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Competing Metal–Metal Bonding in Heterometallic Complexes of Gold and Mercury. Synthesis of Contrasting Fe–Au–Au–Fe and Fe–Hg–Fe Complexes

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By contraction of the s (and p) orbitals and expansion of the d orbitals, relativistic effects promote metal–metal interactions between gold atoms even with a $5d^{10}$ closed-shell electronic configuration.[1] Tangential bonding in gold complexes[2a] results in the marked "aurophilic attraction"[2b] which has become a salient feature of recent experimental[3] and theoretical studies.[4] Yet, more comparative experimental data are desirable to better understand how these effects influence the chemistry (structure and reactivity) of $\mathrm{Au^I}$ vs its neighbor $\mathrm{Hg^{II}}$, another $5d^{10}$ closed-shell ion. Whereas Hg transition metal complexes and clusters are numerous,[5] only few structures are known in which tangential Hg–Hg bonding occurs.[6] We report on the marked differences observed between the new Fe–Au and Fe–Hg complexes $[\mathrm{AuFe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})]_2}$ (**2**) (dppm = $\mathrm{Ph_2PCH_2PPh_2}$) and $\mathrm{Hg[Fe\{Si(OMe)_3\}(CO)_3(dppm\text{-}}P)]_2$ (**3**), respectively, which are due to the preference in the former for Au–Au rather than Au–Fe bonding.

We reacted $[\mathrm{Bu_4N}][\mathrm{AuX_2}]$ (X = Cl, Br) with 2 equiv of the dppm-substituted silyliron metalate $\mathrm{K[Fe\{Si(OMe)_3\}(CO)_3(dppm\text{-}}P)]$ (K[m]) (**1**),[7] anticipating the formation of a $[\mathrm{m\text{-}Au\text{-}m}]^-$ chain. However, a complex analyzing for Au[m] (**2**) was obtained instead (Scheme I)[8] and it was also formed when only 1 equiv of **1** was used. Its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum contains a doublet of doublets, characteristic for the presence of Au- and Fe-bound P atoms coupled to each other (^{2+3}J(P,P) = 43.4 Hz), which is further split by an additional coupling of 14.8 Hz. In addition to the methoxy resonance at δ 3.61 (^{1}H NMR at 333 K), a broad triplet is found at δ 3.23 for the $\mathrm{PCH_2}$ protons. It broadens further when the temperature is lowered, indicating a dynamic behavior for this molecule. The crystal structure of the $\mathrm{CH_2Cl_2}$ solvate of complex **2**[10] revealed that a dimer $(\mathrm{Au[m]})_2$ had formed, as a result of additional Au–Au bonding and partial migration of the dppm ligand (Scheme I). The dimeric complex has an approximate C_2 symmetry, and the Fe–Au–Au–Fe chain possesses a Z shape (Figure 1), with the pairs of atoms Fe(1) and Au(2) and Fe(2) and Au(1) each bridged by a dppm ligand, thus forming two unusual, twisted six-membered rings fused along the Au–Au edge (core of a tetraphosphatetrametalladecaline). The coordination geometry about the Fe atom may be described as distorted octahedral with the P and Si atoms trans to one another and the CO ligands in a *mer* arrangement. Alternatively, if one ignores the Fe–Au bond, it may be viewed as trigonal bipyramidal, a geometry consistent with a formally zerovalent Fe center. The Au–Fe distances are in the expected

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(1) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563 and references therein.

(2) (a) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1163. (b) Scherbaum, F.; Grohmann, A.; Huber, B.; Krüger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1544.

(3) (a) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11. (b) Salter, I. D. *Adv. Organomet. Chem.* **1989**, *29*, 249. (c) Braunstein, P.; Rosé, J. *Gold Bull.* **1985**, *18*, 17 and references cited. (d) Alvarez, S.; Rossell, O.; Seco, M.; Valls, J.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1991**, *10*, 2309 and references cited. (e) Payne, N. C.; Ramachandran, R.; Treurnicht, I.; Puddephatt, R. J. *Ibid.* **1990**, *9*, 880. (f) Khan, Md. N. I.; King, C.; Heinrich, D. D.; Fackler, J. P., Jr.; Porter, L. C. *Inorg. Chem.* **1989**, *28*, 2150. (g) Raptis, R. G.; Fackler, J. P., Jr.; Murray, H. H.; Porter, L. C. *Ibid.* **1989**, *28*, 4057.

(4) (a) Pyykkö, P.; Zhao, Y. *Angew. Chem.* **1991**, *103*, 622; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 604. (b) Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749 and references cited in these papers.

(5) See for example: (a) Charalambous, E.; Gade, L. H.; Johnson, B. F. G.; Kotch, T.; Lees, A. J.; Lewis, J.; McPartlin, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1137. (b) Braunstein, P.; Rosé, J.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Dalton Trans.* **1992**, 911 and references cited.

(6) See, for example: Gäde, W.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 803. Albinati, A.; Moor, A.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 7672. Kergoat, R.; Kubicki, M.; Guerchais, J.-E.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1982**, 633. Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S. *Ibid.* **1983**, 349. Ragosta, J. M.; Burlitch, J. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1187. Gade, L. H.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Kotch, T.; Lees, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 8698 and references cited.

(7) (a) Braunstein, P.; Knorr, M.; Schubert, U.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1507. (b) Braunstein, P.; Knorr, M.; Villarroya, B. E.; Fischer, J. *New J. Chem.* **1990**, *14*, 583 and references cited.

(8) All reactions were performed under purified nitrogen, using standard Schlenk-type techniques. Complex **2**: $[n\text{-}\mathrm{Bu_4N}][\mathrm{AuBr_2}]$[9] (0.599 g, 1.0 mmol) was added at −40 °C to a solution of K[m] (0.685 g, 1 mmol) in THF (35 mL), and the mixture was stirred for 1.5 h. The yellowish solution was filtered and evaporated under reduced pressure. The residue was extracted with warm $\mathrm{CH_2Cl_2}$ (30 mL), and the extract was concentrated and layered with hexane, which afforded colorless crystals after a few days at −20 °C (0.496 g, 56%). IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1978 (s), 1914 (vs), 1899 (vs) $\mathrm{cm^{-1}}$. ^{1}H NMR (in $\mathrm{CDCl_3}$, δ relative to $\mathrm{SiMe_4}$) (333 K): 3.23 (br t, $J \approx 12$ Hz, 2 H, $\mathrm{PCH_2}$), 3.61 (s, 9 H, OMe), 7.10–7.74 (m, 20 H, aromatic). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CH_2Cl_2}$/acetone-d_6, δ relative to external $\mathrm{H_3PO_4}$): 27.9 [dd, J(P,P) = 43.4, 14.8 Hz, P(Au)], 58.4 [dd, J(P,P) = 43.4, 14.8 Hz, P(Fe)].

(9) Braunstein, P.; Clark, R. J. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1845.

(10) Crystal structure determinations: $[\mathrm{AuFe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})]_2\cdot CH_2Cl_2}$ (**2**), $\mathrm{C_{62}H_{62}Au_2Fe_2O_{12}P_4Si_2\cdot CH_2Cl_2}$, M = 1769.79, monoclinic, space group $P2_1/a$ (the matrix /001/010/100/ must be applied to the unit cell in order to change the space group in $P2_1/c$), a = 32.930 (9) Å, b = 17.826 (7) Å, c = 11.297 (5) Å, β = 90.57 (2)°, V = 6631 (4) $\mathrm{Å^3}$, Z = 4, D_c = 1.773 g $\mathrm{cm^{-3}}$, graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, μ = 51.02 $\mathrm{cm^{-1}}$; $\mathrm{Hg[Fe\{Si(OMe)_3\}(CO)_3(dppm\text{-}}P)]_2$ (**3**), $\mathrm{C_{62}H_{62}Fe_2HgO_{12}P_4Si_2}$, M = 1491.52, triclinic, space group $P\bar{1}$ (the matrix /001/100/010/ must be applied to the unit cell in order to obtain the Niggli unit cell), a = 12.706 (6) Å, b = 22.843 (9) Å, c = 12.219 (5) Å, α = 95.79 (2)°, β = 114.15 (2)°, γ = 95.44 (2)°, V = 3183 (2) $\mathrm{Å^3}$, Z = 2, D_c = 1.556 g $\mathrm{cm^{-3}}$, niobium-filtered Mo Kα radiation, λ = 0.710 73 Å, μ = 30.47 $\mathrm{cm^{-1}}$. The intensity data were collected at room temperature on a Philips PW 1100 (**2**) and a Siemens AED (**3**) diffractometer, using the θ–2θ scan technique. A total of 11 218 (**2**) and 13 985 (**3**) unique reflections were measured (with θ in the range 3–24° (**2**) and 3–27° (**3**), of which 5759 (**2**) and 8790 (**3**), having $I > 2\sigma(I)$, were used in the refinement. Corrections for absorption were applied. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for the Au, Fe, P, Si, and O atoms (**2**) and for all the non-hydrogen atom (**3**). The hydrogen atoms were placed at their geometrically calculated positions. The SHELX-76 and SHELXS-86 systems of computer programs were used.[11] The R and R_w values were 0.0665 and 0.0719 (**2**) and 0.0472 and 0.0510 (**3**), respectively. Further details of the crystal structure analyses are available as supplementary material.

(11) Sheldrick, G. M. SHELX-76. Program for Crystal Structure Determination, University of Cambridge, U.K., 1976. SHELXS-86. Program for Crystal Structure Solution. Universität Göttingen, 1986.

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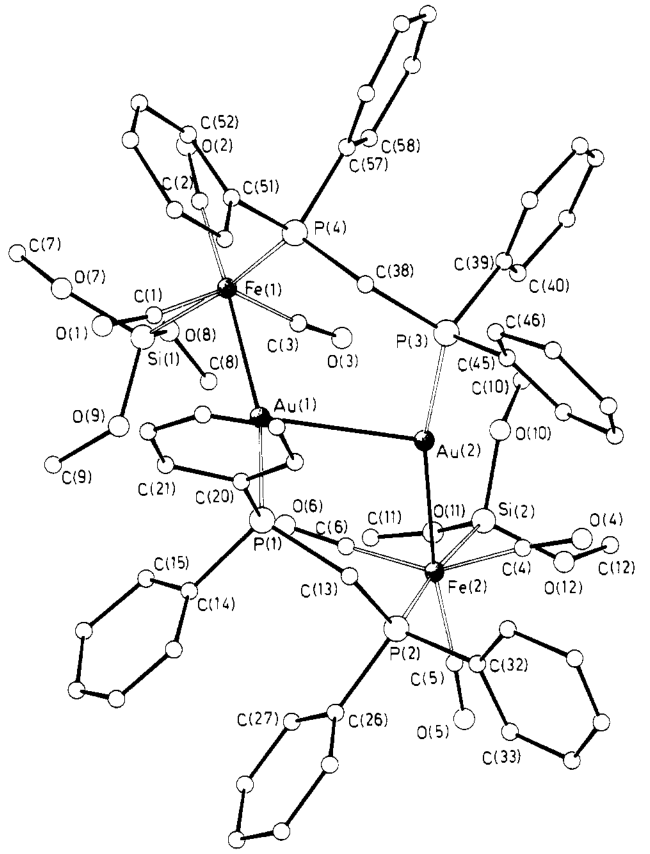
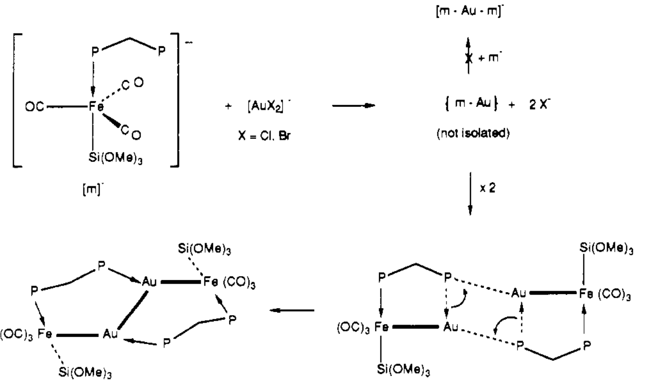


Figure 1. View of the molecular structure of the complex [AuFe{Si(OMe)$_3$}(CO)$_3$(μ-dppm)]$_2$·CH$_2$Cl$_2$ (**2**) together with the atomic numbering system. Selected bond distances (Å) and angles (deg): Au(1)–Au(2) = 2.962 (1), Au(1)–Fe(1) = 2.535 (3), Au(2)–Fe(2) = 2.562 (3), Au(1)–P(1) = 2.266 (6), Au(2)–P(3) = 2.294 (6), Fe(1)–Si(1) = 2.268 (8), Fe(1)–P(4) = 2.226 (6), Fe(2)–Si(2) = 2.282 (7), Fe(2)–P(2) = 2.244 (6); Fe(1)–Au(1)–P(1) = 161.7 (2), Fe(2)–Au(2)–P(3) = 164.0 (2), Fe(1)–Au(1)–Au(2) = 107.2 (1), P(1)–Au(1)–Au(2) = 87.3 (1), Fe(2)–Au(2)–Au(1) = 104.8 (1), P(3)–Au(2)–Au(1) = 88.6 (1), C(1)–Fe(1)–C(3) = 143 (1), C(1)–Fe(1)–C(2) = 108 (1), C(2)–Fe(1)–C(3) = 106 (1), P(4)–Fe(1)–Si(1) = 171.4 (3), C(4)–Fe(2)–C(6) = 150 (1), C(4)–Fe(2)–C(5) = 103 (1), C(5)–Fe(2)–C(6) = 105 (1), P(2)–Fe(2)–Si(2) = 174.3 (3).

Scheme I



2

range,[3d] and the Au(1)–Au(2) separation of 2.962 (1) Å is typical for such interactions that are perpendicular (tangential) to the Fe–Au–P bonding axis [P(1)–Au(1)–Fe(1) = 161.7 (2)°; P(3)–Au(2)–Fe(2) = 164.0 (2)°].[3] It is interesting to note that **2** forms a 10-membered-ring structure in which the Au–Au interaction is reminiscent of the transannular interactions which occur in organic cycles of middle size (8–12).

But why could the trinuclear chain complex ([m]–Au–[m])$^-$ not be isolated in contrast to the behavior observed with other carbonylmetalates?[12] Possibly its Fe–Au bond would be sufficiently labile for dissociation in [m]$^-$ and Au[m], in which the gold atom obviously prefers to increase its coordination by formation of a new Au–Au bonding interaction. This dimerization process would be assisted by the phosphorus atoms P(1) and P(3), which could be either bonded to gold in Au[m] or pendent, resulting for the first time, we believe, in dppm ligands bridging the *termini* atoms of a trinuclear chain. This is supported by the observation that **2** formed in small amounts (5%, ^{31}P{^{1}H} NMR) upon dissolution of pure [Fe{Si(OMe)$_3$}(CO)$_3$(μ-dppm)Au(PPh$_3$)],[7a] owing to partial dissociation of PPh$_3$. The Ag–AsPh$_3$

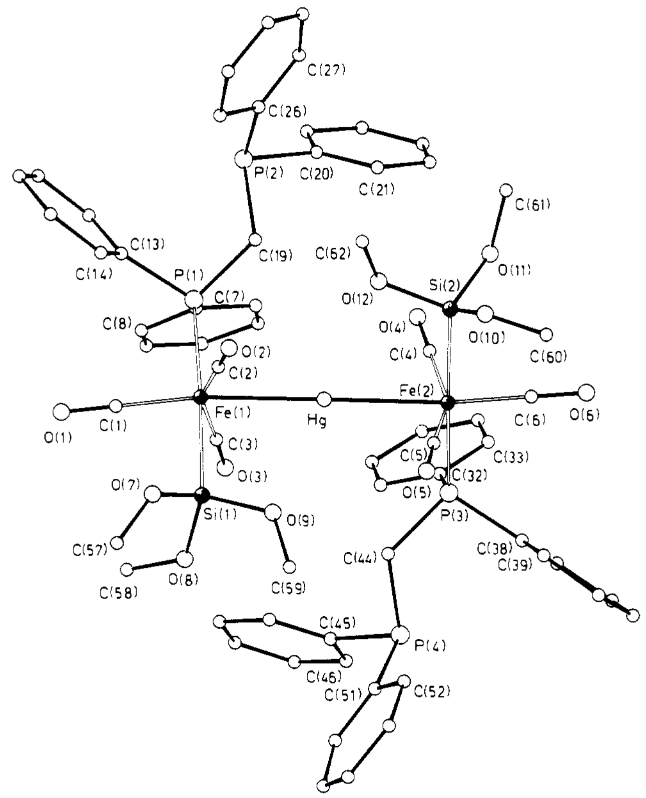
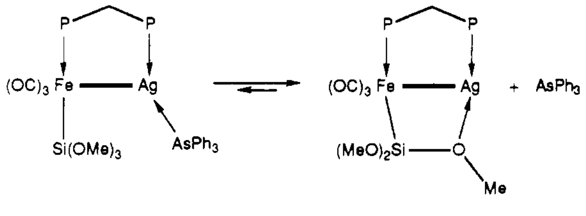


Figure 2. View of the molecular structure of the complex Hg[Fe{Si(OMe)$_3$}(CO)$_3$(dppm-*P*)]$_2$ (**3**) along the pseudo-C_2 axis, together with the atomic numbering system. Selected bond distances (Å) and angles (deg): Hg)–Fe(1) = 2.574 (1), Hg–Fe(2) = 2.576 (1), Fe(1)–Si(1) = 2.290 (3), Fe(1)–P(1) = 2.247 (2), Fe(2)–Si(2) = 2.285 (3), Fe(2)–P(3) = 2.235 (2); Fe(1)–Hg–Fe(2) = 178.0 (1), P(1)–Fe(1)–Si(1) = 177.3 (1), C(1)–Fe(1)–C(2) = 102.6 (4), C(2)–Fe(1)–C(3) = 154.9 (4), C(1)–Fe(1)–C(3) = 99.7 (4).



(1)

analogue of the latter complex readily dissociates AsPh$_3$ in solution,[7a] resulting instead in the occurrence of an unusual μ_2-η^2-SiO bridge (eq 1). The preference for intramolecular stabilization of the electron-deficient Ag center over a dimerization of the type observed above with gold nicely illustrates the much lower affinity of silver for making Ag···Ag contacts. On electronic grounds, Au←O(Si) interactions are therefore not needed in **2**. Note also that excess PPh$_3$ breaks the Au–Au bond of **2**, yielding quantitatively [Fe{Si(OMe)$_3$}(CO)$_3$(μ-dppm)Au(PPh$_3$)].

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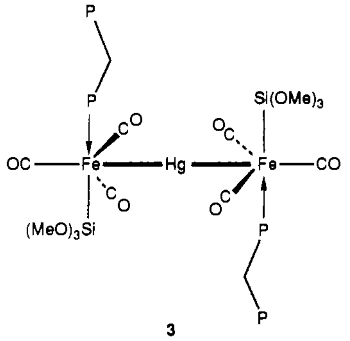
(12) Braunstein, P.; Schubert, U.; Burgard, M. *Inorg. Chem.* **1984**, *23*, 4057 and references cited.

The reaction of 2 equiv of **1** with $HgCl_2$ or of 1 equiv of **1** with the intermediate $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})HgCl]$[7b] afforded in high yield the expected[13] chain complex [m]–Hg–[m] (**3**).[14]



3

Its X-ray structure shows that it has approximate C_2 symmetry[10] and confirms the linearity of the Fe–Hg–Fe array (Figure 2). The Fe–Hg bond distances are slightly longer than those found in neutral or anionic complexes showing a linear Fe–Hg–Fe array.[15] The pendent nature of two P atoms in **3** is maintained in solution, since, even at −30 °C, no $^1J(PHg)$ coupling could be detected in the $^{31}P\{^1H\}$ NMR spectrum. The formation and structure of **3** clearly show that there were no obvious reasons (e.g. steric) why its gold analogue would not form. A comparison of closely related $Fe–Ag^I$, $Fe–Au^I$, and $Fe–Hg^{II}$ systems demonstrates that the $Au^I–Au^I$ attraction (recent estimations are of about −30 kJ/mol[3a,16]) represents a decisive component to the dramatic structural reorganization leading to **2**.

An interesting feature of complex **3** is the orientation of the pendent P atoms. We are currently evaluating the potential of this molecule as an assembling "ligand" of which the trinuclear core could act as a rigid spacer, imparting unique stereochemical features to its complexes.

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Supplementary Material Available: Tables of crystal data and data collection and refinement details, positional parameters, anisotropic thermal parameters, and bond distances and angles for **2** and **3** (26 pages). Ordering information is given on any current masthead page.

Registry No. **1**, 123674-03-3; **2**, 142563-98-2; **2**·CH_2Cl_2, 142632-19-7; **3**, 142563-99-3; $[Bu_4N][AuCl_2]$, 50480-99-4; $[Bu_4N][AuBr_2]$, 50481-01-1; $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})HgCl]$, 142632-20-0; Fe, 7439-89-6; Au, 7440-57-5; Hg, 7439-97-6.

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(13) Kunz, E.; Schubert, U. *Chem. Ber.* **1989**, *122*, 231.

(14) Complex **3**: $HgCl_2$ (0.135 g, 0.5 mmol) was added at 0 °C to a solution of K[m] (0.685 g, 1 mmol) in THF (25 mL), and the mixture was stirred for 1.5 h. The yellow solution was filtered and evaporated under reduced pressure. The residue was recrystallized from toluene/hexane at −20 °C, affording yellow, air-stable crystals of **3** (0.545 g, 73%). IR (THF): ν(CO) 1994 (m), 1965 (sh), 1939 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.22 (br d, $^2J(P,H) = 4.6$ Hz, 2 H, PCH_2), 3.56 (s, 9 H, OMe), 7.10–7.53 (m, 20 H, aromatic). $^{31}P\{^1H\}$ NMR (THF/acetone-d_6, 298 K): −22.4 (d, $^2J(P,P) = 59$ Hz, P), 51.4 (d, $^2J(P,P) = 59$ Hz, $^2J(P,Hg) = 173$ Hz, P(Fe)). ^{199}Hg NMR (Bruker WP 200 SY, CH_2Cl_2/C_6D_6, δ relative to external $HgMe_2$), (312 K): −658 (t, $^2J(P,Hg) = 180$ Hz) (we thank P. Maltese and M. Strampfer for these data).

(15) (a) Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2257. (b) Sosinsky, B. A. S.; Shong, R. G.; Fitzgerald, B. J.; Norem, N.; O'Rourke, C. *Inorg. Chem.* **1983**, *22*, 3124. (c) Alvarez, S.; Ferrer, M.; Reina, R.; Rossell, O.; Seco, M.; Solans, X. *J. Organomet. Chem.* **1989**, *377*, 291.

(16) (a) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417. (b) Jensen, M. *Ibid.* **1987**, *26*, 1098.