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2,4,6-Trifluorophenyl gold(I) and gold(III) complexes

Antonio Laguna, Mariano Laguna, Josefina Jiménez and Antonio J. Fumanal

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza (Spain)

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Abstract

Displacement of tetrahydrothiophen (tht) from AuR(tht) ($R = 2,4,6\text{-}C_6F_3H_2$) by anionic ligands gives $[AuRX]^-$, which reacts with $AgClO_4$ or AgR to give $[AuR]_4$, $[RAuSCNAuR]^-$ or $[AuAgR_2]_x$. Neutral $[AuR_3L$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$, $OPPh_3$, $SPPh_3$, NCMe, NCPr, NCPh, $NC(CH{=}CH_2)$, $o\text{-}(NC)_2C_6H_4$ or py), (μ-4,4′-bipy)AuR_3 or *cis*-$AuR_2Cl(py)$], anionic {$(NBu_4)[AuR_3Br]$ or $(NBu_4)[AuR_4]$} or cationic {*trans*-$[AuR_2(4,4'\text{-bipy})]ClO_4$} gold(III) complexes are obtained by displacement of the ether ligand of $AuR_3(OEt_2)$, $AuR_2Cl(OEt_2)$ or $[AuR_2(OEt_2)_2]ClO_4$.

Introduction

Several gold(I) and gold(III) complexes containing the trifluorophenyl group are known [1–5], but they have received far less attention than the corresponding pentafluorophenyl derivatives [6,7]. For instance, no derivatives of the types $[RAuXAuR]^-$ ($R = C_6F_3H_2$, X = halide or pseudohalide), AuR_3L or $[AuR_2L_2]^+$ (L = neutral ligand) have been reported.

In the present paper we describe the synthesis of several types of trifluorophenyl gold(I) and gold(III) complexes obtained by displacement of tetrahydrothiophen (tht) or diethyl ether from $Au(C_6F_3H_2)(tht)$, $Au(C_6F_3H_2)_3(tht)$, $Au(C_6F_3H_2)_3(OEt_2)$ or $[Au(C_6F_3H_2)_2(OEt_2)_2]ClO_4$ by other neutral or anionic ligands.

Results and discussion

(a) Gold(I) complexes

The tetrahydrothiophen (tht) in AuR(tht) ($R = 2,4,6\text{-}C_6F_3H_2$) is readily displaced by anionic ligands (Eq. 1):

$$AuR(tht) + QX \rightarrow Q[AuRX] + tht \qquad (1)$$

[$R = 2,4,6\text{-}C_6F_3H_2$; QX = $(PPh_3Bz)Cl$ (**1**), $(NBu_4)Br$ (**2**) or $[N(PPh_3)_2]SCN$ (**3**)]

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Complexes **1**–**3** are white solids, air- and moisture-stable at room temperature, and conducting in acetone solutions (1 : 1 electrolytes). The IR spectra show the ν(Au–X) vibration at 323(m) (X = Cl, **1**) or 220 (m) cm^{-1} (X = Br, **2**). The presence of the SCN group in **3** is confirmed by absorptions at 2100(m) [ν(C≡N)], 470(m), 455(m), 440(m) and 402 cm^{-1}(m), which reveal [8,9] that the SCN entity acts as an isothiocyanate ligand, attached through its sulfur atom. The ^{19}F NMR spectrum of **2** shows two resonances at −80.6 (*o*-F) and −118.0 ppm (*p*-F).

An anionic binuclear complex can be prepared from **3** by removing half of the pseudohalide ligands by precipitation it the silver salt (Eq. 2).

$$2[N(PPh_3)_2][AuR(SCN)] + AgClO_4 \rightarrow \underset{(4)}{[N(PPh_3)_2][RAuSCNAuR]} + AgSCN + [N(PPh_3)_2]ClO_4 \qquad (2)$$

The product is an air- and moisture-stable white solid. The absorption due to ν(C≡N) appears at 2160(s) cm^{-1}. The shift towards higher energies (60 cm^{-1}) is that expected for bridging SCN [10]. The ^{19}F NMR spectrum confirms the presence of two different $C_6F_3H_2$ groups and shows multiplets at −83.52 (*o*-F), −83.75 (*o*-F) and −115.12 ppm (*p*-F of the two aryl groups).

Complex **4** reacts with AgR (molar ratio 1 : 2) in diethyl ether to give AgSCN and $[N(PPh_3)_2][AuR_2]$ (**5**). From the solution the previously reported $[AuAgR_2]_x$ [3] can be obtained. Complex **5** can be isolated as a white solid by taking advantage of the insolubility of AgSCN in dichloromethane (Eq. 3).

$$[N(PPh_3)_2][(\mu\text{-SCN})(AuR)_2] + 2\ AgR \rightarrow 1/x[AuAgR_2]_x + [N(PPh_3)_2][AuR_2] + AgSCN \qquad (3)$$

Halide or pseudohalide abstraction (with $AgClO_4$) from complexes **1**–**3** gives the previously reported [2] tetranuclear $[AuR]_4$, according to Eq. 4.

$$Q[AuRX] + AgClO_4 \rightarrow 1/4[AuR]_4 + AgX + QClO_4 \qquad (4)$$

(b) Gold(III) complexes

Addition of stoichiometric amount of TlR_2Cl to a toluene solution of AuR(tht) results in oxidative addition to give the corresponding tris(trifluorophenyl)gold(III) complex, according to Eq. 5.

$$AuR(tht) + TlR_2Cl \rightarrow \underset{(6)}{AuR_3(tht)} + TlCl \qquad (5)$$

Complex **6** is a white solid, which slowly decomposes at room temperature, but remains unchanged for months when stored at −20 °C. It is soluble in acetone, chloroform, dichloromethane, diethyl ether, or toluene, and slightly soluble in hexane. In the solid state and, more markedly in chloroform solution, it has the characteristic smell of the free ligand. The low molecular weight observed in $CHCl_3$ solution is due to partial dissociation of tht. It is non-conducting in acetone. The ^{19}F NMR spectrum shows four resonances at −92.30 (4F, *o*-F, *cis*-$C_6F_3H_2$), −92.69 (2F, *o*-F, *trans*-$C_6F_3H_2$), −113.80 (2F, *p*-F, *cis*-$C_6F_3H_2$) and −115.12 ppm (1F, *p*-F, *trans*-$C_6F_3H_2$).

As in $Au(C_6F_5)_3(tht)$ [11] the tht group in complex **6** is readily displaced by some neutral ($L = PPh_3$, $AsPh_3$, $SbPh_3$) or anionic ligands ($X = Br$) to give AuR_3L [$L = PPh_3$ (**7**), $AsPh_3$ (**8**) or $SbPh_3$ (**9**)] and $(NBu_4)[AuR_3Br]$ (**10**), respectively. Other potential ligands, such as $OPPh_3$, $SPPh_3$, NCMe or C_5H_5N (py), cannot displace the tht group, and no substitution takes place.

Ether solutions of $AuR_3(OEt_2)$ (**11**) are obtained by treating **10** with equimolar amount $AgClO_4$ (Eq. 6).

$$(NBu_4)[AuR_3Br] + AgClO_4 + OEt_2 \rightarrow (NBu_4)ClO_4 + AgBr + AuR_3(OEt_2) \qquad (6)$$

After removal of the (quantitatively precipitated) AgBr and $(NBu_4)ClO_4$, the solutions are stable at room temperature. Evaporation of the solvent and addition of n-hexane gives the white solid AuR_3 (**12**). Complex **12** is unstable at room temperature, but can safely be stored for 2–3 weeks at $-20\,°C$. It is soluble in organic polar solvents as acetone or diethyl ether to give colourless solutions, probably with formation of $AuR_3(S)$, but decomposes in dichloromethane or chloroform with precipitation of metallic gold. It has not been possible to record its NMR spectra or to determine its molecular weight (isopiestic method). By analogy with the results obtained for other 2,4,6-trifluorophenyl gold complexes [2,4], we assume a di- or poly-nuclear structure with gold atoms linked through trifluorophenyl bridges.

It is possible to take advantage of the ease of displacement of OEt_2 from complex **11** to prepare a variety of complexes which cannot be synthesised from the tetrahydrothiophen derivative (**6**). Addition of a neutral ligand to diethyl ether solutions of **11** gives complexes AuR_3L [$L = OPPh_3$ (**13**), $SPPh_3$ (**14**), NCMe (**15**), NCPr (**16**), NCPh (**17**), $NC(CH{=}CH_2)$ (**18**), o-$(NC)_2C_6H_4$ (**19**), py (**20**) or 1/2 (4,4′-bipy) (**21**)].

Complexes **7**–**9** and **13**–**21** were isolated as white solids. Complexes **7**–**9**, **13**, **14**, **20** and **21** are air- and moisture-stable at room temperature, but complexes **15**–**19** slowly decompose to metallic gold and must be stored at $-20\,°C$. The acetone solutions of all the complexes are non-conducting, and their molecular weight confirm their monomeric nature. (The low molecular weight determined for the nitrile derivatives **17** or **19** can be attributed to partial dissociation of the nitrile ligand. The molecular weight of complex **21** could not be determined owing to low solubility.) The vibration $\nu(C{\equiv}N)$ appears in the IR spectra of the nitrile complexes at 2350(s) and 2320(m) (**15**), 2325(s) (**16**), 2285(vs) (**17**), 2300(s) (**18**) or, respectively, 2290(s) cm^{-1} (**20**). The $\nu(P{=}O)$ appears at 1147(s) cm^{-1} for **13** and $\nu(P{=}S)$ at 598(m) cm^{-1} for **14**. The ^{19}F NMR spectra show the same pattern as the tetrahydrothiophen derivative (**6**).

AuR_3 reacts with an equimolar amount of $(NBu_4)[AuR_2]$ to give the homoleptic $(NBu_4)[AuR_4]$ (**22**) according to Eq. 7.

$$(NBu_4)[AuR_2] + AuR_3 \rightarrow Au + 1/2R_2 + (NBu_4)[AuR_4] \qquad (7)$$

Complex **22** is a white solid and a 1:1 electrolyte in acetone. Its ^{19}F NMR spectrum shows two resonances at -88.46 (o-F) and -118.27 ppm (p-F). Reaction 7 involves migration of a trifluorophenyl from the gold(I) atom to the gold(III). Another example of migration of this group is provided by the reaction of equimolar amounts of $Au(C_6F_5)_3(OEt_2)$ and $(NBu_4)[AuR_2]$, but in this case a mixture of $(NBu_4)[Au(C_6F_5)_3R]$ and *cis*- and *trans*-$(NBu_4)[Au(C_6F_5)_2R_2]$ is obtained.

Addition of $AgClO_4$ to diethyl ether solutions of *trans*-$(NBu_4)[AuR_2Cl_2]$ (molar ratio 1:1), followed by the removal of the precipitated AgCl and $(NBu_4)ClO_4$, leads, according to Eq. 8, to stable, colourless solutions, which upon evaporation at reduced pressure at room temperature or below (−20 °C) deposit metallic gold.

$$\textit{trans}\text{-}(NBu_4)[AuR_2Cl_2] + AgClO_4 + OEt_2 \rightarrow \underset{(\mathbf{23})}{AuR_2Cl(OEt_2)} + AgCl + (NBu_4)ClO_4 \quad (8)$$

Fortunately, the solutions of **23** are stable, and addition of a neutral ligand such as pyridine gives the neutral complex *cis*-$AuR_2Cl(py)$ (**24**). Complex **24** is a white, air- and moisture-stable solid. Its ^{19}F NMR spectrum shows four signals at −93.78, −94.20, −113.30 and −113.26 ppm (intensity ratio 2/2/1/1), confirming the presence of two inequivalent $C_6F_3H_2$ groups, which must be now in *cis* positions.

Reaction of $AgClO_4$ and *trans*-$(NBu_4)[AuR_2Cl_2]$ in a molar ratio 2:1 leads (after removal of the precipitated AgCl and $(NBu_4)ClO_4$) to colourless solutions which are stable at room temperature, and which we assume to contain $[AuR_2(OEt_2)_2]^+$ (Eq. 9).

$$\textit{trans}\text{-}(NBu_4)[AuR_2Cl_2] + 2\ AgClO_4 + 2\ OEt_2 \rightarrow \underset{(\mathbf{25})}{\text{trans-}[AuR_2(OEt_2)_2]ClO_4} + 2\ AgCl + (NBu_4)ClO_4 \quad (9)$$

Addition of 4,4′-bipy allows isolation of *trans*-$[AuR_2(4,4'\text{-bipy})]ClO_4$ (**26**). Because of its insolubility in organic solvents it is assumed to have a polymeric structure with bipyridyl bridging two gold centers.

Experimental

Instrumentation and general experimental techniques were as described earlier [11]. Nuclear magnetic resonance spectra were recorded on a Varian XL 200 spectrometer in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ (^1H) and $CFCl_3$ (external, ^{19}F). The yields, C, H, N and Au analyses, molecular weights and conductivities of the novel complexes are listed in Table 1.

Preparation of the complexes

Q[AuRX] [Q = PPh$_3$Bz, X = Cl (1); Q = NBu$_4$, X = Br (2); Q = N(PPh$_3$)$_2$, X = SCN (3)]. To a solution of QX [0.5 mmol, QX = $(PPh_3Bz)Cl$ (0.194 g), $(NBu_4)Br$ (0.161 g) or $[N(PPh_3)_2]SCN$ (0.298 g)] in dichloromethane (30 ml) was added AuR(tht) [12] (0.208 g, 0.5 mmol). After 6 h stirring at room temperature a small amount of metallic gold was filtered off and the filtrate was concentrated in vacuo to ca. 5 ml. Addition of diethyl ether (20 ml) gave complexes **1**–**3**.

[N(PPh$_3$)$_2$][RAu(SCN)AuR] (4). To a solution of **3** (0.462 g, 0.5 mmol) in dichloromethane (30 ml) was added a solution of $AgClO_4$ (0.052 g, 0.25 mmol) in diethyl ether (20 ml) and the mixture was stirred for 12 h at room temperature. The AgSCN was filtered off and the solution evaporated to dryness. The residue was extracted with diethyl ether (20 ml) (to leave behind the insoluble $[N(PPh_3)_2]ClO_4$) and the extract evaporated to leave an oil, which was washed with isopropyl alcohol. The resulting white solid **4** was recrystallized from dichloromethane-hexane.

Table 1

Analytical data for complexes

Complex [a]	Yield (%)	Analysis [Found (calcd)) (%)]				Λ_M [b]	Mol. wt. [c] [Found (calcd.)]	M.p. (°C)
		C	H	N	Au			
1 (PPh$_3$Bz)[AuRCl]	90	52.1	3.55		27.3	113		180
		(51.95)	(3.4)		(27.5)			
2 (NBu$_4$)[AuRBr]	95	41.0	5.85	2.2	29.1	112		92
		(40.6)	(5.9)	(2.15)	(30.3)			
3 [N(PPh$_3$)$_2$][AuR(SCN)]	90	56.1	3.8	2.9	21.4	111		174
		(55.9)	(4.15)	(3.0)	(21.3)			
4 [N(PPh$_3$)$_2$][(μ-SCN)(AuR)$_2$]	80	46.6	2.85	2.35	31.1	92		105(d)
		(46.9)	(2.7)	(2.2)	(31.4)			
5 [N(PPh$_3$)$_2$][AuR$_2$]	70	57.25	3.6	1.5	18.9	131		165(d)
		(57.8)	(3.45)	(1.4)	(19.5)			
6 AuR$_3$(tht)	70	39.25	2.1		28.15	5	580	107(d)
		(38.95)	(2.1)		(29.0)		(678)	
7 AuR$_3$(PPh$_3$)	80	50.5	2.9		22.9	4	899	240(d)
		(50.7)	(2.5)		(23.1)		(852)	
8 AuR$_3$(AsPh$_3$)	75	48.05	2.6		21.9	6	896	205(d)
		(48.25)	(2.35)		(22.0)		(890)	
9 AuR$_3$(SbPh$_3$)	73	45.7	2.5		21.0	3	943	190(d)
		(45.85)	(2.25)		(20.9)		(958)	
10 (NBu$_4$)[AuR$_3$Br]	91	45.0	4.05	1.5	20.8	101		135
		(44.75)	(4.65)	(1.55)	(21.6)			
12 AuR$_3$	60	36.1	1.35		33.0			
		(36.6)	(1.0)		(33.4)			
13 AuR$_3$(OPPh$_3$)	75	49.6	2.4		22.3	2	866	154
		(49.9)	(2.45)		(22.7)		(868)	
14 AuR$_3$(SPPh$_3$)	74	49.0	2.45		22.0	3	830	157
		(48.9)	(2.4)		(22.25)		(885)	
15 AuR$_3$(NCMe)	75	38.05	1.5	2.15	31.0	5	654	130
		(38.05)	(1.45)	(2.2)	(31.2)		(631)	
16 AuR$_3$(NCPr)	70	40.0	2.5	2.0	29.9	10	608	95(d)
		(40.1)	(2.0)	(2.1)	(29.9)		(659)	
17 AuR$_3$(NCPh)	75	42.9	2.0	1.95	28.3	1	497	118(d)
		(43.3)	(1.6)	(2.0)	(28.4)		(693)	
18 AuR$_3$[NC(CH=CH$_2$)]	70	38.55	1.2	2.0	30.65	12	689	105(d)
		(39.0)	(1.4)	(2.2)	(30.0)		(643)	
19 AuR$_3$[*o*-(NC)$_2$C$_6$H$_4$]	65	43.35	1.7	3.3	27.1	5	573	120(d)
		(43.45)	(1.4)	(3.9)	(27.4)		(718)	
20 AuR$_3$(py)	65	41.0	1.9	2.0	30.2	5	676	160(d)
		(41.3)	(1.65)	(2.1)	(29.4)		(669)	
21 (μ-4,4'-bipy)[AuR$_3$]$_2$	85	41.3	1.6	1.95	30.0			170
		(41.35)	(1.5)	(2.1)	(29.45)			
22 (NBu$_4$)[AuR$_4$]	78	50.5	4.75	1.2	19.7	95		210
		(49.85)	(4.6)	(1.45)	(20.4)			
24 *cis*-AuR$_2$Cl(py)	65	36.4	2.2	2.3	34.2	5	580	161
		(35.6)	(1.6)	(2.45)	(34.3)		(574)	
26 *trans*-[AuR$_2$(bipy)]ClO$_4$	71	36.75	1.85	3.9	26.9			180(d)
		(36.95)	(1.7)	(3.9)	(27.55)			

[a] R = 2,4,6-$C_6F_3H_2$. [b] In acetone, ohm^{-1} cm^2 mol^{-1}. [c] In chloroform.

$[N(PPh_3)_2][AuR_2]$ (5). To a solution of AgR [4] (0.2 mmol) in diethyl ether (20 ml) was added **4** (0.125 g, 0.1 mmol) and the mixture was stirred for 2 h at room temperature. The yellow precipitate of AgSCN and **5** was filtered off and washed with diethyl ether (3 × 5 ml) then extracted with dichloromethane (20 ml) to leave behind the insoluble AgSCN. The extract was filtered and concentrated to ca. 5 ml, and diethyl ether (20 ml) added, to give a precipite of **5**. Evaporation of the diethyl ether solution to ca. 2 ml and addition of hexane gave $[AuAgR_2]_x$ as a pale yellow solid.

AuR_3(tht) (6). Addition of AuR(tht) [12] (0.416 g, 1 mmol) to a solution of TlR_2Cl [5] (0.502 g, 1 mmol) in toluene (50 ml) led after few minutes to development of a yellow colour and to precipitation of TlCl. After 5 h stirring at room temperature followed by 3 h refluxing, the TlCl was filtered off and the filtrate evaporated to ca. 2 ml. Addition of hexane (20 ml) gave **6** as a white solid.

AuR_3L [L = PPh_3 (7), $AsPh_3$ (8) or $SbPh_3$ (9)]. The ligand [0.3 mmol, L = PPh_3 (0.078g), $AsPh_3$ (0.092 g) or $SbPh_3$ (0.151 g)] was added to a solution of **6** (0.203 g, 0.3 mmol) in dichloromethane (30 ml). After 2 h stirring at room temperature the solution was evaporated to ca. 5 ml. Addition of hexane gave complexes **7–9**. **7**: ^{19}F NMR −92.56 (4F, *o*-F, *cis*-R), −92.77 (2F, *o*-F, *trans*-R) and −115.78 ppm (3F, *p*-F, *cis*- and *trans*-R). **8**: ^{19}F NMR −90.40 (4F, *o*-F, *cis*-R), −91.90 (2F, *o*-F, *trans*-R) and −116.00 ppm (3F, *p*-F, *cis*- and *trans*-R). **9**: −92.30 (4F, *o*-F, *cis*-R), −92.90 (2F, *o*-F, *trans*-R), −113.95 (2F, *p*-F, *cis*-R) and -115.20 ppm (1F, *p*-F, *trans*-R).

$(NBu_4)[AuR_3Br]$ (10). A mixture of **6** (0.339 g, 0.5 mmol) and $(NBu_4)Br$ (0.161 g, 0.5 mmol) in dichloromethane (30 ml) was stirred for 30 min at room temperature. Concentration of the solution to ca. 5 ml and addition of diethyl ether (20 ml) led to precipitation of **10**.

$AuR_3(OEt_2)$ (11) (solution) and AuR_3 (12). A mixture of $AgClO_4$ (0.042 g, 0.2 mmol) and **10** (0.183 g, 0.2 mmol) in diethyl ether (30 ml) was stirred for 12 h at room temperature. The precipitated AgBr and $(NBu_4)ClO_4$ were filtered off. (The resulting colourless solution of **11** is stable at room temperature.) The solution was evaporated to dryness and the residue of **12** was washed with hexane and dried in vacuo.

AuR_3L [L = $OPPh_3$ (13), $SPPh_3$ (14), py (20) or 1/2(4,4′-bipy) (21)]. To a diethyl ether solution of **10** (0.2 mmol) was added the relevant ligand [L = $OPPh_3$ (0.053 g, 0.2 mmol), $SPPh_3$ (0.056 g, 0.2 mmol), py (0.16 ml, 2 mmol) or 4,4′-bipy (0.015 g, 0.095 mmol)] and the mixture was stirred for 2 h at room temperature. Evaporation of the solution to ca. 2 ml and addition of hexane gave the complex **13**, **14**, **20** or **21**. **13**: ^{19}F NMR −92.56 (4F, *o*-F, *cis*-R), −92.77 (2F, *o*-F, *trans*-R) and −115.78 ppm (3F, *p*-F, *cis*- and *trans*-R). **14**: ^{19}F NMR −90.89 (4F, *o*-F, *cis*-R), −92.76 (2F, *o*-F, *trans*-R), −116.24 (2F, *p*-F, *cis*-R) and −116.72 ppm (1F, *p*-F, *trans*-R). **20**: ^{19}F NMR −94.20 (4F, *o*-F, *cis*-R), −92.68 (2F, *o*-F, *trans*-R), −114.31 (2F, *p*-F, *cis*-R) and −115.39 ppm (1F, *p*-F, *trans*-R).

AuR_3NCR [R = Me (15), Pr (16), Ph (17), CH=CH_2 (18) or o-$(NC)C_6H_4$ (19)]. A diethyl ether solution of **10** (0.2 mmol) was evaporated to 2 ml and hexane (20 ml) was added. To the solution was added the relevant nitrile [NCR, R = Me (0.3 ml, 6 mmol), Pr (0.3 ml, 3.5 mmol), Ph (0.3 ml, 3 mmol), CH=CH_2 (0.3 ml, 4.5 mmol) or *o*-$(NC)C_6H_4$ (0.026 g, 0.2 mmol)], and the mixture was stirred for 3 h at 0 °C. Evaporation of the solvent to ca. 10 ml gave complexes **15–19** as white solids.

15: ^{19}F NMR −92.75 (2F, *o*-F, *trans*-R), −93.54 (4F, *o*-F, *cis*-R), −114.19 (2F, *p*-F, *cis*-R) and −114.60 ppm (1F, *p*-F, *trans*-R). **16**: ^{1}H NMR 6.54 (m, 2H, *trans*-R), 6.4 (m, 4H, *cis*-R), 2.64 (t, 2H, *J*(HH) 7.0 Hz, NC–CH_2), 1.76 (m, 2H, C–CH_2–C) and 1.0 ppm (t, 3H, *J*(HH) 7.3 Hz, CH_3). ^{19}F NMR −92.83 (2F, *o*-F, *trans*-R), −93.62 (4F, *o*-F, *cis*-R), −114.38 (2F, *p*-F, *cis*-R) and −114.84 ppm (1F, *p*-F, *trans*-R). **17**: ^{1}H NMR 7.7 (m, 5H, Ph), 6.56 (m, 4H, *cis*-R) and 6.43 ppm (m, 2H, *trans*-R), ^{19}F NMR −92.75 (2F, *o*-F, *trans*-R), −93.55 (4F, *o*-F, *cis*-R), −114.31 (2F, *p*-F, *cis*-R) and −114.75 ppm (1F, *p*-F, *trans*-R). **18**: ^{1}H NMR 6.55 (m, 4H, *cis*-R), 6.42 (m, 2H, *trans*-R), 6.6 (m, 2H, H_A and H_M) and 5.90 ppm (d of d, 1H, H_x, *J*(AX) 19.0 and *J*(MX) 12.0 Hz), ^{19}F NMR −92.75 (2F, *o*-F, *trans*-R), −93.53 (4F, *o*-F, *cis*-R), −114.10 (2F, *p*-F, *cis*-R) and −114.52 ppm (1F, *p*-F, *trans*-R). **19**: ^{1}H NMR 7.93 (m, 4H, C_6H_4), 6.44 (m, 4H, *cis*-R) and 6.57 ppm (m, 2H, *trans*-R).

$(NBu_4)[AuR_4]$ (22). A mixture of **12** (0.118 g, 0.2 mmol) and $(NBu_4)[AuR_2]$ [9] (0.133 g, 0.2 mmol) in dichloromethane was stirred for 5 h at room temperature. The precipitated metallic gold was removed by filtration through a 1-cm layer of diatomaceous earth and the solution concentrated to ca. 5 ml. Addition of diethyl ether (20 ml) led to precipitation of **22**.

cis-$AuR_2Cl(py)$ (24). To a diethyl ether solution (20 ml) of *trans*-$(NBu_4)[AuR_2Cl_2]$ [9] (0.154 g, 0.2 mmol) was added $AgClO_4$ (0.042 g, 0.2 mmol) and the mixture was stirred for 12 h at room temperature. The precipitated AgCl and $(NBu_4)ClO_4$ were removed by filtration through a 1-cm layer of diatomaceous earth. Pyridine (0.16 ml, 2 mmol) was added to the filtrate. After 1 h stirring the solution was evaporated to ca. 5 ml. Addition of hexane (20 ml) precipitated **24** as a white solid.

trans-$[AuR_2(bipy)]ClO_4$ (26). To a solution of *trans*-$(NBu_4)[AuR_2Cl_2]$ [9] (0.077 g, 0.1 mmol) in diethyl ether (20 ml) was added $AgClO_4$ (0.042 g, 0.2 mmol) and the mixture was stirred for 12 h at room temperature. The precipitated AgCl and $(NBu_4)ClO_4$ were filtered off. To the resulting solution was added 4,4′-bipy (0.031 g, 0.2 mmol) and the mixture was stirred for 5 min. The white precipitate of **26** was filtered off.

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