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Interaction of Methylmercury(II) with N-Substituted Pyrazoles. σ-Donor Ability of Pyridines, Imidazoles, and Pyrazoles

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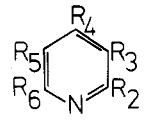
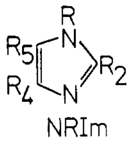
N-Substituted pyrazoles (L) form complexes $[MeHgL]NO_3$ for which $^2J(^1H-^{199}Hg)$ decreases with increasing basicity of L in a very similar manner to that observed for closely related N-substituted imidazole complexes. The relationships differ from that for complexes of pyridines and suggest that for ligands of similar log K_H (pK_a of LH^+ in 50% dioxane–water) the N-substituted imidazoles and pyrazoles are better σ donors toward $MeHg^{II}$ than pyridines. The complexes $[MeHgL]NO_3$ [L = *N*-(2-pyridyl)pyrazole and bis(*N*-pyrazolyl)methane] have the ligands chelated to $MeHg^{II}$ when in methanol.

Introduction

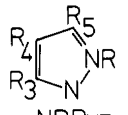
The coupling constant $^2J(^1H-^{199}Hg)$ for the methylmercury(II) group in complexes $[MeHgL]NO_3$ decreases with increasing basicity of pyridyl[1,2] and N-substituted imidazolyl[3] donor ligands L. Although the linear relationship between $^2J(^1H-^{199}Hg)$ and log K_H (pK_a of LH^+ in 50% dioxane–water) is not identical for those two types of donor ligand, the general trend has been useful for more complex systems, e.g., determination of the binding sites for interaction of $MeHg^{II}$ with guanosine.[4] To further explore this relationship, we have extended these studies to include N-substituted pyrazoles (NRPyz, abbreviations given in Experimental Section) which have lower basicities than both pyridines and N-substituted imidazoles (NRIm); these results have been briefly reported.[5]



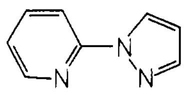
py



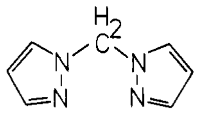
NRIm



NRPyz



NpyPyz



Pyz_2CH_2

X-ray diffraction studies reveal that both NpyPyz and Pyz_2CH_2 in $[MeHgL]NO_3$ are chelated to $MeHg^{II}$,[6] and these complexes have been included in this study to determine the coordination behavior of the ligands in solution.

Experimental Section

Reagents. For synthesis of ligands the reagents pyrazole, 3,5-dimethylpyrazole (Fluka), phenylhydrazine (BDH), and 3,4,5-trimethylpyrazole (Columbia) were used as received. The reagents acetylacetone (distilled), diethyl ether (washed with aqueous 10% $NaHSO_3$ and dried with $CaCl_2$ followed by passage through a column of 4A molecular sieves), dimethyl sulfate (over K_2CO_3 until neutral to Congo red paper, distilled from CaO), methanol (ref 7, p 268), ethanol (ref 7, p 269), and acetone (ref 7, p 275 (method a)) were purified as indicated in parentheses.

Table I. Analytical Data for the New Complexes

complex	% calcd C	% calcd H	% calcd Hg	% found C	% found H	% found Hg
$[MeHg(NMePyz)]NO_3$ [a]	16.7	2.5	55.8	16.8	2.3	55.6
$[MeHg(Me_2NMePyz)]NO_3$	21.7	3.4	51.7	21.7	3.5	51.6
$[MeHg(Me_3NMePyz)]NO_3$	23.9	3.8	50.0	23.7	3.6	49.4
$[MeHg(Me_2NPhPyz)]NO_3$ [b]	32.0	3.4	44.6	31.6	3.3	45.0
$[MeHg(NBzlPyz)]NO_3$ [b]	30.3	3.0	46.0	30.0	3.1	45.8

[a] NMePyz = *N*-methylpyrazole. [b] $Me_2NPhPyz$ = *N*-phenyl-3,5-dimethylpyrazole. Other ligands similarly abbreviated.

The ligands *N*-methylpyrazole[8] (NMePyz, yield 23%, bp 127–134 °C (lit.[9] 126–127 °C)), 1,3,5-trimethylpyrazole[8] ($Me_2NMePyz$, 22%, bp 45–49 °C (5 mm) (lit.[10] 170 °C (755 mm))), 1,3,4,5-tetramethylpyrazole[8] ($Me_3NMePyz$, 22%, bp 72–73 °C (8 mm) (lit.[11] 190–193 °C)), *N*-phenyl-3,5-dimethylpyrazole[12] ($Me_2NPhPyz$, 80%, bp 114–118 °C (5 mm) (lit.[12] 144–148 °C (17 mm))), and *N*-benzylpyrazole[13] (NBzlPyz, 52%, bp 128–131 °C (11 mm) (lit.[13] 134–136 °C (15 mm))) were prepared as reported. The ligands have satisfactory ^1H NMR spectra in $CDCl_3$ and CD_3OD, and their $MeHg^{II}$ derivatives have satisfactory spectra in CD_3OD (Table II).

Complexes. Methylmercuric nitrate[4] and $[MeHgL]NO_3$ (L = *N*-(2-pyridyl)pyrazole and bis(*N*-pyrazolyl)methane)[5] were prepared as described previously; the remaining complexes, except for that of *N*-benzylpyrazole, were obtained as crystals from acetone solutions of $MeHgNO_3$ and ligand (yield 7–71%). The *N*-benzylpyrazole complex formed on evaporation of the solution to dryness and required recrystallization from ethanol (58%). Characterization data for new complexes are presented in Table I. Microanalyses were by the Australian Microanalytical Service, Melbourne.

Physical Measurements. ^1H NMR spectra at 100 MHz were measured in a JEOL JNM-4H-100 spectrometer. Chemical shifts in CD_3OD were measured relative to 1,4-dioxane internal standard; shifts upfield of 1,4-dioxane are taken as negative (Table II).

Apparent protonation constants log K_H (pK_a of LH^+ in 50% dioxane–water) for all ligands were measured following the general procedure described earlier[1,3] modified to account for the lower basicities of some of the ligands studied here. Thus, instead of

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Table II. ^{1}H NMR Data for the Complexes[a]

complex	Me_{Hg}[b]	$\|^2J(^1H-^{199}Hg)\|$[c]	ligand protons[b,d,e] $H_{3(5)}$[f]	H_4	R
$[MeHg(NMePyz)]NO_3$	−2.56	234.3	4.41 d (2.7), 4.24 d (2.4)	2.97 m	0.48 (NMe)
$[MeHg(Me_2NMePyz)]NO_3$	−2.52	228.8		2.56	0.30 (NMe) −1.23, −1.31
$[MeHg(Me_3NMePyz)]NO_3$	−2.53	227.2			0.28 (NMe) −1.30, −1.38, −1.68
$[MeHg(Me_2NPhPyz)]NO_3$	−2.81	229.7		2.80	4.016 (NPh) −1.17, −1.39
$[MeHg(NBzlPyz)]NO_3$	−2.89	234.7	4.67 d (2.3), 4.3 d (2.4)	3.05 m	2.00 (CH_2) 3.6–3.9 m (Ph)
$[MeHg(NpyPyz)]NO_3$	−2.51	245.7		3.33 m	4.93 db ($H_{6'}$) 4.4–4.69 m ($H_{3(5),3',4'}$) 3.99 m ($H_{5'}$), $J_{5',6'} \simeq 5$
$[MeHg(Pyz_2CH_2)]NO_3$	−2.50	243.8	4.54 d (2.4), 4.20 (1.8)	2.91 m	3.16 (CH_2)

[a] Solutions in CD_3OD. Atom numbering schemes are shown in the Introduction. [b] Chemical shift from internal 1,4-dioxane; accuracy to ca. 0.005 ppm. [c] Accuracy to ca. ±0.5 Hz. The sign of the coupling constant is assumed to be negative.[14] [d] Key: m, multiplet; d, doublet; b, broad. [e] First order analysis.[1] [f] Differentiation between H_3 and H_5 not attempted ($J_{x,4}$ given in parentheses).

titration of 0.1 M HCl with 0.01 M solutions of ligand with 1:1 equivalence of HCl and ligand occurring for a 50-mL solution of 50% dioxane in water,[1,3] 1 M HCl was added to 0.1 M solutions of ligands using an autoburette with 1:1 equivalence occurring for a 10-mL solution. For ligands of high log K_H both procedures give similar results, e.g., 2,2′-bipyridyl, 3.24 (with 1 M HCl) and (ref 1, 3.18 with 0.1 M HCl). Measured pH values below 3.0 were corrected by using a plot of expected pH vs. measured pH for the average of three titrations in the absence of ligand.

Results

Formation of complex ions $[MeHg]^+$ in methanol is assumed for unidentate pyridine, *N*-substituted imidazole, and *N*-substituted pyrazole ligands, as both pyridines and *N*-methylimidazole are known to form complexes with appreciable formation constants in water; e.g., complexes $[MeHgL]^+$ have log K_{MeHg} = 4.8,[15] 4.72[16] (pyridine), 4.69 (3-methylpyridine[17]), 5.03 (4-methylpyridine[17]), and 6.96 (*N*-methylimidazole[18]). Polydentate ligands also form stable complex ions, e.g., 2,2′-bipyridyl (log K_{MeHg} = 5.86,[19] 5.93[16]) and 2,2′:6′,2″-terpyridyl (log K_{MeHg} = 6.35[16]).

For unidentate N-substituted pyrazoles the coupling constant $^2J(^1H-^{199}Hg)$, for complexes in methanol, varied with log K_H in a similar manner to complexes of pyridines and N-substituted imidazoles (Figure 1), with the poorer correlation reflecting lower precision in determination of lower K_H values. The relationships for N-substituted pyrazoles (correlation coefficients in parentheses)

$$^2J(^1H-^{199}Hg) = -2.64 \log K_H + 235.9 \text{ Hz} \quad (-0.93)$$

and N-substituted imidazoles[3]

$$^2J(^1H-^{199}Hg) = -2.50 \log K_H + 234.6 \text{ Hz} \quad (-0.98)$$

are displaced from that for pyridines (altered from the previously quoted relationship[2,3,5,20] to include the complex of $pyCHPh_2$[20])

$$^2J(^1H-^{199}Hg) = 2.96 \log K_H + 241.6 \text{ Hz} \quad (-0.99)$$

by approximately 5 Hz.

The $Me_2NPhPyz$ chemical shift of the $MeHg^{II}$ proton for complexes of Me_2PhPyz and NBzlPyz occurs 0.25–0.37 ppm upfield from those for NMePyz, $Me_2NMePyz$, and $Me_3NMePyz$, consistent with orientation of the rings resulting in anisotropic shielding of the methyl group. This effect occurs for several complexes of pyridyl and N-substituted imidazolyl ligands,[1-3,20,21] and for the 2-benzylpyridine complex this orientation results from presence of a weak Hg···π interaction.[22]

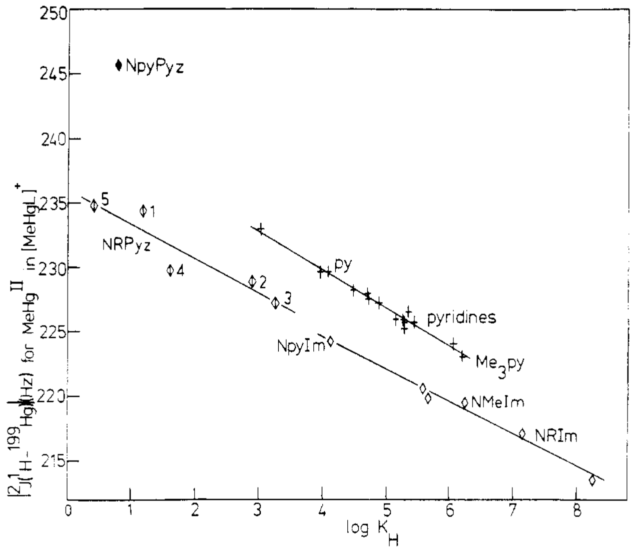
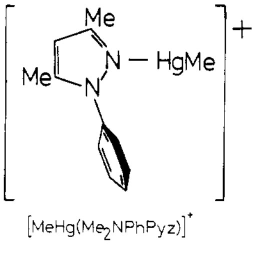
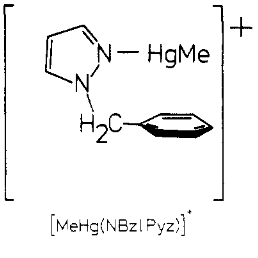


Figure 1. $|^2J(^1H-^{199}Hg)|$ for $[MeHgL]NO_3$ (in CD_3OD) vs. log K_H for the ligands (L). Log K_H values are those obtained for a 50% dioxane–water mixture as solvent: (+) L = pyridines; (◊) N-substituted imidazoles; (⧫) N-substituted pyrazoles. Values of $^2J(^1H-^{199}Hg)$ for N-substituted pyrazole complexes are given in Table II, and values of $^2J(^1H-^{199}Hg)$ and log K_H for the other complexes are given elsewhere.[2,3,20] N-substituted pyrazoles with log K_H values in parentheses are (1) NMePyz (1.19), (2) $Me_2NMePyz$ (2.90), (3) $Me_3NMePyz$ (3.26), (4) $Me_2NPhPyz$ (1.62), (5) N-BzlPyz (0.42), and NpyPyz (0.78).



$[MeHg(Me_2NPhPyz)]^+$



$[MeHg(NBzlPyz)]^+$

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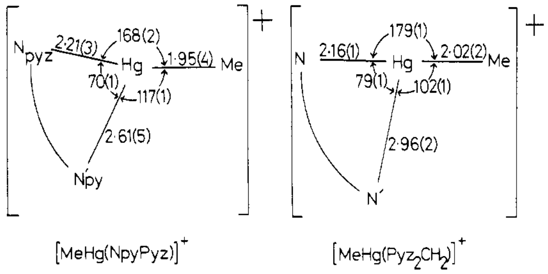


Figure 2. Structures of $[MeHg(NpyPyz)]^+$ and $[MeHg(Pyz_2CH_2)]^+$. The NpyPyz comples has Hg···O distances of 2.97 (3), 3.07 (3), and 3.14 (3) Å, and the Pyz_2CH_2 complex has Hg···O distances of 2.88 (2) and 2.90 (2) Å to form dimeric units $\{[MeHgL]NO_3\}_2$.[6]

Consistent with chelation by NpyPyz and Pyz_2CH_2 in methanol, as found in the solid state[5] (Figure 2), their $MeHg^{II}$ complexes have δ(MeHg) −2.51 and −2.50, respectively, similar to those observed for NMePyz, $Me_2NMePyz$, and $Me_3NMePyz$ (−2.52–2.56 ppm) and well below values for complexes of ligands having an uncoordinated ring adjacent to mercury, −2.81 ($Me_2NPhPyz$) and −2.89 ppm (NBzlPyz). The NpyPyz complex has $^2J(^1H-^{199}Hg)$ = 245.7 Hz, higher than expected for unidentate pyridine or N-substituted pyrazole complexes (Figure 1) and consistent with chelation; e.g., complexes of bidentate 2,2′-bipyridyl[1,23] and py_2CH_2[3,21] have $^2J(^1H-^{199}Hg)$ ca. 6 Hz higher than complexes of unidentate pyridines of similar log K_H. The Pyz_2CH_2 complex has a similar value for $^2J(^1H-^{199}Hg)$, 243.8 Hz, but has a log K_H value too low to measure with the procedure used.

Discussion

For complexes MeHgX and $[MeHgL]^+$ the coupling constant $^2J(^1H-^{199}Hg)$ correlates with the pK_a of HX[18,24-29] or LH^+,[1-3] with each type of ligand giving a different relationship, but similar to those in Figure 1; e.g., for $X^- = RO^-$

$$^2J(^1H-^{199}Hg) = -5.72pK_a + 250.2$$

and for $X^- = RS^-$

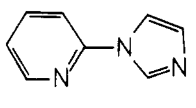
$$^2J(^1H-^{199}Hg) = -3.81pK_a + 193.9 \text{ Hz}^{28}$$

(In these examples the pK_a values were estimated[28] by using the method of Barlin and Perrin.[30])

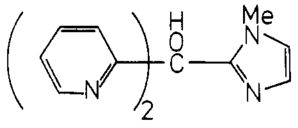
For a particular type of ligand higher basicity or pK_a, reflecting donor ability toward the "hard acid" H^+, also renders a ligand a better donor toward the "soft acid" $MeHg^{II}$, leading to a lower value for the coupling constant. These, and similar relationships, have been attributed to the effect of the major contribution of the Fermi contact interaction to the coupling constant.

For ligands of similar basicity but different donor atom the coupling constant is lower for complexes with higher formation constants; e.g., cysteine containing the soft RS^- group has pK_a = 8.53,[31], similar to that of NH_3 (9.32), but the cysteine complex has log K_{MeHg} = 15.7,[15] $^2J(^1H-^{199}Hg)$ = 174.0,[32] and the NH_3 complex has log K_{MeHg} = 7.25, $^2J(^1H-^{199}Hg)$ = 214.1 Hz.[33]

Relative values of coupling constants thus give an estimate of the order of strength of binding of ligands to $MeHg^{II}$; e.g., formation constants for selenol complexes have not been reported, but since selenol complexes have $^2J(^1H-^{199}Hg)$ lower than analogous thiolates,[34,35] it has been concluded that RSe^- binds more strongly than RS^-.[34] Similarly, the *N*-methylimidazole complex with $^2J(^1H-^{199}Hg)$ = 219.5[3] has formation constant log K_{MeHg} = 6.96[18] and log K_H = 6.25,[3] but the pyridine complex with higher $^2J(^1H-^{199}Hg)$, 229.6 Hz,[1] has both lower log K_{MeHg}, 4.8[15] and 4.72[16] and log K_H, 4.09.[1] Consistent with these results polydentate ligands containing both imidazolyl and pyridyl rings bind more strongly via the imidazolyl ring; e.g., *N*-pyridylimidazole binds via the imidazolyl ring only[3] and $py_2(NMeIm)COH$ acts as a tridentate in the solid state (bidentate in methanol) with Hg–N(NMeIm) = 2.13 (1) Å and Hg···N(py) = 2.66 (1) and 2.77 (1) Å.[20]



NpyIm



$py_2(NMeIm)COH$

An estimate of relative order of bond strengths from $^2J(^2H-^{199}Hg)$ is generally satisfactory provided that the $^2J(^1H-^{199}Hg)$-pK_a correlations are well separated, so that ligands of one donor type will always form complexes having a lower coupling constant than the other type despite variations in p*Ka*, e.g., MeHgOR and MeHgSR (see equations above and Figure 1 in ref 28). Care is required for ligands with similar $^2J(^1H-^{199}Hg)$-pK_a relationships such as pyridines and N-substituted imidazoles and pyrazoles (Figure 1). Thus 1,3,4,5-tetramethylpyrazole has $^2J(^1H-^{199}Hg)$ lower than that for pyridine but higher than that for 2,4,6-trimethylpyridine.

In addition, when comparing relationships for closely related ligands, it is essential that log K_H (pK_a) values be obtained under identical conditions (50% dioxane–water for Figure 1), e.g., reported pK_a values for pyridine in water cover the wide range 5.15–5.52,[36] but values for 10 pyridines in water, obtained by the same workers,[37] give a relationship $^2J(^1H-^{199}Hg) = -2.80pK_a + 244.3$ Hz with an excellent correlation coefficient, −0.99,[2] and different from that obtained by using log K_H values measured in 50% dioxane–water (see above). Similarly, different types of ligands may have log K_H values altered in a different way on change of solvent conditions, and $^2J(^1H-^{199}Hg)$ should refer to measurements in the same solvent.

Thus, with Hg–L bonding in $[MeHgL]^+$ (L = pyridines, N-substituted imidazoles, and pyrazoles) considered to be essentially σ bonding the relative values of coupling constants are expected to indicate the relative σ-bonding

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abilities of the ligands toward the soft acid $MeHg^{II}$, with lower values of $^{2}J(^{1}H-^{199}Hg)$ 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.

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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, $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pt(\mu\text{-}\{(p\text{-tol})NC(H)N(i\text{-}Pr)\})HgBrCl]$, Containing a Pt^{II}-to-Hg^{II} Donor Bond

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The structure of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pt(\mu\text{-}\{(p\text{-tol})NC(H)N(i\text{-}Pr)\})HgBrCl]$ (*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 $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ (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 $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pt\{N(R)C(H)N(R')\}]$ 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*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ with $Hg(O_2CR)_2$ resulted in elimination of metallic mercury and formation of $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt^{IV}(O_2CR)_2]$, reaction of the corresponding cis isomer with $Hg(O_2CR)_2$ afforded quantitatively the stable Pt–Hg bonded complexes $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt(\mu\text{-}O_2CR)Hg(O_2CR)]$ (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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