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Electron−Ligand Interchange Reactions between Palladium(II) Complexes and Mercury and Single-Crystal X-ray Characterization of the d^{10}−d^{10} Binuclear $[Hg_2(dppm)_2Cl_3]Cl$ Complex

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The reactivity of Hg with group VIII metal complexes has been widely investigated,[2] where one of the prime interests is to model the amalgamation with various metals.[3] The resulting products are generally compounds where the Hg atoms oxidatively insert into the M−L bond or add onto the M−M bonds (if any).[2,3] In this work, rapid reactions between the Pd(dppm)X_2 complexes (dppm = $((C_6H_5)_2P)_2CH_2$; X = Cl, Br) and Hg(l) are observed, but for the first time, the products do not fall into one of the categories mentioned above. We now wish to report unprecedented examples of electron−ligand interchange reactions where all ligands belonging to the Pd^{II} complexes are transferred to the Hg^0 metal, in exchange for two electrons, to form novel d^{10}−d^{10} species $[Hg_2(dppm)_2(\mu\text{-}X)(X)_2]^+X^-$ (X = Cl (**1**), Br (**2**)). One of the products has been characterized by X-ray crystallography (X = Cl), and the Hg−Hg interactions have been investigated by Raman spectroscopy.

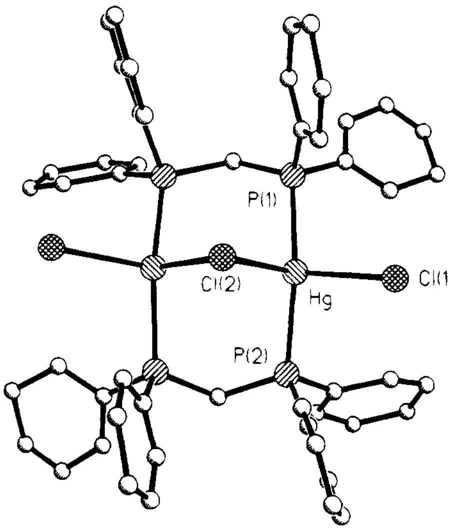

Figure 1. Molecular structure and atom labeling for **1**. The H atoms and Cl^- anion are omitted for clarity. Selected bond distances: Hg−HgA = 3.342(3), Hg−Cl(1) = 2.587(9), Hg−P(1) = 2.452(8), Hg−P(2) = 2.456(9), Hg−Cl(2) = 2.763(9) Å.

When Hg(l) is poured into a Pd(dppm)X_2 (X = Cl, Br)/acetone solution and the mixture is allowed to sit for a period of time, a white precipitate slowly deposits at the Hg(l) surface, and a Pd mirror coats the inner walls of the reaction flasks (as identified by X-ray fluorescence). The reactions are quasi-quantitative, and the products were identified by X-ray crystallography (X = Cl), NMR spectroscopy, and FAB mass spectroscopy:[4]

$$Pd^{II}(dppm)X_2 + Hg(l) \xrightarrow{X + Cl, Br} {}^1/_2[Hg^{II}_2(dppm)_2(\mu\text{-}X)(X)_2]X + Pd(0) \quad (1)$$

The reactions proceed via an interchange process of electrons (redox) and ligands (addition and elimination) where the Pd complexes reductively eliminate the halide (and dppm) ligands, while the Hg(l) oxidatively adds these same ligands. These are the first reactions in which both metals (from the starting materials) are not found within the same product. Hg(l) appears to act as a reducing agent for the Pd^{II} complexes, which, upon a two-electron reduction, eliminate two halides. However, the primary step of the reaction is very unlikely to be an outer-sphere electron transfer from Hg(l) to the Pd^{II} complex.[5] Rather an inner-sphere redox process is more likely to occur via the

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(2) See for instance: (a) Yamamoto, Y.; Takahashi, K.; Matsuda, K.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1987**, 1833. (b) Ehara, K.; Kumagaya, K.; Yamamoto, Y.; Takahashi, K.; Yamazaki, H. *J. Organomet. Chem.* **1991**, *410*, C49. (c) Albinati, A.; Dahmen, K.-H.; Demartin, F.; Forward, J. M.; Longley, C. J.; Mingos, M. P.; Venanzi, L. M. *Inorg. Chem.* **1992**, *31*, 2223. (d) Tanase, T.; Horiuchi, T.; Yamamoto, Y.; Kobayashi, K. *J. Organomet. Chem.* **1992**, *440*, 1. (e) Yamamoto, Y.; Yamazaki, H. *Organometallics* **1993**, *12*, 933. (f) Ehara, K.; Kumagaya, K.; Yamamoto, Y.; Takahuski, K.; Yamazaki, H. *J. Organomet. Chem.* **1991**, *410*, C43.

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(4) (a) Preparation of **1**: To a solution of Pd(dppm)Cl_2 (0.25 g, 4.5×10^{-4} mol) in acetone was added Hg(l) (1 mL). The mixture was stirred for 12 h. A grayish white solid was obtained. The precipitate was washed with ether and dried in vacuo. Yield: 80%. Mp: 250 °C. ^{1}H-NMR (CD_2Cl_2): δ 5.054 ppm at 298 K (br, CH_2) and at 250 K (pentet; J(HP) = 7.8 Hz, CH_2) , 7.2−7.8 ppm (complex, C_6H_5). ^{31}P-NMR (decoupled, $CDCl_3$ at 298 K): δ 21.96 ppm (sharp) vs H_3PO_4. Anal. Calcd: C, 45.77; Hz, 3.36. Found: C, 45.58; Hz, 3.70. FAB MS: m/z 621 (Hg(dppm)$Cl^{\bullet+}$), 653 (Hg(dppm)$Cl_2^{\bullet+}$), 1005 (Hg(dppm)$_2$$Cl^{\bullet+}$), 1037 (Hg(dppm)$_2Cl_2^{\bullet+}$). UV−vis (acetonitrile): 254 nm (59 800 M^{-1} cm^{-1}), 224 nm (60 000 M^{-1} cm^{-1}). Raman (solid state): 266 cm^{-1} (ν(HgCl)), 48 cm^{-1}(ν(Hg_2); see text). The crystals suitable for X-ray crystallography were grown from a CH_2Cl_2/pentane mixture containing a small amount of water. (b) Preparation of **2**: Pd(dppm)Br_2 (0.05 g, 7.7×10^{-5} mol) was dissolved in acetone (25 mL). Hg(l) (1 mL) was added under stirring. After 12 h of stirring, the yellow solution became clear. The product was obtained from an acetone/pentane mixture. Yield: 80%. Mp: 190 °C. ^{1}H-NMR (CD_2Cl_2): δ 5.01 ppm at 250 K (pentet, J(HP) = 8.0 Hz, CH_2). ^{31}P-NMR ($CDCl_3$, decoupled at 298 K): δ 21.47 ppm (sharp) vs H_3PO_4. FAB MS: m/z 665 (Hg(dppm)$Br^{\bullet+}$), 1049 (Hg(dppm)$_2Br^{\bullet+}$). Raman (solid state): 204 cm^{-1} (ν(HgBr)), 46 cm^{-1} (ν(Hg_2)). In the case where Pd(dppm)I_2 was used with Hg(l), the isolated product was not dimeric, but analysis was consistent with the monomeric formulation Hg(dppm)I_2 and was not investigated further.

(5) (a) The reduction potential for Pd(dppm)Cl_2 in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate is observed at −1.21 V vs SCE by polarography. Electrochemical behavior for this derivative and related species will be published in due course. The outer-sphere electron transfer from Hg^0 to the Pd^{II} center appears thermodynamically very unfavorable since the $E°$ value of the Hg^{2+}/Hg couple is 0.851 V vs NHE. (b) The presence of a small amount of free dppm (less than 5%) has occasionally been detected by ^{31}P-NMR (in uncleaned samples). Similarly, the presence of HgX_2 as a residual impurity has been observed from elemental analysis and vibrational spectroscopy, again in unrecrystallized materials.

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insertion of the Hg metal into the Pd^{II} complex (presumably in the Pd–X bond), consistent with other examples known in the literature.[2] The precipitation of Pd(0) can be explained by the possible formation of "Pd(dppm)", which is known to be active in some reactions involving low-valent Pd complexes.[6] To test this hypothesis, the following reactions have been tested and are consistent with our hypothesis:[7]

$$Pd^0_2(dppm)_3 + 2Hg^{II}Cl_2 \rightarrow \mathbf{1} + dppm \qquad (2)$$

$$2Hg^{II}Cl_2 + 2dppm \rightarrow \mathbf{1} \qquad (3)$$

No reaction was observed between $Pd_2(dppm)_3$ and Hg(l) or between $Pd(dppm)Cl_2$ and $HgCl_2$. The weakly soluble compound **1** (Figure 1)[8] exhibits a binuclear structure where two Hg atoms are bridged by two dppm ligands and one chloride ion.[9] Each Hg atom is also covalently bonded to a terminal Cl atom[9] and exhibits a distorted tetrahedral (P_2HgCl_2) structure. The bonded Cl atoms are all on a same plane in a "W" shape. The last Cl^- ion is located inside the cavity (formed by four of the phenyl groups of the dppm ligands) but does not interact with the Hg^{2+} centers ($r(Hg^{2+}\cdots Cl^-)$ = 3.466(9) Å).[10]

The dimers (**1** and **2**) belong to a larger family of bridged diphosphine d^{10}–d^{10} complexes (M = Pd^0, Pt^0, Ag^I, Au^I; see references cited below for examples) in which weak M$\cdots$M interactions exist. The Hg$\cdots$Hg distance is 3.343(3) Å, which is slightly above the sum of the van der Waals radii ($2r_{vdW}$ = 3.01 Å).[11] Hg$\cdots$Hg interactions are present since molecules of the type $Hg_2(g)$ are well-known[12] and belong to the so-called van der Waals molecule family. The low-frequency Raman spectra for the two compounds have been obtained in order to measure $\nu(Hg_2)$.[13] Since the polarization studies failed,[14] the assignments for $\nu(Hg_2)$ are made on the basis of intensity[15] and the comparison with literature data where the $r(M_2)$ values are similar.[13] $\nu(Hg_2)$ is readily detected at 48 and 46 cm^{-1} for **1** and **2**, respectively, being the most intense peaks below 500 cm^{-1}, and compares very favorably with data reported for $Ag_2(dmpm)_2Br_2$ (dmpm = $((CH_3)_2)P)_2CH_2$, $r(Ag_2)$ = 3.60 Å, $\nu(Ag_2)$ = 48 cm^{-1}),[15b] for the $Ag_2(dmb)_2X_2$ complexes (dmb = 1,8-diisocyano-*p*-menthane; X = Cl, $r(Ag_2)$ = 3.451 Å, $\nu(Ag_2)$ = 42 cm^{-1}; X = Br, $r(Ag_2)$ = 3.345 Å, $\nu(Ag_2)$ = 42 cm^{-1}; X = I , $r(Ag_2)$ = 3.378 Å, $\nu(Ag_2)$ = 33 cm^{-1}),[11c] and for $Au_2(tmb)Cl_2$ (tmb = 2,5-dimethyl-2,5-diisocyanohexane; $r(Au_2)$ = 3.536 Å,[17] $\nu(Au_2)$ = 36 cm^{-1} [15b]). To estimate the Hg_2 force constant, *F*, the diatomic approximation and equations relating to linear X–M–M–X systems cannot adequately be used. On the other hand, reparametrized Herschbach–Laurie relationships (H–L; $r(M_2) = a \ln F(M_2) + b$) have proven to be very useful in estimating either $F(M_2)$ (in mdyn $Å^{-1}$) or $r(M_2)$ (in Å).[11,15b] Using literature data,[13] a H–L equation is designed:

$$r(Hg_2) = -0.24 \ln F(Hg_2) + 2.69 \qquad (4)$$

where the correlation coefficient (σ) is 0.96 for 10 data points. The uncertainties are ~±0.16 Å in the Hg_2 cases.[13] For **1**, eq 4 predicts that $F(Hg_2)$ is ~0.07 mdyn $Å^{-1}$. Finally, the comparison of the d^{10}–d^{10} species (M = fifth-row elements) $Pt_2(dppm)_3$, $[Au_2(dppm)_2](PF_6)_2$, and **1**, where $r(M_2)$ are 3.025,[18] 3.045,[15b] and 3.342 Å, $\nu(M_2)$ are 102.5,[19] 69,[15] and 48 cm^{-1}, and $F(M_2)$ are 0.60,[19] 0.28,[15b] and ~0.07 mdyn $Å^{-1}$, respectively, clearly indicates that the charge (promoting both metal orbital contractions and M$\cdots$M repulsion) plays an important role in the M$\cdots$M interactions.

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Supplementary Material Available: Text giving further experimental details, tables giving data collection parameters, all atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and Raman data and interpretation as well as the literature data necessary to design the H–L equation for Hg_2 systems, and figures giving a complete atom-numbering diagram, low-frequency micro Raman spectra, and a plot of ln $F(Hg_2)$ vs $r(Hg_2)$ (16 pages). Ordering information is given on any current masthead page.

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(7) $Pd_2(dppm)_3$ was prepared from literature procedure: Stern, E. W.; Maples, K. *J. Catal.* **1972**, *27*, 120.

(8) (a) The crystal was selected after examination under a polarizing microscope for homogeneity. The unit cell parameters and the reflection data were measured on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα radiation. The intensity of three standard reflections gradually decreased during the data collection. At the end of the collection, the intensity was reduced by about 20%. Scaling on the standard reflections was made as usual. The crystal data and the experimental details are listed in supplementary Table S3. Corrections were made for Lorentz–polarization effects, and the anomalous dispersion terms of Hg, Cl, and P were included in the calculations. The coordinates of the Hg atoms were determined from direct methods, and the positions of all the other non-hydrogen atoms were found by the usual Fourier methods. A residual peak was assigned to a water molecule which was also detected by IR and ^{1}H-NMR spectroscopy. The refinement was done by full-matrix least-squares calculations. The refinement of the other enantiomorphic structure gave higher *R* values. The H atoms were fixed at their calculated positions (riding model) with U = 0.08 $Å^2$. The scattering curves from ref 8b (second citation) were used. The calculations were done with a SHELXTL PLUS system.[8c] (b) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. (c) SHELXTL PLUS, PC version (1990–3), Siemens Analytical X-Ray Instruments Inc., Madison, WI.

(9) (a) $r(Hg-Cl)_{bridge}$ = 2.763(9) Å. The sum of the ionic radii (r_{ion}) is $r_{ion}(Hg^{2+}) + r_{ion}(Cl^-)$ = 1.10 + 1.67 = 2.77 Å.[8b] (b) Cotton, F. A.; Wilkinson, G.; Gauss, P. L. *Basic Inorganic Chemistry*, 2nd ed.; Wiley: Toronto, 1987; p 60. (c) $r(Hg-Cl)_{term}$ = 2.587(9) Å. The sum of the covalent radii (r_{cov}) is $r_{cov}(Hg) + r_{cov}(Cl)$ = 1.51 + 0.99 = 2.50 Å.

(10) The sum of the van der Waals radii is 3.31 Å (r_{vdW} = 1.75 and 1.56 Å for Hg and Cl, respectively).[9b] No counterion metathesis or halide exchange reaction was attempted in this work.

(11) (a) Recent reports on Pd$\cdots$Pd and Pt$\cdots$Pt species have demonstrated that M$\cdots$M interactions are observed even at distances exceeding $2r_{vdW}$, via the measurements of Raman-active ν(M$\cdots$M) (stretching frequencies).[11b,c] (b) Harvey, P. D.; Truong, K. D.; Aye, K. T.; Drouin, M.; Bandrauk, A. D. *Inorg. Chem.* **1994**, *33*, 2347. (c) Perreault, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1993**, *32*, 1901.

(12) $Hg_2(^1\Sigma_g^+)$, $r(Hg_2)$ = 3.63 Å, $\nu(Hg_2)$ = 18.5 cm^{-1}; $Hg_2(^1\Sigma_u^+)$, $r(Hg_2)$ = 3.61 Å, $\nu(Hg_2)$ = 19.7 cm^{-1}: Van Zee, R. D.; Blankespoor, S. C.; Zwier, T. S. *J. Chem. Phys.* **1988**, *88*, 4650.

(13) All the data are provided in the supplementary materials.

(14) Under dilute conditions, the peaks below 100 cm^{-1} are completely covered by the intense Raleigh scatterings.

(15) (a) For the fifth-row elements, $\nu(M_2)$ is the most intense signal in the low-frequency region: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley: New York, 1986. (b) See also for Au_2 systems: Perreault, D.; Drouin, M.; Michel, A.; Miskowski, V. M.; Schaefer, W. P.; Harvey, P. D. *Inorg. Chem.* **1992**, *31*, 695 and the references therein.

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(19) Harvey, P. D.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 2145.