abilities of the ligands toward the soft acid $MeHg^{II}$, with lower values of $^2J(^1H-^{199}Hg)$ indicating greater σ ability; and thus, for ligands with similar log K_H (*as measured*), the N-substituted imidazole and pyrazole ligands are better σ donors than pyridines.

Acknowledgment. We thank the University of Tasmania for a Special Research Project Grant, the Australian Research Grants Committee for financial support, and Mr. A. P. Arnold for assistance with measurement of log K_H values.

Registry No. [MeHg(NMePyz)]NO_3, 80834-23-7; [MeHg(Me_2NMePyz)]NO_3, 80834-25-9; [MeHg(Me_3NMePyz)]NO_3, 80834-27-1; [MeHg(Me_2NPhPyz)]NO_3, 80834-29-3; [MeHg(NBzlPyz)]NO_3, 80834-31-7; [MeHg(NpyPyz)]NO_3, 81420-87-3; [MeHg(Pyz_2CH_2)]NO_3, 81420-89-5; NMePyz, 930-36-9; Me_2NMePyz, 1072-91-9; Me_3NMePyz, 1073-20-7; Me_2NPhPyz, 1131-16-4; NBzlPyz, 10199-67-4; $MeHgNO_3$, 2374-27-8.

Crystal Structure and Molecular Geometry of a Square-Pyramidal Platinum(II) Complex, [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(μ-{(*p*-tol)NC(H)N(*i*-Pr)})HgBrCl], Containing a Pt^{II}-to-Hg^{II} Donor Bond

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The structure of [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(μ-{(*p*-tol)NC(H)N(*i*-Pr)})HgBrCl] (*p*-tol = *p*-tolyl) was determined by X-ray methods and refined to $R = 0.058$, using diffractometer intensities of 5021 independent reflections. The crystals are monoclinic of space group $P2_1/c$ with $a = 9.192$ (5) Å, $b = 12.016$ (5) Å, $c = 26.895$ (4) Å, $\beta = 94.30$ (3)°, and $Z = 4$. The discrete heterodinuclear molecular units comprise a pseudo-square-pyramidally surrounded platinum center. The square plane contains the platinum coordinated terdentate monoanionic ligand [2,6-$(Me_2NCH_2)_2C_6H_3$]$^-$ (Pt–N(3) = 2.097 (9) Å, Pt–N(4) = 2.080 (10) Å, and Pt–C(9) = 1.909 (11) Å), and the two cyclometalated rings show unique puckering geometry (mirror plane type). The fourth coordination site in the square plane is occupied by the donor nitrogen atom of a (*p*-tol)N group (Pt–N(1) = 2.155 (9) Å of a nonsymmetrically substituted formamidino ligand. A HgBrCl unit resides at the apical position of the square pyramid (Pt–Hg = 2.8331 (7) Å), and the formamidino ligand bridges to this mercury center to which it bonds with an (*i*-Pr)N unit (Hg–N(2) = 2.156 (11) Å). The five-membered heterometallic ring is nonplanar, and viewed along the Pt–Hg axis there is a small twist of the HgBrClN unit so that the M–N bonds are not eclipsed (N(2)–Hg–Pt–N(1) = –16.5 (4)°). The title compound can be considered as the first example of a complex formed by coordination of the bidentate [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt{N(R)C(H)N(R′)}] ligand, in which the Pt center and the N(R′) atom act as donor sites to a post-transition-metal salt (HgX_2).

Introduction

Compounds with a bond between two dissimilar metal atoms have been an area of particular interest.[1] In our laboratory a large series of complexes have been synthesized involving d^8 Rh^I (Ir^I) complexes and complexes of Cu^I, Ag^I, Hg^{II}, and Tl^{III} post transition metals having a d^{10} electronic configuration.[2-4] The complexes can formally be divided into those with a covalent metal–metal bond (type I) and those with a metal-to-metal donor bond (type II).[5,6]

Recently, while extending this work to d^8 Pt^{II} complexes, we observed that the geometry of the platinum complexes had a large influence on the products formed. For example, whereas the reaction of *trans*-[(2-$Me_2NCH_2C_6H_4)_2$Pt] with $Hg(O_2CR)_2$ resulted in elimination of metallic mercury and formation of [(2-$Me_2NCH_2C_6H_4)_2Pt^{IV}(O_2CR)_2$], reaction of the corresponding cis isomer with $Hg(O_2CR)_2$ afforded quantitatively the stable Pt–Hg bonded complexes [(2-$Me_2NCH_2C_6H_4)_2$Pt(μ-O_2CR)Hg(O_2CR)] (R = Me, *i*-Pr): see Figure 1.[7] An X-ray structure determination of this latter compound with R = Me revealed the presence of a six-coordinate Pt center and a Pt–Hg bond (2.513 (1) Å) bridged by a carboxylato group.[7,8] Formation of this compound, which belongs to type I, was proposed to occur via an intermediate containing a Pt-to-Hg donor bond (type II).[7] A possible reason for the different reaction

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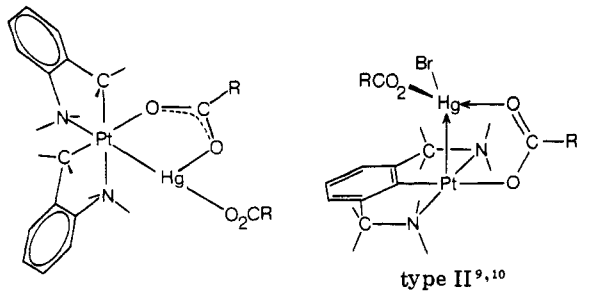

type I[7]

type II[9,10]

Figure 1. Two examples of heterodinuclear Pt–Hg compounds.

courses with *cis*- and *trans*-[(2-$Me_2NCH_2C_6H_4)_2$Pt] lies in the orientation of the N donor atoms which in the trans isomer causes enhanced nucleophilicity of the Pt center.[7]

Recently we succeeded in the isolation of stable heterodinuclear complexes using the terdentate monoanionic ligand system [2,6-$(Me_2NCH_2)_2C_6H_3]^-$, which has a fixed trans arrangement of the N donor sites, and formamidino and triazenido ligands instead of carboxylato groups.[9,10] On the basis of NMR data a type II structure was proposed for these compounds,[11] [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(μ-{*p*-tol)NYNR}MX_n] (Y = CH, N; R = Me, Et, *i*-Pr; M = Ag, X = Br; M = Hg, X_2 = Br, Cl) (see Figure 1).

In this paper we report the X-ray structure determination of one of the Pt–Hg compounds, [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(μ-{*p*-tol)NC(H)N(*i*-Pr)})HgBrCl], thus providing direct evidence for the Pt-to-Hg bonding. Furthermore, the implications of the presence of both a nonsymmetrical formamidino ligand and a rigid terdentate ligand on the molecular geometry are discussed.

Experimental Section

The title compound was prepared according to the method recently described.[10] Single crystals suitable for X-ray structure determination were obtained by crystallization from a CH_2Cl_2/pentane mixture.

Structure Determination and Refinement of $C_{23}H_{34}BrClHgN_4Pt\cdot CH_2Cl_2$. An orange crystal of the title compound was glued on top of a glass fiber and transferred to an ENRAF-NONIUS CAD4 diffractometer for data collection. Unit cell dimensions, their corresponding standard deviations, and a redundant data set were obtained by procedures standard at our laboratory[12] using zirconium-filtered MoKα radiation. The crystal data and details of the data collection and structure refinement are summarized in Table I. The intensity of one reflection was monitored after every hour of X-ray exposure time. A decay of up to 16% at the end of the data collection was observed. The data were subsequently corrected for absorption (via an approximate description of the crystal boundaries) and Lorentz and polarization effects and averaged into a unique set of data in the previously described way.[12] The structure was solved via location of the Pt and Hg from the Patterson synthesis and the other atoms by standard difference Fourier techniques, except for the hydrogen atoms that were located on calculated positions. Refinement by blocked full-matrix least-squares techniques converged at R = 0.058. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined in the riding mode with one overall isotropic thermal parameter.

In addition a rotation parameter was refined for each methyl moiety. Weights based on counting statistics were introduced in the final stages of the refinement. A final difference Fourier

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Table I. Crystal Data and Details of the Structure Analysis

a. Crystal Data

formula	$C_{23}H_{34}BrClHgN_4Pt\cdot CH_2Cl_2$
mol wt	962.52
space group	no. 14; $P2_1/c$
cryst system	monoclinic
a, Å	9.192 (5)
b, Å	12.016 (5)
c, Å	26.895 (4)
β, deg	94.30 (3)
V, Å^3	2962 (2)
Z	4
D(calcd), g·cm^{-3}	2.158
D(obsd), g·cm^{-3}	2.16
F(000), electrons	1808
μ(Mo Kα), cm^{-1}	111
approx cryst size, mm	0.15 × 0.45 × 0.30
cryst vol, mm^3	0.020
no. of grid points	560
max transmissn	0.201
min transmissn	0.053

b. Data Collection

θ(min), θ(max)	0.1, 27.5
radiation, Å	0.710 69 (Mo Kα) Zr filtered
ω-2θ scan, deg	0.60 + 0.35 tan θ
data set	$\pm h,+k,\pm l$
horizontal and vertical aperture, mm	3.0, 3.0
max time per reflctn, s	120
ref reflctn	3, 0, 8
total reflctn data	14134
total unique reflctn	6165
obsd data ($I > 2.5\sigma(I)$)	5021

c. Refinement

no. of refined parameters	329
weighting scheme	$w^{-1} = (\sigma^2(F) + 0.006F^2)/1.3047$
final R_F and R_{wF}	0.058, 0.068

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x/a	y/b	z/c
Hg	0.15274 (6)	0.22051 (4)	0.32429 (2)
Pt	0.28419 (4)	0.04610 (4)	0.38259 (1)
Br	0.3229 (3)	0.3095 (3)	0.2674 (1)
Cl(1)	0.0753 (4)	0.3681 (3)	0.3803 (1)
Cl(2)	0.4297 (7)	0.5237 (6)	0.4364 (2)
Cl(3)	0.510 (1)	0.5835 (8)	0.3384 (3)
N(1)	0.0866 (9)	−0.0397 (8)	0.3572 (3)
N(2)	0.020 (1)	0.0846 (9)	0.2943 (4)
N(3)	0.223 (1)	0.0952 (8)	0.4529 (3)
N(4)	0.415 (1)	−0.0088 (9)	0.3278 (4)
C(1)	0.007 (1)	−0.008 (1)	0.3171 (4)
C(2)	0.034 (1)	−0.132 (1)	0.3821 (4)
C(3)	−0.120 (1)	−0.149 (1)	0.3837 (4)
C(4)	−0.169 (1)	−0.246 (1)	0.4058 (5)
C(5)	−0.073 (1)	−0.325 (1)	0.4299 (4)
C(6)	0.071 (1)	−0.299 (1)	0.4309 (5)
C(7)	0.123 (1)	−0.211 (1)	0.4058 (4)
C(8)	−0.133 (2)	−0.422 (1)	0.4545 (7)
C(9)	0.457 (1)	0.128 (1)	0.4024 (4)
C(10)	0.577 (1)	0.124 (1)	0.3750 (5)
C(11)	0.705 (1)	0.182 (1)	0.3921 (5)
C(12)	0.706 (2)	0.238 (1)	0.4347 (6)
C(13)	0.582 (1)	0.243 (1)	0.4631 (6)
C(14)	0.465 (1)	0.192 (1)	0.4476 (5)
C(15)	0.315 (1)	0.194 (1)	0.4686 (5)
C(16)	0.074 (1)	0.126 (1)	0.4568 (5)
C(17)	0.267 (1)	0.008 (1)	0.4883 (5)
C(18)	0.542 (2)	0.071 (1)	0.3251 (5)
C(19)	0.470 (2)	−0.118 (1)	0.3457 (6)
C(20)	0.354 (2)	−0.024 (1)	0.2779 (5)
C(21)	−0.066 (2)	0.103 (1)	0.2439 (5)
C(22)	0.034 (2)	0.089 (2)	0.2051 (7)
C(23)	−0.152 (2)	0.207 (1)	0.2425 (7)
C(24)	0.451 (3)	0.473 (2)	0.3756 (8)

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

Bond Distances

Hg-Pt	2.8331 (7)	N(2)-C(21)	1.53 (2)	C(6)-C(7)	1.35 (2)
Hg-Cl(1)	2.465 (3)	N(3)-C(15)	1.50 (2)	C(9)-C(14)	1.43 (2)
Hg-N(2)	2.16 (1)	N(3)-C(17)	1.45 (2)	C(9)-C(10)	1.38 (2)
Hg-Br	2.509 (3)	N(3)-C(16)	1.44 (2)	C(10-C(18)	1.49 (2)
Pt-N(1)	2.155 (9)	N(4)-C(19)	1.48 (2)	C(10)-C(11)	1.41 (2)
Pt-C(9)	1.91 (1)	N(4)-C(18)	1.52 (2)	C(11)-C(12)	1.33 (2)
Pt-N(3)	2.097 (9)	N(4)-C(20)	1.43 (2)	C(12)-C(13)	1.42 (2)
Pt-N(4)	2.08 (1)	C(2)-C(7)	1.38 (2)	C(13)-C(14)	1.28 (2)
Cl(2)-C(24)	1.77 (2)	C(2)-C(3)	1.43 (2)	C(14)-C(15)	1.53 (2)
Cl(3)-C(24)	1.77 (3)	C(3)-C(4)	1.40 (2)	C(21)-C(22)	1.45 (2)
N(1)-C(2)	1.40 (1)	C(4)-C(5)	1.42 (2)	C(21)-C(23)	1.48 (2)
N(1)-C(1)	1.32 (1)	C(5)-C(8)	1.47 (2)		
N(2)-C(1)	1.28 (2)	C(5)-C(6)	1.36 (2)		

Bond Angles

Pt-Hg-Cl(1)	108.94 (8)	C(1)-N(2)-C(21)	119 (1)	C(4)-C(5)-C(6)	116 (1)
Pt-Hg-N(2)	81.5 (3)	C(16)-N(3)-C(17)	111 (1)	C(5)-C(6)-C(7)	123 (1)
Pt-Hg-Br	113.17 (7)	Pt-N(3)-C(17)	107.9 (8)	C(2)-C(7)-C(6)	123 (1)
Cl(1)-Hg-N(2)	126.3 (3)	Pt-N(3)-C(15)	107.1 (7)	Pt-C(9)-C(10)	121.1 (9)
Br-Hg-Cl(1)	106.8 (1)	Pt-N(3)-C(16)	117.5 (8)	C(10)-C(9)-C(14)	119 (1)
Br-Hg-N(2)	117.0 (3)	C(15)-N(3)-C(16)	107.3 (9)	Pt-C(9)-C(14)	120.2 (8)
Hg-Pt-N(1)	82.2 (2)	C(15)-N(3)-C(17)	105.2 (9)	C(9)-C(10)-C(11)	119 (1)
Hg-Pt-C(9)	94.8 (4)	Pt-N(4)-C(20)	119.9 (8)	C(9)-C(10)-C(18)	111 (1)
Hg-Pt-N(3)	99.1 (3)	Pt-N(4)-C(19)	104.7 (8)	C(11)-C(10)-C(18)	129 (1)
Hg-Pt-N(4)	95.1 (3)	Pt-N(4)-C(18)	108.5 (8)	C(10)-C(11)-C(12)	119 (1)
N(1)-Pt-C(9)	177.0 (4)	C(18)-N(4)-C(19)	110 (1)	C(11)-C(12)-C(13)	122 (1)
N(1)-Pt-N(3)	98.3 (3)	C(18)-N(4)-C(20)	107 (1)	C(12)-C(13)-C(14)	119 (1)
N(1)-Pt-N(4)	98.2 (4)	C(19)-N(4)-C(20)	107 (1)	C(13)-C(14)-C(15)	129 (1)
N(3)-Pt-C(9)	82.9 (4)	N(1)-C(1)-N(2)	125 (1)	C(9)-C(14)-C(15)	109 (1)
N(4)-Pt-C(9)	81.2 (4)	C(3)-C(2)-C(7)	116 (1)	C(9)-C(14)-C(13)	122 (1)
N(3)-Pt-N(4)	159.5 (4)	N(1)-C(2)-C(3)	120 (1)	N(3)-C(15)-C(14)	113 (1)
Pt-N(1)-C(1)	121.8 (8)	N(1)-C(2)-C(7)	124 (1)	N(4)-C(18)-C(10)	110 (1)
Pt-N(1)-C(2)	122.9 (7)	C(2)-C(3)-C(4)	119 (1)	N(2)-C(21)-C(23)	112 (1)
C(1)-N(1)-C(2)	115.3 (9)	C(3)-C(4)-C(5)	123 (1)	N(2)-C(21)-C(22)	108 (1)
Hg-N(2)-C(1)	123.5 (8)	C(4)-C(5)-C(8)	120 (1)	C(22)-C(21)-C(23)	116 (1)
Hg-N(2)-C(21)	117.6 (8)	C(6)-C(5)-C(8)	125 (1)	Cl(2)-C(24)-Cl(3)	109 (1)

map showed no significant features. The final values of the refined positional parameters are given in Table II (except for the U(iso) = 0.074 (6) Å^2 overall temperature factor of the hydrogen atoms, see supplementary material).

Neutral scattering factors were taken from ref 13 and corrected for anomalous dispersion effects.[14] All calculations were carried out on either the in-house Eclipse S/230 minicomputer with the program ILIAS[15] (structure determination and refinement) or the CYBER-175 computer at the University of Utrecht computer center with the programs from the EUCLID package[16] (molecular geometry and illustrations).

Discussion

Description of the Structure. The crystal structure of [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(μ-{(p-tol)NC(H)N(i-Pr)})-HgBrCl] consists for four discrete heterodinuclear molecules and four CH_2Cl_2 molecules per unit cell that are mutually separated by normal van der Waals distances. The molecular structure along with the adopted numbering scheme is shown in a PLUTO drawing (Figure 2). A ORTEP stereodrawing (Figure 3) shows the thermal vibration ellipsoids in a view down the Pt–Hg bond. Interatomic distances and bond angles are listed in Table III.

The five-coordinate platinum center has a nearly square-pyramidal geometry by virtue of the N,N′,C terdentate ligand 2,6-$(Me_2NCH_2)_2C_6H_3$, one N atom of the formamidino ligand, and the apically positioned mercury atom. The Pt–Hg distance amounts to 2.8331 (7) Å. The formamidino ligand is present in a bridging bonding mode with the second N atom (N(2)) coordinated to the mercury atom. The latter atom is an asymmetric center as a result of coordination of four dissimilar atoms, i.e. Pt, Br, Cl, and N(2) with the two possible stereoisomers present in equal proportions.

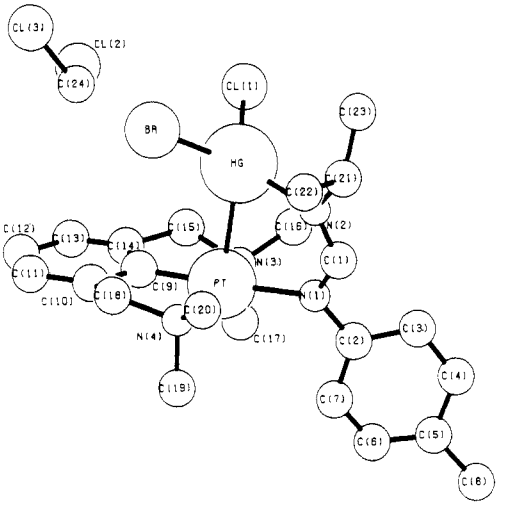

Figure 2. PLUTO drawing of the molecular structure of [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(μ-{(p-tol)NC(H)N(i-Pr)})HgBrCl]·CH_2Cl_2 along with the adopted numbering scheme.

Platinum–Mercury Bond. The Pt–Hg distance in the title compound (2.8331 (7) Å) is much longer than that of previously reported distorted octahedral [(2-$Me_2NCH_2C_6H_4)_2$Pt(μ-O_2CMe)Hg(O_2CMe)] (2.513 (1) Å)[7,8] and that of square-planar *cis*-[$(Ph_3P)_2(F_3C)$PtHg(CF_3)] (2.569 (2) Å).[17] The latter two Pt–Hg distances point to

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(14) Cromer, D. T.; Libermann, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(15) ILIAS, a DG-Eclipse S/230 adaption and extension (by A. L. Spek) of the SHELX-76 package (by G. Sheldrick).

(16) EUCLID, a program package for the calculation and tabulation of geometrical data and structure illustrations including an extended version of the program PLUTO (S. Motherwell, B. Clegg) by A. L. Spek.

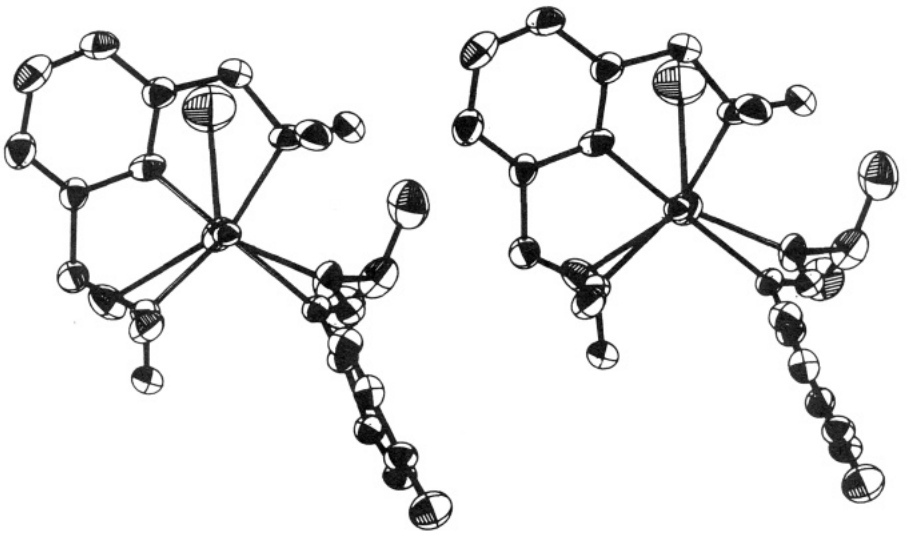


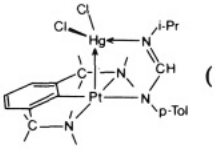
Figure 3. A ORTEP stereodrawing showing the thermal vibration ellipsoids (50% probability) as viewed down the Pt–Hg axis.

a high covalent character of the metal–metal bond (sum of the radii for Pt and Hg amounts to 2.53 Å).[7] This allows a description of these bonds as formal Pt^{III}–Hg^{I} and Pt^{I}–Hg^{I}, respectively, with the smaller covalent radius of Pt^{III} compared to Pt^{I} accounting for the shorter Pt^{III}–Hg^{I} bond.

The title compound is one of the few complexes in which a square-pyramidal coordination around platinum(II) has been found. This geometry in combination with the longer Pt–Hg distance of 2.8331 (7) Å leads to a Pt–Hg interaction which is best described as a Pt-to-Hg donor bond (type II)[9,10] with both metals in a formal oxidation state of 2.

A comparable bonding situation is met with in recently reported $[Pt_2Me_3(Ph_2PCH_2PPh_2)_2]PF_6$ which contains a square-pyramidally surrounded Pt(1) atom with a donor bond to the apically positioned Pt(2) atom (Pt(1)–Pt(2) = 2.769 (1) Å).[18] The relatively small ^1J(Pt(1)–Pt(2)) value of 332 Hz was taken as evidence for a fairly weak Pt(1)–Pt(2) interaction.[19] For covalently Pt–Pt-bonded complexes ^1J(Pt–Pt) values up to 9000 Hz have been reported.[20] Gathering of similar data for the Pt–Hg compound of type I and II from ^{195}Pt NMR spectra was unsuccessful because of extensive line broadening resulting from incomplete collapse of spin–spin coupling to the ^{14}N nuclei of the 2,6-$(Me_2NCH_2)_2C_6H_3$ ligand. However, for the platinum–silver complexes [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt(μ-{(*p*-tol)NC(H)NR}AgBr] (R = Me, Et, *i*-Pr, *p*-tol), which are structurally related to the present Pt–Hg complexes, a $^1J(^{195}Pt–^{109}Ag)$ value of about 170 Hz was observed by INEPT ^{109}Ag NMR spectrometry,[11] thus supporting the presence of a platinum-to-silver interaction. The geometry of these heterodinuclear Pt–Ag and Pt–Hg complexes suggests that the platinum uses a hybrid orbital having a high percentage of d_{z^2} character for its bonding to mercury or silver. The resulting low s content of such an orbital could then explain the low value of the $^1J(^{195}Pt–^{109}Ag)$.[11] Furthermore, these heterodinuclear complexes can be viewed as derived by complex formation of the post-transition-metal salt (HgX_2 of AgX) with the bidentate [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt{N(*p*-tol)C(H)N(*i*-Pr)}] ligand in which the Pt center and the formamidino N atom act as donor sites. This view has support from the trans-metalation route via which these complexes are formed[9,10] as well as from the observation that direct interaction of the platinum–formamidino ligand with $HgCl_2$ yields the corresponding platinum–mercury compound (eq 1).

[{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt{N(*p*-tol)C(H)N(*i*-Pr)}] + $HgCl_2$ →



(1)

The "bite angle"of this new ligand system, which may be expected to be close to 80° (vide infra), is very suitable for the formation of five-membered chelate rings.

Coordination around Mercury. The mercury atom has a pseudotetrahedral geometry with distortions caused by the "bite angle" Pt–Hg–N(2) of 81.5 (3)° of the [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pt{N(*p*-tol)C(H)N(*i*-Pr)}] ligand. The HgBrClN(1) unit is rotated around the Pt–Hg axis (N(2)Hg–PtN(1) = −16.5 (4)°) in such a direction that steric interaction between the halide atoms and the CH_2NMe_2 groups on platinum are reduced. The bulky bromine atom has moved away from the methyl group on N(4) in the direction of the aryl ring (BrHg–PtC(9) = 46.9 (4)°) while the chlorine atom has moved in the direction of N(3) (ClHg–PtC(9) = −71.7 (4)°). This is clearly illustrated by the projection along the Pt–Hg bond (Figure 3).

Coordination around Platinum. When compared to atomic separations in [(2-$Me_2NCH_2C_6H_4)_2Pt(\mu$-$O_2CMe)$-$Hg(O_2CMe)$],[8] the corresponding Pt–C and Pt–N bond lengths in the present Pt–Hg complex are much shorter: i.e., Pt–C(9) = 1.909 (11) Å vs. 2.012 (9) and 2.004 (9) Å; Pt–N(3) = 2.097 (10) Å and Pt–N(4) = 2.080 (10) Å vs. 2.223 (8) and 2.317 (7) Å.

The puckering in the cyclometalated rings[21] that is observed in complexes with the terdentate ligand 2,6-

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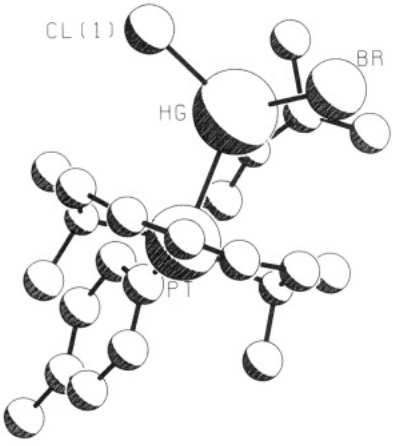

Figure 4. Projection along Pt–N(1) axis showing the puckering of the five-membered cyclometalated rings and the conformation of the Pt–HgNCN part of the molecule.

$(Me_2NCH_2)_2C_6H_3$ may be of either the mirror plane or the twofold axis symmetry variety. One example of the latter type is found in the structure of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(\mu\text{-}Cl)Pd\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]BF_4$ in which the $N(Me_2)$ atoms are at opposite sides of the aryl plane.[23] The present compound is an example of the former type with both N(3) and N(4) donor atoms on the same side of the aryl plane away from the mercury atom (N(3), –0.37 (9) Å, and N(4), –0.26 (8) Å); see Figure 4. Accordingly the two methylene carbon atoms C(15) and C(18) are both positioned above the aryl–PtN(1) plane (+0.15 (9) and +0.23 (8) Å, respectively). As a result the N–Pt–Hg angles (99.1 (3) and 95.0 (3)°) deviate from the ideal value of 90° for a square pyramid. However, these angles are much smaller than 120° which would have been appropriate for an alternative trigonal-bipyramidal description with the two $N(Me_2)$ atoms and mercury in the equatorial plane around platinum. The virtually planar aryl ring and the formamidino N(1) are mutually trans (C(9)–Pt–N(1) = 176.9 (4)°) with the Pt and N(1) atoms lying only –0.09 (8) and –0.08 (8) Å, respectively, out of the least-squares plane defined by the aryl C atoms.

The Bridging Formamidino Ligand. The observed coordination mode of the nonsymmetrically substituted formamidino ligand is in agreement with the structure deduced from the ^1H NMR spectra of this Pt–Hg complex,[10] i.e., *p*-tolyl–N bonded to platinum and isopropyl–N to mercury. The fact that the M–N distances are almost identical (Pt–N(1) = 2.155(9) Å and Hg–N(2) = 2.156 (11) Å) is in remarkable contrast to the nonsymmetrically bridging groups in $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(\mu\text{-}O_2CMe)Hg(O_2CMe)]$ (Pt–O(1) = 2.152 (6) Å and Hg–O(2) = 2.621 (8) Å)[7] and [(cycloocta-1,5-diene)((*p*-tol)NNNEt)$_2$IrHgCl] (Ir–N(1) = 2.10 (1) Å and Hg–N(3) = 2.42 (1) Å).[24] Furthermore, the five-membered ring, formed by the bridging N–C–N ligand and the heterodinuclear Pt–Hg unit, is nonplanar (Hg, +0.15 (3) Å; Pt, –0.15 (3) Å; N(1), 0.19 (3) Å; N(2), –0.18 (3) Å; C(1), –0.01 (3) Å). Distortions from planarity are often observed for bridged heteronuclear[24] and homodinuclear complexes (e.g., $[Me_4(\mu\text{-}O_2CMe)_2Pt_2(SEt_2)_2]$[25,26]). The extent of nonplanarity may be connected with the length of the M–M′ bond which is spanned by the triatomic ligand system. This has recently been discussed for complexes containing a M–P–CH_2–P–M unit.[27]

The substituents on the formamidino ligand, *p*-tolyl and isopropyl, occupy special conformations (see Figure 4). The *p*-tolyl group is positioned such that one of the two ortho hydrogen atoms lies rather close to the Pt center (3.03 (3) Å). Such nonbonding M···H distances even down to values of 2.6 Å have been observed.[28,29] The more bulky isopropyl group is bonded to the N(Hg) atom with the methyl groups turned away from the central formamidino hydrogen atom. These facts indicate that steric interactions between formamidino substituents stabilize the syn relative to the gauche conformation (see discussion in ref 10) and thus to a large extent determine the overall configuration of the $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pt\{N(R)CHN(R')\}$ part of this complex.

Further work is currently in progress to explore the potential of this novel ligand system $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}M\{N(R)YN(R')\}$ for chelate bonding to metal centers $M'L_n$ and its stabilization of M–M′ bonds.

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Registry No. $C_{23}H_{34}BrClHgN_4Pt\cdot CH_2Cl_2$, 82043-92-3.

Supplementary Material Available: Observed and calculated structure factors, final anisotropic thermal parameters, two tables containing least-squares planes, and some relevant torsion angles for $C_{23}H_{34}BrClHgN_4Pt\cdot CH_2Cl_2$ (38 pages). Ordering information is given on any current masthead page.

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