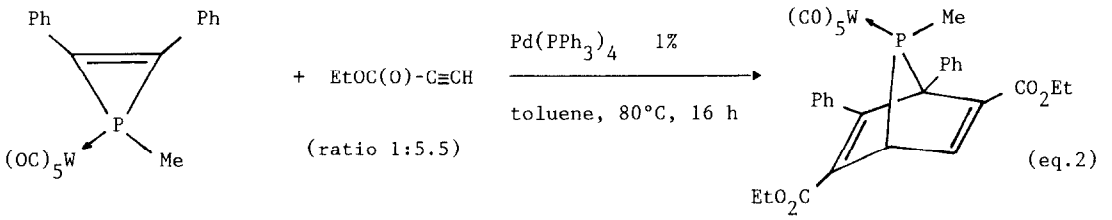


2-8 (eq.1)

1a	$R^1 = R^2 = Ph$,	Z = Ph (ratio 1:2)	80°C, 24 h	2 (45%)
	"	Z = EtO (1:3.4)	100°C, 8 h	3 (33%)
	"	Z = EtOC(O) (1:1.5)	100°C, 15 h	4 (85%)
1b	$R^1 = R^2$ = Et,	Z = EtO(CO) (1:1.5)	100°C, 20 h	5 (50%)
1c	R^1=Ph, R^2=EtO(CO),	Z = EtO(CO) (1:1.5)	100°C, 17 h	6 (47%) + 7 (31%)
				$\{ R^1$= Ph $\{ R^1$=CO_2Et
				$\{ R^2$= CO_2Et $\{ R^2$= Ph
	" "	Z = Ph (1:3.3)	100°C, 17 h	8 (61%)

The various phosphole complexes thus obtained are original and can provide a convenient access to a series of tervalent functional phospholes which are especially difficult to obtain otherwise [7,8] .

When using a huge excess of ZC≡CH , the reaction may go one step further and give the corresponding 7-phosphanorbornadiene complex via an already described [4+2] cycloaddition [9] (eq.2).



1a 9 (42%) (eq.2)

Various attempts with disubstituted alkynes have been unsuccessful.

Spectral data : δ noted positive for downfield shifts from Me_4Si or H_3PO_4. All the products were purified by chromatography on silica gel columns.

1c : This complex was prepared via the reaction of the 1,3,4-trimethylphosphole P-$W(CO)_5$ complex with dimethyl acetylenedicarboxylate and ethylpropiolate (ratio 1:2:1.5) at 108°C in toluene for 16 h (yield: 37%). Similar syntheses have been already described [10] . Yellow solid, m.p. 110°C; ^{31}P NMR (toluene): δ-143 ppm, $^1J(^{31}P-^{183}W)$= 268.6 Hz; ^1H NMR (C_6D_6): δ1.02 (t, ^3J(H-H)= 7.1Hz, 3H, CH_3C), 1.15 (d, ^2J(H-P)=6.1 Hz, 3H, CH_3P), 4.06 (m, 2H, OCH_2),7.1 (m, 3H, Ph), 8.0 (m, 2H, Ph) ppm; ^{13}C NMR (C_6D_6): δ 14.02 (s, CH_3C), 24.60 (s, CH_3P), 62.09 (s, OCH_2), 123.61 (d, J(C-P)= 8 Hz, C), 126.45 (d, J(C-P)= 5.5 Hz, C), 150.01 (d, ^1J(C-P)= 12.6 Hz, Ph-C-P); 160.14 (d, ^2J(C-P)= 9 Hz, CO_2), 195.96 (d, ^2J(C-P)= 8.6 Hz, cis CO), 198.14 (d, ^2J(C-P)= 30.7 Hz, trans CO) ppm; mass spectrum (EI,70eV, ^{184}W): m/z 544 (M^+,55%), 404 (M-5CO,100%); IR (decalin): ν(CO) 2070w, 1945vs, 1720w cm^{-1}.

2 : ^{31}P NMR (C_6D_6): δ -21.2 ppm, $^1J(^{31}P-^{183}W)$= 241.7 Hz; ^1H NMR (C_6D_6): δ1.63 (d, ^2J(H-P)= 6.5 Hz, 3H, CH_3P), 7.63 (d, ^2J(H-P)= 23.3 Hz, =CH-P) ppm; ^{13}C NMR (C_6D_6): δ 20.97 (d, ^1J(C-P)= 34.2 Hz, CH_3P), 141.95 (d, ^1J(C-P)= 24.7 Hz,=CH-P), 197.36 (d, ^2J(C-P)= 6.5 Hz, cis CO), 199.73 (d, ^2J(H-P)= 22.14 Hz, trans CO) ppm; mass spectrum (EI, 70eV, ^{184}W): m/z 650 (M^+, 29%), 538 (M-4CO,90%), 510 (M-5CO,100%); IR (decalin): ν(CO) 2068w, 1940vs cm^{-1}.

3 : Yellow solid, m.p. 89°C; ^{31}P NMR (hexane): δ -0.3 ppm, $^1J(^{31}P-^{183}W)$= 222.2 Hz; ^1H NMR (C_6D_6): δ 0.87 (t, ^3J(H-H)= 7.1 Hz, 3H, CH_3C), 1.56 (d, ^1J(H-P)= 7.6 Hz, 3H, CH_3P), 3.47 (m, 2H, OCH_2), 5.02 (d, ^2J(H-P)= 30.3 Hz, 1H,=CH-P) ppm; ^{13}C NMR (C_6D_6): δ 13.84 (s,CH_3C) 17.38 (d, ^1J(C-P)= 24.2 Hz, CH_3P), 65.65 (s, OCH_2), 96.41 (d, ^1J(C-P)= 48.8 Hz, =CH-P), 143.56 (d, ^2J(C-P)= 11.1 Hz, Ph-C β), 146.94 (d, ^1J(C-P)= 34.2 Hz, Ph-C α), 162.53 (d, ^2J(C-P)= 18.1 Hz, EtO-C), 196.93 (d, ^2J(C-P)= 7.04 Hz, cis CO), 199.39 (d, ^2J(C-P)= 19.6 Hz, trans CO) ppm; mass spectrum (EI, 70eV, ^{184}W): m/z 618 (M^+, 60%), 460 (M-5CO-EtOH, 100%); IR (decalin): ν (CO) 2070w, 1935vs cm^{-1}.

4 : yellow solid, m.p. 110°C ; ^{31}P NMR (C_6D_6): δ 11.8 ppm, $^1J(^{31}P-^{183}W)$= 214.8 Hz; ^1H NMR (C_6D_6): δ 0.69 (t, ^3J(H-H)= 7.6 Hz, 3H, CH_3C), 1.33 (d, ^2J(H-P)= 8.3 Hz, 3H, CH_3P), 3.81 (q, 2H, OCH_2), 7.21 (d, ^2J(H-P)= 33.2 Hz, 1H, =CH-P) ppm; ^{13}C NMR (C_6D_6): δ 13.67 (d, ^1J(C-P)= 24.7 Hz, CH_3P), 13.68 (s, $\underline{C}H_3C$), 61.13 (s, OCH_2), 141.01 (d, ^1J(C-P)= 34.7 Hz, =CH-P), 145.08 (m, 2C β), 147.78 (d, ^1J(C-P)= 35.2 Hz, Ph-C α), 163.59 (d, ^3J(C-P)= 13.6 Hz, CO_2), 195.94 (d, ^2J(C-P)= 6.5 Hz, cis CO), 198.38 (d, ^2J(C-P)= 18.6 Hz, trans CO) ppm; mass spectrum (EI, 70eV, ^{184}W): m/z 646 (M^+,31%), 506 (M-5CO,55%), 374 (100%); IR (decalin): ν(CO) 2070w, 1980w, 1940vs, 1735w cm^{-1}.

5 : ^{31}P NMR (pentane): δ 5.5 ppm, $^1J(^{31}P-^{183}W)$= 212.4 Hz; ^1H NMR (C_6D_6): δ0.86 (t, 3H, Me), 0.93 (t, 3H, Me), 1.04 (t, 3H, Me), 1.12 (d, ^2J(H-P)= 8.5 Hz, 3H, CH_3P), 2.30 (m, 2H, CH_2), 2.49 (m, 2H, CH_2), 2.70 (m, 2H, CH_2), 3.94 (m, 2H, OCH_2), 7.14 (d, ^2J(H-P)=33.9 Hz, =CH-P) ppm; ^{13}C NMR (C_6D_6): δ 13.79 (d, ^1J(C-P)= 28.2 Hz, CH_3P), 14.07, 14.39,14.56 (s,CH_3),20.3 (d,J(C-P)=16.6Hz, CH_2), 21.34(d,J(C-P)=8.6Hz,CH_2), 61.07(s,OCH_2),141.41(d, ^1J(C-P)=37.7Hz, =CH-P),142.85(d, ^2J(C-P)=11.6Hz,$\underline{C}CO_2Et$),146.70(d, ^1J(C-P)= 36.6 Hz, Et-C α), 146.80 (d, ^2J(C-P)= 10.6 Hz, Et-C β), 163.30 (d, ^3J(C-P)= 13.6 Hz, CO_2), 196.27 (d, ^2J(C-P)= 6.5 Hz, cis CO), 198.68 (d, ^2J(C-P)= 17.6 Hz, trans CO) ppm; mass spectrum (EI, 70eV, ^{184}W): m/z 550 (M^+,53%), 438 (100%); IR (CH_2Cl_2): ν(CO) 2070w, 1938vs, 1720w cm^{-1}.

6 : yellow solid, m.p. 110°C; ^{31}P NMR (benzene): δ 17.9 ppm, $^1J(^{31}P-^{183}W)$= 219.7 Hz; ^1H NMR (C_6D_6): δ 0.88(t, ^3J(H-H)= 7.3Hz, 6H, CH_3C), 1.16 (d, ^2J(H-P)= 8 Hz, CH_3P), 3.92 (m, 2H, OCH_2), 4.05 (m, 2H, OCH_2), ≃7.20 (d, ^2J(H-P) ≃ 36 Hz, =CH-P) ppm; ^{13}C NMR (C_6D_6): δ 13.17 (d, ^1J(C-P)= 24.7 Hz, CH_3P), 13.78 and 13.89(s,$\underline{C}H_3C$), 61.59, 61.71 (s, OCH_2), 142.61 (d, ^1J(C-P)= 33.7 Hz, =CH-P), 150.75 (d, ^1J(C-P)= 31.6 Hz, Ph-$\underline{C}$-P), 161.92 (d, J(C-P)= 12.1 Hz, CO_2), 164.76 (d, J(C-P)= 13.6 Hz, CO_2), 195.36 (d, ^2J (C-P)= 6.5 Hz, cis CO), 197.89 (d, ^2J(C-P)= 19.6 Hz, trans CO) ppm; mass spectrum (EI, 70eV, ^{184}W): m/z 642 (M^+,31%), 502 (M-5CO,100%); IR (CH_2Cl_2): ν (CO) 2070w, 1940vs, 1720w cm^{-1}.

7 : ^{31}P NMR (hexane): δ 10.9 ppm, $^1J(^{31}P-^{183}W)$= 217.3 Hz; ^1H NMR (C_6D_6): δ 0.61 (t, ^3J(H-H)= 7 Hz, 3H, CH_3C), 0.72 (t, ^3J(H-H)= 6.8 Hz, 3H, CH_3C), 1.43 (d, ^2J(H-P)= 9 Hz, 3H, CH_3P), 3.8 (m, 4H, OCH_2), 7.29 (d, ^2J(H-P)= 32.5 Hz, =CH-P) ppm; ^{13}C NMR (C_6D_6): δ 13.36 (d, ^1J (C-P)= 26.2 Hz, CH_3P), 13.83(s, CH_3), 13.95 (s, CH_3), 61.47 (s, CH_2), 61.61 (s, CH_2), 138.84 (d, ^1J(C-P)= 38.8 Hz, =$\underline{C}$-CO_2Et), 145.76 (d, ^1J(C-P)= 32.7 Hz, P-CH), 156.18 (d, ^2J (C-P)= 11.07 Hz, =C-Ph), 162.59 (d, ^2J(C-P)= 18.6 Hz, CO_2), 163.18 (d, ^3J(C-P)=13.08Hz,CO_2), 196.21 (d, ^2J(C-P)= 6.5 Hz, cis CO), 198.72 (d, ^2J(C-P)= 19.1 Hz, trans CO); mass spectrum (EI, 70eV, ^{184}W): m/z 642 (M^+,11%), 558 (M-3CO,100%),502 (M-5CO,83%); IR (CH_2Cl_2): ν (CO) 2075w, 1940vs, 1720w cm^{-1}.

8 : yellow solid, m.p. 69°C; ^{31}P NMR (C_6D_6): δ 11.47 $^1J(^{31}P-^{183}W)$= 217.3 Hz; ^1H NMR (C_6D_6) δ 0.58 (t, ^3J(H-H)= 7.1 Hz, 3H, CH_3), 1.37 (d, ^2J(H-P)= 8.06 Hz, 3H, CH_3P), 3.75 (q, 2H, $\underline{C}H_2CH_3$), 6.28 (d, ^2J(H-P)= 36.5 Hz, 1H, =CH-P), 7.0-7.5 (m, 10H, Ph); ^{13}C NMR (C_6D_6) δ 13.53 (s, CH_3), 14.13 (d, ^1J(C-P)= 24.2 Hz, PCH_3), 61.31 (s, CH_2), 132.52 (d, ^1J(C-P)=39.2 Hz, P-CH), 151.53 (d, ^1J(C-P)= 32.2 Hz, P-$\underline{C}$-Ph), 165.60 (d, ^3J(C-P)= 14.6 Hz, CO_2), 195.97 (d, ^2J(C-P)= 6.5 Hz, cis CO), 198.52 (d, ^2J(C-P)= 19.1 Hz, trans CO)ppm; mass spectrum (EI, 70eV, ^{184}W): m/z

IR(CH_2Cl_2): ν (CO) 2070m, 1940vs,1720w cm^{-1}.

9 : yellow solid, m.p. 92°C; ^{31}P NMR (C_6D_6): δ 211.5 ppm, $^{1}J(^{31}P-^{183}W)$= 249.0 Hz; ^{1}H NMR (C_6D_6): δ 0.88 (t, ^{3}J(H-H)= 7.08 Hz, CH_3), 0.90 (t, ^{3}J(H-H)= 7.20 Hz, CH_3), 1.58 (d, ^{2}J(H-P)= 4.4 Hz, 3H , CH_3P), 3.95 (q, 4H, CH_2), 4.02 (dd, ^{2}J(H-P)= 2.2 Hz, ^{3}J(H-H)= 4.64 Hz, 1H, CH-P), 6.8-7.2 (m, Ph), 7.44 (dd, ^{3}J(H-P)= 6.8 Hz, ^{3}J(H-H)= 4.64 Hz, 1H, =CH), 7.9-8.1 (m, 2H, Ph) ppm; ^{13}C NMR (C_6D_6): δ 13.94 (s, CH_3), 22.02 (d, ^{1}J(C-P)= 6.0 Hz, CH_3P), 53.99 (d, ^{1}J(C-P)= 17.1 Hz, CH-P), 61.10 (s, CH_2), 75.51 (d, ^{1}J(C-P)= 19.6 Hz, P-C-Ph), 138.96 (d, ^{2}J(C-P)= 19.6 Hz, =C-CO_2Et), 144.36 (d, ^{2}J(C-P)= 8.6 Hz, =C-CO_2Et), 150.54 (s, =CH), 160.14 (d, ^{2}J(C-P)= 20.6 Hz, =C-Ph), 163.92 (s, CO_2), 164.75 (s, CO_2), 196.03 (d, ^{2}J(C-P)= 6.04 Hz, cis CO), 197.99 (d, ^{2}J(C-P)= 26.7 Hz, trans CO) ppm; mass spectrum (EI, 70eV, ^{184}W): m/z 744 (M^+,15%), 604 (M-5CO,100%); IR (decalin) ν(CO) 2070m, 1940vs, 1720w cm^{-1}.

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