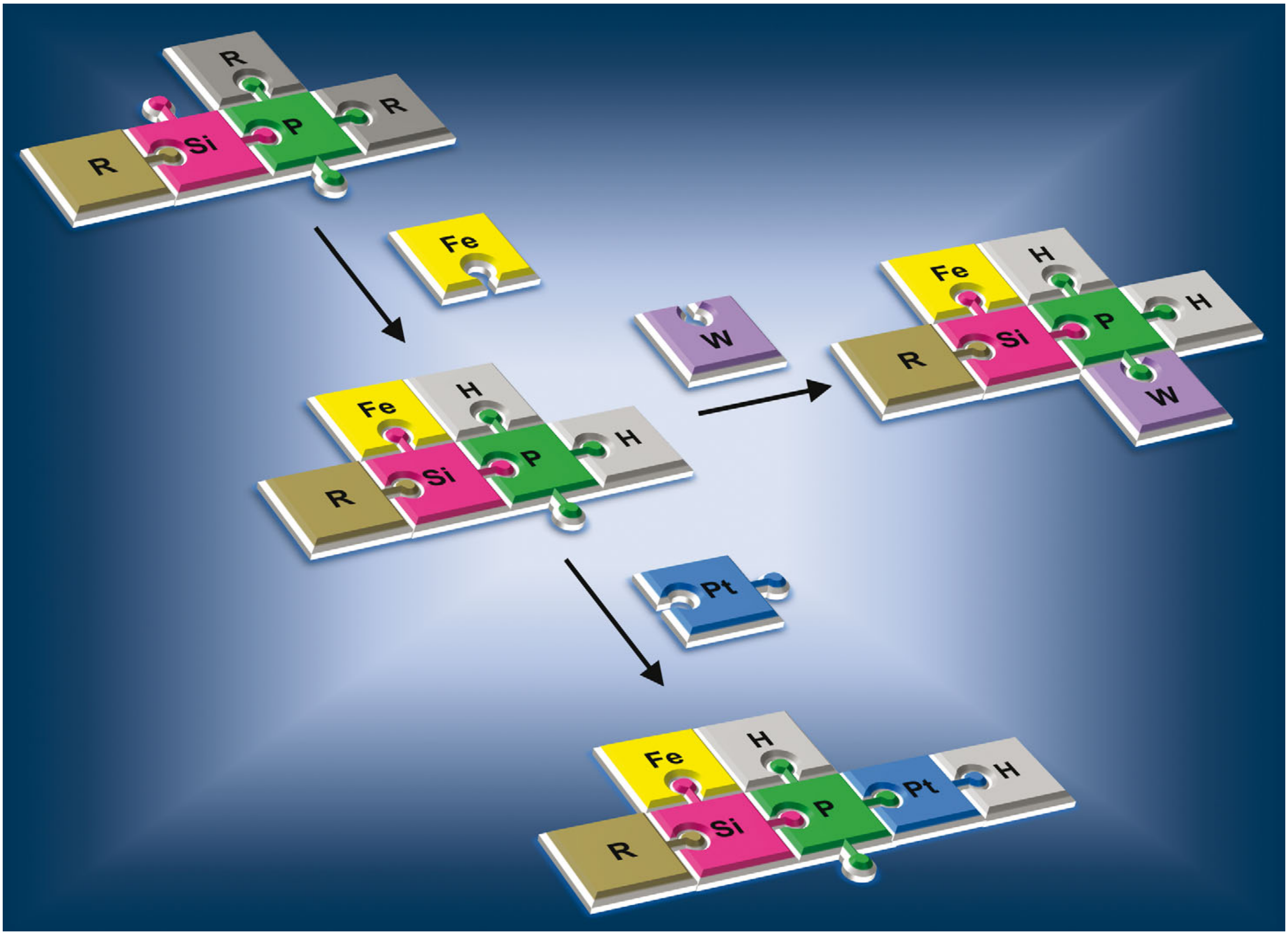

Showcasing research from Professor Shigeyoshi Inoue's group, Department of Chemistry, Technische Universität München, Garching, Germany.

Phosphinosilylenes as a novel ligand system for heterobimetallic complexes

Phosphinosilylenes comprise two interconnected elements with electron lone pairs – silicon and phosphorus. For the first time, both lone pairs were engaged in coordination to different transition metals and heterobimetallic complexes with iron/tungsten and iron/platinum.

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Phosphinosilylenes as a novel ligand system for heterobimetallic complexes†

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A dihydrophosphinosilylene iron complex [LSi{Fe(CO)$_4$}PH$_2$] has been prepared and utilized in the synthesis of novel heterobimetallic complexes. The phosphine moiety in this phosphinosilylene complex allows coordination towards tungsten leading to the iron–tungsten heterobimetallic complex [LSi{Fe(CO)$_4$}PH$_2${W(CO)$_5$}]. In contrast, the reaction of [LSi{Fe(CO)$_4$}PH$_2$] with ethylenebis(triphenylphosphine)-platinum(0) results in the formation of the iron–platinum heterobimetallic complex [LSi{Fe(CO)$_4$}PH{PtH(PPh$_3$)$_2$}] *via* oxidative addition.

Heterobimetallic complexes have received a great deal of attention and have become important targets since they can enhance catalysis through cooperativity.[1] N-heterocyclic carbenes are important compounds as supporting ligands in catalysis and for reactive species.[2,3] Several heterobimetallic species containing one or more carbenes have been reported in the last decade.[1b,4] One inherent problem for the synthesis of heterobimetallic bis(carbene)s (A, Chart 1) is the selectivity of a first monometallation.[1b,4a–e] Incorporating different ligands like phosphines (B, Chart 1) can facilitate selective product formation.[4f,g] Another very recent example of utilizing different donors is the silylene–carbene monometallic complex (C, Chart 1).[5] Various silylene transition metal complexes have been reported to date and some of those have been tested in catalysis and showed very promising results.[6] Also, about a dozen bis(silylene) complexes have been reported to date.[7] In most of them the bis(silylene)s are acting as chelating ligands (D, Chart 1)[8] with a few exceptions of homobimetallic species (E, Chart 1).[8c,9] It should be noted that also few, very interesting heterobimetallic silylene complexes have been described.[8b,f,10] However, to the best of our knowledge, no general route for a systematic synthesis of heterobimetallic complexes with a silylene and an additional donor has been reported to date.

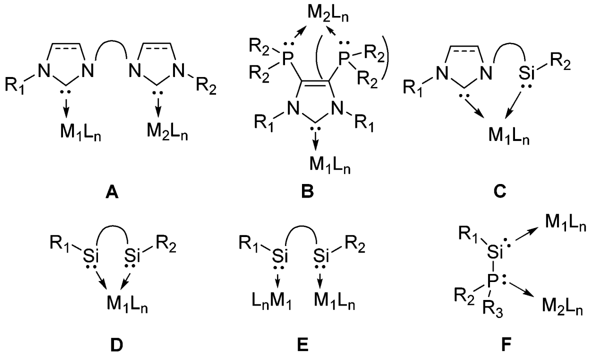

Chart 1 Concept of phosphinosilylenes for heterobimetallic complexes.

In this publication we propose a new ligand system for heterobimetallic complexes with interconnected silylene and phosphine donors, namely the phosphinosilylene (F, Chart 1). Only a few stable phosphinosilylenes have been known to date[11] and their reactivity studies are rather limited.[8c,12]

We lay out the systematic synthesis of phosphinosilylene heterobimetallic complexes (F, Chart 1) based on phoshinosilylene **1** (Scheme 1).[11c] In a stepwise fashion, first the stronger silylene donor should be coordinated to one metal center. Afterwards, the phosphine will be coordinated to the second metal center. In this context, the phosphinosilylene iron carbonyl complex [LSi{Fe(CO)$_4$}P(SiMe$_3$)$_2$] (**2**) [L = PhC(N*t*Bu)$_2$$^-$] was synthesized by the reaction of **1** with [Fe(CO)$_5$] in a good yield of 78% (Scheme 1). The ^{29}Si{^{1}H} NMR spectrum of **2** shows a significant downfield shift from starting material **1**[11c] as well as a downfield shift from the related tungsten complex [LSi{W(CO)$_5$}P(SiMe$_3$)$_2$] (δ = 102.6 ppm, δ = 44.0 ppm,[11c] and δ = 70.7 ppm,[12c] respectively) due to a stronger coordination of the silylene to iron in comparison with tungsten, which was similarly reported for other Si(II) compounds.[13] The ^{31}P{^{1}H} NMR chemical shifts of

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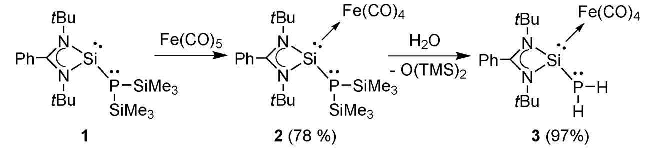
† Electronic supplementary information (ESI) available: Details of experimental procedures and characterization methods, NMR spectra, mass spectra, IR spectra, cyclic voltammograms, and crystallographic data. CCDC 1435730 (**2**), 1435732 (**3**), 1435731 (**4**), and 1435733 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc00601a



Scheme 1 Syntheses of the phosphinosilylene iron carbonyl complexes **2** and **3**.

these compounds display less variation (δ = −194.4 ppm, δ = −211.0 ppm[11c]) in agreement with the coordination of the silylene. The presence of the iron carbonyl group is also confirmed by $^{13}C\{^1H\}$ NMR spectroscopy displaying a signal at δ = 217.2 ppm, which is only slightly downfield shifted from that of $[LSi\{Fe(CO)_4\}OtBu]$ (δ = 216.7 ppm).[14] The IR bands of **2** (ν_{CO} = 2022, 1941, 1904 cm^{-1}) are close to those of $[LSi\{Fe(CO)_4\}OtBu]$ (ν_{CO} = 2026, 1949, 1899 cm^{-1}).[14]

Unfortunately, the phosphinosilylene iron complex **2** does not undergo a reaction with different transition metal complexes ($[Fe_2(CO)_9]$, $[W(CO)_5{\cdot}thf]$, $[Ni(COD)_2]$) presumably due to the steric bulk of the trimethylsilyl groups. We were able to circumvent this issue by replacing the trimethylsilyl groups with hydrogens. Little attention was yet given to the reaction of $RP(SiMe_3)_2$ and H_2O yielding RPH_2 and $O(SiMe_3)_2$.[15] However, it proved to be a viable route for the synthesis of $[LSi\{Fe(CO)_4\}PH_2]$, **3** (Scheme 1). The formation of **3** is quantitative (97% yield) and little excess water seems not to harm this reaction and product. The signals of the PH_2 group in the ^1H and ^{31}P NMR spectra appear as a doublet at δ = 2.50 ppm and a triplet at δ = −198.6 ppm with a coupling constant of $^1J_{P-H}$ = 188 Hz. The $^{29}Si\{^1H\}$ NMR spectrum of **3** reveals a downfield shift from **2** (δ = 112.8 ppm and δ = 102.6 ppm, respectively). The CO signal was found at δ = 216.1 ppm in the $^{13}C\{^1H\}$ NMR spectrum. In the IR spectra a slight change of the ν_{CO}-bands to higher wave numbers was observed (ν_{CO}: 2025, 1946, 1913 cm^{-1} (**3**) and ν_{CO}: 2022, 1941, 1904 cm^{-1} (**2**)).

The structural features of compounds **2** and **3** (Fig. 1) are very similar to those of its tungsten analogue $[LSi\{W(CO)_5\}P(SiMe_3)_2]$.[12c] The Si1–P1 bond lengths of **2** and **3** (2.2281(6) Å and 2.2551(9) Å, respectively) are shortened compared to **1** (2.2838(12) Å[11c]). Their iron–silicon bond lengths (2.2777(5) Å in **2** and 2.2412(7) Å in **3**) are longer than that of $[LSi\{Fe(CO)_4\}OtBu]$ (2.237(7) Å),[14] but shorter than in the bisamidinato species $[(PhC\{NiPr\}_2)_2Si\{Fe(CO)_4\}]$ (2.3175(6) Å).[13a]

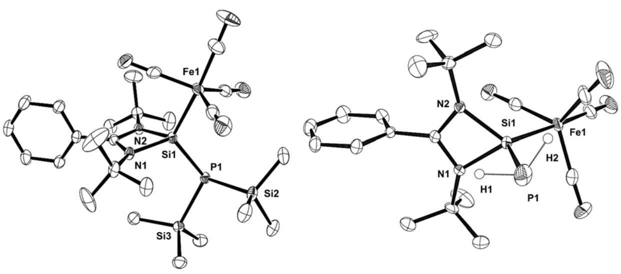
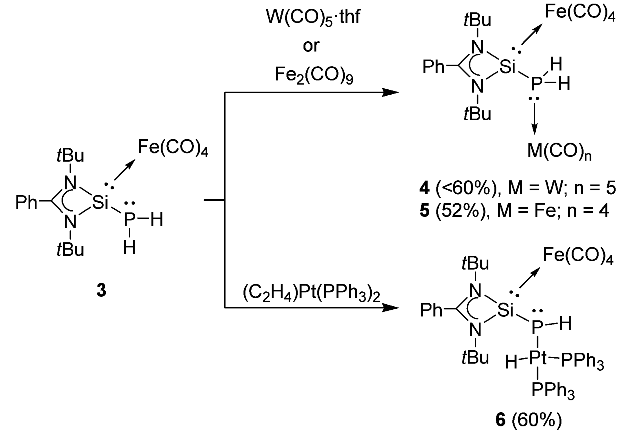


Fig. 1 Molecular structures of compounds **2** (left) and **3** (right). Thermal ellipsoids are drawn at the 40% probability level. One disordered *t*Bu group in **2** and hydrogen atoms except for H1 and H2 in **3** are omitted for clarity. Selected bond lengths (Å) and angles (°) in **2** and **3** (for **3** see the values in brackets): P1–Si1 2.2281(6) {2.2551(9)}, Fe1–Si1 2.2777(5) {2.2412(7)}, P1–Si1–Fe1 119.19(2) {119.97(3)}.



Scheme 2 Syntheses of the hetero- and homobimetallic phosphinosilylene complexes **4**, **5** and **6**.

With the less sterically crowded compound **3** at hand, we were able to successfully synthesize the first heterobimetallic phosphinosilylene complex **4** (Scheme 2). The phosphine of **3** easily coordinates to pentacarbonyl tungsten and **4** was formed as the major product. This coordination is evident from ^1H NMR spectroscopy revealing the shifted PH_2 signal with the expected increased coupling constant ($^1J_{P-H}$ = 302 Hz in **4** and $^1J_{P-H}$ = 188 Hz in **3**; compare also $[PH_2(SiMe_3)\{W(CO)_5\}]$ with $^1J_{P-H}$ = 310 Hz[16]). In addition, the $^{31}P\{^1H\}$ NMR signal at δ = −165.2 ppm exhibits tungsten satellites with a coupling constant of $^1J_{W-P}$ = 187 Hz. This coupling constant lies in between those of $[PH_3\{W(CO)_5\}]$ and $[P(SiMe_3)_3\{W(CO)_5\}]$ ($^1J_{W-P}$ = 216 Hz and $^1J_{W-P}$ = 150 Hz, respectively).[16] The two carbonyl signals appear in the $^{13}C\{^1H\}$ NMR spectrum at δ = 196.4 ppm ($W(CO)_5$) and δ = 215.1 ppm ($Fe(CO)_4$). The $^{29}Si\{^1H\}$ NMR signal of **4** is shifted upfield from **3** and is exhibiting a smaller silicon–phosphorus coupling constant (δ = 98.0 ppm, $^1J_{Si-P}$ = 24 Hz and δ = 112.8 ppm, $^1J_{Si-P}$ = 62 Hz, respectively). This suggests that the coordination of the phosphine to tungsten is having a considerable effect on the silicon–phosphorus bond. Despite our best efforts, the isolation of analytically pure **4** was not possible. The solid obtained in 60% yield contains little impurities of $W(CO)_6$ or other $W(CO)_x$ byproducts that could not be separated.

The molecular structure of **4** was unequivocally assigned by X-ray diffraction analysis (Fig. 2). The iron and tungsten carbonyl moieties are pointing in opposite directions (torsion angle Fe1–Si1–P1–W1: −172.35(4)°) and their interatomic distance amounts to 6.3071(5) Å, which is expected due to their steric requirements. The silicon–phosphorus bond length in **4** increased from 2.2551(9) Å in **3** to 2.2790(13) Å in agreement with the weaker Si–P bond suggested by the coupling constants. The silylene–iron bond is slightly shortened from 2.2412(7) Å in **3** to 2.2307(10) Å in **4**. The P1–W1 interatomic distance of 2.5194(8) Å is in between those of $[PH_3\{W(CO)_5\}]$ and $[PPh(SiMe_3)_2\{W(CO)_5\}]$ (2.493(2) Å and 2.5894(5) Å, respectively).[16]

We utilized iron carbonyl as another source for a bimetallic complex to show that the coordination of phosphorus in **3** is

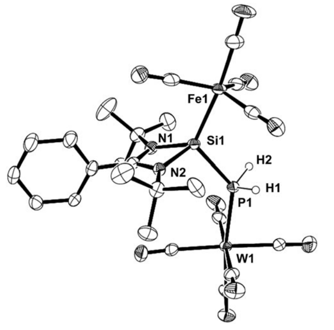


Fig. 2 Molecular structure of compound **4**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms except for H1 and H2, the disorder of the *t*Bu groups and one molecule of pentane are omitted for clarity. Selected bond lengths (Å) and angles (°) in **4**: Si1–P1 2.2790(13), Si1–Fe1 2.2307(10), P1–W1 2.5194(8), P1–Si1–Fe1 116.45(5), Si1–P1–W1 135.28(5).

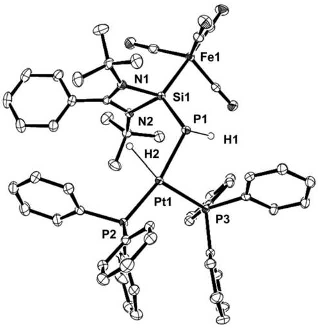


Fig. 3 Molecular structure of compound **6**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms except for H1 and H2 and two molecules of thf are omitted for clarity. Selected bond lengths (Å) and angles (°) in **6**: Si1–P1 2.2176(11), Fe1–Si1 2.2917(9), Pt1–P1 2.3341(7), Pt1–P2 2.2854(8), Pt1–P3 2.3301(7), P2–Pt1–P1 164.20(3), P3–Pt1–P1 92.37(3), P2–Pt1–P3 102.05(3), P1–Si1–Fe1 118.76(4), Si1–P1–Pt1 113.70(4).

also applicable for other than the tungsten carbonyl moiety. The homobimetallic diironcomplex $[LSi\{Fe(CO)_4\}PH_2\{Fe(CO)_4\}]$ (**5**) was obtained from **3** and $[Fe_2(CO)_9]$ in a fair yield of 52% (Scheme 2). The phosphorus–hydrogen coupling constant in **5** is even a bit larger than that of the tungsten analogue **4** ($^1J_{P-H}$ = 321 Hz and $^1J_{P-H}$ = 302 Hz, respectively). The ^{31}P NMR signal of **5** is significantly downfield shifted from **4** (δ = −102.3 ppm and δ = −165.2 ppm, respectively). The $^{29}Si\{^1H\}$ NMR signal of **5** shows little difference from the doublet observed for **4** (δ = 99.2 ppm, $^1J_{Si-P}$ = 25 Hz and δ = 98.1 ppm, $^1J_{Si-P}$ = 24 Hz, respectively). The carbonyl carbons of **5** appear in the $^{13}C\{^1H\}$ NMR spectrum as a doublet at δ = 214.4 ppm ($^2J_{P-C}$ = 17 Hz) and a singlet at δ = 214.9 ppm.

The IR spectrum of **5** exhibits two strong bands at 2055 and 2035 cm^{-1} with many other overlapping bands at 1970, 1955, 1938, 1924 and 1907 cm^{-1}. The IR spectrum of **4** displayed similarly two sharp bands at 2074 and 2040 cm^{-1} in addition to an ill-defined broad region for the other carbonyl bands (2010–1830 cm^{-1}). Based on the IR bands of the parent compounds, $[PH_3\{W(CO)_5\}]$ and $[PH_3\{Fe(CO)_4\}]$ (ν_{CO} = 2083, 1984, 1953, 1921 cm^{-1} and ν_{CO} = 2066, 1994, 1962 cm^{-1}, respectively),[17] the first bands of **4** and **5** at 2074 and 2055 cm^{-1} can be assigned to the phosphine metal carbonyl groups. Furthermore, the bands representing the silylene iron carbonyl groups are expected to be rather close to each other and **3** (ν_{CO} = 2025 cm^{-1}). This matches well with the second bands of **4** and **5** (ν_{CO} = 2040 cm^{-1} and ν_{CO} = 2035 cm^{-1}, respectively).

The PH_2 moiety in **3** could also open up other pathways for the synthesis of heterobimetallic complexes. Compound **6** containing the transition metals iron and platinum, which are largely utilized in catalysis,[18] can be synthesized by the insertion of platinum into the phosphorus–hydrogen bond in 60% yield (Scheme 2).[19] The ^1H NMR spectrum of **6** attests to this reactivity displaying the PtH signal at δ = −4.47 ppm. This doublet of doublet of doublets results from the coupling of the Pt–H with the three different phosphorus moieties ($^2J_{H-P3}$ = 176 Hz, $^2J_{H-P1}$ = 28 Hz, $^2J_{H-P2}$ = 21 Hz) and displays platinum satellites ($^1J_{H-Pt}$ = 906 Hz). The signal of PH (P1) in **6** appears close to **5** (δ = −102.3 ppm) at δ = −105.6 ppm. This doublet of doublets in the $^{31}P\{^1H\}$ NMR spectrum exhibits the expected large and small coupling constants for *trans* and *cis* orientation ($^2J_{P1-P2}$ = 139 Hz and $^2J_{P1-P3}$ = 11 Hz, respectively). This signal is split by the couplings to both the P–H and the Pt–H ($^1J_{P1-H1}$ = 214 Hz and $^2J_{P1-H2}$ = 28 Hz) to a dddd in the ^{31}P NMR spectrum. The ^{31}P–^{195}Pt coupling constant for P1 is significantly smaller than those of P2 and P3 ($^1J_{Pt-P1}$ = 712 Hz, $^1J_{P2-Pt}$ = 2536 Hz and $^1J_{P3-Pt}$ = 2081 Hz). The $^{29}Si\{^1H\}$ NMR signal of **6** (δ = 114.8 ppm) is shaped as a doublet of multiplets presumably due to couplings with the triphenylphosphines. The $^1J_{Si-P1}$ coupling constant in **6** (97 Hz) is higher than that of **3** ($^1J_{Si-P}$ = 62 Hz). The $^{195}Pt\{^1H\}$ NMR spectrum of **6** exhibits the expected doublet of doublet of doublets at δ = −5035.5 ppm. The carbonyl bands in the IR spectrum of **6** are shifted to lower wave numbers compared with **3** suggesting a slightly weaker coordination of the silylene (ν_{CO} = 2014, 1933, 1890 cm^{-1} and ν_{CO} = 2025, 1946, 1913 cm^{-1} respectively). It should be noted that cyclic voltammetry studies of compounds **3** and **6** were also carried out with the results being described in the ESI.†

The iron and platinum centers in **6** are pointing in nearly opposite directions (torsion angle Fe1–Si1–P1–Pt1: 157.10(4)°) with an iron–platinum interatomic distance of 5.8864(6) Å (Fig. 3). The sum of the bond angles around platinum is close to 360°. However, the square coordination sphere of platinum is clearly distorted presumably due to steric reasons (P2–Pt1–P1 164.20(3)°, P2–Pt1–P3 102.05(3)°). The silicon–phosphorus bond in **6** is shorter than in **3**, while its silicon–iron interatomic distance is larger (Si1–P1 2.2176(11) Å, Fe1–Si1 2.2917(9) Å and Si1–P1 2.2551(9) Å, Fe1–Si1 2.2412(7) Å, respectively). This supports the stronger silicon–phosphorus interaction suggested by $^{29}Si\{^1H\}$ NMR spectroscopy and the weaker coordination of the silylene found by IR spectroscopy.

In summary, we succeeded in synthesizing novel heterobimetallic complexes using the phosphinosilylene ligand. Following the coordination of the silylene to iron carbonyl in **2**, the trimethylsilyl groups were replaced with hydrogen to give the corresponding less bulky derivative **3**, an excellent precursor for heterobimetallic complexes. Due to the increased coordination space in **3**, the lone pair on phosphorus can coordinate to tungsten and iron, which produced the iron–tungsten heterobimetallic complex **4** and the homobimetallic diiron complex **5**, respectively. In addition, the iron–platinum heterobimetallic complex **6** was formed *via* oxidative addition of platinum to the P–H bond.

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