stereochemical restraints for the formation of hydrogen bonds.

The poorness of our model is shown by the fact that the absolute configuration of the diamine bound to platinum has very little effect on the antitumor activity of the complexes $[(\text{chiral diamine})PtX_2]$,[10,51] the *R* derivatives being only slightly more active. This difference is small when compared to what is expected on the grounds of the relevant differences of the chiroptical properties of the diastereoisomers $[(\text{chiral diamine})Pt(Guo)_2]^{2+}$. Also, those diamines that do not produce rigid arrangements (en and meso diamines) possess comparable activity.

Although the bis(guanosine) complexes with (*R*)-diamines show exciton splittings lower than those of the corresponding (*S*)-diamines, it is difficult to establish a structure–activity relationship. It is therefore likely that the relevant conformational differences observed here could not have much biological significance presumably because of the small size of the chiral platinum compounds compared with DNA or because more subtle mechanisms are operative. Work is in progress on the interaction of DNA with platinum complexes with chiral ligands in order to elucidate this point.

Acknowledgment. We wish to thank Professor P. Fantucci for helpful discussion of the NMR spectra that were recorded under the skillful technical assistance of Mrs. M. Bonfã.

Registry No. $[(en)Pt(guo)_2]Cl_2$, 50790-42-6; $[((R)\text{-}pn)Pt(guo)_2]Cl_2$, 77943-59-0; $[((S)\text{-}pn)Pt(guo)_2]Cl_2$, 77863-65-1; $[((R,R)\text{-}bn)Pt(guo)_2]Cl_2$, 77902-46-6; $[((S,S)\text{-}bn)Pt(guo)_2]Cl_2$, 77981-96-5; $[(meso\text{-}bn)Pt(guo)_2]Cl_2$, 80629-84-1; $[((R,R)\text{-}chxn)Pt(guo)_2]Cl_2$, 77902-47-7; $[((S,S)\text{-}chxn)Pt(guo)_2]Cl_2$, 77981-97-6; $[(meso\text{-}chxn)Pt(guo)_2]Cl_2$, 80629-85-2; $[((R)\text{-}pen)Pt(guo)_2]Cl_2$, 80583-56-8; $[((R,R)\text{-}dpen)Pt(guo)_2]Cl_2$, 80655-69-2; $[((S,S)\text{-}dpen)Pt(guo)_2]Cl_2$, 80655-70-5; $[(meso\text{-}dpen)Pt(guo)_2]Cl_2$, 80583-57-9; $[((R,R)\text{-}chxn)Pt(9\text{-}MeG)_2]Cl_2$, 80583-58-0; $[((S,S)\text{-}chxn)Pt(9\text{-}MeG)_2]Cl_2$, 80629-86-3; $[(en)Pt(guo)](NO_3)_2$, 79725-46-5; $[((R,R)\text{-}chxn)Pt(guo)](NO_3)_2$, 80593-30-2; $[((S,S)\text{-}chxn)Pt(guo)](NO_3)_2$, 80655-72-7; *cis*-$[(NH_3)_2Pt(guo)_2]Cl_2$, 50790-41-5; Guo, 118-00-3; GpG, 3353-33-1.

Supplementary Material Available: NMR spectra (Table II) of the complexes $[(\text{chiral diamine})Pt(Guo)_2]Cl_2$ (2 pages). Ordering information is given on any current masthead page.

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(51) We have confirmed that the nature of the nonleaving groups is very important in determining the antitumor activity.[52] Such effect is much larger than that of the absolute configuration of the diamine.[10] The particularly high activity of the chxn derivatives has also been confirmed.[52]

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Oxidative-Addition Reactions of Cyclometalated Platinum(II) Compounds with Mercury(II) Carboxylates. X-ray Crystal and Molecular Structure of $rac\text{-}[a\text{-}(\mu\text{-}MeCO_2)\text{-}cf,de\text{-}(2\text{-}Me_2NCH_2C_6H_4)_2PtHg(O_2CMe)]$

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The reactions of *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt^{II}]$, obtained from $[PtCl_2(SEt_2)_2]$ and $[(2\text{-}Me_2NC_6H_4CH_2)Li(TMEDA)]$ (TMEDA = tetramethylethylenediamine), and of *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt^{II}]$ with $Hg^{II}(O_2CR)_2$ (R = Me, *i*-Pr) yielded a novel type of cyclometalated Pt–Hg compound $[(N{-}C)_2(RCO_2)PtHg(O_2CR)]$ (N–C = $2\text{-}Me_2NC_6H_4CH_2{-}$ and $2\text{-}Me_2NCH_2C_6H_4{-}$). An X-ray crystallographic study defined the molecular structure of $[(2\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}MeCO_2)PtHg(O_2CMe)]$. The pertinent crystal data are as follows: orthorhombic, space group *Pccn*, $Z = 8$, $a = 14.817$ (8) Å, $b = 17.339$ (9) Å, $c = 18.602$ (11) Å. The platinum center is six-coordinate with a Pt–Hg bond (2.513 (1) Å) bridged by one acetato group: Pt–O, 2.15 (1) Å; Hg–O′, 2.62 (1) Å. The other acetato ligand is monodentate bonded to Hg: Hg–O, 2.10 (1) Å. The mercury atom and the two carbon ligands are mutually cis. A cis oxidative addition, involving a platinum-to-mercury-bonded intermediate, is proposed for the reaction mechanism. The geometry of the other compounds $[(2\text{-}Me_2NCH_2C_6H_4)_2(i\text{-}PrCO_2)PtHg(O_2C\text{-}i\text{-}Pr)]$ and $[(2\text{-}Me_2NC_6H_4CH_2)_2(RCO_2)PtHg(O_2CR)]$ (R = Me, *i*-Pr), as deduced from ^1H and ^{13}C NMR spectra, is similar. Intramolecular exchange of the two carboxylato groups is not observed. Exchange of these carboxylato groups with free carboxylic acids occurs on different time scales. Reactions of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt^{II}]$ with $Hg^{II}(O_2CR)_2$ proceeded via an unstable Pt–Hg intermediate, which then eliminated Hg^0 to form $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(O_2CR)_2]$ as a mixture of two isomers. Reaction of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Pt^{II}X\}$ (X = Br, O_2CR), containing a terdentate ligand, with $Hg^{II}(O_2CR)_2$ resulted in formation of the stable Pt–Hg-bonded compounds $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](RCO_2)PtHg(O_2CR)X\}$ (X = Br, O_2CR; R = Me, *i*-Pr). For these compounds a structure is proposed containing a five-coordinate Pt center and a carboxylato-bridged Pt-to-Hg donor bond. The structure of the compound with X = Br results from an exchange of the bromide atom and a carboxylato group between the platinum and mercury centers. Intramolecular carboxylato exchange is observed for which a mechanism, involving a six-coordinate Pt intermediate, is proposed. For the compound $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](i\text{-}PrCO_2)PtHgCl_2\}$, prepared from $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Pt(O_2C\text{-}i\text{-}Pr)\}$ and $HgCl_2$, a structure with a carboxylato group bridging between Pt and $HgCl_2$ is proposed. The dynamic behavior of these compounds in solution is discussed.

Introduction

During the last decade interest has been growing in heterodinuclear group 8B metal complexes.[2a] The number of such compounds with CO or phosphine ligands is fairly large. Heterodinuclear complexes with organo groups have also been synthesized, involving either reaction of a metal complex anion with a metal complex cation[2b]

$$(CO)_xM^-Na^+ + RM'Cl \rightarrow NaCl + (CO)_xMM'R$$

or reaction of a neutral transition-metal complex with an electrophilic reagent[3]

$$M + XM'R \rightarrow X{-}M{-}M'{-}R \text{ or } R{-}M{-}M'{-}X$$

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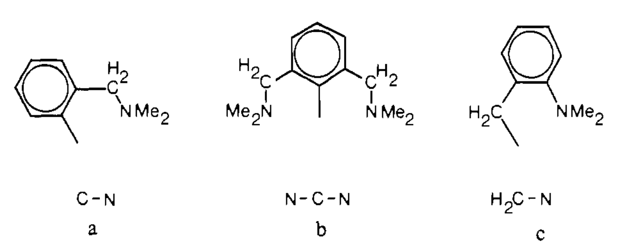
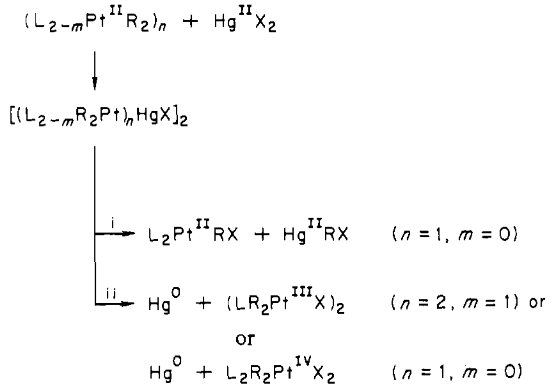


Figure 1. Organo ligands containing CH_2NMe_2 and NMe_2 substituents: (a) $2\text{-}Me_2NCH_2C_6H_4\text{–}$; (b) $2,6\text{-}(Me_2NCH_2)_2C_6H_3\text{–}$; (c) $2\text{-}Me_2NC_6H_4CH_2\text{–}$.

Scheme I



There is much interest in reactions of the latter type with organoplatinum(II) compounds as the transition-metal complex and mercury salts as the electrophilic reagent. These reactions, however, quite generally result in disproportionation. Transmetalation is the preferred reaction route when the donor ligands are soft (L = phosphine).[4] In the case of hard donor ligands either (i) transmetalation[5,6] or (ii) sequential oxidative addition and elimination of metallic mercury leading to dinuclear organoplatinum(III)[7] or mononuclear platinum(IV)[6] compounds has been observed (Scheme I).

Evidence has been presented that dinuclear Pt–Hg compounds are key intermediates in these reactions, but little information is available concerning the structure of the Pt–Hg intermediates and the factors governing product formation via either reaction i or reaction ii.

In order to study these aspects, we have employed organoplatinum compounds in which the organo group contains hard nitrogen-donor atoms (see Figure 1). A common factor of these organo ligands is that they can form five-membered cyclometalated rings by internal coordination of the nitrogen moiety, introduction of such coordinating groups into the organic molecule being a possible approach to prevent transmetalation. Furthermore, whereas for ligand a (Figure 1) the N-donor atoms can be in either the cis or the trans position, for ligand b these atoms are imposed to be mutually trans. This allows the study of the influence of the N-donor atom geometry on reactions of organoplatinum compounds with electrophiles.

In this paper we report (i) the synthesis of *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$, a methyl-substituted biscyclometalated platinum compound, (ii) reactions of several cyclometalated platinum compounds with mercury(II) carboxylates and the isolation of novel mononuclear and heterodinuclear products, and (iii) the first X-ray crystal structure determination of a diorganoplatinum–mercury-bonded compound.[8]

Experimental Section

Reactions involving lithium reagents were carried out under a nitrogen atmosphere. Solvents were dried prior to use by standard techniques. ^1H and ^{13}C NMR spectra were recorded on Varian T-60, Varian XL-100, Bruker WM 250, and Bruker WP-80 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 283 instrument. Molecular weights were determined with a Hewlett-Packard vapor pressure osmometer, Model 320 B. Elemental analyses were carried out at the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

Analytical data and characteristic IR absorptions are given in Table V, while ^1H and ^{13}C NMR data are presented in Tables VI and VII, respectively.

The compounds *cis*-$[PtCl_2(SEt_2)_2]$,[9] *cis*- and *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$,[10] and $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PtBr\}$[11] were prepared according to literature methods.

Preparation of *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ (3). A solution of *cis*-$[PtCl_2(SEt_2)_2]$ (10 mmol, 4.6 g) in toluene (10 mL) was added slowly to a cooled suspension of $[(2\text{-}Me_2NC_6H_4CH_2)Li(TMEDA)]$[12] (20 mmol, 5.2 g) in toluene (10 mL) at −80 °C (TMEDA = tetramethylethylenediamine), and the mixture was stirred at this temperature for a further 2 h. The solution was allowed to warm, filtered, and concentrated to 10 mL. Addition of hexane (30 mL) afforded a white precipitate, which was filtered off and extracted with dichloromethane (20 mL). Evaporation of the solvent resulted in a residue, which was washed with ether and dried in vacuo; yield of *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ 2.9 g, 60%. Attempts to obtain the corresponding trans isomer failed; i.e., when *trans*-$[PtCl_2(SEt_2)_2]$ was used as the starting compound, only the cis isomer was isolated.

Preparation of $[(2\text{-}Me_2NCH_2C_6H_4)_2(RCO_2)PtHg(O_2CR)]$ (R = Me, *i*-Pr) (5). $Hg(O_2CR)_2$(1.0 mmol) was added to a stirred solution of *cis*-$[(Me_2NCH_2C_6H_4)_2Pt]$ (0.466 g, 1.0 mmol) in chloroform (5 mL). The mercury compounds immediately dissolved, a momentary orange-red color was observed, and an almost clear orange-yellow solution was obtained. The solution was filtered and the solvent evaporated, resulting in the solid yellow platinum–mercury compounds, which were obtained in almost quantitative yield. Recrystallisation from CH_2Cl_2/hexane yielded the compounds as rodlike crystals. The compounds are slightly light sensitive. They are stable in solution at room temperature but decompose at temperatures above 50 °C.

Reaction of *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ with $Hg(O_2CR)_2$ (R = Me, *i*-Pr). A 1-equiv quantity of $Hg(O_2CR)_2$ was added to a solution of *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ (0.466 g, 1.0 mmol) in chloroform (5 mL). When the mixture was stirred, the mercury compound dissolved. The resulting slightly colored solution was filtered and evaporated to dryness. The platinum–mercury compound $[(2\text{-}Me_2NC_6H_4CH_2)_2(RCO_2)PtHg(O_2CR)]$ was obtained almost quantitatively as an off-white amorphous residue. The compound was recrystallized from CH_2Cl_2/hexane. It is slightly light sensitive and decomposes slowly in solution above 50 °C.

Reaction of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ with $Hg(O_2CR)_2$ (R = Me, *i*-Pr). $Hg(O_2CR)_2$ (0.5 mmol) was added to a stirred solution of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ (0.233 g, 0.5 mmol) in toluene or chloroform (5 mL), followed, immediately after the mercury compound had dissolved, by addition of 20 mL of hexane. The lemon yellow precipitate obtained was filtered off and dried in vacuo. The yield of the platinum–mercury compound *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2PtHg(O_2CMe)_2]$ was 0.31 g (80%).

When a freshly prepared solution of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2PtHg(O_2CR)_2]$ (0.39 g, 0.5 mmol) in $CDCl_3$ (2 mL) was left standing, metallic mercury started to deposit in a few minutes,

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and this decomposition went to completion within 0.5 h. ^{1}H NMR experiments, after filtration of the solution, showed the presence of one major compound, a, contaminated with a second one, b (4–12%), in a ratio that did not change during 2 weeks. After slow diffusion for 4 days of a layer of THF superposed on the $CDCl_3$ solution, the minor compound b was obtained as colorless leaflets, whereas a greater amount of compound a was obtained as a yellow precipitate. The remaining solution still contained a mixture of the two compounds, but further attempts to obtain the pure products were unsuccessful. The two compounds, which could be obtained as the mixture in a quantitative yield by evaporation of a freshly prepared solution, have been identified later[13] as different isomers of $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(O_2CR)_2]$.

Reaction of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PtBr\}$ with $Hg(O_2CR)_2$ (R = Me, *i*-Pr). Addition of $Hg(O_2CR)_2$ (0.5 mmol) to a stirred solution of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PtBr\}$ (0.233 g, 0.5 mmol) in chloroform (5 mL) resulted in an initially orange and finally yellow solution. Concentration of this solution followed by addition of hexane (10 mL) resulted in the formation of lemon yellow crystals of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](RCO_2)PtHg(O_2CR)Br\}$, yield 90%.

Synthesis of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](RCO_2)PtHgCl_2\}$ (R = *i*-Pr) (9b). $HgCl_2$ (0.135 g, 0.5 mmol) was added to a solution of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Pt(O_2CR)\}$ (0.5 mmol) in $CDCl_3$ or acetone (2.5 mL), and the mixture was heated to 40 °C and stirred for 10 min. The resulting yellow solution was cooled to 0 °C, upon which small cubic crystals of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](RCO_2)PtHgCl_2\}$ were formed. A second fraction could be obtained by decanting the supernatant liquid, adding pentane (5 mL) to it, filtering it, and drying it in vacuo; total yield 90%.

Synthesis of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](RCO_2)PtHg(O_2CR)_2\}$ (R = *i*-Pr) (8b). $Hg(O_2CR)_2$ (0.1 mmol) was added to a solution of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Pt(O_2CR)\}$ (0.1 mmol) in $CHCl_3$ (5 mL) and stirred for 5 min. The solution was concentrated to 2 mL, and pentane (10 mL) was added. When the mixture was stirred, $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](RCO_2)PtHg(O_2CR)_2\}$ precipitated. It was isolated, by filtering, washing with pentane, and drying in vacuo, as a yellow amorphous powder, yield 90%.

Reactions of the Platinum–Mercury Compounds with CO and Phosphines. Freshly prepared solutions of the various Pt–Hg compounds in chloroform were treated both with CO, bubbling through the solution, and with 1 equiv of triphenylphosphine. Only for the compounds $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](RCO_2)PtHg(O_2CR)Br\}$ and PPh_3 was a reaction observed. A white precipitate of $Hg(O_2CMe)_2$ was formed, which was filtered off. Evaporation of the filtrate resulted in a white residue, identified by ^{1}H and ^{31}P NMR as $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Pt(PPh_3)\}Br$ ($\delta(NCH_2)$ 4.31 (53 Hz), $\delta(NCH_3)$ 2.60 (43 Hz), δ(P) 34.33 (2100 Hz)).

Exchange Experiments of the Platinum–Mercury Compounds with Free Carboxylic Acids. Exchange experiments of the various Pt–Hg compounds with free carboxylic acids were performed with freshly prepared solutions of these compounds in deuteriochloroform, to which 2 or 3 equiv of carboxylic acid was added. The ^{1}H and ^{13}C NMR spectra were studied as a function of temperature. Further details and results are discussed in the Results section.

Structure Determination of $[(2\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}MeCO_2)PtHg(O_2CMe)]$ (5a). A yellow crystal, suitable for data collection, was glued on top of a glass fiber and transferred to an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions and their standard deviations were then determined in the usual way from the settings of 16 carefully centered reflections.[14] The quality of the crystal was examined on three Laue photographs, prepared on the diffractometer by 30° oscillations about the three unit cell axes. The crystal data and details of the data collection and structure refinement are summarized in Table I.

Table I. Crystal Data and Details of the Structure Analysis of $[(2\text{-}Me_2NCH_2C_6H_4)_2(MeCO_2)PtHg(O_2CMe)]$ (5a)

a. Crystal Data	
formula	$C_{22}H_{30}HgN_2O_4Pt$
mol wt	782.2
cryst syst	orthorhombic
space group	No. 56, *Pccn*
a, Å	14.817 (8)
b, Å	17.339 (9)
c, Å	18.602 (11)
V, Å^3	4779 (5)
Z	8
D(calcd), g cm^{-3}	2.174
F(000) electrons	2928
μ(Mo Kα), cm^{-1}	118.3
cryst size, mm	$(100)\rightarrow(\bar{1}00)$ 0.36, $(011)\rightarrow(0\bar{1}\bar{1})$ 0.36, $(01\bar{1})\rightarrow(0\bar{1}1)$ 0.36
cryst volume, mm^3	0.046
grid for absorption	8 × 8 × 8
min corrn	3.23
max corrn	7.87
b. Data Collection	
θ min, θ max, deg	0.10, 27.5
radiation, Å	Mo Kα (Zr filtered), 0.710 69
ω, 2θ scan, deg	$0.3 + 0.35 \tan\theta$
data set	$+h, +k, +l$
max time/reflctn, min	2
horizontal and vertical aperture, mm	2.30, 3
ref reflctns	$\bar{1}\bar{1}3$, $10\bar{2}$
total data	6627
total unique data	5463
obsd data ($I > 2.5[\sigma(I)]$)	3743
c. Refinement	
no. of refined parameters	270
weighting scheme	$w^{-1} = (\sigma^2(F) + 0.0001F^2)/2.665$
final $R_F = \Sigma(F_o - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.043
final $R_{wF} = [(\Sigma w(F_o - \lvert F_c\rvert))^2/(\Sigma w\lvert F_o\rvert^2)]^{1/2}$	0.040

The intensities of one octant of the reflection sphere were collected in the $\omega/2\theta$ scan mode, with use of zirconium-filtered Mo Kα radiation. The intensities of two reference reflections were monitored every 0.5 h of X-ray exposure time. A small decay of 5% was observed during data collection. The data were subsequently corrected for absorption,[15] Lorentz and polarization effects, and the observed decay and averaged into a unique set of data in the previously described way.[14]

Solution and Refinement of the Structure. The structure was solved by standard Patterson and Fourier techniques and subsequently refined by blocked full-matrix least-squares techniques with an adapted minicomputer version of SHELX 76.[16] The nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined in the riding mode (U = 0.080 Å^2) on corresponding nonhydrogen atom positions. Weights were introduced in the final refinement stages. The refinement converged at $R_F = 0.043$ for 270 parameters and 3743 reflections and $w^{-1} = (\sigma^2(F) + 0.0001F^2)/2.665$. A final difference Fourier map showed no significant features. Fractional atomic coordinates and anisotropic thermal parameters are given in Table II and selected interatomic distances and angles in Table III. Least-squares planes, to be discussed below, are given in Table IV.

Neutral scattering factors were taken from ref 17 and corrected for anomalous dispersion.[18] All calculations were carried out either on the in-house Eclipse/S230 minicomputer with the program ILIAS[16] (structure determination and refinement) or on the Cyber 175 computer of the University of Utrecht computer center (with the programs ABSORB[15] for absorption correction and EUCLID[19] for molecular geometry calculations and molecular illustrations).

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(13) (a) Reaction of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ with $Tl(O_2CR)_3$ resulted in elimination of $Tl(O_2CR)$ and formation of a mixture of the same two compounds, identified as isomers of $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(O_2CR)_2]$. Conversion of the main isomer, which was consequently assigned a trans(C) geometry, into the other isomer, thus assigned a trans(N) geometry, was performed by addition of free carboxylic acid.[13b] (b) A. F. M. J. van der Ploeg, G. van Koten, and K. Vrieze, *Inorg. Chim. Acta*, **58**, 35 (1982).

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(19) EUCLID is program package for the calculation of geometrical data and structure illustration (A. L. Spek).

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	0.01404 (3)	0.39227 (2)	0.35521 (2)	0.0492 (2)	0.0412 (2)	0.0621 (3)	0.0117 (2)	−0.0077 (2)	−0.0102 (2)
Pt	0.12013 (2)	0.49536 (2)	0.31196 (2)	0.0389 (2)	0.0322 (2)	0.0321 (2)	−0.0000 (1)	−0.0037 (1)	−0.0032 (1)
O(1)	−0.0423 (5)	0.4059 (5)	0.2222 (4)	0.061 (5)	0.079 (5)	0.071 (5)	−0.000 (5)	−0.021 (4)	−0.019 (4)
O(2)	0.0641 (5)	0.4960 (3)	0.2052 (3)	0.057 (4)	0.049 (4)	0.034 (3)	−0.006 (3)	−0.007 (3)	−0.001 (3)
O(3)	−0.0791 (5)	0.3163 (5)	0.4022 (5)	0.064 (5)	0.068 (5)	0.100 (7)	0.025 (5)	−0.005 (5)	−0.019 (4)
O(4)	0.0401 (8)	0.2412 (6)	0.3974 (6)	0.124 (9)	0.080 (7)	0.124 (9)	0.013 (6)	0.012 (8)	−0.006 (7)
N(1)	0.2214 (5)	0.4058 (4)	0.2835 (4)	0.055 (5)	0.040 (4)	0.052 (5)	−0.004 (4)	−0.004 (4)	0.003 (4)
N(2)	0.1875 (5)	0.6070 (4)	0.2693 (4)	0.050 (5)	0.039 (4)	0.042 (4)	0.007 (3)	0.005 (4)	−0.004 (4)
C(1)	0.1830 (6)	0.4869 (5)	0.4075 (5)	0.043 (5)	0.042 (5)	0.043 (5)	0.004 (4)	−0.006 (4)	−0.017 (4)
C(2)	0.1788 (7)	0.5392 (6)	0.4655 (5)	0.060 (7)	0.070 (7)	0.033 (5)	0.004 (5)	−0.003 (5)	−0.019 (5)
C(3)	0.2319 (8)	0.5288 (9)	0.5224 (6)	0.062 (8)	0.12 (1)	0.040 (6)	−0.002 (7)	−0.006 (6)	−0.027 (8)
C(4)	0.2878 (9)	0.469 (1)	0.5285 (7)	0.057 (8)	0.16 (1)	0.049 (8)	0.038 (9)	−0.017 (6)	−0.018 (9)
C(5)	0.2957 (7)	0.4167 (8)	0.4719 (8)	0.044 (6)	0.12 (1)	0.074 (9)	0.044 (8)	−0.007 (6)	−0.002 (7)
C(6)	0.2410 (7)	0.4236 (6)	0.4123 (6)	0.040 (6)	0.057 (6)	0.068 (8)	0.015 (5)	−0.005 (5)	−0.010 (5)
C(7)	0.2393 (8)	0.3657 (6)	0.3550 (7)	0.056 (7)	0.061 (6)	0.092 (9)	0.019 (7)	−0.005 (6)	0.016 (6)
C(8)	0.3091 (7)	0.4352 (6)	0.2573 (7)	0.058 (7)	0.065 (7)	0.068 (8)	−0.012 (6)	0.003 (6)	0.008 (6)
C(9)	0.1897 (9)	0.3503 (7)	0.2287 (8)	0.081 (9)	0.057 (7)	0.11 (1)	−0.037 (7)	−0.007 (8)	0.015 (6)
C(10)	0.0325 (6)	0.5741 (5)	0.3486 (5)	0.036 (5)	0.045 (5)	0.034 (5)	−0.009 (4)	0.002 (4)	−0.003 (4)
C(11)	−0.0288 (7)	0.5708 (6)	0.4045 (5)	0.063 (7)	0.056 (6)	0.046 (6)	−0.000 (5)	−0.005 (5)	−0.004 (5)
C(12)	−0.0793 (7)	0.6313 (7)	0.4278 (6)	0.047 (6)	0.075 (8)	0.059 (7)	−0.007 (6)	0.017 (5)	0.007 (6)
C(13)	−0.0698 (8)	0.7017 (7)	0.3958 (7)	0.061 (7)	0.070 (8)	0.087 (9)	−0.030 (7)	0.011 (7)	0.016 (6)
C(14)	−0.0081 (7)	0.7116 (6)	0.3391 (6)	0.070 (7)	0.041 (6)	0.078 (8)	−0.007 (5)	−0.011 (6)	0.008 (5)
C(15)	0.0404 (6)	0.6485 (5)	0.3160 (5)	0.037 (5)	0.051 (5)	0.046 (5)	0.005 (5)	−0.007 (4)	0.005 (4)
C(16)	0.1064 (6)	0.6559 (5)	0.2560 (5)	0.057 (6)	0.041 (5)	0.040 (5)	0.010 (4)	0.002 (5)	−0.002 (4)
C(17)	0.2399 (8)	0.6028 (6)	0.2027 (5)	0.065 (7)	0.070 (7)	0.050 (7)	0.014 (5)	0.021 (6)	−0.002 (6)
C(18)	0.2458 (7)	0.6411 (5)	0.3257 (6)	0.049 (6)	0.039 (5)	0.067 (7)	0.001 (5)	0.005 (5)	−0.012 (5)
C(19)	−0.0012 (6)	0.4540 (6)	0.1840 (6)	0.035 (5)	0.062 (6)	0.053 (6)	−0.020 (5)	−0.006 (5)	0.007 (5)
C(20)	−0.0273 (8)	0.4627 (8)	0.1085 (6)	0.053 (7)	0.11 (1)	0.056 (7)	−0.009 (7)	−0.014 (6)	0.000 (7)
C(21)	−0.038 (1)	0.2540 (7)	0.4158 (7)	0.11 (1)	0.057 (7)	0.064 (8)	0.020 (7)	−0.028 (8)	−0.038 (8)
C(22)	−0.089 (1)	0.1963 (8)	0.4579 (8)	0.16 (2)	0.09 (1)	0.09 (1)	0.029 (9)	−0.02 (1)	−0.06 (1)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
H(21)	0.1327 (7)	0.5874 (6)	0.4638 (5)	H(141)	0.0014 (7)	0.7674 (6)	0.3143 (6)
H(31)	0.2297 (8)	0.5704 (9)	0.5656 (6)	H(161)	0.1270 (6)	0.7155 (5)	0.2517 (5)
H(41)	0.3270 (9)	0.461 (1)	0.5769 (7)	H(162)	0.0748 (6)	0.6381 (5)	0.2064 (5)
H(51)	0.3449 (7)	0.3708 (8)	0.4748 (8)	H(171)	0.1986 (8)	0.5783 (6)	0.1607 (5)
H(71)	0.3037 (8)	0.3368 (6)	0.3526 (7)	H(172)	0.2987 (8)	0.5671 (6)	0.2108 (5)
H(72)	0.1868 (8)	0.3240 (6)	0.3654 (7)	H(173)	0.2608 (8)	0.6601 (6)	0.1873 (5)
H(81)	0.3361 (7)	0.4761 (6)	0.2954 (7)	H(181)	0.2088 (7)	0.6446 (5)	0.3756 (6)
H(82)	0.2995 (7)	0.4633 (6)	0.2060 (7)	H(182)	0.2667 (7)	0.6982 (5)	0.3095 (6)
H(83)	0.3556 (7)	0.3877 (6)	0.2511 (7)	H(183)	0.3046 (7)	0.6051 (5)	0.3331 (6)
H(91)	0.1254 (9)	0.3267 (7)	0.2450 (8)	H(201)	−0.0829 (8)	0.4245 (8)	0.0967 (6)
H(92)	0.2382 (9)	0.3043 (7)	0.2230 (8)	H(202)	0.0292 (8)	0.4484 (8)	0.0743 (6)
H(93)	0.1821 (9)	0.3798 (7)	0.1779 (8)	H(203)	−0.0475 (8)	0.5216 (8)	0.0988 (6)
H(111)	−0.0371 (7)	0.5160 (6)	0.4314 (5)	H(221)	−0.048 (1)	0.1458 (8)	0.4663 (8)
H(121)	−0.1264 (7)	0.6235 (7)	0.4716 (6)	H(222)	−0.150 (1)	0.1803 (8)	0.4286 (8)
H(131)	−0.1098 (8)	0.7499 (7)	0.4143 (7)	H(223)	−0.108 (1)	0.2205 (8)	0.5093 (8)

[a] The temperature factor has the form of exp(−T) where $T = 8\pi^2 U((\sin\theta)/\lambda)^2$ for isotropic atoms and $T = 2\pi^2 \Sigma_{ij} h_i h_j U_{ij} i^* j^*$ for anisotropic atoms. i^* and j^* are reciprocal axial lengths and h_i are Miller indices. $U = 0.08$ Å^2 for all hydrogen atoms.

Results

General Remarks about the Characterization of the Structures. The ligands used throughout this work, as depicted in Figure 1, have in common the ability to form five-membered cyclometalated rings where in all cases CH_2 and NMe_2 moieties will be members of that ring. In the free ligands inversion about nitrogen in the $CNMe_2$ moiety is rapid on the NMR time scale, which renders the methyl groups homotopic. This inversion at nitrogen can be blocked by coordination, resulting in a stable prochiral nitrogen center. The CH_2 carbon atom is a prochiral center for both the free and the coordinated ligand. Depending on the complex, the prochiral centers on the CH_2 carbon and the NMe_2 nitrogen will have or will lack a plane of symmetry, and as a result both the CH_2 H atoms and the NMe_2 methyl groups will become enantiotopic or diastereotopic, respectively. The latter case can be inferred from inequivalent chemical shifts and magnetic couplings.

Coordination of nitrogen to platinum can thus be inferred for asymmetric complexes from the observation of diastereotopic *N*-methyl groups and, furthermore, from couplings between platinum and NMe_2 nuclei for both symmetric and asymmetric complexes.[20] Such features allow the study of both the stereochemistry at the metal units and the occurrence of an inert Pt–N interaction on the NMR time scale.[21] The deduction of the structure of *cis*-[$(2\text{-}Me_2NC_6H_4CH_2)_2Pt$] on this basis can be used as an illustration.

***cis*-[$(2\text{-}Me_2NC_6H_4CH_2)_2Pt$].** Reaction of *cis*-[$PtCl_2(SEt_2)_2$] with 2 equiv of [$(2\text{-}Me_2NC_6H_4CH_2)Li(TMEDA)$] afforded, in 60% yield, the novel methyl-substituted cyclometalated compound *cis*-[$(2\text{-}Me_2NC_6H_4CH_2)_2Pt$] (**3**). The same cis stereoisomer was obtained when *trans*-[$PtCl_2(SEt_2)_2$] was chosen as the starting material.

The compound, whose solubility is good in CH_2Cl_2 and $CHCl_3$ and somewhat less in benzene and toluene, is monomeric in $CHCl_3$ solution. The ^1H and ^{13}C NMR spectra for **3** indicate the presence of one type of cyclometalated ligand, of which the methylene groups are bonded directly to platinum as is inferred from the coupling values of 74 Hz for

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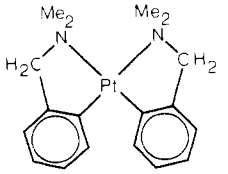
(20) W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).

(21) (a) G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, G. J. Verhoeckx, A. L. Spek, and J. Kroon, *J. Chem. Soc., Dalton Trans.*, 1352 (1980). (b) G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, W. M. G. F. Pontenagel, J. Kroon, and A. L. Spek, *J. Am. Chem. Soc.*, **100**, 5021 (1978).

Table III. Interatomic Distances (Å) and Angles (Deg)

		Bond Distances			
Hg–Pt	2.513 (1)	O(4)–C(21)	1.227 (20)	C(5)–C(6)	1.379 (17)
Hg–O(1)	2.621 (8)	N(1)–C(7)	1.524 (15)	C(6)–C(7)	1.465 (16)
Hg–O(3)	2.100 (8)	N(1)–C(8)	1.478 (13)	C(10)–C(11)	1.383 (13)
Hg–O(4)	2.762 (10)	N(1)–C(9)	1.478 (16)	C(10)–C(15)	1.429 (13)
Pt–O(2)	2.152 (6)	N(2)–C(16)	1.492 (17)	C(11)–C(12)	1.359 (15)
Pt–N(1)	2.223 (8)	N(2)–C(17)	1.464 (13)	C(12)–C(13)	1.366 (17)
Pt–N(2)	2.317 (7)	N(2)–C(18)	1.482 (13)	C(13)–C(14)	1.405 (17)
Pt–C(1)	2.012 (9)	C(1)–C(2)	1.410 (13)	C(14)–C(15)	1.379 (14)
Pt–C(10)	2.004 (9)	C(1)–C(6)	1.397 (13)	C(15)–C(16)	1.489 (13)
O(1)–C(19)	1.254 (13)	C(2)–C(3)	1.332 (15)	C(19)–C(20)	1.464 (16)
O(2)–C(19)	1.274 (12)	C(3)–C(4)	1.331 (21)	C(21)–C(22)	1.484 (21)
O(3)–C(21)	1.266 (16)	C(4)–C(5)	1.395 (21)		
		Bond Angles			
Pt–Hg–O(1)	80.4 (2)	Hg–O(1)–C(19)	116.1 (7)	C(1)–C(6)–C(7)	118.9 (9)
Pt–Hg–O(3)	172.4 (2)	Pt–O(2)–C(19)	125.2 (6)	C(5)–C(6)–C(7)	122.4 (10)
Pt–Hg–O(4)	132.7 (3)	Hg–O(3)–C(21)	107.5 (8)	N(1)–C(7)–C(6)	109.0 (9)
O(1)–Hg–O(3)	103.9 (3)	Hg–O(4)–C(21)	77.0 (8)	Pt–C(10)–C(11)	130.8 (7)
O(1)–Hg–O(4)	113.5 (3)	Pt–N(1)–C(7)	103.2 (6)	Pt–C(10)–C(15)	114.7 (6)
O(1)–Hg–C(21)	112.0 (3)	Pt–N(1)–C(8)	115.6 (6)	C(11)–C(10)–C(13)	114.2 (8)
O(3)–Hg–O(4)	51.6 (3)	Pt–N(1)–C(9)	113.8 (7)	C(10)–C(11)–C(12)	124.7 (10)
O(3)–Hg–C(21)	26.0 (4)	C(7)–N(1)–C(8)	107.0 (8)	C(11)–C(12)–C(13)	119.6 (10)
O(4)–Hg–C(21)	25.7 (4)	C(7)–N(1)–C(9)	111.1 (8)	C(12)–C(13)–C(14)	120.3 (11)
Hg–Pt–C(2)	93.3 (2)	C(8)–N(1)–C(9)	106.1 (9)	C(13)–C(14)–C(15)	118.4 (10)
Hg–Pt–N(1)	90.1 (2)	Pt–N(2)–C(16)	100.7 (5)	C(10)–C(15)–C(14)	122.8 (9)
Hg–Pt–N(2)	166.7 (2)	Pt–N(2)–C(17)	118.5 (6)	C(10)–C(15)–C(16)	116.7 (8)
Hg–Pt–C(1)	87.4 (3)	Pt–N(2)–C(18)	110.0 (5)	C(14)–C(15)–C(16)	120.5 (9)
Hg–Pt–C(10)	88.3 (3)	C(16)–N(2)–C(17)	108.3 (7)	N(2)–C(16)–C(15)	110.8 (7)
O(2)–Pt–N(1)	92.5 (3)	C(16)–N(2)–C(18)	111.1 (7)	O(1)–C(19)–O(2)	125.0 (10)
O(2)–Pt–N(2)	81.1 (3)	C(17)–N(2)–C(18)	108.0 (8)	O(1)–C(19)–C(20)	118.9 (10)
O(2)–Pt–C(1)	173.7 (3)	Pt–C(1)–C(2)	127.5 (7)	O(2)–C(19)–C(20)	116.0 (9)
O(2)–Pt–C(10)	93.5 (3)	Pt–C(1)–C(6)	113.4 (7)	Hg–C(21)–O(3)	46.5 (6)
N(1)–Pt–N(2)	102.2 (3)	C(2)–C(1)–C(6)	118.9 (9)	Hg–C(21)–O(4)	77.3 (8)
N(1)–Pt–C(1)	81.2 (3)	C(1)–C(2)–C(3)	119.7 (11)	Hg–C(21)–C(22)	161.1 (11)
N(1)–Pt–C(10)	173.9 (3)	C(2)–C(3)–C(4)	122.7 (13)	O(3)–C(22)–O(4)	123.7 (13)
N(2)–Pt–C(1)	99.4 (3)	C(3)–C(4)–C(5)	119.7 (12)	O(3)–C(21)–C(22)	115.6 (14)
N(2)–Pt–C(10)	80.0 (3)	C(4)–C(5)–C(6)	120.0 (12)	O(4)–C(21)–C(22)	120.8 (13)
C(1)–Pt–C(10)	92.8 (4)	C(1)–C(6)–C(5)	118.8 (10)		

${}^2J({}^{195}\text{Pt}-{}^1\text{H})$ and 793 Hz for ${}^1J({}^{195}\text{Pt}-{}^{13}\text{C})$. The chemical shifts for the CH_2 C atoms (−1.75 ppm) are in line with a benzylic moiety directly bonded to platinum; $\delta(H(CH_2))$ (3.00 ppm) is somewhat low for a methyl group bonded to platinum. The CH_2 H atoms, and also the NMe_2 methyl groups, are isochronous and thus likely enantiotopic, which points to a plane of symmetry through the CH_2 C atoms and thus accordingly to a planar coordination around platinum. The Pt–N coordination is inert on the NMR time scale, and the ${}^3J({}^{195}\text{Pt}-{}^1\text{H})$ value of 14 Hz for the NMe_2 hydrogen atoms is indicative of coordination of the NMe_2 groups trans to a carbon atom. Therefore, compound **3** will have a cis square-planar structure.



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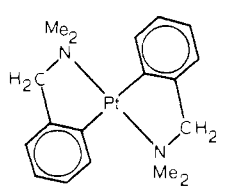

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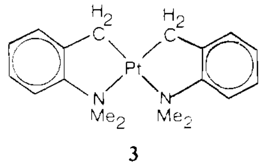

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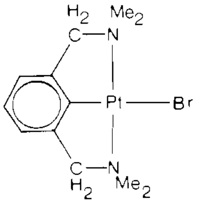

4a

Reactions of Cyclometalated Platinum Compounds with Mercury(II) Carboxylates. Reaction of the cyclometalated complexes *cis*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] (**1**), *cis*-[(2-$Me_2NC_6H_4CH_2)_2Pt$] (**3**), {[2,6-$(Me_2NCH_2)_2C_6H_3$]PtBr} (**4a**), and {[2,6-$(Me_2NCH_2)_2C_6H_3$]Pt(O_2CR)} (**4b**) with mercury(II) carboxylates $Hg(O_2CR)_2$ gave the novel cyclometalated platinum–mercury compounds of formulas [(2-$Me_2NCH_2C_6H_4)_2(RCO_2)PtHg(O_2CR)$] (**5a,b**), [(2-$Me_2NC_6H_4CH_2)_2(RCO_2)PtHg(O_2CR)$] (**6a,b**), {[2,6-$(Me_2NCH_2)_2C_6H_3](RCO_2)PtHg(O_2CR)Br$} (**7a,b**), and {[2,6-$(Me_2NCH_2)_2C_6H_3](RCO_2)PtHg(O_2CR)_2$] (**8a**, R = Me; **8b**, R = *i*-Pr), respectively. The monocarboxylato analogue of **7** and **8** {[2,6-$(Me_2NCH_2)_2C_6H_3](RCO_2)PtHgCl_2$] (**9b**) could be prepared via reaction of {[2,6-$(Me_2NCH_2)_2C_6H_3$]-Pt(O_2CR)} (4b) with $HgCl_2$.

The stoichiometries are based on elemental analytical data and spectroscopic techniques (Tables V–VII). Molecular weight measurements in $CHCl_3$ indicate that the compounds are monomeric in solution. Field desorption mass spectroscopy measurements of **5a** showed an isotope pattern at *m/z* 783, consistent with the molecular ion, along with patterns for degradation products at *m/z* 724, 583, 557, 522, and 463. The compounds **5–7** are soluble in solvents such as CH_2Cl_2, $CHCl_3$, benzene, and acetone, with the greater solubility for R = *i*-Pr, while they are insoluble in ether and hexane. The compounds are air stable, even in solution, but they are slightly light sensitive and decompose in solution at elevated temperatures.

Solutions of the platinum–mercury compounds **5–7** do not react with CO. Only **7** reacted with triphenylphosphine, resulting in elimination of $Hg(O_2CR)_2$ and formation of {[2,6-$(Me_2NCH_2)C_6H_3$]Pt(PPh_3)}Br, as deduced from ${}^1H$ and ${}^{31}P$ NMR spectra.

Reaction of *trans*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] (**2**) with mercury(II) carboxylates $Hg(O_2CR)_2$ gave yellow [(2-$Me_2NCH_2C_6H_4)_2PtHg(O_2CR)_2$] (**10a**, R = Me; **10b**, R =

Table IV. Least-Squares Planes[a]

plane	defining atoms	eq of the least-squares plane[b] P	Q	R	S	max dev, Å	dev of other atoms, Å
1	Hg, Pt, O(1), O(2), C(19)	−9.63 (3)	12.23 (2)	5.25 (4)	6.53 (2)	0.01 (3)	C(20) −0.04 (3)
2	O(3), O(4), C(21), C(22)	5.00 (10)	6.93 (10)	15.85 (8)	8.17 (3)	0.01 (5)	Hg 0.25 (6)
3	Pt, O(2), N(1), C(1), C(10)	9.45 (3)	12.53 (3)	−4.97 (5)	5.78 (2)	0.02 (4)	Hg −2.50 (3), N(2) 2.25 (4)
4	Pt, N(1), C(1), C(6), C(7)	11.54 (3)	10.09 (5)	−4.36 (7)	5.17 (4)	0.25 (5)	
5	Pt, N(2), C(10), C(15), C(19)	7.62 (5)	5.11 (5)	14.98 (4)	8.29 (2)	0.29 (4)	
6	C(1), C(2), C(3), C(4), C(5), C(6)	10.62 (5)	9.52 (7)	−8.00 (8)	3.31 (6)	0.02 (8)	C(7) −0.13 (7), Pt 0.19 (7), N(1) 0.64 (7)
7	C(10), C(11), C(12), C(13), C(14), C(15)	10.70 (4)	4.08 (7)	12.10 (6)	6.90 (5)	0.01 (8)	C(16) 0.00 (7), Pt 0.17 (6), N(2) 0.83 (7)

relevant interplanar angles: 1,2 = 72.4 (6)°; 1,3 = 88.8 (3)°

relevant angles between bonds and planes: (Pt–Hg),3 = 86.8°; (Pt–N(2)),3 = 76.7°

[a] Standard deviations in parentheses. [b] Equation in direct space fractional coordinates: $Px + Qy + Rz = S$.

Table V. Analytical and Physical Data

no.	compd	mol wt (calcd)[a]	anal. found (calcd) % C	% H	% N	% O	color	$\nu(CO_2)$,[d] cm^{-1}
3	*cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$	435 (463)	46.26 (46.65)	5.31 (5.22)	5.94 (6.04)		cream	
5a	$[(2\text{-}Me_2NCH_2C_6H_4)_2(MeCO_2)PtHg(O_2CMe)]$[b]	809 (782)	34.50 (33.77)	4.00 (3.87)	3.47 (3.58)	7.94 (8.18)	yellow	1573, 1376, 1327
5b	$[(2\text{-}Me_2NCH_2C_6H_4)_2(i\text{-}PrCO_2)PtHg(O_2C\text{-}i\text{-}Pr)]$	874 (838)	36.23 (37.25)	4.42 (4.57)	3.30 (3.34)	7.96 (7.63)	yellow	1576, 1385, 1348
6a	$[(2\text{-}Me_2NC_6H_4CH_2)_2(MeCO_2)PtHg(O_2CMe)]$	731 (782)	33.45 (33.77)	4.13 (3.87)	3.47 (3.58)	8.77 (8.18)	cream	1570, 1375
6b	$[(2\text{-}Me_2NC_6H_4CH_2)_2(i\text{-}PrCO_2)PtHg(O_2C\text{-}i\text{-}Pr)]$	826 (838)	36.06 (37.25)	4.73 (4.57)	3.18 (3.34)	7.78 (7.63)	cream	1572, 1389, 1350
7a	$\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](MeCO_2)PtHg(O_2CMe)Br\}$		24.45 (25.38)	2.90 (3.30)	3.24 (3.33)	8.33 (8.46)	yellow	1565, 1408
7b	$\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](i\text{-}PrCO_2)PtHg(O_2C\text{-}i\text{-}Pr)Br\}$	829 (841)	27.97 (28.55)	3.85 (3.92)	4.41 (4.65)	7.06 (7.61)	yellow	1554, 1415, 1370
8b	$\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](i\text{-}PrCO_2)PtHg(O_2C\text{-}i\text{-}Pr)_2\}$		33.38 (33.98)	4.67 (4.75)	3.27 (3.30)	11.66 (11.23)	yellow	
9b	$\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](i\text{-}PrCO_2)PtHgCl_2\}$		25.00 (25.70)	3.77 (3.51)	3.28 (3.76)	3.64 (4.29)	yellow	1525, 1402
10a	$[(2\text{-}Me_2NCH_2C_6H_4)_2PtHg(O_2CMe)_2]\cdot{}^3/_4CH_2Cl_2$[c]		32.42 (33.29)	4.03 (3.73)	3.25 (3.32)	7.52 (7.57)	yellow	1626, 1576, 1383, 1367, 1313

[a] Measured in $CHCl_3$; experimental error is ±10%. [b] Anal. Calcd for Hg: 25.60. Found: 25.65. [c] Presence of solvent adduct was evidenced by ^1H NMR spectra. [d] KBr disk.

Table VI. ^1H NMR Data[a]

compd	cyclometalated ligand aryl	CH_3	CH_2	carboxylato group CH_3	CH
1	6.97	2.81 (15)	3.90 (19)		
2	7.10	3.06 (43)	4.00 (41)		
3	6.90, 7.30	3.20 (14)	3.00 (74)		
4	6.80	3.03 (38)	4.06 (46)		
5a	6.90	2.73, 2.80, 2.75, 3.03 (22)	3.25, 4.19, 3.85, 4.51	2.00	
5b	6.90	2.06 (21), 2.76 (6), 2.70 (30), 3.05 (23)	3.03 (18), 4.18, 3.88 (25), 4.55 (21)	1.09,[b] 1.03,[b] 1.15	2.55
6a	7.10	3.30[c]		2.00	*d*
6b	7.10	3.32[c]		1.15,[b] 1.09,[b] 1.05	*d*
7a	6.90	3.10 (34)	4.25 (46)	1.92	
7b	7.10	3.30 (31)	4.53 (44)	1.25	2.65
8b	6.85	3.10 (34)	4.23 (46)	1.17	2.60
9b[e]	6.80	3.02 (30)	4.21 (44)[f]	0.96	2.60
10a	6.90, 7.26, 7.45	2.71 (38), 2.85 (38)	3.97 (49), 4.14 (49)	1.86	
10b	6.90, 7.25, 7.40	2.69 (40), 2.83 (38)	3.96 (50), 4.10 (48)	0.93, 1.06	2.50

[a] Recorded in $CDCl_3$, $\delta(^1H)$ relative to Me_4Si, $J(^{195}Pt-^1H)$ in parentheses. [b] Diastereotopic Me(*i*-Pr) groups. [c] Various overlapping resonances. [d] Not assigned. [e] Recorded in acetone-d_6. [f] Broad.

i-Pr), on the basis of elemental analytical data and limited spectroscopic data. The compounds are unstable and decompose on dissolution ($CHCl_3$, toluene) with elimination of metallic mercury, even at low temperature. The decomposition yielded one main product contaminated with a second (0–12%), both compounds having stoichiometry $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(O_2CR)_2]$, with trans(C) (**11**) and trans(N) (**12**) geometries for the proposed structures, respectively.[13]

Molecular Geometry of $[(2\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}MeCO_2)PtHg(O_2CMe)]$ (5a). The crystal structure consists of eight discrete monomeric units of $[(2\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}MeCO_2)PtHg(O_2CMe)]$ (**5a**) per unit cell, which are mutually separated by normal van der Waals distances. Both enan-

Table VII. ^{13}C NMR Data^a

	aryl C atoms								carboxylato groups		
compd	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	NCH_2	NCH_3	CO_2	CH_3	CH
1		147.3 (7)	121.0 (40)	122.1	125.2 (86)	138.7 (109)	73.5 (58)	49.9			
2			119.4 (22)	120.8	123.4 (33)	133.3 (39)	78.6 (21)	51.8			
3	148.3 (53)	154.9 (51)	118.8 (18)	124.5	126.4 (10)	130.1 (82)	−1.8 (793)	51.5			
4		144.3	119.6 (35)	123.7			77.9 (67)	55.1 (14)			
5a		145.0	123.2	124.4	127.9	141.4 (124, 22)	73.1 (50, 27)	54.5 (18), 49.1	176.9^b	21.4^b	
		142.9 (20)	122.5	124.2	126.2	135.5 (61, 22)	69.9 (26, 55)	49.9, 47.7	175.6^c	23.7^c	
5b		145.8	123.3	124.4	128.1	141.5 (123, 21)	73.3 (49, 24)	54.9 (21), 49.2	182.6^b	20.0^b	35.1^b
		142.8	123.0	124.1	126.4	135.9 (61, 21)	70.0 (28, 59)	50.2, 48.0	181.1^c	20.0^c	36.4^c
6a	145.6 (40, 30)	152.1 (34, 12)	119.6 (20)	126.5	127.3	129.1 (54)	−2.1 (562, 151)	63.4, 48.7	177.4^b	24.5^b	
	144.1 (48, 12)	150.0 (48, 12)	119.3 (17)	126.2	126.8	129.0 (53)	−5.0 (654, 125)	52.5, 46.7	176.2^c	22.2^c	
6b	145.8 (40, 28)	151.9 (34, 10)	120.1 (22)	126.5	127.3	129.3 (52)	−2.3 (558, 161)	63.6, 48.1	183.0^b	20.3^b	36.4^b
	144.1 (48, 12)	150.0 (48, 11)	119.4 (15)		126.8	129.1 (53)	−4.7 (656, 114)	52.7, 46.6	181.8^c	19.8^c	34.9^c
7a	140.0	145.0	119.7	123.7			77.5	53.8 (19)	179.8, 178.0	24.7, 21.5	
7b	139.1	144.3 (67)	120.6 (31)	125.6			75.6 (57)	53.2 (23)	185.0, 182.3	20.2	37.2, 34.7
8b		144.5	119.7	125.2			*d*	53.5		20.2	34.5

^{a} Recorded in $CDCl_3$, δ(^{13}C) relative to Me_4Si, followed in parentheses by J(^{195}Pt–^{13}C) and by J(^{199}Hg–^{13}C) where appropriate. ^{b} Pt bonded. ^{c} Hg bonded. ^{d} Masked by solvent resonances.

tiomers are equally present. The molecular structure of one enantiomer along with the adopted numbering scheme is shown in a PLUTO drawing (Figure 2). The thermal vibrational ellipsoids are shown in an ORTEP stereoplot (Figure 3). Interatomic bond distances and angles are listed in Table III. The bonding distances and angles of the organic ligands are within the generally observed range. Platinum has a distorted octahedral coordination while the coordination of mercury is T-shaped. The Pt–Hg separation of 2.513 (1) Å is an appropriate value expected for a single Pt–Hg bond. This value corresponds well with the sum of the radii for Pt and Hg (2.532 Å) derived from {[(4-MeC_5H_4N)Me_2(μ-F_3CCO_2)Pt]$_2$} (Pt–Pt = 2.557 (1) Å)[22] and Hg_2Cl_2 (Hg–Hg = 2.507 Å)[23] and is somewhat shorter than the Pt–Hg distance in *cis*-[(Ph_3P)$_2$(F_3C)Pt^{I}Hg^I(CF_3)] (2.569 (2) Å).[24]

One acetato group is coordinated to mercury in a monodentate fashion with a Hg–O(3) bond of 2.10 (1) Å and a Pt–Hg–O(3) angle of 172.5 (2)°. These values are comparable with those for Hg–O and C–Hg–O in $C_6H_5Hg(O_2CMe)$: 2.11 (4) Å and 1.70 (2)°, respectively.[25] The coordination of Hg is completed with a longer Hg–O(1) bond of 2.62 (1) Å to a bridging acetato group. A similar T-shaped coordination with a long Hg–O bond (2.68 (4) Å) is also observed in the organomercury compound {[*t*-Bu–O–O–C(Ph)–C(Ph)]HgBr}.[26] The above results indicate a high covalent character for the Pt–Hg bond.

Interestingly, the bridging acetato group is asymmetrically bonded; the Pt–O(2) distance amounts to 2.15 (1) Å (Pt–O in {[(4-MeC_5H_4N)Me_2(μ-F_3CCO_2)Pt]$_2$} is 2.19 (2) Å[22]). Furthermore, it is noteworthy that the Pt, Hg, O(1), O(2), and C(19) atoms are coplanar (the maximum deviation out of the least-squares plane is 0.007 Å) whereas Hg is displaced out of the plane defined by the monodentate acetato group by 0.253 Å (see Table IV and Figure 4). In contrast to the above planar geometry, similar structures with triazenido- or acetato-bridged Rh–Hg and Pt–Pt bonds all show distortions from planarity.[22,27]

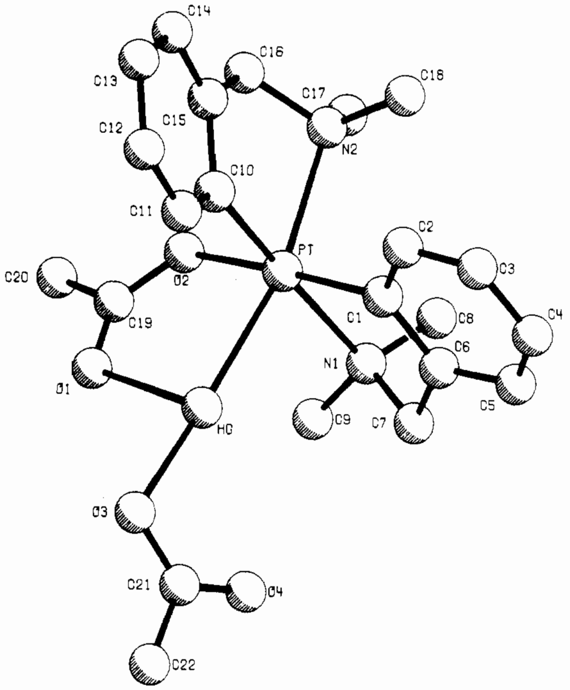

Figure 2. PLUTO drawing of the molecular structure of [(2-$Me_2NCH_2C_6H_4$)$_2$($MeCO_2$)PtHg(O_2CMe)] (**5a**) along with the adopted numbering scheme.

The six-coordination around platinum is completed with two chelate-bonded 2-[(dimethylamino)methyl]phenyl ligands. These ligands are both bonded via a nitrogen-donor bond and a carbon σ bond at the ortho position of the phenyl rings, resulting in five-membered chelate rings. As is normally observed, both five-membered rings are distinctly puckered (see Table IV) and the distortions in the two cyclometalated ligands are quite similar. This puckering may be described with an envelope type of structure, with the N atom moved out of the plane defined by the four other atoms, which furthermore lie in the plane of the aromatic rings (Table IV and Figure 4).

The two Pt–N distances are distinctly different: 0.10 (1) Å. The data point to an exceptionally large trans influence of Hg since Pt–N(2) is longer than Pt–N(1), being trans to

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[22] J. D. Schagen, A. R. Overbeek, and H. Schenk, *Inorg. Chem.*, **17**, 1938 (1978).

[23] E. Dorm, *J. Chem. Soc., Chem. Commun.*, 466 (1971).

[24] L. G. Kuz'mina, Yu. T. Struchkov, V. V. Bashilov, V. I. Sokolov, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 621 (1978); *Chem. Abstr.*, **89**, 43730*t* (1978).

[25] B. Kamenar and M. Penavic, *Inorg. Chim. Acta*, **6**, 191 (1972).

[26] J. Halfpenny and R. W. H. Small, *J. Chem. Soc., Chem. Commun.*, 879 (1979).

[27] P. I. van Vliet, M. Kokkes, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, **187**, 413 (1980).

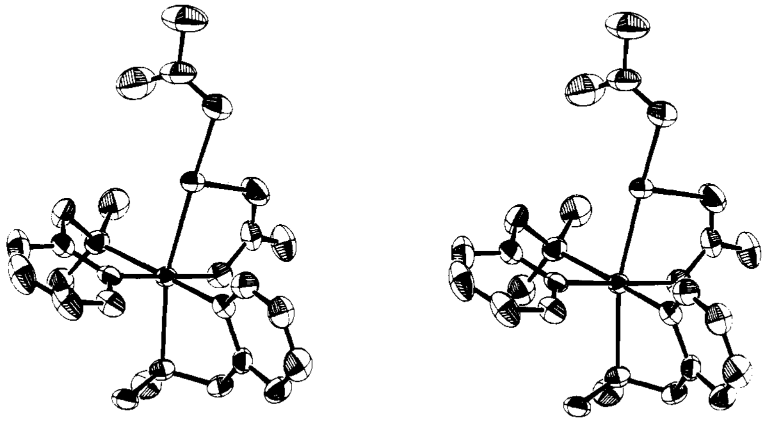
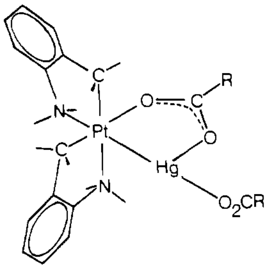


Figure 3. ORTEP stereoview of compound **5a**.

a σ-bonded C atom, which certainly has a high trans influence.[28] The coordinated C atoms and the Hg atom are mutually cis. The atoms C(1), C(10), O(2), N(1) and Pt lie within standard deviations in one plane. The Pt–Hg bond is almost orthogonal to this plane (86.8°) while the Pt–N(2) bond makes an angle of 76.7° with this plane (see Table IV).

The coordination around platinum is distorted from octahedral mainly by the small N–Pt–C bite of the benzylamino ligands: 80.0 (2) and 81.2 (2)°, respectively. These values are comparable with that observed for [(2-$Me_2NCH_2C_6H_4$)$(CO)_4$Mn] (80.2°),[29a] but smaller values have been observed for most other complexes, e.g., 75.3° in [(2-$Me_2NCH_2C_6H_4$)$(C_6H_5)_2$SnBr].[21b] Comparison of those structures shows that the relatively large bite angles in the platinum–mercury complex will be mainly due to the short metal–ligand distances.

Structure in Solution. [(2-$Me_2NCH_2C_6H_4$)$_2$(RCO_2)PtHg(O_2CR)] (5a, R = Me; 5b, R = *i*-Pr). The ^{1}H and ^{13}C NMR data indicate that the acetato and isobutyrato compounds **5a** and **5b** are isostructural and the structural features are in accord with those obtained for **5a** in the solid state. The assignments for the ^{13}C NMR spectra were made by comparison with the proton-coupled and -decoupled ^{13}C NMR spectra of **1**. In the ^{13}C NMR spectra the cyclometalated ligands are inequivalent and signals are observed in accordance with two sets of phenyl groups, differing in chemical shifts and $J(^{195}Pt–^{13}C)$ and $J(^{199}Hg–^{13}C)$ coupling constants. In the ^{1}H and ^{13}C NMR spectra four diastereotopic *N*-methyl groups with different $J(^{195}Pt–^1H)$ and $J(^{195}Pt–^{13}C)$ couplings are observed, indicating that (i) the nitrogen atoms are coordinated to platinum in solution and (ii) the nitrogen atoms and the platinum center lack a plane of symmetry. Taken together, all the above facts indicate that the aryl groups do not exchange and that the platinum–nitrogen bond is inert on the NMR time scale.



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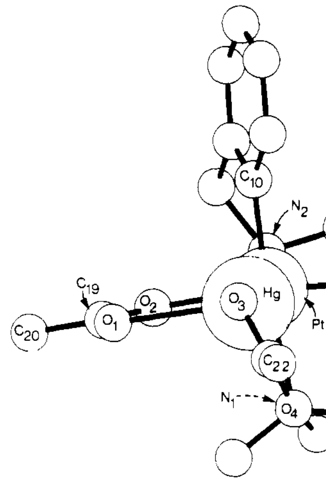

Figure 4. Projection of compound **5a** along the O(4)–N(1) axis showing the planar geometry of the Pt–Hg–O(1)–C(19)–O(2) unit and the puckering of the cyclometalated ring Pt–C(10)–C(15)–C(16)–N(2).

Evidence for a Pt–Hg bond comes from the observation of platinum and mercury couplings to both C(6) and the methylene carbon atoms: 124 and 22 Hz for C(6), 61 and 22 Hz for C(6)′, 50 and 27 Hz for CH_2, and 26 and 55 Hz for C′H_2, respectively (**5a**). Similar behavior was observed by Kuyper for the ^{1}H NMR spectrum of [(bpy)Me_2($MeCO_2$)PtHg(O_2CMe)].[6] The reduction of the $J(^{195}Pt–^{13}C)$ coupling constant for one CH_2 carbon (26 Hz) compared with that of the other (50 Hz) might be the result of the trans influence of mercury vs. carbon on this coupling proceeding via a Pt–N bond. It is noteworthy that the long-range $J(^{199}Hg–^{13}CH_2)$ couplings have an inversed order of magnitude: 55 and 27 Hz, respectively.

The ^{13}C NMR spectra indicate the presence of two inequivalent carboxylato groups. The 250-MHz ^{1}H NMR spectrum of **5b** showed three doublets, with an intensity ratio of 1:1:2, for the isopropyl methyl groups. $Me_2C(H)CO_2$ contains a prochiral carbon center, and connection to an asymmetric center will render the two methyl groups diastereotopic. The resulting chemical shift difference will depend on the distance between the prochiral and the asymmetric Pt center. Therefore the less intense doublets (1:1) are assigned to the platinum-bonded bridging carboxylato group and the remaining more intense doublet is assigned to the terminal mercury-bonded carboxylato group, which is much further from the asymmetric Pt center. The assignments of the carboxylato groups in the ^{13}C NMR spectra are based on exchange experiments with free carboxylic acids (vide infra). The bonding modes of the carboxylato groups, monodentate, chelate, or bridging, cannot be inferred from the NMR spectra,

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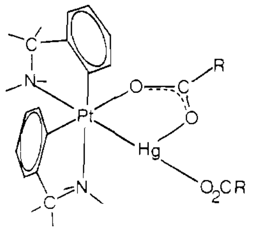
[28] We thank the reviewer for pointing this out.

[29] (a) R. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 844 (1973); (b) G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, A. L. Spek, and J. C. Schoone, *J. Organomet. Chem.* **148**, 233 (1978).

and the IR spectra, which showed several broad bands in the $\nu(CO_2)$ region, are also not very indicative.

[(2-$Me_2NC_6H_4CH_2$)$_2$(RCO_2)PtHg(O_2CR)] (6a, R = Me; 6b, R = *i*-Pr). The following conclusions can be drawn from the ^1H and ^{13}C NMR data of **6a** and **6b** (Tables VI and VII). The methylene groups have become inequivalent but remain bonded to platinum, as indicated by $^1J(^{195}Pt-^{13}C)$ coupling constants of 560 and 655 Hz. The presence of a platinum–mercury bond is unambiguously concluded from the mercury–carbon couplings for the two methylene groups and for several of the aryl carbon atoms. Furthermore, it is evident that both methylene groups are coordinated to platinum cis to the mercury atom, because the $^2J(^{199}Hg-^{13}C)$ coupling constants are of the same order of magnitude (151 and 125 Hz, R = Me; 161 and 114 Hz, R = *i*-Pr). The differences in $J(^{195}Pt-^{13}C)$, and maybe also in $J(^{199}Hg-^{13}C)$, will be due to the influence of the ligands trans to the CH_2 moieties. The platinum–carbon and mercury–carbon coupling constants for the CH_2 and aryl carbon atoms differ only slightly in going from R = Me to R = *i*-Pr.

The observation of four anisochronous NMe carbon resonances indicates platinum–nitrogen coordination, which is stable on the NMR time scale, and methyl group diastereotopicity. The ^{13}C NMR spectra indicated furthermore the presence of two inequivalent carboxylato groups. On the basis of the above facts a structure analogous to that of compound **5** is proposed for **6**. The NMR resonances for the CH_2 and NMe_2 nuclei were rather broad. This is probably due to puckering of the five-membered cyclometalated ring, resulting in different conformers that interchange rather slowly on the NMR time scale.



6

Dynamic Behavior of the Platinum–Mercury Compounds 5 and 6. Compounds **5** and **6** were studied with variable-temperature NMR and free carboxylic acid exchange experiments. In all the experiments described below the $J(^{195}Pt-^1H)$, $J(^{195}Pt-^{13}C)$, and $J(^{199}Hg-^{13}C)$ couplings for the CH_2 and NMe_2 moieties of the cyclometalated ligands were unaffected. Indeed, their resonances broadened at low temperatures (<−50 °C), but this may be due to a slower wagging of the puckered cyclometalated rings. Such a wagging will affect the environment of the benzylic hydrogen atoms as is reported for {[2,6-(Me_2NCH_2)$_2C_6H_3$]SnR_2}X.[29b] The persistence of the coupling data indicates that the arrangement of the cyclometalated ligands around platinum does not change whatever exchange process occurs.

The ^{13}C NMR spectra of compounds **5** and **6** (**a**, R = Me; **b**, R = *i*-Pr) recorded in $CDCl_3$ at room temperature showed for both CO and C_α atoms two resonances, which are attributed to carboxylato groups with different coordination modes, i.e., monodentate platinum (or bridged platinum–mercury) bonded and monodentate mercury bonded, respectively.

The fact that sharp separate signals for the carboxylato groups in the ^{13}C NMR spectra were observed over the whole temperature range studied (−50 to +40 °C) indicates that no exchange process occurs between the Pt- and Hg-bonded carboxylato groups on the NMR time scale.

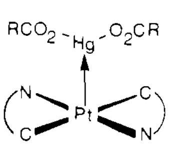
Upon addition of the appropriate carboxylic acid to solutions of **5a** and **5b**, respectively, one of each two resonances remained unaffected, while the others were shifted and collapsed with those of the added acid. When acetic acid was added to a solution of **5b** in $CDCl_3$, the isobutyrato CO_2 and C_α resonances at 185.0 and 37.2 ppm remained unshifted but had decreased intensity while the other isobutyrato resonances, which had increased intensity, shifted in the direction of the free isobutyric acid positions. In addition, two signals for both the acetato CO_2 and the acetato CH_3 carbon atoms were observed. The signals with the lower intensity correspond with those acetato signals in **5a** that remained unaffected in the experiment with free acetic acid.

In a similar experiment for **6b**, when acetic acid was added to a solution of it in $CDCl_3$, broadened ^{13}C NMR signals were observed at room temperature. At −33 °C two sets of sharp signals are present for both the isobutyrato and acetato groups. The positions of the signals with lower intensity were the same as those obtained for one of each two carboxylato resonances obtained for the pure compounds **6a** and **6b**. The signals with higher intensities were positioned between those observed for the other set of signals in the pure compounds **6a** and **6b** and free carboxylic acid.

The above observations lead to the conclusion that (i) both **5** and **6** contain different coordinated carboxylato groups, which do not exchange, or only exchange very slowly, on the NMR time scale, and (ii) exchange with free carboxylic acid is fast on the NMR time scale for one of these carboxylato groups and slow for the other.

The nonobservation of intramolecular exchange of the carboxylato groups in **5** and **6** may be due to the fact that such a process should involve Pt–O bond rupture, which is a difficult process as Pt–O bond rupture for the platinum carboxylato compounds *trans*(*C*)- and *trans*(*N*)-[(2-$Me_2NCH_2C_6H_4$)$_2$Pt(O_2CR)$_2$] is respectively very slow or not observed at all.[13] Such a behavior can also explain that one of the two carboxylato groups in both **5** and **6**, which will be the platinum-bonded one, is exchanged slowly with free carboxylic acid. Consequently, the more labile group in **5** and **6** will be mercury bonded (see Table VII).

[(2-$Me_2NCH_2C_6H_4$)$_2$PtHg(O_2CR)$_2$] (10a, R = Me; 10b, R = *i*-Pr). Only limited ^1H NMR data are available for **10**. Recording of the ^{13}C NMR spectra, which might have given further information, was hampered by the instability of the compounds (vide supra). The ^1H NMR spectra showed the presence of isochronous carboxylato groups, two diastereotopic CH_2NMe_2 methyl groups, and two diastereotopic methylene hydrogen atoms. $J(^{195}Pt-^1H)$ couplings for the CH_2NMe_2 protons indicate the presence of stable platinum–nitrogen coordination in solution. A square-pyramidal structure with an apical platinum-to-mercury bond is in accordance with these observations.



10

{[2,6-(Me_2NCH_2)$_2C_6H_3$]XPtHg(CO_2CR)Y} (7–9). In each of the compounds **7–9** the two Me_2NCH_2 units are coordinated to platinum (cf. $J(^{195}Pt-H_3CN)$ in Table VI) over the whole temperature range studied (−50 to +40 °C) and the meridional spanning of the 2,6-(Me_2NCH_2)$_2C_6H_3$ ligand as imposed by its fixed geometry will be retained. The ^1H NMR spectra of these compounds showed isochronous resonances for both the CH_2 and the NMe_2 hydrogen atoms, suggesting the presence in these molecules of an effective plane of symmetry through the C and N centers (vide infra).

In the IR spectrum of **9** (X = Y = Cl), which contains only one carboxylato group, strong absorptions at 1525 and 1402 cm^{-1} were observed. These absorptions are in the range for

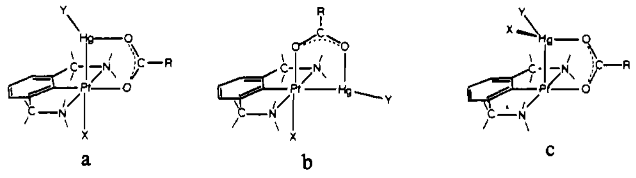


Figure 5. Possible structures for **7** (X = O_2CR, Y = Br), **8** (X = Y = O_2CR), and **9** (X = Y = Cl).

carboxylato groups that are coordinated in a bridging bonding mode.

For **7a** (X = O_2CMe, Y = Br) at low temperature, when the respective resonances from the Me_2NCH_2 unit in the ^1H and ^{13}C NMR spectra are broad, the acetato groups are dissimilar as shown by two singlets for the CH_3 hydrogen atoms (δ 1.87 and 2.10) and carbon atoms (δ 24.70 and 21.50) of the carboxylato groups. This points to different bonding modes for the two carboxylato groups, one probably being bridge bonded as proposed for **9**. At higher temperatures the Me_2NCH_2 resonances became sharp and the carboxylato CH_3 H resonances coalesced (δ 1.93, T_c 10 °C), providing evidence for an intramolecular exchange of the coordination mode of the carboxylato ligands (see Discussion).

The ^{13}C NMR spectra of monomeric **7b** (X = O_2C-*i*-Pr, Y = Br) in $CDCl_3$ showed two sharp resonances for both CO_2 and C_α at −50 °C, which started to coalesce when raising the temperature. The coalescence temperature, above 40 °C, could not be reached due to decomposition of the complex. However, in the ^1H NMR spectrum of **7b** the CH_3 hydrogen atoms appeared as a single sharp doublet ($^3J_{vic}$ 7 Hz) at room temperature.

By contrast the ^1H and ^{13}C NMR spectra of **8** (X = Y = O_2CR) showed the presence of one type of carboxylato group, suggesting a fast exchange of all three carboxylato groups on the NMR time scale.

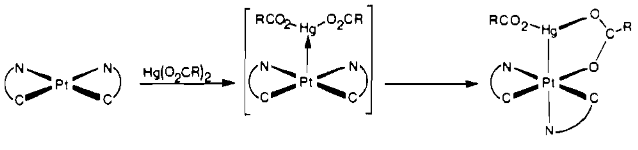
Various structures can be proposed that contain the N,N′,C-bonded 2,6-$(Me_2NCH_2)_2C_6H_3$ terdentate ligand, one bridging carboxylato group, and a Pt–Hg bond as basic structural features. Possible structures are shown in Figure 5 that have as a main difference the presence of either a covalent (a and b) or a donative (c) Pt–Hg bond (see Discussion).

The structures imply that for **7** exchange of a bromide atom and a carboxylato group had occurred between the platinum and mercury centers during complex formation. A similar exchange was observed in reactions of rhodium and iridium halogen complexes with mercury–triazenido or –formamidino compounds, which afforded triazenido- or formamidino-bridged Rh(Ir)–Hg bonds.[27,30] Structures a–c in Figure 5 can explain the observed number of different carboxylato groups, in particular for **7**. Information concerning the bonding mode of the two carboxylato groups in the latter compound is provided by the free carboxylic acid exchange experiments with ^{13}C NMR.

When isobutyric acid was added to a solution of **7b** in $CDCl_3$ at low temperature, the ^{13}C resonances of one carboxylato group remained unchanged, whereas the signals of the second carboxylato group were shifted somewhat and had collapsed with those of the added acid. This points to a fast exchange between this second carboxylato group and free carboxylic acid.

At higher temperature all carboxylato signals start to coalesce, and the observation of one broadened α-carbon resonance indicates that the intramolecular exchange is eclipsed by a much faster exchange of both carboxylato groups with free carboxylic acid. Addition of acetic acid to **7b**, at ambient temperature, also resulted in coalescence of all the carboxylato groups. At low temperature two sets of resonances are observed for both the isobutyrato and the acetato groups. These facts are in line with the view that the carboxylato groups are bonded differently. As was observed for **5** and **6**, one carboxylato group in **7** exchanges much faster with free carboxylic acid than the second, which suggests that the latter carboxylato group is bridge bonded and the former either monodentate or chelate bonded.

Scheme II



Discussion

Stable platinum–mercury complexes $[(2\text{-}Me_2NCH_2C_6H_4)_2(RCO_2)PtHg(O_2CR)]$ (**5**) and $[(2\text{-}Me_2NC_6H_4CH_2)_2(RCO_2)PtHg(O_2CR)]$ (**6**) (R = Me, *i*-Pr) have been prepared from the reactions of the diorgano cyclometalated platinum complexes *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ (**1**) and *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ (**3**). The tendency of *cis*-diorganoplatinum compounds to form platinum–mercury-bonded complexes was shown previously for $[PtMe_2(N\text{–}N)]$ (N–N = bipyridine, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), which also have two cis platinum–carbon bonds.[6] The complexes **5** and **6** are likely isostructural and, as evidenced for **5a** by an X-ray analysis, contain two carbon ligands and the mercury atom mutually cis coordinated to platinum. Mercury is furthermore cis coordinated with respect to the carboxylato O atom.

Thus, the complexes can be thought of as resulting from cis addition of $Hg(O_2CR)_2$ to the platinum complex. This is noteworthy in view of the fact that trans oxidative additions of metal–halogen bonds (germanium, tin, and lead halogen compounds) have been reported with $[PtMe_2(N\text{–}N)]$ (N–N = bipyridine, phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) while both cis and trans additions have been reported for carbon and silicon halogen compounds.[31]

From these facts it can be concluded that there is a general reaction pathway for the formation of such platinum–mercury-bonded species. Although others are possible, we propose the reaction scheme given by Scheme II. The first step is formation of a platinum-to-mercury donor bond,[32] resulting in a square-pyramidal intermediate structure. Adduct complexes with a metal-to-mercury donor bond have been reported for several transition metals, e.g., $[(C_5H_5)(CO)_2MHgCl_2]$ (M = Rh, Co[33]) and $[(C_5H_5)_2RuHgX_2]$ (X = Cl, Br).[34] A charge-transfer interaction leading to ionic radicals, as was proposed for the reduction reaction of $HgCl_2$ with hexaethyldilead,[35] seems less valid for the present case (vide infra).

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(30) P. I. van Vliet, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, **188**, 301 (1980).

(31) J. Kuyper, *Inorg. Chem.*, **16**, 2171 (1977); **17**, 77 (1978).

(32) A metal-to-metal donative bond involving platinum atoms is reported for the compound $[Pt_2Me_3(Ph_2PCH_2PPh_2)_2]BF_4$, which was formulated as a square-planar Pt^{II} unit donating its electrons from the d_{z^2} orbital to another Pt^{II} center.[36] Similarly, the compound $[Pt_2Me_4(O_2CR)_2PPh_3]$,[37] previously formulated as a $Pt^{III}Pt^{III}$ species with a covalent metal–metal bond,[7b] may be looked upon as a $Pt^{II}Pt^{IV}$ species with a similar donative metal–metal bond from the Pt^{II} unit to the Pt^{IV} center. In this way coordination of only one phosphine can be explained: the phosphine completes the six-coordination of the Pt^{IV} center, whereas the position at the Pt^{II} center, opposite to Pt^{IV}, is vacant, resulting in a square-pyramidal geometry.

(33) J. L. Dawes and R. D. W. Kemmitt, *J. Chem. Soc. A*, 1072 (1968); I. N. Nowell and D. R. Russell, *Chem. Commun.*, 817 (1967).

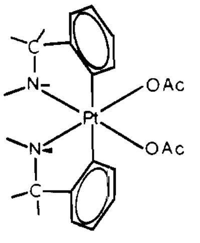
(34) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **6**, 1121 (1972).

There are two different possibilities to go from the intermediate in Scheme II to a six-coordinate platinum compound: i.e., bending away of either the nitrogen or the carbon moiety out of the *xy* plane in the direction of the position trans to mercury. In fact, the reaction proceeds in a unique fashion with only nitrogen migration. This means that the reaction is either completely thermodynamically or completely kinetically controlled. The latter could be interpreted by a greater lability of the Pt–N bond compared to that of the Pt–C bond.

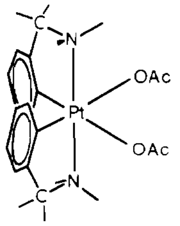
The latter step will be coupled with introduction of one oxygen atom into the coordination sphere of platinum. One can question whether the latter step involves a further electron transfer from platinum to mercury. The solid-state structure of **5a** shows coordination geometries for Pt and Hg that are comparable with those of Pt^{IV} and Hg^{II} when Pt and Hg are conceived as ligands for each other. This may be an indication that the electron pair, originating from the d_{z^2} orbital on platinum, is nicely balanced between the two metals, which can be expressed as a covalent metal–metal bond. This is the situation midway along the two-electron-transfer-reaction pathway, which would result in Pt^{IV} and Hg^0. Possibly, the bridging carboxylato group plays a role in the above electron balance.

The reaction of *trans*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] with Hg-$(O_2CR)_2$ led to the formation of the unstable compound [(2-$Me_2NCH_2C_6H_4)_2PtHg(O_2CR)_2$] (**10**). The proposed structure contains a donative Pt-to-Hg bond, and in that sense it corresponds with the intermediate of the above proposed reaction scheme. Nevertheless, its instability raises questions on the factors governing the reactivity of the several intermediates in the electron-transfer process. Moreover, the next product in the reaction sequence, containing a covalent metal–metal bond, was not observed. Complete electron transfer resulted with elimination of Hg^0, and isolation of [(2-$Me_2NCH_2C_6H_4)_2Pt(O_2CR)_2$] in quantitative yield was possible. These facts exclude ionic radical intermediates in going from *trans*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] to [(2-$Me_2NCH_2C_6H_4)_2Pt]^+$, since such a platinum species might have rearranged its coordination (e.g., from square planar to tetrahedral) and would have been the same as for the cis compound and should have resulted in the same product, in contrast to what is observed.

In fact the product was a mixture of two stereoisomers, in which platinum was six-coordinated with either two C or two N atoms mutually trans. Recently we reported that the same products were obtained with $Tl(O_2CR)_3$ and that the main isomer **11** was thermodynamically unstable and converted, under catalytic action of carboxylic acid, into the second stereoisomer **12**.[13] While generally it is found that *cis*-diorganoplatinum compounds are more stable than *trans*-diorganoplatinum compounds, the structure with the two carbon atoms in the trans position was assigned to stereoisomer **11**.[13]



11



12

Formation of the thermodynamically unfavorable stereoisomer as the main product indicates that the reaction is ruled by kinetic factors. It has been formed by migration of the nitrogen atoms out of the original molecular plane. This is in line with the greater lability of the Pt–N bond as suggested above for the formation of the *cis*-diorganoplatinum–mercury compounds. Furthermore, the presence of the second stereoisomer **12** in variable amounts (0–12%) might be due to impurities in the mercury compounds, which provide catalytically active carboxylato groups, or to a competing reaction.

Support for the proposed reaction sequence and confirmation for the assignments of the structures for the intermediate product **10** and the elimination products **11** and **12** could not be derived from compounds with $Me_2NC_6H_4CH_2$– as the cyclometalated ligand, since we did not succeed in the synthesis of *trans*-[(2-$Me_2NC_6H_4CH_2)_2Pt$]. Reaction of both *cis*- and *trans*-[$PtCl_2(SEt_2)_2$] with [(2-$Me_2NC_6H_4CH_2$)Li(TMEDA)] resulted in the formation of one isomeric form of [(2-$Me_2NC_6H_4CH_2)_2Pt$] (**3**), which was assigned the cis structure. This result may also be due to trans effects governing the stability of cis and trans isomers.[10,38]

The difference in reactivity of the cyclometalated platinum compounds **1** and **2** toward $Hg(O_2CR)_2$ seems to originate solely from the different mutual arrangement of the ligands. In this respect the outcome of reactions of {[2,6-$(Me_2NCH_2)_2C_6H_3$]PtX} with $Hg(O_2CR)_2$ is of importance because in this compound the N-donor atoms are fixed in the trans position. Previously we assigned the product **7**, obtained from the reaction of {[2,6-$(Me_2NCH_2)_2C_6H_3$]PtBr} with Hg-$(O_2CR)_2$, a structure containing a covalent Pt–Hg bond[8] (see Figure 5a). However, on the basis of the ^1H and ^{13}C NMR results and the exchange experiments with free carboxylic acids the structures given by Figure 5b,c might equally well be proposed. Whereas structure b likewise contains a covalent Pt–Hg bond, structure c has a donative Pt-to-Hg interaction, which would imply that, rather than oxidative addition, transfer of Br from Pt to Hg had taken place.

It is important to note that we recently isolated a stable Pt–Hg compound from the reaction of {[2,6-$(Me_2NCH_2)_2C_6H_3$]PtBr} with [Hg(*p*-tolNC(H)N-*i*-Pr)Cl] (*p*-tol = *p*-tolyl) having a molecular geometry analogous to the structure shown in Figure 5c. This was confirmed by an X-ray structure determination.[39] Although the structures a and b cannot be excluded, on the basis of the structure noted above it is assumed that also complexes **7**–**9** belong to a class of compounds having a donative Pt-to-Hg bond. In particular the structure of **9** (X = Y = Cl) would be very much like the structure of the {[2,6-$(Me_2NCH_2)_2C_6H_3$]Pt(formamidino)-HgX_2} complex. The carboxylato ligand, which is isoelectronic with the formamidino and triazenido groups, can likewise stabilize the donative Pt–Hg interaction by a bridging bonding mode. This has been found in many other compounds of this type, e.g., [$(Ph_3P)_2(CO)RhAg(O_2CCF_3)_2$].[40]

Obviously, a conformation with two mutually trans nitrogen ligands stabilizes the Pt-to-Hg donor interaction formed when the $Hg(O_2CR)_2$ electrophile attacks the square-planar Pt complex.

In the case of *trans*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] (**2**) the resulting complex **10** is less stable than the corresponding complexes **7**–**9**, which likewise contain trans N ligands. This is

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(35) J. K. Kochi, "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1978.

(36) M. P. Brown, S. J. Cooper, R. J. Puddephatt, M. A. Thompson, and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1117 (1979).

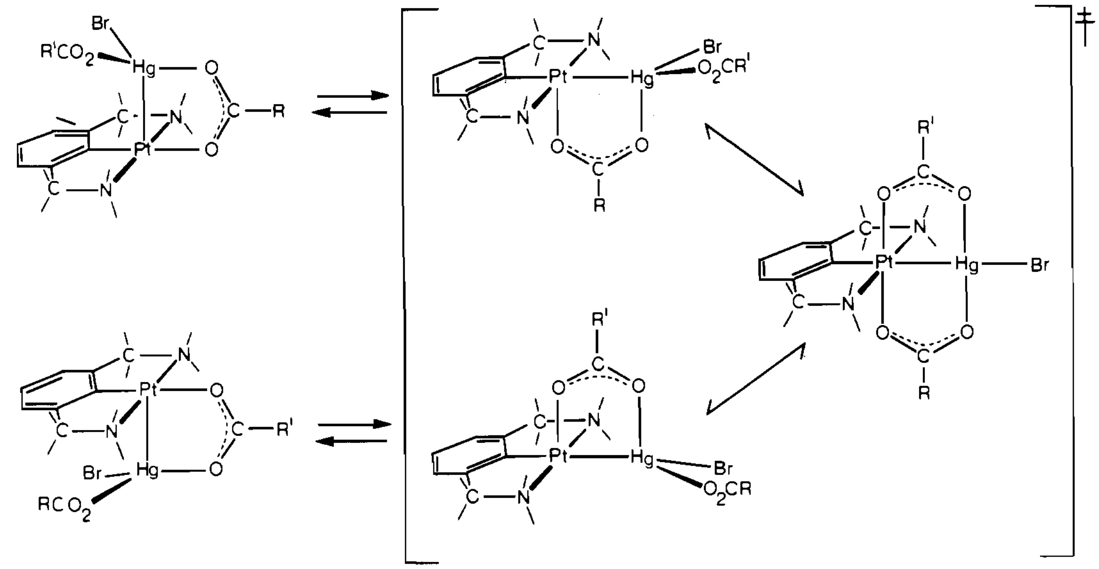
(37) X-ray structure determined by J. D. Schagen, A. R. Overbeek, and H. Schenk, unpublished results.

(38) (a) A. F. M. J. van der Ploeg, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, **222**, 155 (1981). (b) E.g., reaction of *cis*-[(2-$Me_2NCH_2C_6H_4)_2Pd$] with $Hg(O_2CMe)_2$ gave complete transfer of one cyclometalated ligand, resulting in the complexes {[(2-$Me_2NCH_2C_6H_4)Pd(O_2CMe)]_2$} and [(2-$Me_2NCH_2C_6H_4$)Hg-$(O_2CMe)$].[38a]

(39) A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, and A. L. Spek, to be submitted for publication in *Organometallics*.

(40) J. Kuyper and K. Vrieze, *J. Organomet. Chem.*, **107**, 129 (1976).

Scheme III



probably caused by the fact that the square-pyramidal geometry in **7**–**9** is stabilized by the rigid NCN skeleton of the terdentate ligand system. Bending away of a nitrogen ligand into a position trans to the mercury, thus allowing concomitant electron transfer, is not possible. Instead, rearrangement of the ligands around platinum and mercury must have occurred, resulting ultimately in a bridging carboxylato group and transfer of the halogen atom from platinum to mercury. Similar exchanges for heterodinuclear complexes such as $[(Ph_3P)_2(CO)RhAg(RNYNR')Cl]$,[41] $[(COD)(RNYNR')_2RhHgCl]$,[27,30] and $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PtAg(RNYNR')Br\}$[42] (Y = N, CH, CCH_3) also resulted in structures with bridging ligands and chelating ligands bonded to the transition metal and with the halogenide atom bonded to the main-group metal.

There are various indications that in solution the compounds **7**–**9** are dynamic. The NMR resonances of the CH_2 and NMe_2 hydrogen atoms seem to indicate that the molecules **7**–**9** contain an effective plane of symmetry through the C and N centers (see Results). It may very well be possible that these groups are diasterotopic indeed but that the CH_2 and NMe_2 resonances incidentally coincide or, alternatively, these groups become homotopic by inter- or intramolecular processes.

Indeed, for **7** a fluxional process is observed, which involves interchange of the proposed monodentate and bridging carboxylato group. In this respect the monoorganobis(carboxylato) compound **7** differs from the bis(organo)bis(carboxylato) compounds **5** and **6**, which did not show such a dynamic behavior. A possible intramolecular process for **7** involves movement of the mercury atom out of the position perpendicular to the platinum coordination plane, into a position trans to the aryl C atom with retention of the Pt–Hg interaction (see Scheme III). In the resulting transient situation the carboxylato ligands can exchange their respective bridging and monodentate bonding modes, which produces either the initial or the exchanged conformer. The proposed transient situation has great similarity with the structure a (Figure 5), which initially was proposed as a ground-state structure for **7**.[8] A similar mechanism may be operative for compound **8**, containing three carboxylato groups, and can explain the observation of only one carboxylato C_α resonance.

However, for **9**, which has only a bridging carboxylato group, the exchange route proposed for **7** and **8** is not possible. Nevertheless, the CH_2 hydrogen atoms in **9** are isochronous, exhibiting only one somewhat broad resonance. In the related compound $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](p\text{-tolNYNR})PtHgBrCl\}$ the CH_2 hydrogen resonances have a chemical shift difference of 1.5 ppm.[34] These facts may point to the existence of a second exchange mechanism for **9**, e.g., involving initial dissociation of the Pt–Hg donor bond. Further work is needed to clarify these points.

From this work it is clear that rupture of a Pt–O bond is a difficult process, as is illustrated by the stability of the carboxylato groups in **5** and **6** toward intramolecular exchange. (Slightly labile carboxylato groups are observed for **11** while for **12** no Pt–O bond rupture is observed at all.[13]) Furthermore, exchange of the carboxylato groups with free carboxylic acid is possible for the Pt–Hg compounds, but this occurs on a different time scale for carboxylato groups with different coordination properties.

In general, potentially bidentate ligands, present with a different coordination mode in one complex, can be involved in an exchange process. Moreover, such an exchange may proceed via different mechanisms. Robinson et al. have shown that in compounds such as $[Ru(O_2CMe)_2(CO)(PPh_3)_2]$ the monodentate- and chelate-bonded acetato groups can exchange either via a fast process involving cleavage of ruthenium–oxygen bonds trans to phosphorus or via a slower process involving rupture of the ruthenium–oxygen bond trans to the carbonyl.[43] On the basis of the above data, the more stable carboxylato group in the Pt–Hg compounds is assigned to be that bonding to Pt or that bridging the Pt–Hg bond, and consequently, the more labile carboxylato group must be monodentate Hg bonded.

It is noteworthy that during all the exchange experiments with the platinum–mercury compounds the Pt–Hg bond is retained. Also when these complexes are treated with CO, no reaction or decomposition is observed. This points to a rather great stability of this heteronuclear metal–metal bond. It is important to be aware that transmetalation is not observed. As can be expected, oxidative-addition products are favored by hard donor ligands, but for compounds such as $[PtMe_2(bpy)]$ transmetalation reactions, involving the same intermediates, have been reported.[5,6] In the present case,

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(41) P. I. van Vliet, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, **182**, 105 (1979), and references therein.

(42) A. F. M. J. van der Ploeg, G. van Koten, and K. Vrieze, *Inorg. Chem.*, companion paper in this issue.

(43) C. J. Creswell, A. Dobson, D. S. Moore, and S. D. Robinson, *Inorg. Chem.*, **18**, 2055 (1979).

transmetalation may be opposed by internal coordination of the organo group. However, transmetalation of a cyclometalated ligand in similar complexes is possible, as will be shown in a forthcoming paper.[38b]

Conclusions

The reactions of cyclometalated platinum compounds **1**–**4** with $Hg(O_2CR)_2$ involve an oxidative-addition mechanism and most probably proceed via initial nucleophilic attack of the square-planar Pt atom on the Hg center, resulting in formation of an intermediate with a platinum-to-mercury donor bond. The stability of these intermediates depends on the mutual position of the N-donor atoms. The cis intermediates produce via one-electron transfer stable compounds, with a covalent Pt–Hg bond and in which the Pt center is six-coordinate. Differences in the R skeleton, alkyl vs. aryl cyclometalated ligands, as studied for the cis compounds have no influence on the geometry of the complexes formed. In both cases the Hg atom and the organo groups are mutually cis. The reactions of the *cis*-diorgano compounds are governed by kinetic factors; the formed Pt–Hg complexes result from migration of the more labile nitrogen ligand. By contrast, the more stable trans intermediate produces via two-electron transfer and simultaneous transfer of two carboxylato groups the corresponding platinum(IV) dicarboxylato complexes and metallic mercury. When the monoorgano Pt compounds $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PtX\}$ are used in which the N-donor atoms are fixed in the trans position, products are obtained for which structures containing a Pt-to-Hg donor bond have been proposed. This would imply that the terdentate ligand stabilizes, by its rigid skeleton and the trans ligands, a five-coordinate square-pyramidal geometry around Pt^{II}. The possibility of exchange of the carboxylato groups in the Pt–Hg complexes is strongly influenced by their coordination modes. Transfer of cyclometalated nitrogen ligands from platinum to another metal (transmetalation) was not observed during any of the present investigations.

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Registry No. **1**, 38437-99-9; **2**, 38438-00-5; **3**, 37667-90-6; **4a**, 67507-09-9; **4b**, 80484-99; **5a**, 77774-87-9; **5b**, 77774-86-8; **6a**, 80532-09-8; **6b**, 80515-21-5; **7a**, 77774-88-0; **7b**, 77774-85-7; **8b**, 80502-38-1; **9b**, 80502-39-2; **10a**, 80502-40-5; **10b**, 80502-41-6; **11**, 75878-82-9; **12**, 75812-28-1; $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Pt(PPh_3)\}Br$, 80502-42-7; *cis*-$[PCl_2(SEt_2)_2]$, 15442-57-6; $(2\text{-}Me_2NC_6H_4CH_2)Li(TMEDA)$, 80502-43-8; $Hg(O_2CMe)_2$, 1600-27-7; $Hg(O_2C\text{-}i\text{-}Pr)_2$, 19348-33-5.

Supplementary Material Available: A table of observed and calculated structure factors for $[(2\text{-}Me_2NCH_2C_6H_4)_2(MeCO_2)PtHg(O_2CMe)]$ (26 pages). Ordering information is given on any curent masthead page.

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Synthesis of Novel Dinuclear Formamidino and Triazenido Compounds $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](p\text{-}tolNYNR)PtAgBr\}$ (Y = CH, N) Containing a Platinum–Silver Bond

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Received July 15, 1981

Complexes $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3](p\text{-}tolNYNR)PtAgBr\}$ (Y = CH, N, R = Me, Et, *i*-Pr; Y = CH, R = *p*-tolyl (*p*-tol)) are formed by the reaction of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PtBr\}$ with $[Ag(p\text{-}tolNYNR)]_n$. In contrast, $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PtBr\}$ and $[Ag(O_2CR)]_n$ (R = Me, *i*-Pr) undergo ligand methathesis, resulting in formation of the products $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Pt(O_2CR)\}$ and AgBr. The proposed structure for the platinum–silver compounds comprises a five-membered chelate ring in which a Pt^{II}-to-Ag^{I} donor bond is bridged by a triazenido (Y = N) or formamidino (Y = CH) group, while the bromide atom, having migrated from the Pt^{II} center, is on the Ag^{I} atom. The bridging bonding mode is inferred from the observation of both $J(^{195}Pt\text{-}^{1}H)$ (±38 Hz) and $J(^{107,109}Ag\text{-}^{1}H)$ (±16 Hz) for the central H atom of the N–C(H)–N skeleton in the formamidino compounds. Except for *p*-tolNC(H)N-*p*-tol, the compounds exist in two isomers, the relative ratio of which is discussed in terms of steric and electronic factors of the alkyl groups (R), which influence the course of the intimate formation mechanism. Furthermore, it is suggested that the basicity of the Pt center, which has effectively been enhanced by the mutually trans N-donor atoms, contributes to the stability of the Pt–Ag donor bond.

Introduction

In previous reports it has been shown that square-planar d^8-electron species such as $[L_2(CO)MX]$ (L = Ph_3P, Ph_3As, $PhMe_2P$; M = Rh, Ir; X = Cl, Br, I) can form stable covalently bonded dinuclear complexes with Hg^{II} salts[1-4] and stable M-to-M′ donor-bonded complexes with Cu^{I} and Ag^{I} compounds.[5-8] The formation of these complexes can be ascribed to the basic character of the group 8B metal center in $[L_2(CO)MX]$, and the presence of bridging ligands such as nitrato,[7] perchlorato,[7] carboxylato,[2,7,9] amidino, and triazenido[2,3,8] groups determines to a large extent the stability of these dinuclear complexes.

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[1] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1965).
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