Silver and Gold Cationic Diphosphene Complexes: Models for Protonation of the Phosphorus–Phosphorus Double Bond

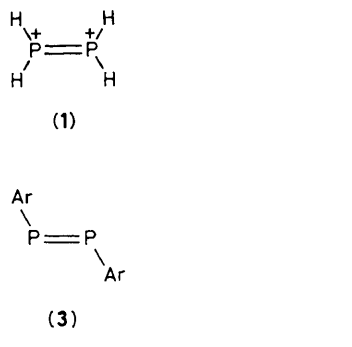
Alan H. Cowley,* Nicholas C. Norman, and Marek Pakulski

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

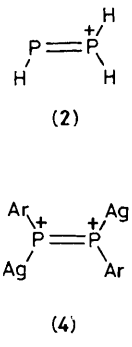
The dication, $[Ar(Ag)P{=}P(Ag)Ar]^{2+}$ (Ar = 2,4,6-$Bu^t_3C_6H_2$) and the monocations, $[ArP{=}P(Ag)Ar]^+$ and $[ArP{=}P(AuPEt_3)Ar]^+$ are formed on treatment of ArP=PAr with $[Ag][SO_3CF_3]$ or $[Et_3PAu][PF_6]$.

Special interest attaches to dication (**1**) because it is isovalent with ethene. Previous attempts to prepare cognates of (**1**) or the corresponding monocation, (**2**), by protonation of the diphosphenes, ArP=PAr, (**3**) (Ar = 2,4,6-$Bu^t_3C_6H_2$) and $(Me_3Si)_3CP{=}PC(SiMe_3)_3$, were thwarted by (i) cyclisation of the monoprotonated product, and/or (ii) P–P bond cleavage.[1] The recognition that the proton is isolobal with Ag^+ and $[R_3PAu]^+$ has stimulated elegant work in transition metal chemistry[2] and, in turn, prompted us to explore the reactivity of these cations towards (**3**).

Treatment of (**3**)[3] with an excess of $Ag[SO_3CF_3]$ in tetrahydrofuran (THF) solution at −90 °C afforded a solution which exhibited two superimposed AXX'A' $^{31}P\{^1H\}$ n.m.r. spectra centred at δ +355 p.p.m. (Figure 1). The following coupling constants were obtained by routine spectral simulation: $^1J(PP)$ 480, $^1J(PAg)$ −760,† $^2J(PPAg)$ +13, and $^3J(AgPPAg)$ −35 Hz. The observation of an AXX'A' $^{31}P\{^1H\}$ n.m.r. pattern indicates structure (**4**) and eliminates structure (**5**) [the *cis* isomer of (**4**) is ruled out on steric grounds]. Moreover, the deshielded ^{31}P chemical shift and large $^1J(PP)$ value are characteristic of a phosphorus–phosphorus double bond.[4] Upon warming the solution of (**4**) to −40 °C, the $^{31}P\{^1H\}$ n.m.r. signals coalesce to a single broad resonance at δ 361 p.p.m. The original AXX'A' pattern reappears on cooling the



(1)



(2)

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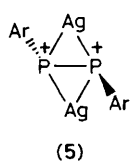
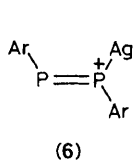
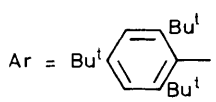


(5)



(6)



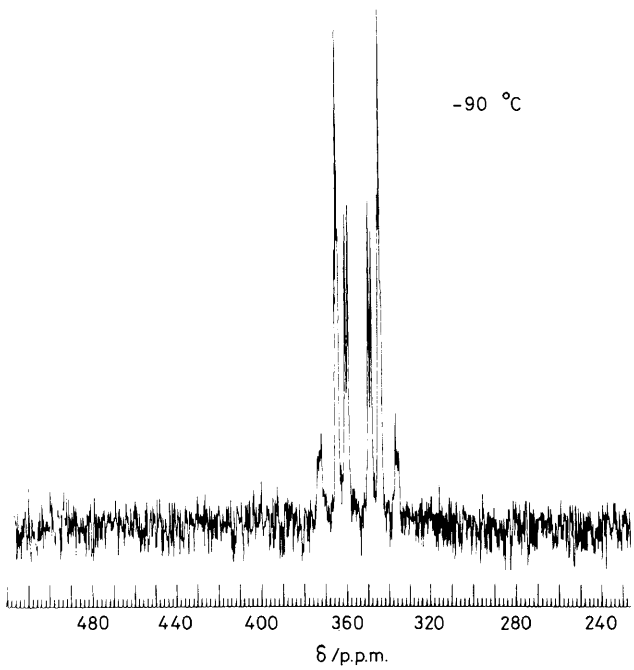


Figure 1. 36.43 MHz $^{31}P\{^1H\}$ N.m.r. spectrum of $[Ar(Ag)P{=}P(Ag)Ar]^{2+}$ (**4**) in THF. ^{31}P Chemical shifts referenced to external 85% H_3PO_4, positive values to high frequency.

† Insufficient spectral resolution was obtained to permit the measurement of separate ^{107}Ag and ^{109}Ag couplings. Averages of ^{107}Ag and ^{109}Ag couplings are therefore reported.

sample to −90 °C. It is possible that exchange proceeds *via* structure (**5**).

When (**3**) is treated with one equivalent of $Ag[SO_3CF_3]$, monocation (**6**) is formed. This structure assignment is consistent with the observed ABX $^{31}P\{^1H\}$ n.m.r. spectral pattern and the fact that the phosphorus nuclei are deshielded: $\delta(P_A)$ 435, $\delta(P_B)$ 378 p.p.m. The coupling constants are also indicative of a P=P bond: $^1J(PP)$ 549, $^1J(P_B{}^{109}Ag)$ −751, $^1J(P_B{}^{107}Ag)$ −750, $^2J(P_AP_B{}^{109}Ag)$ 12, and $^2J(P_AP_B{}^{107}Ag)$ 11.5 Hz. Like that of (**4**), the $^{31}P\{^1H\}$ n.m.r. spectrum of (**6**) is temperature dependent, coalescence to a single broad resonance (δ 379 p.p.m.) being observed on warming to 25 °C.

Treatment of (**3**) with an excess of $[Et_3PAu][PF_6]$ in THF solution resulted in a monocation analogous to (**6**). The ABX $^{31}P\{^1H\}$ n.m.r. spectrum of this cation, which is temperature independent, is assigned as follows: $\delta(P_A)$ 403, $\delta(P_B)$ 358, $\delta(P_X)$ (Et_3P) 41.5 p.p.m.; $^1J(P_AP_B)$ 555, $^1J(P_BP_x)$ −320, and $^2J(P_AP_X)$ 8 Hz. Our inability to prepare a dication akin to (**4**) is presumably a consequence of the steric demands of $[Et_3PAu]^+$.

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