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Formation of Iron Thiolates via Complexes of Molecular Hydrogen

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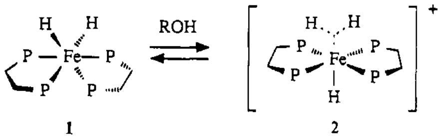
Protonation of $FeH_2(DMPE)_2$ [DMPE = 1,2-bis(dimethylphosphino)ethane] by arene- or alkanethiols affords the molecular hydrogen complex $[Fe(H_2)H(DMPE)_2]^+$, in which the weakly bound η^2-coordinated H_2 is readily displaced by alkane- and arenethiolates to give $FeH(RS)(DMPE)_2$ and $Fe(RS)_2(DMPE)_2$. Both the thiolate iron hydrides and the iron dithiolates exist as equilibrating mixtures of cis and trans stereoisomers in solution, and both readily exchange thiol ligands with added thiols. Crystals of $[\overline{FeSCH_2CH_2S}(DMPE)_2]$ are orthorhombic, of space group *Pcan*, with $a = 10.309$ (2) Å, $b = 13.897$ (2) Å, $c = 15.090$ (4) Å, $Z = 4$, and $R = 0.052$ (4728 *F*). The Fe-S bond length is 2.349 (1) Å.

It is now well established that a variety of metal hydrides can be protonated by strong acids to give molecular hydrogen complexes.[1] In previous work, we reported[2] that the dihydrides of iron 1,2-bis(dialkylphosphino)ethanes, *cis*-$FeH_2(PP)_2$ (**1**) [PP =



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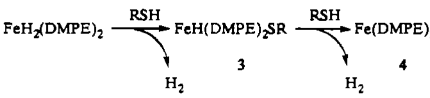
P P = DMPE

$R_2PCH_2CH_2PR_2$, where R = Me (PP = DMPE), Et (PP = DEPE), and *n*-Pr (PP = DPrPE)], are reversibly protonated by ethanol and other simple alcohols to yield the corresponding molecular hydrogen complexes *trans*-$FeH(H_2)(PP)_2^+$ (**2**), and therefore, at least in alcohol solution, these dihydrides exhibit a basicity comparable to alkoxides.

In solution, the complex [*trans*-$FeH(H_2)(DMPE)_2]^+$ undergoes substitution by a variety of species including halides and tertiary phosphines with loss of H_2.[2,3] For inorganic and organometallic synthesis, η^2-coordinated H_2 is a ligand that can be introduced easily under very mild reaction conditions and affords a relatively inert leaving group. If the conjugate base (B^-) of the protonating acid (B-H) is itself a good ligand, protonation, followed by H_2 displacement, leads effectively to substitution of a hydride ligand by B^-. With thiols, $Fe(DMPE)_2H_2$ affords thiolate hydrides **3** and dithiolate complexes **4**.



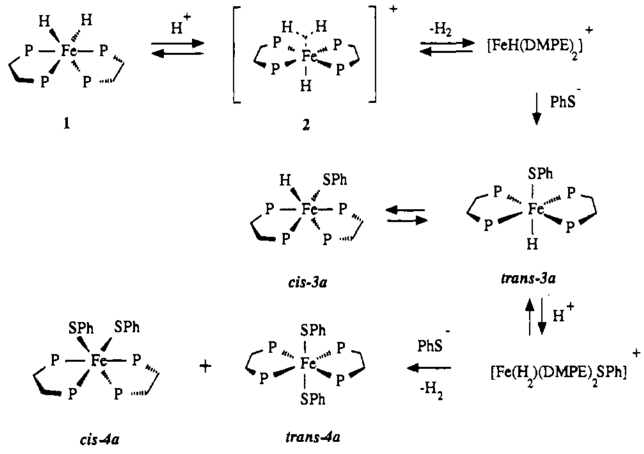
a R = Ph-
b R = CH_3CH_2-
c R = $CH_3CH_2CH_2$-
d R = $PhCH_2$-
e R = $(CH_3)_3C$-

Results and Discussion

Reaction of Thiophenol with $FeH_2(DMPE)_2$. The dihydride *cis*-$FeH_2(DMPE)_2$ is completely protonated by 1 equiv of thiophenol in THF solution to give the known[2] complex [*trans*-FeH(H_2)$(DMPE)_2]^+$ (Scheme I). The trihydride is stable at low temperatures (<230 K) in the reaction mixture, but at temperatures higher than 280 K, hydrogen gas is evolved and substitution by benzenethiolate occurs.[4] Figure 1 shows the progress of the reaction of thiophenol with *cis*-$FeH_2(DMPE)_2$ at 298 K as monitored by ^{31}P NMR spectroscopy.[5]

Under the experimental conditions, the trans molecular hydrogen complex forms rapidly; then substitution affords initially *trans*-FeH(SPh)$(DMPE)_2$ (**3a**). The molecular hydrogen complex never attains a high concentration at 298 K, since subsequent reactions are relatively rapid. The trihydride [FeH(H_2)$(DMPE)_2]^+$ is coordinately saturated, and the reaction probably proceeds by initial loss of the weakly coordinated H_2 ligand with subsequent attack by the thiolate. In other experiments in protic solvents, $[FeH(H_2)(DMPE)_2]^+$ exchanged H_2 for D_2 with added deuterium gas, and this suggests that the reversible loss of H_2 is a facile process and that $[FeH(DMPE)_2]^+$ is a reasonable intermediate in the reaction.[6]

Scheme I



P P = DMPE

The substitution of η^2-coordinated H_2 in *trans*-[FeH(H_2)$(DMPE)_2]^+$ by thiophenolate gives *trans*-**3a** as the kinetic product; however this equilibrates to a mixture of cis and trans isomers in which the cis isomer is the thermodynamically more stable component. The equilibration between *cis*-**3a** and *trans*-**3a** is a relatively facile process, and once the equilibrium *cis*-**3a**:*trans*-**3a** ratio is attained (ca. 3.3:1 under the conditions of the reaction in Figure 1), it is maintained throughout the reaction.

In the presence of excess thiophenol, *trans*-**3a** undergoes a second substitution to give an equilibrium mixture of *cis*- and *trans*-$Fe(SPh)_2(DMPE)_2$ (**4a**). The protonated species [Fe-

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(1) See for example: Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120-8 and references therein.
(2) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, *546*-8.
(3) Baker, M. V.; Field, L. D. *J. Organomet. Chem.* **1988**, *354*, 351-6.
(4) The reaction of thiols with metal hydrides has been noted previously. See for example: Chaudret, B.; Poilblanc, R. *Inorg. Chim. Acta* **1979**, *34*, L209-10. Chatt, J.; Lloyd, J. P.; Richards, R. L. *J. Chem. Soc., Dalton. Trans.* **1976**, 565-8. Lee, C.-L.; Chisholm, J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chim. Acta* **1986**, *121*, L7-9.
(5) ^{31}P NMR spectra (162.0 MHz) were referenced to external, neat trimethyl phosphite, taken as 140.85 ppm. ^1H NMR spectra (400.1 MHz) were referenced to solvent resonances.
(6) The exchange of η^2-coordinated H_2 with D_2 has been noted previously in a number of metal complexes. See for example: Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780-2. Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032-7. Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548-49.

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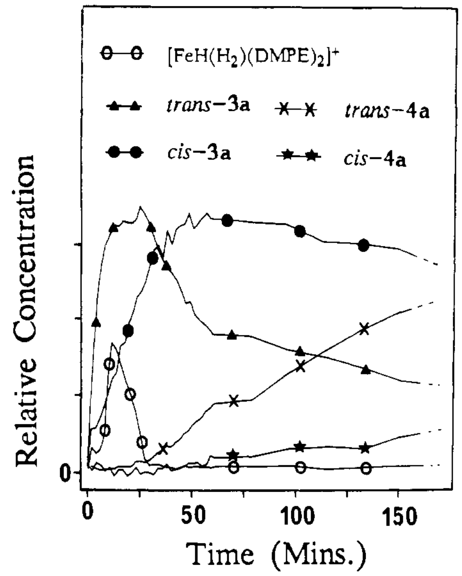


Figure 1. Time course of the reaction of thiophenol (ca. 8 equiv) with $FeH_2(DMPE)_2$ in THF solution at room temperature. The curves are concentrations of the species indicated, as measured by integration of a series of ^{31}P NMR spectra acquired at approximately 2-min intervals.

$(H_2)(SPh)(DMPE)_2]^+$ would be a possible intermediate in the conversion of **3a** to **4a**, but this species has not been observed directly in the reaction mixture.[7]

Reaction of Alkanethiols with $FeH_2(DMPE)_2$. Substitution of *cis*-$FeH_2(DMPE)_2$ is slower with alkanethiols than with thiophenol, presumably due to their lower acidity,[8] and in THF solution the molecular hydrogen complex [*trans*-$FeH(H_2)(DMPE)_2]^+$ does not accumulate in a concentration that can be detected by NMR spectroscopy. In the presence of alkanethiols, *cis*-$FeH_2(DMPE)_2$ exchanges the iron-bound hydrides with added D_2 prior to any substitution reaction, and this supports the formation of a complex of molecular hydrogen $[FeH(H_2)(DMPE)_2]^+$ in solution. In all cases studied, an equilibrium mixture of cis and trans alkanethiolate hydrides is formed with the trans stereoisomer predominating. The monothiolate hydrides slowly undergo a second substitution in the presence of excess alkanethiol to give mixtures of cis and trans dithiolate complexes. In the case of *tert*-butyl mercaptan, the monothiolate hydride failed to undergo a second substitution in the presence of excess thiol, undoubtedly due to the unfavorable steric congestion arising from the bulky *tert*-butyl group. The formation of monothiolate and dithiolate complexes is significantly more rapid in methanol or ethanol solution, and this can be rationalized by stabilization of the charged intermediates in the polar medium.

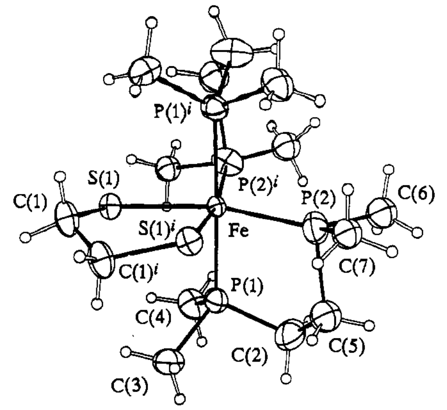


Figure 2. ORTEP plot of $\overline{\text{Fe(SCH}_2\text{CH}_2\text{S}}\text{)(DMPE)}_2$ (**5**). Superscript *i* indicates atoms related by the symmetry operations x, $1 - y$, $^3/_2 - z$.

Table I. Crystal Data for $[\overline{\text{FeSCH}_2\text{CH}_2\text{S}}\text{(DMPE)}_2]$ (**5**)

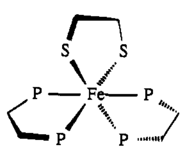
cryst syst	orthorhombic	empirical formula	$C_{14}H_{36}FeP_4S_2$
space group	*Pcan*	fw	448.30
a, Å	10.309 (2)	Z	4
b, Å	13.897 (2)	abs coeff, cm^{-1}	11.25
c, Å	15.090 (4)	T, °C	21
V, $Å^3$	2161.9	λ, Å	0.71069
D_{calc}, g cm^{-3}	1.377	$R(F_o)$	0.052
		R_w	0.062

Table II. Positional Parameters ($\times 10^4$) for $[\overline{\text{FeSCH}_2\text{CH}_2\text{S}}\text{(DMPE)}_2]$ (**5**)[a]

	x	y	z
Fe(1)	3237 (1)	5000	7500
S(1)	4902 (1)	4083 (1)	8146 (1)
C(1)	6393 (6)	4724 (6)	7921 (5)
P(1)	3271 (2)	3933 (1)	6397 (1)
P(2)	1868 (3)	5770 (3)	6623 (5)
P(2B)	1853 (6)	6079 (7)	7023 (6)
C(2)	2098 (16)	4190 (10)	5538 (8)
C(3)	4696 (7)	3665 (5)	5772 (4)
C(4)	2851 (13)	2653 (7)	6715 (9)
C(2B)	2422 (35)	2924 (26)	6473 (24)
C(4B)	2658 (36)	4567 (28)	5231 (23)
C(5)	1913 (17)	5119 (12)	5482 (12)
C(6)	184 (18)	5802 (15)	6597 (14)
C(7)	2388 (10)	6971 (8)	6139 (7)
C(5A)	1007 (27)	4844 (18)	5937 (18)
C(6A)	189 (24)	6169 (16)	7175 (18)
C(5B)	1397 (28)	6893 (20)	7886 (18)
C(6B)	283 (27)	6140 (21)	6677 (21)
C(7B)	2081 (32)	6641 (26)	5903 (22)

[a] A and B indicate minor sites of disordered atoms (see text).

Reaction of $Fe(DMPE)_2H_2$ with Dithiols. The reaction of *cis*-$FeH_2(DMPE)_2$ with 1,2-ethanedithiol or 1,3-propanedithiol in THF solution initially affords the trans monothiolate hydrides but eventually the cyclic dithiametallacycles **5** and **6** are formed as the sole products. With 1,4-butanedithiol and with dithiols where the formation of a chelated dithiolate complex is not possible, dimeric and polymeric products are eventually formed.



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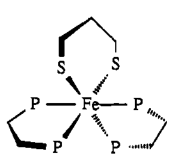

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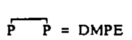

Complexes **5** and **6** are notably more stable than the dithiolates formed from nonchelating thiols, and the crystal structure of **5** is shown in Figure 2.

The structure of **5** consists of the complex unit lying on a 2-fold rotation axis with no significant contact between the units. The 2-fold axis passes through the Fe atom and the center of the C–C bond of the ethanedithiolate ligand. The crystallographic data are summarized in Tables I and II, and bond lengths and angles are given in Table III. Extensive disorder of the one phosphine ligand in the asymmetric unit was observed, apparently resulting from conformational lability and/or crystallization of a complex with symmetry lower than C_2 on the crystallographically imposed 2-fold axis. Attempts at refinement in lower symmetry space groups were unable to resolve this disorder, and the refined populations of the contributing conformations are inconsistent with the latter as being the sole explanation of the disorder. Three conformations contribute to the disorder: the major site with

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(7) $FeH(DMPE)_2SCH_2CH_3$ rapidly exchanges the iron-bound hydride for deuterium when treated with CH_3CH_2SD, prior to the formation of $Fe(DMPE)_2(SCH_2CH_3)_2$. $[Fe(HD)(DMPE)_2SR]^+$ would be a reasonable intermediate for the H/D exchange.

(8) Crampton, M. R. *The Chemistry of the Thiol Group, Part 1*; Patai, S., Ed.; John Wiley and Sons: London, 1974; pp 379–415.

(9) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872.

Table III. Bond Lengths (Å) and Angles (deg) for $[\overline{\mathrm{FeSCH_2CH_2S}}(\mathrm{DMPE})_2]$ (**5**)[a]

S(1)–Fe(1)	2.349 (1)	P(1)–Fe(1)	2.229 (1)
P(2)–Fe(1)	2.210 (3)	P(2B)–Fe(1)	2.191 (6)
C(1)–S(1)	1.808 (7)	C(1)–C(1)	1.485 (14)
C(2)–P(1)	1.807 (9)	C(3)–P(1)	1.785 (6)
C(4)–P(1)	1.892 (10)	C(2B)–P(1)	1.657 (36)
P(1)–C(4B)	2.066 (35)	C(5)–P(2)	1.945 (19)
C(6)–P(2)	1.736 (19)	C(7)–P(2)	1.899 (11)
C(5A)–P(2)	1.875 (26)	C(6A)–P(2)	1.998 (25)
C(5B)–P(2B)	1.786 (29)	C(6B)–P(2B)	1.702 (29)
C(7B)–P(2B)	1.876 (32)	C(5)–C(2)	1.308 (19)
C(5A)–C(2)	1.566 (29)	C(5B)–C(2B)	1.455 (40)
P(1)–Fe(1)–S(1)	86.4 (1)	P(2)–Fe(1)–S(1)	167.7 (2)
P(2)–Fe(1)–P(1)	83.4 (2)	P(2B)–Fe(1)–S(1)	169.4 (3)
P(2B)–Fe(1)–P(1)	102.8 (3)	P(1)–Fe(1)–P(1)	178.2 (1)
P(2)–Fe(1)–P(2)	100.7 (2)	P(2B)–Fe(1)–P(2B)	98.8 (4)
C(1)–S(1)–Fe(1)	106.0 (2)	S(1)–Fe(1)–S(1)	86.1 (1)
C(2)–P(1)–Fe(1)	113.2 (3)	C(3)–P(1)–Fe(1)	123.1 (2)
C(3)–P(1)–C(2)	102.3 (6)	C(4)–P(1)–Fe(1)	115.7 (4)
C(4)–P(1)–C(2)	102.4 (6)	C(4)–P(1)–C(3)	97.2 (5)
C(5)–P(2)–Fe(1)	106.8 (6)	C(6)–P(2)–Fe(1)	131.6 (8)
C(6)–P(2)–C(5)	90.9 (8)	C(7)–P(2)–Fe(1)	118.4 (4)
C(7)–P(2)–C(5)	93.6 (7)	C(7)–P(2)–C(6)	104.5 (8)
C(5)–C(2)–P(1)	109.8 (11)	C(2)–C(5)–P(2)	113.9 (12)

[a] A and B indicate minor sites of disordered atoms (see text).

occupancy 48 (1)%, a second site (A) in which only two of the three C atoms bonded to P(2) have moved (occupancy 26 (1)%), and a third site (B) in which all C atoms and P(2) have moved (occupancy 26 (1)%).

The Fe–P bond lengths in **5** (mean 2.22 (1) Å) are similar to those observed in $[\mathrm{Fe(DMPE)_2Cl_2}]$ (2.230 (1), 2.241 (1) Å).[9] The Fe–P bond trans to the Fe–S bond is marginally shorter than that trans to an Fe–P bond, but given the uncertainty introduced by the disorder, it is difficult to assess whether this is due to a trans effect. The Fe–S bond length is 2.349 (1) Å. This appears to be the first report of the structure of a six-coordinate iron(II) complex with an alkanethiolate ligand.

NMR Spectra of $\mathbf{FeH(DMPE)_2SR}$ and $\mathbf{Fe(DMPE)_2(SR)_2}$ Complexes. Compounds **1**–**6** are neutral, diamagnetic species that are soluble in organic solvents. The thiolate hydride complexes are typically orange in color; the dithiolate complexes of alkanethiols are deep red, and dithiolates of aromatic thiols are green. Both the thiolate hydride complexes and the dithiolates are extremely oxygen sensitive and decompose rapidly on exposure to air. All of the compounds examined exist as mixtures of cis and trans stereoisomers in solution. Equilibration between the stereoisomers is facile but slow on the NMR time scale, so NMR spectra are always complicated by the presence of several isomers. For all of the alkanethiolate hydrides studied, the trans stereoisomer was the dominant component of the equilibrium mixture.

In the ^{1}H NMR of the thiolate hydrides, $\mathrm{FeH(DMPE)_2SR}$, the iron-bound protons resonate at extreme high field and show coupling to four phosphorus nuclei (Table IV). In the trans thiolate hydrides, the iron-bound proton appears characteristically in the range −25 to −28 ppm with a quintet splitting ($^2J_{\mathrm{PH}}$) of approximately 50 Hz; for the corresponding cis isomer, the iron-bound proton occurs in the range −10 to −12 ppm and appears as a 16-line multiplet (dddd) with three splittings of 55–65 Hz ($^2J_{\mathrm{PH_{cis}}}$) and one splitting of approximately 30 Hz ($^2J_{\mathrm{PH_{trans}}}$). In the ^{31}P NMR spectra of the trans thiolate hydride complexes, the equivalent ^{31}P nuclei of the DMPE ligands appear at about 70 ppm (to low field of H_3PO_4). The cis stereoisomers give rise to four multiplets in the ^{31}P spectrum, in the range 50–75 ppm. Selective decoupling experiments established that the phosphorus which is trans to the hydride ligand appears at the highest field and the phosphorus which is trans to the thiolate ligand occurs at lowest field. There is a large P–P coupling (magnitude 150–170 Hz) between the phosphorus nuclei that are mutually trans, and a smaller coupling (magnitude about 20–40 Hz) exists between the phosphorus nuclei that are cis to each other (Table V).

In solutions of the dithiolate complexes, $\mathrm{Fe(DMPE)_2(SR)_2}$, cis and trans isomers exist in comparable concentrations. The proton-decoupled ^{31}P NMR spectra of the cis dithiolate complexes (Table VI), although technically AA′XX′ spin systems, appear as two triplets or a broadened multiplet in cases where the chemical shift separation is small.

Thiol Exchange and Disproportionation in Dithiolate Complexes $\mathbf{Fe(RS)_2(DMPE)_2}$. In solution, the thiolate ligands of the $\mathrm{Fe(RS)_2(DMPE)_2}$ complexes are labile toward exchange with added thiols. Over the space of several minutes in THF solution, $\mathrm{Fe(CH_3CH_2CH_2S)_2(DMPE)_2}$ equilibrates with added ethanethiol to give $\mathrm{Fe(CH_3CH_2CH_2S)(CH_3CH_2S)(DMPE)_2}$ and $\mathrm{Fe(CH_3CH_2S)_2(DMPE)_2}$, i.e. with the $\mathrm{Fe(DMPE)_2}$ skeleton being retained intact. The reaction probably proceeds via the reversible loss of thiolate. 1,2-Ethanedithiol or 1,3-propanedithiol rapidly displaces the monodentate thiols from $\mathrm{Fe(RS)_2(DMPE)_2}$ complexes to produce the cyclic dithiametallacycle **5** or **6** exclusively.

An equimolar mixture of $\mathrm{FeH_2(DMPE)_2}$ and an alkane- or arenedithiolate $\mathrm{Fe(RS)_2(DMPE)_2}$ disproportionates over several days in THF solution to form $\mathrm{FeH(RS)(DMPE)_2}$ as the major product.

Conclusion

The reaction of iron hydrides with weak organic acids such as thiols leads initially to protonation to form complexes of molecular hydrogen. η^2-Coordinated H_2 is only weakly bound and can be

Table IV. Selected ^{1}H and ^{31}P NMR Data for $\mathrm{FeH(DMPE)_2SR}$ Complexes

complex	$\delta(^1\mathrm{H})$, (Fe–H)	$\delta(^{31}\mathrm{P}\{^1\mathrm{H}\})^d$	J_{PH}, Hz
trans-$\mathrm{FeH(DMPE)_2SPh}$ (*trans*-**3a**)	-27.8^b	70.3^a	51.9
cis-$\mathrm{FeH(DMPE)_2SPh}$ (*cis*-**3a**)	-10.4^b	73.3 (P^A), 71.6 (P^B), 66.3 (P^C), 54.6 $(P^D)^a$	$J_{\mathrm{HP^D}} = 31.6$, $J_{\mathrm{HP^A}} = 69.0$, $J_{\mathrm{HP^B}}$ and $J_{\mathrm{HP^C}} = 54.0$
trans-$\mathrm{FeH(DMPE)_2SCH_2CH_3}$ (*trans*-**3b**)	-25.3^b	71.7^b	48.8
cis-$\mathrm{FeH(DMPE)_2SCH_2CH_3}$ (*cis*-**3b**)	-11.23^b	72.1 (P^A), 69.7 (P^B), 66.1 (P^C), 55.4 $(P^D)^b$	$J_{\mathrm{HP^D}} = 32.9$, $J_{\mathrm{HP^A}} = 64.5$, $J_{\mathrm{HP^B}}$ and $J_{\mathrm{HP^C}} = 55.0$
trans-$\mathrm{FeH(DMPE)_2SCH_2CH_2CH_3}$ (*trans*-**3c**)	-25.4^a	71.8^b	49.7
cis-$\mathrm{FeH(DMPE)_2SCH_2CH_2CH_3}$ (*cis*-**3c**)	-11.19^a	72.2 (P^A), 69.5 (P^B), 66.0 (P^C), 55.4 $(P^D)^b$	$J_{\mathrm{HP^D}} = 33.2$, $J_{\mathrm{HP^A}} = 64.7$, $J_{\mathrm{HP^B}}$ and $J_{\mathrm{HP^C}} = 55.6$
trans-$\mathrm{FeH(DMPE)_2SCH_2Ph}$ (*trans*-**3d**)	-25.4^a	71.1^a	49.6
cis-$\mathrm{FeH(DMPE)_2SCH_2Ph}$ (*cis*-**3d**)	-11.6^a	72.2 (P^A), 69.5 (P^B), 65.7 (P^C), 55.4 $(P^D)^c$	$J_{\mathrm{HP^D}} = 32.9$, $J_{\mathrm{HP^A}} = 64.5$, $J_{\mathrm{HP^B}}$ and $J_{\mathrm{HP^C}} = 55.1$
trans-$\mathrm{FeH(DMPE)_2S}$-*t*-Bu (*trans*-**3e**)	-27.6^b	67.7^b	52.5
cis-$\mathrm{FeH(DMPE)_2S}$-*t*-Bu (*cis*-**3e**)	-10.04^a	71.9 (P^A), 65.5 (P^B), 61.7 (P^C), 53.0 (P^D)	*c*
trans-$\mathrm{FeH(DMPE)_2S(CH_2)_2SH}$ (*trans*-**3f**)	-25.8^a	71.0^a	48.8
cis-$\mathrm{FeH(DMPE)_2S(CH_2)_2SH}$ (*cis*-**3f**)	-11.7^a	*c*	*c*
trans-$\mathrm{FeH(DMPE)_2S(CH_2)_3SH}^c$ (*trans*-**3g**)	-25.7^a	71.2^a	44.5

[a] THF solvent, 298 K. [b] Benzene-d_6 solvent, 298 K. [c] Signal intensity too small to accurately resolve signals. [d] P^B and P^C were not assigned conclusively.

Table V. J_{PP}[a] Coupling Constants for *cis*-FeH(DMPE)$_2$SR Complexes

R	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
–Ph (*cis*-**3a**)[b]	38.6	38.9	19.8	152.2	34.5	21.2
–CH$_2$CH$_3$ (*cis*-**3b**)[c]	37.5	37.8	18.0	173.2	34.0	22.7
–CH$_2$CH$_2$CH$_3$ (*cis*-**3c**)[c]	33.7	38.0	17.7	173.0	34.2	22.5
–CH$_2$Ph (*cis*-**3d**)[b]	37.9	38.2	18.5	169.2	33.8	22.6

[a] The signs of coupling constants are not implied. [b] Solvent THF, 298 K. [c] Solvent benzene-d_6, 298 K.

Table VI. Selected ^{1}H and ^{31}P NMR Data for Fe(DMPE)$_2$(SR)$_2$ Complexes

complex	$\delta(^{31}\mathrm{P}\{^1\mathrm{H}\})$[a]	multiplicity
cis-Fe(DMPE)$_2$(SPh)$_2$[b] (*cis*-**4a**)	54.9, 53.6	apparent triplets, splitting 41.0 Hz
trans-Fe(DMPE)$_2$(SPh)$_2$[b] (*trans*-**4a**)	56.1	
cis-Fe(DMPE)$_2$(SCH$_2$CH$_3$)$_2$ (*cis*-**4b**)	57.5	unresolved multiplet
trans-Fe(DMPE)$_2$(SCH$_2$CH$_3$)$_2$ (*trans*-**4b**)	60.5	
cis-Fe(DMPE)$_2$(SCH$_2$CH$_2$CH$_3$)$_2$ (*cis*-**4c**)	57.3	unresolved multiplet
trans-Fe(DMPE)$_2$-(SCH$_2$CH$_2$CH$_3$)$_2$ (*trans*-**4c**)	60.4	
cis-Fe(DMPE)$_2$(SCH$_2$Ph)$_2$ (*cis*-**4d**)	56.8	unresolved multiplet
trans-Fe(DMPE)$_2$(SCH$_2$Ph)$_2$ (*trans*-**4d**)	59.9	
$\overline{\mathrm{SCH_2CH_2S}}\mathrm{Fe(DMPE)_2}$ (**5**)	60.3, 56.7	apparent triplets, splitting 37.6 Hz
$\overline{\mathrm{SCH_2CH_2CH_2S}}\mathrm{Fe(DMPE)_2}$ (**6**)	58.5, 55.9	apparent triplets, splitting 35.6 Hz

[a] Benzene-d_6 solvent, 298 K. [b] THF solvent, 298 K.

displaced readily by better ligands to form new complexes. We believe that the mild protonation of metal hydrides and subsequent displacement of the weakly coordinated molecular hydrogen have considerable potential in the design of synthetic routes to metal thiolates and other classes of inorganic and organometallic compounds.

Experimental Section

FeH$_2$(DMPE)$_2$ was prepared as previously reported.[2] Ethanethiol (BDH), propanethiol (Aldrich), *tert*-butyl mercaptan (Aldrich), thiophenol (Merck), 1,2-ethanedithiol (Aldrich), 1,3-propanedithiol (BDH), and benzyl mercaptan (BDH) were obtained commercially and used without further purification. 1,4-Bis(mercaptomethyl)benzene was synthesized by using the procedure of Whitesides and Houk.[10] THF was distilled from sodium benzophenone ketyl under N$_2$.

Crystallography. Cell constants were determined by a least-squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table I. Data were reduced, and Lorentz, polarization, and decomposition corrections were applied by using a local data reduction program. The structure was solved by Patterson methods and was refined by full-matrix least-squares analysis with SHELX-76.[11] The phosphine ligand was found to be extensively disordered. This disorder was modeled as three contributors each with a different conformation of the phosphine. Hydrogen atoms were included at calculated sites (C–H = 0.97 Å) with group isotropic thermal parameters, and all other atoms except minor contributors to disordered groups were refined anisotropically. A refined empirical extinction correction indicated no significant extinction. Scattering factors and anomalous dispersion corrections for Fe were taken from ref 12, and for all others the values supplied in SHELX-76 were used. Nonhydrogen atom coordinates are listed in Table II. The atomic nomenclature is defined in Figure 2.[13] Listings of H atom coordinates, anisotropic thermal parameters, and observed and calculated structure factor amplitudes have been deposited in the supplementary material.

Reaction of FeH$_2$(DMPE)$_2$ with Alkane- and Arenethiols. General Procedure. Typically, a solution of an alkane- or arenethiol (1.5 M in THF) was deoxygenated by three freeze–thaw cycles. The thiol solution (10 equiv of RSH) was added to a solution of FeH$_2$(DMPE)$_2$ (ca. 10–60 mg) in oxygen-free THF (0.5 mL), and the reaction was monitored by ^{31}P and ^{1}H NMR spectroscopy. At room temperature, the reaction with alkanethiols proceeds slowly, and after 16–24 h, the reaction mixture contains unreacted starting material with the alkanethiolate hydride Fe(RS)H(DMPE)$_2$ as the main product. Formation of the dithiolate complexes was complete after 2–3 weeks, and in most cases the complexes crystallized directly from the reaction mixture.

Benzyl Mercaptan. After 16 h at room temperature, the reaction mixture contained FeH$_2$(DMPE)$_2$, FeH(DMPE)$_2$SCH$_2$Ph, and Fe(DMPE)$_2$(SCH$_2$Ph)$_2$ in the ratio ca. 60:40:10. After 24 h at 50 °C, conversion to Fe(SCH$_2$Ph)$_2$(DMPE)$_2$ was complete as shown by ^{31}P NMR spectroscopy. Removal of the solvent under vacuum followed by recrystallization of the residue from toluene afforded **4d** as a very deep red (almost black) solid, mp 123–5 °C dec. Anal. Calcd for $C_{26}H_{46}FeP_4S_2$: C, 51.83; H, 7.70. Found: C, 51.8; H, 8.1. *cis*-Fe(SCH$_2$Ph)$_2$(DMPE)$_2$ (*cis*-**4d**): ^{1}H{P} NMR (benzene-d_6, 300 K) δ 8.01 (m, 4 H, Ar H_{ortho}), 7.49 (m, 4 H, Ar H_{meta}), 7.32 (m, 2 H, Ar H_{para}), 3.96, 3.90 (AB quartet, 2 H + 2 H, J_{AB} = –12.2 Hz, 2 × PhCH_AH_BS–), 2.05–1.90 (br m, 2 H, 2 × PCHH–), 1.96 (s, 6 H, 2 × CH_3P–), 1.83–1.55 (br m, 2 H, 2 × PCHH–), 1.55–1.25 (br m, 2 H, 2 × PCHH–), 1.44 (s, 6 H, 2 × CH_3P–), 1.35 (s, 6 H, 2 × CH_3P–), 1.15–1.10 (br m, 2 H, 2 × PCHH–), 0.83 (s, 6 H, 2 × CH_3P–); ^{13}C{P,H} NMR (benzene-d_6, 315 K) δ 148.39 (Ar C_{ipso}), 129.56 (Ar C_{ortho}), 126.10 (Ar C_{meta}), 125.42 (Ar C_{para}), 34.04 (PhCH$_2$S–), 33.87, 28.76 (2 × PCH$_2$–), 20.06, 18.80, 16.55, 13.11 (4 × CH$_3$P–). *trans*-Fe(SCH$_2$Ph)$_2$(DMPE)$_2$ (*trans*-**4d**): ^{1}H{P} NMR (benzene-d_6, 300 K) δ 7.60 (m, 4 H, Ar H_{ortho}), 7.38 (m, 4 H, Ar H_{meta}), 7.25 (m, 2 H, Ar H_{para}), 2.73 (br s, 4 H, 2 × PhCH_2S–), 1.99 (br s, 8 H, 4 × PCH_2–), 1.65 (br s, 24 H, 8 × CH_3P–); ^{13}C{P,H} NMR (benzene-d_6, 315 K) δ 147.61 (Ar C_{ipso}), 128.67 (Ar C_{ortho}), 128.31 (Ar C_{meta}), 125.20 (Ar C_{para}), 36.68 (PhCH$_2$S–), 31.07 (PCH$_2$–), 16.61 (CH$_3$P–).

Ethanethiol. After 16 h at room temperature, the reaction mixture contained FeH$_2$(DMPE)$_2$, FeH(DMPE)$_2$SCH$_2$CH$_3$, and Fe(DMPE)$_2$(SCH$_2$CH$_3$)$_2$. After 10 days at room temperature, the reaction was complete. The solvent was removed under vacuum and the residue recrystallized from toluene to give Fe(SCH$_2$CH$_3$)$_2$(DMPE)$_2$ as a deep red crystalline solid, mp 148 °C dec. *trans*-Fe(SCH$_2$CH$_3$)$_2$(DMPE)$_2$ (*trans*-**4b**): ^{1}H{P} NMR (toluene-d_8, 298 K) δ 2.0 (8 H, s, 4 × PCH_2–), 1.67 (24 H, s, 8 × CH_3P–), 1.62–1.54 (4 H, m, 2 × CH$_3$CH_2–), 1.54–146 (6 H, m, 2 × CH_3CH$_2$–); ^{13}C{P,H} NMR (toluene-d_8, 315 K) δ 32.2 (PCH$_2$–), 26.4 (SCH$_2$–), 21.3 (CH$_3$CH$_2$–), 17.5 (CH$_3$P–). *cis*-Fe(SCH$_2$CH$_3$)$_2$(DMPE)$_2$ (*cis*-**4b**): ^{31}P{H} NMR (THF, 298 K) δ 57.9 (br s); ^{1}H{P} NMR (toluene-d_8, 298 K) δ 2.67–2.58 (4 H, m, 2 × SCH_2–), 2.12–2.00 (2 H, m, 2 × PCHH–), 1.95 (6 H, s, 2 × CH_3P–), 1.87–1.78 (8 H, m, 2 × CH_3CH$_2$– and 2 × PCHH–), 1.54–1.46 (2 H, m, 2 × PCHH–), 1.43, 1.42 (12 H, 2 × s, 4 × CH_3P–), 1.22–1.12 (2 H, m, 2 × PCHH–), 0.95 (6 H, s, 2 × CH_3P–); ^{13}C{P,H} NMR (toluene-d_8, 315 K) δ 35.1, 29.7 (2 × PCH$_2$–), 24.1 (SCH$_2$–), 21.3 (CH$_3$CH$_2$–), 21.3, 19.8, 17.4, 13.8 (4 × CH$_3$P–).

Propanethiol. After 1 h at room temperature, the reaction mixture contained FeH$_2$(DMPE)$_2$, FeH(DMPE)$_2$SCH$_2$CH$_2$CH$_3$, and Fe(DMPE)$_2$(SCH$_2$CH$_2$CH$_3$)$_2$. After 10 days at room temperature, the reaction was complete. The solvent was removed under vacuum, and the residue was recrystallized from toluene to give Fe(SCH$_2$CH$_2$CH$_3$)$_2$(DMPE)$_2$ as a deep red crystalline solid, mp 130 °C dec. *trans*-Fe(SCH$_2$CH$_2$CH$_3$)$_2$(DMPE)$_2$ (*trans*-**4c**): ^{1}H{P} NMR (benzene-d_6, 298 K) δ 2.05 (8 H, s, 4 × PCH_2–), 1.91–1.83 (4 H, m, 2 × CH$_3$CH_2–), 1.69 (24 H, s, 8 × CH_3P–), 1.65–1.60 (4 H, m, 2 × SCH_2–), 1.31–1.25 (6 H, m, 2 × CH_3CH$_2$–); ^{13}C{P,H} NMR (benzene-d_6, 310 K) δ 33.4 (SCH$_2$–), 30.2 (PCH$_2$–), 28.0 (CH$_3$$CH_2$–), 15.6 ($CH_3$P–), 13.8 ($CH_3CH_2$–). *cis*-Fe(SCH$_2CH_2CH_3$)$_2$(DMPE)$_2$ (*cis*-**4c**): ^{1}H{P} NMR (benzene-d_6, 298 K) δ 2.78–2.61 (4 H, m, 2 × SCH_2–), 2.35–2.25 (4 H, m, 2 × CH$_3$CH_2–), 2.13–2.00 (2 H, m, 2 × PCHH–), 2.05 (6 H, s, 2 × CH_3P–), 1.83–1.56 (4 H, m, 4 × PCHH–), 1.56–1.47 (6 H, m, 2 × CH_3CH$_2$–), 1.47, 1.43 (12 H, 2 × s, 4 × CH_3P–), 1.23–1.08 (2 H, m, 2 × PCHH–), 0.89 (6 H, s, 2 × CH_3P–); ^{13}C{P,H} NMR (benzene-d_6, 315 K) δ 33.1 (PCH$_2$–), 31.1 (SCH$_2$–), 28.0 (CH$_3$$CH_2$–), 27.8 (P$CH_2$–), 19.3, 17.8 (2 × CH$_3$P–), 14.2 (CH$_3CH_2$–), 13.8, 12.0 (2 × CH$_3$P–).

***tert*-Butyl Mercaptan.** After 10 days at room temperature, the reaction mixture contained *trans*-FeH(S-*t*-Bu)(DMPE)$_2$ as the major

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product (>90%). The solvent was removed under vacuum and the residue recrystallized from benzene to give FeH(S-*t*-Bu)(DMPE)$_2$ as an orange crystalline solid, mp 142–143 °C dec. Anal. Calcd for $\mathrm{C_{16}H_{42}FeP_4S}$: C, 43.06; H, 9.49. Found: C, 43.0; H, 9.8. *trans*-FeH(S-*t*-Bu)(DMPE)$_2$ (*trans*-**3e**): ^{1}H NMR (benzene-d_6, 298 K) δ 2.18–2.38 (br m, 4 H, 4 × $\mathrm{PC}H\mathrm{H}$–), 1.86 (br s, 12 H, 4 × $\mathrm{C}H_3\mathrm{P}$–), 1.76 (s, 9 H, $(\mathrm{C}H_3)_3\mathrm{C}$–), 1.58–1.73 (br m, 4 H, 4 × $\mathrm{PCH}H$–), 1.29 (br s, 12 H, 4 × $\mathrm{C}H_3\mathrm{P}$–), –27.6 (quintet, 1 H, J_{PH} = 52.5 Hz, Fe–H); ^{13}C{P,H} NMR (benzene-d_6, 298 K) δ 39.58 ($(C\mathrm{H_3})_3\mathrm{C}$–), 38.86 ($(\mathrm{CH_3})_3C$–), 32.97 ($\mathrm{P}C\mathrm{H_2}$–), 28.98 ($C\mathrm{H_3P}$–), 18.22 ($C\mathrm{H_3P}$–). Even on prolonged warming with excess *tert*-butyl mercaptan, the disubstituted product, Fe(S-*t*-Bu)$_2$(DMPE)$_2$, was not formed in a detectable quantity.

Thiophenol. Reaction of thiophenol with FeH$_2$(DMPE)$_2$ was significantly more rapid than that of alkanethiols. The cis and trans thiolate hydrides formed over the space of 1 h, and the reaction to form dithiolate complexes was effectively complete after 24 h (see Figure 1). After 24 h at room temperature, the solvent was removed under vacuum and the residue recrystallized from petroleum ether. Fe(SPh)$_2$(DMPE)$_2$ was obtained as a green crystalline solid, mp 170 °C dec. Anal. Calcd for $\mathrm{C_{24}H_{42}FeP_4S_2}$: C, 50.18; H, 7.40; P, 21.57. Found: C, 49.9; H, 7.4; P, 21.4. *trans*-Fe(SPh)$_2$(DMPE)$_2$ (*trans*-**4a**): ^{13}C{P,H} NMR (THF-d_8, 315 K) δ 153.08 (Ar C_{ipso}), 139.48, 129.12 (Ar C_{ortho}, Ar C_{meta}), 124.27 (Ar C_{para}), 32.70 ($\mathrm{P}C\mathrm{H_2}$–), 17.53 ($C\mathrm{H_3P}$–); ^{1}H NMR (benzene-d_6, 300 K) δ 7.64–7.56 (m, 4 H, Ar H_{ortho}), 7.23–7.16 (m, 2 H, Ar H_{para}), 7.12–7.04 (m, 4 H, Ar H_{meta}), 2.23 (br s, 8 H, 4 × $\mathrm{PC}H_2$–), 1.61 (br s, 24 H, 8 × $\mathrm{C}H_3\mathrm{P}$–).

1,2-Ethanedithiol. A solution of FeH$_2$(DMPE)$_2$ (ca. 60 mg) in dry, oxygen-free THF was treated with 1,2-ethanedithiol (400 μL, 1.5 M in THF), and the mixture was left to stand at room temperature. $\overline{\mathrm{SCH_2CH_2SFe}}(\mathrm{DMPE})_2$ (**5**) crystallized from the reaction mixture over a period of 10 days. The solid was removed, washed with pentane, and dried under high vacuum to give the product as deep red plates, mp 236–237 °C dec. Anal. Calcd for $\mathrm{C_{14}H_{36}FeP_4S_2}$: C, 37.51; H, 8.09. Found: C, 37.8; H, 8.4. ^{1}H NMR (benzene-d_6, 298 K): δ 3.00–2.91 (br m, 2 H, 2 × $\mathrm{SC}H\mathrm{H}$–), 2.63–2.52 (br m, 2 H, 2 × $\mathrm{SCH}H$–), 1.64 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–), 1.56–1.42 (br m, 4 H, 4 × $\mathrm{PC}H\mathrm{H}$–), 1.32 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–), 1.23 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–), 1.21–1.09 (br m, 2 H, 2 × $\mathrm{PC}H\mathrm{H}$–), 1.09–0.97 (br m, 2 H, 2 × $\mathrm{PCH}H$–), 0.75 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–). ^{13}C{H,P} NMR (benzene-d_6, 298 K): δ 35.01 ($\mathrm{S}C\mathrm{H_2}$–), 33.69 ($\mathrm{P}C\mathrm{H_2}$–), 28.96 ($\mathrm{P}C\mathrm{H_2}$–), 20.66 ($C\mathrm{H_3P}$–), 17.92 ($C\mathrm{H_3P}$–), 16.90 ($C\mathrm{H_3}$–P), 13.25 ($C\mathrm{H_3P}$–). Slow recrystallization from toluene afforded orange plates suitable for X-ray crystallography.

1,3-Propanedithiol. Reaction of 1,3-propanedithiol was analogous to that of 1,2-ethanedithiol. $\overline{\mathrm{SCH_2CH_2CH_2SFe}}(\mathrm{DMPE})_2$ (**6**) crystallized from the reaction mixture over a period of 10 days. The solid was removed, washed with pentane, and dried under high vacuum to give the product as deep red plates, mp 208–210 °C dec. Anal. Calcd for $\mathrm{C_{15}H_{38}FeP_4S_2}$: C, 38.97; H, 8.29. Found: C, 39.1; H, 8.7. ^{1}H NMR (benzene-d_6, 302 K): δ 2.66–2.60 (br m, 4 H, 2 × $\mathrm{SC}H_2$–), 2.37–2.30 (br m, 2 H, $\mathrm{SC}H_2$–), 2.04 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–), 1.77–1.62 (br m, 4 H, 4 × $\mathrm{PC}H\mathrm{H}$–), 1.43 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–), 1.43–1.28 (br m, 2 H, 2 × $\mathrm{PC}H\mathrm{H}$–), 1.25 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–), 1.11–0.96 (br m, 2 H, 2 × $\mathrm{PC}H\mathrm{H}$–), 0.76 (m, 6 H, 2 × $\mathrm{C}H_3\mathrm{P}$–). ^{13}C{H,P} NMR (benzene-d_6, 302 K): δ 33.4 ($\mathrm{S}C\mathrm{H_2}$–), 33.4 ($\mathrm{P}C\mathrm{H_2}$–), 29.1 ($\mathrm{P}C\mathrm{H_2}$–), 23.6 ($\mathrm{SCH_2}C\mathrm{H_2}$–), 20.6 ($C\mathrm{H_3P}$–), 17.0 ($C\mathrm{H_3P}$–), 16.0 ($C\mathrm{H_3P}$–), 13.2 ($C\mathrm{H_3P}$–).

1,4-Bis(mercaptomethyl)benzene. A solution of FeH$_2$(DMPE)$_2$ (ca. 100 mg) in dry, oxygen-free THF (50 mL) was treated with 1,4-bis(mercaptomethyl)benzene (24 mg, 0.5 equiv), and the mixture was left to stand at room temperature for 4 weeks. HFe(DMPE)$_2$($\mathrm{SCH_2C_6H_4CH_2S}$)FeH(DMPE)$_2$ crystallized directly from the reaction mixture on slow evaporation of the solvent. ^{1}H NMR (benzene-d_6, 302 K): δ 7.8 (s, 4 H, Ar H), 3.35 (s, 4 H, 2 × $\mathrm{SC}H_2$–), 2.10–1.95 (br m, 4 H, 4 × $\mathrm{PC}H\mathrm{H}$–), 1.73 (br s, 24 H, 8 × $\mathrm{C}H_3\mathrm{P}$–), 1.73–1.55 (br m, 8 H, 8 × $\mathrm{PC}H\mathrm{H}$–), 1.31 (br s, 24 H, 8 × $\mathrm{C}H_3\mathrm{P}$–), –25.2 (quintet, 2H, $^1J_{\mathrm{PH}}$ = 50.2 Hz, 2 × Fe–H). ^{13}C{H,P} NMR (benzene-d_6, 315 K): δ 144.9 (Ar C_{ipso}), 128.7 (Ar C), 39.2 ($\mathrm{S}C\mathrm{H_2}$–), 32.6 ($\mathrm{P}C\mathrm{H_2}$), 26.2 ($C\mathrm{H_3P}$–), 16.6 ($C\mathrm{H_3P}$–). Cis isomers were present only to <5%.

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Supplementary Material Available: Tables of crystallographic data, thermal parameters, and hydrogen positional and thermal parameters for **5** (3 pages); tables of calculated and observed structure factors for **5** (8 pages). Ordering information is given on any current masthead page.

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Chemistry of Organometalloid Complexes with Potential Antidotes: Structure of an Organoarsenic(III) Dithiolate Ring

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The reactions of several arylarsenic dichlorides with the vicinal dithiols $\mathrm{HSCH_2CH(SH)CH_2OH}$ (British Anti-Lewisite, BAL) and *meso*-HOOCCH(SH)CH(SH)COOH (dimercaptosuccinic acid, DMSA) were investigated. They readily formed five-membered rings with the dithiolate groups chelated to the arsenic(III) center. The complexes were characterized by a variety of spectroscopic techniques, which indicate that the dithiolates chelate tightly to the arsenic(III) through the sulfur atoms. The complex between tolylarsenic dichloride and BAL was characterized by single-crystal X-ray diffraction. The cell is monoclinic, of space group $P2_1/n$, with $a = 13.343$ (2) Å, $b = 5.116$ (1) Å, $c = 17.196$ (3) Å, $\beta = 96.66$ (1)°, $Z = 4$, $V = 1166.0$ (6) Å^3, $R = 0.039$, and $R_w = 0.048$. The structure contains a five-membered arsenic(III) dithiolate with pyramidal geometry around the arsenic atom. Though both syn and anti isomers are possible, only the anti isomer is isolated. The lone pairs on the oxygen atoms do not appear to be involved in bonding.

Introduction

There is a great deal of concern about the toxicity of post-transition-element ions and their organometallic complexes.[2,3] Despite this, there has been relatively little research done on antidotes to metalloid poisoning in the United States. In fact, the antidote which is most commonly prescribed in the United States is still British Anti-Lewisite, which was developed by the British at the beginning of World War II to counteract anticipated German poison gas attacks.[4]

We have recently initiated a program to investigate the chemistry, spectroscopy, and structure of complexes between heavy p-block elements and their potential antidotes.[5,6] We are initially interested in antidotes to trivalent organoarsenical toxins, such as Lewisite ($\mathrm{ClCH{=}CHAsCl_2}$). The mechanism of toxic action of organoarsenic(III) compounds is not well understood, but is believed to arise from the affinity of As(III) for enzyme sulfhydryl groups.[7-9] The presence of organic groups makes the arsenic

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