Preliminary Communication

Electrophilic additions to the bimetallic silyl complexes [(OC)$_3${(MeO)$_3$Si}-Fe(μ-PR$_2$)Pt(1,5-COD)] (R = Ph, Cy). Crystal structure of [(OC)$_3$Fe(μ-PCy$_2$){μ-Au(PPh$_3$)}$_2$Pt-(1,5-COD)][PF$_6$] (Cy = c-C$_6$H$_{11}$) *

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Abstract

Reactions of the heterobimetallic complexes [(OC)$_3${(MeO)$_3$Si}Fe(μ-PPh$_2$)Pt(PPh$_3$)$_2$] (1) and [(OC)$_3${(MeO)$_3$Si}Fe(μ-PR$_2$)Pt(1,5-COD)] (3a, R = Ph) with HBF$_4$·Et$_2$O result in cleavage of the Fe–Si bond and formation of the dihydrido complexes [(OC)$_3$Fe(μ-PPh$_2$)(μ-H)$_2$Pt(PPh$_3$)$_2$][BF$_4$] (2) and [(OC)$_3$Fe(μ-PR$_2$)(μ-H)$_2$Pt(1,5-COD)][BF$_4$] (4), respectively. Reactions of 3a or 3b (R = Cy) with [(Ph$_3$P)Au][PF$_6$] required 2 equiv. of the electrophile to give the clusters [(OC)$_3$Fe(μ-PR$_2$)(μ-Au(PPh$_3$))$_2$Pt(1,5-COD)][PF$_6$] (5a, R = Ph; 5b, R = Cy). These were fully characterised and the structure of 5b was determined by X-ray diffraction: crystals are monoclinic, space group P2$_1$/n, a = 22.479(6), b = 26.781(8), c = 10.254(3) Å, β = 102.94(2)°, U = 6016.1 Å^3 and Z = 4. This is the first structural determination of a heterobimetallic complex carrying two Au-fragments. The Fe–Pt bond (2.715(3) Å) is bridged by a μ-PCy$_2$ group and by two Au(PPh$_3$) fragments. No Au–Au interaction is observed (4.333(1) Å).

Heterodinuclear metal–metal bonded complexes of the transition metals containing a single bridging unit, such as a μ-PR$_2$ ligand, are particularly suitable for investigating the site-selectivity of reactions with electrophilic reagents [1]. Reactions involving an electron-rich moiety M–(μ-PR$_2$)–M′ may occur at M or M′, at the metal–metal bond or even at the metal–(μ-P) bond [1d]. The bridging ligand holds the metals in close proximity, allowing study of various bimetallic effects that could otherwise not be observed (in case of fragmentation), without shielding the metal centres and decreasing the reactivity of the complex. This may occur when two or more bridging units are present. Cases in which the electrophile simply adds to the dinuclear core should be distinguished from those in which one of the metals carries a ligand, generally anionic, that reacts or is split by the electrophile, often resulting in more complex reactions and molecular rearrangements (*eg.* propene elimination from an allyl complex in the presence of an acidic hydrogen). Here we describe the reactions of (trimethoxy)silyl iron-platinum complexes with the electrophiles H$^+$ and Au(PPh$_3$)$^+$, which lead to the splitting of the Fe–Si bond with formation of new bonds between the metal and the electrophile.

Protonation of [(OC)$_3${(MeO)$_3$Si}Fe(μ-PPh$_2$)Pt-(PPh$_3$)$_2$] (1) [2] with an excess of HBF$_4$·Et$_2$O in cold CH$_2$Cl$_2$ occurred with loss of the –Si(OMe)$_3$ ligand (most likely as FSi(OMe)$_3$), as revealed by ^{1}H NMR and FAB$^+$ mass spectroscopic methods. The cationic dihydride complex [(OC)$_3$Fe(μ-PPh$_2$)(μ-H)$_2$Pt-(PPh$_3$)$_2$][BF$_4$] (2) was isolated in quantitative yield (eqn. (1)).
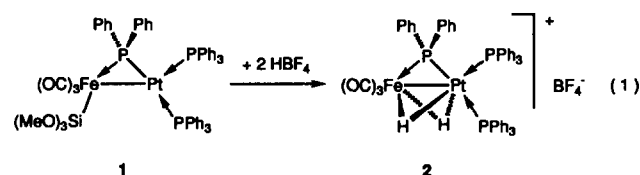
The bridging position of the two equivalent hydrides was deduced from the ^{1}H NMR spectrum, which displays a symmetrical doublet of doublets of doublets in the highfield region, owing to coupling to μ-P (34 Hz), to P$_{trans}$ (36 Hz) and to P$_{cis}$ (10 Hz), flanked by Pt satellites [3]. The coupling to μ-P is similar to that in 4 (40 Hz) (see below). The ^{1}J(PtH) value of 200 Hz is indicative of a bridging position of the hydrides, since it is intermediate between the typical values of ^{1}J(PtH) and ^{2}J(PtH) reported for bimetallic Fe–Pt systems [4]. The ^{31}P{^{1}H} NMR spectrum displays three mutually coupled sets of resonances for the phosphido-bridge (δ = 162.6, ^{2}J(P$_{trans}$P) = 251 Hz, ^{2}J(P$_{cis}$P) = 11 Hz,
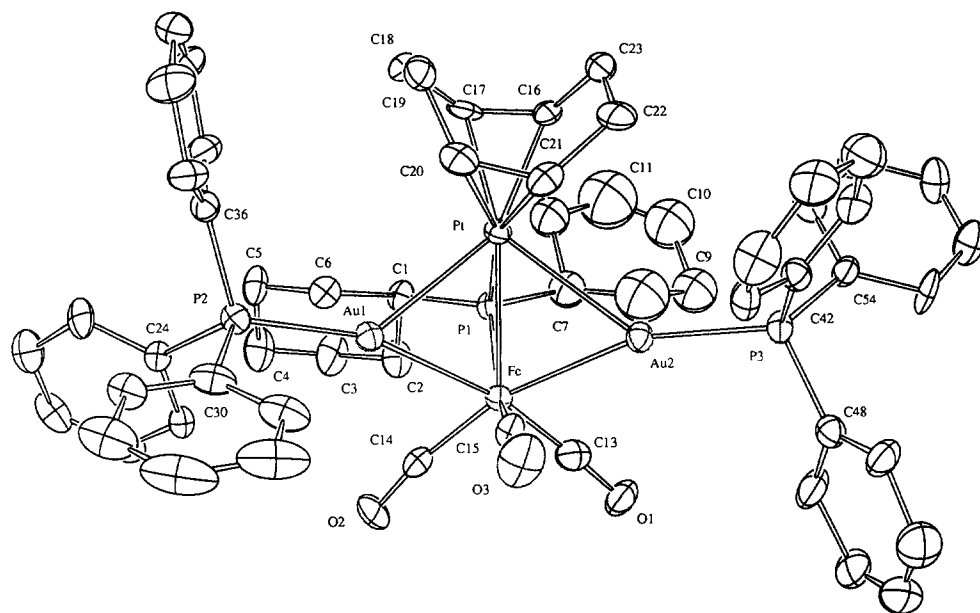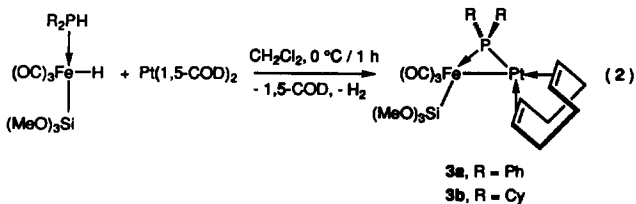
Fig. 1. ORTEP view of the molecular structure of the cation in [(OC)₃Fe(μ-PCy₂)(μ-Au(PPh₂)}₂Pt(1,5-COD)][PF₆] (5b) with the atomic numbering scheme.

^1J(PtP) = 1930 Hz), the cis-PPh₃ ligand (δ = 22.8, ^2J(PP$_{\mu\text{-}P}$) = 11 Hz, ^2J(PP$_{PPh_3}$) = 11 Hz, ^1J(PtP) = 3718 Hz) and the trans-PPh₃ ligand (δ = 12.4, ^2J(PP$_{\mu\text{-}P}$) = 251 Hz, ^2J(PP$_{cis}$) = 11 Hz, ^1J(PtP) = 2460 Hz). On the basis of the NMR data, the ligand arrangement in 2 must be very similar to that in the closely related complex [(OC)₃Fe(μ-PCy₂)(μ-H)₂Pt(PEt₃)₂][BF₄], recently prepared by protonation of [(OC)₃Fe(μ-PCy₂)(μ-H)Pt(PEt₃)₂] [5]. However, there is a marked difference in the position and intensities of its IR ν(CO) vibrations (CH₂Cl₂) (1998 m, 1973 m, br) compared to those of 2 (2079 s, 2027 m, 2012 m).

Although the 1,5-COD-substituted complexes 3a,b, prepared according to eqn. (2), are less electron-rich than the PPh₃-substituted derivative 1, the metal–metal bond in these complexes may be protonated in the same manner.

$$\text{R}_2\text{PH}$$
$$\downarrow$$
$$\text{(OC)}_3\overset{|}{\underset{|}{\text{Fe}}}\text{—H} + \text{Pt(1,5-COD)}_2 \xrightarrow[-1,5\text{-COD, } -\text{H}_2]{\text{CH}_2\text{Cl}_2, 0\,^\circ\text{C / 1 h}} \text{(OC)}_3\text{Fe}\text{—Pt} \quad (2)$$
$$\text{(MeO)}_3\text{Si}$$

3a, R = Ph
3b, R = Cy

Cleavage of the metal–silicon bond also occurs to give [(OC)₃Fe(μ-PPh₂)(μ-H)₂Pt(1,5-COD)][BF₄] (4), the structure of which could be unambiguously deduced from the spectroscopic data (Scheme 1) [6,7]. There was no indication of protonation of the 1,5-COD

ligand, although this reaction may lead to stable allyl-type complexes [8].

When 2 equiv. of [(Ph₃P)Au][PF₆] were added to a CH₂Cl₂ solution of 3, the cationic heteronuclear clusters [(OC)₃Fe(μ-PR₂)(μ-Au(PPh₃)}₂Pt(1,5-COD)]-[PF₆] (R = Ph, Cy) 5 were formed after 10 h in quantitative yield [9]. When a 1 : 1 ratio of the starting materials was used, only 50% of 3 was consumed to give 5. A product of type [(OC)₃{(MeO)₃Si}Fe(μ-PR₂)(μ-Au-(PPh₃)}Pt(1,5-COD)][PF₆] was never observed. The crystal structure of 5b (R = Cy) was determined by X-ray diffraction [10] and an ORTEP view is shown in Fig. 1; selected bond distances and angles are pre-
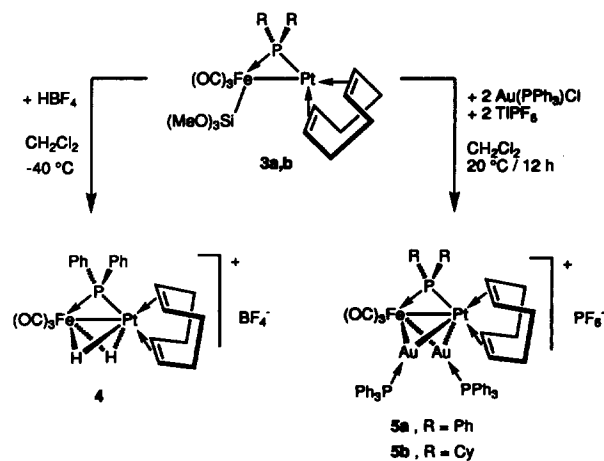

Scheme 1.

TABLE 1. Selected interatomic distances (Å) and angles (°) for **5b**

|			
Au(1)–Au(2)	4.333(1)	Pt–Fe	2.715(3)
Au(1)–Pt	2.821(1)	Fe–P(1)	2.197(6)
Au(1)–Fe	2.614(3)	Pt–C(16)	2.18(2)
Au(2)–Pt	2.875(1)	Pt–C(17)	2.22(2)
Au(2)–Fe	2.576(3)	Pt–C(20)	2.38(2)
Au(1)–P(2)	2.298(5)	Pt–C(21)	2.35(2)
Au(2)–P(3)	2.284(5)	Pt–P(1)	2.229(5)
Fe–C(13)	1.70(3)		
Fe–C(14)	1.77(2)		
Fe–C(15)	1.82(3)		
Fe–Pt–P(1)	51.6(2)	Au(1)–Pt–Au(2)	99.07(3)
Pt–Fe–P(1)	52.7(1)	Fe–Pt–Au(2)	54.81(6)
Fe–P(1)–Pt	75.6(2)	Pt–Fe–Au(2)	65.75(7)
Fe–Pt–Au(1)	56.31(6)	Fe–Au(2)–Pt	59.44(6)
Pt–Fe–Au(1)	63.90(7)	Au(1)–Fe–Au(2)	113.2(1)
Fe–Au(1)–Pt	59.78(6)	P1–Pt–C(16)	107.4(5)
C(13)–Fe–C(14)	96(1)	P1–Pt–C(17)	100.4(7)
C(13)–Fe–C(15)	99(1)	P1–Pt–C(20)	161.2(6)
C(14)–Fe–C(15)	99(1)	P1–Pt–C(21)	160.5(6)
P(1)–Fe–C(15)	151.6(8)		

sented in Table 1. The Fe–Pt bond is bridged by a μ-PCy₂ group and by two Au(PPh₃) fragments. The propeller-like core structure of **5b** is represented in Fig. 2 and is best described as consisting of three triangles sharing the Pt–Fe edge. The dihedral angles between the Fe–Pt–P(1) and the Pt–Fe–Au(1) and Pt–Fe–Au(2) planes are 114.5° and 111.0° respectively, while that between Pt–Fe–Au(1) and Pt–Fe–Au(2) is 134.6°. There is no direct Au–Au interaction, and the interatomic separation of 4.333(1) Å is similar to that observed in [Os₃(CO)₁₀{μ-Au(PPh₃)}₂] [4.304(2) Å] [11]. This is in contrast to [(OC)₄W(μ-PPh₂){(μ-Au-(PPh₃)}₂W(CO)₄], in which an Au–Au distance of 2.749(2) Å was accompanied by a lengthening of the W–W distance to 3.332(1) Å [12]. The structure of **5b** may be compared with those of [Cl(OC)₃Fe(μ-P-Cy₂)Pt-(PEt₃)₂] [5] and [(OC)₃Fe(μ-PCy₂)(μ-H)Pt-(PEt₃)₂] [4b] which contain a similar Pt(μ-P)Fe triangle. The Pt–Fe distance of 2.715(3) Å is in the usual range for this bond [13]. The angles Fe–Au(1)–Pt and Fe–Au(2)–Pt of 59.78(6)° and 59.44(6)°, respectively, are similar to the M–Au–Pt angles in the complexes [(HCy₂P)(CO)Pt(μ-PCy₂)(μ-Au(PPh₂)}W(Cp)(CO)₂] [60.3(1)°] [1a] and [Cp(OC)₂W(μ-PPh₂)(μ-Au(PPh₃)}-Pt(μ-PPh₂)(μ-CO)W(Cp)(CO)₂] [59.7(1)°] [1c]. The Pt–Au distances of 2.821(1) and 2.875(1) Å are very close to those in the latter two complexes and are in the usual range found for this bond [1a,14]. The 1,5-COD ligand is bound to Pt in the usual boat conformation [15]. The geometry at the Pt centre is best described as severly distorted square planar with the olefinic C=C bonds approximately *trans* to (μ-P) and *trans* to the middle of the Au(1)Au(2) unit, respectively. The structure of **5b** appears to be the first reported for an MM′Au₂ cluster [14,16]. The isolobal analogy between [Au(PPh₃)]⁺ and the proton successfully relates complexes **4** and **5**.

The metal–silicon bond in **3** can be considered as a useful synthetic tool which allows, after its cleavage, further addition and increase in cluster nuclearity [17]. Furthermore, complexes **3–5** are potential precursors to a variety of heterometallic complexes since they contain the readily displaced 1,5-COD ligand. Preliminary results have already shown that **3a** reacts with 1 equiv. of [HFe{Si(OMe)₃}(CO)₃(η¹-dppm)] in CH₂Cl₂
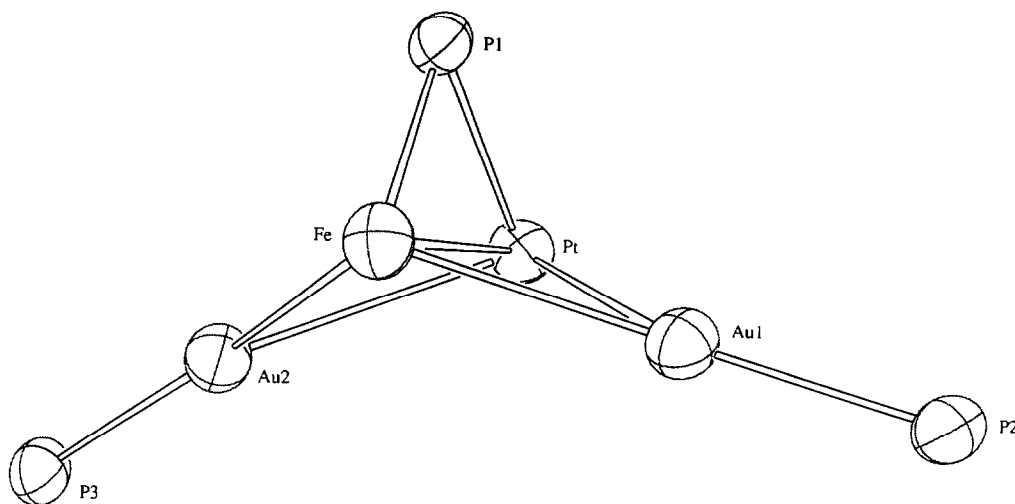
Fig. 2. Perspective view of the core structure of the cation of **5b**.

to give the Fe_2Pt complex **6** which contains two silyl ligands and a hydride (eqn. (3)) [18].

3a

6
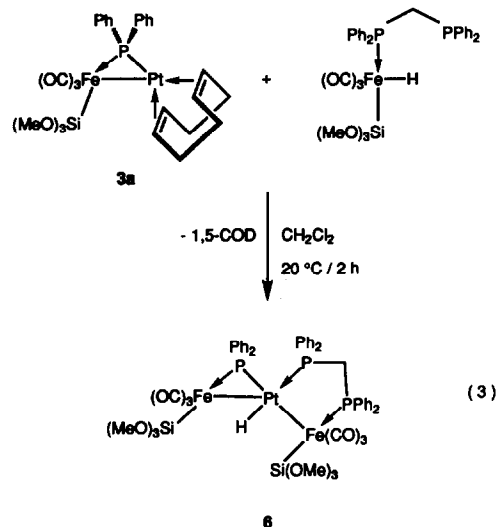
This dppm-assisted synthesis involves displacement of the 1,5-COD ligand and oxidative-addition of the Fe–H bond.

Supplementary material available

Tables of X-ray experimental data (Table S-I), Positional parameters (Table S-II), Bond distances and angles (Table S-III), Thermal parameters (U's) (Table S-IV) and Observed and calculated structure factors (Table S-V) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche information mbH, W-7514 Eggenstein-Leopoldshafen 2 on quoting the depository number CSD-57350, the names of the authors, and the journal citation.

Acknowledgements

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3 Selected data: **2**: ^1H NMR (200 MHz, 28°C, CD_2Cl_2, TMS as external reference): δ –12.15 (ddd, 2H, μ-H, $^2J(PH)$ = 36, 34 and 10 Hz, $^1J(PtH)$ = 200.2 Hz), 7.04–7.47 (m, 40H, aromatic). Mass spectrum (FAB$^+$): 1045.9 (M$^+$, 50%), 959.9 (M$^+$ –2H– 3CO, 100%).

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6 Complex **3a** was obtained by addition of [Fe(H){Si(OMe)$_3$}(CO)$_3$ (PPh$_2$H)] (0.585 g, 1 mmol) to Pt(1,5-COD)$_2$ (0.411 g, 1 mmol) in 3 ml of CH_2Cl_2 at 0°C. After mixing with 3 ml of hexane, the deep orange solution was filtered over Celite and the solvent was removed in vacuum. Yield, 83%, yellow crystalline solid. Selected data: **3a**: IR (CH_2Cl_2): $\nu(CO)$: 1983 s, 1918 s, 1901 s cm^{-1}. ^1H NMR (200 MHz, 28°C, CDCl$_3$): δ 2.1–2.5 (m, 8H, 4CH$_2$), 3.72 (s, 9H, Si(OMe)$_3$), 5.16 (s, 2H, CH, $^2J(PtH)$ = 65 Hz), 6.48 (s, 2H, CH, $^2J(PtH)$ = 56 Hz), 7.2–7.7 (m, 10H, aromatic). $^{31}P\{^1H\}$ NMR (81.02 MHz, 28°C, CH$_2Cl_2$ /C$_6$D$_6$, H$_3$PO$_4$ as external reference): δ 140.9 (s, $^1J(PtP)$ = 3007 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, 28°C, CDCl$_3$): δ 29.7 (s, 2CH$_2$), 30.7 (s, 2CH$_2$), 50.9 (s, 3OCH$_3$), 91.8 (s, 2CH, $^1J(PtC)$ = 116 Hz), 111.0 (d, 2CH, $^2J(PC)$ = 5.0 Hz, $^1J(PtC)$ = 46 Hz), 128–133 (aromatic), 209.7 (d, 3CO, $^2J(PC)$ = 12Hz, $^2J(PtC)$ = 31 Hz). Anal. found: C, 41.50; H, 4.02. C$_{26}$H$_{31}$FeO$_6$PPtSi (M = 749.52) calc.: C, 41.67; H, 4.17%. Selected data: **3b**: Yield: 78%, yellow crystalline solid; IR (CH_2Cl_2): $\nu(CO)$: 1973 s, 1905 s, 1887 s cm^{-1}. ^1H NMR (200 MHz, 28°C, CDCl$_3$): δ 1.24–2.25 (m, 30H, 2Cy+4CH$_2$), 3.72 (s, 9H, Si(OMe)$_3$), 5.27 (s, 2H, CH, $^2J(PtH)$ = 66 Hz), 6.30 (s, 2H, CH, $^2J(PtH)$ = 52 Hz). $^{31}P\{^1H\}$ NMR (81.02 MHz, 28°C, CH$_2Cl_2$/ C$_6$D$_6$): δ 199.6 (s, $^1J(PtP)$ = 2961 Hz). Anal. found: C, 41.22; H, 5.70. C$_{26}$H$_{43}$FeO$_6$PPtSi (M = 761.61) calc.: C, 41.00; H, 5.69%.

7 Complex **4** was obtained by addition of an excess of HBF$_4$·Et$_2$O to a CH_2Cl_2 solution of **3a** (0.110 g, 0.15 mmol) at –40°C. After the reaction mixture was stirred for 0.5 h, the solvent was evaporated and the solid was washed with Et$_2$O (3×0.5 ml). Selected data: **4**: IR (CH_2Cl_2): $\nu(CO)$ 2090 vs, 2041 s, 2027 s cm^{-1}. ^1H NMR (200 MHz, 28°C, CDCl$_3$): δ –11.84 (d, 2 μ-H, $^2J(PH)$ = 40 Hz, $^1J(PtH)$ = 322 Hz), 2.6–2.7 (m, 8H, CH$_2$), 5.28 (s, 2H, CH, $^1J(PtH)$ = 70 Hz), 6.57 (s, 2H, CH, $^1J(PtH)$ = 50 Hz), 7.2–7.6 (m, 10H, aromatic). $^{31}P\{^1H\}$ NMR (81.02 MHz, 28°C, CH$_2Cl_2$ /C$_6$D$_6$): δ 157.1 (s, μ-P, $^1J(PtP)$ = 2290 Hz).

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9 Clusters **5**: They were obtained as yellow crystals by layering a CH_2Cl_2 solution with pentane at low temperature. Selected data: **5a**: IR (KBr): $\nu(CO)$ 1980 vs, 1924 s, 1900 sh cm^{-1}. ^1H NMR (200 MHz, 28°C, CDCl$_3$): δ 1.50–2.35 (m, 8H, CH$_2$), 4.85 (s, 2H, 2CH, $^2J(PtH)$ = 67 Hz), 6.9–8.0 (m, 42H, 2 CH and aromatic). $^{31}P\{^1H\}$ NMR (81.02 MHz, 28°C, CH$_2Cl_2$ /C$_6$D$_6$): δ –143.8 (spt, PF$_6$, $^1J(PF)$ = 713 Hz), 43.7 (d, P(Au), $^3J(PP)$ = 15 Hz, $^2J(PtP)$ = 195 Hz), 154.9 (t, μ-P, $^3J(PP)$ = 15 Hz, $^1J(PtP)$ = 2484 Hz). Anal. found: C, 42.15; H, 3.07. C$_{59}$H$_{52}$Au$_2$F$_6$FeO$_3$P$_4$Pt (M = 1691.87) calc.: C, 41.88; H, 3.10%.

5b: Suitable crystals for X-ray diffraction were obtained from a mixture C$_6$H$_5$Cl/pentane. mp. = 154–156°C (decomp.). IR (KBr): $\nu(CO)$ 1973 vs, 1915 s, 1880 sh cm^{-1}. ^1H NMR (200 MHz, 28°C, CDCl$_3$): δ 0.8–2.4 (m, 30H, aliphatic), 5.05 (s, 2H, CH, $^2J(PtH)$ = 64 Hz), 6.82 (s, 2H, CH, $^2J(PtH)$ = 44 Hz), 7.4–7.5 (m, 30H,

aromatic). $^{31}P\{^1H\}$ NMR (81.02 MHz, 28°C, CH_2Cl_2/C_6D_6): δ -143.7 (spt, PF_6, $^1J(PF) = 713$ Hz), 44.0 (d, P(Au), $^3J(PP) = 16$, $^2J(PtP) = 214$ Hz), 211.0 (t, μ-P, $^3J(PP) = 16$ Hz, $^1J(PtP) = 2370$ Hz). Mass spectrum (FAB$^+$): 1558.1 (M$^+$, 100%), 1366.0 (M$^+$ $-$ 1,5-COD $-$ Cy, 60%), 1103.9 (M$^+$ $-$ 1,5-COD $-$ Cy $-$ PPh$_3$, 40%), 721.1 ([Au(PPh$_3$)$_2$]$^+$, 46%), 459.0 ([Au(PPh$_3$)]$^+$, 50%). Anal. found: C, 41.56; H, 3.53. $C_{59}H_{64}Au_2F_6FeO_3P_4Pt$ (M $= 1703.99$) calc.: C, 41.58; H, 3.79%.

10 Crystal data: $C_{59}H_{64}Au_2F_6FeO_3P_4Pt$ (**5b**) M $= 1703.9$, monoclinic, space group $P2_1/n$, $a = 22.479(6)$, $b = 26.781(8)$, $c = 10.254(3)$ Å, $\beta = 102.94(2)°$, $U = 6016.1$ Å^3, $Z = 4$, ρ(calc) $= 1.881$ g cm^{-3}, $\mu = 75.97$ cm^{-1}, Enraf-Nonius CAD-4 diffractometer, $\lambda = 0.7107$ Å. 11434 independent $\pm h$, $+ k$, $+ l$ reflections were measured ($2 < \theta < 24°$) at 20°C for which 5022 reflections with $I > 3\sigma(I)$ were treated and observed. $R(F) = 0.051$, $R_w(F) = 0.069$, GOF $= 1.675$.

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18 Selected data: **6**: Yield: 88%, orange crystalline solid; IR (KBr): ν(CO): 2067 s, 2016 m, 1992 vs, 1960 s, 1893 m, 1867 s cm^{-1}. ^1H NMR (300.14 MHz, 28°C, CDCl$_3$): δ -7.09 (ddd, 1H, $^2J(PH) = 92$ Hz, $^2J(PH) = 26$ Hz, $^3J(PH) = 7$ Hz, $^1J(PtH) = 462$ Hz), 3.50 (s, 9H, Si(OMe)$_3$), 3.69 (s, 9H, Si(OMe)$_3$), 3.95 (t, 2H, PCH$_2$, $^2J(PH) = 10$ Hz, $^3J(PtH) = 49$ Hz), 6.9–7.3 (m, 30H, aromatic). $^{31}P\{^1H\}$ NMR (121.5 MHz, 28°C, CDCl$_3$): δ 28.8 (d, P(Pt), $^{2+3}J(PP) = 86$ Hz, $^1J(PtP) = 3790$ Hz), 63.3 (d, P(Fe), $^{2+3}J(PP) = 81$ Hz, $^2J(PtP) = 80$ Hz), 149.2 (s, (μ-P), $^1J(PtP) = 1985$ Hz). Anal. found: C, 45.60; H, 4.07. $C_{49}H_{51}Fe_2O_{12}P_3PtSi_2$ (M $= 1287.87$) calc.: C, 45.69; H, 4.00%.