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# Transition-Metal Silyl Complexes. 46.<sup>1</sup> Reaction of Anionic Silyl Complexes [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PR'<sub>3</sub>)]<sup>-</sup> with CdX<sub>2</sub> (X = Cl, Br) To Probe the Influence of PR'<sub>3</sub> and X on Nuclearity and Geometry of the Resulting Polynuclear Complexes

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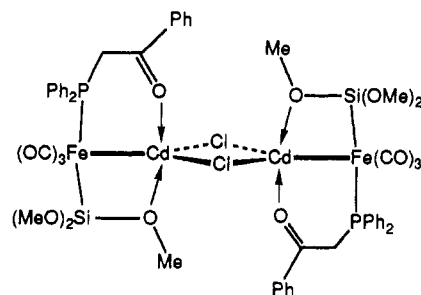
Received September 2, 1992

Reaction of the anionic silyl complexes [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PR'<sub>3</sub>)]<sup>-</sup> with CdX<sub>2</sub> (X = Cl, Br) in THF results in the formation of three different types of products, depending on the nature of the PR'<sub>3</sub> ligand and X. The PMe<sub>3</sub>-substituted complexes [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PMe<sub>3</sub>)]<sup>-</sup> (SiR<sub>3</sub> = SiPh<sub>3</sub>, SiMePh<sub>2</sub>) exclusively give the 2:1 compounds [*fac*-(Me<sub>3</sub>P)(R<sub>3</sub>Si)(CO)<sub>3</sub>Fe]<sub>2</sub>Cd, even if the reaction is carried out with a 2–3-fold excess of CdCl<sub>2</sub>. The 2:1 compounds are also formed in the reactions of [Fe(CO)<sub>3</sub>(SiPh<sub>2</sub>Me){P(OMe)<sub>3</sub>}]<sup>-</sup> or [Fe(CO)<sub>3</sub>(Si(OMe)<sub>3</sub>)(Ph<sub>2</sub>Ppy)]<sup>-</sup> (Ph<sub>2</sub>Ppy = 2-(diphenylphosphino)pyridine) with CdCl<sub>2</sub>. However, the arrangement of the CO ligands in the products [(MeO)<sub>3</sub>Si](Ph<sub>2</sub>MeSi)(CO)<sub>3</sub>Fe]<sub>2</sub>Cd and [(MeO)<sub>3</sub>Si](CO)<sub>3</sub>Fe(μ-Ph<sub>2</sub>Ppy)]<sub>2</sub>Cd is *meridional*. In contrast to these reactions, the 1:1 compounds *mer*-[(R'<sub>3</sub>P)(R<sub>3</sub>Si)(CO)<sub>3</sub>FeCd(μ-X)]<sub>2</sub> are obtained in the reaction of [Fe(CO)<sub>3</sub>(Si(OMe)<sub>3</sub>)(Ph<sub>2</sub>Ppy)]<sup>-</sup> with CdBr<sub>2</sub>, the reaction of [Fe(CO)<sub>3</sub>(SiPh<sub>2</sub>Me){P(OMe)<sub>3</sub>}]<sup>-</sup> with CdCl<sub>2</sub>, and the reaction of [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PPh<sub>2</sub>H)]<sup>-</sup> (SiR<sub>3</sub> = SiPh<sub>3</sub>, SiMePh<sub>2</sub>) with CdCl<sub>2</sub> or CdBr<sub>2</sub>. The bromo bridge in *mer*-[(MeO)<sub>3</sub>Si](CO)<sub>3</sub>Fe(μ-Ph<sub>2</sub>Ppy)Cd(μ-Br)]<sub>2</sub> is cleaved by 4-picoline to give [(MeO)<sub>3</sub>Si](CO)<sub>3</sub>Fe(μ-Ph<sub>2</sub>Ppy)Cd(4-pic)Br. [(Ph<sub>3</sub>Si)(Ph<sub>2</sub>HP)(CO)<sub>3</sub>FeCd(μ-Br)]<sub>2</sub> crystallizes in the triclinic space group *P*1̄ (*Z* = 1) with *a* = 1048.9(5) pm, *b* = 1268.6(4) pm, *c* = 1515.5(7) pm, α = 75.51(3)°, β = 86.58(5)°, and γ = 72.94(5)° (Cd–Fe = 254.0(3) pm, Fe–Si = 236.4(5) pm, and Cd–Br = 268.9(2) and 260.4(2) pm), and [(MeO)<sub>3</sub>Si](CO)<sub>3</sub>Fe(μ-Ph<sub>2</sub>Ppy)]<sub>2</sub>Cd crystallizes in the monoclinic space group *C*2/c (*Z* = 4) with *a* = 2968.4(8) pm, *b* = 1004.3(3) pm, *c* = 2098.8(6) pm, and β = 91.87(2)° (Cd–Fe = 269.70(5) pm, Fe–Si = 228.6(1) pm, Cd–N = 249.3(3) pm).

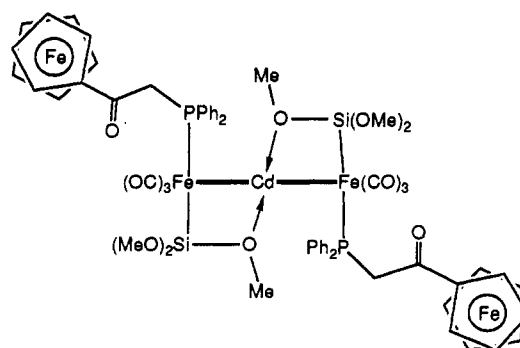
## Introduction

Anionic silyl complexes, such as [MeCpMn(CO)<sub>2</sub>(SiR<sub>3</sub>)]<sup>-</sup> or [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PR'<sub>3</sub>)]<sup>-</sup>, readily undergo substitution reactions with some metal halides to yield di- and trinuclear complexes with unsupported metal–metal bonds.<sup>2</sup> This method was extended to complexes containing bridging phosphine ligands, which also allowed the unusual occurrence of μ-η<sup>2</sup>-SiO bridges with alkoxy-silyl ligands.<sup>3</sup> Silyl-substituted polynuclear complexes are preparatively very interesting. They offer the opportunity to stepwise increase the nuclearity of metal cluster compounds due to the relatively easy cleavage of metal–silicon bonds.

By reaction of HgCl<sub>2</sub> or HgBr<sub>2</sub> with the anionic complexes [MeCpMn(CO)<sub>2</sub>(SiPh<sub>2</sub>Me)]<sup>-</sup> and [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PR'<sub>3</sub>)]<sup>-</sup> the 2:1 complexes [(SiR<sub>3</sub>)<sub>2</sub>L<sub>n</sub>M]<sub>2</sub>Hg and the 1:1 complexes (SiR<sub>3</sub>)<sub>2</sub>L<sub>n</sub>M–HgX (L<sub>n</sub>M = MeCpMn(CO)<sub>2</sub> or Fe(CO)<sub>3</sub>(PR'<sub>3</sub>)) were obtained in a stepwise manner.<sup>2a,d</sup> While both types of complexes were also found in the reaction of [MeCpMn(CO)<sub>2</sub>(SiPh<sub>2</sub>Me)]<sup>-</sup> with CdCl<sub>2</sub>, reaction of [Fe(CO)<sub>3</sub>(SiPh<sub>2</sub>Me)(PPh<sub>3</sub>)]<sup>-</sup> with CdCl<sub>2</sub> only gave the 1:1 complex [(Ph<sub>2</sub>MeSi)(Ph<sub>3</sub>P)(CO)<sub>3</sub>FeCdCl]<sub>2</sub>,<sup>2c</sup> even if the two compounds were reacted in a 2:1 ratio.<sup>2a</sup> Treatment of [Fe(CO)<sub>3</sub>(Si(OMe)<sub>3</sub>)(L)]<sup>-</sup> (L = dppm-P [dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>], Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph, or Ph<sub>2</sub>PCH<sub>2</sub>C(O)(η-C<sub>5</sub>H<sub>4</sub>)FeCp) with 1 equiv of CdCl<sub>2</sub>·2.5H<sub>2</sub>O in THF afforded the 1:1 complexes with the Fe–Cd(μ-Cl)<sub>2</sub>–Fe arrangement



However, the 2:1 complex



with the functional ferrocenyl-substituted ketophosphine could also be isolated and structurally characterized.<sup>4</sup> Surprisingly, interconversion between these different structural types upon reaction of the 2:1 complex with CdCl<sub>2</sub>·2.5H<sub>2</sub>O or by reaction of the 1:1 compound with a second equivalent of the silyl-substituted metalate (bridge-splitting reaction) was not observed.<sup>4</sup>

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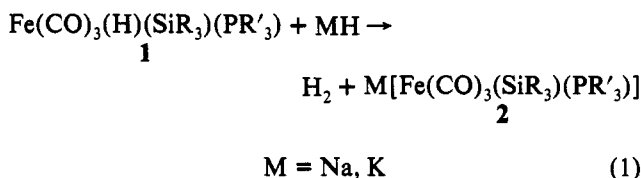
<sup>§</sup> Laboratoire de Cristallographie et de Structurale, Université Louis Pasteur.

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To further study the reactions between anionic silyl complexes and metal dihalides and possibly find an explanation for their different outcome, we reacted  $\text{CdX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with complexes  $[\text{Fe}(\text{CO})_3(\text{SiR}_3)(\text{PR}')^-]$  having different phosphine ligands. The results of these investigations are presented in this paper.

## Results and Discussion

**Reaction of  $[\text{Fe}(\text{CO})_3(\text{SiR}_3)(\text{PR}')^-]$  with  $\text{CdX}_2$ .** The anionic iron silyl complexes **2** were prepared by deprotonation of the corresponding hydrido silyl complexes **1**<sup>2d,5</sup> with NaH or KH as previously described (eq 1).<sup>2d,3f</sup>

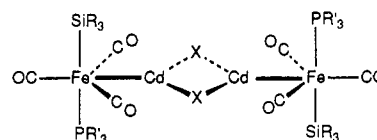
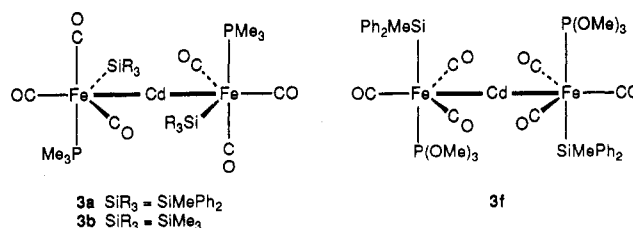


1,2	$\text{PR}'_3$	$\text{SiR}_3$
a	$\text{PMe}_3$	$\text{SiMePh}_2$
b	$\text{PMe}_3$	$\text{SiMe}_3$
c	$\text{PPhPh}_2$	$\text{SiPh}_3$
d	$\text{PPhPh}_2$	$\text{SiMePh}_2$
e	$\text{P}(\text{OMe})_3$	$\text{SiPh}_3$
f	$\text{P}(\text{OMe})_3$	$\text{SiMePh}_2$
g	$\text{PPh}_3$	$\text{SiMePh}_2^{2a}$
h	$\text{PPh}_2(2\text{-C}_5\text{H}_4\text{N})$	$\text{Si}(\text{OMe})_3$

Reaction of **2** with  $\text{CdCl}_2$  in THF results in the formation of three different types of products, depending on the nature of the phosphine (phosphite) ligand. The  $\text{PMe}_3$ -substituted compounds **2a,b** exclusively give 2:1 compounds **3a,b** with a *facial* geometry of the  $\text{Fe}(\text{CO})_3$  unit. Even if the reaction is carried out with an 2–3-fold excess of  $\text{CdCl}_2$ , no 1:1 complexes are formed. A trinuclear compound is also formed if 2 equiv of the  $\text{P}(\text{OMe})_3$ -substituted compound **2f** are reacted with  $\text{CdCl}_2$ . However, the geometry of the product **3f** is *meridional*. Distinction between a *facial* and *meridional* geometry is easily made by the number of  $\nu(\text{CO})$  bands in the infrared spectrum.

While the 2:1 compounds **3a,b** are also formed if equimolar amounts of  $\text{CdCl}_2$  and the  $\text{PMe}_3$ -substituted anionic iron complexes **2a,b** are used, reaction of the  $\text{P}(\text{OMe})_3$ -substituted complex **2e** with  $\text{CdCl}_2$  in a 1:1 ratio gives the 1:1 complex **3e**. The latter type of product is also found, when the anionic complexes **2c,d,g** are analogously reacted with  $\text{CdCl}_2$ . The kind of product does not change when different ratios of **2c,d,g** and  $\text{CdCl}_2$  (2:1 or 1:1) are used. Also, the isolated complex **3d** does not give the corresponding 2:1 complex on further reaction with **2d**. In the 1:1 compounds **3c–g** the geometry of the  $\text{Fe}(\text{CO})_3$  fragment is *meridional*. By analogy with other di- or trinuclear complexes obtained by reaction of  $[\text{Fe}(\text{CO})_3(\text{SiR}_3)(\text{PR}')^-]$  with metal halides,<sup>2,3</sup> the silyl and phosphine ligands are trans, i.e. the  $\text{Fe–Cd}$  bond is cis to both  $\text{SiR}_3$  and  $\text{PR}'_3$ .

Molecular weight determinations of **3c,d** by vapor pressure osmometry and cryoscopy show that these compounds are dimeric in benzene solutions. Although molecular weights were not determined for **3e** and **3g**,<sup>2a</sup> these complexes are probably also



dimeric. A dimeric structure (with unsymmetrical halide bridges) was also found by X-ray crystallography for *mer*- $[(\text{Me}_3\text{P})(\text{Ph}_2\text{MeSi})(\text{CO})_3\text{FeHg}(\mu\text{-Br})]_2^{2d}$  and  $[(\text{MeO})_3\text{Si}](\text{CO})_3\text{Fe}(\mu\text{-dppm})\text{Cd}(\mu\text{-Cl})_2$ .<sup>3f</sup>

To find out to what extent the kind of the products is influenced by the nature of the halide, we also reacted **2c,d** with  $\text{CdBr}_2$ . Bromide instead of chloride results in weaker halide bridges but also in a smaller thermodynamic driving force of the reaction due to the smaller lattice energy of  $\text{NaBr}$  compared to  $\text{NaCl}$ . In these reactions only the 1:1 compounds **3h,i** are formed, even if an excess of **2** is used in the reaction. The bromo-bridged compounds **3h,i** have the same structure as the corresponding chloro-bridged complexes **3c,d** according to the spectroscopic data and molecular weight determinations.

While the nature of the halide does not influence the outcome of the reaction of the diphenylphosphine substituted anionic compounds **2c,d**, it does indeed influence the reaction of the 2-(diphenylphosphino)pyridine-substituted complex **2h**. In this compound only the phosphorus atom is coordinated to the iron atom while the pyridine moiety is pending (Scheme I).

If **2h** is reacted with  $\text{CdBr}_2$ , the 1:1, bromo-bridged compound **4** is formed, while reaction with  $\text{CdCl}_2$  gives the 2:1 compound **6**, irrespective of the **2h**: $\text{CdX}_2$  molar ratio employed. The 2:1 complex **6** cannot be obtained by reaction of **4** with an excess of **2h**. This is not due to a lack of reactivity of **4** toward nucleophiles, since reaction of **4** with 4-picoline results in an easy splitting of the bromo bridges and formation of the monomeric 1:1 compound **5**. Therefore, the reason for the different outcome of the reaction of **2h** with  $\text{CdCl}_2$  and  $\text{CdBr}_2$  (and the fact that **4** cannot be converted to **6**) must be a thermodynamic one. This interpretation is supported by results obtained for the mercury compounds  $\text{XHgA}$  ( $\text{A} = \text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{Bu})$ ), where it has been shown that the equilibrium constant for the redistribution reaction,  $2\text{XHgA} \rightleftharpoons \text{HgX}_2 + \text{HgA}_2$ , is smaller for  $\text{X} = \text{I}$  than for  $\text{X} = \text{Br}$ .<sup>6</sup>

In the complexes **4–6** 2-(diphenylphosphino)pyridine acts as a bridging ligand. While the phosphine part remains bonded to the iron atom, the pyridine moiety is coordinated the cadmium atom. In each compound the cadmium atom is therefore four-coordinate.

**Spectroscopic Characteristics.** Apart from the  $\nu(\text{CO})$  bands in the infrared spectrum and the relative intensity of the  $^1\text{H}$ -NMR signals, the three types of complexes (*fac*-2:1, *mer*-2:1, *mer*-1:1) are easily distinguished by the  $^2J_{\text{CdFeP}}$  coupling constants. For the *facial* 2:1 compounds **3a,b** the coupling constant  $^2J_{^{113}\text{CdFeP}}$

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Scheme I

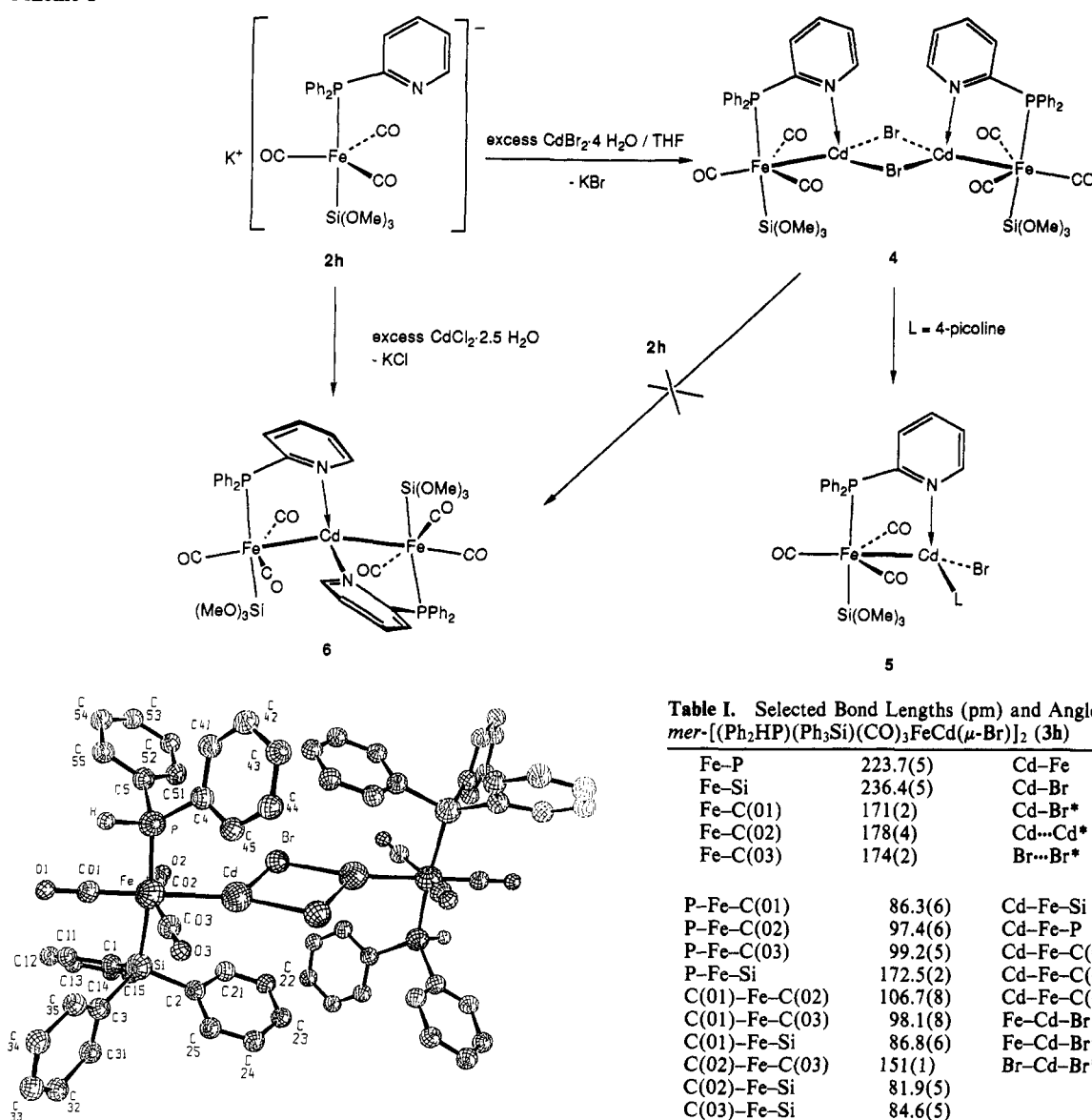


Figure 1. SCHAKAL drawing of the molecular structure of 3h. Hydrogen atoms are omitted.

is about 105 Hz (coupling to  $^{111}\text{Cd}$  is smaller by a factor of 1.0467), while for the *meridional* 2:1 compound 3f  $^2J_{^{113}\text{CdFeP}}$  is 145.1 Hz. Distinctly higher values of  $^2J_{^{113}\text{CdFeP}}$  (about 160–170 Hz) are found for the *meridional* 1:1 compounds 3c–i. In the 1:1 compound 4  $^2J_{^{113}/^{111}\text{CdFeP}}$  (102 Hz) is also higher than in the 2:1 compound 6 (66 Hz). The absolute value of 4 is lower than in 3c–i due to the tetrahedral coordination of cadmium. In the known compounds  $[\{(\text{RO})_3\text{Si}\}(\text{CO})_3\text{Fe}(\mu\text{-dppm})\text{Cd}(\mu\text{-X})]_2$  (X = Cl, 84 Hz; X = Br, 82 Hz<sup>3f</sup>),  $J_{^{113}/^{111}\text{CdFeP}}$  is smaller than in 3c–i probably due to both the tetrahedral coordination at cadmium and/or opposite signs for  $^2J_{\text{CdFeP}}$  and  $^3J_{\text{CdFeP}}$ .

The  $^{31}\text{P}$ -NMR signal in the  $\text{PPh}_2$ -substituted compounds 3c,d,h,i is temperature dependent. At room temperature only a broad singlet (proton decoupled) without cadmium satellites is observed, which appears as a sharp singlet (proton decoupled) with Cd satellites on cooling to 213 or 233 K, showing the expected doublet structure with off-resonance decoupling. This phenomenon is probably not due to a dynamic behavior at Fe, because the  $^{13}\text{C}$ -NMR spectra show two different and well-resolved signals for the CO ligands. A temperature dependent (–45 to +50 °C)

Table I. Selected Bond Lengths (pm) and Angles (deg) for *mer*- $[(\text{Ph}_2\text{HP})(\text{Ph}_3\text{Si})(\text{CO})_3\text{FeCd}(\mu\text{-Br})]_2$  (3h)

Fe–P	223.7(5)	Cd–Fe	254.0(3)
Fe–Si	236.4(5)	Cd–Br	268.9(2)
Fe–C(01)	171(2)	Cd–Br*	260.4(2)
Fe–C(02)	178(4)	Cd...Cd*	371
Fe–C(03)	174(2)	Br...Br*	377
P–Fe–C(01)	86.3(6)	Cd–Fe–Si	92.6(2)
P–Fe–C(02)	97.4(6)	Cd–Fe–P	94.5(2)
P–Fe–C(03)	99.2(5)	Cd–Fe–C(01)	176.0(6)
P–Fe–Si	172.5(2)	Cd–Fe–C(02)	77.1(5)
C(01)–Fe–C(02)	106.7(8)	Cd–Fe–C(03)	77.9(5)
C(01)–Fe–C(03)	98.1(8)	Fe–Cd–Br	127.58(8)
C(01)–Fe–Si	86.8(6)	Fe–Cd–Br*	139.9
C(02)–Fe–C(03)	151(1)	Br–Cd–Br*	90.9
C(02)–Fe–Si	81.9(5)		
C(03)–Fe–Si	84.6(5)		

infrared spectrum of 3i shows a shift of the  $\nu(\text{CO})$  bands to lower wavenumbers (about 10  $\text{cm}^{-1}$ ) on cooling a toluene solution from 298 to 233 K. However, the *meridional* geometry of the  $\text{Fe}(\text{CO})_3$  moiety is retained. We attribute the temperature dependency of the spectra to association phenomena, which currently cannot be quantified, or to a preferred rotational conformer of the phosphine ligand at low temperature.

**Molecular Structures of 3h and 6.** X-ray structure analysis of 3h (Figure 1 and Tables I and II) clearly shows the dimeric nature of this 1:1 compound. Contrary to *mer*- $[(\text{Me}_3\text{P})(\text{MePh}_2\text{Si})(\text{CO})_3\text{FeHg}(\mu\text{-Br})]_2$ , which is only weakly associated ( $\text{Hg–Br} = 253.5(3)$  and  $306.3(1)$  pm;  $\text{Fe–Hg–Br} = 161.0(1)$  and  $113.5(1)^\circ$ ),<sup>2d</sup> the Cd–Br distances in 3h, the complex being centrosymmetric by crystallographic symmetry, are very similar (268.9(2) and 260.4(2) pm), and the Fe–Cd–Br angles only differ by  $12.3^\circ$ . The bromo bridges and the iron atom are approximately coplanar with the cadmium atom.

The 2:1 compound 6 possesses a crystallographically imposed  $C_2$  axis (Figure 2 and Tables III and IV) which passes through the Cd atom and relates the atoms Fe and N to Fe\* and N\*, respectively. The geometry about the Cd center is flattened tetrahedral, with a Fe–Cd–Fe\* angle of  $143.44(3)^\circ$ , a N–Cd–N\* angle of  $80.7(1)^\circ$ , and a N–Cd–Fe angle of  $89.05(7)^\circ$ . The Cd–N distance of 249.3(3) pm is longer than the average value

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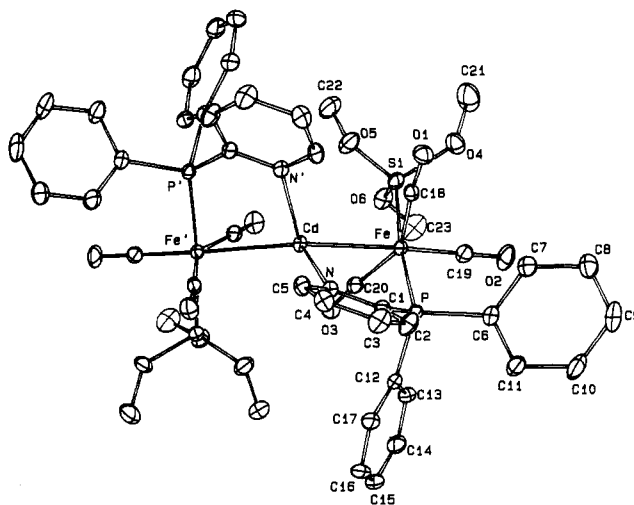
**Table II.** Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for **3h**

atom	x	y	z	B(eq), Å <sup>2</sup>
Cd	0.1279(1)	0.4391(1)	0.09279(9)	5.21(3)
Br	-0.1383(2)	0.4825(2)	0.0827(1)	6.02(5)
Fe	0.2714(2)	0.3878(2)	0.2351(2)	4.06(6)
P	0.2236(5)	0.5669(4)	0.2484(3)	4.5(1)
Si	0.3464(5)	0.1934(4)	0.2337(3)	4.0(1)
O(1)	0.418(1)	0.324(1)	0.4040(8)	7.2(4)
O(2)	0.467(1)	0.401(1)	0.0910(8)	6.9(4)
O(3)	0.027(1)	0.333(1)	0.3066(8)	6.2(4)
C(1)	0.279(2)	0.097(1)	0.332(1)	4.3(4)
C(01)	0.359(2)	0.350(1)	0.335(1)	4.9(5)
C(02)	0.388(2)	0.398(1)	0.146(1)	5.7(5)
C(2)	0.290(2)	0.177(1)	0.124(1)	4.5(4)
C(03)	0.126(2)	0.357(1)	0.280(1)	5.7(5)
C(3)	0.531(2)	0.131(1)	0.243(1)	4.3(4)
C(4)	0.200(2)	0.693(1)	0.152(1)	4.8(4)
C(5)	0.088(2)	0.615(1)	0.323(1)	4.8(5)
C(11)	0.196(2)	0.038(2)	0.321(1)	6.5(5)
C(12)	0.150(2)	-0.031(2)	0.396(2)	9.5(7)
C(13)	0.197(2)	-0.045(2)	0.477(1)	10.1(8)
C(14)	0.288(2)	0.007(2)	0.490(1)	7.7(7)
C(15)	0.329(2)	0.076(1)	0.419(1)	7.0(6)
C(21)	0.155(2)	0.202(1)	0.101(1)	4.6(4)
C(22)	0.109(2)	0.205(1)	0.017(1)	5.4(4)
C(23)	0.201(2)	0.179(2)	-0.049(1)	7.6(6)
C(24)	0.332(2)	0.147(1)	-0.028(1)	6.0(5)
C(25)	0.380(2)	0.147(1)	0.055(1)	5.7(5)
C(31)	0.586(2)	0.015(2)	0.244(1)	6.3(5)
C(32)	0.0721(2)	-0.037(2)	0.253(1)	8.1(7)
C(33)	0.810(2)	0.024(2)	0.257(1)	8.2(7)
C(34)	0.762(2)	0.134(2)	0.260(1)	7.8(7)
C(35)	0.625(2)	0.186(2)	0.248(1)	5.4(5)
C(41)	0.138(2)	0.801(1)	0.161(1)	6.5(6)
C(42)	0.135(2)	0.895(1)	0.095(1)	7.0(6)
C(43)	0.195(2)	0.882(2)	0.014(1)	7.2(6)
C(44)	0.259(2)	0.777(2)	0.001(1)	6.6(6)
C(45)	0.262(2)	0.679(1)	0.069(1)	5.1(5)
C(51)	-0.039(2)	0.623(2)	0.299(2)	7.1(6)
C(52)	-0.146(2)	0.660(2)	0.355(2)	10.1(8)
C(53)	-0.117(2)	0.683(2)	0.435(2)	10.9(8)
C(54)	0.006(3)	0.679(2)	0.454(2)	12(1)
C(55)	0.115(2)	0.638(2)	0.401(1)	8.2(7)
C(100)	0.544(2)	-0.397(2)	0.395(2)	8.5(6)*
C(200)	0.608(2)	-0.475(2)	0.340(2)	9.4(7)*
C(300)	0.595(3)	-0.438(2)	0.246(2)	10.8(8)*
C(400)	0.528(3)	0.663(2)	0.212(2)	11.9(9)*
C(500)	0.461(3)	-0.250(2)	0.250(2)	11.4(8)*
C(600)	0.473(3)	-0.283(2)	0.354(2)	10.3(7)*
C(700)	0.688(4)	-0.585(3)	0.374(3)	16(1)*

\* Starred values denote atoms that were refined isotropically.

of 238.1 pm found for Cd–pyridine distances (where the coordination number is 6 or 7),<sup>8</sup> the average Cd–N value of 237 pm in [(bipy)CdFe(CO)<sub>4</sub>]<sub>3</sub>, in which the cadmium is four-coordinate,<sup>9</sup> and similar to the Cd–N distances (250(1) and 254(1) pm) in four-coordinate (2,2'-bipyridyl)dimethylcadmium.<sup>10</sup>

When the Cd–Fe bond is ignored, then geometry about the Fe atom is of the trigonal bipyramidal type (C(CO<sub>eq</sub>)–Fe–C(CO<sub>eq</sub>)) in **3h** is 151(1)°; in **6** it is 146.9(2)°, as found in other bimetallic complexes containing Fe(PR'<sub>3</sub>)(CO)<sub>3</sub>(SiR<sub>3</sub>) fragments connected to d<sup>10</sup> metal moieties.<sup>2,3</sup> The Cd–Fe distance in **6** (269.70(5) pm) is distinctly longer than in **3h** (254.0(3) pm), *mer*-[(MeO)<sub>3</sub>Si](CO)<sub>3</sub>Fe(μ-dppm)Cd(μ-Cl)<sub>2</sub> (262.4(2) pm),<sup>3f</sup> [L(CO)<sub>3</sub>FeSi(OMe)<sub>2</sub>(μ-OMe)]<sub>2</sub>Cd (L = Ph<sub>2</sub>PCH<sub>2</sub>C(O)(η-C<sub>5</sub>H<sub>4</sub>)FeCp) (261.2(1) pm) and *mer*-[L(CO)<sub>3</sub>FeSi(OMe)<sub>2</sub>(μ-OMe)]<sub>2</sub>Cd(μ-Cl)<sub>2</sub> (260.1(1) pm).<sup>4</sup> The different Cd–Fe bond lengths in these complexes are probably not due to different polarities of this

**Figure 2.** ORTEP drawing of the molecular structure of **6**. Hydrogen atoms are omitted.**Table III.** Selected Bond Lengths (pm) and Angles (deg) for *mer*-[(MeO)<sub>3</sub>Si](CO)<sub>3</sub>Fe(μ-Ph<sub>2</sub>Ppy)]<sub>2</sub>Cd (**6**)

Cd–N	249.3(3)	Fe–P	221.8(1)
Cd–Fe	269.70(5)	Fe–C(18)	175.0(5)
N–C(1)	134.2(5)	Fe–C(19)	175.7(5)
N–C(5)	134.5(5)	Fe–C(20)	176.8(5)
C(1)–C(2)	137.5(6)	Fe–Si	228.6(1)
C(2)–C(3)	138.4(6)	Si–O(4)	164.3(3)
C(3)–C(4)	136.3(6)	Si–O(5)	164.2(3)
C(4)–C(5)	137.0(6)	Si–O(6)	164.0(3)
C(1)–P	184.6(4)	P–C(6)	183.3(4)
		P–C(12)	182.5(4)
P–Fe–Cl(18)	94.7(1)	N–Cd–N*	80.7(1)
P–Fe–C(19)	90.8(1)	N–Cd–Fe	89.05(7)
P–Fe–C(20)	99.2(1)	N–Cd–Fe*	119.64(7)
P–Fe–Si	173.21(5)	Fe–Cd–Fe*	143.45(3)
C(18)–Fe–C(19)	105.5(2)	Cd–N–C(4)	148.5(2)
C(18)–Fe–C(20)	146.9(2)	N–C(1)–P	115.7(3)
C(18)–Fe–Si	82.6(1)	C(1)–P–C(6)	101.1(2)
C(19)–Fe–C(20)	104.2(2)	C(1)–P–C(12)	101.9(2)
C(19)–Fe–Si	84.0(1)	C(1)–P–Fe	116.7(1)
C(20)–Fe–Si	86.3(1)	C(6)–P–C(12)	102.1(2)
Fe–Si–O(4)	108.4(1)	C(6)–P–Fe	114.7(1)
Fe–Si–O(5)	112.0(1)	C(12)–P–Fe	117.8(1)
Fe–Si–O(6)	117.8(1)		

bond, because the ν(CO) bands in the infrared spectra are very similar. The reason for the longer Cd–Fe distances in the dppm- or phosphinopyridine-bridged complexes is probably the different coordination geometry at the cadmium atom or geometric constraints imposed by the bridging ligands.

## Conclusions

Complexes with either Fe–Cd(μ-Cl)<sub>2</sub>Cd–Fe or Fe–Cd–Fe links are formed in the reactions of [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PR'<sub>3</sub>)]<sup>–</sup> with CdX<sub>2</sub> (X = Cl, Br). In the trinuclear complexes the Fe(CO)<sub>3</sub> unit is *meridional* or *facial*. A subtle interplay of the electronic and steric properties of the PR'<sub>3</sub> ligand as well as the nature of the halide is responsible for a particular composition or stereochemistry of the products. For instance, the only difference between the complexes **3a** and **3f** is the basicity of the phosphorus ligand (the cone angle of PMe<sub>3</sub> and P(OMe)<sub>3</sub> is about the same). The higher electron density at the metal atom in **2a** (and **3a**) obviously is responsible for the different structure. A similar phenomenon was found in the complexes Fe(CO)<sub>3</sub>(SiCl<sub>3</sub>)<sub>2</sub>(PR'<sub>3</sub>), where the *facial* isomer is kinetically favored (upon photochemical preparation) over the *meridional* isomer if the phosphine is basic and small (PMe<sub>3</sub> or PMe<sub>2</sub>Ph).<sup>11</sup> In all reactions of the PMe<sub>3</sub> and

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**Table IV.** Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for **6**

atom	x	y	z	B(eq), Å <sup>2</sup>
Cd	0.500	0.08571(4)	0.750	2.680(8)
N	0.5217(1)	-0.1035(3)	0.6805(1)	2.93(7)
C(1)	0.5636(1)	-0.1080(4)	0.6583(2)	2.72(8)
C(2)	0.5803(2)	-0.2225(4)	0.6320(2)	4.2(1)
C(3)	0.5539(2)	-0.3358(4)	0.6275(2)	4.6(1)
C(4)	0.5113(1)	-0.3323(4)	0.6497(2)	3.7(1)
C(5)	0.4968(1)	-0.2150(4)	0.6753(2)	3.40(9)
P	0.59625(3)	0.0479(1)	0.66527(5)	2.57(2)
C(6)	0.6538(1)	-0.0142(4)	0.6567(2)	3.48(9)
C(7)	0.6772(2)	-0.0640(6)	0.7094(2)	5.4(1)
C(8)	0.7208(2)	-0.1081(6)	0.7054(3)	6.5(1)
C(9)	0.7421(2)	-0.1024(6)	0.6492(3)	6.5(1)
C(10)	0.7193(2)	-0.0565(6)	0.5961(3)	6.1(1)
C(11)	0.6755(2)	-0.0111(5)	0.5993(2)	4.8(1)
C(12)	0.5845(1)	0.1253(4)	0.5878(2)	3.01(8)
C(13)	0.6003(1)	0.2525(5)	0.5788(2)	3.66(9)
C(14)	0.5958(2)	0.3129(5)	0.5198(2)	4.8(1)
C(15)	0.5757(2)	0.2477(6)	0.4698(2)	5.4(1)
C(16)	0.5592(2)	0.1211(6)	0.4779(2)	5.2(1)
C(17)	0.5638(2)	0.0598(5)	0.5367(2)	4.2(1)
Fe	0.58631(2)	0.16990(5)	0.75176(2)	2.49(1)
C(18)	0.5882(1)	0.0343(4)	0.8041(2)	3.18(8)
O(1)	0.5922(1)	-0.0563(3)	0.8387(1)	4.92(7)
C(19)	0.6420(1)	0.2288(4)	0.7495(2)	3.65(9)
O(2)	0.6785(1)	0.2667(4)	0.7480(2)	5.95(8)
C(20)	0.5535(1)	0.3000(4)	0.7174(2)	3.31(9)
O(3)	0.5351(1)	0.3908(3)	0.6953(2)	5.01(7)
Si	0.58454(4)	0.2885(1)	0.88463(5)	3.62(3)
O(4)	0.6315(1)	0.2597(4)	0.8860(1)	5.37(8)
C(21)	0.6431(2)	0.3105(8)	0.9463(3)	9.6(2)
O(5)	0.5417(1)	0.2458(4)	0.8878(1)	5.41(8)
C(22)	0.5259(2)	0.3160(7)	0.9394(2)	6.7(2)
O(6)	0.5800(1)	0.4509(3)	0.8395(2)	4.83(7)
C(23)	0.6106(2)	0.5333(6)	0.8101(3)	7.4(2)
C(24)	0.2742(2)	0.5295(6)	0.3929(3)	7.1(2)
C(25)	0.2364(3)	0.4597(7)	0.3895(5)	11.6(3)
C(26)	0.1958(2)	0.5208(8)	0.4021(4)	10.2(2)
C(27)	0.1940(2)	0.6459(9)	0.4111(5)	11.2(2)
C(28)	0.2310(3)	0.7164(9)	0.4122(8)	20.3(5)
C(29)	0.2719(3)	0.6575(8)	0.4005(6)	15.9(3)
Cl	0.32611(7)	0.4566(2)	0.3801(2)	13.14(8)

PHPh<sub>2</sub> substituted anionic silyl complexes reported in this paper only one type of complex is formed, irrespective of the employed ratio of [Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PR'<sub>3</sub>)]<sup>-</sup> and CdX<sub>2</sub>. Contrary to the related Fe–Hg complexes,<sup>2</sup> no conversion from the 1:1 to the 2:1 stoichiometry, or vice versa, was observed for the Fe–Cd complexes **3**, **4**, and **6**.

## Experimental Section

All operations were performed in an atmosphere of dry and oxygen-free nitrogen, using dried and nitrogen-saturated solvents. Melting points were determined by differential thermoanalysis (DuPont Thermal Analyzer). IR spectra: Perkin-Elmer 283, CaF<sub>2</sub>-cells. <sup>1</sup>H NMR spectra: Jeol FX 90 Q; Bruker AC 200 and SY200. <sup>13</sup>C NMR spectra: Bruker AC 200 (50.3 MHz) and Bruker WM 400 (100 MHz). <sup>31</sup>P NMR spectra: Jeol FX-90Q (36.23 MHz), Bruker SY200 (81.02 MHz), and Bruker AMX 400 (161.98 MHz), relative external 85% H<sub>3</sub>PO<sub>4</sub>. Molecular weights were determined by osmometry in benzene with a Knauer vapor pressure osmometer.

Preparation, and spectroscopic data of **1a–d**,<sup>2d</sup> **1e**,<sup>4</sup> and **2a–d**<sup>2d</sup> were already reported.

**Preparation of mer-Fe(CO)<sub>3</sub>(H)(SiMePh<sub>2</sub>)[P(OMe)<sub>3</sub>] (1f).** To a solution of 1.10 g (3.0 mmol) Fe(CO)<sub>4</sub>(H)SiMePh<sub>2</sub><sup>2a</sup> in 50 mL of petroleum ether was added dropwise a solution of 0.372 g (3.0 mmol) of P(OMe)<sub>3</sub> in 15 mL of petroleum ether at 0 °C. Then the solution was stirred at room temperature until gas evolution had ceased and the ν(CO) bands of the reactants had disappeared. The solution was filtered, and the solvent was removed in vacuo. Compound **1f** precipitates from the pentane solution at –78 °C as a brown oil. Yield: 0.86 g (62%). IR (THF; cm<sup>-1</sup>): ν(CO) 2040 (w), 1995 (sh), 1975 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ –9.33 (d, FeH, 1 H, <sup>2</sup>J<sub>HFeP</sub> = 35.3 Hz), 1.36 (s,

SiCH<sub>3</sub>, 3 H), 3.22 (d, POCH<sub>3</sub>, 9 H, <sup>3</sup>J<sub>POCH</sub> = 12.1 Hz), 8.07–7.28 (m, C<sub>6</sub>H<sub>5</sub>, 10 H). <sup>31</sup>P{<sup>1</sup>H} NMR (36.23 MHz, C<sub>6</sub>D<sub>6</sub>): δ 175.8.

**Preparation of mer-Fe(CO)<sub>3</sub>(H)(Si(OMe)<sub>3</sub>)(Ph<sub>2</sub>Ppy) (1h).** To a stirred solution of 2.89 g (11 mmol) of 2-(diphenylphosphino)pyridine in toluene (90 mL) was added a hexane solution (300 mL) of Fe(CO)<sub>4</sub>(H)(Si(OMe)<sub>3</sub>)<sup>3d</sup> (11 mmol). After the reaction mixture was kept at –20 °C for 2–3 days, **1g** crystallized as pale yellow needles. After filtration and washing with 15 mL of hexane, the crystals were dried for 30 min in vacuo. Yield: 4.33 g (75%). Anal. Calcd for C<sub>23</sub>H<sub>24</sub>FeO<sub>6</sub>P<sub>2</sub>Si (M<sub>r</sub> = 525.36): C, 52.58; H, 4.60; N, 2.67. Found: C, 52.10; H, 4.60; N, 2.50. IR (Et<sub>2</sub>O; cm<sup>-1</sup>): ν(CO) 2049 (w), 1985 (s, sh), 1978 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ –8.86 (d, FeH, 1 H, <sup>2</sup>J<sub>PH</sub> = 25.4 Hz), 3.78 (s, 9 H, OCH<sub>3</sub>), 6.41–8.45 (m, 14 H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>D<sub>6</sub>, 303 K): δ 62.8.

**Preparation of Na[Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PR'<sub>3</sub>)] (2e–g)** was performed as already reported for **2a–d**.<sup>2d</sup> Isolation of the compounds is possible but not necessary for the reactions described in this paper. **2e**. IR (THF, cm<sup>-1</sup>): ν(CO) 1850 (s), 1810 (s). **2f**. IR (THF, cm<sup>-1</sup>): ν(CO) 1845 (s), 1805 (s). **2h**. IR (THF, cm<sup>-1</sup>): ν(CO) 1920 (w), 1844 (vs), 1821 (s, sh).

**Preparation of fac-[Fe(CO)<sub>3</sub>(SiR<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cd (3a,b).** A 0.092-g (0.5 mmol) sample of CdCl<sub>2</sub> was added to a solution of 1.0 mmol **2a** or **2b** in 50 mL of THF. After 20–25 min of stirring at 0 °C, the heterogeneous reaction, which was monitored by IR spectroscopy, was finished. From the filtered solution the solvent was removed in vacuo, leaving a residue which was dissolved in 70 mL of toluene. The solution was filtered and concentrated in vacuo to 3–5 mL, and 50–80 mL of pentane was added. After 24 h at –78 °C the complexes **3a** and **3b** precipitated as yellow solids, which were separated from the liquid, washed four times with 15 mL of pentane each, and dried in vacuo.

**3a (SiR<sub>3</sub> = SiMePh<sub>2</sub>).** Yield: 0.83 g (88%). Mp: 74 °C dec. Anal. Calcd for C<sub>38</sub>H<sub>44</sub>CdFe<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Si<sub>2</sub> (M<sub>r</sub> = 938.98): C, 48.61; H, 4.72; Fe, 11.90; Cd, 11.97. Found: C, 48.57; H, 4.75; Fe, 12.18; Cd, 11.83. IR (THF, cm<sup>-1</sup>): ν(CO) 1975 (vs), 1905 (vs). <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.02 (d, P(CH<sub>3</sub>)<sub>3</sub>, 18 H, <sup>2</sup>J<sub>PCH</sub> = 8.8 Hz), 1.40 (s, SiCH<sub>3</sub>, 6 H), 7.09–8.13 (m, phenyl-H, 20 H). <sup>13</sup>C NMR (50.32 Hz, C<sub>6</sub>D<sub>6</sub>): δ 8.30 (s, SiCH<sub>3</sub>), 22.20 (d, P(CH<sub>3</sub>)<sub>3</sub>, <sup>1</sup>J<sub>PC</sub> = 29.5 Hz), 146.10–127.53 (C<sub>6</sub>H<sub>5</sub>), 213.55 (d, CO, <sup>2</sup>J<sub>PFeC</sub> = 14.2 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (36.23 MHz, C<sub>6</sub>D<sub>6</sub>): δ 11.5 (s, <sup>2</sup>J<sub>113/111</sub>CdFeP = 102.6 Hz, <sup>2</sup>J<sub>111</sub>CdFeP = 99.6 Hz).

**3b (SiR<sub>3</sub> = SiMe<sub>3</sub>).** Yield: 0.60 g (87%). Mp: 82 °C dec. Anal. Calcd for C<sub>18</sub>H<sub>36</sub>CdFe<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Si<sub>2</sub> (M<sub>r</sub> = 690.70): C, 31.30; H, 5.25; Fe, 16.17; Cd, 16.27. Found: C, 31.21; H, 5.23; Fe, 15.88; Cd, 16.62. IR (THF, cm<sup>-1</sup>): ν(CO) 1973 (vs), 1897 (vs). <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.99 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 18 H), 1.28 (d, P(CH<sub>3</sub>)<sub>3</sub>, 18 H, <sup>2</sup>J<sub>PCH</sub> = 9.1 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (36.23 MHz, C<sub>6</sub>D<sub>6</sub>): δ 8.8 (s, <sup>2</sup>J<sub>113/111</sub>CdFeP = 107.0 Hz, <sup>2</sup>J<sub>111</sub>CdFeP = 102.6 Hz).

**Preparation of mer-[(Ph<sub>2</sub>HP)(R<sub>3</sub>Si)(CO)<sub>3</sub>FeCd(μ-X)]<sub>2</sub> (3c,d,h,i) and mer-[(MeO)<sub>3</sub>P](Ph<sub>3</sub>Si)(CO)<sub>3</sub>FeCd(μ-Cl)]<sub>2</sub> (3e).** To a solution of 0.8–1.0 mmol of **2c–e** in 40 mL of THF was added an equimolar amount of CdX<sub>2</sub> (X = Cl, Br). The reaction mixture was stirred for 20–40 min at room temperature and monitored by IR spectroscopy. After the ν(CO) bands of **2c–e** have disappeared, the solution was filtered and concentrated in vacuo to 4–5 mL. The product precipitated at –78 °C as a yellow solid after addition of about 50–80 mL of pentane. The solid was separated, washed four times with 15 mL of pentane each, and dried in high vacuum.

**3c (SiR<sub>3</sub> = SiPh<sub>3</sub>, X = Cl).** Yield: 0.89 g (61%). Mp: 60 °C dec. Anal. Calcd for C<sub>66</sub>H<sub>52</sub>Cd<sub>2</sub>Cl<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Si<sub>2</sub> (M<sub>r</sub> = 1466.67): C, 54.05; H, 3.57. Found: C, 53.90; H, 3.76. IR (toluene, cm<sup>-1</sup>): ν(CO) 1984 (m), 1929 (s), 1905 (vs); ν(PH) 2340 (vw). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>): δ 7.14 (d, PH, 2 H, <sup>1</sup>J<sub>PH</sub> = 360.9 Hz), 7.92–6.90 (m, C<sub>6</sub>H<sub>5</sub>, 50 H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>): at 213 K, δ 18.0 (s, <sup>2</sup>J<sub>113/111</sub>CdFeP = 172.9 Hz); at 298 K, δ 31.8 (s, br). Vapor pressure osmometry (benzene, 45 °C): Found (calcd) molecular weight, 1462 (1467). Cryoscopy (benzene): Found, 1463.

**3d (SiR<sub>3</sub> = SiMePh<sub>2</sub>, X = Cl).** Yield: 1.13 g (84%). Mp: 66 °C dec. Anal. Calcd for C<sub>56</sub>H<sub>48</sub>Cd<sub>2</sub>Cl<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Si<sub>2</sub> (M<sub>r</sub> = 1342.52): C, 50.10; H, 3.60; Fe, 8.32; Cd, 16.74. Found: C, 50.38; H, 3.93; Fe, 8.03; Cd, 17.02. IR (toluene, cm<sup>-1</sup>): ν(CO) 1982 (m), 1930 (sh), 1904 (vs); ν(PH) 2330 (vw). <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.46 (s, SiCH<sub>3</sub>, 6 H), 5.56 (s, PH, 1 H, <sup>3</sup>J<sub>113/111</sub>CdFeP = 14.1 Hz, the second part of the doublet is hidden by the phenyl protons), 6.82–7.88 (m, C<sub>6</sub>H<sub>5</sub>, 40 H). <sup>13</sup>C NMR (50.32, C<sub>6</sub>D<sub>6</sub>): δ 6.51 (s, SiCH<sub>3</sub>), 146.49–124.61 (C<sub>6</sub>H<sub>5</sub>), 214.40 (d, CO<sub>ax</sub>, <sup>2</sup>J<sub>PFeC</sub> = 10.1 Hz), 213.16 (d, CO<sub>eq</sub>, <sup>2</sup>J<sub>PFeC</sub> = 14.3 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>): at 233 K, δ 19.0 (s, <sup>2</sup>J<sub>113/111</sub>CdFeP = 164.1 Hz, <sup>2</sup>J<sub>111</sub>CdFeP = 158.2 Hz); 298 K, δ 31.5 (s, br). Vapor pressure osmometry (benzene, 45 °C): found (calcd) molecular weight, 1389 (1343).

**3h** ( $\text{SiR}_3 = \text{SiPh}_3$ ,  $\text{X} = \text{Br}$ ). Yield: 1.12 g (72%). Mp: 117 °C dec. Anal. Calcd for  $\text{C}_{66}\text{H}_{52}\text{Br}_2\text{Cd}_2\text{Fe}_2\text{O}_6\text{P}_2\text{Si}_2$  ( $M_r = 1555.57$ ): C, 50.96; H, 3.37; Fe, 7.18; Cd, 14.45. Found: C, 51.05; H, 3.55; Fe, 6.96; Cd, 14.80. IR (toluene,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1986 (m), 1928 (sh), 1909 (vs);  $\nu(\text{PH})$  2321 (vw).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta$  7.13 (d, PH, 2 H,  $^1J_{\text{PH}} = 360.5$  Hz), 6.22–7.05 (m,  $\text{C}_6\text{H}_5$ , 50 H).  $^{13}\text{C}$  NMR (50.32,  $\text{C}_6\text{D}_6$ ):  $\delta$  145.10–127.47 ( $\text{C}_6\text{H}_5$ ), 213.92 (d,  $\text{CO}_{\text{ax}}$ ,  $^2J_{\text{PFcC}} = 13.2$  Hz), 212.90 (d,  $\text{CO}_{\text{eq}}$ ,  $^2J_{\text{PFcC}} = 16.6$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.98 MHz,  $\text{C}_6\text{D}_5\text{CD}_3$ ): at 213 K,  $\delta$  18.0 (s,  $^2J_{\text{H}/\text{H}}\text{CdFeP} = 172.9$  Hz); at 298 K,  $\delta$  32.8 (s, br). Cryoscopy (benzene): found (calcd) molecular weight, 1533 (1556).

**3i** ( $\text{SiR}_3 = \text{SiMePh}_2$ ,  $\text{X} = \text{Br}$ ). Yield: 1.09 g (76%). Mp: 74 °C dec. Anal. Calcd for  $\text{C}_{56}\text{H}_{48}\text{Br}_2\text{Cd}_2\text{Fe}_2\text{O}_6\text{P}_2\text{Si}_2$  ( $M_r = 1431.42$ ): C, 46.99; H, 3.38; Fe, 7.80; Cd, 15.70. Found: C, 47.05; H, 3.50; Fe, 7.59; Cd, 15.86. IR (toluene,  $\text{cm}^{-1}$ ): at 298 K,  $\nu(\text{CO})$  1990 (m), 1935 (sh), 1915 (vs);  $\nu(\text{PH})$  2320 (vw); at 233 K,  $\nu(\text{CO})$  1980 (m), 1932 (sh), 1913 (vs);  $\nu(\text{PH})$  2307 (vw).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta$  1.53 (s,  $\text{SiCH}_3$ , 6 H), 6.14 (d, PH, 2 H,  $^1J_{\text{PH}} = 353.3$  Hz,  $^3J_{\text{H}/\text{H}}\text{CdFePH} = 12.1$  Hz), 6.90–8.21 (m,  $\text{C}_6\text{H}_5$ , 40 H).  $^{13}\text{C}$  NMR (50.32,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.64 (s,  $\text{SiCH}_3$ ), 146.45–125.63 ( $\text{C}_6\text{H}_5$ ), 213.89 (d,  $\text{CO}_{\text{ax}}$ ,  $^2J_{\text{PFcC}} = 10.2$  Hz), 212.76 (d,  $\text{CO}_{\text{eq}}$ ,  $^2J_{\text{PFcC}} = 13.7$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.98 MHz,  $\text{C}_6\text{D}_5\text{CD}_3$ ): at 233 K,  $\delta$  20.1 (s,  $^2J_{\text{H}/\text{H}}\text{CdFeP} = 164.5$  Hz,  $^2J_{\text{H}/\text{H}}\text{CdFeP} = 154.3$  Hz); at 298 K,  $\delta$  31.9 (s, br). Cryoscopy (benzene): found (calcd) molecular weight, 1353 (1431).

**3e**. Yield: 0.93 g (87%). Mp: 116 °C dec. Anal. Calcd for  $\text{C}_{48}\text{H}_{48}\text{Cd}_2\text{Cl}_2\text{Fe}_2\text{O}_{12}\text{P}_2\text{Si}_2$  ( $M_r = 1342.46$ ): C, 42.95; H, 3.60; Fe, 8.32; Cd, 16.75. Found: C, 43.36; H, 3.68; Fe, 8.15; Cd, 17.03. IR (THF,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1986 (m), 1930 (sh), 1916 (vs).  $^1\text{H}$  NMR (60 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  3.32 (d,  $\text{POCH}_3$ , 18 H,  $^3J_{\text{PH}} = 13.8$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (36.23 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  179.9 (s,  $^2J_{\text{H}/\text{H}}\text{CdFeP} = 156.8$  Hz,  $^2J_{\text{H}/\text{H}}\text{CdFeP} = 149.1$  Hz,  $^2J_{\text{PFcSi}} = 19.0$  Hz).

**Preparation of mer-[(MeO) $_3$ Si](Ph $_2$ MeSi)(CO) $_3$ Fe $_2$ Cd (3f).** A 0.5-mmol sample of  $\text{CdCl}_2$  was added to a solution of 1.0 mmol of **2f** in 50 mL of THF. The reaction mixture was stirred at 0 °C for 10–20 min. The reaction was monitored by IR spectroscopy. Workup was as for **3a,b**. Yield: 0.89 g (86%) of a yellow solid. Mp: 58 °C dec. Anal. Calcd for  $\text{C}_{38}\text{H}_{44}\text{CdFe}_2\text{O}_{12}\text{P}_2\text{Si}_2$  ( $M_r = 1034.98$ ): C, 44.10; H, 4.29; Fe, 10.79; Cd, 10.86. Found: C, 44.58; H, 4.28; Fe, 10.62; Cd, 11.03. IR (THF,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1988 (m), 1935 (sh), 1922 (vs).  $^1\text{H}$  NMR (60 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.52 (s,  $\text{SiCH}_3$ , 6 H), 3.40 (d,  $\text{POCH}_3$ , 18 H,  $^3J_{\text{PH}} = 12.6$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (36.23 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  182.7 (s,  $^2J_{\text{H}/\text{H}}\text{CdFeP} = 145.1$  Hz,  $^2J_{\text{H}/\text{H}}\text{CdFeP} = 139.2$  Hz,  $^2J_{\text{PFcSi}} = 17.6$  Hz).

**Preparation of mer-[(MeO) $_3$ Si](CO) $_3$ Fe( $\mu$ -Ph $_2$ Ppy)Cd( $\mu$ -Br) $_2$  (4).** To a solution of the potassium salt **2h** (0.283 g, 0.5 mmol) in THF (20 mL) was added  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  (0.344 g, 1.0 mmol). The reaction mixture was stirred for 2 h. The clear solution was filtered, and the solvent was removed in vacuo. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL) and filtered again and the solution concentrated to about 10 mL under reduced pressure. Addition of hexane led to the precipitation of colorless microcrystals, which were dried in vacuo. Yield: 0.301 g (84%). Dec at  $T > 200$  °C. Anal. Calcd for  $\text{C}_{46}\text{H}_{46}\text{Br}_2\text{Cd}_2\text{Fe}_2\text{N}_2\text{O}_{12}\text{P}_2\text{Si}_2$  ( $M_r = 1433.32$ ): C, 38.55; H, 3.24; N, 1.95. Found: C, 38.67; H, 3.30; N, 1.90. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1990 (s), 1928 (s), 1908 (vs). IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{CdBr})$  171 (s, br).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.69 (s,  $\text{OCH}_3$ , 9 H), 7.26–9.38 (m,  $\text{C}_6\text{H}_5$ , 14 H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81.02 MHz,  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , 303 K):  $\delta$  84.9 (s,  $^2J_{\text{CdFeP}} = 102$  Hz).

**Preparation of [(MeO) $_3$ Si](CO) $_3$ Fe( $\mu$ -Ph $_2$ Ppy)CdBr(4-pic) (5).** To a solution of 0.072 g (0.05 mmol) of **4** in  $\text{CH}_2\text{Cl}_2$  (6 mL) was added 4-picoline (0.0094 g, 0.1 mmol) by a microsyringe. The clear solution was stirred for 5 min, and then the solvent was removed and the residue dried in vacuo for several hours. Yield: 0.081 g (100%). Dec at  $T > 200$  °C. Anal. Calcd for  $\text{C}_{29}\text{H}_{30}\text{BrCdFeN}_2\text{O}_6\text{PSi}$  ( $M_r = 809.79$ ): C, 43.01; H, 3.73; N, 3.46. Found: C, 43.21; H, 3.75; N, 3.52. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1985 (m), 1925 (s), 1899 (vs). IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{CdBr})$  200 s.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.38 (s, 3 H,  $\text{CH}_3$ ), 3.63

Table V. Crystal Data for **6** and **3h**

	<b>6</b>	<b>3h</b>
formula	$\text{C}_{46}\text{H}_{46}\text{CdFe}_2\text{N}_2\text{O}_{12}\text{P}_2\text{Si}_2 \cdot 2\text{C}_6\text{H}_5\text{Cl}$	$\text{C}_{66}\text{H}_{52}\text{Br}_2\text{Cd}_2\text{Fe}_2\text{O}_6\text{P}_2\text{Si}_2 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$
fw	1386.2	1723.8
space group	$C2/c$	$P\bar{1}$
<i>a</i> , pm	2968.4(8)	1048.9(5)
<i>b</i> , pm	1004.3(3)	1268.6(4)
<i>c</i> , pm	2098.8(6)	1515.5(7)
$\alpha$ , deg		75.51(3)
$\beta$ , deg	91.87(2)	86.58(5)
$\gamma$ , deg		72.94(5)
<i>V</i> , pm <sup>3</sup>	$6254 \times 10^6$	$1866 \times 10^6$
<i>Z</i>	4	1
<i>T</i> , °C	20	25
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.472	1.534
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	10.3	21.2
$\lambda(\text{Mo K}\alpha)$ , pm	71.073	71.073
<i>R</i> <sup>a</sup>	0.028	0.066
<i>R</i> <sub>w</sub> <sup>b</sup>	0.040	0.072

$$^a R = \sum |F_o - F_c| / \sum |F_o|, \quad ^b R_w = \{\sum w(F_o - F_c)^2 / \sum wF_o^2\}^{1/2}.$$

(s, 9 H,  $\text{OCH}_3$ ), 7.16–8.95 (m, 18 H,  $\text{C}_6\text{H}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81.02 MHz,  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , 303 K):  $\delta$  84.9 (s,  $^2J_{\text{PFcCd}} = 82$  Hz).

**Preparation of mer-[(MeO) $_3$ Si](CO) $_3$ Fe( $\mu$ -Ph $_2$ Ppy) $_2$ Cd (6).** To a solution of 0.565 g (1 mmol) of the potassium salt of **2h** in THF (25 mL) was added  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.228 g, 1.0 mmol). The reaction mixture was stirred for 5 h. The clear solution was filtered and concentrated in vacuo. After a few days at  $-20$  °C, 0.401 g (69%) of yellow-green crystals of **6** were formed and collected. Mp: 152–153 °C. Anal. Calcd for  $\text{C}_{46}\text{H}_{46}\text{CdFe}_2\text{N}_2\text{O}_{12}\text{P}_2\text{Si}_2$  ( $M_r = 1161.10$ ): C, 47.59; H, 4.00; N, 2.41. Found: C, 48.43; H, 4.24; N, 2.25. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1990 (m), 1977 (m), 1918 (s), 1894 (vs). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1993 (m), 1980 (m), 1912 (s), 1885 (vs).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.30 (s,  $\text{OCH}_3$ , 9 H), 7.15–8.54 (m,  $\text{C}_6\text{H}_5$ , 14 H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81.02 MHz,  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , 303 K):  $\delta$  83.7 (s,  $^2J_{\text{CdFeP}} = 66$  Hz).

**Crystal Structure Determination of [(Ph $_2$ HP)(Ph $_2$ Si)(CO) $_3$ FeCd( $\mu$ -Br) $_2$  (3h) and [(MeO) $_3$ Si](CO) $_3$ Fe( $\mu$ -Ph $_2$ Ppy) $_2$ Cd (6).** Suitable single crystals of **3h** were obtained by recrystallization from toluene/pentane, those of **6**, by recrystallization from hot chlorobenzene. A crystal of each compound was mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Cell dimensions were determined from 25 reflections with high diffraction angles from different parts of the reciprocal space. Crystal data and experimental parameters for the data collection are given in Table V. For all subsequent calculations the Enraf-Nonius SDP/VAX package was used. The reflections were corrected for polarization and Lorentz effects and by an empirical absorption correction ( $\psi$  scan); no correction for the presence of extinctions was made. The structure was solved by the Patterson method. The positions of the hydrogen atoms were calculated according to an idealized geometry. Refinement was performed by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The parameters of the hydrogen atoms were not refined.

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**Supplementary Material Available:** Tables of complete crystal data, and anisotropic thermal parameters, the calculated coordinates and isotropic thermal parameters for the hydrogen atoms, and all bond distances and angles for **3h** and **6** (11 pages). Ordering information is given on any current masthead page.