

# Unexpected Formation of a Tetranuclear Heterobimetallic Complex by Reaction of a Ruthenium Alkynyl with $\text{AgCF}_3\text{SO}_3$

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$[\text{RuCl}_2(\text{dippe})_2]$  (dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with  $\text{HC}\equiv\text{CR}$  ( $\text{R} = \text{Ph}, \text{H}$ ) in dichloromethane in the presence of  $[\text{NH}_4][\text{PF}_6]$  furnishing the corresponding cationic vinylidene complexes  $\text{trans-}[\text{Ru}=\text{C}=\text{CHR}(\text{Cl})(\text{dippe})_2]^+$ , which were isolated as tetraphenylborate salts. In an analogous fashion, the reaction of  $[\text{RuCl}_2(\text{dippe})_2]$  with substituted propargyl alcohols  $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$  ( $\text{R} = \text{R}' = \text{Me}$ ;  $\text{R} = \text{Me}, \text{R}' = \text{Ph}$ ) yielded the allenylidene derivatives  $[\text{Ru}=\text{C}=\text{C}=\text{CRR}'(\text{Cl})(\text{dippe})_2]^+$ , which were also isolated as  $[\text{BPh}_4]^-$  salts. The reaction of  $\text{trans-}[\text{RuCl}(\text{C}\equiv\text{CPh})(\text{dippe})_2]$ , formed by deprotonation of  $[\text{Ru}=\text{C}=\text{CHPh}(\text{Cl})(\text{dippe})_2][\text{BPh}_4]$  by  $\text{KO}^\text{t}\text{Bu}$ , with  $\text{AgCF}_3\text{SO}_3$  in the presence of  $\text{HC}\equiv\text{CPh}$  was carried out in an attempt to generate a cationic alkynyl–vinylidene species. However, this reaction yielded instead the unexpected tetranuclear heterobimetallic complex  $[\{\text{Ru}(\text{dippe})\}_2(\mu\text{-Cl})_3(\sigma, \eta^2\text{-C}\equiv\text{CPh})_2\{\text{Ag}_2(\mu\text{-dippe})\}]^+$ , isolated as the  $[\text{BPh}_4]^-$  salt, in which two  $\sigma$ -alkynyl ligands attached to ruthenium are bridged by a  $[\text{Ag}_2(\mu\text{-dippe})]^{2+}$  fragment. To understand better the coordination modes of dippe to silver, the complex  $[\{\text{Ag}(\text{dippe})\}_2(\mu\text{-dippe})][\text{BPh}_4]_2$  was synthesized. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of silver-containing derivatives, which display complex second-order patterns, have been analyzed in detail, and the X-ray crystal structures of  $\text{trans-}[\text{Ru}=\text{C}=\text{CH}_2(\text{Cl})(\text{dippe})_2][\text{BPh}_4]$ ,  $[\{\text{Ru}(\text{dippe})\}_2(\mu\text{-Cl})_3(\sigma, \eta^2\text{-C}\equiv\text{CPh})_2\{\text{Ag}_2(\mu\text{-dippe})\}][\text{BPh}_4]$ , and  $[\{\text{Ag}(\text{dippe})\}_2(\mu\text{-dippe})][\text{BPh}_4]_2$  are reported.

## Introduction

The involvement of transition-metal vinylidene complexes in the stoichiometric and catalytic processes of oligomerization of alkynes is now well established. In particular, the metal-mediated dimerization of alkynes to enynes, or even butatrienes,<sup>1</sup> can occur either by alkynyl–vinyl or alkynyl–vinylidene coupling, the enyne being released from either  $\eta^1$ - or  $\eta^3$ -enynyl derivatives on treatment with an additional molecule of alkyne.<sup>2</sup> Examples of such processes are known for a variety of metal complexes of rhodium,<sup>2</sup> tungsten,<sup>3</sup> iron,<sup>4</sup> and osmium.<sup>5</sup> Ruthenium complexes have shown to be especially efficient in achieving alkyne coupling<sup>6</sup> with high regio- and stereoselectivity in some instances: e.g., the catalytic reaction of  $[\text{RuH}(\text{L})(\text{PP}_3)][\text{BPh}_4]$  ( $\text{L} = \text{H}_2, \text{N}_2$ ;  $\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ ) with  $\text{HC}\equiv\text{CSiMe}_3$ <sup>7</sup> or, more recently, the selective formation of 1,3- and 1,4-disubstituted enynes and of a cumulene derivative from the

catalytic dimerization of alkynes mediated by  $[\text{Ru}(\text{C}_5\text{-Me}_5)\text{H}_3(\text{PR}_3)]$  ( $\text{PR}_3 = \text{PPh}_3, \text{PCy}_3, \text{PMe}_3$ ).<sup>8</sup>

Bearing these facts in mind, we had previously studied the reactivity of the coordinatively unsaturated monohydride complex  $[\text{RuH}(\text{dippe})_2][\text{BPh}_4]$ <sup>9</sup> (dippe = 1,2-bis(diisopropylphosphino)ethane) toward 1-alkynes. The alkynyl–dihydrogen complexes  $[\text{Ru}(\text{H}_2)(\text{C}\equiv\text{CR})(\text{dippe})_2][\text{BPh}_4]$  ( $\text{R} = \text{COOMe}, \text{Ph}$ )<sup>10</sup> were the only isolated products from these reactions. Remarkably, these alkynyl–dihydrogen complexes did not react any further with alkynes to furnish either ruthenium buteny-

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nyl or vinyl–vinylidene derivatives. We have now studied the reactivity of the 16-electron fragment  $[\text{RuCl}(\text{dippe})_2]^+$  toward alkynes and alkynols. In an attempt to generate coordinatively unsaturated species of the type  $[\text{Ru}(\text{C}\equiv\text{CR})(\text{dippe})_2]^+$ , with the potential ability to bind an additional alkyne molecule and eventually undergo coupling, we tried abstracting chloride from the chloro–alkynyl complexes  $[\text{Ru}(\text{C}\equiv\text{CR})\text{Cl}(\text{dippe})_2]$  in the presence of 1-alkyne using  $\text{AgCF}_3\text{SO}_3$  as halide scavenger. A novel heterobimetallic tetranuclear ruthenium–silver complex with a remarkable structure has been the only characterized product from such reactions. The preparation, X-ray crystal structure, and NMR spectral properties of this material, as well as of other relevant compounds obtained in our search for alkyne-coupling derivatives, are described in this work.

### Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane<sup>12</sup> and  $[\text{RuCl}_2(\text{dippe})_2]$ <sup>9</sup> were prepared according to reported procedures. IR spectra were recorded in Nujol mulls on Perkin-Elmer 881 or Perkin-Elmer FTIR Spectrum 1000 spectrophotometers. NMR spectra were taken either on Varian Unity 400 MHz or on Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from  $\text{SiMe}_4$  (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) or 85%  $\text{H}_3\text{PO}_4$  (<sup>31</sup>P{<sup>1</sup>H}). The phosphine protons for all the compounds appeared as a series of overlapping multiplets in the range 0.5–3 ppm and were not assigned.<sup>31</sup>P{<sup>1</sup>H} NMR spectral simulation was carried out on a Sun workstation using the software included in the Varian Unity 400 MHz data processing system, which is based on the program LAOCOON.<sup>13</sup> Microanalyses were done by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

**Preparation of the Vinylidene Complexes *trans*-[Ru=C=CHR(Cl)(dippe)<sub>2</sub>][BPh<sub>4</sub>] (R = Ph (1a), H (1b)).** To a slurry of *trans*-[RuCl<sub>2</sub>(dippe)<sub>2</sub>] (0.2 g, ca. 0.3 mmol) and [NH<sub>4</sub>][PF<sub>6</sub>] (0.2 g, excess) in dichloromethane (15 mL) was added an excess of HC≡CPh for preparing **1a**. For the preparation of **1b**, HC≡CH was bubbled through the reaction mixture for a couple of minutes. The mixture was then stirred at room temperature for 3–4 h. A microcrystalline precipitate was formed. The solvent was removed, and the residue was extracted with ethanol. Addition of solid Na[BPh<sub>4</sub>] (0.3 g, excess) afforded a microcrystalline precipitate, which was filtered off, washed with ethanol and petroleum ether, and dried *in vacuo*. These compounds were recrystallized from acetone/ethanol. **1a**: yield 0.26 g, 80%. Anal. Calcd for C<sub>60</sub>H<sub>90</sub>BClP<sub>4</sub>Ru: C, 66.6; H, 8.38. Found: C, 66.7; H, 8.41. IR (Nujol):  $\nu(\text{C}=\text{C})$  1611 cm<sup>-1</sup>; reinforced  $\nu(\text{C}=\text{C})$  in phenyl ring 1592 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): <sup>1</sup>H,  $\delta$  4.07 (q, <sup>4</sup>J(H,P) = 2.8 Hz, Ru=C=CHPh), 6.76, 6.98, 7.14 (m, Ru=C=CH(C<sub>6</sub>H<sub>5</sub>)), <sup>31</sup>P{<sup>1</sup>H},  $\delta$  47.0 s; <sup>13</sup>C{<sup>1</sup>H},  $\delta$  17.8 (m, J(C,P) = 9.4 Hz, PCH<sub>2</sub>), 20.0, 20.3, 20.6 (s, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 26.4 (m, J(C,P) = 5.0 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 110.0 (s, Ru=C=CHPh), 126.5, 127.5, 128.7 (s, Ru=C=CH(C<sub>6</sub>H<sub>5</sub>)), 342.9 (q, <sup>2</sup>J(C,P) = 13.1 Hz, Ru=C=CHPh). **1b**: yield 0.2 g, 67%. Anal. Calcd for C<sub>54</sub>H<sub>86</sub>BClP<sub>4</sub>Ru: C, 64.5;

H, 8.61. Found: C, 64.2; H, 8.58. IR (Nujol):  $\nu(\text{C}=\text{C})$  1607 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): <sup>1</sup>H,  $\delta$  2.95 (s br, Ru=C=CH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H},  $\delta$  53.4 s; <sup>13</sup>C{<sup>1</sup>H},  $\delta$  16.9 (m, J(C,P) = 9.4 Hz, PCH<sub>2</sub>), 19.8, 19.9, 20.3, 20.5 (s, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 25.8 (m, J(C,P) = 5.3 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 29.2 (m, J(C,P) = 5.4 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 105.6 (s, Ru=C=CH<sub>2</sub>), 341.8 (q, <sup>2</sup>J(C,P) = 13.0 Hz, Ru=C=CH<sub>2</sub>).

**Preparation of the Allenylidene Complexes *trans*-[Ru=C=C=CRR'(Cl)(dippe)<sub>2</sub>][BPh<sub>4</sub>] (R = R' = Me, 2a; R = Me, R' = Ph, 2b).** To a solution of *trans*-[RuCl<sub>2</sub>(dippe)<sub>2</sub>] (0.2 g, ca. 0.3 mmol) in dichloromethane (15 mL) was added an excess of the corresponding alkynol and solid [NH<sub>4</sub>][PF<sub>6</sub>] (0.2 g, excess). The mixture was stirred at room temperature for 3–4 h. Solvent removal, extraction with ethanol, and addition of solid Na[BPh<sub>4</sub>] (0.3 g, excess) yielded a microcrystalline precipitate which was filtered off, washed with ethanol and petroleum ether, and dried *in vacuo*. The complexes were recrystallized from acetone/ethanol. **2a**: yield 0.20 g, 66%. Anal. Calcd for C<sub>57</sub>H<sub>90</sub>BClP<sub>4</sub>Ru: C, 65.4; H, 8.67. Found: C, 65.5; H, 8.52. IR (Nujol):  $\nu(\text{C}=\text{C}=\text{C})$  1947 cm<sup>-1</sup>. NMR (CD<sub>3</sub>-COCD<sub>3</sub>): <sup>1</sup>H,  $\delta$  2.16 (s, Ru=C=C=C(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H},  $\delta$  50.8; <sup>13</sup>C{<sup>1</sup>H},  $\delta$  16.6 (m, J(C,P) = 9.8 Hz, PCH<sub>2</sub>), 19.6, 19.8, 20.3, 20.5 (s, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 25.7 (m, J(C,P) = 9.7 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 28.3 (m, J(C,P) = 16.4 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 32.8 (s, Ru=C=C=C(CH<sub>3</sub>)<sub>2</sub>), 147.9 (s, Ru=C=C=C(CH<sub>3</sub>)<sub>2</sub>), 211.8 (s, Ru=C=C=C(CH<sub>3</sub>)<sub>2</sub>), Ru=C not observed. **2b**: yield 0.24 g, 72%. Anal. Calcd for C<sub>62</sub>H<sub>92</sub>BClP<sub>4</sub>Ru: C, 67.1; H, 8.36. Found: C, 67.3; H, 8.49. IR (Nujol):  $\nu(\text{C}=\text{C}=\text{C})$  1965 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): <sup>1</sup>H,  $\delta$  1.74 (s, Ru=C=C=C(CH<sub>3</sub>)Ph), 7.15, 7.33, 7.73 (m, Ru=C=C=C(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H},  $\delta$  50.2; <sup>13</sup>C{<sup>1</sup>H},  $\delta$  16.9 (m, J(C,P) = 9.5 Hz, PCH<sub>2</sub>), 19.4, 19.6, 20.1, 20.4 (s, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 26.0 (m, J(C,P) = 5.4 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 28.3 (m, J(C,P) = 5.4 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 30.9 (s, Ru=C=C=C(CH<sub>3</sub>)Ph), 127.5, 128.2, 132.4 (s, Ru=C=C=C(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>), 143.1 (s, Ru=C=C=C(CH<sub>3</sub>)Ph), 211.8 (s, Ru=C=C=C(CH<sub>3</sub>)Ph), 306.5 (q, <sup>2</sup>J(C,P) = 13.5 Hz, Ru=C=C=C(CH<sub>3</sub>)Ph).

**Preparation of the Neutral Alkynyl Complexes *trans*-[RuCl(C≡CR)(dippe)<sub>2</sub>] (R = Ph (3a), H (3b)).** A tetrahydrofuran solution of the corresponding vinylidene complex **1a** or **1b** was treated with an excess of solid KOBu<sup>t</sup>. The mixture was stirred at room temperature for 1 h. Then, the solvent was removed *in vacuo*. The residue was extracted with toluene and the solution filtered through Celite. Concentration, addition of petroleum ether, and cooling to –20 °C afforded yellow crystals of these compounds. **3a**: yield ca. 60%. Anal. Calcd for C<sub>36</sub>H<sub>69</sub>CIP<sub>4</sub>Ru: C, 56.7; H, 9.12. Found: C, 56.9; H, 9.19. IR (Nujol):  $\nu(\text{C}\equiv\text{C})$  2036 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): <sup>1</sup>H,  $\delta$  7.19, 7.31, 7.45 (m, RuC≡CC<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H},  $\delta$  53.9 s; <sup>13</sup>C{<sup>1</sup>H},  $\delta$  16.7 (m, J(C,P) = 9.7 Hz, PCH<sub>2</sub>); 20.5, 20.6, 20.8, 21.1 (s, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 24.2 (m, J(C,P) = 7.5 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 27.6 (m, J(C,P) = 5.0 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 122.5 (s, RuC≡CPh), 122.8 (q, <sup>2</sup>J(C,P) = 14.9 Hz, RuC≡CPh), 128.8, 130.6, 131.2 (s, C<sub>6</sub>H<sub>5</sub>). **3b**: yield 65%. Anal. Calcd for C<sub>30</sub>H<sub>65</sub>CIP<sub>4</sub>Ru: C, 52.5; H, 9.55. Found: C, 52.2; H, 9.47. IR (Nujol):  $\nu(\text{C}\equiv\text{C})$  2045 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): <sup>1</sup>H,  $\delta$  1.14 (s, RuC≡CH, obscured by phosphine resonances; assigned by a 2D-HETCOR experiment); <sup>31</sup>P{<sup>1</sup>H},  $\delta$  52.3 s; <sup>13</sup>C{<sup>1</sup>H},  $\delta$  16.3 (m, J(C,P) = 9.5 Hz, PCH<sub>2</sub>), 20.3, 20.4, 20.6, 21.0 (s, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 26.0 (m, J(C,P) = 4.2 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 27.0 (m, J(C,P) = 4.7 Hz, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 116.6 (q, <sup>2</sup>J(C,P) = 13.5 Hz, RuC≡CH), 125.4 (s, RuC≡CH).

**[Ag<sub>2</sub>Ru<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>( $\mu$ , $\sigma$ - $\eta^2$ -C≡CPh)<sub>2</sub>( $\mu$ -dippe)(dippe)<sub>2</sub>][BPh<sub>4</sub>] (4).** To a tetrahydrofuran solution of **3a** (0.23 g, ca. 0.3 mmol) were added  $\text{AgCF}_3\text{SO}_3$  (0.075 g, ca. 0.3 mmol) and an excess of HC≡CPh. The mixture was stirred at room temperature for 3 h. The solvent was removed *in vacuo* and the residue extracted with ethanol. Solid Na[BPh<sub>4</sub>] (0.3 g, excess) was added, and a brown microcrystalline precipitate was obtained. This material was filtered off, washed with ethanol and petroleum ether, and dried. Recrystallization from dichloromethane/ethanol yielded two different products: an amorphous, apparently polymeric gray solid and yellow crystals. The yellow crystals were collected and then identified

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**Table 1. Summary of Data for the Crystal Structure Analysis of 1b, 4 and 5**

|   | <b>1b</b>  | <b>4</b>   | <b>5</b>  |
|---|--|--|---|
| formula   | C <sub>54</sub> H <sub>86</sub> BClP <sub>4</sub> Ru | C <sub>82</sub> H <sub>126</sub> Ag <sub>2</sub> BCl <sub>3</sub> P <sub>6</sub> Ru <sub>2</sub> | C <sub>45</sub> H <sub>65</sub> AgBP <sub>3</sub> |
| fw  | 1006.50  | 1832.79  | 817.61  |
| cryst size (mm)   | ca. 0.14 × 0.10 × 0.37                               | 0.25 × 0.14 × 0.34   | 0.18 × 0.05 × 0.19                                |
| cryst system  | monoclinic   | triclinic  | monoclinic  |
| space group   | Cc (No. 9)   | P1̄ (No. 2)  | P2 <sub>1</sub> /n (No. 14)                       |
| cell params   |  |  |   |
| <i>a</i> , Å  | 12.812(3)  | 19.212(5)  | 13.457(10)  |
| <i>b</i> , Å  | 19.261(3)  | 20.753(5)  | 22.067(4)   |
| <i>c</i> , Å  | 22.277(7)  | 10.989(3)  | 15.340(4)   |
| α, deg  |  | 99.02(2)   |   |
| β, deg  | 102.56(2)  | 100.35(2)  | 93.45(4)  |
| γ, deg  |  | 91.20(2)   |   |
| <i>V</i> , Å <sup>3</sup>   | 5365(4)  | 4251(3)  | 4546(5)   |
| <i>Z</i>  | 4  | 2  | 4   |
| ρ <sub>calcd</sub> , g cm <sup>-3</sup>   | 1.246  | 1.431  | 1.194   |
| λ(Mo Kα), Å   | 0.710 69   | 0.710 69   | 0.710 69  |
| μ(Mo Kα), cm <sup>-1</sup>  | 4.86   | 0.37   | 5.69  |
| <i>F</i> (000)  | 2144   | 1892   | 1728  |
| transmissn factor   | 0.90–1.16  | 0.86–1.13  | 0.83–1.17   |
| scan speed (ω), deg min <sup>-1</sup>   | 8  | 8  | 8   |
| 2θ interval, deg  | 5 < 2θ < 50.1  | 5 < 2θ < 50.1  | 5 < 2θ < 50.1                                     |
| no. of measd rflns  | 4112   | 12 068   | 4888  |
| no. of unique rflns   | 4112 ( <i>R</i> <sub>int</sub> = 0.11)               | 11 779 ( <i>R</i> <sub>int</sub> = 0.17)   | 4720 ( <i>R</i> <sub>int</sub> = 0.16)            |
| no. of obsd rflns   | 3023 ( <i>I</i> > σ) <i>i</i> )                      | 5534 ( <i>I</i> > 3σ) <i>i</i> )   | 2649 ( <i>I</i> > 3σ) <i>i</i> )                  |
| no. of params   | 274  | 450  | 216   |
| reflection/parameter ratio  | 11.03  | 12.30  | 12.26   |
| <i>R</i> <sup>a</sup>   | 0.091  | 0.080  | 0.069   |
| <i>R</i> <sub>w</sub> ( <i>w</i> = σ <sub><i>F</i></sub> <sup>-2</sup> ) <sup>b</sup> | 0.073  | 0.097  | 0.080   |
| GOF   | 1.41   | 2.49   | 1.99  |

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$ .

as compound **4**, whereas the amorphous gray solid remained uncharacterized. Yield: 0.092 g, ca. 34% based on Ru. Anal. Calcd for C<sub>82</sub>H<sub>126</sub>Ag<sub>2</sub>BCl<sub>3</sub>P<sub>6</sub>Ru<sub>2</sub>: C, 53.7; H, 6.87. Found: C, 54.2; H, 6.91. IR: ν(C≡C) 2000, 1967 cm<sup>-1</sup>. NMR (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H, δ 7.10, 7.19, 7.27 (m, RuC≡CC<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} at 298 K, δ 26.2 (double multiplet, 2 P, Ag(*μ*-dippe)Ag), 92.7 (s, 4 P, {Ru(*dippe*)<sub>2</sub>}); <sup>31</sup>P{<sup>1</sup>H} at 183 K, δ 26.5 (broad doublet, 2 P, Ag(*μ*-dippe)Ag), 91.6 (d, 2 P), 92.2 (d, 2 P), <sup>2</sup>J(P,P) = 22 Hz, {Ru(*dippe*)<sub>2</sub>}; <sup>13</sup>C{<sup>1</sup>H}, of poor quality due to insufficient solubility of the compound.

[{Ag(*dippe*)<sub>2</sub>(*μ*-dippe)]<sub>2</sub>[BPh<sub>4</sub>]<sub>2</sub> (**5**). To a methanol (50 mL) solution of AgNO<sub>3</sub> (0.085 g, ca. 0.5 mmol) dippe (0.3 mL, 1 mmol) was added. The mixture was stirred at room temperature for 1 h. After this time, the solution was concentrated to 5 mL, and solid Na[BPh<sub>4</sub>] (0.3 g, excess) was added. A microcrystalline white solid was obtained. It was filtered off, washed with ethanol and petroleum ether, and dried in vacuo. Yield: 0.70 g, 85%. Anal. Calcd for C<sub>90</sub>H<sub>136</sub>Ag<sub>2</sub>B<sub>2</sub>P<sub>6</sub>: C, 58.1; H, 7.31. Found: C, 58.4; H, 7.44. NMR (CD<sub>3</sub>COCD<sub>3</sub>): <sup>31</sup>P{<sup>1</sup>H}, δ 23.6 (double doublet of doublets, 4 P, {Ag(*dippe*)<sub>2</sub>(*μ*-dippe)}), 41.4 (double multiplet, 2 P, {Ag(*dippe*)<sub>2</sub>(*μ*-dippe)}); <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>), δ 18.6, 20.0, 23.6 (m, dippe).

**X-ray Structure Determinations of Complexes 1b, 4, and 5.** Crystals suitable for X-ray diffraction were mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer (*T* = 290 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). Accurate unit cell parameters and an orientation matrix were determined by least-squares fitting from the settings of 25 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 1. Data were collected by the ω–2θ scan method. Lorentz and polarization corrections were applied. In the case of the **1b** complex, due to its instability under X-ray radiation, three different crystals were used for data collection. Common reflections allowed the normalization to obtain a unique set of data. Decay was monitored in all the crystals by measuring 3 standard reflections every 100 measurements. An empirical absorption correction was also

applied (DIFABS).<sup>14</sup> The structures were solved by Patterson methods and subsequent expansion of the models using DIRDIF.<sup>15</sup> Reflections having *I* > σ(*I*) in the case of complex **1b** or *I* > 3σ(*I*) in the case of complexes **4** and **5** were used for structure refinement. For compound **1b**, Ru, Cl, and P atoms were anisotropically refined, and the remaining non-hydrogen atoms were refined isotropically. In the case of **4**, Ag, Ru, Cl, and P atoms were anisotropically refined, and the other non-hydrogen atoms were refined isotropically. For compound **5** all non-hydrogen atoms except Ag and P were isotropically refined. In all cases, the hydrogen atoms were included at idealized positions and not refined. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN<sup>16</sup> software system and ORTEP<sup>17</sup> for plotting. Maximum and minimum peaks in the final difference Fourier maps were +0.63 and –0.62 e Å<sup>-3</sup> for **1b**, +1.24 and –1.40 e Å<sup>-3</sup> for **4**, and +0.79 and –0.59 e Å<sup>-3</sup> for **5**.

## Results and Discussion

The vinylidene complexes [Ru=C=CHR(Cl)(dippe)<sub>2</sub>]-[BPh<sub>4</sub>] (R = Ph (**1a**), H (**1b**)) were prepared by reaction of the coordinatively unsaturated complex [RuCl(dippe)<sub>2</sub>]-[PF<sub>6</sub>] (generated *in situ* starting from [RuCl<sub>2</sub>(dippe)<sub>2</sub>] and [NH<sub>4</sub>][PF<sub>6</sub>] in dichloromethane) and the corresponding alkyne and then converted into their [BPh<sub>4</sub>]<sup>-</sup> salts by subsequent treatment with Na[BPh<sub>4</sub>] in ethanol. This synthetic procedure is essentially identical with that used for the preparation of the cationic vinylidene complexes *trans*-[Ru=C=CHR(Cl)(dppm)<sub>2</sub>]-

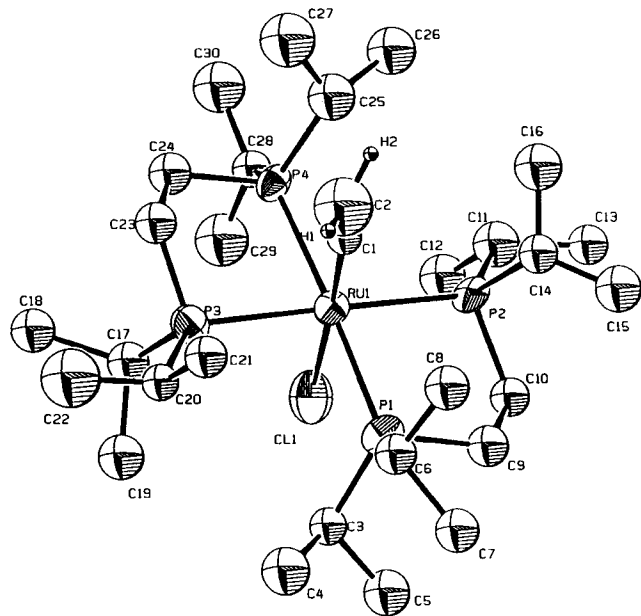
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(15) Beurskens, P. T. DIRDIF; Technical Report 1984/1; Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, The Netherlands, 1984.

(16) TEXSAN, Single-Crystal Structure Analysis Software, version 5.0; Molecular Structure Corp., The Woodlands, TX, 1989.

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**Figure 1.** ORTEP drawing of the cation  $[\text{Ru}=\text{C}=\text{CH}_2(\text{Cl})(\text{dippe})_2]^+$  with 50% probability thermal ellipsoids. Hydrogen atoms, except those attached to C(2), are omitted.

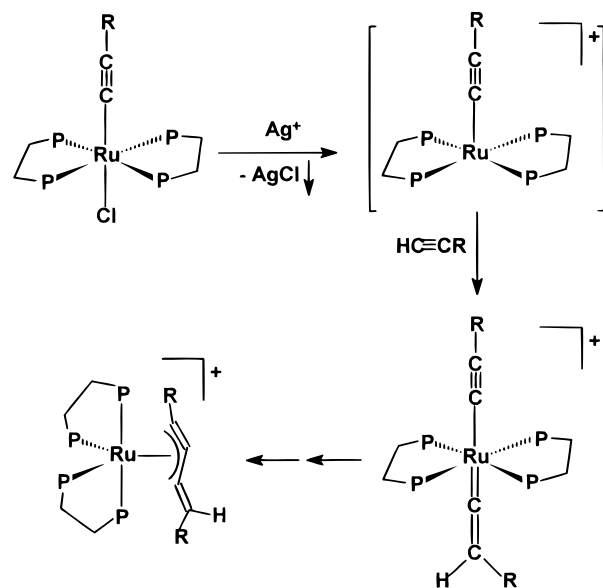
$[\text{PF}_6]$  (dppm = 1,2-bis(diphenylphosphino)methane).<sup>18</sup> Compounds **1a** and **1b** are crystalline solids, moderately stable in air, that display one medium-strong  $\nu(\text{C}=\text{C})$  vinylidene band near  $1600\text{ cm}^{-1}$  in their IR spectra. Their  $^1\text{H}$  NMR spectra show the typical resonance for a proton attached to the  $\beta$ -carbon of the vinylidene ligand, which appears as a quintet in the case of **1a** due to coupling to four equivalent phosphorus atoms, this coupling not being resolved for **1b**. Consistent with this, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra display one singlet, indicative of a *trans* arrangement of the bidentate phosphine ligands. The most characteristic feature of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra is the low-field resonance for the carbon atom of the vinylidene fragment directly attached to ruthenium, which appears as a quintet for both **1a** and **1b** due to coupling with four phosphorus atoms. The X-ray crystal structure of **1b** was determined, supporting the structural assignment made on a spectral basis. An ORTEP view of the complex cation  $[\text{Ru}=\text{C}=\text{CH}_2(\text{Cl})(\text{dippe})_2]^+$  is shown in Figure 1. The ruthenium atom is in an octahedral environment with the chloride and vinylidene ligands in mutually *trans* positions, a geometry that has also been found for the complex *trans*- $[\text{Ru}=\text{C}=\text{CH}_2(\text{Cl})(\text{dppm})_2][\text{PF}_6]$ ,<sup>18</sup>  $[(\text{C}_5\text{H}_5)\text{Ru}=\text{C}=\text{CH}_2(\text{PMePh}_2)_2][\text{BF}_4]$ ,<sup>19a</sup> and  $[(\text{C}_5\text{Me}_5)\text{Ru}=\text{C}=\text{CH}_2(\text{PPh}_3)_2][\text{PF}_6]$ .<sup>19b</sup> Listings of intramolecular bond lengths and angles have been placed in the Supporting Information, for reference.

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(19) (a) Selegue, J. P.; Lompfrey, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (b) Kawata, Y.; Sato, M. *Organometallics* **1997**, *16*, 1093.

The allenylidene derivatives  $[\text{Ru}=\text{C}=\text{C}=\text{CRR}'(\text{Cl})(\text{dippe})_2][\text{BPh}_4]$  ( $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ , **2a**;  $\text{R} = \text{R}' = \text{Me}$ , **2b**) were obtained in a fashion similar to that for the vinylidene derivatives, by reaction of  $[\text{RuCl}_2(\text{dippe})_2]$  with the corresponding propargyl alcohol  $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$  in the presence of  $[\text{NH}_4][\text{PF}_6]$  and subsequent conversion into their  $[\text{BPh}_4]^-$  salts. These crystalline compounds are presumably formed by spontaneous dehydration of an intermediate, undetected hydroxyvinylidene complex, as has been proposed to explain the formation of other allenylidene complexes starting from propargyl alcohols.<sup>20</sup> The IR spectra of **2a** and **2b** are dominated by the strong  $\nu(\text{C}=\text{C})$  band near  $1950\text{ cm}^{-1}$  of the cumulene ligand. The presence of one sharp singlet in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of these compounds is indicative of a *trans* structure, whereas the most relevant signals observed in their  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra correspond to the resonances of the carbon atoms in the unsaturated carbon chain, which appear in the range expected for allenylidene complexes of ruthenium.

In no case did the reaction of an excess of alkyne or substituted propargyl alcohol with  $[\text{RuCl}_2(\text{dippe})_2]$  in the presence of  $[\text{NH}_4][\text{PF}_6]$  lead to spontaneous formation of cationic alkynyl–vinylidene or alkynyl–allenylidene complexes or to C–C coupling derivatives. In an attempt to promote the formation of such species, an alternative route was designed, involving the abstraction of the halide ligand from a neutral alkynyl complex (or from a  $\eta^1$ -enynyl species) using a silver salt as halide scavenger, to generate *in situ* coordinatively unsaturated species of the type  $[\text{Ru}(\text{C}\equiv\text{CR})(\text{dippe})_2]^+$ , which eventually might add another alkyne molecule, according to the overall reaction sequence



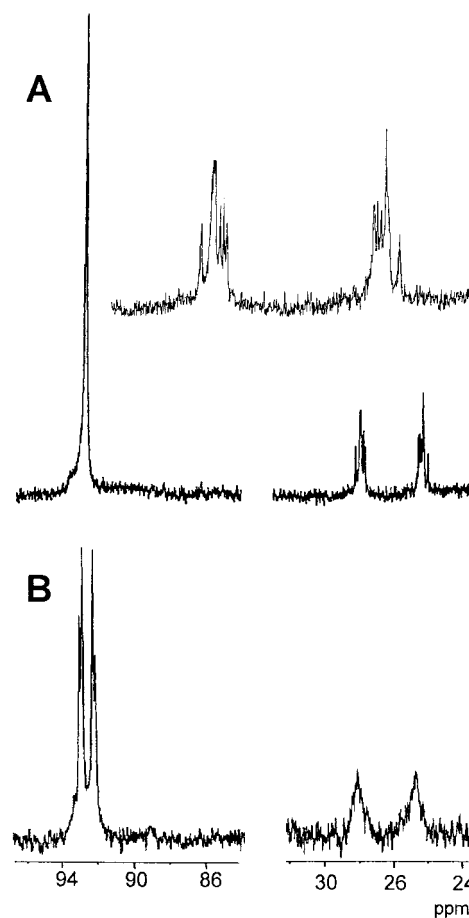
Thus, the vinylidene complexes **1a** and **1b** were deprotonated by  $\text{KO}^t\text{Bu}$  in tetrahydrofuran, yielding the

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corresponding neutral alkynyls  $[\text{Ru}(\text{C}\equiv\text{CR})\text{Cl}(\text{dippe})_2]$  ( $\text{R} = \text{Ph}$  (**3a**),  $\text{H}$  (**3b**)). However, the deprotonation of the allenylidenes **2a** and **2b**, which supposedly would yield the  $\eta^1$ -enynyls  $[\text{Ru}(\text{C}\equiv\text{C}(\text{R})=\text{CH}_2)(\text{Cl})(\text{dippe})_2]$  as has been observed in other cases,<sup>20</sup> gave only oily uncharacterized substances which revealed themselves as a complex mixture of products during  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. The alkynyls **3a** and **3b** are crystalline materials, soluble in nonpolar solvents, which display one strong  $\nu(\text{C}\equiv\text{C})$  band near  $2100\text{ cm}^{-1}$  and one singlet in their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, consistent with a *trans* stereochemistry. The spectral properties of these compounds are quite straightforward and do not require any further comment.

The reactions of **3a** and **3b** with  $\text{AgCF}_3\text{SO}_3$  in tetrahydrofuran in the presence of  $\text{HC}\equiv\text{CPh}$  were carried out. In both cases, a brown solid was obtained upon workup of the reaction mixture and treatment with  $\text{Na}[\text{BPh}_4]$  in ethanol. No pure product could be isolated by recrystallization of the solids from the reaction of **3b**, but in the case of **3a**, two different products were obtained by careful recrystallization of the crude material from dichloromethane/ethanol. One of them was grayish, very insoluble in organic solvents, displaying one broad, strong  $\nu(\text{C}\equiv\text{C})$  band at  $2048\text{ cm}^{-1}$ . The very poor solubility of this material, presumably polymeric, prevented its study in solution by NMR spectroscopy, and hence it remains uncharacterized. At variance with this, the other product obtained from the reaction mixture was a yellow, crystalline substance, slightly soluble in polar organic solvents, which was isolated in moderate yield. This material displays two  $\nu(\text{C}\equiv\text{C})$  bands at  $2000$  and  $1967\text{ cm}^{-1}$  in its IR spectrum. The  $^1\text{H}$  NMR spectrum of this compound shows signals attributable to phosphine and  $[\text{BPh}_4]^-$  protons, plus some multiplets in the aromatic region due to phenyl ring protons of an alkynyl ligand. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (Figure 2) consists of one singlet at  $92.7\text{ ppm}$  and of a complex doublet of multiplets centered at  $26.2\text{ ppm}$ . The spectrum is temperature dependent, and the singlet at  $92.7\text{ ppm}$  becomes two doublets at  $-90\text{ }^\circ\text{C}$ , whereas at this temperature the doublet of multiplets becomes broad and unresolved. These spectral data and the microanalysis figures were uninterpretable until the X-ray crystal structure for this compound was determined. Then, the yellow compound turned out to be an unexpected tetranuclear heterobimetallic complex of formula  $[\{\text{Ru}(\text{dippe})_2(\mu\text{-Cl})_3(\sigma,\eta^2\text{-C}\equiv\text{CPh})_2\{\text{Ag}_2(\mu\text{-dippe})\}] [\text{BPh}_4]$  (**4**) rather than a vinyl-vinylidene or butenyne derivative. The structure of the complex cation is shown in Figure 3. Selected bond lengths and angles are listed in Table 2. The structure consists of one binuclear core of the type  $[\{\text{Ru}(\text{C}\equiv\text{CPh})(\text{dippe})\}_2(\mu\text{-Cl})_3]^-$ , in which each of the Ru atoms adopts a distorted-octahedral coordination, and two of these octahedrons share one face by means of three bridging chloride ligands. The alkynyl groups are almost linearly assembled to ruthenium, the triple  $\text{C}\equiv\text{C}$  bond of each of the alkynyl ligands being  $\eta^2$ -bonded to one silver atom, and the two silver atoms linked together by one bridging dippe ligand. The distances  $\text{Ru}-\text{C}$  ( $1.88(2)$  and  $2.01(2)\text{ \AA}$ ) compare well in general with data in the literature for other ruthenium alkynyls,<sup>10,18,20,21</sup> whereas the  $\text{C}\equiv\text{C}$  bond distances ( $1.30(2)$  and  $1.20(2)\text{ \AA}$ ) are, as expected, slightly longer than those reported due to the effect of  $\eta^2$  coordination to silver. All the  $\text{Ag}-\text{C}$  separations are very similar:  $\text{Ag}(1)-\text{C}(1) = 2.39(2)\text{ \AA}$ ,  $\text{Ag}(1)-\text{C}(2) = 2.42\text{ \AA}$ ,  $\text{Ag}(2)-\text{C}(23) = 2.30(2)\text{ \AA}$ ,  $\text{Ag}(2)-\text{C}(24) = 2.45(2)\text{ \AA}$ . This sequence indicates that the silver- $\pi$ -alkyne bond is essentially symmetrical, as has been found in other bimetallic complexes containing silver bound to a metal-alkynyl moiety, e.g.  $[\{\text{C}_5\text{H}_4\text{SiMe}_3\}_2\text{Ti}(\mu,\sigma\text{-}\eta^2\text{-C}\equiv\text{CSiMe}_3)_2\text{-Ag}(\text{THF})][\text{BF}_4]$ ,<sup>22</sup> in which the  $\text{Ag}-\text{C}$  bond lengths range from  $2.293(6)$  to  $2.472(8)\text{ \AA}$ . The  $\text{Ag}(1)-\text{Ag}(2)$ ,  $\text{Ag}(1)-\text{Cl}(1)$ , and  $\text{Ag}(2)-\text{Cl}(3)$  separations,  $3.106(2)$ ,  $2.770(5)$ , and  $2.842(5)\text{ \AA}$ , respectively, are very close to the value of the sum of covalent radii for the corresponding atoms, suggesting that some sort of bonding interaction might be possible. However, the long  $\text{Ru}(1)-\text{Ru}(2)$  bond distance,  $3.436(2)\text{ \AA}$ , does not indicate any chemically significant direct metal-metal bond.

Once the structure of **4** is known, analytical data can be satisfactorily explained. The use of an excess of phenylacetylene in the synthesis of this compound apparently does not make any sense, and in fact, **4** was also obtained in the absence of added alkyne. However, the yield was very low compared to when the reaction



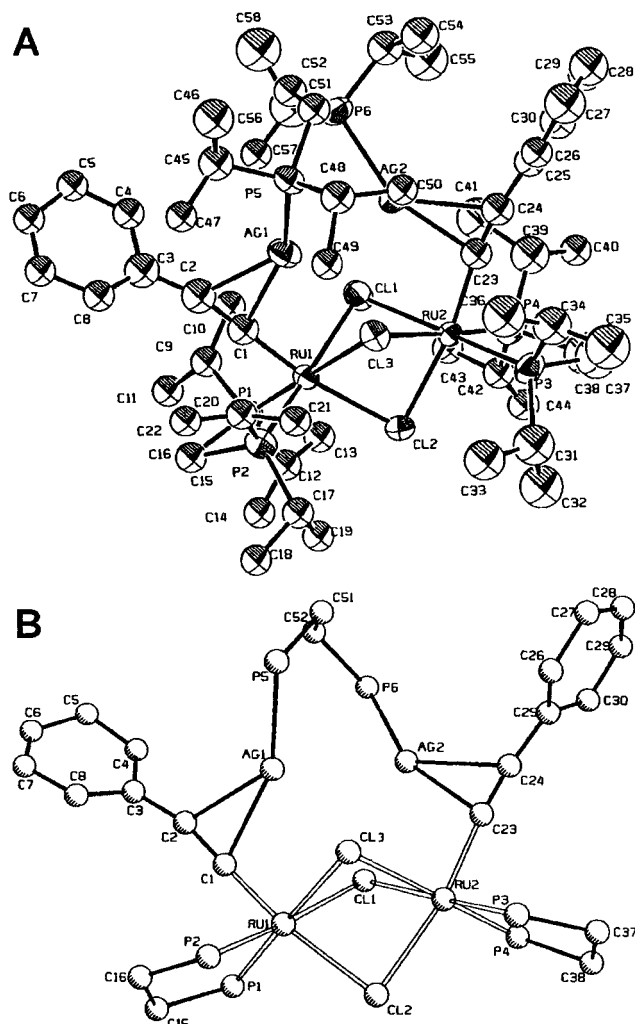
**Figure 2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of compound **4** in  $\text{CD}_2\text{Cl}_2$ : (A) at room temperature; (B) at  $183\text{ K}$ .

nium alkynyls,<sup>10,18,20,21</sup> whereas the  $\text{C}\equiv\text{C}$  bond distances ( $1.30(2)$  and  $1.20(2)\text{ \AA}$ ) are, as expected, slightly longer than those reported due to the effect of  $\eta^2$  coordination to silver. All the  $\text{Ag}-\text{C}$  separations are very similar:  $\text{Ag}(1)-\text{C}(1) = 2.39(2)\text{ \AA}$ ,  $\text{Ag}(1)-\text{C}(2) = 2.42\text{ \AA}$ ,  $\text{Ag}(2)-\text{C}(23) = 2.30(2)\text{ \AA}$ ,  $\text{Ag}(2)-\text{C}(24) = 2.45(2)\text{ \AA}$ . This sequence indicates that the silver- $\pi$ -alkyne bond is essentially symmetrical, as has been found in other bimetallic complexes containing silver bound to a metal-alkynyl moiety, e.g.  $[\{\text{C}_5\text{H}_4\text{SiMe}_3\}_2\text{Ti}(\mu,\sigma\text{-}\eta^2\text{-C}\equiv\text{CSiMe}_3)_2\text{-Ag}(\text{THF})][\text{BF}_4]$ ,<sup>22</sup> in which the  $\text{Ag}-\text{C}$  bond lengths range from  $2.293(6)$  to  $2.472(8)\text{ \AA}$ . The  $\text{Ag}(1)-\text{Ag}(2)$ ,  $\text{Ag}(1)-\text{Cl}(1)$ , and  $\text{Ag}(2)-\text{Cl}(3)$  separations,  $3.106(2)$ ,  $2.770(5)$ , and  $2.842(5)\text{ \AA}$ , respectively, are very close to the value of the sum of covalent radii for the corresponding atoms, suggesting that some sort of bonding interaction might be possible. However, the long  $\text{Ru}(1)-\text{Ru}(2)$  bond distance,  $3.436(2)\text{ \AA}$ , does not indicate any chemically significant direct metal-metal bond.

Once the structure of **4** is known, analytical data can be satisfactorily explained. The use of an excess of phenylacetylene in the synthesis of this compound apparently does not make any sense, and in fact, **4** was also obtained in the absence of added alkyne. However, the yield was very low compared to when the reaction

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**Figure 3.** (A) ORTEP drawing (50% probability thermal ellipsoids) of the tetranuclear cationic complex  $[\{\text{Ru}(\text{dippe})\}_2(\mu\text{-Cl})_3(\sigma,\eta^2\text{-C}\equiv\text{CPh})_2\{\text{Ag}_2(\mu\text{-dippe})\}]^+$ . Hydrogen atoms are omitted. (b) Diagrammatic view of the same complex with isopropyl groups omitted, for the sake of clarity.

was performed with addition of phenylacetylene, for undetermined reasons. Considering the crystal structure of **4**, it is also possible to rationalize the NMR spectral data. Thus, the singlet at 92.7 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at room temperature (Figure 2A) corresponds to the phosphorus atoms attached to ruthenium, whereas the complex doublet of multiplets at higher field is hence attributable to the silver-bound phosphorus atoms. The complex splitting pattern displayed by this resonance is due to the occurrence of three possible combinations of NMR-active  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  nuclei and also to the fact that the  $\text{PCH}_2\text{CH}_2\text{P}$  backbone linking the silver nuclei is not long enough to isolate magnetically each component, leading to a second-order splitting pattern. A similar pattern has been reported for the binuclear silver–phosphine complex  $[\{\text{Ag}(\text{OAc})\}_2(\mu\text{-dppm})]$ .<sup>23</sup> In our case, the spectrum was analyzed by computer simulation (Figure 4), as the sum of three partial subspectra, each of them corresponding to an AA'XX' spin system where A and A' are

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for  $[\{\text{Ru}(\text{dippe})\}_2(\mu\text{-Cl})_3(\sigma,\eta^2\text{-C}\equiv\text{CPh})_2\{\text{Ag}_2(\mu\text{-dippe})\}][\text{BPh}_4]$  with Estimated Standard Deviations in Parentheses

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| Ag(1)–Cl(3)       | 2.770(5) | Ru(1)–C(1)        | 1.88(2)  |
| Ag(1)–P(5)        | 2.385(6) | Ru(2)–Cl(1)       | 2.546(5) |
| Ag(1)–C(1)        | 2.39(2)  | Ru(2)–Cl(2)       | 2.496(5) |
| Ag(1)–C(2)        | 2.42(2)  | Ru(2)–Cl(3)       | 2.554(5) |
| Ag(2)–P(6)        | 2.400(5) | Ru(2)–P(3)        | 2.267(5) |
| Ag(2)–C(23)       | 2.30(2)  | Ru(2)–P(4)        | 2.239(6) |
| Ag(2)–C(24)       | 2.45(2)  | Ru(2)–C(23)       | 2.01(2)  |
| Ru(1)–Cl(1)       | 2.564(5) | C(1)–C(2)         | 1.30(3)  |
| Ru(1)–Cl(2)       | 2.493(5) | C(2)–C(3)         | 1.41(3)  |
| Ru(1)–Cl(3)       | 2.555(5) | C(23)–C(24)       | 1.20(2)  |
| Ru(1)–P(1)        | 2.256(5) | C(24)–C(25)       | 1.42(3)  |
| Ru(1)–P(2)        | 2.257(6) |                   |          |
| Ag(2)–Ag(1)–Cl(3) | 72.8(1)  | Cl(3)–Ru(1)–P(1)  | 177.8(2) |
| Ag(2)–Ag(1)–P(5)  | 89.8(1)  | Cl(3)–Ru(1)–P(2)  | 97.2(2)  |
| Ag(2)–Ag(1)–C(1)  | 111.4(5) | Cl(3)–Ru(1)–C(1)  | 96.3(6)  |
| Ag(2)–Ag(1)–C(2)  | 128.2(5) | P(1)–Ru(1)–P(2)   | 84.5(2)  |
| Cl(3)–Ag(1)–P(5)  | 115.7(2) | P(1)–Ru(1)–C(1)   | 85.2(6)  |
| Cl(3)–Ag(1)–C(1)  | 80.1(5)  | P(2)–Ru(1)–C(1)   | 86.6(6)  |
| Cl(3)–Ag(1)–C(2)  | 110.2(5) | Cl(1)–Ru(2)–Cl(2) | 80.3(2)  |
| P(5)–Ag(1)–C(1)   | 157.2(5) | Cl(1)–Ru(2)–Cl(3) | 77.8(2)  |
| P(5)–Ag(1)–C(2)   | 127.4(6) | Cl(1)–Ru(2)–P(3)  | 177.4(2) |
| C(1)–Ag(1)–C(2)   | 31.4(6)  | Cl(1)–Ru(2)–P(4)  | 96.9(2)  |
| Ag(1)–Ag(2)–P(6)  | 87.6(2)  | Cl(1)–Ru(2)–C(23) | 94.0(5)  |
| Ag(1)–Ag(2)–C(23) | 113.2(5) | Cl(2)–Ru(2)–Cl(3) | 79.4(2)  |
| Ag(1)–Ag(2)–C(24) | 28.7(5)  | Cl(2)–Ru(2)–P(3)  | 99.8(2)  |
| P(6)–Ag(2)–C(23)  | 156.4(5) | Cl(2)–Ru(2)–P(4)  | 100.5(2) |
| P(6)–Ag(2)–C(24)  | 128.3(5) | Cl(2)–Ru(2)–C(23) | 168.7(6) |
| C(23)–Ag(2)–C(24) | 29.1(6)  | Cl(3)–Ru(2)–P(3)  | 99.6(2)  |
| Cl(1)–Ru(1)–Cl(2) | 80.0(2)  | Cl(3)–Ru(2)–P(4)  | 174.7(2) |
| Cl(1)–Ru(1)–Cl(3) | 77.5(2)  | Cl(3)–Ru(2)–C(23) | 89.9(6)  |
| Cl(1)–Ru(1)–P(1)  | 100.9(2) | P(3)–Ru(2)–P(4)   | 85.7(2)  |
| Cl(1)–Ru(1)–P(2)  | 174.1(2) | P(3)–Ru(2)–C(23)  | 85.5(5)  |
| Cl(1)–Ru(1)–C(1)  | 91.3(6)  | P(4)–Ru(2)–C(23)  | 89.8(6)  |
| Cl(2)–Ru(1)–Cl(3) | 79.4(2)  | Ru(1)–C(1)–C(2)   | 176(1)   |
| Cl(2)–Ru(1)–P(1)  | 98.9(2)  | C(1)–C(2)–C(3)    | 164(2)   |
| Cl(2)–Ru(1)–P(2)  | 101.8(2) | Ru(2)–C(23)–C(24) | 173(1)   |
| Cl(2)–Ru(1)–C(1)  | 170.9(6) | C(23)–C(24)–C(25) | 171(2)   |

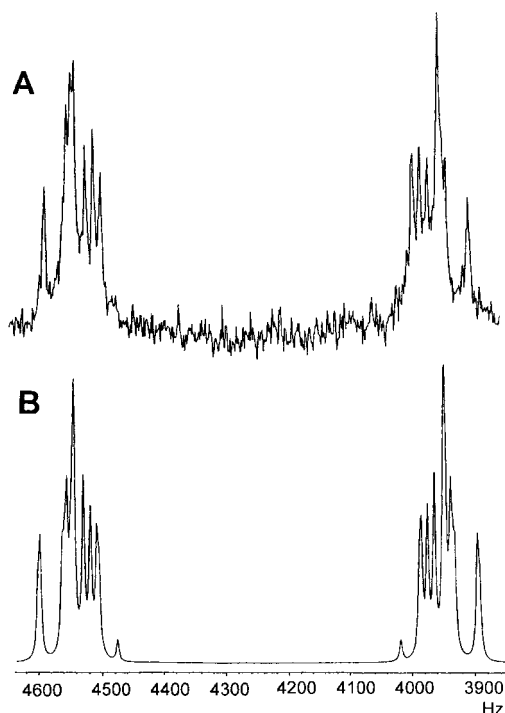
the magnetically inequivalent phosphorus atoms and X and X' correspond to silver nuclei in the three possible isotopic combinations  $^{107}\text{Ag}/^{107}\text{Ag}$ ,  $^{109}\text{Ag}/^{109}\text{Ag}$ , and  $^{107}\text{-Ag}/^{109}\text{Ag}$ , the last having a statistical weight double that of the other two. From this spectral analysis,  $^1J(\text{P},^{107}\text{Ag})$  and  $^1J(\text{P},^{109}\text{Ag})$  were found to be 635 and 556 Hz, respectively, values that fall in the wide range of  $^1J(\text{P},^{107/109}\text{Ag})$  coupling constants reported in the literature for other silver–phosphine complexes.<sup>22–24</sup> It is worth mentioning the large  $^3J(\text{P},\text{P})$  coupling constant of 53 Hz and the negative value of the long-distance coupling constants  $^4J(\text{P},^{107}\text{Ag})$  and  $^4J(\text{P},^{109}\text{Ag})$ , –15 and –10 Hz, respectively. These negative silver–phosphorus coupling constants might arise from through-space coupling given the relative proximity of Ag(1) and P(6) (3.846(6) Å) and of Ag(2) and P(5) (3.911(6) Å), or even through a silver–silver interaction (separation of only 3.106(2) Å) rather than through a sequence of four bonds.

The temperature dependence of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** has been interpreted in terms of its solid-state crystal structure, in which there is no symmetry plane bisecting the P–Ru–P moieties due to the particular conformation of the  $\text{PCH}_2\text{CH}_2\text{P}$  backbone linking the two silver atoms, and therefore the two phosphorus atoms of each dippe ligand attached to a ruthenium atom should be nonequivalent. This is what is observed

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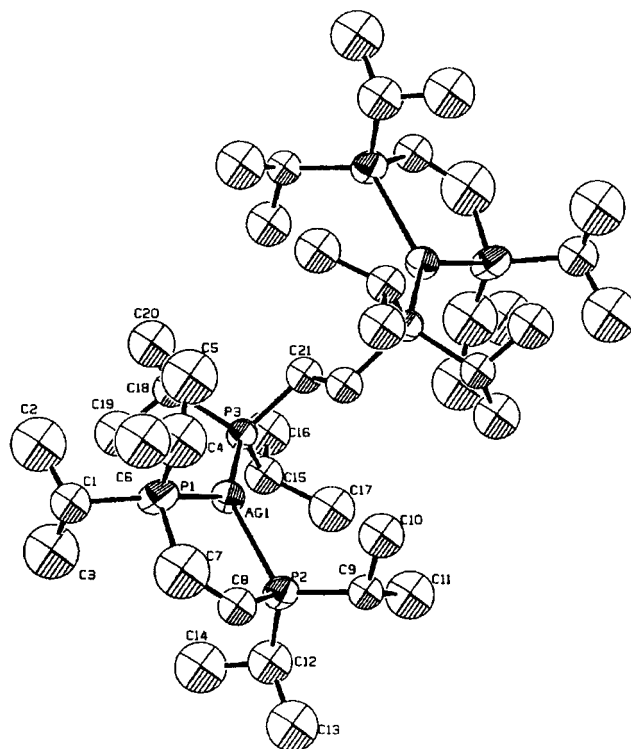


**Figure 4.** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of compound **4** in  $\text{CD}_2\text{Cl}_2$  showing the resonance for the silver-bound phosphorus atoms: (A) experimental; (B) simulated. Simulation parameters: [AA'XX'] spin system;  $\delta(\text{P}_A) = \delta(\text{P}_A) = 4242.1$  Hz (26.2 ppm at 161.9 MHz);  $^3J(\text{P}_A, \text{P}_A) = 53$  Hz;  $^1J(\text{P}_A, ^{107}\text{Ag}) = ^1J(\text{P}_A, ^{109}\text{Ag}) = 635$  Hz;  $^1J(\text{P}_A, ^{109}\text{Ag}) = ^1J(\text{P}_A, ^{107}\text{Ag}) = 556$  Hz;  $^4J(\text{P}_A, ^{107}\text{Ag}) = ^4J(\text{P}_A, ^{109}\text{Ag}) = -15$  Hz;  $^4J(\text{P}_A, ^{109}\text{Ag}) = ^4J(\text{P}_A, ^{107}\text{Ag}) = -10$  Hz.

at low temperature, but at room temperature there is possibly a rapid change in the conformation of the dippe ligands due to the motion of the atoms in solution, and this process, which is rapid on the NMR time scale, would render all ruthenium-bound phosphorus atoms equivalent.

The formation of a heterobimetallic species such as **4** has no precedents in the literature, as far as we are aware, and it is a possibility to be considered when silver salts are used as halide-scavenging reagents against ruthenium alkynyls. Very recently, the structurally related allenylidene complex  $[\{\text{Ru}=\text{C}=\text{C}=\text{CAr}_2(\text{PPh}_3)_2\}_2(\mu\text{-Cl})_3][\text{PF}_6]$  was reported by Dixneuf and co-workers,<sup>25</sup> although this material contains no silver. To explain the formation of **4** starting from **3a**, we must assume that degradation of the alkynyl complex must occur to some extent, releasing dippe and also chloride, the result of such degradation being presumably the grayish material obtained as a byproduct along with **4**.

Complex **4** can be also regarded as the product of the addition of the coordinatively unsaturated complex  $[\text{Ag}_2(\mu\text{-dippe})]^{2+}$  to the  $\pi\text{C}\equiv\text{C}$  bonds of an anionic binuclear ruthenium alkynyl, namely  $[\{\text{Ru}(\text{C}\equiv\text{CPh})(\text{dippe})_2(\mu\text{-Cl}_3)\}^-]$ . To get a better understanding of the coordination modes of dippe to Ag, the reaction of silver nitrate with dippe in methanol was studied, leading to the isolation of the binuclear complex  $[\{\text{Ag}(\text{dippe})\}_2(\mu\text{-dippe})][\text{BPh}_4]_2$  (**5**) in very good yields. Colorless crystals of this compound of analytical purity, suitable for single-crystal



**Figure 5.** ORTEP drawing of the binuclear cation  $[\{\text{Ag}(\text{dippe})\}_2(\mu\text{-dippe})]^{2+}$  with 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for  $[\{\text{Ag}(\text{dippe})\}_2(\mu\text{-dippe})][\text{BPh}_4]_2$  with Estimated Standard Deviations in Parentheses

|                 |          |                 |          |
|-----------------|----------|-----------------|----------|
| Ag(1)–P(1)      | 2.500(4) | Ag(1)–P(3)      | 2.411(4) |
| Ag(1)–P(2)      | 2.492(4) |                 |          |
| P(1)–Ag(1)–P(2) | 86.1(1)  | P(2)–Ag(1)–P(3) | 135.7(1) |
| P(1)–Ag(1)–P(3) | 138.2(1) |                 |          |

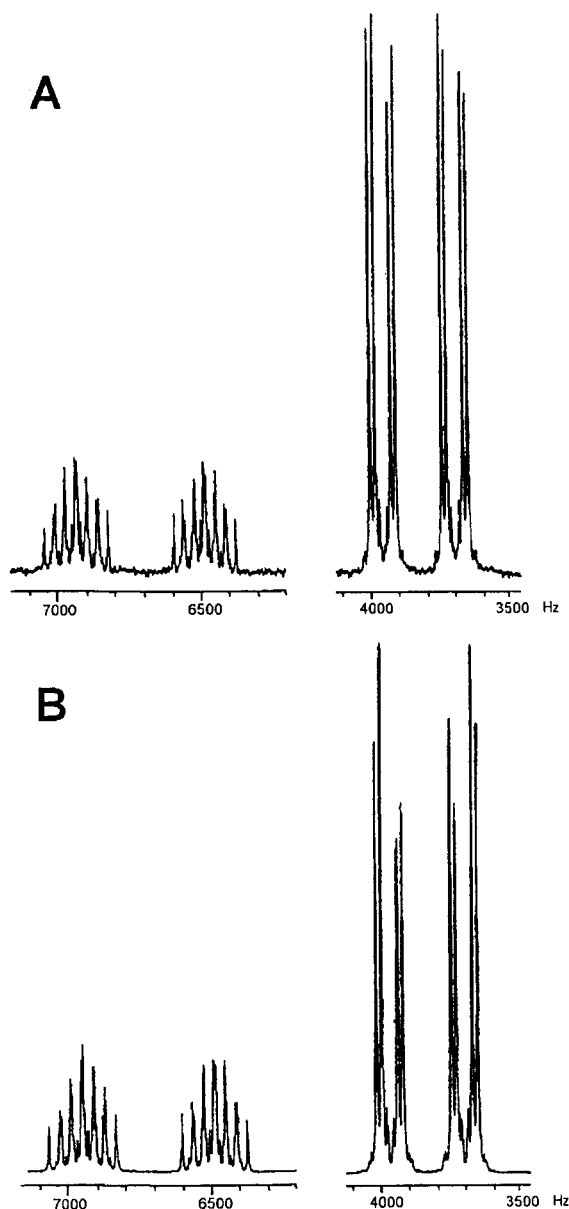
X-ray structure determination, were obtained by recrystallization from acetone/ethanol. The structure of the cation  $[\{\text{Ag}(\text{dippe})\}_2(\mu\text{-dippe})]^{2+}$  is shown in Figure 5. Selected bond lengths and angles are listed in Table 3. Each of the silver atoms adopts a *Y*-distorted trigonal-planar coordination, with one of the dippe ligands acting as a bridge between the two metal centers, in a fashion essentially identical with that found recently in the isoelectronic Pd complex  $[\{\text{Pd}(\text{dippe})\}_2(\mu\text{-dippe})]^{2+}$ <sup>26</sup> by X-ray crystallography. The asymmetric unit consists of one  $[\text{BPh}_4]^-$  anion and half of the dinuclear cation, with a 2-fold axis bisecting the C–C bond of the ethane chain in the bridging dippe. The angle P(1)–Ag(1)–P(2) of the chelating phosphine is 86.1(1)°, smaller than the ideal trigonal 120° and even than 90°. All distances Ag–P are shorter than those corresponding to a  $\sigma$ -bond (2.62 Å),<sup>27</sup> indicative of considerable  $d\pi\text{-}d\pi$  interactions. There are not many previous reports of trigonal-planar structures with only three P donor atoms attached to Ag.<sup>27,28</sup> In fact, genuine three-coordinate silver complexes are rather scarce in

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**Figure 6.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of compound **5** in  $\text{CD}_3\text{-COCD}_3$ : (A) experimental; (B) simulated. Simulation parameters:  $[\text{A}_2\text{BX}]_2$  spin system;  $\delta(\text{P}_\text{A}) = \delta(\text{P}'_\text{A}) = 6709.1$  Hz (41.4 ppm at 161.9 MHz);  $\delta(\text{P}_\text{B}) = \delta(\text{P}'_\text{B}) = 3825.8$  Hz (23.6 ppm at 161.9 MHz);  $^2J(\text{P}_\text{A}, \text{P}_\text{B}) = ^2J(\text{P}'_\text{A}, \text{P}'_\text{B}) = 73.2$  Hz;  $^3J(\text{P}_\text{A}, \text{P}'_\text{A}) = 42$  Hz;  $^1J(\text{P}_\text{A}, ^{107}\text{Ag}) = ^1J(\text{P}'_\text{A}, ^{107}\text{Ag}) = 480$  Hz;  $^1J(\text{P}_\text{A}, ^{109}\text{Ag}) = ^1J(\text{P}'_\text{A}, ^{109}\text{Ag}) = 410$  Hz;  $^1J(\text{P}_\text{B}, ^{107}\text{Ag}) = ^1J(\text{P}'_\text{B}, ^{107}\text{Ag}) = 273.5$  Hz;  $^1J(\text{P}_\text{B}, ^{109}\text{Ag}) = ^1J(\text{P}'_\text{B}, ^{109}\text{Ag}) = 236.8$  Hz;  $^4J(\text{P}_\text{A}, ^{107}\text{Ag}) = ^4J(\text{P}'_\text{A}, ^{107}\text{Ag}) = 0$  Hz;  $^4J(\text{P}_\text{A}, ^{109}\text{Ag}) = ^4J(\text{P}'_\text{A}, ^{109}\text{Ag}) = 0$  Hz.

comparison with those having coordination numbers 2 and 4,<sup>29</sup> the coordination number and geometry being greatly determined by the bulkiness of the phosphine ligand and by the ability of any present counterion to

additionally interact with the metal, as well as by the length of the hydrocarbon chain between the two phosphorus atoms in the case of bidentate phosphine ligands.<sup>24,30</sup>

The binuclear structure displayed by **5** is maintained in solution, as inferred from its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, which resembles that observed for the related complex  $[\{\text{Pd}(\text{dippe})\}_2(\mu\text{-dippe})]$ ,<sup>26</sup> but further complicated by the presence of the two possible NMR-active nuclei  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ . Thus, the observed  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum is again second order, as in the case of compound **4**, and it consists of two groups of multiplets attributable to the phosphorus atoms of the chelating (23.6 ppm) and bridging (41.4 ppm) phosphines, respectively (Figure 6). This complex pattern was satisfactorily analyzed by computer simulation, as the weighted sum of three partial subspectra, one for each possible  $^{107}\text{Ag}/^{109}\text{Ag}$  combination, corresponding to  $[\text{AB}_2\text{X}]_2$  spin systems, X being the silver nucleus. Double weight was given to the partial subspectrum corresponding to the combination  $^{107}\text{Ag}/^{109}\text{Ag}$ , whereas single weight was allowed for  $^{107}\text{Ag}/^{107}\text{Ag}$  and  $^{109}\text{Ag}/^{109}\text{Ag}$  combinations, as was also done for the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectral simulation for compound **4**. From the spectral analysis,  $^1J(\text{P}_\text{A}, ^{107}\text{Ag})$  and  $^1J(\text{P}_\text{A}, ^{109}\text{Ag})$  were found to be 480 and 410 Hz, respectively, whereas the values for  $^1J(\text{P}_\text{B}, ^{107}\text{Ag})$  and  $^1J(\text{P}_\text{B}, ^{109}\text{Ag})$  were 273.5 and 236.8 Hz. The corresponding values for  $^2J(\text{P}_\text{A}, \text{P}_\text{B})$  and  $^3J(\text{P}_\text{A}, \text{P}_\text{A}')$  were 73.2 and 42 Hz. It is interesting to note that the values found for  $^1J(\text{P}, ^{107}\text{Ag})/^1J(\text{P}, ^{109}\text{Ag})$  throughout this work are very sensitive to the Ag–P separations, ranging from 273.5/236.8 Hz for Ag–P bond distances of *ca.* 2.50 Å to 635/556 Hz when the bond lengths are reduced to *ca.* 2.39 Å. The fact that no long-distance coupling constants  $^4J(\text{P}, ^{107}\text{Ag})/^4J(\text{P}, ^{109}\text{Ag})$  have been observed for this compound, at variance with the case for **4**, is in support of the idea that such silver–phosphorus coupling constants arise from through-space coupling or by silver–silver spin interaction rather than by coupling through four bonds, or otherwise such coupling should be also present in the case of compound **5**. For this complex no spectral evidence for dissociation processes in solution leading to other silver–phosphine species such as  $[\text{Ag}(\text{dippe})_2]^+$  and  $[\text{Ag}_2(\mu\text{-dippe})]^{2+}$  was obtained.

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**Supporting Information Available:** Listings of atomic coordinates, thermal parameters, and bond lengths and angles for **1b**, **4**, and **5** (17 pages). Ordering information is given on any current masthead page.

OM9801305

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