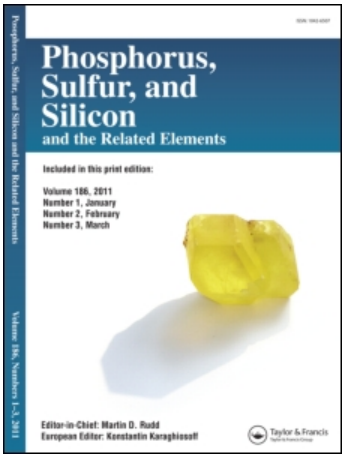

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Michele Soleilhavoup[a]; Olivier Guerret[a]; Jean-Luc Faure[a]; Antoine Baceiredo[a]; Guy Bertrand[a]
[a] Laboratoire de Chimie de Coordination du CNRS, Toulouse Cédex, France

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EVIDENCE FOR A TRANSIENT ACYLPHOSPHENIUM ION*

MICHELE SOLEILHAVOUP, OLIVIER GUERRET, JEAN-LUC FAURE, ANTOINE BACEIREDO and GUY BERTRAND

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cédex (France)

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The reaction of bis(diisopropylamino)pivaloylphosphine **1** and bis(diisopropylamino)p-toluoylphosphine **2** with strong Brönsted acids (HBF_4 and CF_3SO_3H) is reported. In the case of the p-toluoylphosphine **2** a transient acylphosphenium ion **8** is formed and trapped by the starting phosphine affording C-phosphonio phosphaalkene **5.**

Keywords: Phosphenium ions, dicoordinate phosphorus, INEPT ^{31}P-^{13}C

INTRODUCTION

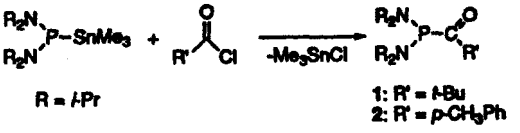
Phosphenium ions are isoelectronic with carbenes. These dicoordinate phosphorus salts are stable providing that they have strong π-donor substituents, classically two amino groups.[1] It is only very recently that a phosphenium ion with a P-C σ bond (i-Pr_2NPMes^+, $AlCl_4^-$) has been isolated and structurally characterized.[2] The chemistry of the related carbenium ions containing an α-destabilizing group has been the subject of considerable attention by organic and theoretical chemists.[3] The carbonyl-substituted carbocations have been the most extensively studied, the relative stability of these compounds was rationalized either by interaction of the oxygen lone pair with the cationic carbon or by a conjugative interaction.[4]

Here we report our attempts to synthesize of dicoordinate phosphorus cations bearing an electron-withdrawing group, namely acylphosphenium ions.

* Dedicated to Robert Wolf for his 70th birthday.

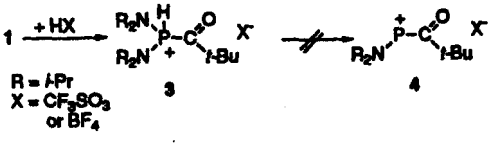
RESULTS AND DISCUSSION

Addition of Lewis[5] or Brönsted[6] acids to amino-substituted phosphines is one of the method to generate phosphenium ions. Therefore, we chose bis(amino)acylphosphines **1** and **2** as starting materials. They were prepared by addition of bis(diisopropylamino)(trimethylstannyl)phosphine[7] to the corresponding acylchloride (Scheme 1).



SCHEME 1

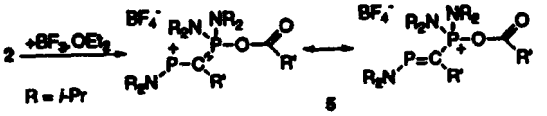
The fate of the reaction of acids to acylphosphines **1** and **2** appeared to be dependent on the nature of the acyl group. With the pivaloyl derivative **1**, addition of one equivalent of trifluoromethanesulfonic or tetrafluoroboric acids at -78°C led to the formation of the phosphonium salt **3**. Its structure was clearly established by spectroscopy: the ^{31}P NMR spectrum showed a doublet of quintets at -20.3 with $^{1}J_{PH}$ = 563.7 Hz and $^{3}J_{PH}$ = 16.8 Hz, while in the ^{13}C NMR spectrum, the CO carbon appeared at 212.6 as a doublet ($^{1}J_{PC}$ = 68.7 Hz). Derivative **3** was stable in solution for a few hours and then decomposed into a complicated mixture of products but didn't lead to the expected phosphenium cation **4** (Scheme 2). Attempts to prepare cation **4** by adding $BF_3.OEt_2$ to **1** also failed.



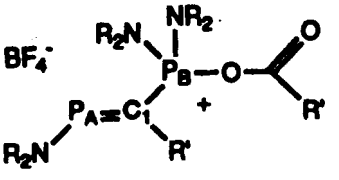
SCHEME 2

One equivalent of $BF_3.OEt_2$ reacted in refluxing dichloromethane with bis(diisopropylamino)(toluoyl)phosphine **2** affording after work up the compound **5** in near quantitative yield (Scheme 3). The $^{31}P\{^{1}H\}$ NMR spectrum indicated the presence of two different phosphorus atoms in the molecule [AX system at δ_P +314.5 (P_A) and +52.3 (P_B) ($^{2}J_{PP}$ = 176.0 Hz)]. The ^{31}P NMR spectrum demonstrated that phosphorus P_A was bonded to only one diisopropylamino group (t, $^{3}J_{PH}$ = 9.4 Hz), while phosphorus P_B was bonded to two diisopropylamino groups (q, $^{3}J_{PH}$ = 15.2 Hz). The values of the $^{3}J_{PH}$ coupling constants showed that P_A was dicoordinated (in agreement with the low field chemical shift), while P_B was tetracoordinated.[8] The presence of a P-C-P sequence was indicated by selective INEPT ^{31}P-$^{13}C\{^{1}H\}$ experiments[δ_C 113.6, dd,

$^1J_{P(A)C}$ = 64.0 Hz and $^1J_{P(B)C}$ = 150.5 Hz] (Fig. 1). All these results compared well with those reported for the very rare other examples of C-phosphonio substituted phosphaalkenes.[5,9] Lastly, infrared (ν_{CO} = 1752 cm^{-1}) and ^{13}C NMR spectroscopy [δ_{CO} 160.4 ppm, $^2J_{P(B)C}$ = 10.3 Hz], showed the presence of a carbonyl-ester group, bonded via oxygen to phosphorus P_B. Formally, compound **5** results from the reaction of the desired phosphenium salt **8** with the starting material **2**.



SCHEME 3



5

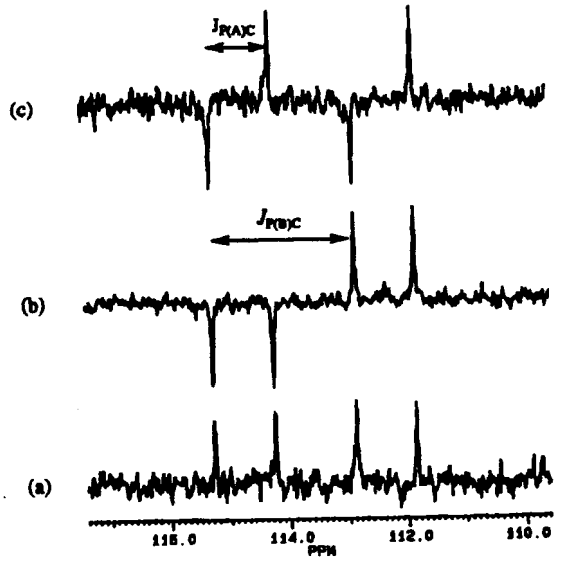
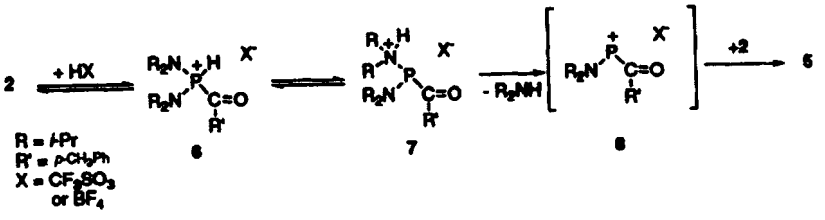


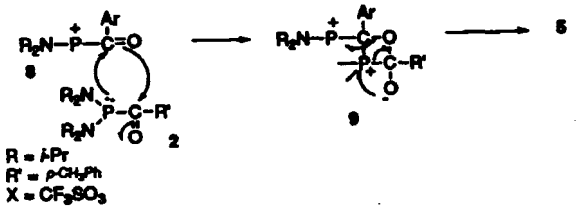
FIGURE 1 Illustration of the use of selective INEPT experiments in order to determine coupling constants at C_1. (a) ^{13}C {^1H} spectrum. (b) Selective ^{31}P. ^{13}C INEPT at P_A. (c) Selective ^{31}P. ^{13}C INEPT at P_B

Compound **8** was also obtained by adding one equivalent of trifluoromethanesulfonic acid to **2**. However, in contrast to $BF_3.OEt_2$, triflic acid already reacted at -78°C. This allowed more insight into the mechanism of the formation of **5** by monitoring the reaction at low temperature. At -70 °C, besides the starting material **2**, the formation of two new products **6** and **7** (1/1 ratio) was observed. The NMR data for **6** (δ_P -12.2, $^1J_{PH}$ = 562 Hz; δ_{CO} = 194.9, $^1J_{PC}$ = 110.5 Hz) compared well with that of **3**, and therefore **6** has a phosphonium structure. Product **7** features a λ^3P as indicated by the value of the ^{31}P chemical shift (δ_P = +93.8), and a carbonyl group directly bonded to the phosphorus atom as shown by the ^{13}C signal at 206.6 ppm (d, $^1J_{PC}$ = 36.8 Hz). Of special interest the four CH carbons of the isopropyl groups are not magnetically equivalent (52.4, $^2J_{PC}$ = 10.8 Hz; 50.9, $^2J_{PC}$ = 9.5 Hz; 50.6, $^2J_{PC}$ = 6.9 Hz; 46.8, $^2J_{PC}$ = 26.1 Hz) strongly suggesting that **7** is an isomer of **6** with the proton bonded to nitrogen. Between -70 and 0 °C, the ^{31}P NMR signals corresponding to **2, 6** and **7** decreased almost at the same rate, while the AX system, corresponding to compound **5** appeared; simultaneously formation of (iPr$_2$NH$_2^+$CF$_3$SO$_3^-$) was observed by ^1H and ^{13}C NMR spectroscopy (Scheme 4).



SCHEME 4

These results as a whole suggest that there is an equilibrium (slow compared to the NMR time scale) between **2, 6** and **7** as already postulated by Dahl in the case of bis(amino)phosphines.[6] Then, after loss of diisopropylamine (quickly converted into the corresponding ammonium salt), the transient phosphenium salt **8** was formed. Therefore, a tentative mechanism to explain the formation of **8** is depicted in scheme 5. The difference observed between **1** and **2** could result from



SCHEME 5

the possible interaction in **8** of the phenyl ring with the phosphenium center, giving a phenonium ion like species.[10]

EXPERIMENTAL

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points were obtained on an Electrothermal capillary apparatus and were not corrected. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker AC80, AC200 or WM250 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1725X. Conventional glassware was used.

Synthesis of bis(diisopropylamino)pivaloylphosphine (**1**). To a toluene solution (10 mL) of bis(diisopropylamino)(trimethylstannyl)phosphine (2.69 g, 6.8 mmol) was added, at 0°C, one equivalent of pivaloyl chloride (0.82 g, 6.8 mmol). After stirring at room temperature for 1 h the solvent and Me_3SnCl were removed under vacuum. The residue crystallized from acetonitrile leading to acylphosphine **1** as yellow crystals (1.29 g, 60 %); mp 70-71 °C, ^{31}P NMR $\{^{1}H\}$ ($CDCl_3$) δ = +34.8; ^{1}H NMR ($CDCl_3$) δ = 1.07 (d, J_{HH} = 6.6 Hz, 12 H, CH_3CH), 1.12 (d, J_{HH} = 6.6 Hz, 12 H, CH_3CH), 1.15 (s, 9 H, CH_3C), 3.45 (sept d, J_{HH} = 6.6 Hz, J_{PH} = 11.0 Hz, 4 H, CH); ^{13}C NMR $\{^{1}H\}$ ($CDCl_3$) δ = 23.2 (d, J_{PC} = 6.5 Hz, CH_3CH), 24.1 (d, J_{PC} = 6.2 Hz, CH_3CH), 26.9 (d, J_{PC} = 5.8 Hz, CH_3C), 45.6 (s, CH_3C), 47.8 (d, J_{PC} = 10.1 Hz, CHN), 234.1 (d, J_{PC} = 43.1 Hz, CO); IR ($CDCl_3$) ν = 1646 cm^{-1} (C=O); Ms *m/z* 316 (M^+); Anal. Calcd for $C_{17}H_{37}N_2OP$: C, 64.52; H, 11.78; N, 8.85. Found: C, 64.91; H, 11.60; N, 8.80.

Synthesis of bis(diisopropylamino)p-toluoylphosphine (**2**). Using the same experimental procedure as for **1** [bis(diisopropylamino)(trimethylstannyl)phosphine(2.69 g, 6.8 mmol); *p*-toluoyl chloride (1.05 g, 6.8 mmol)] and after recrystallization from acetonitrile, acylphosphine **2** was obtained as yellow crystals (2.08 g, 87 %); mp 104 °C (dec); ^{31}P NMR $\{^{1}H\}$ ($CDCl_3$) δ = +57.7; ^{1}H NMR ($CDCl_3$) δ = 1.07 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 1.20 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 2.37 (s, 3 H, CH_3-Ph), 3.33 (sept d, J_{HH} = 7.0 Hz, J_{PH} = 11.4 Hz, 4 H, $CHCH_3$), 7.16-7.93 (m, 4 H, H_{arom}); ^{13}C NMR $\{^{1}H\}$ ($CDCl_3$) δ = 21.7 (s, CH_3-Ph), 23.8 (d, J_{PC} = 6.1 Hz, CH_3CH), 24.1 (d, J_{PC} = 5.6 Hz, CH_3CH), 49.3 (d, J_{PC} = 9.3 Hz, CHN), 128.0 (d, J_{PC} = 11.9 Hz, C_O), 128.8 (s, C_m), 138.1 (d, J_{PC} = 40.5 Hz, C_i), 142.8 (s, C_p), 220.1 (d, J_{PC} = 23.7 Hz, C=O); IR ($CDCl_3$) ν = 1615 cm^{-1} (C=O); Anal. Calcd for $C_{20}H_{35}N_2OP$: C, 68.54; H, 10.07; N, 7.99. Found: C, 68.50; H,10.00; N, 7.83.

Bis(diisopropylamino)pivaloylphosphonium trifluoromethanesulfonate (**3**). To a CD_2Cl_2 solution (1 mL) of **1** (0.16 g, 0.5 mmol) was added at -78°C one equivalent of trifluoromethanesulfonic (or tetrafluoroboric) acid. The reaction was monitored by ^{31}P NMR spectroscopy which indicated the complete transformation of **1** into **3** at -70°C. All attempts to isolate phosphonium salt **3** failed, therefore it was characterized in solution at room temperature: ^{31}P NMR ($CDCl_3$) δ = -20.3 (d q, $^1J_{PH}$ = 563.7 Hz, $^3J_{PH}$ = 16.8 Hz); ^1H NMR ($CDCl_3$) δ = 1.30 (d, J_{HH} = 6.7 Hz, 12 H, CH_3CH), 1.33 (d, J_{HH} = 6.7 Hz, 12 H, CH_3CH), 1.32 (s, 9 H, CH_3C), 3.70 (sept d, J_{HH} = 6.7 Hz, J_{PH} = 16.8 Hz, 4 H, CH), 8.94 (d, J_{PH} = 563.7 Hz, PH); ^{13}C NMR {^1H} ($CDCl_3$) δ = 23.4 (s,CH_3CH), 50.4 (s, CHN), 51.2 (s, CCH_3), 120.9 (q, J_{CF} = 320.8 Hz, CF_3), 212.6 (d, J_{PC} = 68.7 Hz, C=O); IR (CH_2C_2) ν = 2338 (PH), 1683 cm^{-1} (C=O).

Compound (**5**). To a CH_2Cl_2 solution (10 mL) of **2** (0.7 g, 2 mmol) was added at room temperature one equivalent of $BF_3.OEt_2$ (0.25 mL, 2 mmol). After the mixture was refluxed for 18 h, the solvent was removed under vacuum, and the residue was washed several times with ether affording compound **5** as an orange oily mixture with the corresponding ammonium salts (i-$Pr_2NH_2^+$,BF_4^-): ^{31}P NMR ($CDCl_3$) δ = +314.5 (d t, $^2J_{PP}$ = 176.0 Hz, $^3J_{PH}$ = 9.4 Hz, P_A), +52.3 (dq, $^2J_{PP}$ = 176.0 Hz, $^3J_{PH}$ = 15.2 Hz, P_B); ^{13}C NMR {^1H} ($CDCl_3$) δ = 20.9 and 21.7 (s, CH_3Ph), 23.3 (d, J_{PC} = 2.8 Hz, CH_3CH), 23.4 (d, J_{PC} = 2.8 Hz, CH_3CH), 24.0 (s broad, CH_3CH), 49.9 (dd, $J_{P(B)C}$ = 5.1 Hz, $J_{P(A)C}$ = 2.1 Hz, CHN), 51.8 (s broad, CHN), 113.6 (dd, $J_{P(B)C}$ = 150.5 Hz, $J_{P(A)C}$ = 64.0 Hz, PCP), 120.9 (q, J_{CF} = 320.8 Hz, CF_3), 124.3 (d, $J_{P(B)C}$ = 6.5 Hz, C_i), 129.7 (s, C_m), 129.8 (dd, $J_{P(B)C}$ = 6.4 Hz, $J_{P(A)C}$ = 3.2 Hz, C_O), 130.0 (d, $J_{P(B)C}$ = 1.8 Hz, C_O), 130.6 (s, C_m), 132.1 (d, $J_{P(A)C}$ = 6.7 Hz, C_i), 138.5 (d, $J_{P(B)C}$ = 3.0 Hz, C_p), 146.9 (s, C_p), 160.4 (d, $J_{P(B)C}$ = 10.3 Hz, CO); IR (CH_2Cl_2) ν = 1752 cm^{-1} (C=O).

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