Dynamic Trimetallic Clusters

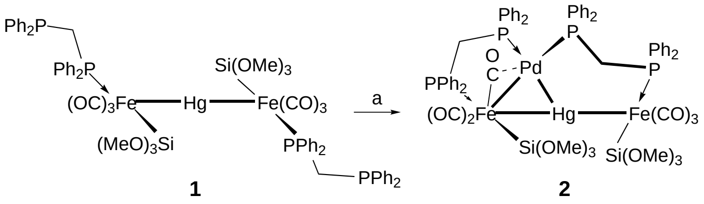
An Unusual Dynamic Fe-Hg-Pd Cluster with a Palladium(0) Fragment Stabilized by d^{10}–d^{10} Heterometallic Bonding**

Walter Schuh, Pierre Braunstein, Marc Bénard, Marie-Madeleine Rohmer, and Richard Welter*

Dedicated to Professor Achim Müller on the occasion of his 65th birthday

The nature of the bonding within metal clusters remains an area of continuing interest; electronic delocalization is often associated with the occurrence of isomeric metal cores and their possible interconversion.[1,2] There is a delicate energetic balance between metal–metal and metal–ligand interactions, and this is even more complex in heterometallic systems owing to the inherent diversity and polarity of the interactions. Unexpected features are therefore not uncommon, and we report here on a heterotetranuclear complex in which a coordinatively unsaturated 14-electron Pd^0 center is bonded to an Fe-Hg-Fe chain through helically arranged diphenylphosphanylmethane (dppm) ligands, along which it exhibits an oscillating motion. Extended Hückel calculations show that the two-electron three-centered Fe/Hg/Pd bonding, which involves interactions between the d^{10} centers Pd^0 and Hg^{II}, results partly from donation from the Fe–Hg σ bond to PdL$_2$, and mostly from back-bonding from the d^{10} Pd^0 center to the d^{10} Hg center and to a semibridging CO group.

The new compound [Hg{Fe[Si(OMe)$_3$](CO)$_3$(μ-dppm)}$_2$Pd] (**2**) was obtained quantitatively (as calculated by ^{31}P NMR spectroscopy) by the reaction of the chain complex [Hg{Fe[Si(OMe)$_3$](CO)$_3$(dppm-P)}$_2$] (**1**)[3] with a Pd^0 precursor (Scheme 1).[4]



Scheme 1. a) 1/2 [Pd$_2$(dba)$_3$]·CHCl$_3$

A single-crystal structural determination[8] revealed that the tetranuclear {Fe$_2$HgPd} core is nearly planar, with the Pd atom located at an asymmetric bridging position across one Hg–Fe bond and being much closer to the Hg center (269.15(8) pm) than to Fe1 (291.26(10) pm, Figure 1). The Pd–Hg bond length is shorter than in compounds with Pd–Hg d^8–d^{10} contacts (287.97(8)–309.8(1) pm).[10]

The P-Pd-P angle of 129.03(6)° and the Pd–P bond lengths of 232.2(2) and 233.2(2) pm are in the range found in trigonal-planar 16-valence-electron Pd^0 complexes.[11] Ignoring the Pd–Fe1 contact, the coordination geometry about each Fe atom may be described as distorted octahedral, with the

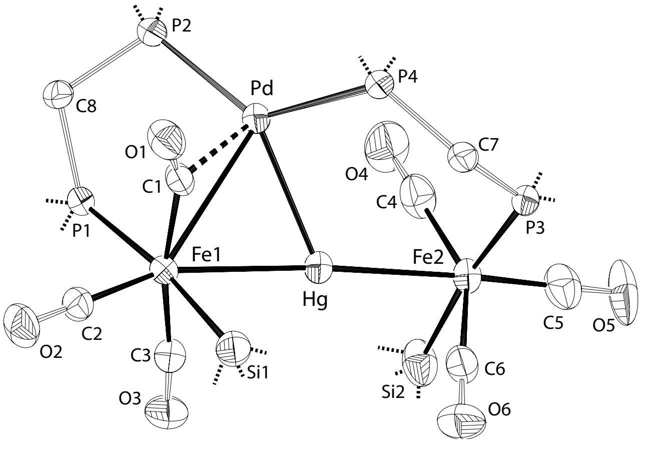


Figure 1. View of the molecular structure of **2**. Phenyl and MeO groups have been omitted for clarity. Ellipsoids enclose 50% of the electron density.

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[*] Dr. P. Braunstein, Dr. W. Schuh
Laboratoire de Chimie de Coordination, UMR 7513 CNRS
Université Louis Pasteur
4, rue Blaise Pascal, 67070 Strasbourg Cédex (France)
Fax: (+33) 3-9024-1322
E-mail: braunst@chimie.u-strasbg.fr

Dr. M. Bénard, Dr. M.-M. Rohmer
Laboratoire de Chimie Quantique, UMR 7551 CNRS
Université Louis Pasteur
4, rue Blaise Pascal, 67070 Strasbourg Cédex (France)

Prof. R. Welter
Laboratoire DECMET, UMR 7513 CNRS
Université Louis Pasteur
4 rue Blaise Pascal, 67070 Strasbourg Cedex (France)

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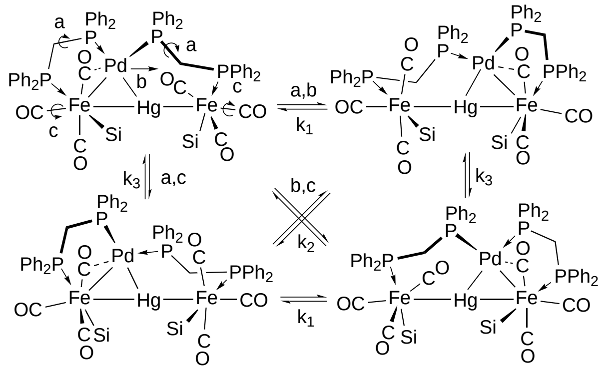
P and Si atoms *trans* to each other and the CO ligands in a *mer* arrangement. A semibridging carbonyl group, attached to Fe1 (Pd1–C11 213.8(6) pm) provides further stability, which was also established by theoretical calculations (see below) and accounts for a $\tilde{\nu}$(CO) vibration at 1821 cm^{-1} in the IR spectrum.[4] The dppm backbones and the Pd atom form a helical arrangement about the Fe-Hg-Fe axis (see Figure S-1 in the Supporting Information). As a result of the asymmetric position of the Pd center, the two dppm domains may be classified as heterotopic, in terms of helicate nomenclature.[12]

The Fe-Hg-Fe array is essentially linear (174.97(3)°) and the Hg–Fe1 bond, which is longer (266.80(9) pm) than the bond to Fe2 (262.12(9) pm), serves as a third "ligand" for the palladium center. The short separation between Pd and Hg suggests a bonding interaction between these two d^{10} metals, a feature related to the Cu^{I}–Hg^{II} interaction (268.9(2) pm) found in [Hg{Fe[Si(OMe)$_3$](CO)$_3$(μ-dppm)}$_2$Cu]PF$_6$ (**3**), which resulted in the 14-valence-electron Cu^{I} center possessing a Y-shaped coordination motif.[13] Here, in contrast, it is not a single atom (Hg) but a metal–metal single bond which allows the Pd^0 center to increase its formal 14-valence-electron count.

The bonding in complex **2** has been analyzed through extended Hückel calculations that were carried out on the model system [Hg{Fe[Si(OH)$_3$](CO)$_3$(PH$_2$CH$_2$PH$_2$)}$_2$Pd] (**2'**), and its fragments {Pd(PH$_3$)$_2$} (**5**) and {Hg[Fe{Si(OH)$_3$}-(CO)$_3$(PH$_3$)]$_2$} (**6**).[14,15] Palladium has a high-energy 5s/5p shell, whereas the 4d orbitals are fairly accessible at −12.0 eV. This means that Pd^0 will behave as a poor acceptor, especially when included in the PdL$_2$ fragment, but will tend to attach to the trimetallic complex through back-bonding. The donation interaction from the Fe1–Hg σ bond to PdL$_2$ does exist however, and can be evidenced from the population increase of the p$_y$ orbital of Pd (from 0.05 to 0.14 e). The greater importance of the back-donation stems from the depopulation of the 4d shell of Pd, which is of the order of 0.48 e (Table S2 of the Supporting Information). Part of this population is transferred to Hg, whose p$_y$ population increases from 0.06 to 0.18 e, and, to a lesser extent, to Fe1. However, the largest share of the density lost by the palladium center is donated to the π* orbital of the C1–O1 bond, which occupies a semibridging position between Pd and Fe1. Upon insertion of the Pd fragment, the C1–O1 bond becomes the most π-accepting carbonyl, with a net charge reversed from +0.09 to −0.11 e. The counterpart of this interaction gives rise to the LUMO+1 of complex **2'** (−9.0 eV) distributed over the π* orbital of C1–O1 (42 %), Fe1 (10 %), and Pd (23 %). This is the only virtual MO with important weight on the d shell of palladium. The LUMO (−9.1 eV) is a combination of the iron π orbitals involved in back-donation towards the other carbonyl groups. The stabilization of complex **2** in the observed conformation should therefore be assigned to a multicentered anchoring of the PdL$_2$ fragment that involves donation interactions from the Fe1–Hg σ bond and back-donation to all atoms of fragment **6** that neighbor the Pd center, especially to the C1–O1 bond. This multicentric network of interactions is lost within the symmetric T-shaped structure, which is assumed to be an intermediate or a transition state in the dynamic exchange of **2** via pathway 1 (Scheme 2). In this conformation, the electronic exchanges between the Pd fragment and the trimetallic moiety are only effective through the Hg atom, which becomes the only atom of **6** to remain in the vicinity of Pd. Both exchanges associated with donation to Pd and back-donation from Pd are strongly reduced in this conformation (0.03 e for donation to the sp shell of Pd, 0.23 e for back-donation from the d shell of Pd; Table S2), which explains that this structure does not correspond to an energy minimum, in contrast to the case of the copper compound **3**.



Scheme 2. Dynamic exchange in **2** involving molecular motion via pathways 1–3: a) Flip of the dppm methylene groups; b) translational motion of Pd along the Fe-Hg-Fe axis; c) torsional motion about the Fe-Hg-Fe axis.

In solution, the kinetic lability of the bonding interactions between Pd and both the Fe–Hg bond and the semibridging carbonyl ligand in **2** is revealed by variable-temperature ^{1}H NMR spectroscopy (see Figure 2). In contrast to the low symmetry found in the crystal structure, there is only one resonance in the ^{1}H NMR spectrum (500 MHz, 310 K, CD$_2$Cl$_2$) for the Si(OMe)$_3$ and the dppm methylene protons, respectively. At 164 K however, four resonances for the CH$_2$ groups in dppm and two resonances for the methoxysilyl groups are observed, in accordance with the solid-state structure. In the temperature range 164–310 K, two distinct mutual exchange processes are observed, with activation

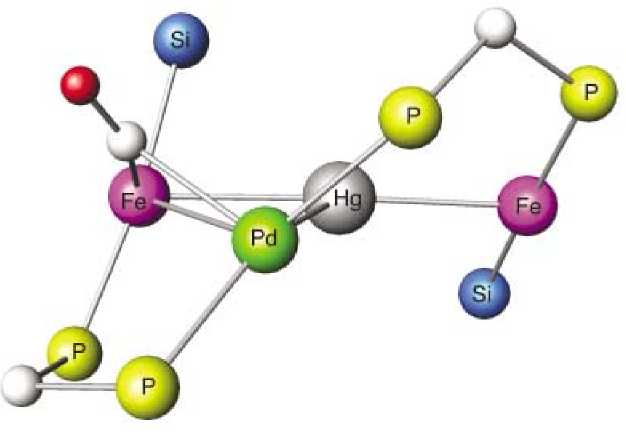


Figure 2. View of the core structure of **2** showing the helical arrangement of the diphosphane ligands.

parameters $\Delta G^{\ddagger}_{182\mathrm{K}} = 38 \pm 3\ \mathrm{kJ\,mol^{-1}}$, $\Delta H^{\ddagger} = 43 \pm 2\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger} = 27 \pm 9\ \mathrm{J\,K^{-1}\,mol^{-1}}$, and $\Delta G^{\ddagger}_{270\mathrm{K}} = 55 \pm 3\ \mathrm{kJ\,mol^{-1}}$, $\Delta H^{\ddagger} = 45 \pm 2\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger} = -37 \pm 6\ \mathrm{J\,K^{-1}\,mol^{-1}}$, respectively, obtained by computational line-shape analysis of the spectra.[4,6,7] Since the exchange rates are retained when approximately 10% of **1** is added to a solution of **2**, the dynamic behavior may therefore be considered to proceed through an intramolecular mechanism.[16] The exchange pathways illustrated in Scheme 2 are discussed in the Supporting Information.

A comparison of the activation entropies reveals that the two dynamic processes must involve essentially different motions, since $\Delta S^{\ddagger}$ is clearly positive for exchange 1 and negative for exchange 2. The value of $\Delta H^{\ddagger}$ for exchange 1 is very similar to the activation enthalpy of the cyclohexane chair-conformation inversion, which also displays a positive $\Delta S^{\ddagger}$;[17] this strengthens the assignment of the low-energy dynamic process to pathway 1. Consequently, the torsional motion appears related to the negative activation entropy found for the high-energy dynamic process. This may be understood by considering that such a motion is a high-order concerted process. It may be hindered by increased random thermal motion or by molecular vibrations.

In conclusion, we have prepared an unprecedented heteropolymetallic complex by "capture" of a $\mathrm{Pd^0}$ center by the trimetallodiphosphane **1**. Its metal–metal bonding has been analyzed in detail and shown to involve, for the first time to our knowledge, direct interactions between the d^{10} centers $\mathrm{Pd^0}$ and $\mathrm{Hg^{II}}$. The complex fluxional behavior of compound **2** has been shown to consist of an apparent "sliding" of the palladium along the trimetallic chain.[16] Further studies are in progress, and we can already indicate that Pt does not form a direct analogue of **2**, which emphasizes the delicate energetic balance that characterizes such complex molecules.

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Keywords: cluster compounds · coordination modes · heterometallic complexes · metal–metal interactions · molecular dynamics

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[4] Details for the synthesis are given in the Supporting Information. Selected spectroscopic data for **2**: IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu} = 1994$ (s), 1978 (vs), 1930 (vs, br), 1821 cm^{-1} (m). $^1\mathrm{H}\{^{31}\mathrm{P}\}$ NMR ($\mathrm{CD_2Cl_2}$, 164 K, 500 MHz, TMS): $\delta = 8.8$–6.5 (m, br, 40 H, Ph), 3.79 (br, 1 H, $\mathrm{CH_2}$), 3.70 (s, 9 H, $\mathrm{(MeO)_3Si}$), 3.61 (s, 9 H, $\mathrm{(MeO)_3Si}$), 3.56 (br, 2 H, $\mathrm{CH_2}$), 3.10 ppm (br, 1 H, $\mathrm{CH_2}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 166 K, 202.5 MHz, 85% $\mathrm{H_3PO_4}$): $\delta = 9.4$ ($^2J(\mathrm{P^2,P^4}) = 80$ Hz, $^{2+4}J(\mathrm{P^3,P^4}) = 55$ Hz, $^{3+4}J(\mathrm{P^1,P^4}) = -18$ Hz, $\mathrm{P^4}$), 9.6 ($^4J(\mathrm{P^2,P^3}) = 11$ Hz, $^{2+3+4}J(\mathrm{P^1,P^2}) = 197$ Hz, $\mathrm{P^2}$), 45.9 ($^4J(\mathrm{P^1,P^3}) = 0$ Hz, $\mathrm{P^3}$), 59.3 ppm ($\mathrm{P^1}$). For the numbering of the phosphorus atoms, see Figure 1. The assignment of the phosphorus resonances is based on the very large P–P coupling constant of 197 Hz between $\mathrm{P^2}$ and $\mathrm{P^3}$, which indicates a bonding interaction between the dppm-bridged metals Fe and Pd.[5] $^{199}\mathrm{Hg}$ NMR ($\mathrm{CD_2Cl_2}$, 298 K, 71.6 MHz, $\mathrm{HgMe_2}$): $\delta = -134$ (s, br). Simulation of second-order spectra were performed with WinDaisy,[6] and computational line-shape analysis with SpinWorks.[7] More spectroscopic data, technical details, and Eyring plots are provided in the Supporting Information.

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[8] Crystal data for $\mathbf{2}\cdot 1/2\,\mathrm{Et_2O}\cdot 1/2\,\mathrm{H_2O}$: Crystals suitable for X-ray diffraction were obtained upon slow evaporation of a solution of **2** in $\mathrm{Et_2O}$ that was in contact with air; monoclinic, space group $C2/c$, $a = 41.564(5)$, $b = 15.716(5)$, $c = 22.117(5)$ Å, $\beta = 95.715(5)°$, $V = 14375(6)$ Å^3, $Z = 8$, $T = 183(2)$ K, $\mathrm{Mo_{K\alpha}}$ ($\lambda = 0.70930$ Å), 24981 data collected, 11149 data with $I > 2\sigma(I)$, θ min/max = 0.998/32.032°. The structure was solved by direct methods (SHELXS-97)[9a] and refined by full-matrix least-squares methods on F^2 (SHELXL-97).[9b] $R = 0.0583$, $wR2$(all data) = 0.1446, GOF = 0.894. CCDC-188689 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] The axis x is assumed to be collinear to Fe-Hg-Fe and xy is the average plane of the four metals. The chelating diphosphanes have been replaced by $\mathrm{PH_3}$ in order to avoid unwanted interactions. In the trimetallic fragment **6**, neutral mercury (in the $d^{10}s^2$ configuration) acts as a donor by means of its deep 6s orbital (−13.7 eV) and as an acceptor through its 6p shell (−8.47 eV). The donation and the back-donation are operative

respectively through the in-phase and the out-of-phase combinations of the Fe σ orbitals resulting from the approximate square-pyramidal conformation of the two $\{Fe[Si(OH)_3](CO)_3(PH_3)\}$ moieties. The out-of-phase combination is stabilized and becomes the HOMO of fragment **6**, whereas the in-phase combination contributes to a low-energy MO with major weight on the mercury 6s orbital. The orbital populations of Hg in **6** are 1.29 e for 6s and 0.44 e, 0.06 e, and 0.07 e for the p_x, p_y, and p_z orbitals, respectively (Table S2 in the Supporting Information).

[16] We cannot state whether the intramolecular Pd motion corresponds to a contact sliding along the Fe-Hg-Fe chain or results from successive Pd detaching and reattaching to the Fe-Hg bond. At the moment, we have no way of separating the two enantiomers resulting from the presence of both *P* and *M* helical arrangements of the phosphanes.

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