

Synthesis and Reactivity of a Stable η^2 -(Diphosphirenylium)W(CO)₅ Complex

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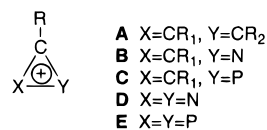
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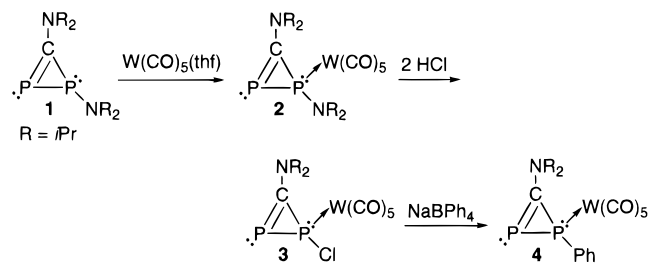
Several cyclopropenium salts **A** (Scheme 1), the prototype for 2- π -electron Hückel aromatic systems, have been prepared over the last 40 years.¹ According to calculations,² the azirinylium cations **B** exhibit a less-pronounced aromatic character due to the π -polarization toward nitrogen; to date, these compounds remain unknown. Replacement of the nitrogen atom by a phosphorus center should decrease the ring strain and allow better delocalization of the (2 π) electrons. However, phosphirenyl cations **C** have been observed spectroscopically only in SO₂ solution at -78 °C,³ or when complexed in an η^3 -fashion to an electron-rich Ni⁰ center.⁴ In the series of cationic 2- π -electron three-membered rings, no derivatives featuring two heteroatoms are known; even the postulated involvement⁵ of the diazirinylium cation **D** in the exchange reaction of nucleophiles with halodiazirines has been refuted.⁶ Here, we report the synthesis and reactivity of the first stable diphosphirenylium salt **E** bound in an η^2 -manner to a transition metal center.

It is well-known that amino substituents and transition metal centers dramatically stabilize electron-deficient species^{1c,7} and low-coordinate phosphorus compounds,⁸ respectively. More-

Scheme 1



Scheme 2



over, it has been clearly established that coordinated phosphonium salts can be easily obtained by heterolytic cleavage of the P–X bond of halogenophosphine complexes.⁹ Therefore, 1-halogeno-3-aminodiphosphirene complexes¹⁰ seemed to be ideal precursors for the desired diphosphirenylium salts. Treatment of the 1H-diphosphirene **1**¹¹ with 1 equiv of W(CO)₅(THF) at low temperature in THF readily affords complex **2** as a yellow oil, in 65% yield.¹² The spectroscopic data observed for **2** are comparable to those described for analogous compounds prepared by other routes.^{10b,c} Reaction of **2** with 2 equiv of hydrogen chloride in pentane¹³ gives 1-chloro-1H-diphosphirene (**3**) as a yellow oil in 69% yield¹² (Scheme 2). The substitution of the amino group at the λ^3 -phosphorus atom is clearly evident from mass spectrometry (Cl, CH₄, m/z = 534) and from the NMR spectra (data observed for **2** and **3** are similar). Interestingly, the mass spectrum features fragment peaks which correspond to both complexed and uncomplexed diphosphirenylium cations [m/z = 498 (M – Cl)⁺ and 174 [M – Cl – W(CO)₅]⁺].

Treatment of **3** with sodium tetraphenylborate in dichloromethane at room temperature affords the P-phenyl-1H-diphosphirene **4**¹² (Scheme 2). The replacement of the chlorine atom by a phenyl group at the λ^3 -phosphorus center is again apparent from the mass spectrum (Cl, NH₃, m/z = 576) and the ³¹P NMR spectra [–177.5, dt, $J(P-P)$ = 148.4 Hz, $J(P-H)$ = 13.2 Hz, λ^3 -P]. The formation of **4** probably results from the ionization of the P–Cl bond of **3** leading to a transient diphosphirenylium, which abstracts a phenyl group from the tetraphenylborate counterion. In order to prevent nucleophile

(11) To be published elsewhere.

(12) Selected spectroscopic data for **2**: ³¹P NMR (C₆D₆) –123.0 (d, $^1J(P-P)$ = 164.3 Hz, $^1J(P-W)$ = 295.1 Hz, P-NiPr₂), 15.0 ($^1J(P-P)$ = 164.3 Hz, σ^2 -P); ¹³C NMR (C₆D₆) 195.9 (dd, $^1J(P-C)$ = 80.6 Hz, 48.4 Hz, PCP), 197.6 (d, $^1J(P-C)$ = 8.7 Hz, $^1J(C-W)$ = 126.9 Hz, CO_e), 200.2 (d, $^1J(P-C)$ = 33.1 Hz, $^1J(C-W)$ = 149.9 Hz, CO_a); IR (THF) 1930 (vs), 1938 (vs), 1979 (s), 2069 (s) cm⁻¹ (ν_{CO}). For **3**: ³¹P NMR (C₆D₆) –78.5 (d, $^1J(P-P)$ = 218.0 Hz, $^1J(P-W)$ = 307.8 Hz, PCl), 34.6 ($^1J(P-P)$ = 218.0 Hz, σ^2 -P); ¹³C NMR (C₆D₆) 189.0 (dd, $^1J(P-C)$ = 88.6, 34.7 Hz, PCP), 196.7 (d, $^1J(P-C)$ = 8.6 Hz, $^1J(C-W)$ = 127.1 Hz, CO_e), 199.5 (d, $^1J(P-C)$ = 46.8 Hz, CO_a); IR (pentane) 1949 (vs), 1959 (vs), 2079 (s) cm⁻¹ (ν_{CO}). For **4**: ³¹P NMR (C₆D₆) –177.5 (d, $^1J(P-P)$ = 148.4 Hz, $^1J(P-W)$ = 257.1 Hz, P–Ph), –60.0 ($^1J(P-P)$ = 148.4 Hz, σ^2 -P); ¹H NMR (C₆D₆) 6.9–7.1 (m, 3 H, H_{ar}), 7.65 (ddd, $^3J(H-H)$ = 8.0 Hz, $^4J(H-H)$ = 1.5 Hz, $^3J(P-H)$ = 13.2 Hz, 2 H, H_{ar}); IR (pentane) 1935 (vs), 1943 (vs), 1938 (vs), 2071 (s) cm⁻¹ (ν_{CO}). For **5**: ¹H NMR (CDCl₃) 1.39 (d, $^3J(H-H)$ = 6.7 Hz, 6 H, CH₃), 1.44 (d, $^3J(H-H)$ = 6.7 Hz, 6 H, CH₃), 4.34 (sept, $^3J(H-H)$ = 6.7 Hz, 2 H, CHN); ¹³C NMR (CDCl₃) 20.2 (s, CH₃), 20.9 (s, CH₃), 61.0 (s, CHN), 119.7 (q, $^1J(C-F)$ = 318.6 Hz, CF₃), 189.3 (t, $^1J(P-C)$ = 4.3 Hz, $^1J(C-W)$ = 121.5 Hz, CO_e), 194.4 (t, $^1J(P-C)$ ≤ 1 Hz, CO_a), 205.1 (t, $^1J(P-C)$ = 90.9 Hz, PCP); IR (CH₂Cl₂) 1950 (vs), 2055 (s) cm⁻¹ (ν_{CO}); MS (Cl, CH₄) m/z 498 (M⁺), 470 {[M – (CO)]⁺}, 442 {[M – 2(CO)]⁺}. Anal. Calcd for **5**·(GaCl₄⁻), C₁₂H₁₄NO₅P₂WGaCl₄: C, 20.31; H, 1.99; N, 1.97. Found: C, 19.60; H, 2.39; N, 2.10.

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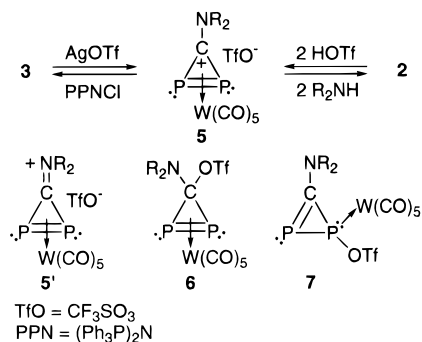
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Scheme 3

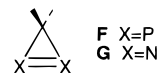


transfer, ionization of **3** was carried out with silver triflate at -78°C . The dichloromethane solution immediately turned to deep red, and after the solution was warmed to room temperature and filtration, the ^{31}P NMR spectrum showed only one singlet at -157.4 ppm (no P–W or P–H coupling was observed), in the range expected for a three-membered phosphorus heterocycle.¹⁴ The presence of a $\text{W}(\text{CO})_5$ fragment is readily apparent from the IR spectrum (CH_2Cl_2 , $\nu_{\text{CO}} = 1950$ and 2055 cm^{-1}). The multiplicity of the ^{31}P resonance can be explained either by a symmetrical structure with 2 equiv phosphorus atoms such as **5** or **6**, or alternatively from a rapid exchange of both the $\text{W}(\text{CO})_5$ fragment and the triflate group between the adjacent phosphorus nuclei of **7**¹⁵ (Scheme 3). The two triplets observed in the ^{13}C NMR spectrum for the carbonyl groups [189.3 , t, $J(\text{P}-\text{C}) = 4.3$ Hz, CO_e and 194.4 , t, $J(\text{P}-\text{C}) \leq 1$ Hz, CO_a] ruled out the rapid exchange of the metal fragment, confirmed the η^2 -coordination of the heterocycle (via the P=P bond), but did not exclude an equilibrium between the ionic and covalent structures **5** and **6**. However, it should be noted that no significant modification of the NMR spectra was detected on cooling the solution to -60°C and that the complex was only soluble in polar solvents.

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Scheme 4



The definitive proof for the ionic nature of **5** arises from the formation of complexes presenting identical ^{31}P , ^1H , and ^{13}C NMR data, by treatment of **3** with a slight excess of aluminium or gallium trichloride.¹⁶ All of these complexes are highly air- and moisture-sensitive brown oils.

The diphosphirenylium cation **5** readily reacts with 2 equiv of diisopropylamine and 1 equiv of bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), quantitatively affording complexes **2** and **3**, respectively. Lastly, note that **5** can be obtained directly along with 1 equiv of diisopropylammonium triflate, by treatment of a dichloromethane solution of **2** with 2 equiv of triflic acid at low temperature (Scheme 3).

The stability of **5** (stable for weeks in solution at room temperature) is certainly not only due to the presence of the metal fragment but also to the effective π -donation of the nitrogen: the mesomeric form **5'** is likely to be the major contributing structure (Scheme 3). Complex **5** is the first compound featuring a phosphorus–phosphorus double bond in a three-membered ring, and we are currently investigating the possibility of *C*-functionalization of such diphosphirenylium salts that would lead to the previously unknown *3H*-diphosphirenes **F**,¹⁷ the phosphorus analogues of *3H*-diazirine **G** (Scheme 4).

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Supporting Information Available: Listings of complete spectroscopic data for compounds **2–4** (2 pages). See any current masthead page for ordering and Internet access instructions.

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