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# New Ylide−, Alkynyl−, and Mixed Alkynyl/Ylide−Gold(I) Complexes

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Reactions of AuCl(tht) (tht = tetrahydrothiophene) with various ylides in equimolar amounts give the complexes [AuCl(ylide)]$X_n$ ($n$ = 0, ylide = $C(PPh_3)_2$ (**1a**), 4-$MeC_6H_4SO_2$-$CHPPh_3$ (**1b**); $n$ = 1, X = TfO, ylide = $[HC(PPh_3)_2]^+$ (**2**)) and $[(AuCl)_2\{\mu\text{-}C(PPh_3)_2\}]$ (**3**) when using a 2:1 molar ratio. The complex **1a** reacts (i) with Tl(acac) to give $[Au(acac)\{C(PPh_3)_2\}]$ (**4**) and (ii) with terminal alkynes (with or without added $Et_3N$) to give $[HC(PPh_3)_2][Au(C{\equiv}CC_6H_4R\text{-}4)Cl]$ (R = H (**5a**), CN (**5b**), OMe (**5c**), $NO_2$ (**5d**)) instead of the desired complexes $[Au(C{\equiv}CC_6H_4R\text{-}4)\{C\{PPh_3\}_2\}]$. These complexes (R = H (**6a**), CN (**6b**), OMe (**6c**), $NO_2$ (**6d**), C≡CPh (**6e**)) were prepared by the reaction of $[Au(acac)\{C(PPh_3)_2\}]$ (**4**) with a large excess of alkynes (ca. 1:25−30). Complex **1b** reacts with terminal alkynes in the presence of $Et_3N$ differently from **1a**, giving the complexes $[Au(C{\equiv}CC_6H_4R\text{-}4)\{CH(PPh_3)\{S(O)_2C_6H_4Me\text{-}4\}\}]$ (R = H (**7a**), NC (**7b**), OMe (**7c**), $NO_2$ (**7d**), C≡CPh (**7e**)). The reaction of PPN$[Au(acac)_2]$ with the phosphonium salt $[H_2C(PPh_3)_2](TfO)_2$ or $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]$TfO in 1:2 stoichiometry afforded the cationic complex $[Au(ylide)_2](TfO)_n$, where the ylide is $[HC(PPh_3)_2]^+$ ($n$ = 3, **8a**) or 4-$MeC_6H_4S(O)_2CHPPh_3$ ($n$ = 1, **8b**), respectively. The crystal structures of $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]$TfO, **1b**·$0.5CH_2Cl_2$, **3**·$3CH_2Cl_2$, **5a**, **5c**, **6d**·THF, and **8b** have been determined.



## Introduction

Gold(I) complexes are interesting from both theoretical and applied standpoints. Thus, in addition to the well-known applications as antiarthritic agents,[1] other medicinal applications have been reported, extending from chemotherapy[2,3] to treatments of tropical diseases,[4] thrombosis,[5] or cancer.[6] An increasing number of publications have documented the potential of soluble gold catalysts.[7] Recent reports have detailed alkane oxygenation[8] and hydrosilylation reactions.[9] Many gold(I) complexes show Au···Au interactions that are weaker than normal covalent bonds but stronger than van der Waals forces. These interactions are termed aurophilic[10,11] and determine the supramolecular structure of many gold(I) complexes as well as the formation of rare hypercoordinate complexes;[12,13] they are partially responsible for the interesting photophysical properties of many of these compounds.[14−16]

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The preference of gold(I) for linear dicoordination, together with the linearity of the C≡C bond in alkynyl ligands, makes alkynylgold(I) complexes attractive candidates for the design of linear-chain metal-containing polymers with extended electronic conjugation along the backbone.[17] The rapidly growing interest in alkynylgold(I) complexes is associated with the expectation that these electronically flexible rigid-rod polymers might exhibit interesting properties either difficult or impossible to achieve with conventional organic polymers. Thus, some alkynyl gold(I) complexes have liquid crystalline properties,[18] nonlinear optical behavior,[19,20] or interesting photophysical or photochemical properties.[14,21] The objective of the present work was to prepare alkynylgold(I) complexes containing ylides to study their NLO properties. Although they did not show such properties, the results were nonetheless remarkable, as presented below.

Phosphorus ylides are an interesting group of ligands, and their coordination chemistry with transition and nontransition elements has been thoroughly reviewed.[22−24] A large number of gold(I) complexes with phosphorus ylides are known.[25−28]

The only previously known gold complex with the diylide $C(PPh_3)_2$ is $[AuCl\{C(PPh_3)_2\}]$ (**1a**),[29] preliminarily reported by Schmidbaur and obtained by reacting $C(PPh_3)_2$ with [AuCl(CO)]. In this work, we report a different way to synthesize **1a** and other complexes with this ligand, including the unusual dinuclear complex $[(AuCl)_2\{\mu\text{-}\{C(PPh_3)_2\}\}]$ (**3**), the first acetylacetonato−ylide gold complex, $[Au(acac)\{C(PPh_3)_2\}]$ (**4**), and the family of alkyne complexes $[Au(C{\equiv}CR)\{C(PPh_3)_2\}]$ (**6**). We have previously reported some complexes containing bridging ylides, but in contrast to **3**, they are cationic species of the general formula $[(AuPR_3)_2\{\mu\text{-}\{CR'(PR_3)\}\}]^+$.[30−33] Related to **3** are the complexes $[(AuMe)_2\{\mu\text{-}C(PMe_3)_2\}]$[34] and $[(AuPPh_3)_2\{\mu\text{-}C(PMePh_2)_2\}]^{2+}$.[35]

The number of complexes with the ligand $C(PPh_3)_2$ is very limited, despite several attempts to coordinate it to low- and high-valent transition elements. Thus, reactions with $[MBr(CO)_5]$ (M = Mn, Re), $[Fe(CO)_5]$, $[Fe(CS)(CO)_4]$, and $[W(CO)_6]$ led to the Wittig products $[MBr(C{\equiv}CPPh_3)(CO)_4]$,[36] $[Fe(C{\equiv}CPPh_3)(CO)_4]$, and $[Fe_3(C{\equiv}CPPh_3)(CO)_9]$[37] and the hydrolysis product $[W(CO)_5(OPPh_2CHPPh_3)]$,[38] respectively. Similarly, all attempts to prepare Pt(IV) complexes were unsuccessful. Thus, the reaction of $[PtMe_3I]$ with $C(PPh_3)_2$ was sluggish and incomplete and, in the presence of $AgPF_6$ or $AgOSO_2CF_3$, led to methane, $[HC(PPh_3)_2]^+$, and Pt(II) complexes containing derivatives of $C(PPh_3)_2$, depending on the molar ratio of the reagents. Likewise, reduction of Cu(II) to Cu(I) was observed when $C(PPh_3)_2$ was reacted with $CuCl_2$, giving $[ClC(PPh_3)_2][CuCl_2]$.[29] Despite these difficulties, some complexes have been isolated: for example, $[W(CO)_5\{C(PPh_3)_2\}]$,[39] $[Ni(CO)_n\{C(PPh_3)_2\}]$ ($n$ = 3,[36,40] 2[40]), $[MX\{C(PPh_3)_2\}]$ (M = Cu, Ag, Au, X = Cl,

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Cp, Cp*),[29,41] and $[O_3Re\{C(PPh_3)_2\}][ReO_4]$.[42] However, only the crystal structures of $[Ni(CO)_n\{C(PPh_3)_2\}]$ ($n$ = 3, 2),[40] $[CuX\{C(PPh_3)_2\}]$ (X = Cl, Cp*),[29,41] and $[O_3Re\{C(PPh_3)_2\}][ReO_4]$[42] have been solved. Here we report the synthesis of eight new gold(I) complexes with the ligand $C(PPh_3)_2$ and the crystal structure of two of them.

Only a few [Au(C≡CR)(ylide)] complexes have been prepared, by reacting $[Au(ylide)(tht)]ClO_4$ (tht = tetrahydrothiophene) with KC≡CR.[43] Here we report two new synthetic methods for such complexes. One of them uses $[Au(acac)\{C(PPh_3)_2\}]$ (**4**), following the method we have widely used to prepare gold(I) complexes by reacting $[Au(acac)(PR_3)]$ or $[Au(acac)_2]^-$ with acids.[27] We report the first complexes with the ylide $4\text{-}MeC_6H_4S(O)_2CHPPh_3$ and the ylide cation $[HC(PPh_3)_2]^+$. Kaska et al. reported unsuccessful attempts to prepare $[(OC)_5W\{HC(PPh_3)_2\}]^+$.[39] M. Laguna has recently reported complexes related to **2**, $[Au(X)\{CH(PPh_2Me)_2\}]^+$ (X = Cl, $C_6F_5$).[26]

## Experimental Section

Infrared spectra were recorded in the range 4000−200 $cm^{-1}$ on a Perkin-Elmer 16F PC FT-IR spectrophotometer with Nujol mulls between polyethylene sheets. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, N, and S analyses were carried out with a Carlo Erba 1106 microanalyzer. Unless otherwise stated, $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts are referenced to the internal chloroform peak ($^1H$ and $^{13}C$) and to external $H_3PO_4$ ($^{31}P$). Most of the carbon resonances have not been assigned, but signals corresponding to quaternary or ternary carbons are indicated as C or CH with the help of DEPT experiments. $[CH_2(PPh_3)_2]Br_2$, $[HC(PPh_3)_2]Br$, $C(PPh_3)_2$,[44] $4\text{-}MeC_6H_4S(O)_2CH_2I$,[45] $4\text{-}NCC_6H_4C{\equiv}CH$, $4\text{-}MeOC_6H_4C{\equiv}CH$, $4\text{-}O_2NC_6H_4C{\equiv}CH$,[46a] $PhC{\equiv}CC_6H_4C{\equiv}CH$,[46b] and $PPN[Au(acac)_2]$[47] were prepared by following either published methods or extensions of them. Thus, in the preparation of $C(PPh_3)_2$ from $[HC(PPh_3)_2]Br$ and NaH in diglyme, the reaction mixture was heated at 90−100 °C until the $H_2$ evolution ceased (usually for 1−1.5 h), because decomposition occurs if refluxed as reported.[44] In the purification of alkynes or their silyl derivatives by column chromatography, a solvent mixture of $Et_2O$ and hexane (1:4) was used instead of the reported benzene−hexane mixture.[46a] $[CH_2(PPh_3)_2](TfO)_2$ and $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]TfO$ (TfO = $CF_3SO_3$) were prepared by the metathesis reactions of $[CH_2(PPh_3)_2]Br_2$ and $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]I$ with thallium(I) triflate, respectively. Crystals of $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]TfO$ (Anal. Calcd for $C_{27}H_{24}F_3O_5PS$: C, 55.85; H, 4.16; S, 11.05. Found: C, 56.02; H, 4.31; S, 10.92) suitable for the X-ray study were obtained by slow evaporation of a $d_6$-acetone solution. All complexes are stable at room temperature in the air, except complex **4**. Complex **3** is not stable in solution (see Discussion).

**Synthesis of $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]I$.** A mixture of $4\text{-}MeC_6H_4S(O)_2CH_2I$ (7.83 g, 2.64 mmol), triphenylphosphine (6.96 g, 2.65 mmol), and 25 g of triphenyl phosphate was heated at 125−130 °C for 36 h. A highly viscous solution was obtained. Toluene (30 mL) was added to the cooled reaction mixture, whereupon a white solid precipitated. It was filtered by suction and recrystallized from a $CH_2Cl_2$−hexane mixture to give the title compound. Yield: 6.9 g, 46.4%. Mp: 236−238 °C. Anal. Calcd for $C_{26}H_{24}IO_2PS$: C, 55.92; H, 4.33; S, 5.74. Found: C, 55.82; H, 4.40; S. 5.47. $^1H$ NMR ($CDCl_3$): $\delta$ 2.40 (s, 3 H, Me), 6.18 (d, 2 H, $CH_2$, $^2J$(HP) = 13 Hz), 7.35 (d, 2 H, $C_6H_4$, $^3J$(HH) = 8 Hz), 7.64−7.70 (m, 6 H, Ph or $C_6H_4$), 7.77−7.83 (m, 2 H, Ph or $C_6H_4$), 7.93−8.01 (m, 9 H, Ph or $C_6H_4$). $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): $\delta$ 17.6 (s).

**Synthesis of $4\text{-}MeC_6H_4S(O)_2CHPPh_3$.** To a suspension of $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]I$ (1.04 g, 1.86 mmol) in THF (30 mL) was added an $^nBuLi$ solution in hexane (1.6 M, 1.20 mL, 1.92 mmol), and the reactants were stirred at room temperature for 6 h. The resulting pale yellow solution was evaporated to dryness, and the resulting solid was thoroughly washed with water (3 × 5 mL) and recrystallized from a $CH_2Cl_2$−hexane mixture to give the ylide as an off-white solid. Yield: 0.65 g, 81%. Mp: 184 °C. Anal. Calcd for $C_{26}H_{23}O_2PS$: C, 72.54; H, 5.38; S, 7.44. Found, C, 72.05; H, 5.40; S, 6.96. $^1H$ NMR ($CDCl_3$): 2.31 (s, 3 H, Me), 2.96 (br, 1 H, $HCPPh_3$), 6.99, 7.32 (AB system, $^3J$(HH) = 8 Hz, 4 H, $C_6H_4$), 7.38−7.70 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 14.8 (s).

**Synthesis of $[AuCl\{C(PPh_3)_2\}]$ (1a).** To a suspension of [AuCl(tht)] (0.68 g, 2.1 mmol) in THF (40 mL) was added a THF solution (40 mL) of $C(PPh_3)_2$ (1.18 g, 2.2 mmol) dropwise over a period of 20 min under a nitrogen atmosphere. The reactants were further stirred for 3 h, during which time a white solid precipitated. It was filtered, washed with $Et_2O$ (2 × 5 mL), and air-dried to give **1a** as a white crystalline solid. Yield: 1.31 g, 80%. The concentration of the filtrate to ca. 1 mL and addition of $Et_2O$ (20 mL) afforded 0.2 g more of **1a**, taking the total yield up to 92%. Dec pt: 250 °C; lit.[29] 250 °C for a THF monoadduct. Anal. Calcd for $C_{37}H_{30}AuClP_2$: C, 57.78; H, 3.93. Found: C, 57.51; H, 4.33. IR ($cm^{-1}$): $\nu$(Au−Cl), 326 (s). $^1H$ NMR ($CDCl_3$): $\delta$ 7.18−7.22, 7.33−7.54, 7.63−7.72, 7.96−8.06 (m, 30 H, Ph). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): $\delta$ −1.46 (t, $^1J$(CP) = 102 Hz, $C(PPh_3)_2$), 128.23 (m, *o*-C), 131.14 (s, *p*-C), 133.20 (apparent triplet, AA′X, $|^1J(CP) + {}^3J(CP)|$ = 114 Hz, *ipso*-C), 133.28 (m, *m*-C). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 14.4 (s).

**Synthesis of $[AuCl\{CH(PPh_3)\{S(O)_2C_6H_4Me\text{-}4\}\}]$ (1b).** To a $CH_2Cl_2$ (15 mL) solution of AuCl(tht) (0.23 g, 0.7 mmol) was added a $CH_2Cl_2$ (5 mL) solution of the ylide $4\text{-}MeC_6H_4SO_2CHPPh_3$ (0.31 g, 0.71 mmol). The reactants were stirred for 2 h. The solvent was evaporated in vacuo, and the white residue so obtained was washed with $Et_2O$ (3 × 2 mL). Recrystallization of the residue from a $CH_2Cl_2$−$Et_2O$ mixture afforded **1b** as a white crystalline solid. Yield: 0.42 g, 89%. Mp: 218−220 °C dec. Anal. Calcd for $C_{26}H_{23}AuClO_2PS$: C, 47.10; H, 3.49; S, 4.83. Found: C, 46.69, H, 3.60; S, 4.56. IR ($cm^{-1}$): $\nu$(Au−Cl), 328 (s). $^1H$ NMR: $\delta$ 2.38 (s, 3 H, Me), 4.93 (d, $^2J$(PH) = 10 Hz, 1 H, $CHPPh_3$), 7.21, 7.81 (AB system, $^3J$(HH) = 9 Hz, 4 H, $C_6H_4$), 7.54−7.60 (m, 6 H, Ph), 7.68−7.74 (m, 3 H, Ph), 7.92−7.99 (m, 6 H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 21.79 (Me), 50.28 (d, $^1J$(CP) = 34 Hz, C−$PPh_3$), 122.98 (d, $^1J$(CP) = 88 Hz, *ipso*-C), 127.57 (CH), 129.49 (CH), 129.7 (CH), 134.08 (br, CH), 134.38 (CH), 134.51 (CH) 143.25 (br, C), 144.24 (C). $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): $\delta$ 20.7 (s). Single crystals of **1b**·$0.5CH_2Cl_2$ were obtained by slow diffusion of hexane into a $CH_2Cl_2$ solution of **1b**.

**Synthesis of $[Au\{HC(PPh_3)_2\}Cl]TfO$ (2).** A $CH_2Cl_2$ solution (5 mL) of $[HC(PPh_3)_2]TfO$ (0.33 g, 0.48 mmol) was added to a $CH_2Cl_2$ (15 mL) solution of [AuCl(tht)] (0.15 g, 0.47 mmol). The reactants were stirred for 2 h. The solvent volume was concentrated to ca. 2 mL under reduced pressure, and $Et_2O$ (15 mL) was added to precipitate a white solid. It was filtered by suction, air-dried, and recrystallized from $CH_2Cl_2/Et_2O$ to give **2** as a white crystalline solid. Yield: 0.39 g, 90%. Mp:

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190 °C dec. $\Lambda_M$ = 159 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{38}H_{31}AuClF_3O_3P_2S$: C, 49.66; H, 3.40; S, 3.49. Found: C, 49.63; H, 3.38; S, 3.36. IR (cm$^{-1}$): $\nu$(Au−Cl), 338 (s). $^1$H NMR: $\delta$ 5.58 (t, $^2J$(PH) = 17 Hz, 1 H, HC(PPh$_3$)$_2$), 7.34−7.59, 7.62−7.89 (m, 30 H, Ph). $^{13}$C{$^1$H} (50 MHz, $CD_2Cl_2$): $\delta$ 7.17 (t, $^1J$(CP) = 45 Hz, HC(PPh$_3$)$_2$), 121.69 (m, AA′X, |$^1J$(CP) + $^3J$(CP)| = 92 Hz, *ipso*-C), 129.69 (m, *o*-C), 133.29 (m, *m*-C), 134.13 (s, *p*-C). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 22.1 (s).

**Synthesis of [(AuCl)$_2${$\mu$-C{PPh$_3$}$_2$}] (3).** To a THF solution (5 mL) of C(PPh$_3$)$_2$ (0.17 g, 0.31 mmol) was added AuCl(tht) (0.20 g, 0.62 mmol). A white solid started precipitating as soon as the two reactants were mixed. After 1 h of stirring it was filtered off, washed with Et$_2$O (2 × 5 mL), and air-dried to give **3** as a white solid. Yield: 0.22 g, 70%. Dec pt: 168−172 °C. Anal. Calcd for $C_{37}H_{30}Au_2Cl_2P_2$: C, 44.37; H, 3.02. Found: C, 44.58; H, 3.18. IR (cm$^{-1}$): $\nu$(Au−Cl), 330 (s). $^1$H NMR: $\delta$ 7.20−7.24, 7.41−7.46, 7.98−8.05 (m, Ph). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 21.2 (s). Single crystals of **3** were obtained by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution.

**Synthesis of [Au(acac){C(PPh$_3$)$_2$}] (4).** Solid Tl(acac) (0.2 g, 0.66 mmol) was added to a degassed CH$_2$Cl$_2$ (20 mL) solution of **1a** (0.46 g, 0.6 mmol) under a nitrogen atmosphere. After it was stirred for 40 min, the resulting suspension was filtered through Celite, the filtrate was concentrated to ca. 1 mL under reduced pressure, and Et$_2$O (20 mL) was added to precipitate a solid, which was filtered and dried under nitrogen to give complex **4** as a pale yellow solid. Yield: 0.47 g, 94%. Dec pt: 101−102 °C. IR (cm$^{-1}$): $\nu$(C═O), 1632 (s), 1646 (s). Anal. Calcd for $C_{42}H_{37}AuO_2P_2$: C, 60.58; H, 4.48. Found: C, 60.62; H, 4.56. $^1$H NMR: $\delta$ 1.77 (s, 6 H, Me), 4.1 (s, 1 H, CH), 7.23 (br, 9 H, Ph), 7.35−7.39 (m, 9 H, Ph), 7.57−7.64 (m, 12 H, Ph). $^{13}$C{$^1$H} NMR (50 MHz, CDCl$_3$): $\delta$ 7.59 (t, $^1J$(CP) = 94 Hz, C(PPh$_3$)$_2$), 29.71(s, Me), 128.25 (apparent triplet, AA′X, |$^3J$(CP) + $^5J$(CP)| = 12 Hz, *o*-C), 131.10 (CH), 133.02 (apparent triplet, AA′X, |$^4J$(CP) + $^6J$(CP)| = 10 Hz, *m*-C), 132.72 (m, AA′X, |$^1J$(CP) + $^3J$(CP)| = 95 Hz, *ipso*-C), 201.78 (s, CO). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 14.3 (s).

**Synthesis of the Complexes [HC(PPh$_3$)$_2$][Au(C≡CR)-Cl] (5).** Complexes **5** were obtained by reacting **1a** (0.09−0.13 mmol) with a slight excess of the corresponding alkyne (molar ratio ca. 1:1.2) in CH$_2$Cl$_2$. The reactants were stirred at room temperature for 10 h. The solvent was removed under reduced pressure, and the residue thus obtained was recrystallized from CH$_2$Cl$_2$ and Et$_2$O.

**[HC(PPh$_3$)$_2$][Au(C≡CPh)Cl] (5a).** Yield: 78%. Dec pt: 145−148 °C. $\Lambda_M$ = 136 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{45}H_{36}AuClP_2$: C, 62.04; H, 4.17. Found: C, 61.98; H, 4.20. IR (cm$^{-1}$): $\nu$(Au−Cl), 332 (s); $\nu$(C≡C), 2118 (w). $^1$H NMR: $\delta$ 1.91 (t, $^2J$(HP) = 5 Hz), 7.07−7.10, 7.33−7.34, 7.42−7.50, 7.56−7.62 (m, Ph). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ −1.89 (t, $^1J$(CP) = 124 Hz, HC(PPh$_3$)$_2$), 98.28 (C), 110.14 (C), 125.08 (CH), 126.20 (m, AA′X system, |$^1J$(CP) + $^3J$(CP)| = 102 Hz, *ipso*-C), 127.45 (CH), 129.49 (apparent triplet, AA′X, |$^3J$(CP) + $^5J$(CP)| = 12 Hz, *o*-C), 132.22 (CH), 132.76 (apparent triplet, AA′X, |$^4J$(CP) + $^6J$(CP)| = 10 Hz, *m*-C), 133.25 (CH). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 21.1 (s). Single crystals of **5a** suitable for an X-ray diffraction study were obtained by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution.

**[HC(PPh$_3$)$_2$][Au(C≡CC$_6$H$_4$CN-4)Cl] (5b).** Yield: 72%. Dec pt: 130−132 °C. $\Lambda_M$ = 121 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{46}H_{35}AuClNP_2$: C, 61.65; H, 3.94; N, 1.56. Found: C, 61.85; H, 4.16; N, 1.63. IR (cm$^{-1}$): $\nu$(Au−Cl), 328 (s); $\nu$(C≡N), 2222 (s); $\nu$(C≡C), 2112 (w). $^1$H NMR: $\delta$ 1.87 (t, $^2J$(HP) = 5 Hz), 7.35 (s), 7.43−7.49, 7.57−7.63 (m, Ph or CNC$_6$H$_4$). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ −1.58 (t, $^1J$(CP) = 124 Hz, HC{PPh$_3$}$_2$), 97.63 (C), 107.87 (C), 119.38 (CN), 119.70 (C), 126.39 (m, AA′X, |$^1J$(CP) + $^3J$(CP)| = 102 Hz, *ipso*-C), 129.66 (apparent triplet, AA′X, |$^3J$(CP) + $^5J$(CP)| = 12 Hz, *o*-C), 131.45 (CH), 132.91 (apparent triplet, AA′X, |$^4J$(CP) + $^6J$(CP)| = 10 Hz, *m*-C), 133.46 (CH). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 21.1 (s).

**Synthesis of [HC(PPh$_3$)$_2$][Au(C≡CC$_6$H$_4$OMe-4)Cl] (5c).** Yield: 66%. Dec pt: 138−140 °C. $\Lambda_M$ = 126 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{46}H_{38}AuClOP_2$: C, 61.31; H, 4.25. Found: C, 60.78; H, 4.43. IR (cm$^{-1}$): $\nu$(Au−Cl), 332 (s); $\nu$(C≡C), 2118 (w). $^1$H NMR: $\delta$ 1.93 (t, $^2J$(HP) = 5 Hz), 3.74 (s, 3 H, OMe), 6.67, 7.29 (AB system, $^3J$(HH) = 9 Hz, 4 H, C$_6$H$_4$), 7.41−7.51 (m, 24 H, Ph), 7.56−7.62 (m, 6 H, Ph). $^{13}$C{$^1$H} NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ −1.93 (t, $^1J$(CP) = 124 Hz, HC{PPh$_3$}$_2$), 55.09 (s, Me), 96.98 (CAu), 108.84 (C), 113.31 (CH), 120.05 (C), 126.37 (m, AA′X, |$^1J$(CP) + $^3J$(CP)| = 102 Hz, *ipso*-C), 129.39 (apparent triplet, AA′X, |$^3J$(CP) + $^5J$(CP)| = 12 Hz, *o*-C), 132.84 (apparent triplet, AA′X, |$^4J$(CP) + $^6J$(CP)| = 10 Hz, *m*-C), 132.91 (CH) 133.20 (CH) 157.51 (C). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 21.1 (s). Single crystals of **5c** suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a CH$_2$Cl$_2$ solution.

**Synthesis of [HC(PPh$_3$)$_2$][Au(C≡CC$_6$H$_4$NO$_2$-4)Cl] (5d).** Yield: 83%. Dec pt: 146−148 °C. $\Lambda_M$ = 119 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{45}H_{35}AuClNO_2P_2$: C, 59.00,. H, 3.85, N, 1.53. Found: C, 58.54; H, 3.82, N, 1.74. IR (cm$^{-1}$): $\nu$(Au−Cl), 336 (s); $\nu$(C≡C), 2116 (w); $\nu_{asym}$(NO$_2$), 1504 (s); $\nu_{sym}$ (NO$_2$), 1336 (s). $^1$H NMR: $\delta$ 1.86 (t, $^2J$(HP) = 5 Hz), 7.38−7.48 (m, Ph or C$_6$H$_4$NO$_2$), 7.56−7.62 (m, Ph or C$_6$H$_4$NO$_2$), 7.96 (d, Ph or C$_6$H$_4$NO$_2$). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ −1.86 (t, $^1J$(CP) = 124 Hz, HC{PPh$_3$}$_2$), 97.70 (C−Au), 121.53 (C), 123.06 (CH) 126.18 (m, AA′X, |$^1J$(CP) + $^3J$(CP)| = 102 Hz, *ipso*-C), 129.49 (apparent triplet, AA′X, |$^3J$(CP) + $^5J$(CP)| = 12 Hz, *o*-C), 132.40 (CH) 132.73 (apparent triplet, AA′X, |$^4J$(CP) + $^6J$(CP)| = 10 Hz, *m*-C), 133.29 (CH) 135.14 (C), 144.65 (C). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 21.1 (s).

**Synthesis of [Au(C≡CPh){C(PPh$_3$)$_2$}] (6a).** To a freshly distilled and degassed chloroform (5 mL) solution of **4** (0.10 g, 0.12 mmol) was added phenylacetylene (0.372 g, 3.64 mmol) under a nitrogen atmosphere. The reactants were stirred for 1.5 h, after which the volume of the solution was reduced to 1 mL under reduced pressure and Et$_2$O (10 mL) was added to precipitate a solid which was filtered, washed with Et$_2$O (2 × 2 mL), and air-dried to afford **6a** as a cream-colored solid. Yield: 90 mg, 90%. Dec pt: 252−254 °C. Anal. Calcd for $C_{45}H_{35}AuP_2$: C, 64.75; H, 4.22. Found: C, 64.81; H, 4.32. IR (cm$^{-1}$): $\nu$(C≡C), 2104 (w). $^1$H NMR: $\delta$ 7.03−7.13, 7.19−7.25, 7.32−7.37, 7.44−7.48, 7.65−7.72 (m, 35 H, Ph). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ 9.62 (t, $^1J$(CP) = 94 Hz, C(PPh$_3$)$_2$), 101.57 (C), 102.65 (C), 125.11 (C), 127.51 (CH), 128.15 (apparent triplet, AA′X, |$^3J$(CP) + $^5J$(CP)| = 11.5 Hz, *o*-C), 130.90 (CH), 132.27 (CH), 133.43 (apparent triplet, AA′X, |$^4J$(CP) + $^6J$(CP)| = 9 Hz, *m*-C), 133.13 (m, AA′X system, |$^1J$(CP) + $^3J$(CP)| = 94 Hz, *ipso*-C). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 16.06 (s).

**Synthesis of [Au(C≡CC$_6$H$_4$CN-4){C(PPh$_3$)$_2$}] (6b).** The off-white complex **6b** was prepared as for **6a** from **4** (0.17 g, 0.2 mmol) and 4-NCC$_6$H$_4$C≡CH (0.7 g, 5.5 mmol) after 3 h of stirring. Yield: 0.125 g, 71%. Mp: 198−200 °C. Anal. Calcd for $C_{46}H_{34}AuNP_2$: C, 64.26; H, 3.98; N, 1.62. Found: C, 63.62; H, 4.00; N, 1.60. IR (cm$^{-1}$): $\nu$(C≡C), 2106 (w); $\nu$(C≡N), 2218 (s). $^1$H NMR: $\delta$ 7.1 (m, Ph or C$_6$H$_4$CN), 7.12 (m, Ph or C$_6$H$_4$CN), 7.15 (m, Ph or C$_6$H$_4$CN), 7.23 (m, Ph or C$_6$H$_4$CN), 7.53−7.60 (m, Ph or C$_6$H$_4$CN). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$): $\delta$ 10.68 (t, $^1J$(CP) = 95 Hz, C(PPh$_3$)$_2$), 100.19 (C), 107.63 (C), 119.32 (C), 128.00 (apparent triplet, AA′X, |$^3J$(CP) + $^5J$(CP)| = 11.5 Hz, *o*-C), 130.90 (CH), 131.36 (CH), 132.07 (CH), 133.06 (apparent triplet, AA′X, |$^4J$(CP) + $^6J$(CP)| = 9 Hz, *m*-C), 132.72 (m, AA′X system, |$^1J$(CP) + $^3J$(CP)| = 95 Hz, *ipso*-C). $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 16.5 (s).

**Synthesis of [Au(C≡CC$_6$H$_4$OMe-4){C(PPh$_3$)$_2$}] (6c).** The pale yellow complex **6c** was prepared as for **6a** from **4** (64 mg, 0.077 mmol) and 4-MeOC$_6$H$_4$C≡CH (0.308 g, 2.3 mmol) after stirring the reaction mixture for 4 h. Yield: 55 mg, 82%. Dec pt: 140−142 °C. Anal. Calcd for **6c**·0.5CH$_2$Cl$_2$, $C_{46.5}H_{38}AuClOP_2$: C, 61.56; H, 4.22. Found: C, 61.13; H, 4.25. IR (cm$^{-1}$): $\nu$(C≡C), 2106 (w). $^1$H NMR: $\delta$ 3.74 (s, 3 H, OMe), 5.29 (s, 1 H, 0.5 CH$_2$Cl$_2$), 6.66, 7.14 (AB system, $^3J$(HH) = 9 Hz, 4

H, $C_6H_4$), 7.24−7.29 (m, 12 H, Ph), 7.38−7.42 (m, 6 H, Ph). 7.67−7.74 (m, 12 H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CD_2Cl_2$): $\delta$ 10.86 (t, $^1J$(CP) = 95 Hz C($PPh_3$)$_2$), 55.47 (s, Me), 100.52 (C), 113.73 (CH), 120.47 (C), 126.75 (C), 128.48 (apparent triplet, AA′X, $|^3J(CP) + {}^5J(CP)|$ = 11 Hz, *o*-C), 131.34 (CH), 133.04 (CH), 133.40 (m, AA′X system, $|^1J(CP) + {}^3J(CP)|$ = 95 Hz, *ipso*-C). 133.51 (CH), 133.43 (apparent triplet, AA′X, $|^4J(CP) + {}^6J(CP)|$ = 9 Hz, *m*-C), 157.81 (C). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 15.9(s).

**Synthesis of [Au(C≡CC$_6$H$_4$NO$_2$-4){C(PPh$_3$)$_2$}] (6d).** The orange crystalline complex **6d** was prepared as for **6a** from **4** (0.164 g, 0.19 mmol) and 4-$NO_2C_6H_4$C≡CH (0.70 g, 4.75 mmol) after stirring the reaction mixture for 2.5 h. Yield: 0.12 g, 71%. Dec pt: 164 °C. Anal. Calcd for $C_{45}H_{34}AuNO_2P_2$: C, 61.44; H, 3.90, N, 1.59. Found: C, 61.62; H, 4.06; N, 1.97. IR (cm$^{-1}$): $\nu$(C≡C), 2096 (w); $\nu_{asym}(NO_2)$, 1504 (s); $\nu_{sym}(NO_2)$, 1334 (s). $^1H$ NMR: $\delta$ 7.20−7.21 (m, 12 H, $C_6H_4NO_2$ or Ph), 7.34−7.41 (m, 8 H, $C_6H_4NO_2$ or Ph), 7.64−7.71 (m, 12 H, $C_6H_4NO_2$ or Ph), 7.97 (d, 9 Hz, 2 H, $C_6H_4NO_2$ or Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 10.52 (t, $^1J$(CP) = 93 Hz, C($PPh_3$)$_2$), 101.09 (C), 123.22 (CH), 128.24 (apparent triplet, AA′X, $|^3J(CP) + {}^5J(CP)|$ = 11.5 Hz, *o*-C), 131.07 (CH), 132.90 (m, AA′X system, $|^1J(CP) + {}^3J(CP)|$ = 95 Hz, *ipso*-C). 132.55 (CH) 133.39 (apparent triplet, AA′X, $|^4J(CP) + {}^6J(CP)|$ = 9 Hz, *m*-C), 138.04 (C), 135.12 (C), 144.80 (C−$NO_2$). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 16.6 (s). Single crystals of **6d** suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a THF solution of **6d**.

**Synthesis of [Au(C≡CC$_6$H$_4$C≡CPh-4){C(PPh$_3$)$_2$}] (6e).** Pale yellow **6e** was prepared as for **6a** from **4** (70 mg, 0.084 mmol) and 4-PhC≡C$C_6H_4$C≡CH (0.432 g, 3.62 mmol) after stirring the reaction mixture for 5 h. Yield: 55 mg, 70%. Mp: 96−98 °C. Anal. Calcd for $C_{53}H_{39}AuP_2$: C, 68.10; H, 4.20. Found: C, 68.68; H, 4.20. IR (cm$^{-1}$): $\nu$(C≡C), 2100 (w). $^1H$ NMR: $\delta$ 6.92−6.99, 7.20−7.38, 7.40−7.48, 7.51−7.53, 7.63−7.72 (m, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 9.78 (t, $^1J$(CP) = 96 Hz, C{$PPh_3$}$_2$), 89.73 (C), 90.35 (C), 101.61 (C), 122.00 (C), 123.07 (C), 123.82 (CH), 128.19 (apparent triplet, AA′X, $|^3J(CP) + {}^5J(CP)|$ = 12 Hz, *o*-C), 128.38 (CH), 128.5 (CH), 130.97 (CH), 131.60 (CH) 132.0 (m, AA′X system, $|^1J(CP) + {}^3J(CP)|$ = 95 Hz, *ipso*-C), 132.19 (CH), 133.40 (apparent triplet, AA′X, $|^4J(CP) + {}^6J(CP)|$ = 9 Hz, *m*-C). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 16.2 (s).

**Synthesis of [Au(C≡CPh){CH(PPh$_3$){S(O)$_2$C$_6$H$_4$Me-4}}] (7a).** A $CH_2Cl_2$ (10 mL) solution of **1b** (0.112 g, 0.17 mmol) was added to a stirred $CH_2Cl_2$ (5 mL) solution of phenylacetylene (0.0186 g, 0.18 mmol) and triethylamine (0.0218 g, 0.21 mmol). The reaction mixture was stirred for 8 h. The volume of the solution was reduced to ca. 2 mL under reduced pressure, and $Et_2O$ (20 mL) was added to precipitate a white solid, which was filtered and washed with water (2 × 5 mL) to remove [$NHEt_3$]Cl. The solid residue was dissolved in $CH_2Cl_2$ (20 mL), the solution was passed through anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was recrystallized from $CH_2Cl_2$/hexane to afford **7a** as a white crystalline solid (0.098 g, 79.6%). Mp: 160 °C. $\Lambda_M$ = 3 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{34}H_{28}AuO_2PS$: C, 56.05; H, 3.87; S, 4.40. Found: C, 56.23; H, 4.02; S, 4.12. IR (cm$^{-1}$): $\nu$(C≡C), 2118 (w). $^1H$ NMR: $\delta$ 2.38 (s, 3 H, Me); 4.60 (d, $^2J$(PH) = 11 Hz, 1 H, HCP), 7.33, 7.81 (AB system, $^3J$(HH) = 9 Hz, 4 H, $C_6H_4$), 7.09−7.23 (m, 4 H, Ph), 7.52−7.59 (m , 6 H, Ph), 7.66−7.70 (m, 4 H, Ph), 7.91−7.98 (m, 6 H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 21.75 (s, Me); 55.34 (d, $^1J$(CP) = 32 Hz, H*C*PPh$_3$), 102.14 (Au−C), 123.45 (d, 89 Hz, *ipso*-C), 125.10 (C), 125.95 (CH), 126.31 (C), 127.37 (CH), 127.77 (CH), 128.7 (C), 129.49 (d, $^1J$(CP) = 13.0 Hz, *o*-C), 132.27 (CH), 133.79 (d, 2.3 Hz, *p*-C), 134.51 (d, 9.7 Hz, *m*-C), 143.46 (C−$SO_2$), 143.51 (C−Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 21.4 (s).

**Synthesis of [Au(C≡CC$_6$H$_4$CN-4){CH(PPh$_3$){S(O)$_2$-C$_6$H$_4$Me-4}}] (7b).** The off-white complex **7b** was prepared as for **7a** using **1b** (0.2 g, 0.30 mmol), 4-NC$C_6H_4$C≡CH (42 mg, 0.33 mmol), and $Et_3N$ (34 mg, 0.33 mmol). Yield: 0.16 g, 68%. Dec pt: 162−163 °C. $\Lambda_M$ = 3 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for **7b**·0.15$CH_2Cl_2$, $C_{35.15}H_{27.3}Cl_{0.3}AuNO_2PS$: C, 55.09; H, 3.59; N, 1.83; S, 4.18. Found: C, 55.18; H, 3.66; N, 1.93; S, 3.86. IR (cm$^{-1}$): $\nu$(C≡C), 2116 (w); $\nu$(C≡N), 2222 (s). $^1H$ NMR: $\delta$ 2.38 (s, 3 H, Me), 4.6 (d, $^2J$(PH) = 11 Hz, 1 H, CHP), 5.29 (s, 0.3 H, $CH_2Cl_2$), 7.2, 7.7 (AB system, $^3J$(HH) = 8 Hz, 4 H, $C_6H_4SO_2$), 7.34−7.50 (m, 4 H, $C_6H_4$C≡C), 7.52−7.58 (m, 3 H, Ph), 7.66−7.71 (m, 6 H, Ph), 7.89−7.96 (m, 6 H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 21.76 (s, Me), 55.52 (d, $^1J$(CP) = 32 Hz, CPPh$_3$), 101.04 (C), 108.84 (C), 119.41 (CN), 123.33 (d, $^1J$(CP) = 89 Hz, *ipso*-C), 127.34 (CH), 129.52 (d, 12.7 Hz, *o*-C), 129.67 (CH), 131.63 (CH), 132.69 (CH), 133.90 (d, 3 Hz, *p*-C), 134.45 (d, 10 Hz, *m*-C), 143.48 (*C*−$SO_2$), 143.79 (*C*−Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 21.6 (s).

**Synthesis of [Au(C≡CC$_6$H$_4$OMe-4){CH(PPh$_3$){S(O)$_2$-C$_6$H$_4$Me-4}}] (7c).** White crystalline complex **7c** was prepared as for **7a** using using **1b** (0.155 g, 0.23 mmol), 4-MeO$C_6H_4$C≡CH (32 mg, 0.24 mmol), and $Et_3N$ (26 mg, 0.25 mmol). Yield: 0.125 g, 70%. Dec pt: 108−110 °C. $\Lambda_M$ = 4 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{35}H_{30}AuO_3PS$: C, 55.41; H, 3.99; S, 4.23. Found: C, 54.94; H, 4.00; S, 4.12. IR (cm$^{-1}$): $\nu$(C≡C), 2114 (w). $^1H$ NMR: $\delta$ 2.38 (s, 3 H, Me), 3.74 (s, 3 H, OMe), 4.58 (d, $^2J$(PH) = 11 Hz, 1 H, CHP), 6.7 (d, $^3J$(HH) = 9 Hz, 2 H, $C_6H_4$C≡C), 7.2, 7.8 (AB system, $^3J$(HH) = 8 Hz, 4 H, $C_6H_4$-Me), 7.52−7.61 (m, 6 H, Ph or $C_6H_4$C≡C), 7.62−7.71 (m, 5 H, Ph or $C_6H_4$C≡C), 7.91−7.98 (m, 6 H, Ph or $C_6H_4$C≡C). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 21.4 (s).

**Synthesis of [Au(C≡CC$_6$H$_4$NO$_2$-4){CH(PPh$_3$){S(O)$_2$-C$_6$H$_4$Me-4}}] (7d).** Yellow crystalline complex **7d** was prepared as for **7a** using **1b** (0.18 g, 0 27 mmol), 4-$O_2NC_6H_4$C≡CH (54.2 mg, 0.37 mmol), and $Et_3N$ (38 mg, 0.37 mmol). Yield: 0.15 g, 71%. Mp: 160 °C. $\Lambda_M$ = 4 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for **7d**·0.25$CH_2Cl_2$, $C_{34.25}H_{27.5}AuCl_{0.5}NO_4PS$: C, 51.76; H, 3.49; N, 1.76; S, 4.03. Found: C, 51.80; H, 3.47; N, 1.83; S, 3.94. IR (cm$^{-1}$): $\nu$(C≡C), 2116 (w); $\nu_{asym}$ ($NO_2$), 1510 (s); $\nu_{sym}$($NO_2$), 1348 (s). $^1H$ NMR: $\delta$ 2.39 (s, 3 H, Me), 4.61 (d, $^2J$(PH) = 11 Hz, 1 H, CHP), 5.29 (s, 0.5 H, $CH_2Cl_2$), 7.22, 7.78 (AB system,$^3J$(HH) = 8 Hz, 4 H, $C_6H_4SO_2$), 7.4, 8.03 (AB system, $^3J$(HH) = 9 Hz, 4 H, $C_6H_4$C≡C), 7.54−7.67 (m, 6 H, Ph), 7.69−7.72 (m, 3 H, Ph), 7.9−8.00 (m, 6 H, Ph), $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 21.79 (s, Me), 55.48 (d, $^1J$(CP) = 32 Hz, CHP), 101.10 (C), 123.22 (d, $^1J$(CP) = 89 Hz, *ipso*-C), 123.34 (C), 127.30 (CH), 127.56 (CH), 129.54 (d, $^2J$(CP) = 13 Hz, *o*-C), 132.69 (CH), 133.77 (C), 134.43 (d, $^3J$(CP) = 10 Hz, *m*-C), 134.76 (CH), 143.36 (C−$SO_2$), 143.83 (C−Me), 145.37 (C−$NO_2$). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 21.8 (s)

**Synthesis of [Au(C≡CC$_6$H$_4$C≡CPh-4){CH(PPh$_3$){S(O)$_2$-C$_6$H$_4$Me-4}}] (7e).** The yellow complex **7e** was prepared as for **7a** from **1b** (0.12 g, 0 18 mmol), PhC≡C$C_6H_4$C≡CH (44 mg, 0.21 mmol), and $Et_3N$ (22 mg, 0.21 mmol). Yield: 75 mg, 50%. Dec pt: 134−136 °C. $\Lambda_M$ = 8 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{42}H_{32}AuO_2PS$: C, 60.87; H, 3.89; S, 3.86. Found: C, 61.05; H, 4.11; S, 3.62. IR (cm$^{-1}$): $\nu$(C≡C), 2108 (w). $^1H$ NMR: $\delta$ 2.39 (s, 3 H, Me), 4.60 (d, $^2J$(PH) = 11 Hz, 1 H, CHP), 7.23, 7.81 (AB system, $^3J$(HH) = 8 Hz, 4 H, $C_6H_4SO_2$), 7.30−7.34 (m, 6 H, $C_6H_4$C≡C or Ph), 7.42−7.70 (m, 12 H, $C_6H_4$C≡C or Ph), 7.91−7.98 (m, 6 H, $C_6H_4$C≡C or Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 21.71 (s, Me), 55.04 (d, $^1J$(CP) = 32 Hz, CHP), 89.86 (C), 90.35 (C), 101.45 (C), 120.62 (C), 123.42 (d, $^1J$(CP) = 89 Hz, *ipso*-C), 125.10 (C), 125.58 (C), 126.73 (C), 127.03 (C), 127.30 (CH), 127.56 (C), 128.56 (CH), 129.67 (d, $^2J$(CP) = 12.7 Hz, *o*-C), 129.79 (CH), 131.44 (CH), 131.79 (CH), 132.11 (CH), 134.13 (d, $^4J$(CP) = 2.9 Hz, *p*-C), 134.63 (d, $^3J$(CP) = 10 Hz, *m*-C), 143.42 (CSO$_2$), 144.11 (CMe). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 21.6 (s).

**Synthesis of [Au{HC(PPh$_3$)$_2$}$_2$](TfO)$_3$ (8a).** Solid [$CH_2$-($PPh_3$)$_2$](TfO)$_2$ (0.553 g, 0.660 mmol) was added to a solution of PPN[Au(acac)$_2$] (0.308 g, 0.330 mmol) in 1.5 mL of $CH_2Cl_2$. The resulting mixture was stirred for 5 h, during the course

**Table 1. Summary of X-ray Data for [4-MeC$_6$H$_4$S(O)$_2$CH$_2$PPh$_3$]TfO and the Complexes 1b·0.5CH$_2$Cl$_2$ and 3·3CH$_2$Cl$_2$**

| | [4-MeC$_6$H$_4$S(O)$_2$CH$_2$PPh$_3$]TfO | **1b**·0.5CH$_2$Cl$_2$ | **3**·3CH$_2$Cl$_2$ |
|---|---|---|---|
| formula | $C_{27}H_{24}F_3O_5PS_2$ | $C_{26.5}H_{24}AuCl_2O_2PS$ | $C_{40}H_{36}Au_2Cl_8P_2$ |
| $M_r$ | 580.55 | 705.35 | 1256.16 |
| cryst syst | triclinic | monoclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 9.3844(10) | 10.7675(16) | 13.3093(8) |
| $b$ (Å) | 11.1949(12) | 14.957(2) | 18.7357(12) |
| $c$ (Å) | 13.4673(14) | 16.499(2) | 17.7001(12) |
| α (deg) | 69.404(8) | 90 | 90 |
| $\beta$ (deg) | 84.271(8) | 96.827(10) | 105.100(3) |
| $\gamma$ (deg) | 83.508(8) | 90 | 90 |
| $V$ (Å$^3$) | 1313.2(2) | 2638.3(6) | 4261.31(5) |
| $Z$ | 2 | 4 | 4 |
| $T$ (K) | 173(2) | 173(2) | 133(2) |
| $D_{calcd}$ (Mg m$^{-3}$) | 1.468 | 1.776 | 1.958 |
| $F$(000) | 600 | 1372 | 2400 |
| $\mu$ (mm$^{-1}$) | 0.322 | 5.941 | 7.484 |
| no. of indep rflns | 4528 | 4641 | 12 473 |
| no. of data/restraints/params | 4528/373/377 | 4641/266/312 | 12 473/432/469 |
| $S(F^2)$ | 1.030 | 0.899 | 0.978 |
| wR2 (all rflns) | 0.0899 | 0.0446 | 0.0539 |
| R1 ($I > 2\sigma(I)$) | 0.0342 | 0.0233 | 0.0225 |
| max $\Delta\rho$ (e Å$^{-3}$) | 0.303 | 0.619 | 1.602 |

**Table 2. Summary of X-ray Data for Complexes 5a, 5c, 6d·THF, and 8b**

| | **5a** | **5c** | **6d**·THF | **8b** |
|---|---|---|---|---|
| formula | $C_{45}H_{36}AuClP_2$ | $C_{46}H_{38}AuClOP_2$ | $C_{49}H_{42}AuNO_3P_2$ | $C_{53}H_{46}AuF_3O_7P_2S_3$ |
| $M_r$ | 871.09 | 901.12 | 951.74 | 1206.98 |
| cryst syst | monoclinic | monoclinic | triclinic | monoclinic |
| space group | $Cc$ | $Cc$ | $P\bar{1}$ | $P2_1/n$ |
| $a$ (Å) | 16.7631(12) | 17.1531(11) | 11.7875(11) | 16.098(3) |
| $b$ (Å) | 15.7320(11) | 15.8402(11) | 13.4391(12) | 15.402(2) |
| $c$ (Å) | 15.0215(11) | 15.1264(8) | 14.8753(12) | 20.668(3) |
| α (deg) | 90 | 90 | 78.828(3) | 90 |
| $\beta$ (deg) | 111.100(4) | 112.657(3) | 68.060(3) | 106.222(10) |
| $\gamma$ (deg) | 90 | 90 | 68.627(3) | 90 |
| $V$ (Å$^3$) | 3695.8(5) | 3792.8(4) | 2030.9(3) | 4920.4(13) |
| $Z$ | 4 | 4 | 2 | 4 |
| $T$ (K) | 133(2) | 133(2) | 133(2) | 173(2) |
| $D_{calcd}$ (Mg m$^{-3}$) | 1.566 | 1.578 | 1.556 | 1.629 |
| $F$(000) | 1728 | 1792 | 952 | 2416 |
| $\mu$ (mm$^{-1}$) | 4.171 | 4.069 | 3.745 | 3.247 |
| no. of indep rflns | 10 759 | 10 986 | 11 826 | 8654 |
| no. of data/restraints/params | 10 759/147/443 | 10 986/152/462 | 11 826/163/ 505 | 8654/551/616 |
| $S(F^2)$ | 0.951 | 0.982 | 1.013 | 0.853 |
| wR2 (all rflns) | 0.0401 | 0.0359 | 0.0597 | 0.0517 |
| R1 ($I > 2\sigma(I)$) | 0.0218 | 0.0179 | 0.0249 | 0.0266 |
| max $\Delta\rho$ (e Å$^{-3}$) | 1.604 | 0.995 | 2.110 | 0.596 |



of which a white solid precipitated. The solid was filtered by suction, washed with cold CH$_2$Cl$_2$ (2 × 1 mL), and air-dried to give **8a** as a white solid. Yield: 70%. Dec pt: 250−252 °C. $\Lambda_M$ = 254 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{75}H_{62}AuF_9O_9P_4S_3$: C, 53.14; H, 3.69; S, 5.67. Found: C, 52.94; H, 3.57; S, 5.26. $^1$H NMR ($d_6$-acetone): $\delta$ 5.69 (t, $^2J$(HP) = 16 Hz, 2 H, CH), 7.29−7.77 (m, 60 H, Ph). $^{31}$P{$^1$H} NMR (121 MHz, $d_6$-acetone): $\delta$ 26.1 (s).

**Synthesis of [Au{CH(PPh$_3$){S(O)$_2$C$_6$H$_4$Me-4}}$_2$]TfO (8b).** White complex **8b** was prepared as for **8a** from PPN[Au(acac)$_2$] (0.100 g, 0.108 mmol) and [4-MeC$_6$H$_4$S(O)$_2$CH$_2$PPh$_3$]TfO (0.126 g, 0.217 mmol) in 1 mL of THF. Yield: 66%. Dec pt: 188−190 °C. $\Lambda_M$ = 147 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Anal. Calcd for $C_{53}H_{46}AuF_3O_7P_2S_3$: C, 52.74; H, 3.84; S, 7.97. Found: C, 52.40; H, 3.93; S, 7.68. $^1$H NMR ($d_6$-acetone): $\delta$ 2.34 (s, 6 H, Me), 5.32 (d, 11 Hz, 2 H, CH), 7.09 (d, $^3J$(HP) = 8 Hz, 4 H, C$_6$H$_4$), 7.43−7.51 (m, 16 H, Ph or C$_6$H$_4$), 7.75−7.86 (m, 18 H, Ph or C$_6$H$_4$). $^{31}$P{$^1$H} NMR (121 MHz, $d_6$-acetone): $\delta$ 20.2 (s).

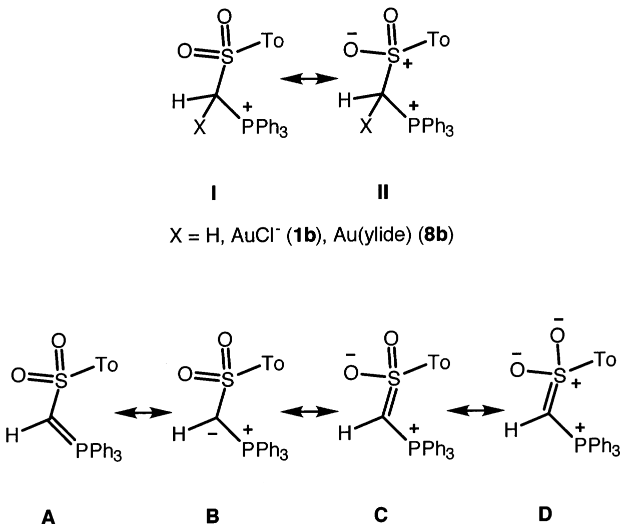
**X-ray Structure Determinations.** Data were collected using Mo Kα radiation ($\lambda$ = 0.710 73 Å). For compounds [4-MeC$_6$H$_4$S(O)$_2$CH$_2$PPh$_3$]TfO, **1b**, and **8b** a Siemens P4 diffractometer was used ($\omega$-scans, $2\theta_{max}$ = 50°, absorption correction by $\psi$-scans); for the other structures, a Bruker SMART 1000 CCD ($\omega$- and $\phi$-scans, $2\theta_{max}$ = 60°, absorption correction using multiple scans). Structures were refined anisotropically on $F^2$ using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model or rigid methyl groups. Light atom $U$ values were restrained to be approximately equal (commands SIMU, DELU). Disordered groups were refined using appropriate systems of similarity restraints. Other details of the data collection and refinement are given in Tables1 and 2.

**Special Features of the Refinement.** [4-MeC$_6$H$_4$S(O)$_2$-CH$_2$PPh$_3$]TfO: the triflate anion is disordered over two positions with occupations of ca. 89:11. Compound **1b**: the solvent is disordered over two positions with occupations ca. 70:30. Compounds **5a** and **5c**: the structures were refined as enantiomorphic twins, with twinning ratios 0.333:0.667 and 0.433:0.567, respectively. Compound **8b**: the triflate is disordered over two equally occupied sites.

## Results and Discussion

**Synthesis of [4-MeC$_6$H$_4$SO$_2$CH$_2$PPh$_3$]X (X = I, CF$_3$SO$_3$).** The triflate salt of the phosphonium cation [4-MeC$_6$H$_4$SO$_2$CH$_2$PPh$_3$]$^+$ has recently been described

**Chart 1**

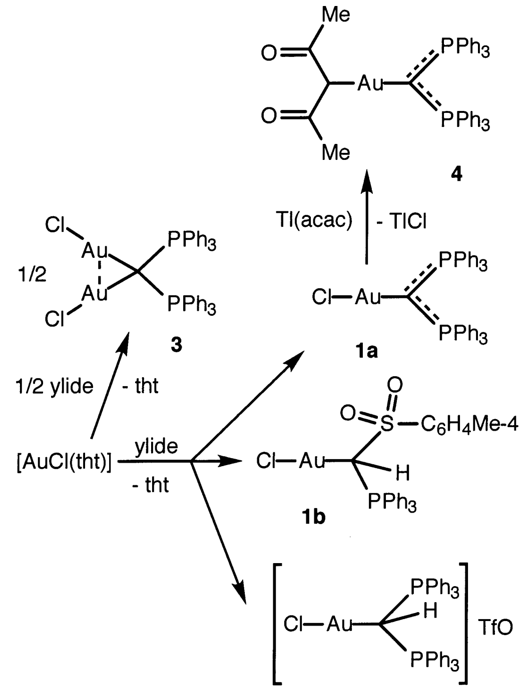



by Zhdankin starting from 4-$MeC_6H_4SO_2CH_2I$ and following a three-step synthetic procedure.[48] We report the synthesis of the iodide salt by heating the same starting material, triphenylphosphine, and triphenyl phosphate at 125–130 °C for 36 h, extending the procedure used for the synthesis of the diphosphonium salt $[CH_2(PPh_3)_2]Br_2$.[44] The triflate salt was prepared by reacting the iodide with thallium(I) triflate and the ylide by dehydroiodination of the iodide salt by $^{n}$BuLi in THF. *C*-Sulfonyl-substituted ylides are among the most stable ylides, as attributable to the efficient delocalization of the negative charge on the ylide carbon over the oxygen atoms (see Chart 1). They have been obtained by various methods as stable crystalline substances. We are not aware of the existence of metal complexes of these ligands.[22,23]

**Synthesis of the Complexes [AuCl(ylide)], [AuCl(ylide)]TfO, [(AuCl)$_2${$\mu$-ylide}], and [Au(acac)(ylide)].** The reaction of AuCl(tht) (tht = tetrahydrothiophene) with the ylide $C(PPh_3)_2$ in THF or with 4-$MeC_6H_4SO_2$-$CHPPh_3$ or $[HC(PPh_3)_2]$TfO in $CH_2Cl_2$ (1:1 molar ratio) readily afforded the corresponding complexes [AuCl(ylide)]$X_n$ ($n$ = 0, ylide = $C(PPh_3)_2$ (**1a**), 4-$MeC_6H_4SO_2$-$CHPPh_3$ (**1b**), $n$ = 1, X = TfO, ylide = $[HC(PPh_3)_2]^+$ (**2**)) in good to excellent yields (Scheme 1). The only previously known gold complex with the diylide $C(PPh_3)_2$ is **1a**,[29] preliminarily reported by Schmidbaur and obtained by reacting $C(PPh_3)_2$ with [AuCl(CO)]. Complex **2** is the first gold complex with the ylide cation $[HC(PPh_3)_2]^+$.[25]

When we attempted to prepare **1a** in a large quantity (about 1 g), a white solid precipitated immediately. On isolation, this showed NMR data different from those of **1a**, and C and H analyses indicated that the complex could be the dinuclear [$(AuCl)_2${$\mu$-$C(PPh_3)_2$}] (**3**) (Scheme 1). This was confirmed by reacting [AuCl(tht)] and $C(PPh_3)_2$ in a 2:1 molar ratio. The insolubility of **3** and a localized excess of AuCl(tht) in the 1:1 reaction could explain its unexpected formation in the large-scale synthesis of **1a**. These results indicate that the coordinated ylide $C(PPh_3)_2$ in **1a** retains some basic character after coordination to AuCl, because it replaces the tht

**Scheme 1**



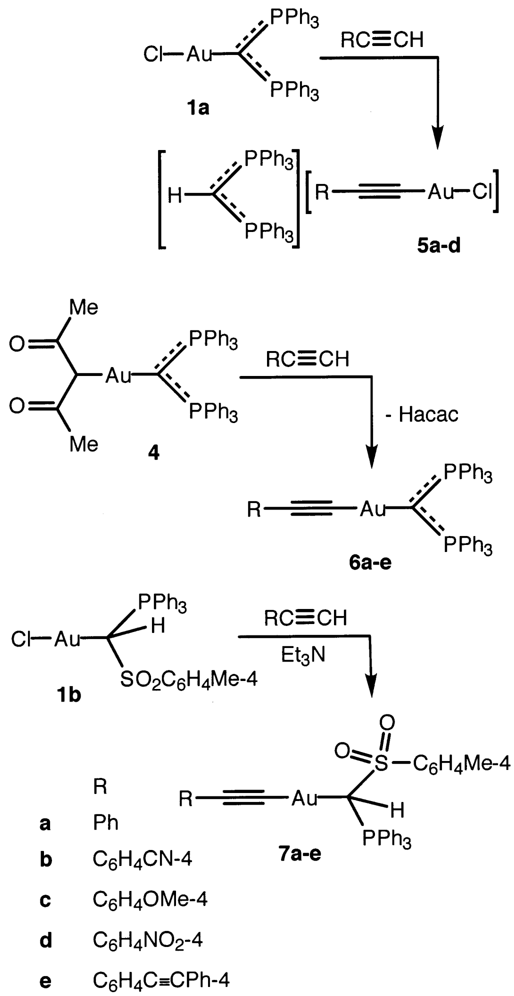

ligand of [AuCl(tht)]. In other words, complex **1a** behaves as a ligand. Solutions of complex **3** in chlorinated solvents ($CH_2Cl_2$ or $CHCl_3$) decompose slowly. We have reported di-, tri-, and tetranuclear complexes containing C-bridging ylides which, in contrast to **3**, are all cationic and have been prepared by reacting the phosphonium or arsonium salts $[R_3AsCH_2C(O)R']^+$, [Au{$HC(PPh_3)(CO_2R)$}$_2$]$^+$, [OC{$CH_2L'$}$_2$]$^{2+}$, and $[Ph_2P(CH_2CO_2R)_2]ClO_4$ with [Au(acac)$PR'_3$] or PPN[Au(acac)$_2$]. The resulting complexes are of the following types: [$(AuEPh_3)_2${$\mu$-$C(PPh_3)R$}]$^+$ (E = P, As; R = C(O)Me, C(O)Ph, C(O)$NMe_2$, $CO_2Me$, $CO_2Et$, CN, pyridyl-2), [Au{$C(PPh_3)(AuPPh_3)(CO_2R)$}$_2$]$^+$ (R = Me, Et), [$(AuL)_2${$\mu$-{C(L)C(O)CH(L)(AuL)}}]$^{2+}$ (L = $PPh_3$), [$(AuL)_4${$\mu$-{C(L')}$_2$C(O)}}]$^{2+}$ (L = $PMe_2Ph$, L' = $PPh_3$), and [$(AuL)_2${$\mu$-$C(CO_2R)PPh_2CH(AuL)CO_2R$)}]$^+$ (L = $PPh_3$, R = Me, Et; L = $PMe_2Ph$, R = Me; L = $PPh_2(C_6H_4OMe$-4), R = Et).[30–33] Schmidbaur also reported the cationic complex [$(AuPPh_3)_2${$\mu$-$C(PMePh_2)_2$}]$^{2+}$ by reacting the ylide with 2 equiv of [$AuBr(PPh_3)$].[35] The only complex related to **3** is [$(AuMe)_2${$\mu$-$C(PMe_3)_2$}],[34] reported as the product of the reaction of the ylide with 2 equiv of [$AuMe(PMe_3)$]; it starts decomposing slowly if left in chlorinated solvents ($CH_2Cl_2$ or $CHCl_3$). The rest of all the complexes could be handled in air without any problem.

The reaction of **1a** with Tl(acac) using a 1:1.4 molar ratio gives [Au(acac){$C(PPh_3)_2$}] (**4**), which is the first (acetylacetonato)gold(I) complex with an ylide ligand (Scheme 1). As shown below, it can be used to prepare the complexes [Au(C≡CR){$C(PPh_3)_2$}] by reaction with alkynes. Complex **4** decomposes slowly at room temperature if left in the air, but it can be stored indefinitely at −10 °C under nitrogen.

**Reactivity of [Au{$C(PPh_3)_2$}Cl] (1a) toward Alkynes. Synthesis of the Complexes $[HC(PPh_3)_2]$[Au(C≡CR)Cl] (5).** In an attempt to prepare the complexes [Au(C≡CR){C{$PPh_3$}$_2$}] (R = Ph, 4-$MeOC_6H_4$) we reacted [Au{$C(PPh_3)_2$}Cl] (**1a**) with the correspond-

(48) Zhdankin, V. V.; Erickson, S. A.; Hanson, K. J. *J. Am. Chem. Soc.* **1997**, *119*, 4775.

**Scheme 2**



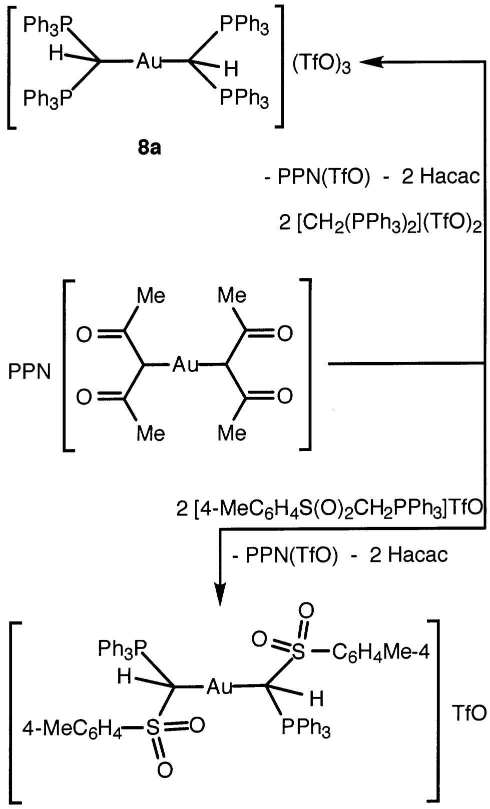

ing terminal alkynes in the presence of $Et_3N$ (1:1:1 molar ratio). However, we isolated instead complexes of the type $[HC(PPh_3)_2][Au(C{\equiv}CR)Cl]$ (**5**) (Scheme 2). This result indicates that the deprotonating character of the coordinated ylide $C(PPh_3)_2$ in **1a** is better than that of the free $Et_3N$. This result is in agreement with the basic or ligand character of **1a** when it reacts with [AuCl(tht)], replacing tht to give the dinuclear complex **3**. To ascertain whether the triethylamine was necessary in these reactions, we monitored the reactions of **1a** with alkynes in the absence of $Et_3N$ by $^{31}P$ NMR spectroscopy. It was observed that the reactions took place and were complete in about 5−6 h. However, a parallel study in the presence of $Et_3N$ showed that these reactions were much faster than in the absence of the base, being complete in 0.5 h. Although $Et_3N$ acts as a catalyst in these reactions, we decided to prepare the complexes $[HC(PPh_3)_2][Au(C{\equiv}CC_6H_4R\text{-}4)Cl]$ (R = H (**5a**), CN (**5b**), OMe (**5c**), $NO_2$ (**5d**)) in the absence of $Et_3N$ to avoid contaminations. The only reported complexes of the type Q[Au(C≡CR)X] are those with R = Ph and X = Cl, Br, I[49] and with R = H and X = Cl, Br, I.[50,51] The former were only preliminarily reported as the result of reactions of the polymeric complex $[Au(C{\equiv}CPh)]_n$ with the corresponding halides. The latter complexes were prepared by reacting $[Au(C{\equiv}CH)_2]^-$ with the corresponding $[AuX_2]^-$. The method used to prepare complexes **5** represents a third way to synthesize these types of complexes.

**Synthesis of the Complexes [Au(C≡CR){C(PPh$_3$)$_2$}] (6).** The desired complexes $[Au(C{\equiv}CC_6H_4R\text{-}4)\{C\{PPh_3\}_2\}]$ (R = H (**6a**), CN (**6b**), OMe (**6c**), $NO_2$ (**6d**), C≡CPh (**6e**)) were prepared by the reaction of $[Au(acac)\{C(PPh_3)_2\}]$ (**4**) with a large excess of alkynes (ca. 1:25−30) in freshly distilled and degassed chloroform (Scheme 2). This is a new example of the "acac" method of synthesis of gold complexes.[27] To establish the exact course of the reactions, they were first monitored by $^{31}P$ NMR spectroscopy. The main peaks were observed at $\delta$ 14.35 ppm for **4**, around $\delta$ 16 ppm for complexes **6**, and $\delta$ 21.1 ppm (weak, coincident with that of $[HC(PPh_3)_2]^+$). The 1:1 reaction with PhC≡CH was incomplete even after 40 h. This slowness contrasts with the usually fast reactions of other acac gold(I) complexes use to proceed and also with the reactions of **1a** with alkynes to give complexes **5**. The reaction rate increased with the molar ratio of the alkyne to complex **4**, but not significantly. For example, in the reaction with a 3:1 molar ratio, **4** was only 50% consumed after 10 h and was totally consumed after 30 h. With a 10:1 molar ratio only 33% was consumed after 3 h and 100% after 24 h. If the reaction is left for a longer time, then the peak at 21.1 ppm ($[HC(PPh_3)_2]^+$), always present in the mixture in minor amounts, grows with respect to that corresponding to **6a**. All these data suggest that the first reaction is $[Au(acac)\{C(PPh_3)_2\}]$ + PhC≡CH → $[Au(C{\equiv}CPh)(C\{PPh_3\}_2)]$ (**6a**) + Hacac and that the excess of the alkyne slowly protonates and replaces the ylide ligand from **6a** following the reaction: $[Au(C{\equiv}CPh)\{C(PPh_3)_2\}]$ + PhC≡CH → $[HC(PPh_3)_2][Au(C{\equiv}CR)_2]$. Finally, a 30:1 molar ratio reaction allowed a complete conversion of reactants in **6a** in 1.5 h with only minor amounts of the 21.1 ppm peak in the $^1H$ NMR spectrum of the mixture. In view of these observations, reactions in NMR tubes were carried out between **4** and variable amounts of alkynes to optimize the molar ratios and the time required to prepare complexes **6**. Depending on the alkyne, the reactions were complete within 2−5 h of mixing when 25−30 equiv of the alkyne was used. Complex **4** starts decomposing if kept in solution for a longer time. The large excess of the alkyne could be easily recovered from the ether washings and can be purified either by chromatography or recrystallization for further use.

**Synthesis of Complexes [Au(C≡CC$_6$H$_4$R-4){CH(PPh$_3$){S(O)$_2$C$_6$H$_4$Me-4}}] (R = H (7a), NC (7b), OMe (7c), NO$_2$ (7d), C≡CPh (7e)).** The complex $[AuCl\{CH(PPh_3)\{S(O)_2C_6H_4Me\text{-}4\}\}]$ (**1b**) reacts with terminal alkynes in the presence of $Et_3N$ differently from **1a**, giving complexes **7** (Scheme 2). Complexes **7** are air and moisture stable and show the expected NMR spectra. However, $CDCl_3$ solutions of complexes **7a**, **7c**, and **7e** show small peaks at around 22.3 (±0.01) and 14.82 (±0.01) ppm in their $^{31}P$ NMR spectra, integrated to approximately 1/8 and 1/10 for **7a**, 1/6 and 1/7 for **7c**, and 1/13 and 1/16 with respect to the main peak of complex **7** at around 21.5 ppm. Such peaks could not

(49) Abu-Salah, O. M.; Al-Ohaly, A. R. *Inorg. Chim. Acta* **1983**, *77*, L159.
(50) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 497.
(51) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

**Scheme 3**




arise from impurities, because they remain with the same intensity ratio after several recrystallizations. This led us to believe that, although in the solid these complexes are pure compounds, in agreement with their elemental analyses, when dissolved, they decompose to give other product(s) with which they are in equilibrium. The peak at 14.82 ppm could be due to free ylide ($\delta$ 14.8 ppm), suggesting an equilibrium of complexes **7** with the ylide and $[Au(C{\equiv}CR)]_n$. The peak at 22.3 ppm could be caused by the ionic species $[Au\{CH(PPh_3)\{S(O)_2C_6H_4\text{-}Me\text{-}4\}\}_2][Au(C{\equiv}CR)_2]$ (the resonance in the complex $[Au\{CH(PPh_3)\{S(O)_2C_6H_4Me\text{-}4\}\}_2]TfO$ (**8b**) appears at 20.2 ppm). The molar conductivities of solutions in acetone of complexes **7** are in the range 3−8 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Because of the different concentrations required to measure $^{31}P$ NMR spectra and conductivities, it is not possible to calculate the molar conductivities referenced to the ionic species.

**Synthesis of the Cationic Complexes [Au{HC(PPh$_3$)$_2$}$_2$](TfO)$_3$ (8a) and [Au{CH(PPh$_3$){S(O)$_2$C$_6$H$_4$Me-4}}$_2$]TfO (8b).** The reactions of PPN[Au(acac)$_2$] with the phosphonium salts $[H_2C(PPh_3)_2](TfO)_2$ and $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]TfO$ in a 1:2 stoichiometry afforded the cationic complexes **8a** and **8b**, respectively (Scheme 3). These complexes are white crystalline solids, and their solutions in acetone-$d_6$ show singlets at $\delta$ 26.1 and 20.4, respectively, indicating that the two phosphorus atoms are equivalent in the complexes.

**Structures of the Complexes.** The crystal structures of $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3]TfO$ (Figures 1 and 2), **1b**·0.5CH$_2$Cl$_2$ (Figures 3−5), **3**·3CH$_2$Cl$_2$ (Figure 6), **5a** (Figures 7 and 8), **5c** (Figure 9), **6d**·THF (Figures 10 and 11), and **8b** (Figures 12 and 13) have been determined. Tables 1 and 2 give a summary of X-ray data for these complexes.

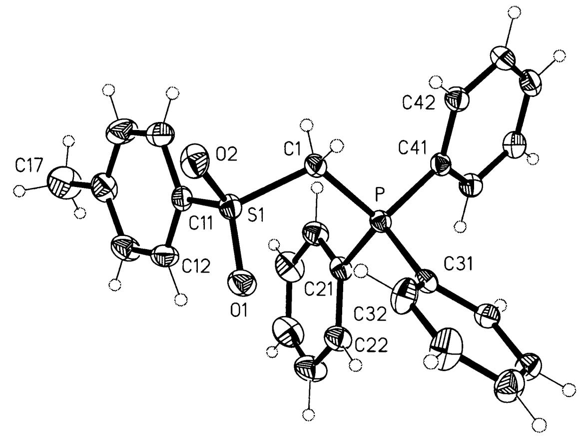



**Figure 1.** Thermal ellipsoid plot of the cation $[4\text{-}MeC_6H_4S(O)_2\text{-}CH_2PPh_3\}]^+$ (50% probability level) with the labeling scheme. Selected bond lengths (Å) and angles (deg): P−C(41) = 1.7927(18), P−C(21) = 1.7932(18), P−C(31) = 1.7935(19), P−C(1) = 1.8145(18), S(1)−O(1) = 1.4358(14), S(1)−O(2) = 1.4385(14), S(1)−C(11) = 1.7549(19), S(1)−C(1) = 1.7968(18), S(2)−O(5) = 1.426(2), S(2)−O(3) = 1.428(3), S(2)−O(4) = 1.429(2), S(2)−C(99) = 1.809(3), C(99)−F(1) = 1.306(4), C(99)−F(3) = 1.311(3), C(99)−F(2) = 1.329(4); C(41)−P−C(21) = 107.90(9), C(41)−P−C(31) = 110.13(8), C(21)−P−C(31) = 110.07(9), C(41)−P−C(1) = 106.37(8), C(21)−P−C(1) = 110.95(8), C(31)−P−C(1) = 111.31(9), O(1)−S(1)−O(2) = 119.45(9), O(1)−S(1)−C(11) = 108.71(9), O(2)−S(1)−C(11) = 107.68(9), O(1)−S(1)−C(1) = 108.33(8), O(2)−S(1)−C(1) = 105.05(8), C(11)−S(1)−C(1) = 106.98(9), S(1)−C(1)−P = 116.42(10).

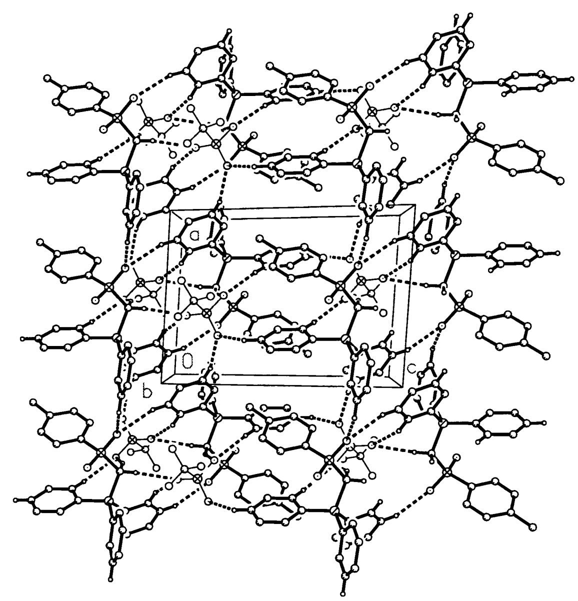



**Figure 2.** Packing diagram showing hydrogen bond interactions in $[4\text{-}MeC_6H_4S(O)_2CH_2PPh_3\}]TfO$.

The structure of the phosphonium salt $[4\text{-}MeC_6H_4S(O)_2\text{-}CH_2PPh_3\ ]TfO$ (Figure 1) reveals the expected distorted-tetrahedral geometry around the phosphorus and sulfur atoms. The C−P−C bond angles are similar to those found in the corresponding ylide complexes **1b** and **8b**. The O−S−O bond angle (119.45(9)°) is wider than the C−S−O and C−S−C bond angles (105.05(8)−108.71(9)°), probably due to the multiple-bond character of the

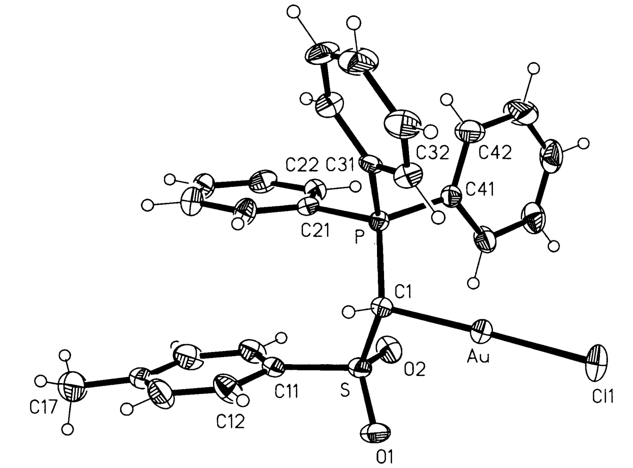



**Figure 3.** Thermal ellipsoid plot of the complex **1b**·0.5$CH_2Cl_2$ (50% probability level) with labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(1) = 2.067(4), Au−Cl(1) = 2.2914(10), S−O(1) = 1.437(3), S−O(2) = 1.446(3), S−C(11) = 1.771(4), S−C(1) = 1.771(4), P−C(1) = 1.792(4), P−C(21) = 1.800(4), P−C(41) = 1.803(4), P−C(31) = 1.804(4); C(1)−Au−Cl(1) = 178.36(11), O(1)−S−O(2) = 118.39(18), O(1)−S−C(11) = 105.53(18), O(2)−S−C(11) = 107.21(18), O(1)−S−C(1) = 106.91(18), O(2)−S−C(1) = 108.96(18), C(11)−S−C(1) = 109.62(18), C(1)−P−C(21) = 111.88(18), C(1)−P−C(41) = 114.17(18), C(21)−P−C(41) = 108.44(18), C(1)−P−C(31) = 108.23(18), C(21)−P−C(31) = 106.02(18), C(41)−P−C(31) = 107.70-(18), S−C(1)−P = 118.2(2).

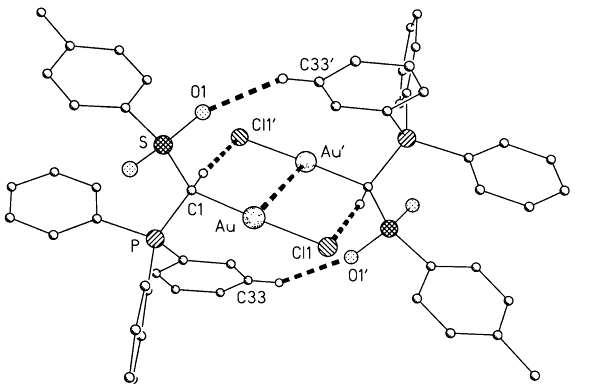



**Figure 4.** Packing diagram showing Au⋯Au and hydrogen bond interactions in the dimeric unit of **1b**·0.5$CH_2Cl_2$.

S−O bonds (see Chart 1). The S−O (1.4358(14), 1.4385-(14) Å) and P−Ph (1.7927−1.7935 Å) bond distances are not significantly different from those in its metalated derivatives (**1b**, S−O = 1.437(3), 1.446(3) Å, P−Ph = 1.800−1.804(4) Å; **8b**, S−O = 1.440(2)−1.446(3) Å, P−Ph = 1.792−1.813(4) Å). However, the P−$C_{sp^3}$ bond length (1.8145(18) Å) in the phosphonium salt is significantly longer than the corresponding distance in **1b** (1.792(4) Å). In **8b**, one P−$C_{sp^3}$(Au) distance is significantly shorter (1.798(4) Å) and the other one marginally shorter (1.805(4) Å) than that in the phosphonium salt. The crystal structure of the ylide 4-$MeC_6H_4S(O)_2$-$CHPPh_3$ has been solved.[52] Although it is not too reliable, the P−CH bond length is considerably shorter (1.709(19) Å) and one of the S−O values (1.469(14) Å) longer than the above values. The other S−O distance (1.444(15) Å) is similar to those found in the phosphonium salt or complexes **1b** and **8b**. Probably, the P−C bond order in these complexes is intermediate between the single bond in the phosphonium salt and that in the free ylide (see Chart 1). A similar conclusion was reached when IR and $^1$H NMR spectra were compared

(52) Speziale, A. J.; Ratz, K. W. *J. Am. Chem. Soc.* **1965**, *87*, 5603.

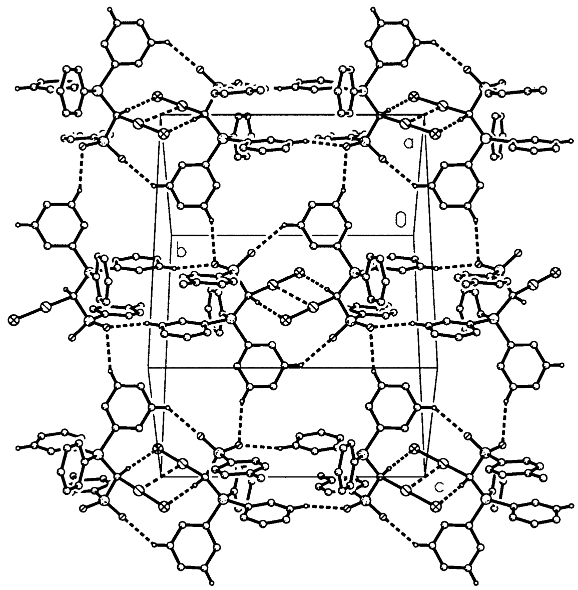



**Figure 5.** Packing diagram showing all hydrogen bond interactions in **1b**·0.5$CH_2Cl_2$.

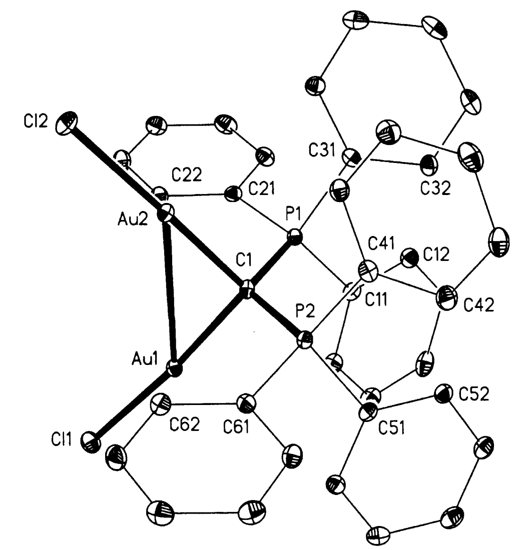



**Figure 6.** Thermal ellipsoid plot of the complex **3**·3$CH_2Cl_2$ (30% probability level) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) = 2.078(3), Au(1)−Cl(1) = 2.2974(8), Au(1)−Au(2) = 3.1432-(2), Au(2)−C(1) = 2.074(3), Au(2)−Cl(2) = 2.2946(7), P(2)−C(1) = 1.776(3), P(2)−C(61) = 1.809(3), P(2)−C(51) = 1.819(3), P(2)−C(41) = 1.825(3), P(1)−C(1) = 1.776(3), P(1)−C(31) = 1.809(3), P(1)−C(11) = 1.819(3), P(1)−C(21) = 1.819(3); C(1)−Au(1)−Cl(1) = 175.29(8), C(1)−Au(2)−Cl(2) = 176.96(8), C(1)−P(2)−C(61) = 113.42(13), C(1)−P(2)−C(51) = 111.09(13), C(61)−P(2)−C(51) = 104.64(13), C(1)−P(2)−C(41) = 115.35(13), C(61)−P(2)−C(41) = 103.55-(13), C(51)−P(2)−C(41) = 107.97(13), C(1)−P(1)−C(31) = 111.16(13), C(1)−P(1)−C(11) = 116.40(13), C(31)−P(1)−C(11) = 107.49(13), C(1)−P(1)−C(21) = 112.20(13), C(31)−P(1)−C(21) = 105.25(13), C(11)−P(1)−C(21) = 103.50(13), P(1)−C(1)−P(2) = 117.30(15), P(1)−C(1)−Au(2) = 108.06-(13), P(2)−C(1)−Au(2) = 111.14(13), P(1)−C(1)−Au(1) = 110.20(13), P(2)−C(1)−Au(1) = 110.07(14).

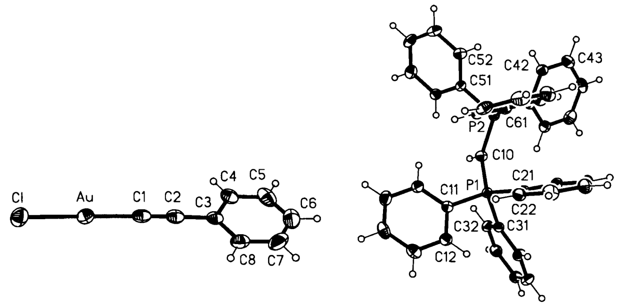



**Figure 7.** Thermal ellipsoid plot of the complex **5a** (50% probability level) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(1) = 1.968(5), Au−Cl = 2.2838(13), C(1)−C(2) = 1.189(5), C(2)−C(3) = 1.427(4), C(10)−P(1) = 1.698(2), C(10)−P(2) = 1.702(2), P(1)−C(21) = 1.805(2), P(1)−C(31) = 1.810(2), P(1)−C(11) = 1.817(2), P(2)−C(61) = 1.803(2), P(2)−C(51) = 1.806(2), P(2)−C(41) = 1.812(3); C(1)−Au−Cl = 175.31(9), C(2)−C(1)−Au = 175.1(3), C(1)−C(2)−C(3) = 178.8(4), P(1)−C(10)−P(2) = 128.60(13).

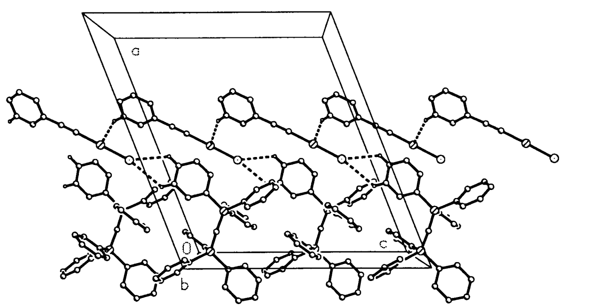


**Figure 8.** Packing diagram showing C−H···Au and three-center C−H···Cl interactions in complex **5a**.

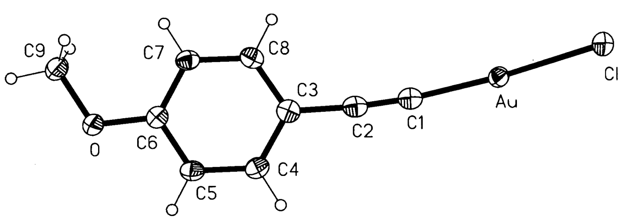



**Figure 9.** Thermal ellipsoid plot of the anion of complex **5c** (50% probability level) with the labeling scheme. The cation is numbered as for **5a.** Selected bond lengths (Å) and angles (deg): Au−C(1) = 1.952(4), Au−Cl = 2.2917-(10), C(1)−C(2) = 1.201(4), C(2)−C(3) = 1.436(4), C(6)−O = 1.370(3), O−C(9) = 1.437(3), C(10)−P(1) = 1.700(2), C(10)−P(2) = 1.703(2), P(1)−C(21) = 1.796(2), P(1)−C(11) = 1.810(2), P(1)−C(31) = 1.811(2), P(2)−C(61) = 1.804(2), P(2)−C(41) = 1.810(2), P(2)−C(51) = 1.814(2); C(1)−Au−Cl = 174.66(7), C(2)−C(1)−Au = 171.8(2), C(1)−C(2)−C(3) = 175.5(3), C(6)−O−C(9) = 115.83(19), P(1)−C(10)−P(2) = 128.77(12).

(see below). Eight hydrogen bonds of the type C−H···O, with H···O distances in the range 2.39−2.57 Å, are observed in [4-$MeC_6H_4S(O)_2CH_2PPh_3$]TfO; one of the sulfone oxygens and the three triflate oxygen atoms are each involved in two such hydrogen bonds to form a layer parallel to the *xz* plane (see Figure 2). The final sulfone oxygen O(1) forms a three-center $(C-H)_2$···O system that connects adjacent layers.

In complex **1b** the ligand arrangement around the gold atom is essentially linear, with an C(1)−Au−Cl bond angle equal to 178.36(11)° (Figure 3). This is a common feature of all complexes here reported (range 173.20(14)−178.36(11)°). The Au−C bond length, 2.067-(4) Å, is similar to Au−$C_{ylide}$ distances found in the other complexes (**3**: 2.078(3), 2.074(3) Å; **6d**, 2.083(2) Å; **8b**, 2.079(3), 2.088(3) Å). The Au−Cl bond length (2.2914-(10) Å) is similar to that found in complex **3** (2.2974(8) Å). An intramolecular H(46)···O(2) hydrogen bond (2.25 Å) is observed. The molecules of **1b** form dimers through C−H···O and C−H···Cl hydrogen bonds and a weak aurophilic interaction (H(33)···O(1) = 2.46 Å, H(1)···Cl(1) = 2.56 Å, Au···Au = 3.5539(5) Å; see Figure 4). The dimers are connected by two further C−H···O interactions (H35···O2 = 2.53 Å, H23···O2 = 2.45 Å) to form layers parallel to the plane (101) (see Figure 5). There are several examples of these two different types of interactions supporting the polymerization of gold complexes.[53]

In complex **3** (Figure 6), the Au···Au distance is 3.1432(2) Å, a typical value for an aurophilic contact

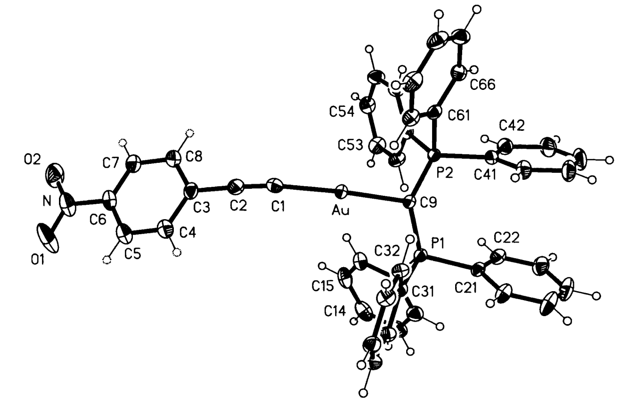



**Figure 10.** Thermal ellipsoid plot of the complex **6d**·THF (50% probability level) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(1) = 1.999(2), Au−C(9) = 2.082(2), P(1)−C(9) = 1.688(2), P(1)−C(21) = 1.814(2), P(1)−C(31) = 1.819(2), P(1)−C(11) = 1.834(2), P(2)−C(9) = 1.682(2), P(2)−C(41) = 1.819(2), P(2)−C(61) = 1.824(2), P(2)−C(51) = 1.822(2), C(1)−C(2) = 1.181(4), C(2)−C(3) = 1.437(4), C(6)−N = 1.462(3), N−O(1) = 1.222-(3), N−O(2) = 1.225(3); C(1)−Au−C(9) = 174.36(9), C(2)−C(1)−Au = 168.9(2), C(1)−C(2)−C(3) = 172.5(3), O(1)−N−O(2) = 123.1(2), O(1)−N−C(6) = 118.2(2), O(2)−N−C(6) = 118.7(2), P(2)−C(9)−P(1) = 133.64(13), P(2)−C(9)−Au = 110.66(11), P(1)−C(9)−Au = 111.06(11).

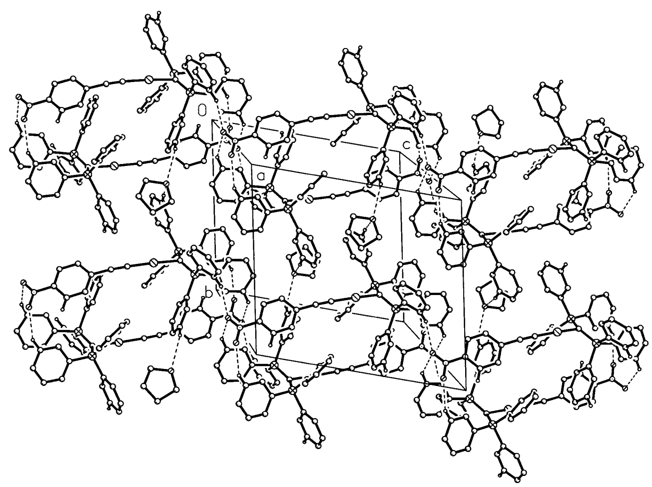


**Figure 11.** Packing diagram showing C−H···O interactions in the complex **6d**·THF.

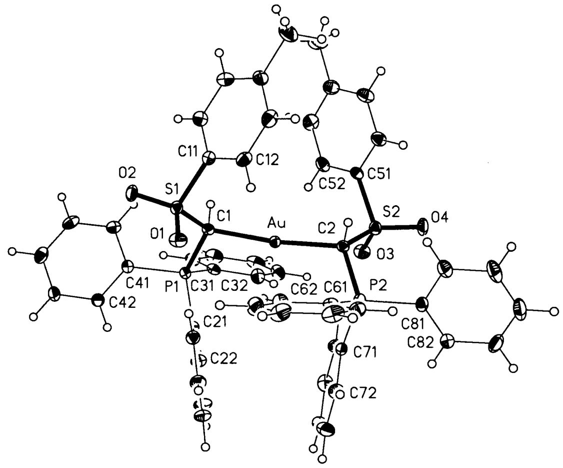



**Figure 12.** Thermal ellipsoid plot of the complex **8b** (50% probability level) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(2) = 2.079(3), Au−C(1) = 2.088(3), S(1)−O(2) = 1.440(2), S(1)−O(1) = 1.446(3), S(1)−C(11) = 1.763(4), S(1)−C(1) = 1.782(4), S(2)−O(4) = 1.441(2), S(2)−O(3) = 1.444(3), S(2)−C(51) = 1.763(4), S(2)−C(2) = 1.791(4), P(1)−C(1) = 1.798(4), P(2)−C(2) = 1.805(4); C(2)−Au−C(1) = 173.20(14), O(2)−S(1)−O(1) = 117.02(17), C(11)−S(1)−C(1) = 101.27(19), O(4)−S(2)−O(3) = 117.04(17), C(51)−S(2)−C(2) = 101.50(19), S(1)−C(1)−P(1) = 119.0(2), S(1)−C(1)−Au = 108.13(17), P(1)−C(1)−Au = 113.0(2), S(2)−C(2)−P(2) = 117.77(19), S(2)−C(2)−Au = 108.61(17), P(2)−C(2)−Au = 114.2(2).

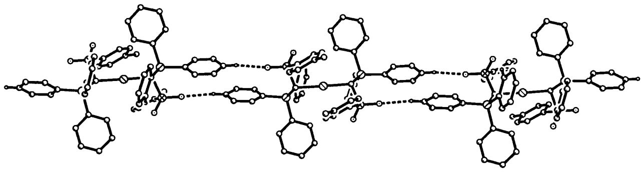


**Figure 13.** Packing diagram showing intermolecular hydrogen bond interactions in **8b**.

supported by a bridging carbon donor ligand.[10] However, shorter Au⋯Au distances have been found in similar but cationic complexes (2.7999(7)−3.008(1) Å).[13,30,31,32a,b,33] Correspondingly, the Au(1)−C(1)−Au(2) angle (98.44(11)°) is narrower than expected for two $C_{sp^3}$ hybrid orbitals. The P(1)−C(1) and P(2)−C(1) bond lengths are equal (1.776(3) Å) and shorter than P−Ph distances (1.809(3)−1.825(3) Å), showing a certain multiple character of the bonds in the P(1)−C(1)−P(2) group; in phosphonium salts P−$C_{sp^3}$ and P−Ph distances tend to be around 1.800 Å.[54] As indicated above, the electron density for such an increase in bond order probably comes from the gold atoms. The P(1)−C(1)−P(2) angle in **3** is 117.30(15)°, a value approaching that corresponding to two $C_{sp^2}$ hybrid orbitals.

The packing of complex **3** involves 13 C−H⋯Cl contacts, a number promoted in part by the presence of three ordered dichloromethane molecules, and shows no easily assimilable features such as layers or chains.

The structure of complexes **5a** (Figures 7 and 8) and **5c** (Figure 9), which are isostructural, show the ylide cation $[HC(PPh_3)_2]^+$ and the anionic gold complex. The Cl−Au−C(1), Au−C(1)−C(2), and C(1)−C(2)−C(3) bond angles are near 180° (range 171.8(2)−178.8(4)°). The Au−Cl bond distance in **5a** (2.2838(13) Å) is, unexpectedly, shorter than that in **5c** (2.2917(10) Å). The latter is similar to those found in complexes **1b** and **3**. The Au−C(1) distances in **5a** and **5c** are similar (1.968(5) and 1.952(4) Å, respectively) but significantly shorter than that found in the alkynyl complex **6d** (1.998(2) Å). However, all these distances are in the range found in other neutral and anionic alkynyl gold(I) complexes (1.972(8)−2.080(12) Å),[19,51,54] although that of **5c** establishes a new minimum in this range. The C(1)−C(2) and C(2)−C(3) bond distances in **5a**, **5c**, and **6d** are not significantly different.

In compounds **5a** and **5c**, the packing shows broad chains of anions and cations parallel to the *z* axis, connected by a short C−H⋯Au contact (H(7)⋯Au = 2.91 Å; values apply to **5a**) between anions and a three-center $(C-H)_2$⋯Cl system (H(44,45)⋯Cl = 2.83 and 2.98 Å) between anion and cation (Figure 8). The chains are linked by a further C−H⋯Cl interaction (H(24)⋯Cl = 2.84 Å) to form the final three-dimensional structure.

Most of the structural data on complexes **6d** (Figures 10 and 11) and **8b** (Figures 12 and 13) have been discussed above. The only reported crystal structures of $C(PPh_3)_2$ complexes are those of $[Ni(CO)_n\{C(PPh_3)_2\}]$ ($n$ = 2, 3),[40] $[CuX\{C(PPh_3)_2\}]$ (X = Cl, Cp*),[29,41] and $[O_3Re\{C(PPh_3)_2\}][ReO_4]$.[42] The P−C bond distances in complex **6d** (Figure 10) (1.688(2), 1.682(2) Å) are in the range 1.66−1.70 Å found in the above Ni(0) and Cu(I) complexes but longer than those in the free ylide $C(PPh_3)_2$ (1.610−1.633 Å).[55] The significant double character of the Re−$C(PPh_3)_2$ bond in $[O_3Re\{C(PPh_3)_2\}]$-$[ReO_4]$, as a consequence of the $\pi$-donor capacity of the ylide, is consistent with the longest P−C bond distances (1.777(8), 1.764(8) Å).[42] However, the P−C−P angles do not generally follow the expected increase when the P−C bond order increases. Thus, the expected order should be $C(PPh_3)_2$ > **6d** ≈ Ni(0) and Cu(I) complexes > $[O_3Re\{C(PPh_3)_2\}][ReO_4]$ but the actual order is $C(PPh_3)_2$ (130.1−143.8°) ≥ $[Cu(Cp^*)\{C(PPh_3)_2\}]$ (135.97°) ≈ **6d** (133.71°) ≈ $[Ni(CO)_2\{C(PPh_3)_2\}]$ (132.13°) > $[Ni(CO)_3\{C(PPh_3)_2\}]$ (124.58°) ≈ $[CuCl\{C(PPh_3)_2\}]$ (123.8°) ≈ $[O_3Re\{C(PPh_3)_2\}][ReO_4]$ (123.1°). A theoretical study on $[Ni(CO)_3\{C(PH_3)_2\}]$ gives an excellent agreement between the calculated (124.6°) and the experimental value of the P−C−P angle in $[Ni(CO)_3\{C(PPh_3)_2\}]$ (124.58°).[40] However, the calculated value in $[Ni(CO)_2\{C(PH_3)_2\}]$ (126.6°) is lower than the experimental one for $[Ni(CO)_2\{C(PPh_3)_2\}]$ (132.13°). No explanation was given. Charge decomposition analysis of these Ni complexes shows that carbodiphosphoranes are much better $\sigma$ donors than $\pi$ acceptors and that this component is more important for $[Ni(CO)_2\{C(PH_3)_2\}]$ than for $[Ni(CO)_3\{C(PH_3)_2\}]$.[40] Because the P−C−P angles and P−C bond distances in $[Ni(CO)_2\{C(PPh_3)_2\}]$ and in **6d** are

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very similar, it is reasonable to asume that the M−C-($PPh_3)_2$ bonds are analogous in both complexes.

Hydrogen bond interactions involving C−H of the phenyl groups of the ligand $PPh_3$ and the oxygen atoms of the nitro group, which both accept two H bonds (H···O = 2.34−2.62 Å), link the molecules in a three-dimensional network (Figure 11). The H bonds involving the nitro group occupy the regions at $z \approx 0$, 1, etc., with each molecule displaying donor and acceptor functions separated by a translation of approximately **c**. The THF oxygens are also acceptors of two C−H···O hydrogen bonds (H···O = 2.53, 2.62 Å).

In **8b** there are two very short intramolecular C−H···O hydrogen bonds involving two ortho hydrogens (H(26)···O(1) = 2.30 Å and H(76)···O(3) = 2.26 Å) groups (Figure 13) of $PPh_3$ and two oxygen atoms of the $SO_2$ groups. In addition, two intermolecular hydrogen bonds from para hydrogens (H(84)···O(2) = 2.37 Å and H(44)···O(4) = 2.55 Å) connect the cations to form chains parallel to the diagonal [1,0,−1].

**Spectroscopic Properties of Complexes.** The ylide 4-$MeC_6H_4SO_2CHPPh_3$ shows two strong bands at 1270 and 1126 $cm^{-1}$ that have been assigned to $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ modes, respectively.[52] The salts [4-$MeC_6H_4S(O)_2CH_2PPh_3$]X (X = I, TfO) show these bands at higher energy (1342−1324 and 1160−1156 $cm^{-1}$, respectively) in agreement with the assignments made for the bromide salt (1330 and 1165 $cm^{-1}$, respectively).[52] This shift to higher energy of these bands can be explained as a consequence of the contribution of resonance forms **C** and **D**, which cannot be formulated for the phosphonium salt, to the electronic structure of the ylide (Chart 1). In aryl/alkyl sulfones, two bands in the ranges 1334−1325 and 1160−1150 $cm^{-1}$ have been assigned to the $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ modes, respectively.[56] However, Zhdankin has assigned a band at 1441 $cm^{-1}$ to $\nu$(S═O) in [$PhS(O)_2CH_2PPh_3$]-TfO.[48]

When the IR spectra of complexes differing only in the ylide ligand are compared (e.g., **1a** with **1b**, **6a** with **7a**, etc.), those containing the sulfonylylide ligand show a strong band at around 1300 (s) (see the Experimental Section), usually appearing with two shoulders at lower and higher energies, and a medium or strong band in the range 1138−1124 $cm^{-1}$, which could be assigned to $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$, respectively. The lower values of the wavenumbers of these bands with respect to those of in the phosphonium salts suggest that metallic substituents at the methine group (X in Chart 1) are more electron-releasing than a hydrogen. This conclusion was also reached when studying the IR spectra of gold complexes of carbonyl-stabilized ylides.[31]

Because the assigned $\nu(SO_2)$ bands appear in regions where other bands are present, IR spectroscopy is not as useful as in the case of carbonyl-stabilized ylides to indicate the mode of coordination of the ligand. In our case, the determination of the crystal structure of complexes **1b** and **8b**, along with the use of NMR spectroscopy, allows us to propose the C-coordination of the sulfonylylide ligand in all complexes. Thus, the $^1$H NMR resonance of the methine proton in complexes **1b**, **7**, and **8b** (4.58−5.32 ppm) is intermediate between that of the ylide (2.96 ppm) and that corresponding to the methylene protons of [4-$MeC_6H_4S(O)_2CH_2PPh_3$]I (6.18 ppm). The same behavior has been observed in other gold complexes with carbonyl-stabilized ylides.[30,31] The same order is observed for the $\delta(^1H)$ value of the methine proton of the ylide cation $[HC(PPh_3)_2]^+$ (1.86−1.93 ppm in complexes **5**, 1.83 ppm in $[HC(PPh_3)_2]$Br, and 1.86 ppm in $[HC(PPh_3)_2]$TfO) < that in complexes **2** and **8** (5.58, 5.69 ppm) < that in the methylene protons of the phosphonium salt $[CH_2(PPh_3)_2](TfO)_2$ (6.30 ppm). Therefore, replacement of a proton in a phosphonium salt by a gold moiety increases the shielding of the remaining methine proton. This is in agreement with the conclusion we have reached from the IR spectra (see above).

The $\delta(^{31}P)$ values tend to follow a different order: ylide 4-$MeC_6H_4S(O)_2CHPPh_3$ (14.8 ppm) < [4-$MeC_6H_4S$-$(O)_2CH_2PPh_3$]I (17.6 ppm) < complexes **1b**, **7**, and **8b** (20.2−21.8 ppm). The same order is followed by the $\delta(^{31}P)$ values of the ylide $C(PPh_3)_2$ (−3.5 ppm)[57] < the ylide cation $[HC(PPh_3)_2]^+$ (21.1 ppm in complexes **5**) < complexes **1a**, **4**, and **6** (14.3−16.6 ppm). The same series was observed with the ylide $Me_2NC(O)CHPPh_3$ with respect to some $[Me_2NC(O)CH_2PPh_3]^+$ salts and a series of its gold complexes, although not then appreciated at the time.[33] However, a different sequence is found for the ylide cation $[HC(PPh_3)_2]^+$ (21.1 ppm in complexes **5** and the bromide and triflate salts), which is very similar to that of its phosphonium salts $[CH_2(PPh_3)_2]$X (X = Br, 20.99 ppm; X = TfO, 20.47 ppm), although both are smaller than the $\delta(^{31}P)$ values in its complexes **2** and **8a** (22.1, 26.1 ppm, respectively).

## Conclusions

We have prepared the first complexes containing the ylide 4-$MeC_6H_4SO_2CHPPh_3$ or the ylide cation $[HC(PPh_3)_2]^+$ and some of the few complexes containing the double ylide $C(PPh_3)_2$. To prepare the alkynyl−ylide complexes [Au(C≡CR)(ylide)] (we wanted to study their NLO properties), we have studied the reactivity of the corresponding [AuCl(ylide)] complexes toward terminal alkynes in the presence $Et_3N$. This method was successful for the synthesis of the complexes [Au(C≡CR)-{CH($PPh_3$){$S(O)_2C_6H_4Me$-4}}], but when the ylide was $C(PPh_3)_2$, the complexes $[HC(PPh_3)_2]$[Au(C≡CR)Cl] were obtained. To synthesize the desired alkynyl−ylide complexes [Au(C≡$CC_6H_4R$-4){C{$PPh_3$}$_2$}], we prepared [Au-(acac){$C(PPh_3)_2$}] and studied its reactivity toward alkynes by NMR spectroscopy. We concluded that a large excess of the alkyne (ca. 1:25−30) and 1−4 h of reaction is required to obtain the pure compounds with good yields. The tri- and monocationic complexes [Au-$(ylide)_2](TfO)_n$, where the ylide is $[HC(PPh_3)_2]^+$ ($n$ = 3) or 4-$MeC_6H_4S(O)_2CHPPh_3$ ($n$ = 1), have been obtained by reacting PPN[Au$(acac)_2$] with the corresponding phosphonium salt. IR and NMR criteria have been established to prove the C-coordination of the ylide 4-$MeC_6H_4S(O)_2CHPPh_3$. The crystal structures of some of the reported complexes show interesting aurophilic

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interactions and/or hydrogen bond interactions. Two of these crystal structures are the first gold complexes containing the ligand $C(PPh_3)_2$.

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**Supporting Information Available:** Listings of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for [4-$MeC_6H_4S(O)_2$-$CH_2PPh_3$]TfO, **1b**·0.5$CH_2Cl_2$, **3**·3$CH_2Cl_2$, **5a**, **5c**, **6d**·THF, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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