Reactions of Heterodinuclear Fe−Pt and Fe−Pd Complexes with Cyclic Bis(amino)germylenes and -stannylenes: A Bridging Metal(II) Amide Unit between Two Different Transition Metal Centers and Donor Stabilization of Terminal Germylene and Stannylene Ligands by $Si(OMe)_3$[†]

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Reaction of the cyclic amides $\overline{\mathrm{EN^tBuSiMe_2N}}{}^t\mathrm{Bu}$ (E = Ge, Sn) with the heterobimetallic complexes $[(\mathrm{OC})_3\mathrm{Fe}(\mu\text{-CO})(\mu\text{-Ph_2PXPPh_2})\mathrm{Pt}(\mathrm{PR_3})](\mathit{Fe{-}Pt})$ (X = CH_2, NH; R = phenyl, *p*-tolyl) occurs by selective substitution of the bridging carbonyl ligand and yields the stannylene- and germylene-bridged complexes $[(\mathrm{OC})_3\mathrm{Fe}\{\mu\text{-}\overline{\mathrm{EN^tBuSiMe_2N}}{}^t\mathrm{Bu}\}(\mu\text{-Ph_2PXPPh_2})\mathrm{Pt}(\mathrm{PR_3})](\mathit{Fe{-}Pt})$ (**2a**, X = CH_2, E = Sn, R = Ph; **2b**, X = NH, E = Sn, R = Ph; **2c**, X = CH_2, E = Sn, R = *p*-tol; **3a**, X = CH_2, E = Ge, R = Ph; **3b**, X = NH, E = Ge, R = Ph). When $\overline{\mathrm{GeN^tBuSiMe_2N}}{}^t\mathrm{Bu}$ was added in excess to the germylene complex **3a**, the tetranuclear complex $[(\mathrm{OC})_3\mathrm{Fe}\{\mu\text{-}\overline{\mathrm{GeN^tBuSiMe_2N}}{}^t\mathrm{Bu}\}(\mu\text{-dppm})\mathrm{Pt}\ \{\overline{\mathrm{GeN^tBuSiMe_2N}}{}^t\mathrm{Bu}\}](\mathit{Fe{-}Pt})$ (**4**) was formed, which is in equilibrium with **3a**. The heterobimetallic $Si(OMe)_3$-substituted complexes *mer*-$[(\mathrm{OC})_3\mathrm{Fe}\{\mu\text{-Si(OMe)}_2(\overline{\mathrm{OMe)\}(\mu\text{-dppm})M}})(\mathrm{Me})](\mathit{Fe{-}M})$ (M = Pd, Pt) react with $\overline{\mathrm{EN^tBuSiMe_2N}}{}^t\mathrm{Bu}$ (E = Ge, Sn) by opening of the four-membered $\overline{\mathrm{Fe{-}Si{-}O{-}M}}$ ring to give the complexes *mer*-$[(\mathrm{OC})_3\mathrm{Fe}\{\mu\text{-Si(OMe)}_2(\overline{\mathrm{OMe)\}\{}}\underline{\mathrm{EN^tBuSiMe_2N}}{}^t\mathrm{Bu}\}\{\mu\text{-dppm})\mathrm{M}\}(\mathrm{Me})](\mathit{Fe{-}M})$ (**5**, M = Pt, E = Sn; **6**, M = Pd, E = Sn; **7**, M = Pd, E = Ge) which contain a five-membered $\overline{\mathrm{Fe{-}Si{-}O{-}E{-}M}}$ ring. The expected insertion of the amides $\overline{\mathrm{EN^tBuSiMe_2N}}{}^t\mathrm{Bu}$ into the M−Me bond was not observed. The dynamic behavior of these intramolecularly base-stabilized trimetallic germylene and stannylene complexes, which is due to a rapid exchange of the methoxy groups coordinated on E, was investigated by variable-temperature ^{1}H-NMR spectroscopy. All complexes were characterized by multinuclear NMR spectroscopy, and the solid-state structure of **7** was determined by X-ray diffraction.

Introduction

Heterodinuclear complexes containing a metal−metal bond represent ideal molecules to study the influence of different metal centers on their reactivity, including chemo- and regioselectivity aspects. In addition to metallosite-selective reactions, insertion into the metal−metal bond may occur. It has been shown recently that a $Si(OR)_3$ group may display novel features in heterometallic complexes which include hemilabile bridging behavior,[1a−e] migration from one metal center to another[1a,f] or to organic ligands,[1a,h−i] or transformation into silylene species.[1j] On the other hand, cyclic germylenes and stannylenes have been shown to be very versatile reagents toward transition metals[2] and lead to simple ligand substitutions,[2f] insertions into metal−carbon bonds,[2g,h] or more complex reactions such as tin−tin coupling in the tetrametallic chain complex $[\mathrm{CpFe(CO)_2}\{\overline{\mathrm{SnN^tBuSiMe_2N}}{}^t\mathrm{Bu}\}]_2$.[2g] Assuming that poly-

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[†] Dedicated to Prof. M. Herberhold on the occasion of his 60th birthday with our sincere congratulations.

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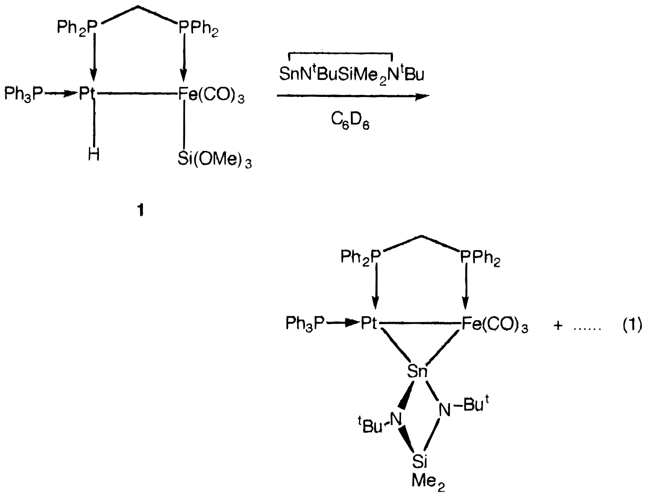
metallic systems associating such silicon and germanium/tin centered ligands would exhibit interesting new features, we envisaged to combine these two facets in a collaborative approach.

Here we report that metal(II) amides of the type $\overline{\text{EN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}$ (E = Ge, Sn)[2a,b] can be used for the systematic buildup of trimetallic compounds containing both main group and transition metals with unprecedented dative interactions between $Si(OMe)_3$ groups and the metal amides.

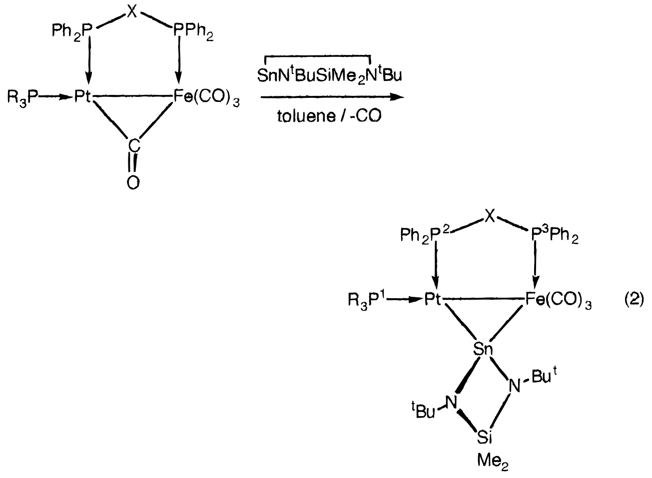
Results and Discussion

A. Complexes with a Bridging Stannylene or Germylene Ligand. Synthesis. We began this study with the bimetallic precursor complex $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-dppm})Pt(H)(PPh_3)]$(*Fe−Pt*) (**1**), which contains a terminal hydride ligand on platinum.[3] We were interested to see whether treatment of **1** with a slight excess of $\overline{\text{SnN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}$ in toluene would substitute the PPh_3 ligand or insert into the Pt−H bond. Such insertions of tin amides of the type $[Sn\{N(SiMe_3)_2\}_2]$ into the M−H bonds of mononuclear complexes have previously been reported by Lappert and Rowe.[4] However, the outcome of this reaction was very surprising. IR and ^{31}P NMR monitoring of the course of the reaction showed that all starting material had been consumed after ca. 45 min, leading to the orange-red trimetallic cluster $[(OC)_3Fe(\mu\text{-}\overline{\text{SnN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}})(\mu\text{-dppm})Pt(PPh_3)]$(*Fe−Pt*) (**2a**) as the only observable phosphorus-containing species (eq 1). This compound has been fully characterized by elemental analyses and multinuclear NMR techniques (see below).



Formal donor-induced reductive elimination of $HSi(OMe)_3$ has occurred, a reaction previously observed upon treatment of the related hydrido complex $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-dppm})Rh(H)(Cl)]$(*Fe−Rh*) with carbon monoxide.[5a] Similarly, elimination of $HSi(OMe)_3$ was observed upon reaction of $[HFe\{Si(OMe)_3\}(CO)_3(\eta^1\text{-dppm})]$ with *fac*-$[Re(CO)_3(THF)(\mu\text{-Br})]_2$ affording the bromide-bridged complex $[\overline{(OC)_3Fe(\mu\text{-dppm})(\mu\text{-Br})Re}(CO)_3]$.[5b] In the present case, however, we found no evidence by NMR or IR spectroscopy for the formation of $HSi(OMe)_3$ in the reaction mixture. We can also rule out the formation of hexamethoxydisilane or tetramethoxysilane, since the singlet resonance observed at δ 3.94 (in C_6D_6) does not correspond with their chemical shifts (commercial samples). Therefore the mechanism of this transformation remains still unclear.

A more rational access to **2** was provided by the selective substitution of the bridging CO ligand of the complexes $[(OC)_3Fe(\mu\text{-CO})(\mu\text{-dppm})Pt(PR_3)]$(*Fe−Pt*) (R = Ph, *p*-Tol)[6] by $\overline{\text{SnN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}$ in toluene under mild conditions (eq 2).



2a R = Ph, X = CH2
2b R = Ph, X = NH
2c R = *p*-Tol, X = CH2

The orange red clusters **2a,c** have been isolated in high yields and are air-stable for short periods of time. In a similar manner, the yellow bis(diphenylphosphino)amine-bridged cluster **2b** was obtained in 74% yield by the reaction of $[(OC)_3Fe(\mu\text{-CO})(\mu\text{-dppa})Pt(PPh_3)]$(*Fe−Pt*)[7] with $\overline{\text{SnN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}$. The replacement of the dppm bridge by dppa in complex **2b** lowers the stability both in the solution and solid state, which may be due to a slow reaction of the N−H group with the tin amide.[2b] Note that, in contrast to the numerous examples of dppm-bridged bi- and polymetallic complexes, only two

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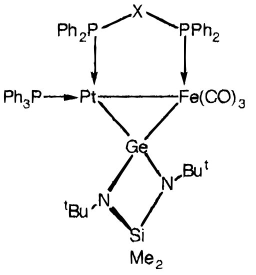
examples of dppa-bridged heterometallics have been described in the literature, to the best of our knowledge.[8]

For comparison, we also examined the reactivity of $[(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}Ph_2PXPPh_2)Pt(PPh_3)]$(*Fe*−*Pt*) toward the cyclic germanium(II) amide $\overline{\text{GeN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}$. Upon stoichiometric addition of this germylene reagent, substitution of the bridging CO ligand readily occurred to afford the stable, yellow complexes $[(OC)_3Fe\{\mu\text{-}\overline{\text{GeN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}\}(\mu\text{-}Ph_2PXPPh_2)Pt(PPh_3)]$(*Fe*−*Pt*) (**3a**, X = CH_2; **3b**, X = NH) in nearly quantitative yields. Their spectroscopic data (see below) are very similar to their tin congeners. Therefore, we assume **3** to be isostructural with **2**. In the trimetallic cores of **2** and **3**, the three metal centers are mutually connected by metal−metal bonds, conferring to the Pt and Fe centers their usual 16 and 18 e count, respectively.

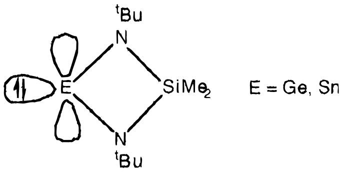


3a X = CH_2
3b X = NH

No reaction took place when the lead(II) amide $\overline{\text{PbN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}$ was mixed with $[(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}dppm)Pt(PPh_3)]$(*Fe*−*Pt*). However, plumbylene-bridged clusters have been prepared very recently by the reaction of $[Ru_3(CO)_{12}]$ with $[Pb\{CH(SiMe_3)\}_2]$.[9]

Cluster compounds in which metal(II) amides or related tin species bridge two identical transition metals to form a triangular core were already known. Examples include $[(M\{\mu\text{-}E(NR_2)_2\}CO)_3]$ (M = Pd, Pt; R = $SiMe_3$),[10a,b] $[(PPh_3)Pt\{\mu\text{-}Sn(acac)_2\}_3Pt(PPh_3)]$,[10c] $[(Ru_3(\mu\text{-}SnR_2)_2(CO)_{10}]$,[10d] and $[(PPh_3)Pd\{\mu\text{-}\overline{\text{SnN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}\}_3Pd(PPh_3)]$.[2i] Compounds **2** and **3** extend this class of mixed main group−transition metal clusters and represent the first examples where a germylene or stannylene unit bridges *different* metals connected by a metal−metal bond. A related Fe−Sn−Pt array was recently established in the μ-$SnCl_2$ complex $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-}dppm)(\mu\text{-}SnCl_2)Pt(Cl)(PEt_3)]$,[11] although in this case there was no metal−metal bond between the Pt and Fe centers.

One may ask why the germylene or stannylene ligands exclusively adopt a bridging position in compounds **2** and **3**. These ambivalent metal(II) amides possess both a filled σ-donor orbital and a low-lying empty p-orbital and can therefore act as σ-donor and/or π-acceptor ligands.[2d,e]



It is known that the π-acceptor ability of σ-donor/π-acceptor ligands like CO, CS, CNR, or SO_2 generally increases when these ligands are coordinated in a bridging mode. We therefore conclude that it is the electron-donating influence of the three phosphorus ligands (combined with two transiton metals in low oxidation states) which induces a bridging mode for the the μ-$[\overline{\text{EN}^t\text{BuSiMe}_2\text{N}^t\text{Bu}}]$ ligands which can then better evacuate electron density than in a terminal mode.

Spectroscopic Studies. The structure of complexes **2** and **3** could be unambiguously deduced from the combined NMR and IR data as exemplified below for cluster **2a**. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet of doublets at δ 83.6 for the iron-bound phosphorus atom, which is strongly coupled ($^{2+3}J(P{-}P)$ = 148 Hz) with the platinum-bound dppm phosphorus, which is found at δ 43.5. This signal is further split owing to the presence of the PPh_3 ligand which resonates at δ 41.9 as a doublet of doublets with a typical "cis-coupling" of 13 Hz and a further weak $^{3+4}J(P{-}P)$ coupling of 6 Hz with the dppm phosphorus on iron. All resonances are flanked by ^{195}Pt satellites with couplings of 80, 2841, and 4491 Hz, respectively. Owing to the presence of the bridging tin nucleus, all resonances show additional sets of $^{119/117}Sn$ satellites. These $^2J(Sn{-}P)$ couplings are also found in the $^{119}Sn\{^1H\}$ NMR spectrum, which exhibits a ddd pattern centered at δ 615.1. The PPh_3 ligand is only weakly coupled by *ca.* 45 Hz, whereas the two dppm phosphorus nuclei, which are in a transoid position with respect to tin, are coupled by *ca.* 130 and 1373 Hz. The $^{31}P\{^1H\}$ NMR spectrum of **2c** is very similar and is depicted in Figure 1. On the basis of the very different $^2J(P^2{-}Sn)$ and $^2J(P^3{-}Sn)$ coupling constants, one could anticipate that the tin amide ligand bridges the Fe−Pt bond in an unsymmetrical manner, with the larger value being associated with a shorter Pt−(μ-Sn) distance. However, the almost symmetrically bridging position of the carbene ligand in the related μ-siloxycarbene complex $[(OC)_3Fe\{\mu\text{-}C(Et)OSi(OMe_3)\}(\mu\text{-}dppm)Pt(PPh_3)]$(*Fe*−*Pt*) is associated with $^2J(P{-}\mu\text{-}C)$ couplings of 14 and 84 Hz.[1h] By analogy, we therefore assume a rather symmetric bridging position of the tin center between the two transition metals.

A ddd pattern is found in the $^{195}Pt\{^1H\}$ NMR spectrum of **2a**. This signal at δ −3188 displays $^1J(Pt{-}P)$ couplings of 2840 Hz (dppm) and 4490 Hz (PPh_3) and a $^{2+3}J(Pt{-}P)$ coupling of 79 Hz with the iron-bound phosphorus. In addition, a $^1J(Pt{-}Sn)$ coupling of 9708 Hz is observed. In the $^{13}C\{^1H\}$ NMR spectra two doublets are observed for the inequivalent iron carbonyls in a 1:2 ratio at δ 220.1 (see Experimental Section) and 210.8. Both in the ^{13}C and ^1H NMR spectrum the $SiMe_2$ groups appear as two distinct signals due to the bridging bonding mode of the tin atom.

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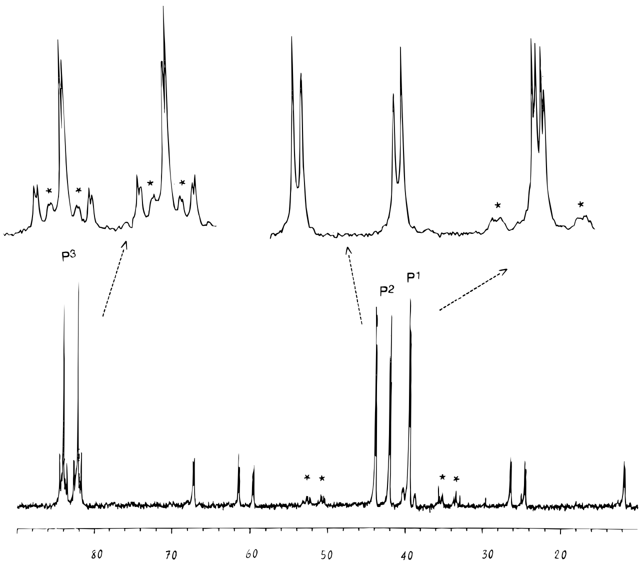
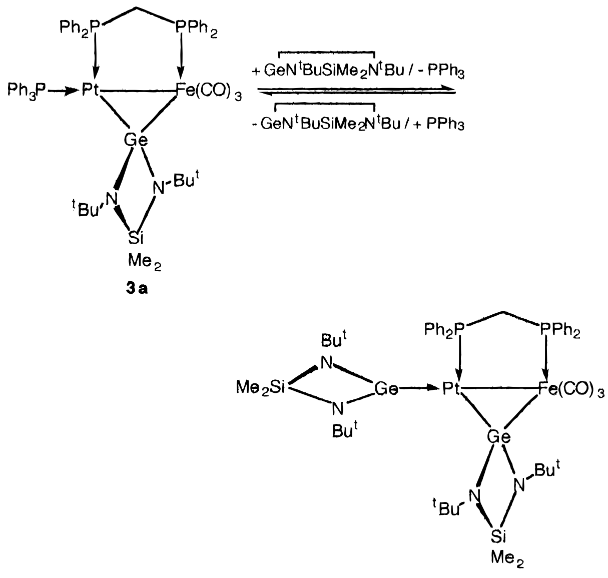


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-SnN}^tBuSiMe_2N^tBu\}Pt\{P(p\text{-tol})_3\}]$(*Fe−Pt*) (**2c**). The asterisks denote the $^{117/119}Sn$ satellites.

In the $^{31}P\{^1H\}$ NMR spectrum of the dppa-bridged derivative **2b** the resonances of the dppa ligand are significantly shifted to lower field. The doublet at δ 122.1 is assigned to the iron-bound phosphorus atom, which is strongly coupled ($^{2+3}J(P-P) = 173$ Hz) with the platinum-bound dppa phosphorus at δ 92.6. This signal is further split owing to the presence of the PPh_3 ligand. This latter gives rise to a doublet at δ 41.5 with a cis-coupling of 28 Hz. Whereas the $^1J(Pt-P^1)$ coupling for the platinum-bound PPh_3 ligand is similar to that in **2a** (4506 vs 4491 Hz), the $^1J(Pt-P^2)$ coupling for the platinum-bound dppa phosphorus is however markedly increased (3235 vs 2841 Hz for **2a**). The chemical shift of the ^{195}Pt nucleus (δ −3260) is not much affected by the nature of the bridging phosphine backbone and appears as a doublet of doublets of doublets with coupling constants of 68, 3235, and 4505 Hz. The NMR data of the dppa-bridged germylene homologue **3b** are very similar (see Experimental Section).

The IR spectra of **2** and **3** show three distinct ν(CO) vibrations, as expected for a meridional arrangement of these ligands. The position of these bands is not much influenced by the nature of the bridging Sn or Ge ligand. However, a significant shift to higher wavenumbers is observed for the dppa-bridged derivatives **2b** and **3b**, which may be caused by a lower electron donating ability of the dppa backbone. The solid-state IR spectra of **2b** and **3b** contain a sharp absorption assigned to the N−H vibration (3309 and 3318 cm^{-1}) which is indicative for the absence of hydrogen bonds, otherwise often encountered in dppa complexes.[12]

Reactivity Studies. Reaction of **2a** with 1 equiv of 2,6-dimethylphenyl isocyanide led to quantitative displacement of the tin amide to afford the known isocyanide-bridged complex $[(OC)_3Fe\{\mu\text{-CN-xylyl}\}(\mu\text{-dppm})Pt(PPh_3)]$(*Fe−Pt*).[3b] Interestingly, $GeN^tBuSiMe_2N^tBu$ substitutes the bridging benzyl isonitrile ligand of $[(OC)_3Fe\{\mu\text{-CN-benzyl}\}(\mu\text{-dppa})Pt(PPh_3)]$(*Fe−Pt*)[7] to give **3b.** Attempts to obtain a bis(stannylene) complex remained unsuccessful. Even on addition of a further 2 equiv of $[Sn(N^tBu)_2SiMe_2]$ to a solution of **2a** and gentle heating, only **2a** was recovered. Upon addition of a second 1 equiv of germylene to a toluene solution of **3a**, ^{31}P NMR monitoring revealed partial substitution of the PPh_3 ligand with formation of the bis(germylene) complex $[(OC)_3Fe\{\mu\text{-GeN}^tBuSiMe_2N^tBu\}(\mu\text{-dppm})Pt\{GeN^tBuSiMe_2N^tBu\}]$ (**4**) (eq 3).



(3)

The existence of an equilibrium between **3a** and **4** is indicated in $^{31}P\{^1H\}$ NMR by a broad resonance at δ −4.5 due to PPh_3 in rapid exchange with **3a**. This equilibrium can be shifted completely to the right side using a 5-fold excess of $GeN^tBuSiMe_2N^tBu$. However, attempts to isolate pure **4** failed since **3a** was recovered when excess $GeN^tBuSiMe_2N^tBu$ was removed. We tried also to trap the phosphine by CH_3I; however, a complex mixture of unknown compounds was obtained. The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits a AX pattern centered at δ 78.3 and δ 46.5 for the iron-bound and platinum-bound phosphorus atoms, respectively ($^{2+3}J(P-P) = 150$ Hz). The observation of both a $^{2+3}J(Pt-P)$ of 86 Hz and a $^1J(Pt-P)$ of 2871 Hz supports our assumption that a Fe−Pt bond is preserved.

B. Complexes with a Cyclic Structure. The versatility of these cyclic metal(II) amide reagents[2] led us to consider their reactivity toward heterobimetallic alkyl complexes of the type $[(OC)_3Fe(\mu\text{-Si}\{OMe\}_2(OMe)\}(\mu\text{-dppm})M(Me)]$(*Fe−M*) (M = Pd, Pt), related to **1** but in which the $Si(OMe)_3$ ligand is bridging between the metals.[1a,b] The stability of the resulting four-membered cycle Fe−Si−O→M is associated with a lability of the dative O→M interaction. This confers a unique hemilabile character to the $Si(OMe)_3$ ligand and plays a central role for e.g. the migratory insertion of small molecules like isocyanides, CO, and olefins[1c,d] into the metal−alkyl bond or the catalytic dehydrogenative coupling of stannanes.[1e]

Insertion of the reactive metal amides $EN^tBuSiMe_2N^tBu$ into the M−C σ-bond was therefore anticipated,

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[12] (a) Liehr, G.; Szucsanyi, G.; Ellermann, J. *J. Organomet. Chem.* **1984**, *265*, 95. (b) Steil, P.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1989**, *366*, 313.

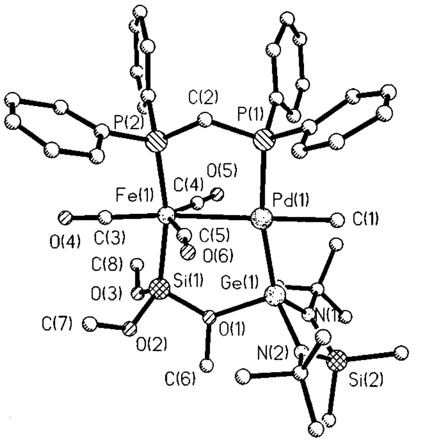
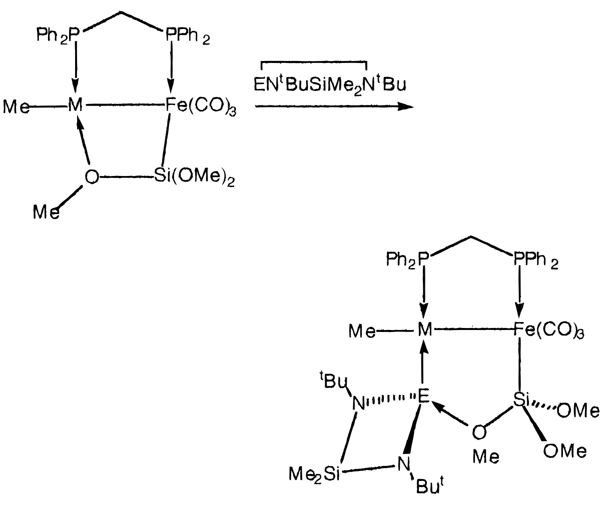


Figure 2. Perspective view and numbering scheme for *mer*-[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}{GeN^{t}BuSiMe$_2$N^{t}Bu}(μ-dppm)Pd(Me)](*Fe−Pd*) (**7**).

by analogy also with their insertion into the Fe−Me bond of [CpFe(CO)$_2$Me], which yielded [CpFe(CO)$_2$-{EN^{t}BuSiMe$_2$N^{t}Bu}Me].[2g] However, on the basis of the spectroscopic data, insertion of EN^{t}BuSiMe$_2$N^{t}Bu (E = Ge, Sn) into the M−methyl bond of [(OC)$_3$Fe(μ-Si{OMe)$_2$(OMe)}(μ-dppm)M(Me)](*Fe−M*) (M = Pd or Pt) was ruled out, even in the presence of excess reagent and after long reaction times. Instead the trimetallic stannylene or germylene adducts **5**−**7** were formed in high yields: the reagent has inserted into the dative O→M bond to form an unprecedented five-membered ring structure (eq 4). Again, no reaction took place with the plumbylene PbN^{t}BuSiMe$_2$N^{t}Bu reagent.



(4)

5 E = Sn, M = Pt
6 E = Sn, M = Pd
7 E = Ge, M = Pd

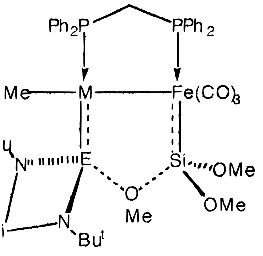
An X-ray diffraction study was performed on a single crystal of **7** (Figure 2). Unfortunately, extensive decomposition occurred during the data collection, and due to the insufficient data quality, we will not discuss the structural features in detail. Selected bond lengths and angles are listed in Table 1. The structure shown is consistent with IR and multinuclear NMR data at variable temperatures, as exemplified for [(OC)$_3$Fe-{μ-Si(OMe)$_2$(OMe)}{SnN^{t}BuSiMe$_2$N^{t}Bu(μ-dppm)Pt}(Me)]-(*Fe−Pt*) (**5**). The meridional arrangement of the carbonyls is retained, but a shift of the three ν(CO) vibrations (1947 m, 1884 s, 1848 s) of *ca.* 10 cm^{-1} to lower wavenumbers results from insertion of the stannylene. The electron-donating effect of the metal amides appears to be larger than their back-bonding abilities. The ^{31}P{^{1}H} NMR data are consistent with this structure (see Experimental Section). In the ^{195}Pt{^{1}H} NMR spectrum, the dd resonance at δ −2825 shows the expected ^1J(Pt−$^{117/119}$Sn) couplings in the range of 16 634 and 17 430 Hz, respectively. Compared to the low-field ^{119}Sn chemical shifts of *ca.* 600 ppm for the μ-stannylene complexes **2a,c**, the ^{119}Sn chemical shifts of **5** and **6** are dramatically high-field shifted at δ 128.7 for **5** and δ 81.2 for **6**.

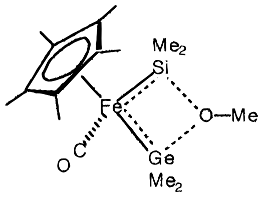
Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 7

Pd(1)−Ge(1)	2.36(5)	Pd(1)−P(1)	2.31(9)
Pd(1)−Fe(1)	2.74(6)	Pd(1)−C(1)	2.10(3)
Ge(1)−O(1)	2.10(2)	Si(1)−O(1)	1.70(2)
Fe(1)−Si(1)	2.26(12)	Si(1)−O(2)	1.64(3)
Fe(1)−P(2)	2.23(11)	Si(1)−O(3)	1.65(4)
Pd(1)−Fe(1)−Si(1)	96.8(3)	P(2)−Fe(1)−Pd(1)	95.3(3)
Fe(1)−Si(1)−O(1)	115.1(8)	P(1)−Pd(1)−Fe(1)	92.0(2)
Si(1)−O(1)−Ge(1)	124.2(11)	P(1)−Pd(1)−Ge(1)	169.2(3)
Pd(1)−Ge(1)−O(1)	104.2(6)	P(2)−Fe(1)−Si(1)	167.2(5)
C(1)−Pd(1)−Ge(1)	81.9(9)		

Proton NMR spectroscopy of **5**−**7** at variable temperatures revealed rapid exchange of the methoxy groups. For **5**, a sharp singlet for the Si(OMe)$_3$ ligand is observed at δ 3.70, which broadens on lowering the temperature, whereas the other signals remained unaffected. Coalescence was reached at 255 K. Below this temperature, the methoxy resonance gives two distinct signals which are found in a 1:2 ratio at 233 K at δ 3.87 and 3.57, indicating the presence of a rigid five-membered Fe−Si−O→Sn−Pt cycle. Using the Eyring equation, we estimate for **5** a $\Delta G^{\ddagger}$ of 51.3 kJ/mol and for the palladium derivatives **6** and **7** a $\Delta G^{\ddagger}$ of 53.6 and 54.7 kJ/mol, respectively. This intramolecular base stabilization may also be responsible for the fact that no insertion reaction into the M−methyl bond was observed.

One may speculate about the validity of a bonding description of complexes **5**−**7** with a silylene-like bonding of the silyl moiety, base-stabilized by a bridging methoxy group. Such a formalism has been used by Ogino *et al.* to describe the molecular structure of the fluxional complex [(η-C$_5$Me$_5$)Fe(CO)GeMe$_2$OMeSiMe$_2$], for which rotation about the Fe−Ge bond has been deduced from NMR experiments.[13]





We confidently rule out this description for our compounds which involves rotation around the M−E axis. In the temperature range examined we always observed *two* distinct resonances for the nonequivalent Si−CH$_3$ groups, which should become identical if the above mechanism were operative. Furthermore, the ^{29}Si NMR chemical shift for the Si(OMe)$_3$ group of **7** (δ 29.4) is in the usual range for M−Si(OMe)$_3$ complexes (*e.g.* δ(^{29}Si) 17.6 for [(OC)$_3$Fe(μ-Si{OMe}$_2$(OMe)}(μ-dppm)Pd(Me)]-(*Fe−Pd*)), whereas that for [η-C$_5$Me$_5$)Fe(CO)GeMe$_2$-OMe-SiMe$_2$] appears in the low-field region at δ 114.3.[34]

As noticed above for the EN^{t}BuSiMe$_2$N^{t}Bu-bridged clusters **2** and **3**, the germylene derivative **7** is more stable than the stannylene analogues **5** and **6**. Upon standing in solution, the latter gradually loose the tin amide ligand to regenerate [(OC)$_3$Fe(μ-Si{OMe}$_2$(OMe)}-(μ-dppm)M(Me)](*Fe−M*), whereas the germylene complex **7** remained unchanged after 2 days in CDCl$_3$. This may explain our failure to get correct elemental analyses for **5** and **6**.

(C) Attempted Preparation of Fe−Rh Stannylene and Germylene Complexes. We then tried to extend the observations made in eq 4 to a related Fe−Rh complex containing a four-membered ring Fe−Si−O→Rh.[5a] Surprisingly, no reaction took place when [(OC)$_3$Fe(μ-Si{OMe}$_2$(OMe)}(μ-dppm)Rh(PPh$_3$)](*Fe−Rh*) was reacted with an excess of EN^{t}BuSiMe$_2$N^{t}Bu. Even after gentle heating, only the starting materials were recovered. Although stable complexes with Rh−Sn and Rh−Ge bonds have recently been reported from the reactions of [RhCl(PPh$_3$)$_3$] with EN^{t}BuSiMe$_2$N^{t}Bu,[2d,i] the strength of the dative MeO→Rh interaction appears to prevent adduct formation under ring opening, as found for the related systems **5**−**7**.

Conclusion

We have shown that heterotrimetallic clusters containing both main group and transition metals are obtained in high yields by reaction of cyclic bis(amino)-germylenes and -stannylenes with heterobimetallic complexes. The amides adopt exclusively a bridging bonding mode in the clusters **2** and **3** and a terminal base-stabilized bonding mode in complexes **5**−**7**. These heterotrimetallic systems are not reactive (under mild conditions) toward displacement of other ligands, e.g. CO or PPh$_3$. Future work using more severe reaction conditions or photochemical activation will be required to see whether these compounds can be used for the construction of higher nuclearity clusters. Another aspect which deserves further investigation is the possibility to chemically transform the coordinated metal amides. The present findings demonstrate again the diversity of reaction patterns that may be observed when polymetallic systems are reacted with low-valent main group compounds.

Experimental Section

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use, with tetrahydrofuran over sodium benzophenone ketyl, toluene and hexane over sodium, and dichloromethane from P$_4$O$_{10}$. Nitrogen was passed through BASF R3−11 catalyst and P$_4$O$_{10}$ columns to remove residual oxygen or water. Elemental C, H, and N analyses were performed on a Leco CHN 900 elemental analyzer. Infrared spectra were recorded in the 4000−400 cm^{-1} region on Perkin-Elmer 883 spectrometer. The ^{1}H, ^{31}P{^{1}H}, ^{119}Sn{^{1}H}, ^{29}Si-INEPT, and ^{13}C{^{1}H} NMR spectra were recorded at 200.13, 81.01, 74.60, 39.76, and 50.32 MHz, respectively, on a Bruker ACP 200 instrument. Phosphorus chemical shifts were referenced to 85% H$_3$PO$_4$ in water and ^{119}Sn chemical shifts to SnMe$_4$ with downfield shifts reported as positive. ^{195}Pt chemical shifts were measured on a Bruker ACP 200 instrument (42.95 MHz) and externally referenced to K$_2$PtCl$_4$ in water with downfield chemical shifts reported as positive. Unless otherwise stated, NMR spectra were recorded in pure CDCl$_3$. The reactions were generally monitored by IR in the ν(CO) region. The presence of 0.5 molecules of toluene in **2a,b** has been determined from the ^{1}H NMR spectrum.

[(OC)$_3$Fe(μ-SnN^{t}BuSiMe$_2$N^{t}Bu))(μ-dppm)Pt(PPh$_3$)]-(*Fe−Pt*) (2a). Method A. SnN^{t}BuSiMe$_2$N^{t}Bu (0.21 mmol, 56 μL) was added slowly to a suspension of [(OC)$_3${(MeO)$_3$Si}-Fe(μ-dppm)Pt(H)(PPh$_3$)] (**1**) (220 mg, 0.2 mmol) in C$_6$D$_6$ (2 mL) at room temperature. The resulting deep red solution was stirred for 45 min. ^{31}P NMR-monitoring showed the presence of **2a** as the only P-containing species in solution. Layering the solution with hexane afforded **2a** in form of orange-yellow microcrystals (0.161 g, 63%).

Method B. A solution of SnN^{t}BuSiMe$_2$N^{t}Bu (0.55 mmol, 160 μL) in toluene (5 mL) was added slowly to a stirred suspension of [(OC)$_3$Fe(μ-dppm)(μ-CO)Pt(PPh$_3$)](*Fe−Pt*) (505 mg, 0.5 mmol) in toluene (10 mL) at room temperature. The clear red mixture was stirred for 15 min and then evaporated under reduced pressure to *ca.* 4 mL. Addition of hexane yielded **2a** as an orange-yellow powder (0.620 g, 92%). (Anal. Found: C, 52.81; H, 4.46; N, 1.50. Calc for C$_{56}$H$_{61}$N$_2$O$_3$P$_3$-FePtSiSn·0.5C$_7$H$_8$ (M = 1300.76 + 46.07): C, 53.06; H, 4.86; N, 2.08). IR (toluene): ν(CO) 1955 m, 1908 s, 1873 s cm^{-1}. ^{1}H NMR: δ 0.34 (s, 3H, SiMe), 0.43 (s, 3H, SiMe), 0.99 (s, 18H, ^{t}Bu), 3.32 (t, 2H, PCH$_2$P, ^2J(P−H) = 9.6, ^3J(Pt−H) = 38), 7.08−7.38 (m, 35H, C$_6$H$_5$). ^{31}P{^{1}H} NMR: δ 41.9 (dd, P^1(Pt), ^2J(P^1−P^2) = 13, ^{3+4}J(P^1−P^3) = 6, ^1J(P−Pt) = 4491, ^2J(P−Sn) = 130), 43.5 (dd, P^2(Pt), ^2J(P^2−P^1) = 13, ^{2+3}J(P^2−P^3) = 148, ^1J(P−Pt) = 2841, ^2J(P−Sn) = 1373), 83.6 (dd, P^3(Fe), ^{2+3}J(P^3−P^2) = 148, ^{3+4}J(P^3−P^1) = 6, ^{2+3}J(P−Pt) = 80, ^2J(P−Sn) = 43). ^{13}C{^{1}H} NMR (253 K): δ 7.0 (d, 1C, SiMe, ^5J(P−C) = 2.6), 8.8 (s, 1C, SiMe), 34.8 (s, 6C, C−*Me*), 51.2 (s, 2C, N−*C*), 125.2−136.6 (m, 42C, C$_6$H$_5$), 210.8 (d, 2C, CO, ^2J(P−C) = 24), 220.1 (d, 1C, CO, ^2J(P−C) = 8). ^{29}Si-INEPT NMR: δ 3.35 (d, SiMe$_2$, ^4J(P^2−Si) = 2). ^{119}Sn{^{1}H} NMR: δ 615.1 (ddd, ^2J(Sn−P^1) = 132, ^2J(Sn−P^2) = 1373, ^2J(Sn−P^3) = 50). ^{195}Pt{^{1}H} NMR: δ −3188 (ddd, ^1J(Pt−P^1) = 4491, ^1J(Pt−P^2) = 2841, ^{2+3}J(Pt−P^3) = 79, ^1J(Pt−^{119}Sn) = 9708 Hz).

[(OC)$_3$Fe(μ-SnN^{t}BuSiMe$_2$N^{t}Bu)(μ-dppa)Pt(PPh$_3$)]-(*Fe−Pt*) (2b). The yellow cluster **2b** was prepared similarly to **2a** (method B), using SnN^{t}BuSiMe$_2$N^{t}Bu (0.55 mmol, 160 μL) and [(OC)$_3$Fe(μ-CO)(μ-dppa)Pt(PPh$_3$)](*Fe−Pt*) (0.5 mmol, 505 mg) (prepared from [Fe(CO)$_4$(η^1-dppa)] and [Pt(H$_2$C=CH$_2$)-(PPh$_3$)$_2$]. Yield: 0.498 g, 74%. (Anal. Found: C, 51.93; H, 4.92; N, 2.98. Calc for C$_{55}$H$_{60}$N$_3$O$_3$P$_3$FePtSiSn·0.5C$_7$H$_8$ (M = 1301.75 + 46.07): C, 52.13; H, 4.92; N, 2.98). IR (toluene): ν(CO) 1964 m, 1913 s, 1893 s. IR (KBr): ν(CO) 1956 m, 1912 sh, 1891 s, ν(NH) 3309 w cm^{-1}. ^{1}H NMR: δ 0.33 (s, 3H, SiMe), 0.41 (s, 3H, SiMe), 0.92 (s, 18H, ^{t}Bu), 4.70 (t br, 1H, NH, ^3J(Pt−H) = 86.0), 7.08−7.44 (m, 35H, C$_6$H$_5$). ^{31}P{^{1}H} NMR: δ 41.5 (d, P^1(Pt), ^2J(P−P^2) = 28, ^1J(P−Pt) = 4506), 92.6 (dd, P^2(Pt),

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(13) (a) Koe, J.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 2479. (b) For a very recent example of a mononuclear tungsten silyl germylene see: Figge, L. K.; Carroll, P. J.; Berry, D. H. *Organometallics* **1996**, *15*, 209.

^{2}J(P−P^{1}) = 28, ^{2+3}J(P−P^{3}) = 173, ^{1}J(P−Pt) = 3235), 122.1 (d, P^{3}(Fe), ^{2+3}J(P−P^{2}) = 173, ^{2+3}J(P−Pt) = 68, ^{2}J(P−Sn) = 40). ^{195}Pt {^{1}H} NMR: δ −3260 (ddd, ^{1}J(P^{1}−Pt) = 4506, ^{1}J(P^{2}−Pt) = 3235, ^{2+3}J(P^{3}−Pt) = 68 Hz).

[(OC)$_3$Fe(μ-SnN^{t}BuSiMe$_2$N^{t}Bu)(μ-dppm)Pt{P(p-tol)$_3$}]-(*Fe*−*Pt*) (2c). To a suspension of [(OC)$_3$Fe(μ-CO)(μ-dppm)Pt{P(p-tol)$_3$}] (0.5 mmol, 525 mg) in toluene (10 mL) was added dropwise a solution of SnN^{t}BuSiMe$_2$N^{t}Bu (0.55 mmol, 160 μL) in toluene (5 mL) within 5 min. The clear red mixture was stirred for 15 min, and then the solvent was reduced under vacuum to 4 mL. Addition of hexane yielded **2c** as a red powder (0.632 g, 91%). (Anal. Found: C, 54.03; H, 5.84; N, 1.88. Calc for $C_{59}H_{67}N_2O_3P_3FePtSiSn\cdot0.5C_7H_8$ (M = 1342.84 + 46.07): C, 54.05; H, 5.13; N, 2.02). IR (toluene): ν(CO): 1956 m, 1907 s, 1871 m. ^{1}H NMR: δ 0.32 (s, 3H, SiMe), 0.43 (s, 3H, SiMe), 1.01 (s, 18H, ^{t}Bu), 2.28 (s, 9H, tolyl−Me), 3.30 (t, 2H, PCH$_2$P, ^{2}J(P−H) = 9.5, ^{3}J(Pt−H) = 38), 6.87−7.41 (m, 32H, C$_6$H$_5$). ^{31}P{^{1}H} NMR: δ 39.5 (dd, P^{1}(Pt), ^{2}J(P^{1}−P^{2}) = 13, ^{3+4}J(P^{1}−P^{3}) = 6, ^{1}J(P−Pt) = 4490, ^{2}J(P−Sn) = 130), 43.0 (dd, P^{2}(Pt), ^{2+3}J(P^{2}−P^{3}) = 149, ^{2}J(P^{2}−P^{1}) = 13, ^{1}J(P−Pt) = 2841, ^{2}J(P−Sn) = 1383), 83.2 (dd, P^{3}(Fe), ^{3+4}J(P^{3}−P^{1}) = 6, ^{2+3}J(P^{3}−P^{2}) = 149, ^{2+3}J(P−Pt) = 79, ^{2}J(P−Sn) = 36). ^{119}Sn{^{1}H} NMR: δ 608.2 (ddd, ^{2}J(P^{1}−Sn) = 132, ^{2}J(P^{2}−Sn) = 1383, ^{2}J(P^{3}−Sn) = 36). ^{195}Pt{^{1}H} NMR: δ −3182.1 (ddd, ^{1}J(P^{1}−Pt) = 4490, ^{1}J(P^{2}−Pt) = 2841, ^{2}J(P−Pt) = 79 Hz).

[(OC)$_3$Fe(μ-GeN^{t}BuSiMe$_2$N^{t}Bu)(μ-dppm)Pt(PPh$_3$)]-(*Fe*−*Pt*) (3a). It was prepared similarly to **2a** (method B), using GeN^{t}BuSiMe$_2$N^{t}Bu (0.6 mmol, 100 μL) and [(OC)$_3$Fe(μ-CO)(μ-dppm)Pt(PPh$_3$)](*Fe*−*Pt*) (0.5 mmol, 505 mg), and isolated in the form of yellow microcrystals (0.546 g, 87%). (Anal. Found: C, 54.00; H, 5.45; N, 2.16. Calc for $C_{56}H_{61}N_2O_3P_3FePtSiGe$ (M = 1254.66): C, 53.61; H, 4.90; N, 2.23). IR (toluene): ν(CO) 1960 m, 1910 s, 1872 s. IR (KBr): ν(CO) 1958 m, 1897 s, 1871 s cm^{-1}. ^{1}H NMR: δ 0.42 (s, 3H, SiMe), 0.49 (s, 3H, SiMe), 0.98 (s, 18H, ^{t}Bu), 3.21 (t, 2H, PCH$_2$P, ^{2}J(P−H) = 9.1, ^{3}J(Pt−H) = 33.5), 7.05−7.28 (m, 35H, C$_6$H$_5$). ^{31}P{^{1}H} NMR: δ 39.6 (dd, P^{1}(Pt), ^{2}J(P^{1}−P^{2}) = 13, ^{3+4}J(P^{1}−P^{3}) = 6, ^{1}J(P−Pt) = 4534), 42.4 (dd, P^{2}(Pt), ^{2+3}J(P^{2}−P^{3}) = 149, ^{2}J(P^{2}−P^{1}) = 13, ^{1}J(P−Pt) = 2419), 81.6 (dd, P^{3}(Fe), ^{2+3}J(P^{3}−P^{2}) = 149, ^{3+4}J(P^{3}−P^{1}) = 6, ^{2+3}J(P−Pt) = 91). ^{13}C{^{1}H} NMR: δ 5.6 (d, 1C, SiMe), 8.2 (s, 1C, SiMe), 33.6 (s, 6C, C−*Me*), 51.8 (s, 2C, N−*C*), 127.8−134.6 (m, 42C, C$_6$H$_5$), 214.1 (d, 2C, CO, ^{2}J(PC) = 27), 220.7 (d, 1C, CO, ^{2}J(PC) = 7). ^{195}Pt{^{1}H} NMR; δ −3125 (ddd, ^{1}J(P^{1}−Pt) = 4534, ^{1}J(P^{2}−Pt) = 2419, ^{2+3}J(P^{3}−Pt) = 91 Hz).

[(OC)$_3$Fe(μ-GeN^{t}BuSiMe$_2$N^{t}Bu)(μ-dppa)Pt(PPh$_3$)]-(*Fe*−*Pt*) (3b). This complex was prepared similarly to **2a** (method B), using GeN^{t}BuSiMe$_2$N^{t}Bu (0.6 mmol, 100 μL) and [(OC)$_3$Fe(μ-CO)(μ-dppa)Pt(PPh$_3$)](*Fe*−*Pt*) (0.5 mmol, 505 mg), and isolated as a yellow microcrystalline powder (0.521 g, 83%). (Anal. Found: C, 52.55; H, 4.49; N, 2.95. Calc for $C_{55}H_{60}N_3O_3P_3FePtSiGe$ (M = 1255.65): C, 52.61; H, 4.82; N, 3.35). IR (toluene): ν(CO) 1968 m, 1915 s, 1894 s. IR (KBr): ν(CO) 1966 m, 1912 sh, 1892 s, ν(NH) 3318 w cm^{-1}. ^{1}H NMR: δ 0.45 (d, 3H, SiMe), 0.50 (s, 3H, SiMe), 0.95 (s, 18H, ^{t}Bu), 4.58 (t br, 1H, PNHP, ^{2}J(H−P) = 79), 7.04−7.43 (m, 35H, C$_6$H$_5$). ^{31}P{^{1}H} NMR: δ 39.3 (d, P^{1}(Pt), ^{2}J(P^{1}−P^{2}) = 29, ^{1}J(P^{1}−Pt) = 4562), 90.5 (dd, P^{2}(Pt), ^{2+3}J(P^{2}−P^{3}) = 173, ^{2}J(P^{2}−P^{1}) = 29, ^{1}J(P−Pt) = 2840), 118.3 (d, P^{3}(Fe), ^{2+3}J(P^{3}−P^{2}) = 173, ^{2+3}J(P−Pt) = 82). ^{13}C{^{1}H} NMR: δ 5.7 (d, 1C, SiMe), 8.4 (s, 1C, SiMe), 33.8 (s, 6C, C−*Me*), 51.3 (s, 2C, N−*C*), 127.4−141.1 (m, 42C, C$_6$H$_5$), 212.9 (d, 2C, CO, ^{2}J(P−C) = 29), 219.9 (d, 1C, CO, ^{2}J(P−C) = 7). ^{29}Si-INEPT NMR: δ 1.95 (d, SiMe$_2$, ^{4}J(P^{2}-Si) = 3,^{3}J(Pt−Si) = 27), ^{195}Pt{^{1}H} NMR: δ −3190 (ddd, ^{1}J(P^{1}−Pt) = 4562, ^{1}J(P^{2}−Pt) = 2840, ^{2+3}J(P^{3}−Pt) = 82 Hz).

[(OC)$_3$Fe(μ-GeN^{t}BuSiMe$_2$N^{t}Bu)(μ-dppm)Pt(GeN-^{t}BuSiMe$_2$N^{t}Bu)](*Fe*−*Pt*) (4). To a solution of **3a** (0.5 mmol, 630 mg) in 10 mL of toluene was added dropwise a solution of GeN^{t}BuSiMe$_2$N^{t}Bu (2.0 mmol, 540 μL) in 5 mL of toluene within 30 min. The clear orange yellow solution was stirred for 15 min and then examined by spectroscopic methods. Attempts to isolate pure **4** always led to mixtures containing both **4** and **3a**. IR (toluene): ν(CO) 1961 m, 1910 s, 1878 m cm^{-1}. ^{31}P{^{1}H} NMR (C$_6$D$_6$/toluene): δ 46.5 (d, P^{1}(Pt), ^{2+3}J(P−P) = 150, ^{1}J(P−Pt) = 2871), 78.3 (d, P^{2}(Fe), ^{2}J(P−Pt) = 86). ^{195}Pt{^{1}H} NMR (C$_6$D$_6$/toluene): δ −3301 (dd, ^{1}J(P^{1}−Pt) = 2871, ^{2+3}J(P^{2}−Pt) = 86 Hz).

[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(SnN^{t}BuSiMe$_2$N^{t}Bu}-(Me)](*Fe*−*Pt*) (5). To a suspension of [(OC)$_3$Fe{μ-Si(OMe)$_2$-(OMe)}(μ-dppm)Pt(Me)](*Fe*−*Pt*) (0.5 mmol, 430 mg) in 10 mL of Et$_2$O was added dropwise a solution of SnN^{t}BuSiMe$_2$N^{t}Bu (0.55 mmol, 150 μL) in 2 mL of toluene. The reaction mixture was stirred at room temperature for 1 h. ^{31}P-NMR monitoring revealed that **5** was the sole P-containing species in solution. Reduction of the volume to ca. 6 mL and addition of hexane yielded **5** as a yellow powder, which was washed with hexane and dried under vacuum. ^{31}P-NMR analysis of the yellow powder revealed that after removal of all volatiles *ca*. 15% of the starting material has been re-formed by partial stannylene dissociation. IR (toluene): ν(CO) 1947 s, 1884 s, 1848 s cm^{-1}. ^{1}H NMR: δ 0.19 (s, 3H, SiMe), 0.23 (s, 3H, SiMe), 0.40 (d, 3H, PtMe, ^{3}J(P−H) = 8.5, ^{2}J(Pt−H) = 55), 1.11 (s, 18H, ^{t}Bu), 3.45 (t, 2H, PCH$_2$P, ^{2}J(P−H) = 10.4, ^{3}J(Pt−H) = 43), 3.69 (s, 9H, Si(OMe)$_3$), 7.15−7.58 (m, 20H, C$_6$H$_5$), ^{31}P{^{1}H} NMR: δ 32.0 (d, P^{1}(Pt−P), ^{2+3}J(P^{1}−P^{2}) = 102, ^{1}J(P−Pt) = 3513, ^{2}J(P−^{117}Sn) = 3498, ^{2}J(P−^{119}Sn) = 3576), 71.3 (d, P^{2}(Fe−P), ^{2+3}J(P−Pt) = 50, ^{3+4}J(P−Sn) = 212). ^{29}Si-INEPT NMR: δ 3.05 (d, SiMe$_2$, ^{4}J(P^{1}−Si) = 2), 26.9 (dd, Si(OMe)$_3$, ^{2}J(Si−P^{2}) = 38, ^{4}J(Si−P^{1}) = 4). ^{119}Sn{^{1}H} NMR: δ 128.6 (dd, ^{2}J(P^{1}−Sn) = 3571, ^{3+4}J(P^{2}−Sn) = 219, ^{1}J(Pt−Sn) = 17376). ^{195}Pt{^{1}H} NMR: δ −2825 (dd, ^{1}J(P^{1}−Pt) = 3513, ^{2+3}J(P^{2}−Pt) = 50, ^{1}J(Pt−^{117}Sn) = 16634, ^{1}J(Pt−^{119}Sn) = 17430 Hz).

[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}{SnN^{t}BuSiMe$_2$N^{t}Bu}(μ-dppm)Pd(Me)](*Fe*−*Pd*) (6). To a suspension of [(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)Pd(Me)](*Fe*−*Pd*) (1.0 mmol, 768 mg) in diethyl ether (15 mL) was added dropwise SnN^{t}BuSiMe$_2$N^t-Bu (1.1 mmol, 300 μL). The reaction mixture was stirred at room temperature for 1 h, and then the volume was reduced to 6 mL. Addition of hexane yielded **6** as a red orange powder, which was washed with hexane and dried under vacuum. IR (KBr): ν(CO) 1949 s, 1885 s, 1858 s, ν(SiOCH) 2840 w. IR (Et$_2$O): ν(CO) 1954 m, 1894 s, 1864 s cm^{-1}. ^{1}H NMR: δ 0.25 (s, 3H, SiMe), 0.28 (s, 3H, SiMe), 0.33 (d, 3H, PdMe, ^{3}J(P−H) = 8.3), 1.22 (s, 18H, ^{t}Bu), 3.53 (t, 2H, PCH$_2$P, ^{2}J(P−H) = 10.4), 3.75 (s, 9H, Si(OMe)$_3$), 7.19−7.53 (m, 20H, C$_6$H$_5$). ^{31}P{^{1}H} NMR: δ 32.25 (d, P^{1}(Pd−P), ^{2+3}J(P^{1}−P^{2}) = 113, ^{2}J(P−^{117}Sn) = 3417, ^{2}J(P−^{119}Sn) = 3550), 70.9 (d, P^{2}(Fe−P), ^{3+4}J(P−Sn) = 195). ^{29}Si-INEPT NMR: δ 2.68 (d, SiMe$_2$, ^{4}J(Si−P^{1}) = 1.9, ^{2}J(Si−Sn) = 23.6), 26.8 (dd, SiOMe, ^{2}J(P^{2}−Si) = 34.1, ^{4}J(P^{2}−Si) = 3.6). ^{119}Sn{^{1}H} NMR: δ 81.2 (dd, ^{2}J(P^{1}−Sn) = 3554, ^{3+4}J(P^{2}−Sn) = 197 Hz).

[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}{GeN^{t}BuSiMe$_2$N^{t}Bu}(μ-dppm)Pd(Me)](*Fe*−*Pd*) (7). It was prepared similarly to **6**, using [(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)Pd(Me)](*Fe*−*Pd*) (1.0 mmol, 768 mg) and GeN^{t}BuSiMe$_2$N^{t}Bu (1.1 mmol, 300 μL). The complex was isolated in form of nearly colorless thin plates from a cold Et$_2$O/hexane mixture (0.697 g, 67%). (Anal. Found: C, 48.92; H, 5.91; N, 2.65. Calc for $C_{42}H_{58}N_2O_6P_2FePdSi_2Ge$ (M = 1039.86): C, 48.51; H, 5.62; N, 2.69). IR (KBr): ν(CO) 1947 s, 1878 s, 1851 s, ν(SiOCH) 2831 w. IR (toluene): ν(CO) 1947 m, 1881 s, 1850 s cm^{-1}. ^{1}H NMR: δ 0.30 (s, 3H, SiMe), 0.35 (s, 3H, SiMe), 0.40 (d, 3H, PdMe, ^{3}J(P−

H) = 8.4), 1.24 (s, 18H, ^{t}Bu), 3.46 (t, 2H, PCH_2P, ${}^{2}J$(P−H) = 10.3), 3.73 (s, 9H, $Si(OMe)_3$), 7.23−7.56 (m, 20H, C_6H_5). ^{31}P-{^{1}H} NMR: δ 31.1 (d, P^1(Pd−P), ${}^{2+3}J(P^1-P^2)$ = 118), 72.4 (d, P^2(Fe−P)). ^{29}Si-INEPT NMR: δ 4.07 (d, $SiMe_2$, ${}^{4}J(Si-P^1)$ = 3.6), 29.36 (dd, SiOMe, ${}^{4}J(P^1-Si)$ = 4.4, ${}^{2}J(P^2-Si)$ = 35). ^{13}C-{^{1}H} NMR: δ 2.5 (d, 1C, SiMe, ${}^{5}J$(P−C) = 1), 4.7 (s, 1C, SiMe), 6.1 (d, 1C, PdMe, ${}^{2}J$(P−C) = 3), 33.8 (s, 6C, C−*Me*), 38.1 (t, 1C, PCH_2P), 50.4 (s, 3C, SiOMe), 51.0 (s, 2C, N−*C*), 127.8 - 136.2 (m, 24C, C_6H_5), 211.1 (d, 2C, CO, ${}^{2}J$(P−C) = 25), 214.9 (d, 1C, CO, ${}^{2}J$(P−C) = 14 Hz).

Crystallographic Data for Complex 7: Crystal system, triclinic; space group, $P\bar{1}$; a = 10.704(10), b = 20.53(2), c = 25.76(3) Å; α = 68.88(4), β = 79.33(4), γ = 80.20(4)°; V = 5155-(9) Å^3; Z = 4; d(calc) = 1.340 g/cm^3. Data were collected at 293 K on a Siemens Stoe AED 2 diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). Intensities were collected from 1.58−22.52° in Θ, using the $\omega-\Theta$ scan mode: total number of unique data, 8263; number of observed unique data, 5298; final R_1 ($I > 2\sigma(I)$) = 0.1318; wR_2 = 0.3770.

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Supporting Information Available: Tables of crystallographic data, atom parameters, thermal parameters, and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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