Journal of Organometallic Chemistry, 226 (1982) 93—103
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

DINUCLEAR FORMAMIDINO AND TRIAZENIDO COMPOUNDS [{2,6-($Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtHgBrCl] (Y = CH, N) CONTAINING A PLATINUM-TO-MERCURY DONOR BOND

A.F.M.J. VAN DER PLOEG, G. VAN KOTEN * and K. VRIEZE

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

(Received September 3rd, 1981)

Summary

Complexes [{2,6-($Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtHgBrCl] (Y = CH, N; R = Me, Et, i-Pr) have been prepared by the reaction of [{2,6-($Me_2NCH_2)_2C_6H_3$} PtBr] with [Hg(*p*-tolylNYNR)Cl]. Similar complexes were obtained, although in lower yields, from exchange reactions of [{2,6-($Me_2NCH_2)_2C_6H_3$}(RCO_2)-PtHg(O_2CR)Br] with *p*-tolylNNN(H)-*p*-tolyl and *p*-tolylNC(H)N(H)Et.

The proposed structure for these heterodinuclear compounds involves a Pt-to-Hg donor bond which is bridged by a triazenido (Y = N) or a formamidino (Y = CH) group, the five-membered ring thus formed acting as a stabilizing factor. The absence of a subsequent electron transfer reaction is ascribed to the constraints of the terdentate 2,6-($Me_2NCH_2)_2C_6H_3$ ligand, which fixes the N-donor atoms in mutual *trans*-positions.

The use of *p*-tolylNYNR, where R is an alkyl group, results in the formation of two isomers of [{2,6-($Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtHgBrCl] with *p*-tolyl-N and alkyl-N sites bonded either to Pt or Hg. The relative abundance of these isomers varies systematically with the nature of the group R. It is suggested that the ratio is determined during the formation of the complexes and that both steric and electronic factors are important.

Introduction

A series of publications from our laboratory has dealt with the chemistry of heterodinuclear Rh(Ir)—Cu(Ag, Hg) complexes with formamidino or triazenido groups bridging the metal centres [1—7]. Such complexes were synthesized by

---

* To whom correspondence should be addressed.

0022-328X/82/0000—0000/$02.75

combination of a d^8 transition metal complex with a d^{10} post-transition metal complex.

Recently, we directed our interest towards the synthesis of heterodinuclear complexes involving, instead of Rh^I or Ir^I, the isoelectronic platinum(II) as the d^8 transition metal. It became apparent that a large series of stable dinuclear Pt—Hg complexes could be prepared from cyclometallated platinum(II) compounds containing N-donor ligands [8,9]. For $[(2\text{-}Me_2NCH_2C_6H_4)_2(MeCO_2)\text{-}PtHg(O_2CMe)]$ (I) an X-ray structure determination confirmed the presence of a covalent Pt—Hg bond bridged by one carboxylato group, the other carboxylato group being monodentate bonded to Hg. No intramolecular exchange of these differently-bonded carboxylato groups was observed. In $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(RCO_2)PtHg(O_2CR)Br]$ (II: R = Me, i-Pr) a different structure was observed; the two N-donor atoms in this compound are fixed in *trans*-positions, which excludes formation of a Pt—Hg compound containing a ligand donor atom arrangement around platinum, similar to that found in I. Moreover, in II the carboxylato groups, which are inequivalently bonded, do undergo intramolecular exchange. From these observations alone no conclusion could be reached about the nature of the Pt—Hg interaction in II. Since it is known that formamidino and triazenido ligands are better bridging ligands, and can therefore give rise to more stable dinuclear complexes [10], the synthesis of complexes containing these ligands has been studied. In a recent paper we reported the stabilization of platinum—silver bonds by such ligands [11]. In this paper we describe the synthesis and structural characterization of Pt—Hg bonded complexes formed in the reaction of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$ with formamidino- and triazenido-mercury compounds.

Experimental

^1H NMR spectra were recorded on Varian T-60, Varian XL 100-15 and Bruker WM-250 spectrometers. The IR spectra were measured on a Perkin—Elmer 283 instrument. Elemental analyses were carried out at the Institute for Organic Chemistry TNO, Utrecht.

The complexes $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$ [12], $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}(RCO_2)PtHg(O_2CR)Br]$ [9], and $[Ag(p\text{-}tolylNYNR)]_n$ (Y = CH, N; $n = 2, 4$) * [13] were prepared by published methods. Formamidino and triazenido mercury compounds were prepared in situ from the corresponding silver salts [5,6].

Synthesis of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\{p\text{-}tolylNC(H)NR\}PtHgBrCl]$ *(R = Me, Et, i-Pr)*

$HgCl_2$ (0.054 g, 0.2 mmol) and silver formamidine, $[Ag\{p\text{-}tolylNC(H)NR\}]_n$ (1/5 n mmol) were stirred in THF (8 ml). After 15 min $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}PtBr]$ (0.092 g, 0.2 mmol) was added and stirring was continued for 2 h. The suspension was filtered and the residue extracted with CH_2Cl_2 (5 ml). Concen-

---

* In solution $[Ag(RNYNR')]_n$ exists in both dimer and tetramer isomeric forms which are in equilibrium with each other [13].

tration of the combined solutions, addition of pentane and stirring gave a yellow solid (90%), which was filtered off.

Synthesis of [{2,6-($Me_2NCH_2)_2C_6H_3$}(p-tolylNNNR)PtHgBrCl] (R = Me, Et, i-Pr)

A solution of $HgCl_2$ (0.054 g, 0.2 mmol) and silver triazene, $[Ag(p\text{-tolylNNNR})]_n$ (1/5 *n* mmol) in THF (8 ml) was stirred for 20 min. [{2,6-($Me_2NCH_2)_2C_6H_3$}PtBr] (0.092 g, 0.2 mmol) was added, the mixture was stirred overnight and then filtered. The residue was washed with CH_2Cl_2 (5 ml), and the combined filtrates were concentrated to 3 ml. Addition of pentane (20 ml) gave a yellow precipitate. This was filtered off, washed with pentane, and dried in vacuo to give pure [{2,6-($Me_2NCH_2)_2C_6H_3$}(*p*-tolylNNNR)PtHgBrCl] in 70% yield.

Reaction of [{2,6-($Me_2NCH_2)_2C_6H_3$}PtBr] with bis-formamidino and bis-triazenido mercury compounds

A solution of $HgCl_2$ (0.054 g, 0.2 mmol) and $[Ag(p\text{-tolylNYNR})]_n$ (Y = CH, N; R = Me, Et, i-Pr, *p*-tolyl) (2/5 *n* mmol) in THF (10 ml) was stirred for 30 min, [{2,6-($Me_2NCH_2)_2C_6H_3$}PtBr] (0.092 g, 0.2 mmol) was added and the mixture stirred for 18 h. The precipitate formed was filtered off and extracted with CH_2Cl_2. Work-up of the combined liquids gave a mixture of the starting platinum compound and mono-formamidino or mono-triazenido Pt—Hg compounds.

Reaction of [{(2,6-($Me_2NCH_2)_2C_6H_3$}(RCO_2)PtHg(O_2CR)Br] (R = Me, i-Pr) with EtNC(H)N(H)-p-tolyl

[{2,6-($Me_2NCH_2)_2C_6H_3$}(RCO_2)PtHg(O_2CR)Br] (0.2 mmol) was dissolved in toluene (10 ml). EtNC(H)N(H)-*p*-tolyl (0.2 mmol) was added and the mixture stirred for 2 h. Addition of hexane (5 ml) gave an orange precipitate, which was filtered off, washed with hexane and dried in vacuo to give pure [{2,6-($Me_2NCH_2)_2C_6H_3$} {EtNC(H)N-*p*-tolyl}$PtHgBr_2$], yield 35%.

Reaction of [{2,6-($Me_2NCH_2)_2C_6H_3$}(RCO_2)PtHg(O_2CR)Br] (R = Me, i-Pr) with p-tolylNNN(H)-p-tolyl

p-TolylNNN(H)-*p*-tolyl (0.2 mmol) was added to a solution of [{2,6-($Me_2NCH_2)_2C_6H_3$}(RCO_2)PtHg(O_2CR)Br] (0.2 mmol) in toluene (10 ml) and stirred for 4 h. An orange precipitate was formed which was filtered off, washed with hexane and dried in vacuo, to give pure [{2,6-($Me_2NCH_2)_2C_6H_3$}-(*p*-tolylNNN-*p*-tolyl)$PtHgBr_2$] in 28% yield.

Results

Reactions of [{2,6-($Me_2NCH_2)_2C_6H_3$}PtBr] with formamidino- and triazenido-mercury compounds [Hg(*p*-tolylNYNR)Cl] (Y = CH, N) [5] resulted in almost quantitative formation of platinum—mercury bonded compounds according to eq. 1:

$$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr] + [Hg(p\text{-tolylNYNR})Cl] \rightarrow [\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(p\text{-tolylNYNR})PtHgBrCl] \quad (1)$$

(Y = CH, N; R = Me, Et, i-Pr)

Similar products were obtained from reaction between pure Pt—Hg-carboxylato compounds [9] and the free ligands (eq. 2).

$$2[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(R'CO_2)PtHg(O_2CR')Br] + p\text{-tolylNYN(H)R} \rightarrow$$
$$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(p\text{-tolylNYNR})PtHgBr_2] + R'CO_2H$$
$$+ [\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(R'CO_2)PtHg(O_2CR')_2] \quad (2)$$

(Y = CH, R = Et; Y = N, R = *p*-tolyl; R' = Me, i-Pr)

According to the stoichiometry of eq. 2, quantitative conversion would give a 50% yield of the bis-bromo product based on the amount of starting material. The somewhat lower yields observed (±30%) may be partly due to decomposition of the nitrogen ligands by reaction with the liberated carboxylic acid. Isolation of the pure bis-bromo products of reaction 2 was possible because of their low solubilities in the reaction solvents. Their formation must have involved exchange of one carboxylato group for a formamidino (or triazenido) group and exchange of a second carboxylato group for a bromide atom. This bromide atom probably comes from a second starting complex, thus leading to formation of the proposed tris-carboxylato Pt—Hg compounds. These latter compounds were not isolated from the reaction mixture, but the characterization of such compounds has been reported elsewhere [9].

Reaction of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$ with both the bis-formamidino- and bis-triazenido-mercury compounds $[Hg(p\text{-tolylNYNR})_2]$ (Y = CH, N; R = Me, Et, i-Pr, *p*-tolyl) (prepared in situ from $HgCl_2$ and $[Ag(p\text{-tolylNYNR})]_n$ [5]) did not result in the isolation of compounds identifiable as the bis-form-

TABLE 1

ANALYTICAL DATA AND CHARACTERISTIC INFRARED ABSORPTIONS

Compound	Anal. (found (calcd.)(%))			1600—1100 cm^{-1} region [a]
	C	H	N	
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}\{p\text{-tolylNC(H)NMe}\}PtHgBrCl]$	29.70 (29.69)	3.60 (3.53)	6.49 (6.59)	1588; 1336
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}\{p\text{-tolylNC(H)NEt}\}PtHgBrCl]$	30.79 (30.61)	3.83 (3.71)	6.29 (6.49)	1578; 1340; 1271; 1224
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}\{p\text{-tolylNC(H)N-i-Pr}\}PtHgBrCl]$	32.37 (31.49)	4.00 (3.90)	6.48 (6.38)	1568; 1338; 1226
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}(p\text{-tolylNNNMe})PtHgBrCl]$	28.12 (28.24)	3.42 (3.44)	8.04 (8.23)	1460; 1432; 1366; 1316; 1290
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}(p\text{-tolylNNNEt})PtHgBrCl]$	29.14 (29.17)	3.68 (3.61)	7.87 (8.10)	1460; 1410; 1315; 1275
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}(p\text{-tolylNNN-i-Pr})PtHgBrCl]$	31.90 (30.07)	4.07 (3.79)	7.47 (7.97)	1460; 1399; 1255
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}(p\text{-tolylNNN-}p\text{-tolyl})PtHgBr_2]$				1380; 1332; 1199
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}\{p\text{-tolylNC(H)NEt}\}PtHgBr_2]$	28.76 (29.11)	3.50 (3.53)	6.16 (6.17)	1578; 1340; 1232

[a] In KBr; only bands associated with formamidino and triazenido groups.

TABLE 2

^{1}H NMR DATA FOR [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}(*p*-tolylNYNR)PtHgBrCl] [a]

Substituents		Isomer [b]	{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$} resonances						*p*-tolylNYNR resonances					
			aryl		CHH' [c]		N(Me)Me' [d]		CH	*p*-tolyl			alkyl	
Y	R		*m*-H [e]	*p*-H [c]						*o*-H	*m*-H	CH$_3$	C$^\alpha$H	C$^\beta$H
CH	Me	A	7.02	6.87	5.18 (<5)	3.78	3.01	2.98	8.77 (30; 291)	7.11(s)		2.31	3.41	
CH	Me	B		6.78	4.98 (<5)	3.79	3.39	3.14	8.68 (38)	7.18		2.27		
CH	Et	A	7.02	6.86	5.19 (<5)	3.73 (89)	3.07 (34)	2.99 (35)	8.72 (33; 310)	7.11(s)		2.31	3.56	1.38
CH	Et	B							8.75			2.37	3.35	1.22
CH	i-Pr	A	7.03	6.86	5.28 (<5)	3.71 (89)	3.07 (33)	3.01 (36)	8.78 (25; 303)	7.12(s)		2.31	3.93	1.41
CH	i-Pr	B [f]												
N	Me	A	7.19	6.90	5.16 (<5)	3.77	3.18	2.98 (38)		7.61	7.15	2.33	3.66	
N	Me	B			5.18 (<5)	3.78	3.27 (30)	3.10 (37)		7.50	7.11	2.28	3.83	
N	Et	A	7.09	6.90	5.19 (<5)	3.76 (91)	3.18	2.99 (37)		7.62	7.09	2.33	3.95	1.46
N	Et	B			5.18 (<5)	3.77	3.25 (32)	3.10		7.50	7.10	2.29	3.82	1.28
N	i-Pr	A	7.09	6.89	5.28 (<5)	3.74 (91)	3.17 (32)	3.00 (36)		7.63	7.15	2.33	4.36	1.50
N	i-Pr	B [g]				3.72	3.26	3.11				2.31		

[a] In CD$_2$Cl$_2$; δ(^{1}H) in ppm relative to TMS; J(^{195}Pt—^{1}H), followed by J(^{199}Hg—^{1}H) where appropriate, between parentheses. [b] A = alkyl-N atom bonded to Hg; B = alkyl-N atom bonded to Pt. [c] Doublets with J(H—H')$_{gem}$ 13 Hz. [d] Singlets. [e] Multiplets. [f] Not observed. [g] Owing to the low abundance of this isomer not all resonances were observable.

amidino- or triazenido-Pt—Hg compounds, the original platinum compound being recovered along with some mono-substituted Pt—Hg compounds.

The stoichiometry of the Pt—Hg compounds was confirmed by elemental analysis (Table 1) and ^{1}H NMR data (Table 2). Formation of the bis-bromo products by exchange of a carboxylato group for a bromide atom in reaction 2 is confirmed by their ^{1}H NMR and IR spectra, which did not show resonances or absorptions for any carboxylato group.

The solid compound [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$(*p*-tolylNNN-*p*-tolyl)PtHgBr$_2$] showed intense absorptions in the IR spectrum at 1380 and 1199 cm^{-1}, which are in accordance with criteria [14,15] for a bridging bonding mode of the triazenido group. The IR spectra of the other formamidino and triazenido compounds showed strong absorptions in the 1100—1600 cm^{-1} region at quite different positions (Table 1), but these are also likely to be due to vibrations in the N—Y—N skeleton of a bridging ligand (see ref. 11). The positions of these bands are very similar to those observed for the related formamidino and triazenido compounds [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$(*p*-tolylNYNR)PtAgBr], for which a structure with a Pt-to-Ag donor bond bridged by a NYN ligand was proposed [11]. Furthermore, the absorptions for the *p*-tolylNNNMe-Pt-Hg compound (1366, 1316 and 1290 cm^{-1}) are also very similar to those of [(PPh$_3$)$_2$(CO)-(*p*-tolylNNNMe)RhCuCl] which contains a bridging *p*-tolylNNNMe group (1371, 1318, 1274 cm^{-1}) [1].

For the asymmetrically substituted ligands *p*-tolylNYNalkyl the bridging bonding mode, i.e. one N bonded to Pt and the other to Hg, raises the possibility that the substituents *p*-tolyl and alkyl can be either N(Pt) or N(Hg) bonded. This is confirmed by the ^{1}H NMR spectra, in which two resonance patterns have been observed for the various ligand moieties of all the complexes, thereby indicating the presence of two isomers. The ^{1}H NMR data for the two isomers A (alkyl-N bonded to Hg) and B (alkyl-N bonded to Pt) are summarized in Table 2. The assignments have been made on the basis of comparison of chemical shifts, relative intensities and NMR data of related Pt—Ag compounds.

Several structures can be proposed which fit the NMR and IR data. These structures differ in respect of the coordination at Pt, i.e. six-coordination (a and b) or five-coordination (c), the relative orientation of the Pt—Hg and Pt—C bonds, and the position of the halides (see Fig. 1).

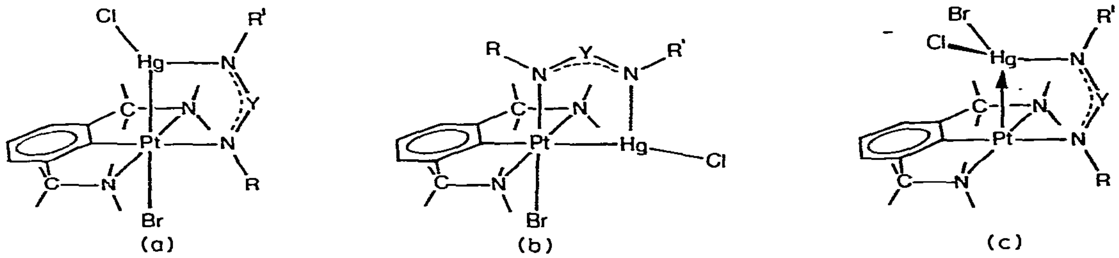


Fig. 1. Proposed structures for the compounds [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$(*p*-tolylNYNR)PtHgBrCl] (Y = CH, N); structure c was established by X-ray diffraction for [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$(*p*-tolylNC(H)N-i-Pr$\}$-PtHgClBr] [16].

To distinguish between the possibilities an X-ray crystal structure determination of [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$} {*p*-tolylNC(H)N-i-Pr} PtHgClBr] was undertaken, and the preliminary results show the molecular geometry agrees with that depicted in Fig. 1c [16].

Discussion

The results presented reveal that stable dinuclear Pt—Hg compounds can be derived from the reaction of [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}PtBr] with [Hg(*p*-tolylNYNR)Cl] (Y = CH, N). On the basis of ^{1}H NMR data alone, several structures can be considered for these compounds (see results, Fig. 1). Structure a and b contain a covalent Pt—Hg bond and would imply a reaction sequence similar to that proposed for the formation of [(2-Me$_2$NCH$_2$C$_6$H$_4$)$_2$(MeCO$_2$)PtHg(O$_2$CMe)] [9], i.e. initial formation of an activated dinuclear complex containing a Pt-to-Hg donor bond, transfer of *p*-tolylNYNR and Br ligands, and subsequent single electron-transfer. However, the formamidino and triazenido Pt—Hg compounds show considerable similarity with respect to spectroscopic features (Table 2) and isomer ratios (Table 3) to related Pt—Ag complexes [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}(*p*-tolylNYNR)PtAgBr] [11]. For the latter a square pyramidal structure was proposed, having the Ag atom at the apex and a bridging NYN ligand coordinated at Pt *trans* to the aryl ligand. Such a structure for the PtHg compounds (cf. Fig. 1c) would indicate that exchange of NYN and Br ligands as well as the formation of a complex with a Pt-to-Hg donor bond had occurred.

For one of these complexes, i.e. [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$} {*p*-tolylNC(H)N-i-Pr} PtHgBrCl], the structure is in accordance with the square pyramidal geometry at Pt as shown in Fig. 1c [16].

A configuration at Pt with the N-donor ligands fixed in a mutual *trans*-position, as in [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}(*p*-tolylNYNR)PtHgX$_2$], obviously stabilizes the Pt-to-Hg donor bond and prevents subsequent electron transfer. An essential step in this process would be the bending back of one of the N donor ligands into a position *trans* to the Pt—Hg bond, which is obviously not possible for configuration 1c (cf. isomer a or b in Fig. 1). It is just this latter *trans* arrangement which was found in [(2-Me$_2$NCH$_2$C$_6$H$_4$)$_2$(MeCO$_2$)PtHg(O$_2$CMe)] which has a covalent Pt—Hg bond [8].

TABLE 3

RELATIVE ABUNDANCE OF THE ISOMERS OF [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}(*p*-tolylNYNR)PtHgBrCl] [a]

Y	R	Isomer A [b]	Isomer B [c]	ln{[A]/[B]}
CH	Me	50	50	0
CH	Et	82	18	1.52
CH	i-Pr	>99	<1	—
N	Me	39	61	−0.45
N	Et	83	17	1.47
N	i-Pr	97	3	3.48

[a] Based on the relative intensities of the ^{1}H NMR resonances. [b] Alkyl-N atom bonded to Hg. [c] Alkyl-N atom bonded to Pt.

It is interesting to compare the ^{1}H NMR data of [{2,6-$(Me_2NCH_2)_2C_6H_3$}-(*p*-tolylNYNR)PtHgBrCl] with those of the carboxylato analogue [{2,6-$(Me_2NCH_2)_2C_6H_3$)(RCO_2)PtHgCl_2]. For the latter compounds both the CH_2 and NMe_2 H resonances were observed as singlets which was ascribed to either too small a $\Delta\delta$ for diastereotopic H resonances or to the occurrence of a dynamic process by which these hydrogen atoms become homotopic. In contrast, the ^{1}H NMR spectra of [{2,6-$(Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtHgBrCl] clearly show that the benzylic and the NMe_2 H atoms are diastereotopic over the range —50 to 40°C. Moreover the $\Delta\delta$ and J values appeared to be temperature invariant. This indicates that processes leading to intramolecular rearrangements and which involve the NYN ligand system are either blocked or very slow on the NMR time scale.

The rigidity of the formamidino and triazenido complexes may arise from the higher stability of the *syn*-MNYN'M' relative to the *gauche* configuration. Steric interactions between alkyl (or aryl) and M substituents would be smaller in the *syn* than in the *gauche* conformer. For bridging carboxylato groups such interactions are not important because the oxygen donor sites do not bear R substituents. Accordingly, for [{2,6-$(Me_2NCH_2)_2C_6H_3$}(RCO_2)PtHgCl_2] a dynamic process involving initial dissociation of the Pt-to-Hg donor bond and concomitant rotation around the (Hg)O- C bond becomes likely [9].

The NMR spectra of [{2,6-$(Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtHgBrCl] furthermore suggest that the molecule has a mirror plane, containing the NYN bridging system, and being perpendicular to the plane of the terdentate ligand 2,6-$(Me_2NCH_2)_2C_6H_3$. This points to occurrence of a dynamic process involving exchange of the relative positions of the Br and Cl atoms at the Hg centre. Alternatively, the chemical shift differences of the NMe and benzylic H atoms pointing towards either the Cl or the Br atom (see Fig. 1c) are too small to be observed.

From Table 2 it is clear that in the isomeric complexes the chemical shifts for the N-alkyl and N-*p*-tolyl groups are different according to whether they are Pt or Hg bonded. Similar behaviour was observed for the related Pt- Ag compounds [{2,6-$(Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtAgBr] [11].

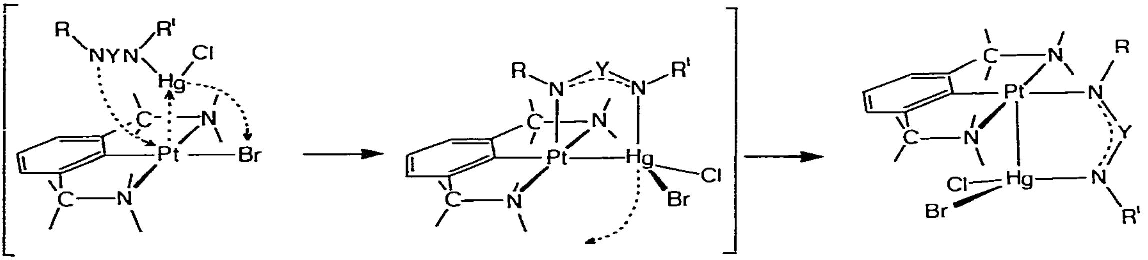
Of more importance are the differences in chemical shifts between Pt bonded N-groups in the Hg and Ag complexes. The N(Pt) bonded groups are much more deshielded in the Pt—Ag compounds than in the Pt—Hg compounds, e.g. 7.52 versus 7.11 ppm for the *ortho*-(*p*-tolyl) H atom of the formamidino group. In general, protons which reside close to the metal and above or below the bonding plane of the molecule will experience downfield shifts as a result of the magnetic anisotropy around the metal centre [11,17]. For the present square pyramidal complexes this can be explained in terms of a geometry in which the N(Pt) bonded *p*-tolyl groups can be folded between the two NMe_2 groups bringing the *ortho*-N atoms near Pt. Rotation around the N-*p*-tolyl axis makes the two *ortho*-H atoms equivalent.

It may be possible that the difference in extent of deshielding is a reflection of the difference in electrophilicity of the post-transition metal unit (HgBrCl compared with AgBr).

Formation of the complexes

As has been noted above, the Pt—Hg complexes with asymmetric bridging ligands *p*-tolylNYNalkyl exist in two isomeric forms. The isomer ratios, which appear to be dependent on the alkyl group used, can provide valuable information concerning the mechanism by which these complexes are formed. Before doing this it must be noted that the isomer ratios as given in Table 3, must be treated with some reservation, since they may not be completely reliable in view of the non-quantitative yields. Furthermore, the accuracy for R = i-propyl is rather low due to the low abundance of isomer B. Nevertheless, Table 3 suggests that the order of preference for the group bonded to N(Pt) is methyl > *p*-tolyl > ethyl > i-propyl.

The same dependence was observed for the isomer ratio of the bridged Pt—Ag compounds [{2,6-$(Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtAgBr] [11]. The main conclusion from that work was that the isomer ratio is determined by kinetic factors and not by the relative stability of the isomers. The experimental results were explained in terms of a proposed formation mechanism involving a Pt—Ag intermediate with a monodentate or chelate bonded RNYNR ligand on silver. Accomplishment of the bridging bonding mode for the NYN ligand then involves breaking of one Ag—NR bond and approach of that NR group to Pt. This process will be influenced by the basicity of the ligand halves and of the metal centres and by the steric interaction between the substituents in *p*-tolylNYNR and the Pt—NMe_2 moieties.



SCHEME 1

A similar sequence for formation of the present Pt—Hg compounds is visualized in Scheme 1. The initial step in this process is nucleophilic attack of the Pt centre on the Hg atom followed by intramolecular attack of the free RN site of the monodentate bonded RNYNR ligand on Pt and formation of a Hg—Br bond. In line with this is the failure to synthesize Pt—Hg compounds from reactions of [{2,6-$(Me_2NCH_2)_2C_6H_3$}PtBr] with the mercury compounds [Hg(*p*-tolylNYNR)$_2$] in which, compared to [Hg(*p*-tolylYNR)Cl], is a reduced electron acceptor ability of the mercury atom.

No indication was obtained of any intramolecular process involving exchange of the N-donor sites of the *p*-tolylNYNalkyl bridging system bonded either to Pt or Hg. Accordingly, the stereochemistry in the final isomers may be due to a different rate of attack of the Pt centre on the isomers of [Hg(*p*-tolylNYNalkyl)Cl] having a monodentate NYN ligand bonded to Hg via either N(alkyl) or N(*p*-tolyl). However, the possible formation of an intermediate (or transition state) with a chelating *p*-tolylNYNalkyl ligand on Hg can also play a role in the mechanism of formation of the Pt—Hg complexes, because in such an intermediate, exchange of (Hg)N-alkyl with (Hg)N-*p*-tolyl is also possible. In this respect, it is noteworthy that a dynamic behaviour for monodentate bonded triazenido ligands (intramolecular exchange of the N-atom bonded to Hg) has been reported for mononuclear [Hg(RNNNR)Cl] [18].

Finally, the somewhat enhanced preference for the *p*-tolyl-N group to be bonded to Pt in the Pt—Hg complexes compared with the position in Pt—Ag complexes may reflect the influence of the post-transition metal (Hg versus Ag).

The fact that a bis-halogenido complex [{2,6-$(Me_2NCH_2)_2C_6H_3$}(RNYNR')-$PtHgBr_2$] was obtained from the reaction of [{2,6-$(Me_2NCH_2)_2C_6H_3$}(RCO_2)-$PtHg(O_2CR)Br$] with RNYN(H)R' indicates that extensive disproportionation with exchange of carboxylato groups and halide atoms must have occurred. Such exchanges have been observed before, i.e. an intramolecular process in heterodinuclear complexes, which generally ends with the bidentate ligand bonded to the transition metal centre and the halogen atom on the post-transition metal [6,7,11].

This indicates that in the case of the reactions with mercury salts a second mechanism for the formation of the compounds [{2,6-$(Me_2NCH_2)_2C_6H_3$}-(*p*-tolylNYNR)PtHgBrCl] cannot be excluded. This mechanism involves prior formation of HgX_2 and [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(*p*-tolyl)NYNR)], in a ligand exchange reaction, followed by recombination of these units. In particular the formation of [{2,6-$(Me_2NCH_2)_2C_6H_3$}(RCO_2)$PtHgCl_2$] from [{2,6-$(Me_2NCH_2)_2$-C_6H_3}$Pt(O_2CR)$] and $HgCl_2$ indicates that such a mechanism is possible.

Conclusions

The structural features of the complexes [{2,6-$(Me_2NCH_2)_2C_6H_3$}(*p*-tolyl-NYNR)PtHgBrCl] show much similarity to those of related Pt—Ag complexes [{2,6-$(Me_2NCH_2)_2C_6H_3$}(*p*-tolylNYNR)PtAgBr], i.e. there is a five-coordinate, square pyramidal Pt centre, a bridging bonding mode for the bidentate *p*-tolyl-NYNR ligand and the presence of two isomers differing in the position of the alkyl group R. The Pt-to-Hg donor bond is stabilized against subsequent one electron transfer, which would lead to a complex with a covalent Pt—Hg bond, by the fixed geometry of the 2,6-$(Me_2NCH_2)_2C_6H_3$ ligand.

Acknowledgement

Dr. D.M. Grove is gratefully acknowledged for his continuing interest and critical reading of the manuscript. Investigations were supported in part by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Pure Research (ZWO) (A.F.M.J. v.d. P.).

References

1 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 96 (1975) 289.
2 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 105 (1976) 379.
3 J. Kuyper and K. Vrieze, J. Organometal. Chem., 107 (1976) 129.
4 P.I. van Vliet, G. van Koten and K. Vrieze, J. Organometal. Chem., 182 (1979) 105.
5 P.I. van Vliet, J. Kuyper and K. Vrieze, J. Organometal. Chem., 122 (1976) 99.
6 P.I. van Vliet, M. Kokkes, G. van Koten and K. Vrieze, J. Organometal. Chem., 187 (1980) 413.

7 P.I. van Vliet, G. van Koten and K. Vrieze, J. Organometal. Chem., 188 (1980) 301.
8 A.F.M.J. van der Ploeg, G. van Koten, K. Vrieze, A.L. Spek and A.J.M. Duisenberg, J. Chem. Soc., Chem. Commun., 469 (1980).
9 A.F.M.J. van der Ploeg, G. van Koten, K. Vrieze and A.L. Spek, Inorg. Chem., in press.
10 F.A. Cotton, W.H. Ilsley and W. Kaim, Inorg. Chem., 19 (1980) 1450 and (1980) 2360 and references therein; K.R. Laing, S.D. Robinson and M.F. Uttley, J. Chem. Soc., Dalton Trans., (1974) 1205; L. Tonioli, A. Immirzi, U. Croatto and C. Bombieri, Inorg. Chim. Acta, 19 (1976) 209.
11 A.F.M.J. van der Ploeg, G. van Koten and K. Vrieze, Inorg. Chem., in press.
12 G. van Koten, K. Timmer, J.G. Noltes and A.L. Spek, J. Chem. Soc., Chem. Commun., (1978) 250.
13 P.I. van Vliet, G. van Koten and K. Vrieze, J. Organometal. Chem., 179 (1979) 89.
14 E. Pfeiffer, A. Oskam and K. Vrieze, Transition Met. Chem., 2 (1977) 240.
15 S.D. Robinson and M.F. Uttley, J. Chem. Soc., Chem. Commun., (1972) 184.
16 A.F.M.J. van der Ploeg, G. van Koten, K. Vrieze and A.L. Spek, to be published.
17 M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 15 (1975) 137, and ref. therein; H. van der Poel, G. van Koten and K. Vrieze, Inorg. Chem., 19 (1980) 1145.
18 P. Peringer, Inorg. Nucl. Chem. Letters, 16 (1980) 461; Inorg. Chim. Acta, 42 (1980) 129.