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

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The dication,  $[Ar(Ag)P=P(Ag)Ar]^2+ (Ar = 2,4,6-But_3C_6H_2)$  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 =  $2,4,6-Bu^{1}_{3}C_{6}H_{2}$ ) and (Me<sub>3</sub>Si)<sub>3</sub>CP=PC(SiMe<sub>3</sub>)<sub>3</sub>, were thwarted by (i) cyclisation of the monoprotonated product, and/or (ii) P–P bond cleavage.<sup>1</sup> The recognition that the proton is isolobal with Ag<sup>+</sup> and [R<sub>3</sub>PAu]<sup>+</sup> has stimulated elegant work in transition metal chemistry<sup>2</sup> and, in turn, prompted us to explore the reactivity of these cations towards (3).

Treatment of (3)<sup>3</sup> with an excess of Ag[SO<sub>3</sub>CF<sub>3</sub>] in tetrahydrofuran (THF) solution at -90 °C afforded a solution which exhibited two superimposed AXX'A' <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectra centred at  $\delta$  +355 p.p.m. (Figure 1). The following coupling constants were obtained by routine spectral simula-

 $Ar = Bu^{t} \qquad Ar = Bu^{t} \qquad Bu^{t} \qquad$ 

tion: <sup>1</sup>*J*(PP) 480, <sup>1</sup>*J*(PAg) -760, <sup>†</sup> <sup>2</sup>*J*(PPAg) +13, and <sup>3</sup>*J*(AgP-PAg) -35 Hz. The observation of an AXX'A' <sup>31</sup>P{<sup>1</sup>H} 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 <sup>31</sup>P chemical shift and large <sup>1</sup>*J*(PP) value are characteristic of a phosphorus–phosphorus double bond.<sup>4</sup> Upon warming the solution of (**4**) to -40 °C, the <sup>31</sup>P{<sup>1</sup>H} n.m.r. signals coalesce to a single broad resonance at  $\delta$  361 p.p.m. The original AXX'A' pattern reappears on cooling the



Figure 1. 36.43 MHz  ${}^{31}P{}^{1}H$  N.m.r. spectrum of [Ar(Ag)P=P(Ag)Ar]^{2+} (4) in THF.  ${}^{31}P$  Chemical shifts referenced to external 85% H<sub>3</sub>PO<sub>4</sub>, positive values to high frequency.

<sup>&</sup>lt;sup>+</sup> Insufficient spectral resolution was obtained to permit the measurement of separate <sup>107</sup>Ag and <sup>109</sup>Ag couplings. Averages of <sup>107</sup>Ag and <sup>109</sup>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<sub>3</sub>CF<sub>3</sub>], monocation (6) is formed. This structure assignment is consistent with the observed ABX  ${}^{31}P{}^{1}H{}$  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:  ${}^{1}J(PP)$  549,  ${}^{1}J(P_B{}^{109}Ag)$  -751,  ${}^{1}J(P_B{}^{107}Ag)$  -750,  ${}^{2}J(P_AP_B{}^{109}Ag)$  12, and  ${}^{2}J(P_AP_B{}^{107}Ag)$ 11.5 Hz. Like that of (4), the  ${}^{31}P{}^{1}H{}$  n.m.r. spectrum of (6) is temperature dependent, coalescence to a single broad resonance ( $\delta$  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 <sup>31</sup>P{<sup>1</sup>H} 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<sub>3</sub>P) 41.5 p.p.m.; <sup>1</sup>J(P\_AP\_B) 555, <sup>1</sup>J(P\_BP\_X) -320, and

 ${}^{2}J(P_AP_X)$  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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