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Preparation and Properties of Monothio- and Monoselenocarbamate Complexes of Gold(I) and Rhodium(I)

F. W. PIJPERS, A. H. DIX and J. G. M. VAN DER LINDEN
Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

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The complexes $(C_6H_5)_3PAuL$ and $((C_6H_5)_3P)_2Rh(CO)L$ ($L = SC(O)NR_2$ and $SeC(O)NR_2$) have been prepared. Infrared data reveal the monothio- and selenocarbamate complexes to be monodentate coordinated with the metal atom via the sulfur or selenium, respectively.

The kinetic parameters of the hindered rotation around the ($C\overset{...}{-}N$) bonds in the gold complexes have been determined from n.m.r. spectra. The values for the activation energies have the same order of magnitude as those found for other hindered rotation processes in dithiocarbamate complexes.

Introduction

After the extensive investigations being made on transition metal dithiocarbamates[1] there is now a growing interest in the monothiocarbamate ligand as a complexing agent.[2–7] Relatively few diselenocarbamates have been reported[8–11] and only two reports concerning monoselenocarbamato metal complexes have appeared so far.[12,13] Interest in selenium containing compounds arises from the occurrence of selenium as a trace element in enzymatic reactions and as a cancer inhibitor.[14]

The recent characterisation of di-alkylammonium monoselenocarbamates as intermediates in the reaction of amines with selenium and carbon monoxide[15] opens the possibility to compare the coordinating properties of these monoseleno- and monothiocarbamates.

In the present work the preparation and some physical properties of monothio- and monoselenocarbamato complexes of gold(I) and rhodium(I) are described. The kinetic parameters of the hindered rotation around the $R_2N–C(O)S$ and $R_2N–C(O)Se$ bonds in the gold complexes, $(C_6H_5)_3PAuSC(O)NR_2$ and $(C_6H_5)_3PAuSeC(O)NR_2$, have been determined from proton n.m.r. spectra.

Results and Discussion

With simple reactions $(C_6H_5)_3PAuL$ and $((C_6H_5)_3P)_2Rh(CO)L$ ($L = SC(O)NR_2$ and $SeC(O)NR_2$, $R = Me$, $R_2 = C_5H_{10}$) could be prepared from $(C_6H_5)_3PAuCl$ and $((C_6H_5)_3P)_2Rh(CO)Cl$ and the ammonium (or sodium) salts of the monothio- and monoseleno carbamato ligands. Attempts to prepare the sodium salt of the monoselenocarbamate failed, because addition of sodium hydroxide to the reaction mixture led to red coloured decomposition products.

The purification of the monoselenocarbamato complexes offered some difficulty because during the preparation also formed di-alkyl-ammonium chloride shows the same solubility behaviour as these complexes.

The analogous tricyclohexylphosphine derivatives of rhodium differ remarkably in chemical behaviour, in most cases due to the bulky cyclohexylgroups.[16] Thus, in benzene solutions no reaction took place between the N-piperidyl-thiocarbamate and $((C_6H_{11})_3P)_2Rh(CO)Cl$ or $(C_6H_{11})_3P(C_6H_5)_3PRh(CO)Cl$,* while the last compound failed to react in tetrahydrofurane. All of the reactions with the seleno containing ligands require careful deoxygenation of solvents and reaction vessels in order to avoid oxidation of the ligand with formation of ureas.[15] When kept in a nitrogen atmosphere the gold and rhodium thio- and selenocarbamates are stable in solution as well as in the solid state. When exposed to the air the dissolved complexes are decomposed and the solid selenocarbamates became black, due to the separation of selenium.

A molecular weight determination revealed $(C_6H_5)_3PAuSC(O)NC_5H_{10}$ to be monomeric in chloroform solutions (osmometric method; found: 616; calcd.: 604).

Infrared Spectra

In the 1600–1400 cm⁻¹ region the infrared spectra of the various complexes contained only one strong

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* This known mixed phosphine complex[17] can easily be obtained by treating $[RhCl(C_8H_{14})_2]_2$ with two equivalents of $(C_6H_5)_3P$ in THF and passing carbon monoxide over the solution until a colour change to yellow occurred, giving $[RhCl(CO)P(C_6H_5)_3]_2$. This last complex is treated with two equivalents of $P(C_6H_{11})_3$ giving the desired mixed complex ($\nu(CO) = 1930$ cm^{-1}, $\nu(Rh–Cl) = 310$ cm^{-1}).

TABLE I. Infrared Data for the Complexes.

	$\nu(\mathrm{C}\equiv\mathrm{O})$	$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$		$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$
$(C_6H_5)_3PAuSC(O)N(CH_3)_2$		1595,	1590	
$(C_6H_5)_3PAuSeC(O)N(CH_3)_2$		1610,	1600	
$(C_6H_5)_3PAuSC(O)NC_5H_{10}$		1595,	1585	
$(C_6H_5)_3PAuSeC(O)NC_5H_{10}$		1605,	1595	
$(C_6H_5)_3PAuSC(O)N(C_6H_5)_2$		1620,	1590	
$[AuS_2CN(C_6H_5)_2]_2$				1355
$(C_6H_5)_3PAuSC(S)N(C_6H_5)_2$				1340
$[AuS_2CN(C_4H_9)_2]_2$				1488
$(C_6H_5)_3PAuSC(S)NC_5H_{10}$				1430
$((C_6H_5)_3P)_2Rh(CO)(SC(O)NC_5H_{10})$	1960	1565		
$((C_6H_5)_3P)_2Rh(CO)(SeC(O)NC_5H_{10})$	1980	1585		

broad band (Table I) apart from the sharp peaks at 1590, 1570, 1480 and 1440 cm^{-1} which are characteristic for the vibrations of the phenyl groups of the phosphine.[18] This broad band, which splits up to some extent for the gold complexes, is assigned to the coupled $(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{O})$ and $(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$ stretching modes of the thio- and selenocarbamate moiety. Both vibrations are generally found in this region.[19]

The molecular structure determination of the dithio analog, $(C_6H_5)_3PAuSC(S)N(C_2H_5)_2$ revealed that the dithiocarbamate ligand acts as a monodentate ligand; the sulfur–gold distance of the not co-ordinated sulfur atom is somewhat less than the expected Van der Waals distance.[20]

From these data and the observed high values of the $\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{O})$ it can be concluded that in the newly prepared complexes the metal atom is co-ordinated with the thio- and selenocarbamate ligand only through the sulfur or selenium atom, respectively.

It is well known that in the N,N-di-phenyl substituted dithiocarbamates the $(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$ stretching frequency is considerably lowered due to the electron-withdrawing phenyl groups (Table I). For the N,N-diphenyl substituted monothiocarbamates there is a competition for electrons between the carbonyl oxygen and the phenylgroups.[21] The $\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$ should be lowered and the $\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{O})$ should be increased. However, apart from the absorption band at 1590 cm^{-1} no other band appeared in the 1500–1400 cm^{-1} region, which could be assigned to the $\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N}$ stretching frequency.

In view of the observed position of the coupled $(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{O})$ and $(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$ vibrations we suggest that also in the rhodium complexes the thio- and selenocarbamate ligands are coordinated only via the sulfur and selenium, respectively. The position of the $\nu(\mathrm{C}\equiv\mathrm{O})$ at 1980 cm^{-1} strongly suggest that the carbonyl group is situated trans to the carbamate ligand. In similar square planar Rh(I) complexes with phosphine trans to CO this carbonyl stretching frequency is found well above 2000 cm^{-1} (ref. 22).

After this study was essentially complete we learned of the work of Krankovitsch, Magee and O'Connor,[4b] who via another route obtained and characterised the analogous N,N-diethylthiocarbamate complex, $((C_6H_5)_3P)_2Rh(CO)SC(O)N(C_2H_5)_2$. The collective infrared data compare satisfactorily and these authors came to the same conclusions by other arguments.

N.m.r. Spectra

When the proton n.m.r. spectra of the thio- and seleno gold complexes are measured in $CDCl_3$ solutions at sufficiently low temperatures, the signal for the N–CH_x protons splits into two signals of equal intensity α–1 and α–2. The chemical shift of these protons together with the temperature required for maximum splitting is listed in Table II. According to Tanaka *et al.*[13] the high field signal of the selenium compound, which is smaller in height and broader than the low field one, should be assigned to the CH_x-α protons *trans* to the selenium atom with respect to the $(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$ bond in the planar monoselenocarbamate. This broadening is due to the coupling with ^{77}Se (natural abundance 7,5%) that is higher for trans than for *cis* α-protons. The signals of the α-protons in the monothio compounds cannot be assigned to a particular site. The magnetic coupling between the α and β protons of the piperidine ring is hidden in the line width of these signals, which is considerably higher than that of the aromatic ring protons of the triphenylphosphine ligand ($1/T_{2,0} = 6$ rad sec^{-1}).

At room temperature the limit of fast exchange is reached, whereas at temperatures below –30° C the splitting is at its maximum value. At still lower temperatures the signals of the piperidine ring protons somewhat broaden. This is probably due to a decrease of the rate of the boat–chair interconversion process, which at higher temperature averages the coupling between the α-protons (axial and equatorial) with the β axial and equatorial ones. The effect of an increased viscosity of the solvent on the linewidth can be ne-

TABLE II. Proton N.m.r. Data.

Complex in $CDCl_3$	δ_{arom}[b] (p.p.m.)	$\delta_{CH_2}\alpha_1$ (p.p.m.)	$\delta_{CH_2}\alpha_2$ (p.p.m.)	$\delta_{CH_2}(\beta+\gamma)$ (p.p.m.)	T (°C)	$1/T_{2,0}$ (rad/sec)
$(C_6H_5)_3PAuSC(O)N(CH_3)_2$	7.40	3.16	2.92	–	+1	6.3
$(C_6H_5)_3PAuSeC(O)N(CH_3)_2$	7.50	3.24	3.00	–	+12	6.3
$(C_6H_5)_3PAuSC(O)NC_5H_{10}$	7.42	3.68	3.50	1.50	–30	25
$(C_6H_5)_3PAuSeC(O)NC_5H_{10}$	7.40	3.62	3.50	1.50	–30	41
$(C_6H_5)_3PAuSC(S)NC_5H_{10}$	7.40	4.10	4.10	1.62	–60[c]	38
$(C_6H_5)_3PAuSC(S)NC_5H_{10}$[a]	–	4.05	4.05	1.62	–90[c]	47

[a] In CH_2Cl_2 solution. [b] $\delta = \frac{H_{comp}-H_{ref}}{H_{ref}} \times 10^6$; TMS was the internal standard. Shift accuracy is about 0.01 p.p.m. For the multiplets of the aromatic protons the values of the centers have been tabulated; the intensity ratio of the two α-CH_2 signals is always 1:1. The $J_{H\alpha-H\beta}$ is always smaller than the linewidth $(1/T_{2,0})$ of the α proton signal. [c] Lowest available temperature for this solvent.

glected as is seen from the linewidth of the aromatic ring protons signals, which does not alter as the temperature is lowered.

All n.m.r. spectra have been simulated by using the modified Bloch equations describing the exchange between two equally populated sites.[23] The simulation requires three independent parameters only, *viz.* $T_{2,0}^{-1}$, the linewidth parameter in the absence of exchange the lifetime of a particular configuration and the positions of lines at conditions of very slow rotation ($\tau \rightarrow \infty$) (see Table II). $T_{2,0}^{-1}$ was chosen in such a way that the line shape of the CH_2-$\beta+\gamma$ protons is matched in the experimental spectra (Table II).

The lifetime τ at a given temperature was found by trial and error; it was varied until the line-shape of the α-CH_2 protons in the simulated n.m.r. spectra matched perfectly with the experimental ones.

Figure 1 shows the Eyring plots for hindered rotation around the ($C\overset{..}{-}N$) bond in $(C_6H_5)_3PAuSC(O)NC_5H_{10}$ and $(C_6H_5)_3PAuSeC(O)NC_5H_{10}$ in $CDCl_3$. The thermodynamic constants derived from these plots are listed in Table III. These constants for the activated complex, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ result from the application of the Eyring equation with a path degeneracy factor of 1. The values for $\Delta H^{\ddagger}$ have the same order of magnitude as those found for other hindered rotation processes in dithiocarbamates.[24]

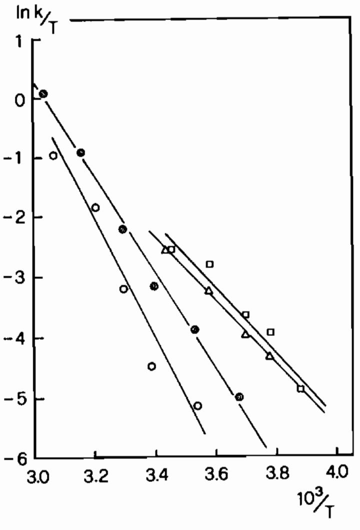

Figure 1. Eyring plots for the intramolecular rearrangement reactions of $(C_6H_5)_3PAuSC(O)N(CH_3)_2$ (●), $(C_6H_5)_3PAuSeC(O)N(CH_3)_2$ (○), $(C_6H_5)_3PAuSC(O)NC_5H_{10}$ (□), $(C_6H_5)_3PAuSeC(O)NC_5H_{10}$ (△).

TABLE III. Thermodynamic Constants for the $C\overset{..}{-}N$ Bond Rotation.

Compound	$\Delta G^{\ddagger}_{300°K}$ (kcal/mol)	$\Delta H^{\ddagger}_{300°K}$ (kcal/mol)	$\Delta S^{\ddagger}_{300°K}$ (e.u.)
$(C_6H_5)_3PAuSC(O)N(CH_3)_2$	15.8	15.8	0.0
$(C_6H_5)_3PAuSeC(O)N(CH_3)_2$	16.4	19.2	+9.2
$(C_6H_5)_3PAuSC(O)NC_5H_{10}$	15.2	10.8	–14.7
$(C_6H_5)_3PAuSeC(O)NC_5H_{10}$	15.4	10.7	–15.7

[a] The inaccuracy in $\Delta G^{\ddagger}$ is approximately 0.1 unit; in $\Delta H^{\ddagger}$ 1.0 unit and in $\Delta S^{\ddagger}$ 3 units.

In contrast to our expectations based upon the molecular structure of $(C_6H_5)_3PAuSC(S)N(C_2H_5)_2$, which reveals two chemically different sulfur atoms in this complex,[20] the n.m.r. pattern of the α-CH_2 protons in the piperidine ring of $(C_6H_5)_3PAuSC(S)NC_5H_{10}$ showed only one signal. Even at −90°C the lowest temperature that could be obtained when CH_2Cl_2 was used as solvent no splitting of this signal was observed. Assuming that the bond rotation around the S_2C——NR_2 bond is frozen out, which is highly probable at this low temperature, this means that the two sulfur atoms are equivalent, probably due to a process in which the metal–ligand bond alternates rapidly between the gold atom and both the sulfur atoms.

The width of this signal ($1/T_2 = 47$ rad sec^{-1}) is only slightly more than that found at +32°C in $CDCl_3$ ($1/T_2$ = 38 rad sec^{-1}) or that of the $\beta+\gamma$ protons signal at −60°C ($1/T_2$ = 31 rad sec^{-1}). So this process is rapid on the n.m.r. time scale.

Experimental

Infrared spectra in the region 4000–625 cm^{-1} were measured on a Perkin Elmer 257 spectrophotometer in KBr pellets. The spectra in the 700–200 cm^{-1} region were measured on a Hitachi EPI–L instrument in CsI discs. ^1H n.m.r. spectra were recorded on a Varian HA–100 spectrometer operating at 100 MHz equipped with a variable temperature unit. Temperatures were measured with a copper–constantane couple in the probe. Molecular weights were determined using a Hewlett Packard 302B osmometer.

Analyses were carried out in the micro analytical department of this university. Gold was analysed by atomic absorption spectrophotometry.

Preparations

All reactions were carried out in a dry nitrogen atmosphere.

Ligands

N,N-dimethyl- and N-piperidylthiocarbamates were prepared as the ammonium or sodium salts from the amines and carbonyl sulfide as described.[19] The selenocarbamates were prepared from the amines, selenium and carbon monoxide in tetrahydrofurane solutions following a procedure described recently.[15]

The procedures used to prepare the various gold complexes were basically the same and the following procedure is a typical example.

$(C_6H_5)_3PAuSC(O)NC_5H_{10}$

To a solution of 0.32 g (2 mmol) $C_5H_{10}NC(O)SNa$ in 10 ml of THF was added an equimolar amount of triphenylphosphinegoldchloride in 50 ml toluene. The mixture was stirred for five minutes, filtered, and the solvent was removed *in vacuo*. The obtained product was dissolved in 5 ml THF, colled to −30°C and the complex was precipitated with 15 ml hexane. This last procedure was repeated once, a white solid resulted, 0.5 g, m.p. 123–4°C. Found: C, 47.8; H, 4.2; N, 2.6; Au, 33.3. Calc. for $AuC_{24}H_{25}NOPS$: C, 47.8; H, 4.2; N, 2.3; Au, 32.8.

$(C_6H_5)_3PAuSeC(O)NC_5H_{10}$

M.p. 131–4°C. Found: C, 44.6; H, 3.9; N, 2.2. Calc. for $AuC_{24}H_{25}NOPSe$: C, 44.3; H, 3.9; N, 2.2.

$(C_6H_5)_3PAuSC(O)N(CH_3)_2$

M.p. 141–4°C. Found: C, 45.9; H, 3.9; N, 2.7. Calc. for $AuC_{21}H_{21}NOPS$: C, 44.8; H, 3.8; N, 2.5.

$(C_6H_5)_3PAuSeC(O)N(CH_3)_2$

M.p. 149.5–151.5°C. Found: C, 42.3; H, 3.7; N, 2.4. Calc. for $AuC_{21}H_{21}NOPSe$: C, 41.3; H, 3.5; N, 2.3.

$(C_6H_5)_3PAuSC(O)N(C_6H_5)_2$

M.p. 192–4°C.

$((C_6H_5)_3P)_2Rh(CO)SC(O)NC_5H_{10}$

To a solution of 0.06 g (0.28 mmol) $[C_5H_{10}NH_2]$ $[C_5H_{10}NC(O)S]$ (or the corresponding selenium compound) was added an equimolar amount of $((C_6H_5)_3P)_2Rh(CO)Cl$ in 10 ml THF. The mixture was stirred for 30 minutes, filtered and the filtrate cooled to −60°C. The complex was precipitated with 15 ml hexane. The last procedure was repeated once, and a yellow solid resulted. Found: C, 64.6; H, 5.4; N, 1.8. Calc. for $RhC_{43}H_{40}NO_2P_2S$: C, 64.6; H, 5.0; N, 1.5.

$((C_6H_5)_2Rh(CO)SeC(O)NC_5H_{10}$

This complex was identified by the similarity of its i.r. spectrum with the analogous sulfur compound.

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