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A Protected Metallophosphine Ligand: Synthesis, Structure, and Reactivity of the Silylphosphinidene Cluster $(\mu\text{-H})_2Fe_3(CO)_9[\mu_3\text{-PSi}(i\text{-Pr}_3)]$

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Summary: An anionic "metallophosphine" ligand with a lone pair available for coordination is the result of cleaving the P–Si bond in the first example of a monocapped silylphosphinidene cluster, $(\mu\text{-H})_2Fe_3(CO)_9[\mu_3\text{-PSi}(i\text{-Pr})_3]$. *The bulky triisopropylsilyl group, which serves as a protecting group for the phosphorus atom during the cluster synthesis, can be removed by reaction with* $[NBu_4]F$, $[(Ph_3P)_2N]Cl$, *and* $(Ph_3P)AuCl$. *In the case of the gold halide reaction, the* $(Ph_3P)Au^+$ *fragment coordinates the resulting metallophosphine ligand.*

Substituent-free heteroatoms of group 15 that cap M_3 or M_4 faces of a metal cluster offer a lone electron pair that is capable of acting as a ligand. Surprisingly, very few examples of metal cluster analogues to amine or phosphine ligands, which possess face-capping N or P donor atoms, are known.[1] This rarity is, in part, due to the tendencies of such clusters to undergo self-oligomerization reactions that result in coordination of the basic pnictide atom lone pair.[2] We are interested in systematically accessing the coordinating potential of cluster-bound phosphorus atoms in bicapped M_3 and M_4 clusters (such as $[Fe_3(CO)_9(\mu_3\text{-P})_2]^{2-}$) to assemble extended chains of clusters.[3] These "metallophosphine" ligands can be accessed through the synthesis of phosphinidene clusters[4] that incorporate a readily cleavable silyl substituent on the phosphorus atom as a protecting group during the cluster synthesis. We report here the synthesis and the structural characterization of the first example of a monocapped silylphosphinidene[5] transition metal cluster, $(\mu\text{-H})_2Fe_3(CO)_9[\mu_3\text{-PSi}(i\text{-Pr})_3]$ (1), as well as the reactivity of 1 with the halide salts $[NBu_4]F$ and $[(Ph_3P)_2N]Cl$ and the metal halide complex $(Ph_3P)AuCl$. This system permits the fundamental chemistry of the P–Si bond as well as the coordinating properties of the resulting metallophosphine ligand to be studied.

The silylphosphinidene cluster, 1, isostructural with previously reported alkyl- and arylphosphinidene clusters,[6] can be prepared under mild conditions by warming a 10% *cis*-cyclooctene/hexanes reaction mixture containing 3 equiv of $Fe(CO)_3(cis\text{-cyclooctene})_2$[7] and 1 equiv of $H_2PSi(i\text{-Pr})_3$[8] from −40 °C to room temperature (eq 1); following purification by low-temperature chromatography, black

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(1) (a) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104. (b) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41.

(2) (a) Vizi-Orosz, A. *J. Organomet. Chem.* **1976**, *111*, 61. (b) Vizi-Orosz, A.; Galamb, V.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1976**, *107*, 235.

(3) Bautista, M. T.; White, P. S.; Schauer, C. K. *J. Am. Chem. Soc.* **1991**, *113*, 8963.

(4) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743.

(5) The (trimethylsilyl)nitrene complex $Fe_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-NSiMe}_3)$ has been prepared in very low yield from reaction of $Fe_2(CO)_9$ and Me_3SiN_3. Hydrogenation of $Fe_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-NSiMe}_3)$ produces $(\mu\text{-H})_2Fe_3(CO)_9(\mu_3\text{-NSiMe}_3)$. (a) von Gustorf, E. K.; Wagner, R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 910. (b) Barnett, B. L., Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 910.

(6) Thermolytic syntheses analogous to those employed in the synthesis of alkyl and aryl phosphinidene clusters (Huttner, G.; Schneider, J.; Mohr, G.; von Seyerl, J. *J. Organomet. Chem.* **1980**, *191*, 161) do not produce good yields of silylphosphinidene clusters.

(7) Fleckner, H.; Grevels, F.-W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

(8) Fritz, G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1971**, *385*, 243.

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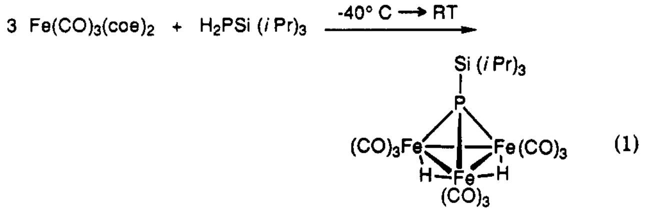

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crystals of pure 1 are isolated in 40% yield.[9] The P–Si(i-Pr)$_3$ linkage is able to survive chromatography using conventional supports without hydrolysis, unlike P–SiMe$_3$ groups.[3] The structure of 1 was determined by a single-crystal X-ray diffraction study (Figure 1)[10] and consists of a μ_3-PSi(i-Pr)$_3$ ligand bound to an isosceles Fe$_3$ triangle. The Fe–P bond distances in 1 (Figure 1) are ca. 0.04 Å longer than those observed for (μ-H)$_2$Fe$_3$(CO)$_9$(μ_3-PPh),[5] indicating slightly weaker bonding of the silylphosphinidene ligand than the phenylphosphinidene ligand to the Fe$_3$ frame. The P–Si distance of 2.292 (3) Å for 1 is elongated over that observed in the cubane cluster [(iBuAl)(PSiPh$_3$)]$_4$ with face-capping silylphosphinidene ligands (2.236 (4) Å).[11]

Both the silyl group as well as the acidic hydride ligands[12] in 1 are potential sites of reaction with basic reagents capable of removing the silyl group. For instance, in tetrahydrofuran solution, [NBu$_4$]F,[13] a common desilylating agent, stoichiometrically *deprotonates* 1 to yield red-brown [NBu$_4$]{(μ-H)Fe$_3$(CO)$_9$[μ_3-PSi(i-Pr)$_3$]} ([NBu$_4$]$^+$[2]) (Scheme I).[14] The presence of a silyl substituent on the phosphorus atom influences the observed ^{31}P chemical shift of the anion. The ^{31}P resonance of 1 (δ 300.4) shifts downfield by more than 100 ppm upon deprotonation, with a concomitant increase in $^1J_{\text{P-Si}}$ from 23 Hz in 1 to 34 Hz in 2. Only very small shifts are observed in the ^{31}P NMR resonances when the P–Ph and P–tBu analogues to 1 are deprotonated (2 ppm downfield and 3 ppm downfield, respectively).[15] Presumably the observed difference in the spectroscopic properties of 2 and the alkyl- and arylphosphinidene analogues is a result of the known ability of a silyl group to act as an acceptor.[16]

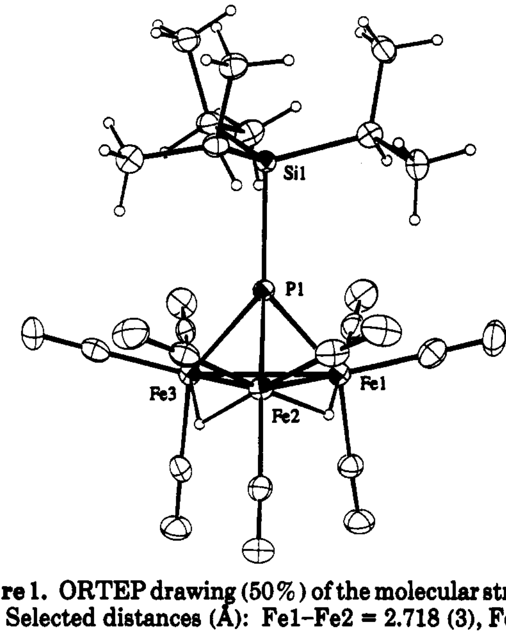
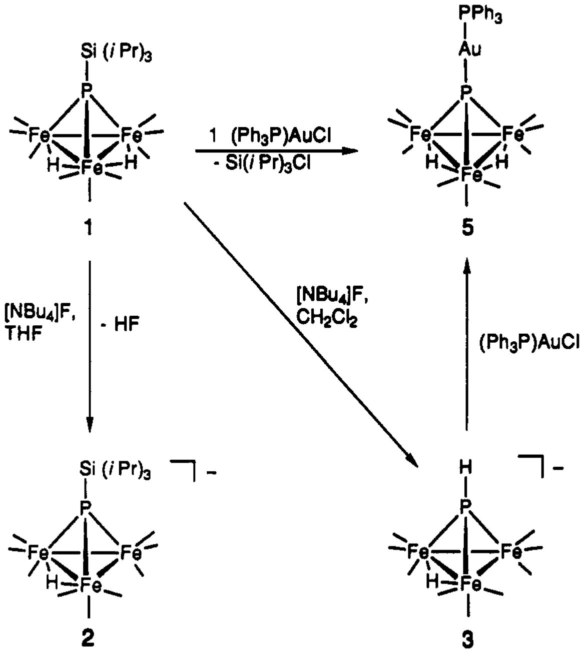


Figure 1. ORTEP drawing (50%) of the molecular structure of 1. Selected distances (Å): Fe1–Fe2 = 2.718 (3), Fe1–Fe3 = 2.665 (2), Fe2–Fe3 = 2.710 (2), Fe1–P1 = 2.186 (2), Fe2–P1 = 2.241 (2), Fe3–P1 = 2.195 (2), P–Si = 2.297 (3).

Scheme I



The [NBu$_4$]F reaction is highly solvent dependent, and in CH$_2$Cl$_2$ solution, [NBu$_4$]F *desilylates* 1 instead to produce the red-purple rearranged product [NBu$_4$][(μ-H)Fe$_3$(CO)$_9$(μ_3-PH)] ([NBu$_4$]$^+$[3]).[17] The pattern observed in the infrared spectrum for [NBu$_4$]$^+$[3] is identical to [NBu$_4$]$^+$[2] but is shifted approximately 6 cm^{-1} to higher energy. The presence of a hydrogen terminally bound to phosphorus in 3 is evident in the ^{31}P NMR spectrum, where the resonance for the μ_3-P atom at δ 289.8 is a doublet of doublets, with a characteristically large coupling ($^1J_{\text{P-H}}$ = 347 Hz) to the directly bound hydrogen atom and a smaller coupling (31 Hz) to the hydride ligand. Although formation of a Si–Cl bond provides a smaller thermodynamic driving force for a desilylation reaction than Si–F bond

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(9) Data for 1. IR (hexanes, ν_{CO}, cm^{-1}): 2089 w, 2054 s, 2028 vs, 2000 s, 1983 w. ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.73 (A$_6$$B$X pattern, ^3J(H,H) = 7.5 Hz, ^3J(H,P) = 6.7 Hz, CH), 1.37 (A_6B, ^3J(H,H) = 7.5 Hz, CH_3), −24.16 (d, ^2J(P,H) = 23.8 Hz, μ-H). ^{31}P NMR (CD$_2$Cl$_2$): δ = 300.4 (t of q, ^2J(P,H) = 22 Hz, ^3J(P,H) = 6.5 Hz). Anal. Calcd (found) for C$_{18}$H$_{23}$O$_9$Fe$_3$PSi: C, 35.42 (35.39); H, 3.80 (3.69); P, 5.08 (4.97).

(10) Crystal data for 1: a = 33.822 (14) Å, b = 14.299 (14) Å, c = 10.365 (3) Å, and β = 93.33 (5) at −150 °C; space group $C2/c$ (Z = 8). Least-squares refinement of 290 least-squares parameters and 3390 reflections converged at R (R_w) = 0.069 (0.089).

(11) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1409.

(12) (a) Deck, W.; Schwarz, M.; Vahrenkamp, H. *Chem. Ber.* **1987**, *120*, 1515. (b) Kristjánsdóttir, S. S.; Moody, A. E.; Wedberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983.

(13) Purchased from Aldrich as a 1 M solution in tetrahydrofuran containing <5% H$_2$O.

(14) Quantitative conversion to [NBu$_4$]$^+$[2] was confirmed by ^{31}P NMR spectroscopy. We have been unable to isolate [NBu$_4$]$^+$[2] as a pure solid. A ^{1}H NMR spectrum of 2, unobscured by THF or [Bu$_4$N]$^+$, was obtained by deprotonation of 1 with 1 equiv of Et$_3$N in CD$_2$Cl$_2$. IR (THF, ν_{CO}, cm^{-1}): 2035 w, 1992 s, 1969 vs, 1954 m. ^{1}H NMR ([HNEt$_3$]$^+$[2], CD$_2$Cl$_2$): δ = 1.55 (A$_6$$B$X, ^3J(H,H) = 7.5 Hz, ^3J(H,P) = 5.6 Hz, CH), 1.31 (A_6B, ^3J(H,H) = 7.5 Hz, CH$_3$), −21.99 (d, ^2J(P,H) = 26 Hz, μ-H). ^{31}P NMR (CD$_2$Cl$_2$): δ = 406.2 (d of q, ^2J(P,H) = 24.3 Hz, ^2J(P,H) = 6.1 Hz, μ_3-P).

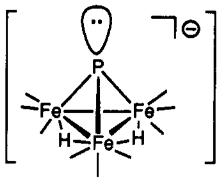
(15) Knoll, K.; Huttner, G.; Zsolnai, L.; Orama, O.; Wasiucionek, M. *J. Organomet. Chem.* **1986**, *310*, 225.

(16) Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1968**, *90*, 4478.

(17) Quantitative conversion to [NBu$_4$]$^+$[3] was confirmed by ^{31}P NMR spectroscopy. [NBu$_4$]$^+$[3] decomposes during workup, so reactions of 3 were performed on solutions generated from 1. IR (CH$_2$Cl$_2$, ν_{CO}, cm^{-1}): 2045 w, 2000 s, 1974 vs, 1959 m. ^{1}H NMR (CD$_2$Cl$_2$): δ = 5.69 (d, ^1J(P,H) = 348 Hz, PH), −22.55 (d, ^2J(H,P) = 31 Hz, μ-H). ^{31}P NMR (CH$_2$Cl$_2$): δ = 289.8 (dd, ^1J(P,H) = 347 Hz, ^3J(P,H) = 31 Hz).

formation, $[(Ph_3P)_2N]Cl$ ([PPN]Cl) also reacts with 1 in CH_2Cl_2 to produce $[PPN]^+[3]$ with evolution of $(i\text{-}Pr)_3SiCl$.

The rearrangement of the desilylated cluster to generate the P–H capped cluster 3 formally consists of a transfer of one cluster-bound hydride ligand, as H^+, to the phosphorus atom lone pair. The metastable intermediate cluster with a naked μ_3-P atom can be observed by ^{31}P NMR spectroscopy. At −90 °C, after addition of 1 equiv of $[NBu_4]F$, conversion of 1 to a new species, 4, is observed



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with a resonance at δ 577.9 that shows no resolved hydrogen coupling. Upon warming the solution from −90 to −70 °C, rearrangement of 4 to 3 is observed. Evidently, after desilylation of the cluster, the P-atom site is more basic than the Fe–Fe edge, providing the driving force for the proton migration.

The reactivity of the bulky silyl group in 1 was also evaluated with $(Ph_3P)AuCl$. Metal halides have been previously employed to cleave $P\text{–}SiMe_3$ bonds in the synthesis of H_2P-bridged dimers[18] and large clusters with capping PR ligands.[19] The complex $(Ph_3P)AuCl$ was chosen in this initial study because the presence of only a single halogen ligand reduces the number of possible reaction products. In addition, an interesting question is presented with regard to the site of preferred coordination for a $(R_3P)Au^+$ fragment[20] on a $[(H)_2Fe_3(CO)_9(\mu_3\text{-}P)]^-$ cluster framework. A reaction between 1 and 1 equiv of $(Ph_3P)AuCl$ occurs over a period of 3 h to produce $(\mu\text{-}H)_2Fe_3(CO)_9[\mu_3\text{-}PAu(PPh_3)]$ (5) with evolution of $(i\text{-}Pr)_3SiCl$.[21] In the $^{31}P\{^1H\}$ NMR spectrum of 5, the gold-bound phosphine ligand (δ 40.8) and the μ_3-P atom (δ 390.3) are coupled by a large $^2J_{P\text{-}P}$ of 314 Hz suggesting that the gold fragment is exclusively bound to cluster through the μ_3-P atom (as opposed to interacting with an Fe–P edge or an Fe_2P face).[22] This substitution of the R_3Si^+ group in 1 by $(R_3P)Au^+$ results in more electron density being localized on the cluster; the infrared spectrum for 5 has a pattern similar to that of the parent silyl cluster 1 but is shifted by 10 cm^{-1} to lower energy. The P–H capped anion, 3, reacts with $(Ph_3P)AuCl$ instantaneously to also produce 5, demonstrating that the capping phosphorus-bound proton serves as a labile protecting group, allowing access to the thermodynamically preferred coordination site for the gold fragment. Attempts to observe an intermediate with the $(Ph_3P)Au^+$ fragment bridging an Fe–Fe edge by a low-temperature ^{31}P NMR experiment have thus far been unsuccessful.

To the best of our knowledge, terminal coordination of a $(Ph_3P)Au^+$ fragment exclusively to a substituent-free main-group atom in a metal carbonyl cluster has not previously been observed. In the gold-substituted sulfido cluster $Fe_3(CO)_9S[Au_2(PPh_3)_2]$, which is based on the Fe_3S cluster isoelectronic with 1, no interaction is observed between the sulfur heteroatom and gold.[23] Direct interactions between gold substituents and the carbon atoms in four- and five-metal carbide clusters[24] as well as the boron atoms in four-metal borane clusters have been observed;[25] however, the coordination environment of the substituent-free main-group atoms in these clusters necessitates additional interactions with the cluster metal atoms. Because of the limited number of gold derivatives characterized for trinuclear clusters with a substituent-free main-group atom as a ligand, it is not clear if the apical coordination of gold is a feature unique to our system.

Systematic access to the phosphorus lone pair in 1 is achieved by cleavage of the silyl group bound to phosphorus with both halide salts and metal halide complexes. Our current studies on this system are directed toward understanding how fragments with different coordination preferences (such as $Mn(CO)_3^+$ and $(PPh_3)Cu^+$) bind to 3.

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Supplementary Material Available: Complete crystallographic results for $(\mu\text{-}H)_2Fe_3(CO)_9[\mu_3\text{-}PSi(i\text{-}Pr)_3]$, including a figure showing atom numbering and tables of crystal data, positional and thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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[18] For example: (a) Schäfer, H. *Z. Anorg. Allg. Chem.* **1980**, *467*, 105. (b) Ebsworth, E. A. V.; Henner, B. J. L.; Redd, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 272. (c) Schäfer, H.; Zipfel, J.; Gutekunst, B.; Lemmert, U. *Z. Anorg. Allg. Chem.* **1985**, *529*, 157.

[19] Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277.

[20] Gold derivative of clusters have been extensively studied. (a) Salter, I. D. *Adv. Organomet. Chem.* **1989**, *29*, 249. (b) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237. (c) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171.

[21] Infrared spectroscopy shows nearly quantitative conversion to 5. A red band was eluted by chromatography at −40 °C (Kieselgel 60, 3:1 hexanes/CH_2Cl_2). Crystallization from hexanes at −10 °C yielded dark red crystals of 5. Isolated yield: 11 mg (10%). The low isolated yield is a result of product loss during chromatography. IR (hexanes, ν_{CO}, cm^{-1}): 2079 w, 2044 s, 2018 vs, 1990 m, 1972 w. ^1H NMR (C_6D_6): δ = 7.47, 7.25 (m, C_6H_5), −23.53 (d, $^2J(H,P)$ = 20.1 Hz, μ-H). $^{31}P\{^1H\}$ NMR (C_6H_6): δ = 390.3 (d, $^2J(P,P)$ = 316 Hz, μ_3-P), 40.8 (d, $^2J(P,P)$ = 312 Hz, PPh_3). Anal. Calcd (found) for $C_{27}H_{17}O_9AuFe_3P_2$: C, 35.56 (35.88); H, 1.88 (1.99).

[22] Further support for assigning the $(R_3P)Au^+$ fragment exclusive coordination to the phosphorus atom is the structural characterization of a Au_2 derivative of 1, where the gold unit bound in an analogous position to 5 displays a similar $^2J_{P\text{-}P}$: Sunick, D. L.; White, P. S.; Schauer, C. K. Manuscript in preparation.

[23] Roland, E.; Fischer, K.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 326.

[24] Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Organomet. Chem.* **1982**, *231*, C59.

[25] Housecroft, C. E. *Adv. Organomet. Chem.* **1991**, *33*, 1 and references therein.