Multidonor Ligands. 2.[1] Room-Temperature C(sp^3)−H Activation of 2-(Alkylthio)pyridine by Gold(III) Complexes

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Received September 2, 1998

$Na[AuCl_4]$ reacts with [py{$SCH_2C(O)R$}-2] (py-2 = 2-pyridyl) at room temperature to give cyclometalated alkylgold(III) complexes [$AuCl_2${py{SCHC(O)R}-2}] [R = Ph (**1a**), Me (**1b**), OMe (**1b**)], which in turn react with NaBr or with PR'_3 in the presence of $NaClO_4$ to give [$AuBr_2${py{SCHC(O)R}-2}] [R = Ph (**2a**), Me (**2b**)] or a mixture of SP4-3- and SP4-4-[AuCl{py{SCHC(O)R}-2}(PPh_3)]ClO_4 [R = Ph (**3a**), Me (**3b**)]. This mixture of isomers converted to the isomer SP4-4 upon refluxing in chloroform. When the last reaction was made using $P(C_6H_4OMe\text{-}4)_3$, the main products were [AuCl{$P(C_6H_4OMe\text{-}4)_3$}] and [Hpy{$SCH_2C(O)Ph$}-2]ClO_4. The crystal structure of the latter has been determined.

Introduction

Some cyclometalated gold(III) complexes have been shown to have antitumor activity[2,3] or luminescent properties.[4] Cyclometalated gold(III) complexes are rather more scarce than those of palladium(II) and platinum(II)[5−7] probably because until only recently cyclometalation reactions had not been applied to gold(III) and moreover the range of organic reagents prone to being cycloaurated is narrower.[4,8−17] The fact that for many years gold(III) was thought unable to give cyclometalation reactions is also responsible for this situation.[18−21] In fact, most cycloaurated complexes have been obtained by transmetalation reactions using organotin(II)[22−25] or organomercury(II) compounds.[2,3,26−36]

Most cycloauration reactions involve C(sp^2)−H activation processes. The number of cycloaurated complexes containing a C(sp^3)−Au(III) bond is very low indeed, and the reactivity of these derivatives is almost unexplored. As far as we are aware, only a few alkylcycloaurated derivatives have been described. The complexes [Au{PPh_2{C_6H_4($CHCH_2Br$)-2}}Br_2] and [Au{PPh_2{C_6H_4-(CH_2CHCH_2Br)-2}}Br_2][37] were obtained by oxidizing with bromine, [AuBr{PPh_2{C_6H_4($CH{=}CH_2$)-2}}] and

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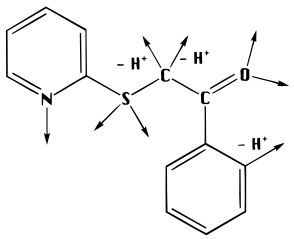
10.1021/om980747m CCC: $18.00
Publication on Web 01/27/1999

Chart 1



[AuBr{PPh_2{C_6H_4($CH_2CH{=}CH_2$)-2}}], respectively, while [Au{$N_2C_{10}H_7$(CH_2CMe_2)-6}Cl][17] results from the reaction of Na[$AuCl_4$] with 6-*tert*-butyl-2,2′-bipyridine. Very recently, the first auracyclobutan-3-one [Au{CH(CO_2Me)C(O)CH(CO_2Me)}L] and aurathietane-3,3-dioxide [Au{CH{C(O)Ph}SO_2CH{C(O)Ph}}L] [L = $C_6H_3CH_2NMe_2$-2-OMe-5] complexes have been reported.[11] They are obtained by reacting the dichlorocomplex [Au(L)Cl_2] with dimethyl-1,3-acetonedicarboxilate or diphenacyl sulfone, respectively, in the presence of silver oxide.

All cycloauration reactions described so far require the refluxing of a solution of a gold(III) complex containing the substrate to be metalated as a ligand (usually [$AuCl_3$(LH)]) or the use of some additional basic reagent to promote the metalation (usually a silver salt). Sometimes, both these reaction conditions are required. Here, we describe the first cycloauration reactions that occur at room temperature and without the need of any basic promoter. In addition, we also show that better results are obtained by using a different basic reagent, Na_2CO_3. This paper reports new cycloaurated complexes involving a C(sp^3)−Au(III) bond, [Au{py{SCHC(O)R}-2}], and is a part of a series dedicated to the study of a family of ligands that can coordinate through nitrogen, sulfur, or oxygen and, after a C−H bond activation, through the methylene carbon atom or a carbon atom of the group R (see Chart 1). We call these multidonor ligands. We have previously reported[1] some mono-, di-, and trinuclear silver(I) and gold(I) derivatives of 2-phenacylthiopyridine showing the different coordination affinity of these cations toward the sulfur and nitrogen atoms.[1]

Experimental Section

The IR spectra, elemental analyses, conductance measurements in acetone, and melting-point determinations were carried out as described earlier.[38] A Varian Unity-300 spectrometer was used to record ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra. Chemical shifts are referred to TMS [^{1}H, ^{13}C{^{1}H}] or H_3PO_4 [^{31}P{^{1}H}]. Otherwise stated the reactions were carried out at room temperature without special precautions against moisture. 2-Mercaptopyridine (HSpy) and chloroacetone were purchased from Fluka, 2-bromoacetophenone [$BrCH_2C(O)Ph$] from Aldrich, methylchloroacetate from Merck, and Na[$AuCl_4$] from Sociedad Española de Metales Preciosos (SEMPSA). Na[$AuBr_4$] was prepared by reacting Na[$AuCl_4$] (450 mg, 1.18 mmol) in acetone (15 mL) with NaBr (731 mg, 7.11 mmol). The brown-red suspension formed was stirred at room temperature for 2 h and then concentrated to dryness. The residue was extracted with dichloromethane (3 × 15 mL), and the extracts were filtered through Celite. The solution was concentrated (5 mL) and diethyl ether (20 mL) added to precipitate Na[$AuBr_4$] (485 mg, 0.9 mmol) as a brown-red solid that was filtered, washed with diethyl ether (2 × 5 mL), and suction dried. Yield: 76%.

Warning: Perchlorate salts with organic cations can be explosive and should be prepared in small amounts.

The ligands py{$SCH_2C(O)R$}-2 (R = Me, OMe) have been prepared following the procedure used for py{$SCH_2C(O)Ph$}-2.[1]

py{$SCH_2C(O)Me$}-2. ^{1}H NMR ($CDCl_3$, δ): 2.32 (s, 3 H, *Me*), 3.99 (s, 2 H, CH_2), 6.96 [m, 1 H, *H4* (py)], 7.21 [m, 1 H, *H3* (py)], 7.49 (m, 1H, *H5* (py)], 8.37 (m, 1H, *H6* (py)]. IR (cm^{-1}): ν_{CO}, 1706.

py{SCH_2CO_2Me}-2. ^{1}H NMR ($CDCl_3$, δ): 3.61 (s, 3 H, O*Me*), 3.88 (s, 2 H, CH_2), 6.86 [m, 1 H, *H4* (py)], 7.09 [m, 1 H, *H3* (py)], 7.34 (m, 1H, *H5* (py)], 8.26 (m, 1H, *H6* (py)]. IR (cm^{-1}): ν_{CO}, 1738.

Syntheses of [$AuCl_2${py{SCHC(O)R}-2}] [R = Ph (1a), Me(1b), OMe (1c)]. py{$SCH_2C(O)R$}-2 (ca. 1 mmol), Na[$AuCl_4$], and Na_2CO_3 were reacted in acetone (25 mL) in 2:2:1 molar ratio for 2.5 (**1a**), 7 (**1b**), or 22 (**1c**) h, respectively. The resulting suspension was concentrated to dryness, and the residue was extracted with dichloromethane (5 × 50 mL) and filtered through anhydrous $MgSO_4$. Complexes **1a**−**c** precipitated as orange solids upon concentration of the solution (to ca. 5 mL) and addition of diethyl ether (20 mL).

1a. Yield: 72%. Mp: 112 °C (decomp). Λ_M: 12 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν_{CO}, 1679; ν_{AuCl}, 358, 312. ^{1}H NMR ($CDCl_3$, δ): 5.86 (s, 1 H, C*H*Au), 7.44−7.53 [m, 3 H, *m-H* (COPh) + *p-H* (Ph)], 7.63 [m, 1 H, *H5* (py)], 7.85 [m, 1 H, *H3* (py)], 7.95 [m, 1 H, *H4* (py)], 8.07 [d, 2 H, *o-H* (COPh), $^3J_{HH}$ = 7.5 Hz], 9.26 [d, 1 H, *H6* (py), $^3J_{HH}$ = 6 Hz]. ^{13}C{^{1}H}: 59.17 (s, *C*HS), 98.56 [s, *ipso-C* (CO*Ph*)], 121.99, 123.06 [s, *C4* (py) + *p-C*′ (CO*Ph*)], 128.75, 129.77 [s, *o-C* + *m-C* (CO*Ph*)], 134.48 [s, *C5* (py)], 141.37 (s, *C3* (py)], 150.26 [s, *C6* (py)], 172.27 [s, *C2* (py)], 191.2 (s, *C*OPh). Anal. Calcd for $C_{13}H_{10}AuCl_2NOS$: C, 31.47; H, 2.03; N, 2.82; S, 6.46. Found: C, 31.32; H, 2.07; N, 3.05; S, 6.63.

1b. Yield: 58%. Mp: 120 °C (decomp). Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν_{CO}, 1697; ν_{AuCl} 354, 305. ^{1}H NMR ($CDCl_3$, δ): 2.47 (s, 3 H, *Me*), 5.05 (s, 1 H, C*H*Au), 7.40 [t, 1 H, *H4* (py)], 7.81−7.99 [m, 2 H, *H3* + *H5* (py)], 9.21 [d, 1 H, *H6* (py), $^3J_{HH}$ = 8.6 Hz]. Anal. Calcd for $C_8H_8AuCl_2NOS$: C, 22.13; H, 1.86; N, 3.23; S, 7.39. Found: C, 22.33; H, 1.71; N, 3.22; S, 7.63.

1c. Yield: 49%. Mp: 105 °C. Λ_M 6 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν_{CO}, 1733; ν_{AuCl}, 362, 273. ^{1}H NMR ($CDCl_3$, δ): 3.78 (s, 3 H, *Me*) 3.96 (s, 1 H, C*H*), 7.57 [t, 1 H, *H4* (py)] 7.95−8.06 [m, 2 H, *H3* + *H5* (py)], 8.58 [d 1 H, *H6* (py), $^3J_{HH}$ = 6.3 Hz]. Anal. Calcd for $C_8H_8AuCl_2NO_2S$: C, 21.35; H, 1.79; N, 3.11; S, 7.12. Found: C, 21.10; H, 1.89; N, 2.92; S, 6.50.

Synthesis of [$AuBr_2${py{SCHC(O)Ph}-2}] (2a). py{$SCH_2C(O)Ph$}-2 (425 mg, 1.85 mmol), Na[$AuBr_4$] (1 g, 1.85 mmol), and Na_2CO_3 (265 mg, 0.93 mmol) were reacted in acetone (10 mL) in 2:2:1 molar ratio for 1.5 h, and the resulting suspension was concentrated to dryness. The oily residue was dried in vacuo for 1 h and vigorously stirred with cold *n*-pentane (5 mL, 0 °C) for 0.5 h to give a solid that was filtered and dried under a nitrogen stream to give **2a** as a brick-red solid. Yield: 478 mg, 46%. Mp: 123 °C. Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν_{CO}, 1651; ν_{AuBr}, 251, 219. ^{1}H NMR ($CDCl_3$, δ): 5.99 (s, 1 H, C*H*Au), 7.41−7.54 [m, 3 H, *m-H* + *p-H* (CO*Ph*), 7.62 [m, 1 H, *H5* (py)], 7.86 [m, 1 H, *H3* (py)], 7.96 [m, 1 H, *H4* (py)], 8.06 [d, 2 H, *o-H* (CO*Ph*), $^3J_{HH}$ = 8.1 Hz], 9.41 [d, 1 H, *H6* (py), $^3J_{HH}$ = 6.1 Hz]. Anal. Calcd for $C_{13}H_{10}AuBr_2NOS$: C, 26.69; H, 1.72; N, 2.39; S, 5.48. Found: C, 26.82; H, 1.76; N, 2.46; S, 5.47.

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Synthesis of [AuBr$_2${py{SCHC(O)Ph}-2}] (2b). To a suspension of **1b** (501 mg, 1.15 mmol) in acetone (40 mL) was added NaBr (309 mg, 3.0 mmol). The reaction mixture was stirred for 15 h and then concentrated to dryness. The residue was extracted with CH_2Cl_2 (5 × 50 mL), the combined extracts were filtered through anhydrous $MgSO_4$, and the solution was concentrated to ca. 3 mL. Addition of diethyl ether (10 mL) gave a solid that was filtered and dried under a nitrogen stream to give **2b** as a red solid. Yield: 262 mg, 44%. Mp: 131 °C (decomp). Λ_M: 10 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν_{CO}, 1690; ν_{AuBr}, 297, 257. ^{1}H NMR ($CDCl_3$, δ): 2.49 (s, 3 H, *Me*), 5.20 (s, 1 H, C*H*Au), 7.39 (t, 1 H, *H4*), 7.82−7.93 [m, 2 H, *H3* + *H5* (py)], 9.33 [d, 1H, *H6* (py), $^3J_{HH}$ = 8 Hz]. Anal. Calcd for $C_8H_8AuBr_2NOS$: C, 18.37; H, 1.54; N, 2.68; S, 6.13. Found: C, 18.52; H, 1.59; N, 2.54; S, 5.91.

Syntheses of [AuCl{py{SCHC(O)R}-2}(PPh$_3$)]ClO$_4$ [R = Ph (3a), Me (3b)]. To a suspension of **1a** or **1b** (ca. 0.2 mmol) in acetone (15 mL) were added equimolar amounts of $NaClO_4$·H_2O and the corresponding phosphine. The resulting suspension was stirred at room temperature for 3 h and then concentrated to dryness. The residue was extracted with dichloromethane (3 × 10 mL) and filtered through anhydrous $MgSO_4$. The solution was concentrated (1 mL) and diethyl ether (20 mL) added to give an orange precipitate, which was filtered and dried under a nitrogen stream. In the case of **3b** [AuCl(PPh$_3$)] was also observed. This can be removed by washing repeatedly with 20 mL portions of $CHCl_3$/Et_2O (1:5).

3a. Yield: 63%. Mp: 152 °C. Λ_M: 96.3 Ω^{-1} cm^2 mol^{-1}. NMR ($CDCl_3$, δ): ^{1}H, 4.60 (s, br, 1 H, C*H*Au, isomer SP4-3), 5.86 (s, 1 H, C*H*Au, isomer SP4-4), 7.26−8.41 [m, 23 H, P*Ph*$_3$, + C(O)-*Ph* + *H3* (py) + *H4* (py) + *H5* (py)], 9.26 (d, 1 H, *H6* (py), $^3J_{HH}$ = 6 Hz). ^{31}P{^{1}H}: 29.75 (s, isomer SP4-4), 32.70 ([AuCl(PPh$_3$)]), 43.15 (s, isomer SP4-3). Anal. Calcd for $C_{31}H_{25}AuCl_2NO_5PS$: C, 45.27; H, 3.07; N, 1.70; S, 3.90. Found: C, 45.01; H, 3.24; N, 1.74; S, 4.10.

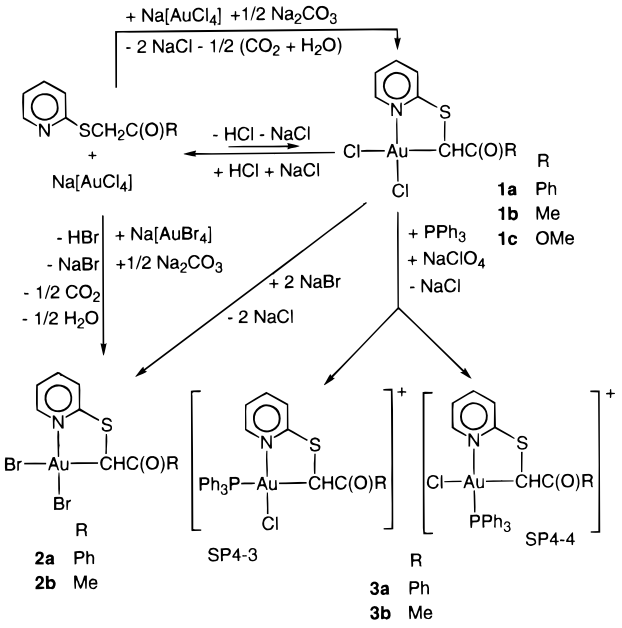
3b. Yield: 81%. Mp: 70 °C Λ_M: 86 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν_{CO}, 1685; ν_{AuCl} 282. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 2.46 (s, 3 H, *Me*, isomer SP4-3), 2.52 (s, 3 H, *Me*, isomer SP4-4), 4.54 (d, 1 H, C*H*, $^3J_{HP}$, 3 Hz, isomer SP4-3), 5.04 (s, 1 H, C*H*, isomer SP4-4), 7.40−9.26 (m, 19 H, *H3* + *H4* + *H5* + *H6* (py) + P*Ph*$_3$). ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$, δ): 27.19 (s, isomer SP4-3), 29.00 (s, isomer SP4-4), 32.70 ([AuCl(PPh$_3$)]). Anal. Calcd for $C_{26}H_{23}AuCl_2NO_5PS$: C, 41.07; H, 3.05; N, 1.84; S, 4.22. Found: C, 40.88; H, 3.07; N, 2.05; S, 4.28.

[Hpy{SCH$_2$C(O)Ph}-2]ClO$_4$. Following the procedure used to prepare complexes **3**, but starting from **1a** and P(C$_6$H$_4$OMe-4)$_3$, a solid was obtained. This was refluxed in chloroform for 1 h and the suspension concentrated to dryness. The residue was extracted with dichloromethane/diethyl ether (1:9, 10 mL) and the suspension filtered to remove colloidal gold and [AuCl{P(C$_6$H$_4$OMe-4)$_3$}]. Upon slow evaporation of the filtrate, crystals of [Hpy{SCH$_2$C(O)Ph}-2]ClO$_4$ were obtained. This salt was prepared independently by reacting the corresponding bromide salt[1] (ca. 6 mmol) with $NaClO_4$·H_2O (1:1.3 molar ratio) in acetone for 0.5 h. The resulting suspension was concentrated to dryness and the residue extracted with dichloromethane (15 mL). The suspension was filtered through Celite, the solution concentrated (1 mL), and diethyl ether (25 mL) added to give a white precipitate that was filtered off, washed with diethyl ether (2 × 10 mL), and air-dried. Yield: 90%. Mp: 123 °C. Λ_M: 114 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{13}H_{12}ClNO_5S$: C, 47.35; H, 3.68; N, 4.25; S, 9.72. Found: C, 47.47; H, 3.69; N, 4.32; S, 9.64.

Results and Discussion

Synthesis of Complexes. The ligands pySCH$_2$C(O)R-2 (R = Ph, Me, OMe) react at room temperature with Na[AuCl$_4$] (1:1) in acetone giving the cyclometalated complexes [AuCl$_2${py{SCHC(O)R}-2}] [R = Ph (**1a**), Me(**1b**), OMe (**1c**)] (see Scheme 1) along with NaCl and some colloidal gold. Upon extraction of the mixture with dichloromethane, pure **1a**−**c** are obtained in low yield (14−17%). However, complexes **1a**−**c** are best prepared in medium to good yields by reacting py{SCH$_2$C(O)R}-2, Na[AuCl$_4$], and Na_2CO_3 in a 2:2:1 molar ratio at room temperature. This fact suggests that the metalation reaction is an equilibrium that can be displaced by removing the HCl formed with Na_2CO_3 (see Scheme 1).

Scheme 1



Complexes **1a** and **1b** react with an excess of NaBr in acetone to give the analogous dibromo complexes **2a** and **2b**, respectively. This procedure gives only a poor yield (26%) in the case of **2a**, which can be improved by reacting py{SCH$_2$C(O)Ph}-2, Na[AuBr$_4$], and Na_2CO_3 (2:2:1). The high solubility of these bromo complexes in the most common organic solvents, including diethyl ether and *n*-hexane, may account for the moderate yields (ca. 50%) obtained. The reaction of **1a** with NaI (1:2) in acetone, designed to produce the corresponding diiodogold(III) complex, instead gave elemental gold and iodine.

Complexes **1a** and **1b** react with PPh$_3$ in the presence of $NaClO_4$·H_2O (1:1:1) (see Scheme 1) to give complexes [AuCl{py{SCHC(O)R}-2}(PPh$_3$)]ClO$_4$ [R = Ph (**3a**), Me (**3b**)] along with [AuCl(PPh$_3$)]. The latter can easily be separated by precipitating complex **3a** or **3b** with diethyl ether. ^{31}P NMR spectra of analytically pure samples of **3a** or **3b** always give the resonance due to [AuCl(PPh$_3$)], indicating that these complexes are unstable in solution. Any excess of $NaClO_4$ in the synthesis of **3a** or **3b** must be avoided; otherwise, some unstable hygroscopic products are obtained. These probably contain the complex [Au(OClO$_3$){py{SCHC(O)R}-2}(PPh$_3$)]ClO$_4$ (the IR spectrum shows the presence of the coordinated OClO$_3$ ligand). In the reaction of complex **1a** with P(C$_6$H$_4$OMe-4)$_3$ and $NaClO_4$·H_2O, in addition to [AuCl{P(C$_6$H$_4$OMe-4)$_3$}] (by IR, ^{1}H, and ^{31}P NMR; this product was also

obtained from **1b**), single crystals of [Hpy{$SCH_2C(O)$-Ph}-2]ClO_4 suitable for a X-ray diffraction study were obtained.[39]

According to ^{1}H NMR data (see below) both complexes are obtained as mixtures of the two possible isomers, namely that containing the phosphine ligand trans to the pyridine nitrogen (isomer SP4-4) or to the CH group (isomer SP4-3). The most abundant is the latter (4:1 and 2:1, respectively). Upon refluxing these complexes in chloroform, mixtures containing mainly [AuCl(PPh_3)] along with small amounts of the SP4-4 isomers are obtained. According to these results, the SP4-3 isomer would seem to be the kinetic product, while SP4-4 is the thermodynamic one. The adverse effect of mutually trans soft ligands,[40−42] termed "transphobia",[43,44] can explain this isomerization. The trans to cis isomerization of [Au(aryl)Cl_2(PR_3)] complexes[45−47] is also an example of the same effect. The formation of [Hpy{$SCH_2C(O)Ph$}-2]ClO_4 in the reaction of complex **1a** with P(C_6H_4OMe-4)$_3$ and $NaClO_4$·H_2O could be a hydrolytic process due to the water added with the $NaClO_4$.

Many reactions aimed to prepare derivatives containing the cyclometalated [Au{py{SCHC(O)R}-2}] moiety failed. Thus, reactions of **1a** with NaCN in 1:2 or 1:4 molar ratio gave mixtures that we could not resolve. All attempts to prepare [Au$(SH)_2$py{SCHC(O)R}-2}] by reacting **1a** with NaSH (1:2, or with a large excess of NaSH) in the presence or not of H_2S gave a red complex analyzing as [Au(S){py{SCHC(O)R}-2}]. However, we could not prove its true nature because its extreme insolubility prevented NMR studies while its FAB mass spectrum gave only the matrix peaks. The reactions of **1a** with Tl(acac) (1:1 or 1:2) gave irresolvable mixtures (by NMR). If the 1:1 reaction is carried out in the presence of $NaClO_4$ (1 equiv), extensive decomposition occurs. Attempts to prepare the dinuclear complex [Au(μ-Cl){py{SCHC(O)R}-2}]$_2^{2+}$ by reacting **1a** with $AgClO_4$ or Tl(O_3SCF_3) (1:1) gave unstable oily products that we could not characterize. The reactions of **1a** with $NaClO_4$ and ^{t}BuNC or γ-picoline (1:1:1 or 1:1.5:1) gave mixtures of unstable compounds. Complex **1a** reacts with 1,2-bis(diphenylphosphino)methane (dppm) and $NaClO_4$ (1:1:2) to give a mixture in which only [$(AuCl)_2$-(dppm)] was identified. The reaction of **1a** with 1,10-phenanthroline and $NaClO_4$ (1:1:2) is incomplete after 3 h. Longer reaction times produce decomposition, while if an excess of 1,10-phenanthroline is used, it cannot be removed from the resulting mixture. These unfruitful results from **1a** induced us not to explore the reactivity of the less stable **1b** or **1c** derivatives.

NMR Spectra. The resonances due to the CH group in the neutral chloro complexes **1** appear as singlets at 5.86 (**1a**), 5.05 (**1b**), or 3.96 (**1c**) ppm. This is the expected order according to the inductive effect of the R group. These values are shifted downfield with respect to those of the CH_2 group in the free ligands pySCH_2C-(O)R (4.68, 3.99, 3.88 ppm, respectively). The bromo complexes **2** show this resonance at δ 5.99 (**2a**) or 5.20 (**2b**) ppm shifted slightly downfield with respect to the homologous chloro complexes **1**, despite the higher electronegativity of the chloro ligand. The ^{1}H NMR spectra of **3a** and **3b** show (besides the presence of [AuCl(PPh_3)]) a duplicity of resonances that we attribute to the presence of the isomers with the CH group trans to the phosphine (SP4-3) or to the chloro ligand (SP4-4). We assign the singlet CH resonance at lower field [5.87 (**3a**), 5.04 (**3b**)] to the SP4-4 isomer with the CH group trans to the more electronegative chloro ligand and that at higher field [4.60 (br) (**3a**), 4.54 (d) (**3b**)] to the SP4-3 isomer, in which the CH group is trans to the phosphine. The ^{31}P{^{1}H} NMR spectrum of **3a** or **3b** shows two singlet resonances corresponding to both isomers along with a resonance due to the product of decomposition [AuCl(PPh_3)]. The mixture obtained by refluxing **3a** or **3b** contains [AuCl(PPh_3)] (by ^{31}P NMR) and a small amount of the corresponding SP4-4 isomer (by ^{1}H NMR). This allows us to assign the singlet corresponding to each isomer in the ^{31}P NMR spectrum of **3a** or **3b**. The isomers SP4-3-**3b** (P trans to C) and SP4-4-**3b** (P trans to N) show the ^{31}P resonances at 27.19 and 29 ppm, respectively, in agreement with the greater electronegativity of nitrogen compared to carbon. Unexpectedly, the ^{31}P resonances in **3a** appear at 43.15 (SP4-3-**3a**) and 29.75 (SP4-4-**3a**), respectively. This indicates that, in this case, the chemical shift is dependent on other more important contributions than the electronic one.

IR Spectra. The formation of the auracycle does not significantly affect the $\nu_{C=O}$ band, which is, in the IR spectra of complexes **1**−**3**, close to that of the py{SCH_2C-(O)R}-2 ligands [1678 (R = Ph), 1706 (Me), 1737 (OMe) cm^{-1}]. According to the greater trans influence of carbon with respect to nitrogen donor ligands, we assign the bands at 358 (**1a**), 354 (**1b**), and 362 (**1c**) to ν_{AuCl} trans to nitrogen mode and those at 312 (**1a**), 305 (**1b**), and 273 (**1c**) to ν_{AuCl} trans to carbon mode. These assignments are consistent with many others reported in the literature.[26,28−31,33−35,48−54] The wavenumber of the bands corresponding to the ν_{AuCl} trans to carbon mode increases with the electron-withdrawing ability of the R group, being OMe (273 cm^{-1}) < Me (305 cm^{-1}) < Ph (312 cm^{-1}).

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This suggests that the R group influences the strength of the pπ(Cl)→dπ(Au) bond component. The dibromo complexes **2** show the ν_{AuBr} bands at 251, 219 (**2a**) and 297, 257 (**2b**). These are all shifted toward the low-energy region, as expected for the heavier bromo ligand, and as above, the higher ones must correspond to ν_{AuBr} trans to N. We could not record the IR spectra of **3a** because it was impossible to prepare an adequate Nujol mull. Complex **3b** shows two bands at 374 and 318 cm^{-1} that we assign to ν_{AuCl} trans to nitrogen mode and to ν_{AuCl} trans to carbon mode of the two isomers. The cationic nature of these complexes can explain the increase of the frequency of these absorptions with respect to the corresponding ones in the neutral complex **1b**.[26,28−31,33−35,48−54]

Acknowledgment. We thank Dirección General de Enseñanza Superior for financial support (PB PB97-1047), and S.H. is grateful to the Spanish Ministerio de Educación y Cultura for a grant. The authors appreciate the helpful suggestions of Prof. R. V. (Dick) Parish.

OM980747M