J. Am. Chem. Soc. **1989**, *111*, 8049–8051 8049

Table II. Oxidation of Aldehydes with Oxoferryl Porphyrin Cation Radical

substrate	product(s)[a]	%
4	**10** (as methyl ester)	92[b]
$PhCH_2CHO$	$PhCH_2COOH$	88
$Ph(CH_3)CHCH_2CHO$	$Ph(CH_3)CHCH_2COOH$	87
$Ph(CH_3)_2CHO$	$Ph(CH_3)_2COOH$	92

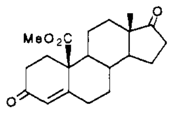
[a] Yields were determined by ^{1}H NMR and GLC as free acids. [b] Yield was determined as methyl ester by GLC.

formation after the decarboxylation of acylperoxo metalloporphyrins has been observed in the consequence of the homolytic O–O bond cleavage reactions.[11b,c,16] Increased formation of **9** and unknown products either upon the use of an excess amount of 18-crown-6 or in the reaction without Fe^{III}PFP(Cl) might be caused by iron porphyrin-free superoxide ion and/or its decomposed products.[17]

While treatment of **7** with 4-N HCl (aqueous) readily gave an aromatized product, **2**, the enzyme system directly affords **2** at physiological pH.[18] Therefore, if the peroxo intermediate is responsible for the aromatization, the activation of the C-1 hydrogen of **4** by such as enolization due to the hydrogen bond interaction with the active site of the enzyme[7,19] could be involved during the course of oxygen rebound process as shown in Scheme III. A possible participation of the enolate of **4** in the aromatization reaction has been reported.[7,10d]

Then, we carried out the reaction of **4** and a model system of the oxenoid species of P-450*arom* to compare the reactivity of the C-2 hydrogens to that of the C-19 oxo group.

Oxidation of 4 with Oxoferryl Porphyrin Cation Radical. To a methylene chloride solution (3 mL) of **4** (23 mg, 73 μmol) and Fe^{III}PFP(Cl) (2 mg, 1.9 μmol) was added 15 mg of mCPBA (87 μmol) at −78 °C and stirred for 20 min. After confirming the disappearance of **4** on Al_2O_3–TLC, an excess amount of diazomethane was added at 0 °C. Methyl *m*-chlorobenzoate and the oxidation product were separated by column chromatography (Al_2O_3), and the structure of the product was identified to be 4-androsten-19-oic-3,17-dione methyl ester (**10**) by ^{1}H NMR, IR, and mass spectra.[20] No formation of the acid was observed when Fe^{III}PFP(Cl) was absent. Further, oxidation of several alkyl aldehydes, which possess reactive positions for the hydroxylation,[7,21] was examined with the same system by employing 1.1–1.2 equiv of mCPBA. As shown in Table II, the corresponding carboxylic acids were obtained as the sole products. Thus, if the oxenoid species was involved in the final step of the aromatase reaction, the corresponding carboxylic acid (or possibly **9** due to facile decarboxylation) either with or without **5** should be observed. In fact, Suhara et al. have recently reported that when **4** was oxidized by purified adrenal cortex mitochondrial P-45011β,[22] a concurrent formation of **2** and **9** was observed.



10

While the oxenoid species has been generally considered to be responsible for oxidations catalyzed by cytochrome P-450,[2a,b,5] the results shown above indicate a possible participation of the peroxo-iron(III) intermediate instead of the oxenoid species, if the substrate contains an electrophilic site. Reactions of the peroxo complex of synthetic metalloporphyrins and electrophiles such as acyl halides and CO_2 have been reported to afford the corresponding adducts,[23] consistent with these considerations.

Detection of **7** in the enzymatic oxidation of **4** with purified cytochrome P-450*arom* is now under investigation in this laboratory.

Acknowledgment. This work was supported in part by Grant-in-Aid for Scientific Research on Priority Area No. 035 from the Ministry of Education, Science, and Culture, Japan (Y.I.) and by grants from Keio University (Y.I. and Y.W.).

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(15) Cross, A. D.; Denton, E.; Acevedo, R.; Urquiza, R.; Bowers, A. *J. Org. Chem.* **1964**, *29*, 2195–2200. **7**: IR (KBr) 3400, 1730, 1670 cm^{-1}; λ_{max} (MeOH) 243 nm; mass spectrum, *m/e* 288 (M^+, 23.5) 260 (42.8) 99 (100); HRMS for $C_{18}H_{24}O_3$ requires 288.1722, found, 288.1692; ^{13}C NMR ($CDCl_3$) δ 220.36 (C-17), 198.73 (C-3), 163.69 (C-5), 124.99 (C-4), 70.35 (C-10), 52.58, 50.47, 47.59, 35.76, 34.85, 33.77, 33.61, 31.76, 31.03, 30.55, 21.62, 19.72, 13.72.

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(18) At physiological pH (0.2 M phosphate buffer, pH = 7.2), **7** was not converted to **2**.

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(20) **10**: IR (KBr) 1740, 1730 (sh), 1675 cm^{-1}; mass spectrum, *m/e* 331 (M + 1, 23.7), 330 (M^+, 100), 271 (46.9), 270 (70.4), 253 (38.7); HRMS for $C_{20}H_{26}O_4$ requires 330.1819, found 330.1811; ^{1}H NMR ($CDCl_3$) δ 5.91 (s, 1 H), 3.76 (s, 3 H, $-CO_2Me$; ^{13}C ($CDCl_3$) δ 220.14 (C-17), 198.73 (C-3), 177.19 (C-19), 162.06 (C-5), 126.85 (C-4), 53.80, 52.16, 50.92 (O-Me), 50.88, 47.5, 35.73, 35.62, 34.94, 33.85, 32.59, 31.38, 30.10, 21.95, 21.66, 13.79.

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Facile Arene C–H Bond Activation by Tantalum Silyl Complexes

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In 1970 Barefield, Parshall, and Tebbe demonstrated the exchange of hydrogen and deuterium between benzene and the hydride ligands on Cp_2TaH_3 (Cp ≡ η^5-C_5H_5).[1] Although a tantalum phenyl complex could not be isolated, this was one of the earliest indications of intermolecular arene C–H activation by a transition-metal complex.[2] Over the past two decades many research groups have investigated the activation of both saturated and unsaturated hydrocarbons by a wide variety of metal complexes.[3] Although several different mechanisms for C–H activation have been identified, the most common pathway, oxidative addition of a C–H bond to an unsaturated, electron-rich metal center, is still believed to proceed as originally postulated in 1970. In this report we show that the addition of benzene to an otherwise unreactive Ta(III) alkyl complex can be catalyzed by di-*tert*-butylsilane and that an isolated silyl complex, $Cp_2Ta(PMe_3)(SiH(t\text{-}Bu)_2)$, will itself activate benzene under extremely mild conditions.

In the presence of 0.7–2.0 equiv of di-*tert*-butylsilane, the 18 e$^-$, Ta(III) alkyl complex $Cp_2Ta(CH_3)(PMe_3)$ (**1**) reacts with

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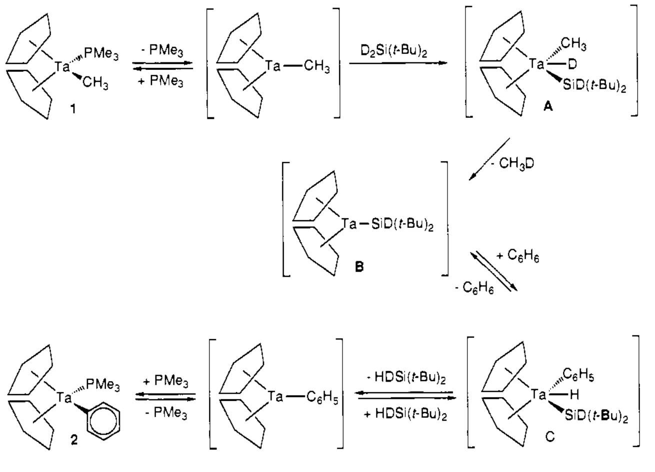
(1) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1970**, *92*, 5234–5235.

(2) The first example of homogeneous intermolecular arene C–H activation by a transition-metal complex was observed by Chatt and Davidson in 1965: Chatt, J., Davidson, J. M. *J. Chem. Soc.* **1965**, 843–855.

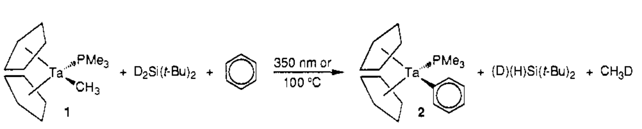
(3) For recent reviews, see: (a) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Deem, M. L. *Coord. Chem. Rev.* **1986**, *74*, 101. (d) Bergman, R. G. *Science* **1984**, *223*, 902–908. (e) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91–100.

Scheme I

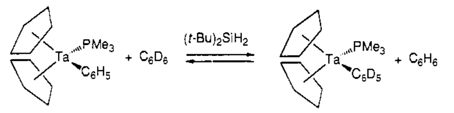


benzene solvent under photolytic (350 nm) or thermal (100 °C) conditions to form methane and the phenyl complex $Cp_2Ta(C_6H_5)(PMe_3)$ (**2**) in virtually quantitative yield. The reaction is typically complete within 3 h at 100 °C. Compound **2** has been isolated in 91% yield from a preparative scale reaction.[4] However, in the absence of $H_2Si(t\text{-}Bu)_2$, **1** only slowly decomposes in benzene under these reaction conditions (ca. 50% in 24 h) to a complex mixture of products containing less than 1% of the phenyl derivative **2**.

The role of the silane in promoting the reaction of **1** with benzene has been probed with isotope labeling experiments. Thus reaction of excess $D_2Si(t\text{-}Bu)_2$ with **1** and C_6H_6 produces **2**, CH_3D, and $(D)(H)Si(t\text{-}Bu)_2$ (eq 1), clearly indicating the active participation of the silane. Furthermore, although **2**-d_0 does not react with benzene-d_6 thermally or photolytically to produce **2**-d_5 in the absence of $H_2Si(t\text{-}Bu)_2$, the exchange occurs readily when the silane is present (eq 2).



(1)

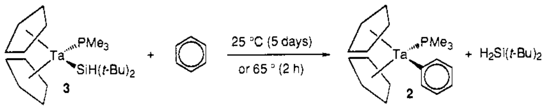


(2)

Consistent with these observations, a proposed mechanism for the reaction of **1** with benzene in the presence of $D_2Si(t\text{-}Bu)_2$ is shown in Scheme I. This mechanism is predicated on the assumption that all C–H and Si–H activation steps proceed by oxidative addition to the Ta(III) centers as opposed to four-center σ-bond metathesis, which to date has only been observed at highly electron-deficient, d^0 metal centers.[5] Furthermore, the oxidative additions must occur such that the hydride is positioned in the central position between the silyl and alkyl or phenyl ligands.[6]

In the proposed mechanism, the 16 e^- $Cp_2Ta(CH_3)$ is generated either thermally or photolytically and subsequently adds $D_2Si(t\text{-}Bu)_2$ to form the 18 e^-, Ta(V) species A. Reductive elimination of methane-d_1 generates the 16 e^-, Ta(III) silyl B. We currently have no information concerning the possible reversibility of this step. Addition of benzene to B generates a new Ta(V) species, C, which eliminates either benzene reverting to B, or silane-d_1, generating the unsaturated phenyl complex. Phosphine coordination to the latter species then leads to **2**. The reversibility of all steps connecting **2** and B may be inferred from the silane-catalyzed exchange between **2** and labeled benzene (eq 2).

To further probe the species involved in the C–H activation process the photolysis of **1** at 10 °C in neat $H_2Si(t\text{-}Bu)_2$ was examined. In this case the Ta(III) silyl complex $Cp_2Ta(PMe_3)(Si(t\text{-}Bu)_2H)$ (**3**) is produced in excellent yield (92% isolated).[7] Dissociation of phosphine from **3** in solution should lead to intermediate B in the scheme. Indeed, **3** activates benzene under remarkably mild conditions. Conversion of **3** to **2** and $H_2Si(t\text{-}Bu)_2$ in benzene solution is complete within 5 days at 25 °C (in the dark) or 2 h at 65 °C (eq 3). Consistent with the intermediacy of a 16e^- species, conversion of **3** to **2** in benzene is strongly inhibited by added PMe_3.



(3)

Perhaps the central issue raised by these observations is the remarkable difference in reactivity toward benzene suggested for the 16e^-, Ta(III) intermediates $Cp_2Ta\text{-}R$ (R = CH_3, Ph, $Si(H)(t\text{-}Bu)_2$). Although this complex question cannot be fully addressed at this time, two points are noteworthy. First, silicon is much more electropositive than carbon ($\chi_C = 2.55$; $\chi_{Si} = 1.90$)[8] suggesting there will be higher electron density at the metal, and hence a greater driving force for oxidative addition, in the Ta(III) silyl B relative to the alkyl and phenyl species. It should be noted that $Cp_2Ta\text{-}H$ ($\chi_H = 2.20$) also reacts with benzene, although the resulting Ta(V) species is not stable with respect to loss of benzene.[1] Secondly, the extreme bulk of the di-*tert*-butylsilyl group, in conjunction with the steric constraints of the cyclopentadienyl rings, should serve to destabilize silyl products such as **3**, increasing the steady-state concentration of the unsaturated intermediate C. In addition, these steric factors should also weaken the metal–silyl bond in C, favoring silane elimination and formation of the phenyl complex.[9] In contrast to the reactions with $H_2Si(t\text{-}Bu)_2$, complexes **1** and **2** react with an excess of smaller silanes at 100 °C in benzene to completion, forming the bis(silyl) complexes $Cp_2Ta(SiR_3)_2(H)$ ($R_3 = Me_2H, Me_3$),[10] stable Ta(V) species analogous to intermediate C. Formation of a bis(silyl) complex from $H_2Si(t\text{-}Bu)_2$ is apparently precluded by adverse steric interactions. Significantly, arene C–H activation by smaller silyls is *kinetically* feasible; an equilibrium mixture containing ca. 10% of the phenyl product **2** is established from a benzene solution of $Cp_2Ta(PMe_3)(SiMe_3)$[10] after several hours at 100 °C. In this instance, however, the silyl complex is thermodynamically favored over **2**, underscoring the delicate balance of steric and electronic effects necessary for C–H activation which is maintained by the di-*tert*-butylsilyl ligand. Studies aimed at obtaining relative M–C and M–Si bond strengths from more quantitative equilibrium

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(4) Compound **2**: A solution containing 500 mg (1.24 mmol) of **1** and 206 mg (1.43 mmol) of $H_2Si(t\text{-}Bu)_2$ in 10 mL of benzene was heated at 100 °C for 4 h, filtered, and the volatiles removed under vacuum to yield 528 mg (91%) of **2** (pure by ^1H NMR), which may be recrystallized from toluene/hexanes. All NMR data for **2** and **3** were recorded in benzene-d_6 solution: ^1H NMR δ 7.68 (m, 2 H, o-C_6H_5), 7.04 (m, 3 H, *m* + *p*-C_6H_5), 4.35 (d, 10 H, C_5H_5, $^3J_{PH} = 1.8$ Hz), 0.93 (d, 9 H, $P(CH_3)_3$, $^2J_{PH} = 7.0$ Hz); $^{13}C\{^1H\}$ NMR δ 158.6 d, *ipso*-C_6H_5, $^2J_{PC} = 5$ Hz), 148.4 (d, *o*-C_6H_5, $^3J_{PC} = 5$ Hz), 125.4 (*m*-C_6H_5), 121.0 (*p*-C_6H_5), 86.5 (C_5H_5), 20.5 (d, $P(CH_3)_3$, $^1J_{PC} = 25$ Hz); $^{31}P\{^1H\}$ NMR δ -24.8; mass spec (CI) calcd 464.110, obsd 464.105. Anal. Calcd for $C_{19}H_{24}PTa$: C, 49.15; H, 5.21. Found: C, 51.13; H, 5.36.

(5) See, for example: (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (b) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425–437. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 204–219.

(6) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701–707.

(7) Compound **3**: A solution containing 200 mg (0.50 mmol) of **1** in 20 mL of $H_2Si(t\text{-}Bu)_2$ was irradiated (low-pressure mercury lamps, 350 nm) at 10 °C for 20 h; filtered, and the silane removed under vacuum to yield 243 mg (92%) of dark red, microcrystalline **3**, which can be recrystallized from hexanes: ^1H NMR δ 4.26 (d, 10 H, C_5H_5, $^3J_{PH} = 2.4$ Hz), 4.06 (s, 1 H, Si-*H*), 1.37 (s, 18 H, $SiC(CH_3)_3$), 0.85 (d, 9 H, $P(CH_3)_3$, $^2J_{PH} = 6.0$ Hz); $^{13}C\{^1H\}$ NMR δ 84.4 (C_5H_5), 34.6 ($SiC(CH_3)_3$), 24.6 (d, $P(CH_3)_3$, $^1J_{PC} = 25$ Hz), 26.7 ($SiC(CH_3)_3$); $^{31}P\{^1H\}$ NMR δ -24.6. Anal. Calcd for $C_{21}H_{38}PSiTa$: C, 47.54; H, 7.22. Found: C, 47.72; H, 7.21.

(8) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(9) The steric congestion in **3** is reflected in an extremely long Ta–Si bond (2.741 (2) Å). The full X-ray diffraction study on **3** will be reported separately: Berry, D. H.; Jiang, Q.; Carroll, P. J., manuscript in preparation.

(10) Berry, D. H.; Jiang, Q.; Koloski, T. S., manuscript in preparation.

measurements are currently in progress.

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Protonation Sites in Thiolato Iron Carbonylates: Evidence for an Arrested Fe(RS–H) Oxidative Addition

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The recently synthesized series of iron thiolate complexes *trans*-RSFe(CO)$_3$L$^-$ [1] and selenium analogues[2] contains particularly interesting functional groups, RSFe or RSeFe, in which both the chalcogen and the iron center are potential sites of reactivity with electrophiles. The Mulliken atomic charges derived from Fenske–Hall calculations[3] roughly quantify charge distribution in the complexes MeSFe(CO)$_4^-$ (δ_-(S) = –0.43; δ_-(Fe) = –0.22) and *trans*-MeSFe(CO)$_3$PH$_3^-$ (δ_-(S) = –0.45; δ_-(Fe) = –0.29). The sensitivity of charge distribution to substituents on sulfur[4] is noted in PhSFe(CO)$_4^-$, where the charges on S and Fe are almost equal (δ_-(S) = –0.28 and δ_-(Fe) = –0.23) and similar to that of H and Fe in HFe(CO)$_4^-$ (δ_-(H) = –0.22; δ_-(Fe) = –0.26).[5] The latter anion forms a dihydride on protonation, H$_2$Fe(CO)$_4$, and its P-donor substituted derivatives H$_2$Fe(CO)$_3$PR$_3$ are stabilized relative to the all-carbonyl derivative.[6] The thermodynamic dihydride product does not necessarily reflect the initial, presumably charge-controlled, collision complex. Nevertheless, the negative charge on Fe is available for transformation into an additional Fe–H bond as the electron-rich d^8 Fe(0) in trigonal bipyramidal (TBP) HFe(CO)$_4^-$ is converted into the d^6 Fe(II) in O_h H$_2$Fe(CO)$_4$. The similar stabilities of HFe(CO)$_3$L$^-$ and REFe(CO)$_3$L$^-$ (E = S, Se) raised the question of whether examples of iron hydrido thiolates (RS)(H)Fe(CO)$_3$L might be prepared, or if all reactions with electrophiles should occur only at the more accessible, electron-rich sulfur site. The results presented below demonstrate *both possibilities* as well as evidence for a three-center η^2-Fe(RS–H) bond, arrested[7,8] along its way to an oxidative addition product.

The carbonyl stretching frequencies, ν(CO), for various RSFe(CO)$_3$L$^-$ in Table I reflect expected changes as the donor abilities of RS$^-$ (MeS > PhS) and L (PEt$_3$ > P(OEt)$_3$ > CO) are varied. In contrast to the anionic acyls RC(O)Fe(CO)$_4^-$, where metal site vs ligand (acyl oxygen) site reactivity depends on choice of alkylating agent,[10] reaction of all entries of Table I with either soft or hard alkylating agents resulted in formation of neutral, hexane-soluble thioether or selenoether derivatives, (RER′)Fe(CO)$_4$.[1] Such reactions are characterized by moderate increases in ν(CO) values consistent with formation of the neutral Fe(0) carbonyls, eq 1. There was no indication of iron-site alkylation.

$$\underset{\substack{2016\ (\mathrm{w}),\\ 1910\ (\mathrm{s})\ \mathrm{cm^{-1}}}}{\mathrm{PhSFe(CO)_4^-}} \xrightarrow{\mathrm{MeI\ or\ Me_3O^+}} \underset{\substack{2054\ (\mathrm{m}),\\ 1969\ (\mathrm{m}),\\ 1946\ (\mathrm{s})\ \mathrm{cm^{-1}}}}{\mathrm{(PhSMe)Fe(CO)_4}} \tag{1}$$

$$\mathrm{2[PPN][PhSFe(CO)_4] + 2HBF_4 \xrightarrow{-78\ ^\circ C} H_2 + (\mu\text{-}PhS)_2Fe_2(CO)_6 + 2CO + 2[PPN][BF_4]} \tag{2}$$

Protonation of the phenyl thiolate complex at –78 °C formally oxidizes the iron(0) to iron(I), forming the well-known dimer,[11] with elimination of H$_2$, eq 2. When the protonation reaction was carried out with the more electron rich derivatives listed in Table I, thermally unstable intermediates could be detected by ν(CO) IR and ^{1}H NMR spectroscopy in the temperature range of –78 to –30 °C. The ν(CO) IR spectral shifts to higher energies of ca. 50 cm^{-1}, for protonation of **1**$^-$, are similar to those observed for the alkylation reaction, eq 1, and consistent with protonation at sulfur. The chemical shift of the complexed thiol, MeS–H = 2.4 ppm, is shifted ca. 0.6 ppm downfield from that of the free thiol.[12] Successive addition of Et$_3$N and HBF$_4$ permitted reformation of the thiolato anion and thiol derivatives without degradation at –78 °C, eq 3. Upon warming of the solution of (RSH)Fe(CO)$_4$ (R = Me, Et), decomposition yielding hydrogen and thiolato-bridged dimers analogously to eq 2 occurred with no intermediates observed.

In contrast, **2H** and **3H** showed no resonances attributable to a metal-bound thiol, but rather upfield doublets in the –7 to –8-ppm "hydride" region with splittings similar to the $J_{\mathrm{H-P}}$ values earlier observed for HFe(CO)$_3$P(OEt)$_3^-$ and H$_2$Fe(CO)$_3$P(OEt)$_3$.[13,14] At similar temperatures,[9] the ν(CO) showed increases in the average ν(CO) values over that of the anion precursors of ca. 150 cm^{-1}, also consistent with the HFe(CO)$_3$P(OEt)$_3^-$ protonation, eq 4.[14]

$$\underset{\mathrm{R\ =\ Me,\ Et}}{\mathrm{RSFe(CO)_4^-}} \xrightleftharpoons[\mathrm{NEt_3}]{\mathrm{HBF_4}} \mathrm{(HSR)Fe(CO)_4} \tag{3}$$

$$\underset{\mathbf{2^-}}{\mathrm{PhSFe(CO)_3P(OEt)_3^-}} \xrightarrow{\mathrm{HBF_4}} \underset{\mathbf{2H}}{\mathrm{(H)(PhS)Fe(CO)_3P(OEt)_3}} \tag{4}$$

The observation of two hydride resonances in the ^{1}H NMR spectrum for the complex **2H** is interpreted as indicative of two isomeric forms, consistent with the difference in $J_{\mathrm{H-P}}$ values of the two species[15] and by comparison to analogous derivatives of (H)(Ph$_3$Si)Fe(CO)$_3$PPh$_3$.[16,17] These latter complexes also have average ν(CO) values near 2000 cm^{-1} and high-field hydride resonances at –9 to –10 ppm.

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[1] Liaw, W.-F.; Kim, C.; Darensbourg, M. Y.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 3591.

[2] [PPN][*trans*-MeSeFe(CO)$_3$(P{OEt}$_3$)] was prepared by reaction of [PPN][HFe(CO)$_3$(P{OEt}$_3$)] with Me$_2$Se$_2$ analogous to the synthesis of [PPN][*trans*-PhSFe(CO)$_3$(P{OEt}$_3$)] described in ref 1.

[3] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. Bond distances and angles were taken from the crystal structure of [PPN][PhSFe(CO)$_4$]^1 and from the following: Ash, C. E.; DeLord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17.

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[5] Ash, C. E.; Darensbourg, M. Y.; Kao, S. C.; Silva, R.; Springs, J. *Pure Appl. Chem.* **1988**, *60*, 131.

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