mation of $\mathbf{2}\text{-}d_2{}^+\mathrm{BF_4}^-$. The tube was cooled to −78 °C, and liquified $\mathrm{Me_2O}$ (ca. 0.2 mL) was added by cannula. The tube was shaken and again placed in a −70 °C NMR probe. No reaction had occurred. The probe was warmed to −40 °C, and ^{1}H and ^{31}P NMR spectra were recorded over the course of 4 h, after which time conversion to $\mathbf{4}^+\mathrm{BF_4}^-$ was ca. 90% complete. ^{1}H NMR (δ): 7.50–7.56 (m, 3 $\mathrm{C_6H_5}$), 5.63 (s, $\mathrm{C_5H_5}$), 3.72 (s, 2 $\mathrm{CH_3}$); 3.23 (free $\mathrm{Me_2O}$). ^{31}P NMR (ppm): 18.1 s.

Reaction B. This reaction is representative of those in Scheme IV. A 5 mm NMR tube was charged with $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(NO)(PPh_3)(OCH_3)}$ (**8**;[11,12] 0.051 g, 0.060 mmol) and $\mathrm{Me_3O^+BF_4^-}$ (0.089 g, 0.60 mmol), capped with a septum, evacuated, filled with nitrogen, and cooled to −78 °C. Then $\mathrm{CD_2Cl_2}$ was slowly added by syringe. The heterogeneous reaction mixture was transferred to a −60 °C NMR probe. Spectra showed **8** to be consumed, and the clean formation of $\mathbf{4}^+\mathrm{BF_4}^-$. ^{1}H NMR ($\delta$): 5.61, 3.72. ^{31}P NMR (ppm): 18.7. The $\mathbf{4}^+\mathrm{BF_4}^-$ was warmed in 20 °C increments, and additional ^{1}H and ^{31}P NMR spectra were recorded. Complex $\mathbf{4}^+\mathrm{BF_4}^-$ slowly decomposed. ^{1}H NMR (δ, 20 °C): $\mathrm{C_5H_5}$ (s) at 5.60 ($\mathbf{4}^+\mathrm{BF_4}^-$), 5.52, 5.48; free $\mathrm{Me_2O}$ at 3.28. ^{31}P NMR (ppm, 20 °C): 18.2 ($\mathbf{4}^+\mathrm{BF_4}^-$), 19.6, 22.8.

Acknowledgment. We thank the Department of Energy for support of this research.

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Synthesis and Spectroscopic Characterization of (Triethylphosphine)gold(I) Complexes $\mathrm{AuX(PEt_3)}$ (X = Cl, Br, CN, SCN), $[\mathrm{AuL(PEt_3)^+}]$ (L = $\mathrm{SMe_2}$, $\mathrm{SC(NH_2)_2}$, $\mathrm{H_2O}$), and $(\mu\text{-S})[\mathrm{Au(PEt_3)}]_2$

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Received April 18, 1989

Neutral complexes of the type $\mathrm{AuX(PEt_3)}$ (X = Br, CN, SCN) were prepared and characterized by infrared and Raman spectroscopy, with the major emphasis on the assignment of the gold–ligand vibrations and discerning the mode of bonding for the ambidentate ligands. The photosensitive cationic complexes $[(\mathrm{Au(SMe_2)(PEt_3)})]\mathrm{PF_6}$ and $\{\mathrm{Au[SC(NH_2)_2](PEt_3)}\}\mathrm{Cl}$ in addition to $[\mathrm{Au(OH_2)(PEt_3)}]\mathrm{NO_3}$ and $(\mu\text{-S})[(\mathrm{PEt_3})\mathrm{Au}]_2$ were also prepared and characterized by infrared and NMR spectroscopy. In both cases in which the ambidentate ligands $\mathrm{SCN^-}$ and $\mathrm{SC(NH_2)_2}$ were complexed with Au(I), the sulfur atom coordinates to the metal, providing evidence for a symbiotic relationship in these complexes.

Introduction

Interest in the characterization of Au(I) complexes for the type $\mathrm{AuL(PEt_3)}$ has been rekindled by reports that indicated oral administration of chloro(triethylphosphine)gold(I) in rats revealed its potential in the treatment of arthritis.[1,2] Subsequent studies have shown that a number of gold(I) complexes of the type $\mathrm{Au(SR)(PEt_3)}$ also display activity in the treatment of rheumatoid arthritis,[3-6] in addition to in vivo antitumor activity.[7] Auranofin, a Au(I) compound containing triethylphosphine and tetraacetylthioglucose ligands, is currently being used clinically in the treatment of arthritis.[6]

The linear geometry of $\mathrm{AuL(PEt_3)}$ about a heavy metal provides an especially attractive system for characterization by vibrational spectroscopy, in that vibrational frequencies can be readily assigned for the M–L vibrational modes in complexes containing other complex ligands. In addition, these complexes are ideal for studying the mode of bonding of ambidentate ligands in terms of their electronic control and in the absence of steric factors, in addition to serving as excellent models for further exploring the symbiotic or antisymbiotic trans influence.[8,9] Relatively few reports have appeared in the literature on the metal–ligand vibrations in gold(I) complexes of the type $\mathrm{AuL(PEt_3)}$. A factor partially responsible for this is that Au(I) compounds are often unstable, many being especially photosensitive. In this report, we have synthesized a number of neutral and cationic Au(I) complexes and characterized them with infrared, Raman, and proton NMR spectroscopy. In addition to the Au–P vibrations, assignments for the Au–L vibrations and those diagnostic of the mode of binding for ambidentate ligands are presented and compared to the relevant literature.

Experimental Section

General Data. The elemental analysis was performed by Galbraith Microanalytical Laboratories, Knoxville, TN. The $\mathrm{AuCl(PEt_3)}$ was kindly provided by Smith, Kline and French Laboratories, Philadelphia, PA.

$\mathrm{AuBr(PEt_3)}$. An ethanolic solution of $\mathrm{AuCl(PEt_3)}$ (0.20 g, 0.57 mmol in 3 mL of ethanol) was mixed with an aqueous solution of $\mathrm{AgNO_3}$ (0.09 g, 0.51 mmol in 2 mL of $\mathrm{H_2O}$) and the precipitated AgCl removed by filtration. The colorless, aqueous solution of $[\mathrm{Au(OH_2)(PEt_3)}]\mathrm{NO_3}$ was treated with aqueous NaBr solution (0.23 g, 2.0 mmol in 2 mL of $\mathrm{H_2O}$) to give immediate white crystals of $\mathrm{AuBr(PEt_3)}$. These were filtered out and washed with $\mathrm{H_2O}$. The product was recrystallized from hot ethanol: yield 89% (0.18 g); mp 88–89 °C (lit.[10,11] mp 88–89 °C).

$\mathrm{Au(CN)(PEt_3)}$. An aqueous solution of $[\mathrm{Au(OH_2)(PEt_3)}]\mathrm{NO_3}$ (1 mmol) was treated with an aqueous solution of KCN (0.07 g, 1.0 mmol in 3 mL of $\mathrm{H_2O}$). The solution mixture initially turned white and then became colorless upon further addition of the KCN. The solution was stirred for 5 min at room temperature and then cooled in an ice bath to give white needle-shaped crystals of $\mathrm{Au(CN)(PEt_3)}$. These were filtered out, washed with $\mathrm{H_2O}$, and then dried over $\mathrm{P_4O_{10}}$ under vacuum: yield

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Table I. Infrared and Raman Data (below 500 cm^{-1}) for AuX(PEt$_3$) (X = Cl, Br, CN, SCN)[a]

X = Cl		X = Br		X = CN		X = SCN		
IR	R	IR	R	IR	R	IR	R	assgnt
							119 vs	δ(PAuS)
	129 m		132 m					
	162 s		150 s		150 s		168 s	δ(PC$_3$)
		215 vs	213 s					ν(AuBr)
240 w	240 w		238 w		233 s	240 w	237 w	δ_s(PC$_3$)
278 vw	278 m		276 w					δ_s(PC$_3$)
						292 s	288 s	ν(AuS)
					294 vs			δ(AuCN)
315 s	312 vs							ν(AuCl)
310 s								
	336 m		334 w		330 s		332 s	ν(CCP)
385 w	390 m	385 w	382 w		381 w	375 w	388 w	ν(AuP)
				420 m	442 m			ν(AuCN)
						423 w, sh		ν(SCN)
						435 m		
						445 w, sh		
						455 m		

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; δ, bending or deformation; ν, stretching; s, symmetric; a, asymmetric; sh, shoulder; IR, infrared; R, Raman.

52% (0.09 g); mp 113–114 °C (lit.[12] mp 112.7–113.1 °C). Anal. Calcd for C$_7$H$_{15}$AuNP: C, 24.78; H, 4.42. Found: C, 24.55; H, 4.51.

Au(SCN)(PEt$_3$). An aqueous solution of [Au(OH$_2$)(PEt$_3$)]NO$_3$ (0.86 mmol) was treated with KSCN (0.19 g, 2 mmol in 2 mL of H$_2$O). The white solid formed was recrystallized from hot ethanol to produce a yield of 87% (0.25 g); mp 49–50 °C (lit.[10] mp 50.5–51 °C). Anal. Calcd for C$_7$H$_{15}$AuNPS: C, 22.52; H, 4.02; Au, 52.81. Found: C, 21.97; H, 4.06; Au, 52.26.

(μ-S)[(Et$_3$P)Au]$_2$. The dinuclear Au(I) complex was prepared by modification of the method of Kowala and Swan.[13] A solution of AuCl(PEt$_3$) (0.20 g, 0.57 mmol) in 4 mL of chloroform was added to a stirred aqueous solution of Na$_2$S·9H$_2$O (0.27 g, 1.14 mmol) in 3 mL of H$_2$O. An oily product immediately formed in solution, which changed to a yellowish white solid after heating to 60 °C. The filtered product was washed with H$_2$O and dried over P$_4$O$_{10}$ under vacuum: yield 100% (0.19 g); mp 225–227 °C dec (lit.[13] mp 225–227 °C). Anal. Calcd for C$_{12}$H$_{30}$Au$_2$P$_2$S: C, 21.75; H, 4.53; Au, 59.52. Found: C, 21.60; H, 4.45; Au, 59.07.

[Au(SMe$_2$)(PEt$_3$)]PF$_6$. This complex was prepared by a modification of the method reported by Jones et al.,[14] being similar to that used for the synthesis of [Au(py)(PEt$_3$)]PF$_6$.[15] The yield was 55% (0.22 g) compared to 80% reported previously.[14] The melting point was 126–127 °C dec. Anal. Calcd for C$_8$H$_{21}$AuF$_6$P$_2$S: C, 18.40; H, 4.00; Au, 37.72. Found: C, 18.46; H, 4.09; Au, 37.72.

[Au(tu)(PEt$_3$)]Cl (tu = Thiourea). The complex was prepared by the method used by Coates et al. to prepare the bromide analogue, Au(tu)(PEt$_3$)Br:[10] yield 90% (0.22 g); mp 148–150 °C (lit.[16] mp 140–143 °C). Anal. Calcd for C$_7$H$_{19}$AuClN$_2$PS: Au, 46.18. Found: Au, 46.22.

Spectral Data. The infrared spectra were obtained with the Beckman IR-12 spectrometer using the split Nujol–halocarbon mull technique with KBr windows. The far-infrared spectra (200–400 cm^{-1}) were obtained as Nujol mulls with polyethylene windows. Calibration of the instrument was effected by using a polystyrene film. The frequencies of sharp bands are believed accurate to 2 cm^{-1}, while those for broad bands should be within 5 cm^{-1}. Raman spectra were obtained as previously described,[17] by using 514.5-nm excitation, at a power of 500–1200 mW and a resolution of 8 cm^{-1}. Proton NMR spectra were obtained in DMSO-d_6 by using a Varian A-60 spectrometer, with chemical shifts (δ/ppm) reported in reference to tetramethylsilane (TMS).

Results and Discussion

Vibrational Spectra of AuX(PEt$_3$). The Raman spectra of crystalline AuX(PEt$_3$) (X = Cl, Br, CN, SCN) shown in Figure 1 and the infrared spectra (not shown) exhibit very similar vibrations, with most frequencies greater than 500 cm^{-1} common to the (Et$_3$P)Au^I moiety. These vibrations are readily assigned on the basis of spectra reported for free and metal-complexed triethylphosphine.[18] Although the entire spectra were obtained, of particular interest were (1) the assignment of Au–X vibrations, (2) the vibrations associated with the ambidentate ligands, which are diagnostic of the mode of binding, and (3) the extent of the trans influence of the ligands on the Au–X and Au–P stretching frequencies. Table I shows primarily these selected vibrations.

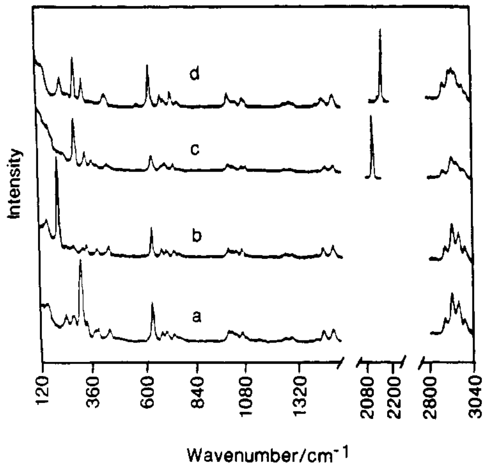

Figure 1. Laser Raman spectra (120–1500, 2100–2200, and 2800–3050 cm^{-1}) of solid (a) AuCl(PEt$_3$), (b) AuBr(PEt$_3$), (c) Au(CN)(PEt$_3$), and (d) Au(SCN)(PEt$_3$).

A single, strong band, with no discernible splitting, observed at 312 cm^{-1} in the Raman spectrum of solid AuCl(PEt$_3$), is assigned to the AuCl stretching mode. This is comparable to the same mode observed at 307 cm^{-1} in the Raman spectrum of solid AuCl(PMe$_3$).[19] The far-infrared spectrum of AuCl(PEt$_3$) shows intense bands at 315 and 310 cm^{-1} associated with the isotopic splitting for ν(Au^{35}Cl) and ν(Au^{37}Cl), respectively. These are comparable to 312 and 305 cm^{-1} reported by Coates and Parkin.[20] The ν(AuCl) stretching frequencies are also similar to those at 311 and 305 cm^{-1} for AuCl(PMe$_3$) but lower than those at 329 and 323 cm^{-1} for AuCl(PPh$_3$), at 325 and 320 cm^{-1} for AuCl(SMe$_2$), and at 330 cm^{-1} for the AuCl$_2^-$ anion.[20,21]

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The Raman spectrum of solid AuBr(PEt_3) shows a strong band at 213 cm^{-1}, which is assigned to ν(AuBr). In the far-infrared region, we observed this mode at 215 cm^{-1}, slightly higher than the previously reported value of 210 cm^{-1}.[20] This frequency is, in fact, midway between that at 205 cm^{-1} for AuBr(PMe_3) and 229 cm^{-1} for AuBr(PPh_3).[20,22] It is also at lower frequency than that at 228 cm^{-1} for AuBr(SMe_2) but comparable to that at 210 cm^{-1} for Au($AsMe_3$)Br.[20,22]

On the basis of Raman and the infrared frequencies for ν(AuBr) in AuBr(PEt_3) and ν(AuCl) in AuCl(PEt_3), a ratio of 0.68 is calculated for ν(AuBr)/ν(AuCl). This supports these assignments, since this ratio is virtually the same as the 0.70 value found for a variety of complex anions of Au(III).[23] This value infers that the force constant for the gold–chloride bond is about 10% greater than that for the gold–bromide bond.[23-25] Additionally, ν(AuP) in AuCl(PEt_3) is assigned at 385 cm^{-1} (IR) and 390 cm^{-1} (R), while assigned at 385 cm^{-1} (IR) and 382 cm^{-1} (R) for AuBr(PEt_3).[20]

Au(CN)(PEt_3). The linear, neutral complex Au(CN)(PEt_3) is known to be unstable in solution by undergoing ligand scrambling.[12] The Raman spectrum of solid Au(CN)(PEt_3) shows a single intense band at 2153 cm^{-1} and a very weak band at 2137 cm^{-1}. The first band is assigned to ν(CN), consistent with a C-bonded cyanide group. In the infrared spectrum, only one band for ν(CN) at 2140 cm^{-1} is observed for the solid complex compared to 2080 cm^{-1} for the free cyanide group in KCN. Hormann et al., who characterized the complex only in the cyanide absorption region, also reported a single band at 2138 cm^{-1}.[12] The infrared ν(CN) for Au(CN)(PEt_3) is essentially of the same frequency as those reported in the infrared spectra of Au(CN)(PPh_3) (2141 cm^{-1}),[26] Au(CN)(NH_3) (2142 cm^{-1}),[27] and K[Au$(CN)_2$] (2141 cm^{-1}).[28] These complexes, which contain terminal C-bonded cyanides, are characterized by having a significantly lower ν(CN) than those containing bridging cyanides, such as that at 2261 cm^{-1} (IR) for AuCN.[28] The reason for the higher ν(CN) in the Raman relative to the infrared spectrum for solid Au(CN)(PEt_3) is not clear but may be in part due to factor group coupling. ν(AuC) for solid Au(CN)(PEt_3) is assigned at 420 cm^{-1} (IR) and at 440 cm^{-1} (R). These values are comparable to the reported infrared ν(AuC) at 414 cm^{-1} for Au(CN)(PMe_3) in CH_2Br_2.[8] These values are also in the region found for ν(AuC) at 447 cm^{-1} (IR) for K[Au$(CN)_2$][29] but much lower than 530 cm^{-1} found for ν(AuC) in AuMe(PEt_3).[20] δ(AuCN) for Au(CN)(PEt_3) occurs at 294 cm^{-1}, which is lower than δ(AuCN) at 348 cm^{-1} (IR) reported for Au(CN)(PMe_3).[8] ν(AuP) for Au(CN)(PEt_3) occurs at 381 cm^{-1} (R), which is higher than 363 cm^{-1} (IR) found for Au(CN)(PMe_3)[8] but lower than 388 cm^{-1} (IR) for AuMe(PEt_3).[20]

Au(SCN)(PEt_3). The complex Au(SCN)(PEt_3) is of particular interest due to the fact that the thiocyanate group is an ambidentate ligand, capable of bonding via the sulfur or the nitrogen atom, and therefore can be used to support a symbiotic or antisymbiotic character of bonding.[8] The vibrational bands, ν(CN), ν(CS), and δ(SCN), are diagnostic of the mode of binding for the SCN group. ν(CN), which occurs at 2053 cm^{-1} for uncomplexed SCN^-, is increased in the solid Au(SCN)(PEt_3) to 2117 cm^{-1} (IR) and to 2119 cm^{-1} (R). These values for ν(CN) are in the range 2108–2120 cm^{-1} expected for a terminally S-bonded thiocyanate group.[8,30] ν(CS) for the S-bonded thiocyanate group in Au(SCN)(PEt_3), which is expected at about 700 cm^{-1},[30] is masked by the strong absorption of the PEt_3 moiety. The infrared spectrum of Au(SCN)(PEt_3) in Figure 2 shows two major bands at 435 and 455 cm^{-1}, which are assigned to δ(SCN) with much weaker shoulders at 423, 442, and 445 cm^{-1}. It has been found that, for an N-bonded thiocyanate group, a single band of medium intensity is expected at about 475 cm^{-1}, while, for an S-bonded thiocyanate, δ(SCN) usually occurs at a lower frequency (410–430 cm^{-1}), with multiple weaker splittings of higher frequencies.[30] The infrared spectra of Au(SCN)(PPh_3) and Au(SCN)(PMe_3) showed δ(SCN) at 422 and 454 cm^{-1} for the former and at 422 cm^{-1} for the latter.[8] Unfortunately, bands possibly associated with δ(SCN) are very weak in the Raman spectrum of crystalline Au(SCN)(PEt_3) and cannot be assigned with any certainty. Nonetheless, the evidence is entirely consistent with a SCN terminally bound through the sulfur atom, as would be expected for symbiotic bonding to a soft acid such as the (Et_3P)Au^I moiety.

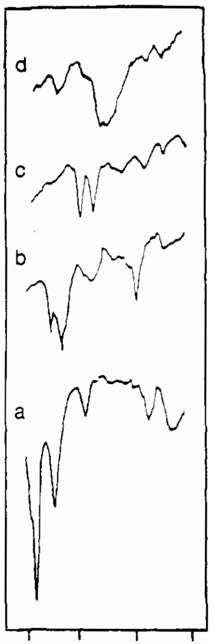

Figure 2. Infrared spectra (200–500 cm^{-1}) of (a) (Au(tu)(PEt_3))Cl, (b) Au(SCN)(PEt_3), (c) [Au(SMe_2)(PEt_3)]PF_6, and (d) (μ-S)[(Et_3P)Au$]_2$.

In addition to these diagnostic modes, modes associated with the S-bonded thiocyanate complex include ν(AuS) and the δ(AuSC) and δ(PAuS) bending modes. ν(AuS), which is expected to be of higher frequency than the remaining two modes, occurs at 288 cm^{-1} in the Raman spectrum (figure not shown), while it is observed at 292 cm^{-1} in the infrared spectrum (Figure 2). This assignment is consistent with those values in the range 296–304 cm^{-1} reported for several Au(SCN)L complexes in solution infrared spectra,[8] revealing the insensitivity of ν(AuS) to the nature of neutral trans ligand. Interestingly, ν(AuS) for a variety of tricoordinate Au(SCN)$(PR_3)_2$ complexes was also found in the region 291–304 cm^{-1} revealing, in this case, the lack of variation in ν(AuS) with the increase in the coordination number around Au(I).[31] The lowest frequency, yet strong, Raman band at 119 cm^{-1} for Au(SCN)(PEt_3) is assigned to δ(PAuS). This assignment is reasonable if compared to δ(SAuS) at 112 cm^{-1} (IR) for the Au$(SMe)_2^-$ anion[32] and δ(ClAuCl) at 116 cm^{-1} (IR) for the $AuCl_2^-$ anion.[21] Finally, the δ(AuSC) mode is apparently very weak and is not evident in the infrared or the Raman spectrum of solid Au(SCN)(PEt_3). However, ν(AuP) for the complex Au(SCN)(PEt_3) appears as a weak band at 375 cm^{-1} (IR) and at 388 cm^{-1} (R).

(μ-S)[Et_3PAu]$_2$. This dinuclear Au(I) complex is, unlike the triphenylphosphine analogue, (μ-S)[Ph_3PAu]$_2$,[13] stable at room temperature yet undergoes rapid photodecomposition in the laser

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Table II. Infrared Data (below 1100 cm^{-1}) for SMe_2 and $[Au(SMe_2)(PEt_3)]PF_6$

SMe_2(l)	$[Au(SMe_2)(PEt_3)]PF_6$	assgnt
	235 w	δ(AuSC)
	270 w	$\delta(PC_3)$
286 m, b	312 w, b	$\delta(SC_2)$
	366 m	ν(AuS)
	392 m	ν(AuP)
	560 s	PF_6^-
695 s	673 w	ν_s(CS)
	688 vw	$\nu_a(PC_3)$
	704 w	
740 m	725 m	ν_a(CS)
	756 s	$\rho(CH_2)$
	765 s	
	840 vvs	PF_6^-
900 w	932 w	$\rho(CH_3)$
975 m	1003 s	$\rho(CH_3)$
1030 vs	1052 s	$\rho(CH_3)$

Table III. Infrared Data (cm^{-1}) for Thiourea (tu) and $[Au(tu)(PEt_3)]Cl^a$

thiourea	$[Au(tu)(PEt_3)]Cl$	assgnt
	225 m	δ(AuSC)
	268 m	ν(AuS)
	388 m	ν(AuP)
411 m	402 m	τ(NH)
463 m	442 m	δ(NCN)
486 s	482 s	δ(SCN)
	493 m, sh	
630 s		β(SCN)
730 s	724 s	ν(CS)
769 vw		w(NH)
	740 s	$\rho(CH_2)$
	765 s	$\rho(CH_2)$
	775 s	$\rho(CH_2)$
	1040 s	$\rho(CH_3)$
	1055 m, sh	$\rho(CH_3)$
1086 m		ν(NCN), $\rho(NH_2)$
1413 s	1385 m, sh	ν(NCN), $\rho(NH_2)$, ν(C=S)
	1405 s	
	1450 m, sh	
1473 s	1500 w	ν(NCN)
1610 s	1610 s, sh	$\delta(NH_2)$
	1625 s	
	1640 s, sh	
3097 s	3110 w, b	$\nu(NH_2)$
3156 s	3180 w, b	
3258 s	3260 w, b	
3365 s	3400 w, b	

[a] Abbreviation: w, wagging; ρ, rocking; τ, torsion; β, out-of-plane deformation.

beam. The far-infrared spectrum, shown in Figure 2, of the complex revealed a weak band at 390 cm^{-1} and a strong band at 350–362 cm^{-1} assigned to ν(AuP) and ν(AuS), respectively. This latter frequency is only slightly higher than ν(AuS) observed in the region 339–343 cm^{-1} for the disulfur-bridged complex $ClAu(\mu\text{-}SR(CH_2)_nRS)AuCl$ (R = Me, Et, Ph; n = 2–10).[31]

$[Au(OH_2)(PEt_3)]NO_3$. In aqueous media and in the absence of other additional coordinating ligands, water occupies the second coordination site in this complex. At room temperature, aqueous solutions of $[Au(OH_2)(PEt_3)]NO_3$ are extremely sensitive to the laser frequency and rapidly decompose to produce metallic gold. The photodecomposition can be minimized at low temperature, and accordingly, the Raman spectrum (not shown) of an 0.5 M aqueous solution was analyzed at 5 °C in the region 180–1300 cm^{-1}. Most of the observed bands in this region are, as expected, weak and broad with the exception of an intense band at 1046 cm^{-1}, which is undoubtedly due to ν(NO) for the ionic nitrate. Vibrational bands are assigned to ν(AuP) at 381 cm^{-1}, $\delta(PC_3)$ at 372 and 642 cm^{-1}, and the combination mode of ν(CC) and $\nu_a(PC_3)$ at 980 cm^{-1} and are essentially of the same frequencies as those observed in the solid $AuL(PEt_3)$ complexes. The ν(AuO) vibration for the aquo complex was assigned to a weak band at 426 cm^{-1}, which is comparable to that at 418 cm^{-1} for $\nu(AuO_2)$ observed in the Raman spectrum of an aqueous solution of $[Au(OH_2)_2Me_2]ClO_4$.[34]

$[Au(SMe_2)(PEt_3)]PF_6$. The solid white crystals of the complex are very sensitive to the laser beam, and therefore the Raman spectrum was not obtained; however, the entire infrared spectrum was analyzed. The assignments of the infrared bands (1100–200-cm^{-1} region) for the complex are summarized in Table II. The most prominent changes that occur in neat SMe_2 are associated with the CS stretching vibrations and the methyl rocking modes. ν_s(CS) at 695 cm^{-1} in free SMe_2 is both reduced in intensity and lowered in frequency to 673 cm^{-1} upon coordination. ν_a(CS), which occurs at 740 cm^{-1} in the spectrum of the free ligand, is also lowered in frequency to 725 cm^{-1} in the complex. The methyl rocking modes at 900, 975, and 1030 cm^{-1} for free dimethyl sulfide increase significantly upon complexation to 932, 1003, and 1052 cm^{-1}, respectively.

There are five distinct bands in the far-infrared spectrum (Figure 2) of the complex $[Au(SMe_2)(PEt_3)]PF_6$. The ν(AuP) mode is assigned to the medium band at 392 cm^{-1}, somewhat higher than that at 385 cm^{-1} for $[Au(py)(PEt_3)]PF_6$.[14] The presence of the new band in the cationic complex at 366 cm^{-1} for the complex is assigned to ν(AuS). This assignment is reasonable in light of the reported ν(AuS) at 345 cm^{-1} (IR) and 343 cm^{-1} (R) for $AuCl(SMe_2)$,[35] at 331 cm^{-1} (IR) and 329 cm^{-1} (R) for $AuBr(SMe_2)$,[35] and at 342 cm^{-1} (IR) for the anionic $Au(SMe)_2^-$.[32] These values for ν(AuS) are also in the same region discussed earlier for the sulfur-bridged complex $(\mu\text{-}S)[(Et_3P)Au]_2$. The weak band at 235 cm^{-1} for $[Au(SMe_2)(PEt_3)]PF_6$ may be due to the δ(AuSC) deformation mode, since it occurs for $AuCl(SMe_2)$ at 226 cm^{-1} (R)[35] and at 204 cm^{-1} (IR).[36] Moreover, the infrared band at 270 cm^{-1} for the complex appears to be due to $\delta(PC_3)$, since it occurs also in this region for $AuL(PEt_3)$ (L = Cl, Br, CN, SCN).

The ^1H NMR spectrum of $[Au(SMe_2)(PEt_3)]PF_6$ in DMSO-d_6 shows a single peak at δ = 2.68 ppm for the coordinated SMe_2, downfield from that at 2.08 ppm for free SMe_2. This chemical shift in these methyl protons is essentially the same as those observed for $AuCl(SMe_2)$ (2.67 ppm) and $AuBr(SMe_2)$ (2.69 ppm)[31] and slightly greater than those reported at 2.57 ppm for the Au(III) complex $[AuMe_2(SMe_2)_2]NO_3$[37] and at 2.50 ppm for the 1:1 Ag(I) complex $Ag(SMe_2)NO_3$.[38] The chemical shift for triethylphosphine in the cationic complex $[Au(SMe_2)(PEt_3)]PF_6$ is essentially the same as those observed for $AuL(PEt_3)$ (L = Cl, Br, CN, SCN).

$[Au(tu)(PEt_3)]Cl$. As with SCN, the ambidentate $SC(NH_2)_2$ ligand is potentially capable of bonding via the sulfur or nitrogen atom. Although the crystals of $[Au(tu)(PEt_3)]Cl$ decompose in the laser beam, full infrared analysis of the solid complex was obtained and assignments of most observed bands are given in Table III.

There are at least three major infrared vibrational bands that are generally diagnostic of the binding mode of thiourea to metals. These include ν(C=S), ν(CN), and $\nu(NH_2)$. Upon coordination of thiourea to a metal via the sulfur atom, the carbon–sulfur double-bond character is reduced and that of the carbon-nitrogen single bond is increased and reaches that of a double bond. As a result, a decrease in ν(C=S) with a concomitant increase in ν(CN) and $\nu(NH_2)$ is to be expected. The opposite would be true if thiourea were coordinated via the nitrogen. ν(CS) for uncomplexed thiourea at 730 cm^{-1} is simultaneously reduced in intensity and decreased to 724 cm^{-1}, while ν(CN) at 1473 cm^{-1} increases to 1500 cm^{-1} in $[Au(tu)(PEt_3)]Cl$. Also consistent with S-bonding is the increase to higher frequencies in the symmetric and asym-

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metric stretches for the NH$_2$ groups in free thiourea upon complex formation. These bands, which occur at 3097, 3156, 3258, and 3365 cm^{-1} for thiourea, are observed at 3110, 3180, 3260, and 3400 cm^{-1} for the complex, respectively.

Although the parent complex, AuCl(PEt$_3$), exhibits strong ν(AuCl) bands at 315 and 310 cm^{-1}, no bands are observed in this region, as evident in Figure 2, for the [Au(tu)(PEt$_3$)]Cl complex. This suggests that the chloride is not coordinated to gold(I) as in the case of Au(tu)$_2$Cl.[39] Most importantly, the medium-intensity infrared band at 268 cm^{-1} for [Au(tu)(PEt)$_3$]Cl is assigned to ν(AuS), being comparable to that at 284 cm^{-1} for ν(AuS) in the Au(tu)$_2$Cl.[39] Finally, ν(AuP) for [Au(tu)(PEt$_3$)]Cl is observed at 388 cm^{-1}.

Uncomplexed thiourea has a single, sharp ^{1}H NMR resonance at δ = 7.18 ppm, which upon complexation shifts downfield to 7.80 ppm. This chemical shift is comparable to that at 7.90 ppm found for the linear S-bonded complex Ag(tu)$_2$NO$_3$ containing the soft and isoelectronic Ag(I).[38] The NMR data clearly show that the complex [Au(tu)(PEt$_3$)]Cl does not dissociate in solution to give free thiourea and AuCl(PEt$_3$) as was believed to occur in chloroform solutions containing the bromide analogue, Au(tu)(PEt$_3$)Br.[13] In addition, these data reveal that the complex remains S-bonded in solution and that the N-bonded isomer does not form.

Conclusions. Of the eight complexes investigated, we have found that the ν(AuP) values in almost all cases fall within 385 ± 5 cm^{-1} and show little sensitivity as a function of the trans ligand and/or charge on the complex. The infrared data do not parallel findings that show ν(AuP) decreases in the order L = Cl > SCN > CN for the trimethylphosphine analogues.[8] These findings are also in further evidence against significant coupling between ν(AuX) or ν(AuL) and ν(AuP).[19,25] In the cases where the ν(AuX) values for AuX(PEt$_3$) can be compared to those of other complexes of the type AuX(PR$_3$) and referred to within the text, they agree well with the relative trans influence of ligand Et$_3$P.[25] In both cases in which the ambidentate ligands SCN$^-$ and SC(NH$_2$)$_2$ were complexed with (PEt$_3$)Au$^{\mathrm{I}}$, the soft base, sulfur, selectively bound to the (PEt$_3$)Au$^{\mathrm{I}}$ moiety as would be expected if the bonding was symbiotic. Finally, assignments for the gold-ligand vibrations in the studied complexes have been made and compared to the relevant literature.

Acknowledgment. We wish to thank Smith, Kline and French Laboratories, Philadelphia, PA, for providing AuCl(PEt$_3$). This work was supported by a Bowling Green State University FRC grant.

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NMR Relaxation and π Bonding in Group 6 Transition-Metal Hexacarbonyls

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Received May 24, 1989

Carbon-13 and oxygen-17 spin-lattice relaxation times were measured for the series M(CO)$_6$, M = Cr, Mo, and W, at two temperatures in the solvent, CDCl$_3$. Values of T_1(^{13}C) at two magnetic field strengths were utilized to calculate reorientational correlation times, τ_c, which, together with T_1(^{17}O), yielded values for the oxygen's quadrupole coupling constant, χ(^{17}O); results at the two temperatures were in good agreement. The Townes-Dailey theory of QCC's was applied to obtain estimates of the CO's 2π (or π*) orbital populations, [2π], in each of the carbonyls. It was found that the orbital occupancies and, hence, π-bond strengths vary in the order $[2\pi]_{\mathrm{Mo}} < [2\pi]_{\mathrm{Cr}} \approx [2\pi]_{\mathrm{W}}$. This is the same order observed for the majority of spectroscopic, thermodynamics, and kinetic measures of overall, $\sigma + \pi$, bond energies. Therefore, π-bond variations play an important role in determining the relative M-CO bond stabilities in the group 6 hexacarbonyls.

Introduction

There is now an abundance of evidence that the bonding in transition-metal carbonyl complexes is synergistic in nature, with reinforcement of the otherwise weak σ bond between the CO 5σ and metal d$_\sigma$ orbitals by metal d$_\pi$ back-bonding to the CO's 2π framework. Rather surprisingly, though, the relative magnitude of the contributions of the σ and π components to the M-CO bond stability remains poorly understood.[2] This comparative dearth of knowledge is due to the fact that most experimental properties, including the widely used $C\equiv O$ vibrational force constants[3] and NMR chemical shifts,[4] are affected by variations in both the σ- and π-bond interactions.

Nuclear quadrupole coupling constants (QCC's), defined by $\chi = e^2qQ/h$, are proportional to the electric field gradient (eq) and, thus, directly dependent upon the electronic charge symmetry in the immediate environment of the nucleus.[5] For nuclei involved in multiple bonds, it is generally observed that changes in χ are influenced primarily by variations in π bonding.[5,6]

In recent years, a number of investigators[7,8] have employed NMR spin-lattice relaxation time measurements to estimate oxygen-17 QCC's in a variety of metal carbonyl complexes and have observed that the magnitude of χ(^{17}O) and, hence, π-bond strengths are markedly dependent upon the metal to which the

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