

Synthesis of $[Au_3]^{3+}$, $[Au_2Ag]^{3+}$, and $[Au_2Cu]^{3+}$ Loose Clusters

José Vicente, María-Teresa Chicote,* and María-Cristina Lagunas

Grupo de Química Organometálica, Departamento de Química Inorgánica, Universidad de Murcia, Apdo 4021, Murcia 30071, Spain

Received January 5, 1993

(2-Pyridylmethyl)triarylphosphonium salts, $[R_3PCH_2(py-2)]X$ ($py =$ pyridyl-2) react (i) with AgX , in 1:1 or 2:1 molar ratios, to give N-coordinated complexes $[AgX_2(py-CH_2PTO_3-2)]$ [$X = ClO_4$, $To = C_6H_4Me-4$ (1)] or $[AgX_3\{py-CH_2PTO_3-2\}_2]$ [$X = ClO_4$ (2a), $CF_3SO_3 = TfO$ (2b)], respectively, or (ii) with $[AuCl_n(tht)]$ ($n = 1$ or 3, $tht =$ tetrahydrothiophene) to afford $[R_3PCH_2(py-2)][AuCl_{n+1}]$ ($n = 1$, $R = Ph$ (5a), To (5b); $n = 3$, $R = Ph$ (6a), To (6b)) or (iii) with $Tl(acac)$ (1:1, $acacH =$ acetylacetone, $X = AuCl_2$) or $ppn[Au(acac)_2]$ [2:1, $ppn =$ bis(triphenylphosphoranylidene)ammonium] or $[Au(acac)(PR'_3)]$ (1:2) to yield the ylide complexes $[AuCl\{CH-(PR'_3)\}(py-2)]$ [$R = Ph$ (7a), To (7b)], $[Au\{CH(PTO_3)(py-2)\}_2]ClO_4$ (8), $[(AuPR'_3)_2\{\mu\cdot\{C(PR'_3)(py-2)\}\}]ClO_4$ [$R = R' = Ph$ (9a), $R = To$, $R' = C_6H_4OMe-4 = pmp$ (9b)], respectively. Complex 1 reacts with PR'_3 (1:1) to give $[Ag(ClO_4)_2\{PR'_3\}\{py-CH_2PTO_3-2\}]$ [$R' = Ph$ (3a), pmp (3b)]. 3a reacts with $[AuCl(tht)]$ (1:1) leading to $[Au(PPh_3)\{py-CH_2PTO_3-2\}](ClO_4)_2$ (4). Complex 9a reacts with $AgNO_3$ (1:1) to give $[(AuPPh_3)_2\{\mu\cdot\{C(PPh_3)(py-2)\}\}\mu\cdot\{Ag(\eta^2-O_2NO)(OCIO_3)\}]$ (10), which reacts with $[AuCl(PPh_3)]$ and $NaClO_4\cdot H_2O$ (1:1:1) leading to $[(AuPPh_3)_2\{\mu\cdot\{C(PPh_3)(py-2)\}\}(AuPPh_3)](ClO_4)_2\cdot H_2O$ (11). Complexes 9a and 9b react with $CuCl$ to give $[(AuPR'_3)_2\{\mu\cdot\{C(PR'_3)(py-2)\}\}(CuCl)](ClO_4)$ [$R = R' = Ph$ (12a); $R = To$, $R' = pmp$ (12b)], respectively. The X-ray crystal structures of 9b and 10- $CH_2Cl_2\cdot H_2O$ at 178 K show that weak interactions between both Au centers occur [2.949(1) and 3.078(1) Å, respectively]. The configuration of the N lone pair with respect to the Au_2 moiety is *anti* in 9b while *syn* in 10 because two $Au\cdots Ag$ weak interactions [2.926(1), 3.006(1) Å] seem to act as a conformation-determining force.

Introduction

Weak attractive $Au(I)\cdots Au(I)$ interactions¹ lead to the formation of very interesting gold(I) complexes. Thus, for example, hypercoordinated compounds such as $[C(AuL)]^+$, $[RC(AuL)_4]^+$, $[C(AuL)_6]^{2+}$, $[N(AuL)]^{2+}$, $[P(AuL)]^{2+}$, or $[RP(AuL)]^{2+}$ (where $R =$ aryl, $L =$ triarylphosphine), prepared by Schmidbaur,² owe their stabilities to such weak interactions. The tendency of the AuL^+ units to form aggregates is termed “aurophilicity”,^{1b} and it has been suggested that it arises in part from relativistic effects.³ However, as Schmidbaur points out,^{1b} this term will not survive time. In fact, similar interactions have been found in some complexes containing $[Au_2Ag_2]^{4+}$ ring moieties with⁴ or without⁵ bridging ligands and in some $Au(I)/Cu(I)$ ⁶ and $Ag(I)/Cu(I)$ ⁷ polynuclear complexes. All these species have in common a cluster of closed-shell d^{10} centers without the metal-metal bonds present in conventional clusters. We prefer to call them “loose clusters”. These, and the trinuclear $[Au_2Ag]^{3+}$ complex we report in this paper, suggest that we should use a new word (for example, numismophilicity from the Latin *numisma* = money, coin) to account for this common feature of the three coinage metals. These weak bonds are different from those they form in some clusters in which low valent metal centers behave as basic electron donors towards the acidic $Cu(I)$, $Ag(I)$, or $Au(I)$ centers.⁸

- (1) (a) Jones, P. G. *Gold Bull.* 1981, 14, 102, 159; 1983, 16, 114; 1986, 19, 46. (b) Schmidbaur, H. *Gold Bull.* 1990, 23, 11.
- (2) Schmidbaur, H. *Inorg. Chem.* 1992, 31, 2370 and references therein.
- (3) Pykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* 1979, 12, 276. Pykkö, P. *Chem. Rev.* 1988, 88, 563.
- (4) Abu-Salah, O. M.; Knobler, C. B. *J. Organomet. Chem.* 1986, 302, C10.
- (5) (b) Usón, R.; Laguna, A.; Laguna, M.; Usón, A.; Jones, P. G.; Erdbrügger, C. F. *Organometallics* 1987, 6, 1778. (c) Usón, R.; Laguna, A.; Laguna, M.; Manzano, B. R.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* 1984, 285.
- (6) See, for example: Abu-Salah, O. M.; Al-Ohaly, A. R. A.; Knobler, C. B. *J. Chem. Soc., Chem. Commun.* 1985, 502.
- (7) See, for example: Abu-Salah, O. M.; Hussain, M. S.; Schlemper, E. O. *J. Chem. Soc., Chem. Commun.* 1988, 212.

In this paper we report the synthesis of complexes derived from cationic phosphonium salts $[R_3PCH_2(py-2)]X$ ($R =$ aryl, $py-2$ (pyridyl-2); $X = ClO_4$, CF_3SO_3). We chose these ligands because they could coordinate through the nitrogen atom and also, by a single or double deprotonation process, through the methylene carbon atom. Thus, up to three metal centers could be arranged near enough as to establish metal-metal contacts. The synthesis of homo- or hetero-, -di- and -trinuclear complexes have been attempted. X-ray crystal structures of two new complexes containing $[Au_2]^+$ or $[Au_2Ag]^+$ moieties support the above mentioned numismophilicity. Some of these results have been the subject of a preliminary communication.⁹ When this article was already written a paper of Schmidbaur appeared in which a similar strategy, but involving N-H instead of C-H activation processes, was used to prepare, from 8-aminoquinoline, one tri- and one tetranuclear gold(I) complex.¹⁰

Experimental Section

The IR, the Au analyses, conductance measurements, and melting point determinations were carried out as described elsewhere.¹¹ Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ on a Varian Unity 300 and conductivity measurements were made in acetone. Chemical shifts are in ppm and referred to TMS [1H and $^{13}C\{^1H\}$] or H_3PO_4 [$^{31}P\{^1H\}$]. C, H, and N analyses were carried out with a Carlo Erba EA 1108 or a Perkin-Elmer 240C microanalyzer.

Caution! Perchlorato complexes are potentially explosive. Preparations in larger scale than that here reported should be avoided.

$[Ag(ClO_4)_2(py-CH_2PTO_3-2)]$ (1). To a solution of $[To_3PCH_2(py-2)]ClO_4$ (166.4 mg, 0.335 mmol) in acetone (10 mL) was added $AgClO_4$

- (8) See, for example: Carreño, R.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *Organometallics* 1992, 11, 2923. Pergola, R. D.; Demartin, F.; Garlaschelli, L.; Manassero, M.; Martinengo, S.; Masciocchi, N.; Sansoni, M. *Organometallics*, 1991, 10, 2239 and references therein.
- (9) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* 1991, 1730.
- (10) Schmidbaur, H.; Kolb, A.; Bissinger, P. *Inorg. Chem.* 1992, 31, 4370.
- (11) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* 1991, 2579.

(69.6 mg, 0.335 mmol). The resulting suspension was stirred in the dark for 2 h, the solvent was removed under vacuum, and the residue was stirred with diethyl ether (20 mL) and filtered. The white solid obtained was recrystallized from dichloromethane/diethyl ether to give **1** (208 mg, 88% yield). Anal. Calcd for $C_{27}H_{27}AgCl_2NO_8P$: C, 46.12; H, 3.87; N, 1.99. Found: C, 46.28; H, 4.27; N, 2.13. Mp: 246 °C dec. $\Delta_M = 257 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data (in CD_2Cl_2): ^1H (200 MHz) 2.49 [s, 9H, Me(To)], 4.88 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.6 \text{ Hz}$), 7.3–7.5 (m, 14H, To + py), 7.85 [m, 1H, py (H4)], 8.44 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ (80 MHz) 24.0 (s) ppm.

[$\text{AgX}_3[\text{py}-\text{CH}_2\text{PTO}_3-2]_2$] [$\text{X} = \text{ClO}_4$ (**2a**), $\text{CF}_3\text{SO}_3 = \text{TfO}$ (**2b**)]. To a solution of [$\text{TO}_3\text{PCH}_2(\text{py}-2)$]X ($\text{X} = \text{ClO}_4$, 204.9 mg, 0.413 mmol, TfO, 520.5 mg, 0.954 mmol) in acetone (15 or 30 mL, respectively), was added AgClO_4 (42.8 mg, 0.206 mmol) or $\text{AgTfO}^{-1}/\text{PhMe}$ (144.5 mg, 0.477 mmol). The resulting suspension was stirred in the dark for 2 or 14 h, respectively. In the case of **2a**, the suspension was concentrated (1 mL) and diethyl ether (20 mL) added to complete the precipitation of a white solid which was collected and recrystallized from dichloromethane/diethyl ether (229 mg, 92% yield). In the case of **2b**, the suspension was concentrated to dryness and the residue stirred with diethyl ether (30 mL) to yield a white solid which was recrystallized from dichloromethane/diethyl ether (570 mg, 88% yield). Data for **2a** follow. Anal. Calcd for $C_{54}H_{54}AgCl_3N_2O_{12}P_2$: C, 54.08; H, 4.54; N, 2.34. Found: C, 53.96; H, 4.52; N, 2.24. Mp: 177 °C. $\Delta_M = 259 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H (200 MHz) 2.44 [s, 9H, Me(To)], 4.98 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.7 \text{ Hz}$), 7.3–7.6 (m, 14H, To + py), 7.75 [m, 1H, py (H4)], 8.34 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ (80 MHz) 22.0 (s) ppm. Data for **2b** follow. Anal. Calcd for $C_{57}H_{54}AgF_9N_2O_9P_2S_3$: C, 50.79; H, 4.04; N, 2.08. Found: C, 50.55; H, 4.19; N, 1.84. Mp: 103 °C. $\Delta_M = 298 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H 2.45 [s, 9H, Me(To)], 5.01 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.7 \text{ Hz}$), 7.1–7.6 (m, 14H, To + py), 7.77 [m, 1H, py (H4)], 8.32 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 22.45 (s) ppm.

[$\text{Ag}(\text{ClO}_4)_2(\text{PR}'_3)[\text{py}-\text{CH}_2\text{PTO}_3-2]$] [$\text{R}' = \text{Ph}$ (**3a**), pmp (**3b**)]. An acetone solution containing PR'_3 ($\text{R}' = \text{Ph}$, 183.3 mg, 0.699 mmol, pmp, 88.4 mg, 0.251 mmol) and **1** in equimolar amounts was stirred in the dark for 2 h and then concentrated (1 mL). Addition of diethyl ether (20 mL) gave **3a** (631 mg, 93% yield) or **3b** (220 mg, 83% yield) as white solids which were recrystallized from acetone/diethyl ether. Data for **3a** follow. Anal. Calcd for $C_{45}H_{42}AgCl_2NO_8P_2$: C, 55.98; H, 4.38; N, 1.45. Found: C, 56.03; H, 4.36; N, 1.36. Mp: 220 °C. $\Delta_M = 218 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($3.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H (200 MHz) 2.42 [s, 9H, Me(To)], 5.03 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.7 \text{ Hz}$), 7.3–7.5 (m, 29H, Ph + To + py), 7.81 [m, 1H, py (H4)], 8.56 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ (20 °C) 21.77 (s, PTO_3); at low temperatures **3a** is a mixture of two complexes which are in a 2:1 ratio in CDCl_3 and 8:1 in ($\text{CD}_3)_2\text{CO}$ (the resonances due to the most abundant isomer are followed by an asterisk) (-60 °C, CDCl_3) 11.69 (dd, PPH_3 , $^1J_{\text{AgP}} = 494.3 \text{ Hz}$, $^1J_{\text{AgP}} = 570.7 \text{ Hz}$), 14.36* (dd, PPH_3 , $^1J_{\text{AgP}} = 667.6$, $^1J_{\text{AgP}} = 770.5 \text{ Hz}$), 21.51 (s, PTO_3) ppm; [-60 °C, ($\text{CD}_3)_2\text{CO}$] 16.19 (dd, Ph_3 , $^1J_{\text{AgP}} = 493.6 \text{ Hz}$, $^1J_{\text{AgP}} = 569.9 \text{ Hz}$), 18.28* (dd, PPH_3 , $^1J_{\text{AgP}} = 676.7 \text{ Hz}$, $^1J_{\text{AgP}} = 780.5 \text{ Hz}$), 27.18 (s, PTO_3) ppm. Data for **3b** follow. Anal. Calcd for $C_{48}H_{48}AgCl_2NO_{11}P_2$: C, 54.61; H, 4.58; N, 1.33. Found: C, 54.43; H, 4.58; N, 1.36. Mp 184 °C. $\Delta_M = 261 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H 2.44 [s, 9H, Me(To)], 3.83 [s, 9H, OMe(pmp)], 5.00 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.7 \text{ Hz}$), 6.9–7.5 (m, 26H, pmp + To + py), 7.69 [m, 1H, py (H4)], 8.50 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ (20 °C) 21.94 (s, PTO_3); (-60 °C): 10.61 (dd, $P(\text{pmp})_3$, $^1J_{\text{AgP}} = 676.8 \text{ Hz}$, $^1J_{\text{AgP}} = 781.9 \text{ Hz}$), 21.66 (s, PTO_3) ppm.

[$\text{Au}(\text{py}-\text{CH}_2\text{PTO}_3-2)(\text{PPH}_3)$] [ClO_4] (**4**). To a solution of **3a** (324.7 mg, 0.336 mmol) in acetone (30 mL) was added [$\text{AuCl}(\text{tht})$] (107.8 mg, 0.336 mmol) and the resulting suspension stirred for 30 min and then filtered over Celite. The solution was concentrated (1 mL) and diethyl ether (30 mL) added to precipitate **4** as a white solid (331 mg, 93% yield), which was recrystallized from acetone/diethyl ether, washed with diethyl ether (2 × 5 mL), and air dried. Anal. Calcd for $C_{45}H_{42}AuCl_2NO_8P_2$: C, 51.25; H, 4.01; N, 1.33; Au, 18.67. Found: C, 51.55; H, 4.00; N, 1.25; Au, 18.15. Mp: 203 °C dec. $\Delta_M = 227 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($3.1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H 2.39 [s, 9H, Me(To)], 5.32 (d, 2H, CH_2 , $^2J_{\text{PH}} = 15 \text{ Hz}$), 7.1–7.7 (m, 30H, Ph + To + py), 8.89 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 20.97 (s), 28.36 (s) ppm.

[$\text{R}_3\text{PCH}_2(\text{py}-2)\text{AuCl}_2$] [$\text{R} = \text{Ph}$ (**5a**), To (**5b**)]. To a solution of [$\text{R}_3\text{PCH}_2(\text{py}-2)$]Cl ($\text{R} = \text{Ph}$, 444.1 mg, 1.139 mmol, To, 267.6 mg, 0.619 mmol) in CH_2Cl_2 (15 to 20 mL, respectively) was added [$\text{AuCl}(\text{tht})$] in an equimolar amount. The resulting solution was stirred for 1 h and then concentrated (1 mL). Diethyl ether (20 mL) was added to precipitate a white solid, which was recrystallized from dichloromethane/diethyl

ether to give **5a** (638 mg, 90% yield) or **5b** (372 mg, 90% yield). Data for **5a** follow. Anal. Calcd for $C_{24}H_{21}AuCl_2NP$: C, 46.32; H, 3.40; N, 2.25; Au, 31.65. Found: C, 46.20; H, 3.66; N, 2.30; Au, 32.29. Mp: 162 °C. $\Delta_M = 137 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($5.8 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). IR: [$\nu(\text{AuCl})$] 350 cm⁻¹. NMR data: ^1H 5.16 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.4 \text{ Hz}$), 7.14 [m, 1H, py (H5)], 7.6–7.8 (m, 17H, Ph + py), 8.27 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 22.09 (s) ppm. Data for **5b** follow. Anal. Calcd for $C_{27}H_{27}AuCl_2NP$: C, 48.81; H, 4.09; N, 2.11; Au, 29.65. Found: C, 49.01; H, 4.42; N, 2.13; Au, 29.68. Mp: 135 °C. $\Delta_M = 141 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($3.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). IR: [$\nu(\text{AuCl})$] 350 cm⁻¹. NMR data: ^1H 2.47 [s, 9H, Me(To)], 4.94 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.4 \text{ Hz}$), 7.16 [m, 1H, py (H5)], 7.4–7.6 (m, 14H, To, py), 8.33 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 22.17 (s) ppm.

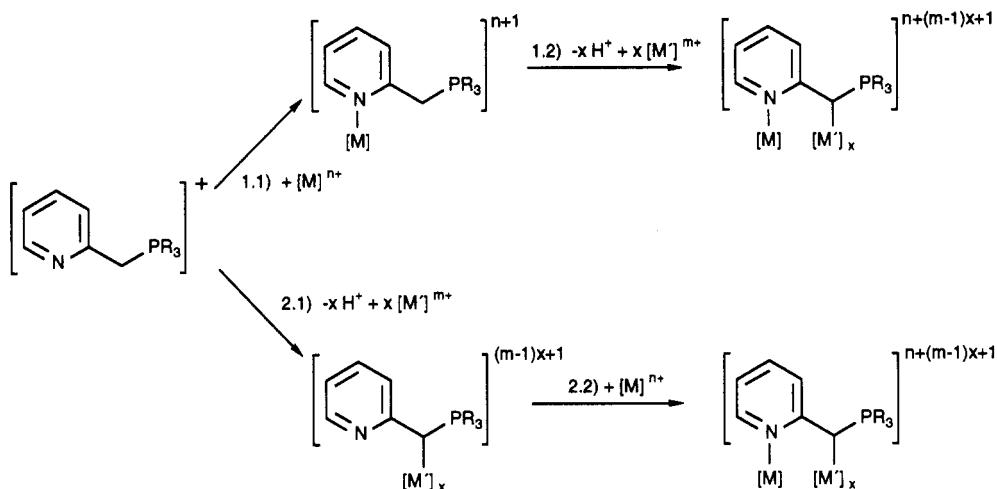
[$\text{R}_3\text{PCH}_2(\text{py}-2)\text{AuCl}_4$] [$\text{R} = \text{Ph}$ (**6a**), To (**6b**)]. To a solution of $\text{Na}[\text{AuCl}_4]$ ($\text{R} = \text{Ph}$, 148.6 mg, 0.411 mmol, To, 182.4 mg, 0.504 mmol) in ethanol/water (1/1) was added [$\text{R}_3\text{PCH}_2(\text{py}-2)$]Cl ($\text{R} = \text{Ph}$, 146.9 mg, 0.377 mmol, To, 200.0 mg, 0.463 mmol). The resulting yellow suspension was stirred for 10 min and the crystalline yellow solid filtered and washed with ethanol (1 × 2 mL) and diethyl ether to give **6a** (194 mg, 74% yield) or **6b** (320 mg, 94% yield). Data for **6a** follow. Anal. Calcd for $C_{24}H_{21}AuCl_4NP$: C, 41.58; H, 3.05; N, 2.02; Au, 28.41. Found: C, 41.47; H, 3.10; N, 1.88; Au, 28.30. Mp: 137 °C. $\Delta_M = 123 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($5.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). IR: [$\nu(\text{AuCl})$] 354 cm⁻¹. NMR data: ^1H 4.93 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.4 \text{ Hz}$), 7.1–7.8 (m, 18H, Ph + py), 8.31 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 23.37 (s) ppm. Data for **6b** follow. Anal. Calcd for $C_{27}H_{27}AuCl_4NP$: C, 44.11; H, 3.70; N, 1.90; Au, 26.79. Found: C, 44.38; H, 3.77; N, 1.94; Au, 26.44. Mp: 92 °C. $\Delta_M = 107 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($4.8 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). IR: [$\nu(\text{AuCl})$] 360 cm⁻¹. NMR data: ^1H 2.44 [s, 9H, Me(To)], 4.80 (d, 2H, CH_2 , $^2J_{\text{PH}} = 14.1 \text{ Hz}$), 7.3–7.6 (m, 15H, To, py), 8.35 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 22.26 (s) ppm.

[$\text{AuCl}[\text{CH}(\text{PR}'_3)(\text{py}-2)]$] [$\text{R} = \text{Ph}$ (**7a**), To (**7b**)]. To a solution of **5a** (411.1 mg, 0.661 mmol) or **5b** (120.8 mg, 0.182 mmol) in dichloromethane (15 mL) was added [$\text{Ti}(\text{acac})_4$] (0.727 or 0.218 mmol, respectively), and the suspension was stirred in an ice bath under N_2 for 1 h and then filtered off. The solution was concentrated (1 mL) and diethyl ether (30 mL) added to precipitate a white solid, which was washed with acetone (2 mL) and air dried (**7a**, 331 mg, 85% yield; **7b**, 80.4 mg, 70% yield). Data for **7a** follow. Anal. Calcd for $C_{24}H_{20}AuClNP$: C, 49.20; H, 3.44; N, 2.39; Au, 33.62. Found: C, 49.18; H, 3.63; N, 2.58; Au, 34.18. Mp: 184 °C dec. $\Delta_M = 0 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). IR: [$\nu(\text{AuCl})$] 320 cm⁻¹. NMR data: ^1H (200 MHz) 4.50 (d, 1H, CH , $^2J_{\text{PH}} = 7.8 \text{ Hz}$), 6.74 [m, 1H, py (H5)], 7.17 [m, 1H, py (H3)], 7.2–8.0 (m, 17H, Ph + py) ppm; $^{31}\text{P}\{\text{H}\}$ (80 MHz) 27.6 (s) ppm. Data for **7b** follow. Anal. Calcd for $C_{27}H_{26}AuClNP$: C, 51.65; H, 4.17; N, 2.23; Au, 31.37. Found: C, 52.14; H, 4.50; N, 2.04; Au, 32.12. Mp: 161 °C dec. $\Delta_M = 0 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($4 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). IR: [$\nu(\text{AuCl})$] 320 cm⁻¹. NMR data: ^1H (200 MHz) 2.39 [s, 9H, Me(To)], 4.44 (d, 1H, CH , $^2J_{\text{PH}} = 8.4 \text{ Hz}$), 6.74 [m, 1H, py (H5)], 7.12 [m, 1H, py (H3)], 7.23–7.27 (m, 6H, To), 7.39 [m, 1H, py (H4)], 7.65–7.75 (m, 6H, To), 7.98 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ (80 MHz), 26.3 (s) ppm.

[$\text{Au}[\text{CH}(\text{PTO}_3)(\text{py}-2)]_2\text{ClO}_4$ (**8**). To a solution of [$\text{TO}_3\text{PCH}_2(\text{py}-2)$] ClO_4 (421.4 mg, 0.849 mmol) in degassed dichloromethane (20 mL) was added $\text{ppn}[\text{Au}(\text{acac})_2]^2$ (396.2 mg, 0.425 mmol) under N_2 . The resulting suspension was stirred in an ice bath for 3 h and then evaporated to dryness. The residue was extracted with an 1:10 mixture of dichloromethane/diethyl ether (3 × 10 mL). The extract was filtered through Celite, the solution concentrated (1 mL), and diethyl ether (20 mL) added to precipitate **8** as a white solid (354 mg, 76% yield). Anal. Calcd for $C_{54}H_{52}AuCl_2NO_4P_2$: C, 59.65; H, 4.82; N, 2.57; Au, 18.11. Found: C, 60.22; H, 5.37; N, 2.21; Au, 17.87. Mp: 132 °C. $\Delta_M = 118 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data (resonances due to the most abundant diastereoisomer (ratio 1:3:1) are followed by an asterisk): ^1H (200 MHz) 2.38*, 2.39 [s, 9H, Me(To)], 3.92, 4.05* (d, 1H, CH , $^2J_{\text{PH}} = 7.6 \text{ Hz}$), 6.69–8.0 (m, 16H, To + py) ppm; $^{31}\text{P}\{\text{H}\}$ 26.06* (s), 26.56 (s) ppm.

[$(\text{AuPR}'_3)_2[\mu\cdot\{\text{C}(\text{PR}_3)(\text{py}-2)\}]_2\text{ClO}_4$, $\text{R} = \text{R}' = \text{Ph}$ (**9a**); $\text{R} = \text{To}$, $\text{R}' = \text{pmp}$ (**9b**)]. To a solution of the corresponding phosphonium salt [$\text{R}_3\text{PCH}_2(\text{py}-2)$] ClO_4 [$\text{R} = \text{Ph}$, 63.6 mg, 0.140 mmol; $\text{R} = \text{To}$, 75.3 mg, 0.152 mmol] in dichloromethane [20 mL] was added [$\text{Au}(\text{acac})(\text{PR}'_3)$] [$\text{R}' = \text{Ph}$, 234.7 mg, 0.420 mmol; $\text{R}' = \text{pmp}$, 295.3 mg, 0.455 mmol], and the suspension was stirred [46 h, (**9a**); 24 h (**9b**)] and filtered over Celite. The solution was concentrated (1 mL) and diethyl ether (50 mL)

(12) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Lagunas, M. C. *J. Chem. Soc., Chem. Commun.* 1992, 915.

Scheme I^a

^a [M] and [M'] represent metallic moieties such as $[\text{AuPPPh}_3]^+$ or AuCl , etc. (see Scheme II); $x = 1$ or 2 , n and $m = 0$ or 1 .

added to precipitate an off-white solid, which was recrystallized from dichloromethane/diethyl ether [1:20], washed with diethyl ether (3×10 mL), and air dried to give **9a** (171 mg, 89%) or **9b** (189 mg, 78% yield). Data for **9a** follow. Anal. Calcd for $C_{60}H_{49}Au_2ClNO_4P_3$: C, 52.58; H, 3.60; N, 1.02; Au, 28.74. Found: C, 52.90; H, 3.86; N, 1.14; Au, 28.61. Mp: 218 °C dec. $\Delta_M = 129 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($1.4 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H (200 MHz) 6.64 [m, 1H, py (H5)], 7.1–8.2 (m, 48H, Ph + py) ppm; $^{31}\text{P}\{\text{H}\}$ (80 MHz) 33.4 (t, CPPPh₃, $^3J_{\text{PP}} = 2$ Hz), 37.9 (d, AuPPPh₃) ppm. Data for **9b** follow. Anal. Calcd for $C_{69}H_{67}Au_2ClNO_{10}P_3$: C, 52.04; H, 4.24; N, 0.88; Au, 24.73. Found: C, 51.92, H, 4.44; N, 0.68; Au, 24.34. Mp: 133 °C dec. $\Delta_M = 142 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($1.5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H (200 MHz) 2.37 [br s, 9H, Me(To)], 3.82 [s, 18H, OMe (pmp)], 6.61 [m, 1H, py (H5)], 6.7–7.2 (m, 36H, To + pmp), 7.38 [m, 1H, py (H4)], 7.57 [m, 1H, py (H3)], 7.71 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ (80 MHz) 31.8 (t, CPTO₃, $^3J_{\text{PP}} = 2$ Hz), 34.1 (d, AuP(pmp)) ppm.

$[(\text{AuPPPh}_3)_2\mu\{-\text{C}(\text{PPPh}_3)(\text{py}-2)\}\{\mu\text{-Ag}(\eta^2\text{-O}_2\text{NO})(\text{OCIO}_3)\}]$ (**10**). To a solution of **9a** (123.6 mg, 0.090 mmol) in acetone (15 mL) was added AgNO_3 in an equimolecular amount. The resulting suspension was stirred in the dark for 20 h and then filtered through Celite. The solution was concentrated (1 mL) and diethyl ether (25 mL) added to precipitate an off-white solid, which was recrystallized from dichloromethane/diethyl ether to give **10** (108 mg, 78% yield). Anal. Calcd for $C_{60}H_{49}\text{AgAu}_2\text{ClN}_2\text{O}_7\text{P}_3$: C, 46.79; H, 3.21; N, 1.82. Found: C, 46.81, H, 3.56; N, 1.74. Mp: 140 °C dec. $\Delta_M = 156 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($1.7 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H (200 MHz) 6.73 [m, 1H, py (H3)], 6.9–7.7 (m, 47H, Ph + py), 8.35 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ (80 MHz) 24.9 (t, CPPPh₃, $^3J_{\text{PP}} = 5$ Hz), 37.6 (d, AuPPPh₃) ppm.

$[(\text{AuPPPh}_3)_2\mu\{-\text{C}(\text{PPPh}_3)(\text{py}-2)\}\{\text{AuPPPh}_3\}(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (**11**). To a solution of **10** (92.1 mg, 0.060 mmol) in acetone (20 mL) was added $[\text{AuCl}(\text{PPPh}_3)]$ (29.6 mg, 0.060 mmol), and the suspension was stirred for 1.5 h and filtered through Celite. To the solution was added $\text{NaClO}_4\cdot\text{H}_2\text{O}$ (17.3 mg, 0.123 mmol), and the suspension was stirred for 2.5 h and then concentrated to dryness. The residue was extracted with dichloromethane (15 mL), the extract filtered through Celite, and the solution concentrated (2 mL). Addition of diethyl ether (10 mL) gave an off-white solid, which was recrystallized from acetone/diethyl ether to give **11** (83 mg, 71% yield). Anal. Calcd for $C_{78}H_{68}\text{Au}_3\text{Cl}_2\text{NO}_{10}\text{P}_4$: C, 47.67; H, 3.49; N, 0.71; Au, 30.07. Found: C, 47.69; H, 3.44; N, 0.82; Au, 30.10. Mp: 170 °C dec. $\Delta_M = 254 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($3.9 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H 1.60 (s, 4H, H_2O), 6.8–7.9 (m, 63H, Ph + py), 8.79 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 22.58 (br s, NaAuPPPh_3), 27.87 (s, CPPPh₃), 36.90 (d, CAuPPPh₃, $^3J_{\text{PP}} = 6.1$ Hz) ppm.

$[(\text{AuPR}'_3)_2\{\mu\{-\text{C}(\text{PR}_3)(\text{py}-2)\}\}(\text{CuCl})](\text{ClO}_4)$ [$\text{R} = \text{R}' = \text{Ph}$ (**12a**); $\text{R} = \text{To}$, $\text{R}' = \text{pmp}$ (**12b**)]. To a solution of **9a** (113.4 mg, 0.083 mmol) or **9b** (117.3 mg, 0.074 mmol) in acetone (20 mL) was added CuCl (0.099 or 0.088 mmol, respectively). The resulting suspension was stirred under N_2 atmosphere (5 or 16 h, respectively) and then filtered through MgSO_4 . The solution was concentrated (2 mL) and diethyl ether (20 mL) added to precipitate **12a** (95.6 mg, 78% yield) or **12b** (89.3 mg, 71% yield) as off-white solids, which were recrystallized from dichloromethane/diethyl ether. Data for **12a** follow. Anal. Calcd for $C_{60}H_{49}\text{Au}_2\text{Cl}_2\text{CuNO}_4\text{P}_3$: C, 49.05; H, 3.36; N, 0.95. Found: C, 49.11; H, 3.58; N, 1.01. Mp:

190 °C dec. $\Delta_M = 128 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H 6.63 [m, 1H, py (H3)], 6.88 [m, 1H, py (H5)], 7.1–7.6 (m, 46H, Ph + py), 8.30 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 20.32 (br, s CPPPh₃), 36.04 (d, AuPPPh₃, $^3J_{\text{PP}} = 4.6$ Hz) ppm. Data for **12b** follow. Anal. Calcd for $C_{69}H_{67}\text{Au}_2\text{Cl}_2\text{CuNO}_{10}\text{P}_3$: C, 48.99; H, 3.99; N, 0.83. Found: C, 48.68; H, 4.11; N, 0.81. Mp: 145 °C. $\Delta_M = 126 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$). NMR data: ^1H 2.41 [br s, 9H, Me(To)], 3.81 [s, 18H, OMe (pmp)], 6.6–7.4 (m, 39H, To + pmp + py), 8.30 [m, 1H, py (H6)] ppm; $^{31}\text{P}\{\text{H}\}$ 19.45 (br s, CPTO₃), 32.74 (d, P(pmp)₃, $^3J_{\text{PP}} = 3.6$ Hz) ppm.

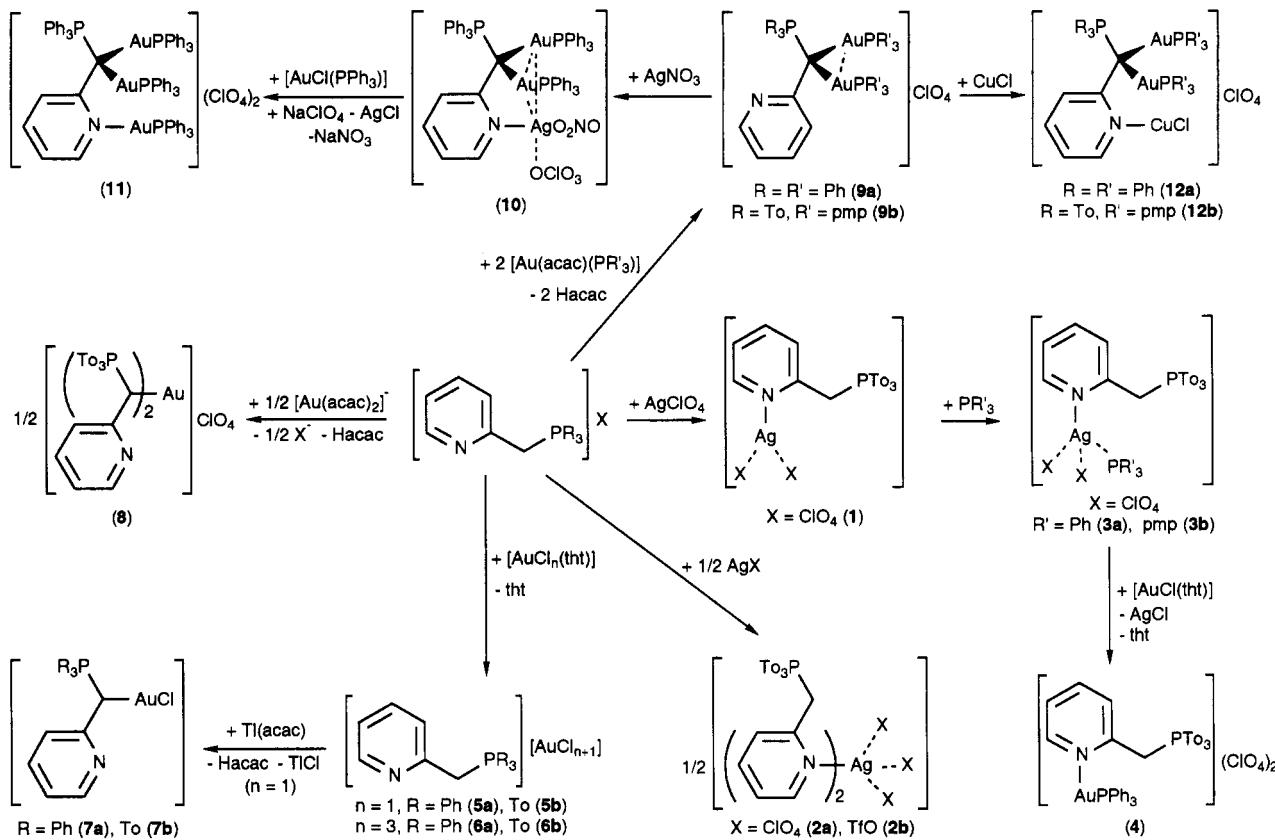
Results

Synthesis of Complexes. Two different strategies were planned to prepare the desired di- and trinuclear complexes derived from the functionalized phosphonium salts $[\text{R}_3\text{PCH}_2(\text{py}-2)]\text{X}$ ($\text{py}-2 = \text{pyridyl}-2$; see Scheme I). The first involved the coordination of one metal ion to the pyridyl N atom (step 1.1) followed by deprotonation and coordination of a second or third metal center (step 1.2) while the opposite order was followed in the second route.

Direct coordination of a metal center to the pyridyl N atom was only achieved in the case of Ag(I) salts of labile perchlorate and triflate ions (see Scheme II). Thus, $[\text{TO}_3\text{PCH}_2(\text{py}-2)]\text{X}$ [$\text{To} = \text{C}_6\text{H}_4\text{Me}-4$] reacts with silver salts, AgX , in 1:1 or 2:1 molar ratios, to give N-coordinated complexes $[\text{Ag}(\text{ClO}_4)_2\{\text{py}-(\text{CH}_2\text{PTO}_3-2)\}]$ (**1**) or $[\text{AgX}_3\{\text{py}-(\text{CH}_2\text{PTO}_3-2)\}_2]$ [$\text{X} = \text{ClO}_4$ (**2a**), $\text{CF}_3\text{SO}_3 = \text{TfO}$ (**2b**)], respectively. **2b** can also be obtained by reacting $[\text{TO}_3\text{PCH}_2(\text{py}-2)]\text{Cl}$ and $\text{AgCF}_3\text{SO}_3 \cdot 1/2\text{PhMe}$ (2:3 molar ratio) in acetone. Other N-bonded complexes were obtained by reacting **1** with PR'_3 (1:1) to give $[\text{Ag}(\text{ClO}_4)_2(\text{PR}'_3)\{\text{py}-\text{CH}_2\text{PTO}_3-2\}]$ [$\text{R}' = \text{Ph}$ (**3a**), $\text{C}_6\text{H}_4\text{OMe}-4 = \text{pmp}$ (**3b**)] and by reacting **3a** with $[\text{AuCl}(\text{tht})]$ ($\text{tht} = \text{tetrahydrothiophene}$; 1:1) to give $[\text{Au}(\text{PPPh}_3)\{\text{py}-\text{CH}_2\text{PTO}_3-2\}](\text{ClO}_4)_2$ (**4**). Other attempts to prepare N-bonded complexes were unsuccessful (see Scheme III). However, when $[\text{R}_3\text{PCH}_2(\text{py}-2)]\text{Cl}$ ($\text{R} = \text{Ph}$ or To) reacts with $[\text{AuCl}_n(\text{tht})]$ ($n = 1, 3$; 1:1) the labile tht ligand is replaced by chloride to give $[\text{R}_3\text{PCH}_2(\text{py}-2)][\text{AuCl}_2]$ [$\text{R} = \text{Ph}$ (**5a**), $\text{To} = (\text{5b})$] or $[\text{R}_3\text{PCH}_2(\text{py}-2)][\text{AuCl}_4]$ [$\text{R} = \text{Ph}$ (**6a**), $\text{To} = (\text{6b})$], respectively. Complexes **6a,b** can also be obtained by reacting $\text{Na}[\text{AuCl}_4]$ with the corresponding phosphonium chlorides. The cationic nature of these pyridine ligands is likely responsible for their reduced basic character.

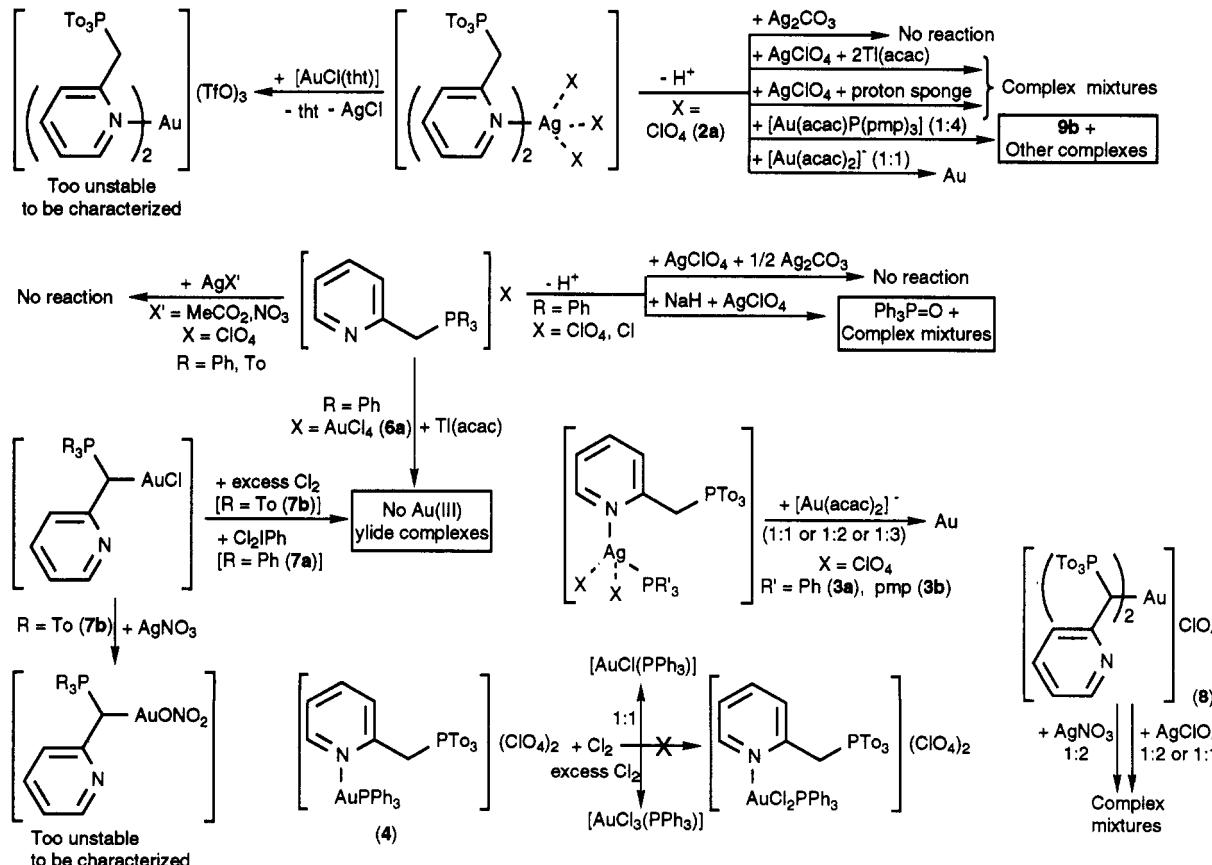
We did not succeed in the first route designed to prepare the di- and trinuclear complexes because several reactions of **2a** with deprotonating reagents failed to give the expected complexes (see Scheme III and step 1.2 in Scheme I).

Two attempts to coordinate Ag(I) to the methylene carbon atom (step 2.1 in Scheme I) using AgClO_4 plus Ag_2CO_3 or NaH also failed (see Scheme III). We have previously used Ag_2CO_3

Scheme II^a

^a To = C₆H₄Me-4; pmp = C₆H₄OMe-4; TfO = CF₃SO₃; tht = tetrahydrothiophene; Hacac = acetylacetone.

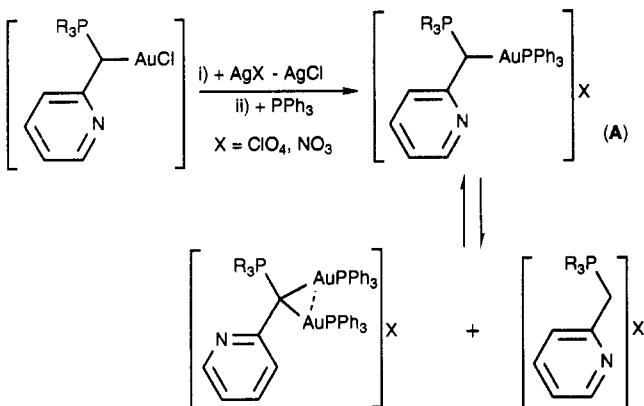
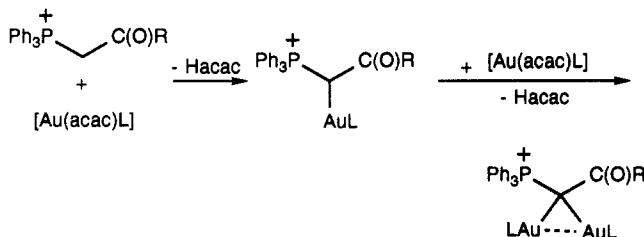
Scheme III. Unsuccessful Reactions



as a deprotonating agent to prepare silver(I) ylide complexes from $[\text{Ph}_2\text{P}(\text{CH}_2\text{CO}_2\text{R})_2]\text{Cl}$ (R = Me, Et)¹³ whereas the

pyridylphosphonium salts (R = Ph and X = ClO₄ or Cl) do not react with Ag₂CO₃ in the presence of AgClO₄.

Scheme IV

Scheme V^a

^a R = OMe, OEt, Me, Ph, NMe₂; L = PPh₃, AsPh₃.

Two alternative ways were used to coordinate one or two Au(I) centers to the methylene carbon atom. Reaction of $[R_3PCH_2(py-2)][AuCl_2]$ with the deprotonating reagents Tl(acac) or NaH (1:1), generates *in situ* the ylide from the phosphonium cation and precipitates one chloride anion from $[AuCl_2]^-$. The coordinative vacancy created on the gold(I) center is then occupied by the ylide to give the complex $[AuCl\{CH(PR_3)(py-2)\}]$ [R = Ph (**7a**), To (**7b**) (see Scheme II)]. The method using NaH has already been reported.¹⁴ In our case it gave lower yields (*ca.* 50–60%) than that using Tl(acac) (70–85%).

On the other hand, reactions of $[R_3PCH_2(py-2)]ClO_4$ with (acetylacetone)gold(I) complexes, such as $ppn[Au(acac)]_2$ ¹² in a 2:1 molar ratio or with $[Au(acac)(PR'_3)]$ (1:3), also lead to ylide complexes $[Au\{CH(PR_3)(py-2)\}_2]ClO_4$ (**8**) or $[(AuPR'_3)_2\{\mu-[C(PR_3)(py-2)]\}]ClO_4$ [R = R' = Ph (**9a**), R = To, R' = pmp (**9b**)], respectively. In these reactions the acac ligands act as the deprotonating agent to give acacH so creating the vacant sites on gold. The reactions between $[Ph_3PCH_2(py-2)]ClO_4$ and $[Au(acac)(PPh_3)]$ in 1:1 or 1:2 molar ratios give mixtures containing (by NMR) the starting material and **9a** along with a product that could be the expected, $[Au(PPh_3)\{CH(PR_3)(py-2)\}]ClO_4$ (**A**). The same mixture is obtained by reacting **7a** with $AgClO_4$ and, after removing $AgCl$, adding PPh_3 (1:1:1). This last experiment proves that **A** disproportionates to **9a** and the phosphonium salt preventing its isolation (see Scheme IV). In addition, the reaction of **7a** with PPh_3 gives $[AuCl(PPh_3)]$. We have previously obtained complexes $[AuL\{CH(PR_3)C(O)R\}]ClO_4$ and $\{[AuL]_2\{\mu-[C(PR_3)C(O)R]\}\}ClO_4$ by reacting the carbonyl-stabilized phosphonium salts $[Ph_3PCH_2C(O)R]ClO_4$ (R = OMe, OEt, Me, Ph, NMe₂) with $[Au(acac)L]$ (L = PPh₃, AsPh₃) in different molar ratios (see Scheme V).¹⁵ The less acidic character of the pyridylphosphonium salts with respect to those containing a carbonyl group may be responsible for this different behavior.

We unsuccessfully attempted to prepare the corresponding Au(III) complexes $[AuCl_3\{CH(PR_3)(py-2)\}]$ starting from **6a**, **7a**, or **7b** (see Scheme III). However, we have used chlorine to pre-

(13) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Jones, P. G. *Organometallics* **1989**, *8*, 767.

(14) Laguna, A.; Laguna, M.; Rojo, A.; Fraile, M. N. *J. Organomet. Chem.* **1986**, *315*, 269 and references therein.

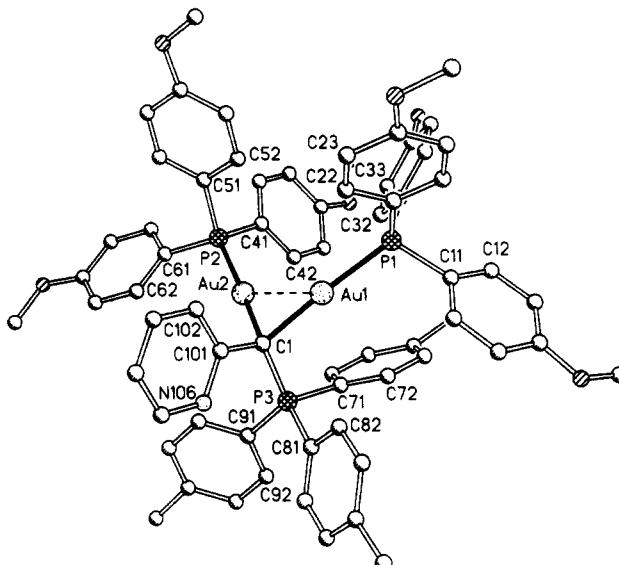


Figure 1. Structure of the cation of complex **9b**. Reprinted with permission from ref 9. Copyright 1991 Royal Society of Chemistry. Radii are arbitrary, H atoms omitted for clarity. Only one position of the disordered methoxy group is shown.

Table I. Selected Bond Lengths (Å) and Angles (deg) for Complex **9b**

Bond Lengths			
Au(1)-Au(2)	2.949(1)	Au(1)-C(1)	2.102(10)
Au(2)-C(1)	2.110(10)	P(3)-C(1)	1.753(11)
C(1)-C(101)	1.470(13)		
Bond Angles			
Au(2)-Au(1)-C(1)	45.7(3)	P(1)-Au(1)-C(1)	174.8(3)
Au(1)-Au(2)-C(1)	45.4(3)	P(2)-Au(2)-C(1)	173.5(3)
Au(1)-C(1)-Au(2)	88.9(4)	Au(1)-C(1)-P(3)	111.1(5)
Au(2)-C(1)-P(3)	112.9(5)	Au(1)-C(1)-C(101)	115.6(6)
Au(2)-C(1)-C(101)	112.2(6)	P(3)-C(1)-C(101)	113.8(7)

pare $[AuCl_3\{CH(PPh_3)C(O)R\}]$ from $[AuCl\{CH(PPh_3)C(O)R\}]$ (R = OMe, OEt, Me, Ph, NMe₂).¹⁵

Several attempts to use complexes **7a,b** or **8** as N-donor ligands failed to give the expected products (see Scheme III). Thus, $AgNO_3$ reacts with **7b** (1:1) to give $AgCl$ and the corresponding (nitrate)gold(I) complex, which was too unstable to be fully characterized. However, addition of PPh_3 to its solutions gave mixtures resulting from the disproportionation of complex **A** (see Scheme IV).

Complexes of the desired type were obtained (step 2.2, see Scheme I) starting from **9a,b**. Thus, complex **9a** reacts with $AgNO_3$ (1:1) to give $[(AuPPh_3)_2\{\mu-[C(PPh_3)(py-2)]\}\{\mu-Ag(\eta^2-O_2NO)(ClO_3)\}]$ (**10**) which, in turn, reacts with $[AuCl(PPh_3)]$ and $NaClO_4$ (1:1:1) leading to $[(AuPPh_3)_2\{\mu-[C(PPh_3)(py-2)]\}(AuPPh_3)](ClO_4)_2$ (**11**). Complexes **9a,b** react with $CuCl$ to give $[(AuPR'_3)_2\{\mu-[C(PR_3)(py-2)]\}(CuCl)](ClO_4)$ [R = R' = Ph (**12a**), R = To, R' = pmp (**12b**)], respectively.

Structure of Complexes. The X-ray crystal structures of **9b** (see Figure 1 and Table I) and $10 \cdot CH_2Cl_2 \cdot H_2O$ (See Figure 2 and Table II) at 178 K have been published⁹ and show that weak interactions between both Au centers occur [2.949(1) and 3.078(1) Å, respectively]. These values are in the range 3.00 ± 0.25 Å found in related complexes,^{15a,c,16} and in many di- or polynuclear gold(I) complexes.¹ The configuration of the N lone pair with

(15) (a) Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernandez-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163. (b) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Turpin, J.; Fernandez-Baeza, J. *J. Organomet. Chem.* **1987**, *333*, 129. (c) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc. Dalton Trans.* **1991**, 2579.

(16) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Jones, P. G.; Meyer-Bäse, K.; Erdbrügger, C. F. *Organometallics* **1988**, *7*, 997.

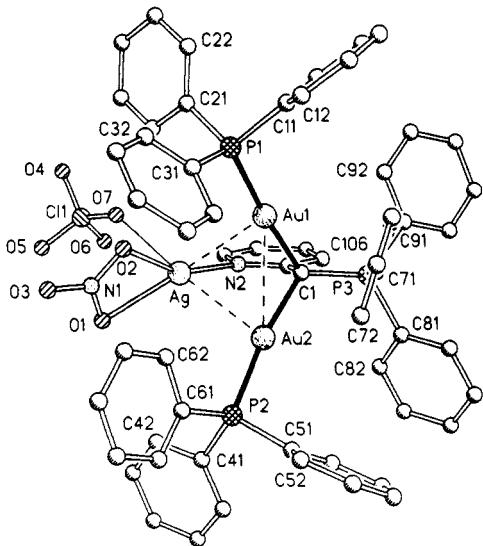


Figure 2. Structure of the cation of complex **10**· $\text{CH}_2\text{Cl}_2\text{H}_2\text{O}$. Reprinted with permission from ref 9. Copyright 1991 Royal Society of Chemistry. Radii are arbitrary, H atoms omitted for clarity.

respect to the Au_{2+} moiety is *anti* in **9b** while *syn* in **10** because two $\text{Au}\cdots\text{Ag}$ weak interactions seem to act as a conformation-determining force. The $\text{Au}\cdots\text{Ag}$ bonds are similar in nature to weak $\text{Au}\cdots\text{Au}$ bonds, at least in terms of the bond distances [2.926(1), 3.006(1) Å]. These $\text{Au}\cdots\text{Ag}$ bond lengths are similar to those reported for $[\{\text{Au}(\text{C}_2\text{Ph})_2\}_2(\mu\text{-AgPPPh}_3)_2]$ [2.894(1), 2.913(1) Å]⁴ but longer than those in some $[\text{Au}_2\text{Ag}_2]^{4+}$ clusters [2.702(2)–2.792(2) Å].⁵

The coordination at silver in complex **10** may be regarded as distorted octahedral or distorted trigonal prismatic [end faces $\text{Au}(1)$, $\text{Au}(2)$, $\text{N}(2)$; $\text{O}(1)$, $\text{O}(2)$, $\text{O}(7)$]. However, it is possible to consider a trigonal bipyramidal geometry with the group $(\text{AuPPPh}_3)_2^{2+}$ occupying only one coordination site, and the perchlorato ligand in axial positions. Recently, the isolobal relationship of this group with H_2 , CO , or PhC_2Ph has been discussed; thus, $[(\text{Ph}_3\text{PAu})_2\{\mu\text{-Fe}(\text{CO})_4\}]$ or $[\text{Ru}_3(\mu_2\text{-NPh})\{\mu_3\text{-}(\text{AuPPPh}_3)_2\}(\text{CO})_9]$ are isostructural with $[\text{Fe}(\text{CO})_5]$ or $[\text{Ru}_3(\mu_2\text{-NPh})(\mu_3\text{-CO})(\text{CO})_9]$, respectively,¹⁷ and $[(\text{Ph}_3\text{PAu})_2\{\mu\text{-PtCl}(\text{PEt}_3)\}]^+$ is isostructural with $[\text{PtCl}(\text{PR}_3)(\text{PhC}_2\text{Ph})]^+$.¹⁸ The coordination of the η^1 -perchlorato-ligand [$\text{Ag}\cdots\text{O}(7)$: 2.663(9) Å] is significantly weaker than that of the η^2 -nitrato-ligand [$\text{Ag}\cdots\text{O}(1)$, 2.442(8) Å; $\text{Ag}\cdots\text{O}(2)$, 2.396(8) Å].

Molar conductivities (Λ_M) in acetone of the gold complexes **5a,b**, **6a,b**, **8**, and **9a,b** ($107\text{--}142 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) are in the range reported in the literature for 1:1 electrolytes.¹⁹ The value of Λ_M found for **4** and **11** (227 and 254 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively) is slightly over the range reported for 2:1 electrolytes (160–200 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$).¹⁹ On the basis of the above data, **10** and **12a,b** ($\Lambda_M = 156$, 128, and 126 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively) and the silver complexes **1**, **2a**, and **3a,b** ($\Lambda_M = 218\text{--}261 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) behave in acetone as 1:1 or, respectively, as 2:1 electrolytes. The Λ_M of **2b** ($298 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) suggests that an equilibrium between 2:1 and 3:1 electrolytes exists in acetone solution. Molar conductivities of these complexes in dichloromethane, as has previously been shown, are not so reliable.^{19,20}

Although triflate or perchlorate anions in the silver complexes **1**, **2a,b**, and **3a,b** can be coordinated in the solid state, the above conductivity data suggest that they are weakly bonded, as it occurs in **10** because in acetone solutions the solvent replaces two such

Table II. Selected Bond Lengths (Å) and Angles (deg) for Complex **10**

Bond Lengths			
$\text{Au}(1)\text{-Au}(2)$	3.078(1)	$\text{Au}(1)\text{-Ag}$	3.006(1)
$\text{Au}(1)\text{-P}(1)$	2.274(2)	$\text{Au}(1)\text{-C}(1)$	2.110(8)
$\text{Au}(2)\text{-Ag}$	2.926(1)	$\text{Au}(2)\text{-P}(2)$	2.273(3)
$\text{Au}(2)\text{-C}(1)$	2.130(10)	$\text{Ag}\cdots\text{O}(1)$	2.442(8)
$\text{Ag}\cdots\text{O}(2)$	2.396(8)	$\text{Ag}\cdots\text{N}(2)$	2.178(8)
$\text{Ag}\cdots\text{O}(7)$	2.663(9)	$\text{N}(1)\text{-O}(1)$	1.270(12)
$\text{N}(1)\text{-O}(2)$	1.235(13)	$\text{N}(1)\text{-O}(3)$	1.233(13)
$\text{C}(1)\text{-C}(101)$	1.469(12)		

Bond Angles			
$\text{Au}(2)\text{-Au}(1)\text{-Ag}$	57.5(1)	$\text{Ag}\cdots\text{Ag}(1)\text{-C}(1)$	74.3(3)
$\text{P}(1)\text{-Au}(1)\text{-C}(1)$	174.4(3)	$\text{Au}(1)\text{-Au}(2)\text{-Ag}$	60.0(1)
$\text{Ag}\cdots\text{Au}(2)\text{-P}(2)$	112.0(1)	$\text{Ag}\cdots\text{Au}(2)\text{-C}(1)$	75.8(2)
$\text{P}(2)\text{-Au}(2)\text{-C}(1)$	172.1(2)	$\text{Au}(1)\text{-Ag}\cdots\text{Au}(2)$	62.5(1)
$\text{Au}(1)\text{-Ag}\cdots\text{O}(1)$	130.1(2)	$\text{Au}(2)\text{-Ag}\cdots\text{O}(1)$	100.0(2)
$\text{Au}(1)\text{-Ag}\cdots\text{O}(2)$	84.6(2)	$\text{Au}(2)\text{-Ag}\cdots\text{O}(2)$	104.2(2)
$\text{O}(1)\text{-Ag}\cdots\text{O}(2)$	53.1(3)	$\text{Au}(1)\text{-Ag}\cdots\text{N}(2)$	76.9(2)
$\text{Au}(2)\text{-Ag}\cdots\text{N}(2)$	79.3(2)	$\text{O}(1)\text{-Ag}\cdots\text{N}(2)$	149.5(3)
$\text{O}(2)\text{-Ag}\cdots\text{N}(2)$	157.1(3)	$\text{Au}(1)\text{-Ag}\cdots\text{O}(7)$	115.9(2)
$\text{Au}(2)\text{-Ag}\cdots\text{O}(7)$	171.4(2)	$\text{O}(1)\text{-Ag}\cdots\text{O}(7)$	87.3(3)
$\text{O}(2)\text{-Ag}\cdots\text{O}(7)$	83.8(3)	$\text{N}(2)\text{-Ag}\cdots\text{O}(7)$	92.1(3)
$\text{O}(1)\text{-N}(1)\text{-O}(2)$	119.3(10)	$\text{O}(1)\text{-N}(1)\text{-O}(3)$	119.1(10)
$\text{O}(2)\text{-N}(1)\text{-O}(3)$	121.5(9)	$\text{Au}(1)\text{-C}(1)\text{-Au}(2)$	93.1(4)
$\text{Au}(1)\text{-C}(1)\text{-P}(3)$	106.3(4)	$\text{Au}(2)\text{-C}(1)\text{-P}(3)$	107.0(4)
$\text{Au}(1)\text{-C}(1)\text{-C}(101)$	113.2(6)	$\text{Au}(2)\text{-C}(1)\text{-C}(101)$	113.7(6)
$\text{P}(3)\text{-C}(1)\text{-C}(101)$	120.0(7)		

anions or, in the case of **2b**, partially a third one. To represent the structures of all these silver complexes in Scheme II, we have tentatively assumed these weak interactions. In fact, the strong band appearing around 1100 cm⁻¹ in the IR spectra of the cationic gold(I) complexes **4**, **8**, **9a,b**, and **11**, assignable to the stretching $\nu(T_2)$ mode of the ClO_4^- anion, is split in the Ag(I) complexes **1**, **2a,b**, and **3a,b** (corresponding to the change of symmetry from T_d to C_{3v} or C_{2v}). In addition, a weak band, around 925 cm⁻¹, assignable to $\nu(A_1)$ mode (only active if the symmetry of ClO_4^- is C_{3v} or C_{2v}), is also observed. Although this band is found in **10**, curiously, the expected splitting of the 1100 cm⁻¹ band is not observed. The same occurs in Au(I)/Cu(I) complexes **12a,b**.

To relate conductivity data with variable temperature NMR spectra of **3a** (see below), we have measured its conductivity in acetone at -60 °C. The lowering of the molar conductivity, from 218 at room temperature to 81 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ at -60 °C (approximately $10^4 \text{ mol}\cdot\text{L}^{-1}$), is similar to that found in the related Au(I) complex **4** (from 227 to 97 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$). Because dicoordination in **4** can reasonably be assumed (in the solid state and in solution), we conclude that in acetone solutions of **3a** perchlorate anions are not coordinated either at room or at low temperature (-60 °C). A 1:1 electrolyte such as $(\text{PhCH}_2\text{PPh}_3)\text{-ClO}_4$ shows molar conductivities of 123 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ at room temperature and 60 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ at -60 °C.

Low temperature (-40 to -60 °C) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (CDCl_3) of the phosphine complexes **3a,b** show, in addition to the singlet corresponding to the PTO_3 group, two or one doublet of doublets, respectively, corresponding to the phosphine bonded to Ag(I). Because each doublet of doublets arises from $^{109}\text{Ag}\cdots\text{P}$ and $^{107}\text{Ag}\cdots\text{P}$ spin–spin coupling, we interpret that two or one complexes are present in CDCl_3 solutions of **3a** or **3b**, respectively, at low temperatures. The doublets were identified from the relative peak intensities and ratio of $J_{^{109}\text{Ag-P}}/J_{^{107}\text{Ag-P}}$ both being approximately 1.15. These doublets broaden when the temperature rises and coalesce at 20 °C. At 40–50 °C a broad singlet (approximately 14 ppm) is observed for complex **3a**. Of the two complexes formed in CDCl_3 solutions of **3a** (approximate molar ratio 2:1) the most abundant one shows $\delta(\text{PPh}_3)$ at lower field (14.36 ppm) and has $J_{^{109}\text{Ag-P}}$ (667.6 and 770.5 Hz) greater than those of the less abundant one (11.69 ppm; 494.3 and 570.7 Hz). Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3a** in $(\text{CD}_3)_2\text{CO}$ solutions are similar to those in CDCl_3 but the molar ratio of the

- (17) Bruce, M. I.; Corbin, P. E.; Humphrey, P. A.; Koutsantonnis, G. A.; Liddel, M. J.; Tiekkink, E. R. T. *J. Chem. Soc., Chem. Commun.* 1990, 674.
 (18) Braunstein, P.; Lehner, H.; Matt, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 304.
 (19) Geary, W. J. *Coord. Chem. Rev.* 1971, 7, 81.
 (20) Rosenthal, M. R.; Drago, R. S. *Inorg. Chem.* 1965, 4, 11.

Table III. Chemical Shifts of the Pyridine Protons

compd	H(3)	H(4)	H(5)	H(6)
(py-CH ₂ PR ₃ -2)X				
R = Ph, X = Cl	7.12		8.20	
R = To, X = Cl	7.15		8.29	
R = Ph, X = AuCl ₂ (5a)	7.14		8.27	
R = To, X = AuCl ₂ (5b)	7.16		8.33	
R = Ph, X = AuCl ₄ (6a)			8.31	
R = To, X = AuCl ₄ (6b)			8.35	
M ← py-CH ₂ PTo ₃ -2				
M = Ag(ClO ₄) ₂ (1)	7.85		8.44	
M = Ag(ClO ₄) ₃ (py-CH ₂ PTo ₃ -2) (2a)	7.75		8.34	
M = Ag(TfO) ₃ (py-CH ₂ PTo ₃ -2) (2b)	7.77		8.32	
M = Ag(ClO ₄) ₂ (PPh ₃) ₃ (3a)	7.81		8.56	
M = Ag(ClO ₄) ₂ P(pmp) ₃ (3b)	7.67		8.56	
M = Au(PPh ₃) ₄ (4)			8.89	
M ← C(X)(PR ₃)(py-2)				
M = AuCl, X = H, R = Ph (7a)	7.17		6.74	
M = AuCl, X = H, R = To (7b)	7.12	7.39	6.74	
M = AuC(X)(PR ₃)(py-2), X = H, R = To (8)				
M = AuPR' ₃ , X = AuPR' ₃ , R = R' = Ph (9a)			6.64	
M = AuPR' ₃ , X = AuPR' ₃ , R = To, R' = pmp (9b)	7.57	7.38	6.61	7.71
M ← C(AuPR' ₃)(PR ₃)(py-2) → M'				
M = AuPR' ₃ , R = R' = Ph, M' = Ag(NO ₃)(ClO ₄) (10)	6.73			8.35
M = AuPR' ₃ , R = R' = Ph, M' = AuPR' ₃ (11)				8.79
M = AuPR' ₃ , R = R' = Ph, M' = CuCl (12a)	6.63		6.88	8.30
M = AuPR' ₃ , R = To, R' = pmp, M' = CuCl (12b)				8.30

two species increases to approximately 8:1. Because $^1J_{AgP}$ increases with the percentage of s character, the most abundant complex in solution is that of lower coordination number.²¹ According to the conductivity data in acetone the most abundant complex in solution at low temperatures is the dicoordinate [Ag-(PPh₃)(py-CH₂PTo₃-2)](ClO₄)₂. Therefore, the other one could be the tricoordinate [Ag(ClO₄)(PPh₃)(py-CH₂PTo₃-2)]ClO₄. The very similar values of $^1J_{AgP}$ in acetone and chloroform suggest that the same species are present in both solvents. At room temperature and above a rapid exchange between the phosphine ligand and perchlorate could account for the $^{31}P\{^1H\}$ NMR spectral data.²¹

$^{31}P\{^1H\}$ NMR spectral data of complex **11** show that AuPPh₃ groups are not interchangeable as occurs in $\{[C_9H_6N(AuPPh_3)]-\{N(AuPPh_3)_3\}\}^{2+}$ (C_9H_6N = 8-quinolinyl). Because this scrambling occurs by cleavage of the N–Au bonds, it is reasonable to assume that in **11** the interchange does not occur because the C–Au bond energy is too high to allow a dissociation process.¹⁰

(21) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386. Goel, R. G.; Pilon, P. *Inorg. Chem.* **1978**, *17*, 2876. Socol, S. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 88. Alyea, E. C.; Malito, J.; Nelson, J. H. *Inorg. Chem.* **1987**, *26*, 4294. Baker, L. J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Steigelmann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656.

Table III gives chemical shifts of the pyridine protons. Overlapping of some of these resonances with those of phenyl protons prevents some assignments. While H(4) and H(5) use to appear as apparent triplets or doublets of doublets, H(3) and H(6) have the apparent of doublets. Data from Table III clearly show that chemical shifts of the pyridine protons depend on the type of coordination of this cationic ligand.

Discussion

We have designed two routes to prepare homo- or hetero-, -di- or -trinuclear complexes of the d¹⁰ coinage metals. Although many experiments have been unsuccessful, this study has shown that the cationic ligands [R₃PCH₂(py-2)]X are able (1) to form gold(I) and silver(I) complexes using the pyridine substituent, (2) to give mono- and dinuclear gold(I) complexes by substituting one or two of the methylene hydrogen atoms, and (3) from these dinuclear complexes, to form trinuclear copper(I), silver(I), and gold(I) complexes.

The crystal structures of **9b** and **10** show short Au...Au distances. In both complexes these distances are in the range of 3.00 ± 0.25 Å found in many gold(I) complexes containing or not a bridging ligand.¹ The energy of this weak bond is similar to a hydrogen bond and it gives a reason, for example, of the formation of hypercoordinated compounds (see Introduction) as well as some interesting conformational changes.^{1,2} Thus, the diphosphinylide Me₃P=C(PPh₂)₂ has a *syn/anti* orientation of lone pairs both in solution and in the crystalline state. However, in the complex $[(AuCl)_2\{\mu-(PPh_2)_2C=PMe_3\}]$ the ligand changes to a *syn/syn* conformation to bring the gold atoms at 3.000(1) Å.²²

This, and other examples,¹ can be considered precedents for the change of orientation of the pyridyl group we observe from complex **9b** to **10**. The short Au...Ag distances suggest that this change of conformation can be due to the two weak Au...Ag bonds. In addition, these interactions seem to weaken the Au...Au bond because a significant lengthening of the Au–Au bond distance is observed [2.949(1) → 3.078(1) Å]. We show in this paper, for the first time, that these weak conformation-determining forces are not exclusive for gold–gold interactions. Because there are examples of similar weak bonds between all the coinage metals (numismophilicity; see Introduction) it is probable that other examples of change of conformation could be found which allow one to measure the energy of these weak interactions. If we do not consider these Au...Ag interactions in complex **10**, the geometry around the Ag atom would be an unprecedented trigonal pyramidal geometry with the metal center in the base.

Acknowledgment. We thank Dirección General de Investigación Científica y Técnica (PB89-0430) for financial support and Prof. Peter G. Jones for the determination of crystal structures of complexes **9b** and **10**. M.-C. L. is grateful for a grant from Ministerio de Educación y Ciencia (Spain).

(22) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417.