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Addition of Nitrogen-Containing Heteroallenes to Iron(II)-Hydrides

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The reactions between *cis*-Fe(dmpe)$_2$H$_2$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) (**1**) or *cis*-Fe(PP$_3$)H$_2$ (PP$_3$ = P(CH$_2$CH$_2$PMe$_2$)$_3$) (**2**) and phenyl isothiocyanate (PhNCS), ethyl isothiocyanate (EtNCS), and phenyl isocyanate (PhNCO) were investigated. PhNCS reacts with **1** to form a variety of insertion products at low temperature, and the thermodynamic product hydridoiron *N*-phenylthioformimidate *trans*-Fe(dmpe)$_2$(SCHNPh)H (**3a**) at 300 K. Addition of an excess of PhNCS to **1** produces the bis(insertion) product *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (**3c**). EtNCS inserts into the iron−hydride bond of **1** to form a mixture of *trans*-Fe(dmpe)$_2$(SCHNEt)H (**4a**, thermodynamic product) and *cis*-Fe(dmpe)$_2$(SCHNEt)H (**4b**, kinetic product). Addition of an excess of EtNCS does not result in a second insertion but rather attack at the thioformimidato ligand to form *trans*-Fe(dmpe)$_2$(SCHN$^+$(Et)C(S)N$^-$Et)H (**4c**). PhNCO reacts rapidly with **1** to form *trans*-Fe(dmpe)$_2$(OCHNPh)H (**5a**) and higher oligomeric products. The addition of PhNCS, EtNCS, and PhNCO to **2** permits the formation of thermally stable, geometrically constrained *cis* products *cis*-Fe(PP$_3$)(SCHNPh)H (**6a**), *cis*-Fe(PP$_3$)(SCHNEt)H (**7a**), and *cis*-Fe(PP$_3$)(OCHNPh)H (**8a**) in clean reactions. The hydridoiron *N*-phenylthioformimidate **6a** reacts with a second equivalent of PhNCS to form *cis*-Fe(PP$_3$)(SCHNPh)$_2$ (**6c**), but oligomerization of EtNCS or PhNCO does not occur. All complexes have been characterized by multinuclear NMR andIR spectroscopy and mass spectrometry (electrospray), with elemental analysis or high resolution mass spectrometry confirming the structures of thermally stable complexes where possible. Complexes **3c** and **4c** were characterized by single-crystal X-ray crystallography.

Introduction

Transition metal hydrides are important compounds due to their chemical reactivity and importance in catalysis. The insertion of small unsaturated molecules into the transition metal hydride bond is an equally important step in catalytic functionalization reactions.

The insertion of simple heteroallenes, most notably CO$_2$, into transition metal hydride bonds has received much recent attention due to their potential usefulness as C1 building blocks in constructing higher organic structures. The isocyanate or isothiocyanate functionality is particularly useful as a source of carbon, nitrogen, and oxygen or sulfur in one chemical step. Isocyanates (or isothiocyanates) typically insert into a metal−hydride bond to form formamido (or thioformamido) ligands which bind to the metal in an η^2 fashion through both nitrogen and oxygen[1−5] (or nitrogen and sulfur[5−7]) atoms. Examples of binding η^1 through the nitrogen atom[8] and η^1 through the carbonyl moiety to form a carboxamido ligand[9,10] are also known.

There is, to date, only a single confirmed report of a thioformimidato ligand which binds η^1 through the sulfur atom,[11] although this form of binding has been postulated in other cases.[5,12,13] There have been no reports of a formimidato ligand binding η^1 through the oxygen atom. Jetz and Angelici[10] have reported the insertion of *tert*-butyl isocyanate into the iron−hydride bond of CpFe(CO)$_2$H to form the carboxamido complex CpFe(CO)$_2$(CONH^{t}Bu).

We have recently reported the propensity of iron(II) dihydride complexes with phosphine donor ligands to insert the heteroallenes CO$_2$, CS$_2$, and COS into both iron−hydride bonds.[14] In this paper, we report insertion and further reactions of the heteroallenes phenyl isothiocyanate (PhNCS), ethyl isothiocyanate (EtNCS), and phenyl isocyanate (PhNCO) with the iron(II)−hydride bonds of the related iron phosphine complexes *cis*-Fe(dmpe)$_2$H$_2$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) (**1**) and *cis*-Fe(PP$_3$)H$_2$ (PP$_3$ = P(CH$_2$CH$_2$PMe$_2$)$_3$) (**2**).

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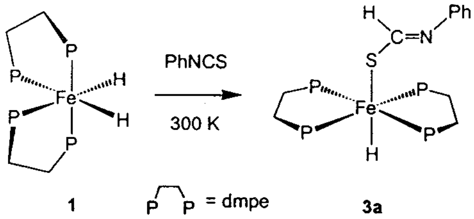
Table 1. Summary of ^{1}H, ^{31}P, ^{13}C NMR and IR Data for Complexes 1−8A

compound	^{1}H		^{31}P	^{13}C (C = X)	IR	
	hydride	FeXC*H*N			M−H	ν(XCHN)
cis-Fe(dmpe)$_2$H$_2$ (**1**)	−14.33		83.7, 74.1		1777	
cis-Fe(PP$_3$)H$_2$ (**2**)	−11.03		187.2, 68.7		1828, 1713	
trans-Fe(dmpe)$_2$(SCHNPh)H (**3a**)	−24.93	9.49	70.7	177.8	1789	1590, 2900
cis-Fe(dmpe)$_2$(SCHNPh)H (**3b**)	−11.46	8.71	56.2, 67.6, 72.6, 74.6			
trans-Fe(dmpe)$_2$(SCHNPh)$_2$ (**3c**)		8.76	60.3	174.2		1593, 2898
trans-Fe(dmpe)$_2$(SCHNEt)H (**4a**)	−25.38	9.03	71.3	172.4	1785	1540, 2898
cis-Fe(dmpe)$_2$(SCHNEt)H (**4b**)	−11.33	8.71	54.9, 66.5, 71.0, 73.1	181.7		
trans-Fe(dmpe)$_2$(SC(H)N^{+}(Et)C(S)N^{-}(Et))H (**4c**)	−24.47	11.06	68.5	169.8, 193.5	1811	984, 1225, 1551, 2900
trans-Fe(dmpe)$_2$(OCHNPh)H (**5a**)	−34.31	8.13	70.7	167.8	1792	1595, 2903
cis-Fe(PP$_3$)(SCHNPh)H (**6a**)	−14.05	9.70	180.4 (P$_A$), 62.8 (P$_T$), 60.8 (P$_E$)	178.7	1802	1494, 2897
cis-Fe(PP$_3$)(SCHNPh)$_2$ (**6b**)		9.26, 9.63	178.4 (P$_A$), 73.3 (P$_E$), 53.6 (P$_T$)	176.4, 176.8		1590, 2903
cis-Fe(PP$_3$)(SCHNEt)H (**7a**)	−13.92	9.31	181.0 (P$_A$), 62.8 (P$_T$), 61.2 (P$_E$)	173.6	1803	1543, 2898
cis-Fe(PP$_3$)(OCHNPh)H (**8a**)	−13.07	8.81	173.3 (P$_A$), 56.2 (P$_T$), 55.1 (P$_E$)	170.3	1794	1571, 2900

Scheme 1



Results and Discussion

A solution of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) in benzene-d_6, toluene-d_8, or tetrahydrofuran-d_8 reacted with phenyl isothiocyanate (PhNCS, 1 equiv) at 300 K to form the insertion product *trans*-Fe(dmpe)$_2$(SCHNPh)H (**3a**) (Scheme 1, Table 1).

The $^{31}P\{^{1}H\}$ NMR spectrum of *trans*-Fe(dmpe)$_2$(SCHNPh)H (**3a**) comprises a singlet resonance at δ 70.7 (Table 1), indicating a *trans* geometry for the dmpe ligands about the iron center. The ^{1}H NMR spectrum of **3a** exhibits a high-field pentet at δ −24.93 due to the metal-bound hydride coupled to four equivalent ^{31}P nuclei ($^{2}J_{PH}$ = 50 Hz) and a singlet at δ 9.49, indicative of a thioformamido or thioformimidato proton.[4]

The ligand formed upon insertion of phenyl isothiocyanate into the iron−hydride bond can bind to the iron center in an η^1 fashion through either the sulfur (thioformimidato ligand) or the nitrogen (thioformamido ligand) atom or in an η^2 fashion (thioformamido ligand). The trend in chemical shift for hydrides *trans* to sulfur, oxygen, and phosphorus atoms in iron(II) complexes of this type (containing formate, dithioformate, or thioformate ligands) has been established.[14] **3a** exhibits an η^1 S-bound thioformimidato ligand as evidenced by the characteristic chemical shift (δ −24.93) for a hydride *trans* to an S-donor.

The $^{13}C\{^{1}H\}$ NMR spectrum of **3a** exhibited a singlet at δ 177.8 for the imido carbon, while the IR spectrum (KBr disk) of **3a** confirmed the presence of a thioformimidato ligand with two bands at 1590 (C=N stretch) and 2900 (thioformimidato C−H stretch) cm^{-1}.[4,13]

The reaction between *cis*-Fe(dmpe)$_2$H$_2$ (**1**) and phenyl isothiocyanate was carried out at lower temperature in tetrahydrofuran-d_8. Reaction was initiated only at temperatures higher than 260 K, at which point ^{1}H NMR suggested the reaction mixture contained five products: *trans*-Fe(dmpe)(SCHNPh)H (**3a**, major product) and four other minor products with iron-hydride and thioformimidato proton resonances at δ −11.46 (ddt, $^{2}J_{PH}$ = 31, 54, 64 Hz) and δ 8.71 (**3b**, *cis* stereochemistry), δ −10.15 and δ 9.63 (*cis*), δ −25.38 (p, $^{2}J_{PH}$ = 50 Hz) and δ 8.33 (*trans*), and δ −23.43 (p, $^{2}J_{PH}$ = 51 Hz) and δ 11.17 (*trans*).

Product **3b** was the most stable of these, and remained stable in solution at temperatures up to 280 K, and is probably *cis*-Fe(dmpe)(SCHNPh)H, the expected intermediate in the formation of **3a**. The $^{31}P\{^{1}H\}$ NMR spectrum of **3b** exhibits four 8-line multiplet resonances at δ 56.2 (dt), 67.6 (ddd), 72.6 (ddd), and 74.6 (dt) for four inequivalent ^{31}P nuclei, confirming the *cis* stereochemistry.[14]

The other products formed at low temperature, one *cis* and two *trans* products, could not be characterized further and are presumably unstable isomers of **3b** which contain the thioformimidato ligand in a different binding mode, such as η^1 or η^2 thioformamido.

The addition of a second equivalent (or indeed excess) of PhNCS to **3a** or **3b** at a variety of temperatures resulted in the formation of a single product, *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (**3c**), the product of insertion of phenyl isothiocyanate into the second iron−hydride bond of **1** (Scheme 2). The *cis* isomer, *cis*-Fe(dmpe)$_2$(SCHNPh)$_2$, was not detected.

The $^{31}P\{^{1}H\}$ NMR spectrum of **3c** exhibits a singlet at δ 60.3. The ^{1}H NMR spectrum displays equivalent thioformimidato proton resonances at δ 8.76. IR spectroscopy gave evidence only for thioformimidato ligands in the product (no metal hydrides) while the $^{13}C\{^{1}H\}$ NMR spectrum exhibited a ^{31}P coupled pentet at δ 174.2 ($^{3}J_{CP}$ = 6 Hz) for equivalent imido carbon nuclei (Table 1).

Scheme 2

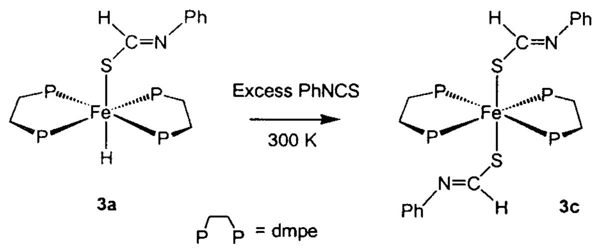


Table 2. Selected Bond Distances (Å) and Angles (deg) for *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (3c)

bond distances (Å)		bond angles (deg)	
Fe(1)−P(1)	2.2547(8)	P(2)−Fe(1)−P(1) (intra-ligand)	86.05(2)
Fe(1)−P(2)	2.2529(7)	P(1)−Fe(1)−S(1)	84.42(2)
Fe(1)−S(1)	2.3213(7)	P(2)−Fe(1)−S(1)	85.04(3)
S(1)−C(7)	1.7108(18)	Fe(1)−S(1)−C(7)	128.15(6)
C(7)−N(1)	1.283(2)	S(1)−C(7)−N(1)	130.42(14)
N(1)−C(8)	1.420(2)	C(7)−N(1)−C(8)	118.41(15)

Table 3. Selected Bond Distances (Å) and Angles (deg) for *trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (4c)

bond distances (Å)		bond angles (deg)	
Fe(1)−P(1)	2.2024(10)	P(1)−Fe(1)−P(2)	85.18(4)
Fe(1)−P(2)	2.1998(10)	P(2)−Fe(1)−P(3)	94.24(4)
Fe(1)−P(3)	2.1990(10)	P(1)−Fe(1)−P(3)	168.86(4)
Fe(1)−P(4)	2.1964(10)	P(2)−Fe(1)−P(4)	171.47(4)
Fe(1)−S(1)	2.2927(9)	P(1)−Fe(1)−S(1)	90.46(4)
S(1)−C(1)	1.667(3)	P(3)−Fe(1)−S(1)	100.67(4)
C(1)−N(1)	1.314(4)	Fe(1)−S(1)−C(1)	114.83(11)
N(1)−C(2)	1.503(5)	S(1)−C(1)−N(1)	127.4(2)
C(2)−C(3)	1.401(7)	C(1)−N(1)−C(2)	120.6(3)
N(1)−C(4)	1.475(4)	C(1)−N(1)−C(4)	120.3(3)
C(4)−S(2)	1.705(4)	C(4)−N(1)−C(2)	119.0(3)
C(4)−N(2)	1.273(5)	N(1)−C(4)−S(2)	118.3(3)
N(2)−C(5)	1.469(4)	N(1)−C(4)−N(2)	110.9(3)
C(5)−C(6)	1.388(7)	S(2)−C(4)−N(2)	130.7(3)
		C(4)−N(2)−C(5)	117.2(4)

Table 4. Crystallographic Data for *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (3c) and *trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (4c)

	3c	4c
emperical formula	$C_{26}H_{44}FeN_2P_4S_2$	$C_{21}H_{44}FeN_2P_4S_2$
formula weight	628.48	568.43
crystal system	monoclinic	triclinic
crystal habit	blade	prism
crystal color	dark brown	red
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Z value	2	2
a (Å)	10.669(3)	10.435(2)
b (Å)	9.176(3)	16.783(4)
c (Å)	16.199(5)	9.226(2)
α (deg)		104.933(7)
β (deg)	104.836(5)	92.245(8)
γ (deg)		98.482(7)
V (Å^3)	1533.0(8)	1539.1(6)
T (°C)	−100	21
λ (Mo Kα, Å)	0.710 73	0.710 73
μ (Mo Kα, mm^{-1})	0.856	0.845
ρ_{calcd} (g cm^{-3})	1.362	1.227
R1(F)^a	0.0318	0.0498
wR2(F^2)^a	0.0810	0.1534
$T_{min,max}$	0.853, 1.000 (SADABS)	0.772, 0.926 (Gaussian)
N	13 795	12 535
N_{ind}	3617	6847
N_{obs}	3311 ($I > 2\sigma(I)$)	4949 ($I > 2\sigma(I)$)
R_{merge}	0.0208	0.0335

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w F_c^2)^2)^{1/2}$, all reflections $w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 1.8264P]$ for **3c** and $w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$ for **4c** where $P = (F_o^2 + 2F_c^2)/3$.

Dark brown bladelike single crystals of *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (**3c**), suitable for structure determination by X-ray crystallography, were grown in benzene-d_6. Selected bond lengths and angles are listed in Table 2 and crystallographic data are listed in Table 4. The dmpe ligand backbone adopts at least two different orientations (Figure 1), with disordered site populations refined and then fixed at 0.5. The structure confirmed the presence of two η^1 S-bound thioformimidato ligands in a *trans* disposition, the first example of such binding to a first-row transition metal. Only one other structurally characterized example of an η^1 S-bound thioformimidato ligand, the rhodacarborane 3-(η^1-SCHNPh)-3,3-(PMe$_2$Ph)$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$, is known.[11] The C═N (1.283(2) Å) and C−S (1.7108(18) Å) bond lengths and NCS (130.42(14)°) bond angle of **3c** compare favorably with those of the rhodacarborane (1.254(4) Å, 1.724(3) Å, and 126.7(2)° respectively).

A solution of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) in benzene-d_6, toluene-d_8, or tetrahydrofuran-d_8 reacted with ethyl isothiocyanate (EtNCS, 1 equiv) at a variety of temperatures to form a mixture of the insertion products *trans*-Fe(dmpe)$_2$(SCHNEt)H (**4a**) and *cis*-Fe(dmpe)$_2$(SCHNEt)H (**4b**) (Scheme 3). The *cis* isomer **4b**, an intermediate in the formation of **4a**, was the dominant product at lower temperatures (kinetic product), and at 300 K the immediate ratio of products **4a**:**4b** in the reaction was 1:1.25. With heat or standing, complete conversion from **4b** to **4a** was observed within 3 h.

The ^{31}P{^{1}H} NMR spectrum of *trans*-Fe(dmpe)$_2$-(SCHNEt)H (**4a**) exhibited a singlet at δ 71.3, while the ^{1}H NMR spectrum exhibited a high-field pentet at δ −25.38 for a hydride coupled to four equivalent ^{31}P nuclei ($^2J_{PH}$ = 51 Hz) and *trans* to a sulfur donor. A singlet at δ 9.03 was indicative of a thioformimidato proton. The ^{13}C{^{1}H} NMR spectrum of **4a** exhibited a phosphorus-coupled pentet at δ 172.4 ($^3J_{CP}$ = 5 Hz) for the imido carbon. IR spectroscopy of the stable *trans* product confirmed the presence of an *N*-ethylthioformimidato ligand.

The ^{31}P{^{1}H} NMR spectrum of *cis*-Fe(dmpe)$_2$-(SCHNEt)H (**4b**) exhibited four 8-line multiplets for four inequivalent ^{31}P centers at δ 54.9, 66.5, 71.0, and 73.1. The ^{1}H NMR spectrum displayed a multiplet at δ −11.33 for a hydride *trans* to a phosphorus donor and coupled to four inequivalent ^{31}P centers and a singlet at δ 8.71 for the thioformimidato proton.

When a further equivalent of EtNCS was added to **4a** or **4b**, the product of insertion into the second iron−hydride bond of **1** was not detected. Quantitative conversion of **4a** or **4b** to a new product **4c**, containing a hydride resonating as a phosphorus-coupled pentet ($^2J_{PH}$ = 50 Hz) at δ −24.47 (*trans* to a sulfur atom) and equivalent ^{31}P environments (δ 68.5), was observed (Scheme 4). The ^{13}C{^{1}H} NMR spectrum featured an imido carbon resonance at δ 169.8 and a further resonance at δ 193.5 which is consistent with a thiocarbonyl carbon.[14] IR indicated the presence of an iron-hydride and both C═N and C═S functionalities.

Red prismatic single crystals of **4c** of suitable quality for structure determination by X-ray crystallography

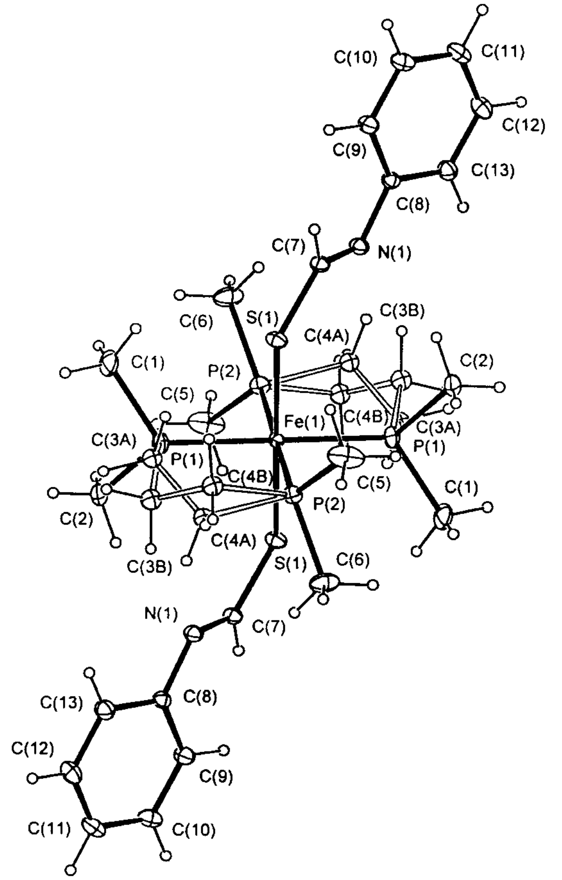
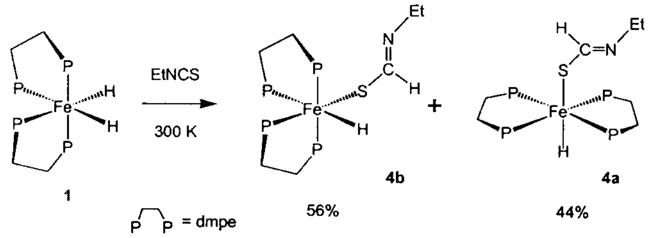
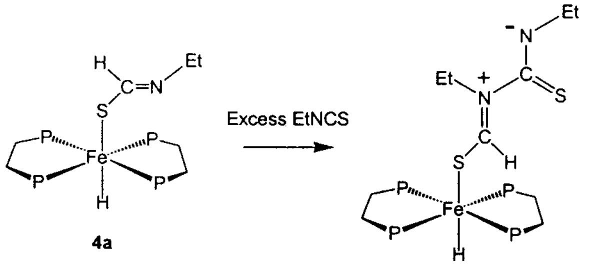


Figure 1. ORTEP[15] diagram of the complex *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (**3c**) (20% atomic displacement ellipsoids). The molecule resides on an inversion site.

Scheme 3



Scheme 4



were grown from benzene-d_6, and **4c** was identified as *trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (Figure 2). Selected bond lengths and angles are listed in Table 3, and crystallographic data are listed in Table 4.

The X-ray structure of **4c** shows that the dimerized ligand is bound η^1 through the sulfur atom, indirectly confirming the structure of *trans*-Fe(dmpe)$_2$(SCHNEt)H (**4a**) as having an η^1 S-bound thioformimidato ligand.

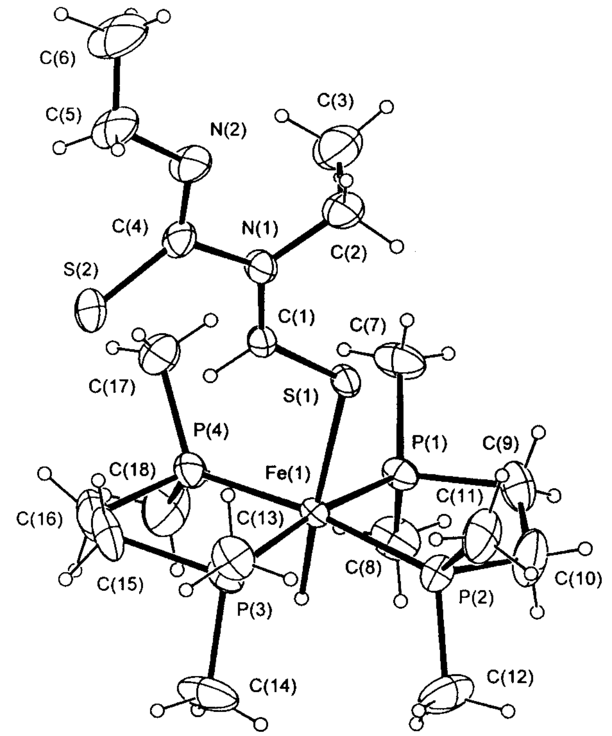


Figure 2. ORTEP[15] diagram of the complex *trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (**4c**) (20% atomic displacement ellipsoids).

The dimerized ligand is formally zwitterionic and contains both quaternary (positive) and anionic nitrogen centers. The outer C−S bond length of 1.705(4) Å suggests a C−S single bond and indicates that the negative charge of the zwitterion is probably delocalized over the outer S−C−N moiety in the solid state.

trans-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (**4c**) is formally the product of nucleophilic attack by the lone pair on the nitrogen of the *N*-ethylthioformimidato ligand of **4a** at the thiocarbonyl carbon of EtNCS. The complex **4c** represents the product of the initial step in a possible polymerization of EtNCS at an iron(II) center; however no higher order oligomers of EtNCS were detected (by NMR or electrospray MS) in this reaction. Transition metal catalysts for the oligomerization (or polymerization) of isothiocyanates and isocyanates are relatively rare.[16−19] Notable examples include a titanium complex, TiCl$_3$(OCH$_2$CF$_3$), which has been reported to polymerize alkyl isocyanates in a "living" fashion,[20] and Ru(CCC$_6$H$_9$)(PMe$_3$)$_2$(Cp) which forms tri- and poly(methylisocyanate) products from methyl isocyanate.[21]

A solution of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) in benzene-d_6 or tetrahydrofuran-d_8 reacted with phenyl isocyanate (PhNCO) at 300 K to form a mixture of the insertion product *trans*-Fe(dmpe)$_2$(OCHNPh)H (**5a**), four other products (containing hydrides with ^{1}H NMR resonances

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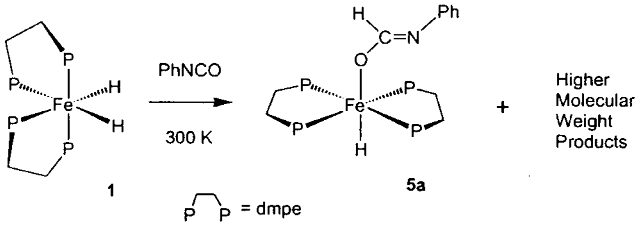
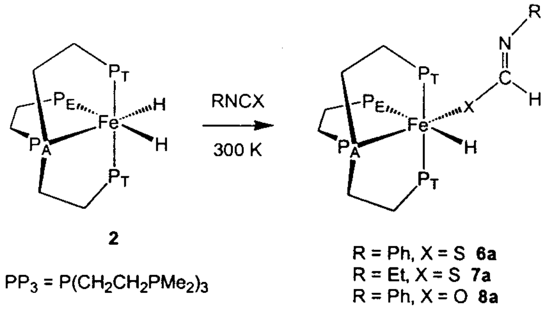
Scheme 5



Scheme 6



similar to those of **5a**) in solution, and a red oily precipitate (Scheme 5). Notably, at least 1.5 equiv of PhNCO was required to completely convert *cis*-Fe(dmpe)$_2$H$_2$ (**1**) to products, indicating a high reactivity of the initial thermodynamic product **5a**. When the reaction was carried out at low temperature, up to eight unstable products with *cis* geometries for the phosphine ligands were formed, each in very small amounts compared to the formation of **5a**.

The ^{31}P{^{1}H} NMR spectrum of *trans*-Fe(dmpe)$_2$-(OCHNPh)H (**5a**) exhibited a singlet at δ 70.7. The ^{1}H NMR spectrum exhibited a high-field pentet at δ −34.31 for a hydride coupled to four equivalent ^{31}P nuclei ($^2J_{PH}$ = 49 Hz) and *trans* to an oxygen donor[14] and a formimidato proton resonance at δ 8.13. The imido carbon resonated at δ 167.8 in the ^{13}C{^{1}H} NMR spectrum. IR spectroscopy of a partially purified mixture containing mostly (>90%) **5a** confirmed the presence of an *N*-phenylformimidato ligand.

Electrospray mass spectrometry of the product mixture and of the oily precipitate showed a parent ion (M − 1)$^+$ at 476 (M = **5a**), a peak at 595 (M + PhNCO − 1)$^+$, and some higher mass peaks which do not obviously correspond to products containing higher order oligomers of PhNCO. The cation with a mass of 595 amu probably corresponds to the product *trans*-Fe(dmpe)$_2$-(OC(H)N$^+$(Ph)C(O)N$^-$(Ph))H, by analogy with the formation of **4c** from **4a**.

The insertion of isothiocyanates and isocyanates into the metal−hydride bond in this work resulted exclusively in Fe−S or Fe−O bonded products rather than metal−N bonded products. This observation is consistent with previous observations of hydridoiron thioformates.[14] The selectivity for S or O binding over N binding in these potentially ambident donors probably involves the affinity of the relatively soft Fe(II) center for the softer S or O centers. Steric factors may also play a role since the sterically more encumbered C=N−R fragment is directed away from the metal center with O- or S-binding of the thioformimidate fragment.

No thermally stable products with a *cis* disposition of the two dmpe ligands were observed in this work. Iron complexes containing two bidentate phosphine ligands are well-known to be stereochemically labile with ready interconversion of *cis* and *trans* isomers at or near room temperature. The relative stability of the Fe(PP)$_2$X$_2$ complexes can be rationalized by the fine balance between steric and electronic factors. The substituted tertiary phosphines are crowded at the Fe(II) center, and depending on the bulk of the substituents on P and the nature of X ligands, Fe(PP)$_2$X$_2$ complexes have been characterized with either *trans* stereochemistry, e.g., Fe(dmpe)$_2$Cl$_2$,[22] Fe(dmpe)$_2$HCl,[23] Fe(dmpe)$_2$(CCR)$_2$,[24] [Fe(dmpe)$_2$(H$_2$)H]$^+$,[25] *cis* stereochemistry, e.g., Fe(dmpe)$_2$H$_2$,[26,27] Fe(BPE5)$_2$Cl$_2$ (BPE5 = 1,2-bisphospholanoethane),[28] or as an equilibrating mixture of the two, e.g., Fe(dprpe)$_2$Cl$_2$ (dprpe = 1,2-bisdi(*n*-propyl)phosphinoethane),[29] Fe(dmpe)$_2$(SR)$_2$.[30]

A stable *cis* stereochemistry was imposed on the metal system, by replacement of the two dmpe ligands with the tetradentate phosphine ligand P(CH$_2$CH$_2$PMe$_2$)$_3$ (PP$_3$). Addition of 1 equiv of PhNCS, EtNCS, or PhNCO in benzene-d_6 to a benzene-d_6 solution of *cis*-Fe(PP$_3$)H$_2$ (**2**) at 300 K resulted in a clean quantitative reaction to form *cis*-Fe(PP$_3$)(SCHNPh)H (**6a**), *cis*-Fe(PP$_3$)(SCHNEt)H (**7a**), or *cis*-Fe(PP$_3$)(OCHNPh)H (**8a**), respectively (Scheme 6).

The ^{31}P{^{1}H} NMR spectrum of *cis*-Fe(PP$_3$)(SCHNPh)H (**6a**) is typical of most octahedral complexes of the type *cis*-Fe(PP$_3$)XY,[31,32] showing a characteristic doublet of triplet resonance for the apical, central phosphorus of the chelating PP$_3$ ligand (P$_A$) at δ 180.4, with signals at δ 62.8 and 60.8 for the axial terminal phosphorus resonances (P$_T$) and the equatorial terminal phosphorus resonance (P$_E$), respectively. The ^{1}H NMR spectrum exhibited a one-proton resonance at δ 9.70 for the thioformimidato proton, and this is somewhat downfield from the corresponding protons in Fe(dmpe)$_2$(SCHNPh)H (**3a**,**b**) and *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (**3c**). The ^{1}H NMR spectrum also exhibits a doublet of doublets of triplets resonance at δ −14.05 for a hydride coupled to three different ^{31}P environments and at a chemical shift characteristic of a hydride *trans* to a phosphorus donor. In the ^{13}C{^{1}H} NMR spectrum, a C=N resonance appears at δ 178.7. For the alternate N-coordinated isomer, the spectrum would exhibit a C=S resonance in the range δ 200−250.[14] IR stretches at 1494 (C=N stretch) and 2897 (thioformimidate C−H stretch) cm^{-1} also confirm an η^1 S-bound *N*-phenylthioformimidato ligand.

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The $^{31}P\{^1H\}$ NMR spectrum of *cis*-Fe(PP$_3$)(SCHNEt)H (**7a**) exhibited a doublet of triplets ($^2J_{PP} = 30, 24$ Hz) at δ 181.0 (P$_A$), a doublet of doublets ($^2J_{PP} = 30, 24$ Hz) at δ 62.8 (P$_T$), and a quartet ($^2J_{PP} = 24$ Hz) at δ 61.2 (P$_E$). The ^{1}H NMR spectrum exhibited a resonance at δ 9.31 for the thioformimidato proton and a doublet of doublets of triplets resonance at δ −13.92 for the metal hydride. The imido carbon resonance at δ 173.6 in the $^{13}C\{^1H\}$ NMR spectrum and IR stretches at 1543 and 2898 cm^{-1} again confirm the presence of an η^1 S-bound *N*-ethylthioformimidato ligand.

The $^{31}P\{^1H\}$ NMR spectrum of *cis*-Fe(PP$_3$)(OCHNPh)H (**8a**) exhibited a doublet of triplets ($^2J_{PP} = 33, 23$ Hz) at δ 173.3 (P$_A$), a doublet of doublets ($^2J_{PP} = 33, 23$ Hz) at δ 56.2 (P$_T$), and a quartet ($^2J_{PP} = 23$ Hz) at δ 55.1 (P$_E$). The ^{1}H NMR spectrum exhibited a resonance at δ 8.81 for the formimidato proton and a doublet of doublets of triplets resonance at δ −13.07 for the metal-bound hydride. The imido carbon resonance at δ 170.3 in the $^{13}C\{^1H\}$ NMR spectrum, the IR stretches at 1571 and 2900 cm^{-1}, and the comparison of ^{31}P and ^{1}H NMR data with that of the known *cis*-Fe(PP$_3$)(OCHO)H[14] confirm the presence of an η^1 O-bound *N*-phenylformimidato ligand.

2D NOESY and COSY nmr,[31,32] and X-ray crystallography[33] have been used to determine the geometry of *cis*-Fe(PP$_3$)XH complexes, and for all complexes of this type studied to date, the metal-bound hydride ligand has been located exclusively in a position cis to the apical phosphorus P$_A$. The downfield chemical shift, splitting pattern and proton-phosphorus couplings confirm that *cis*-Fe(PP$_3$)(SCHNPh)H (**6a**), *cis*-Fe(PP$_3$)(SCHNEt)H(**7a**), and *cis*-Fe(PP$_3$)(OCHNPh)H (**8a**) also have this stereochemistry.

The addition of a further equivalent (or an excess) of PhNCS to a solution of *cis*-Fe(PP$_3$)(SCHNPh)H (**6a**) in benzene-d_6 results in the rapid formation of a cream-colored precipitate. This product was insoluble in most solvents and only partially soluble in tetrahydrofuran and acetonitrile. The $^{31}P\{^1H\}$ NMR spectrum shows the formation of two products in the approximate ratio of 2.5:1. The major product exhibits an apparent quartet ($J = 23$ Hz) at δ 178.4 (P$_A$), a doublet of triplets ($J = 42, 23$ Hz) at δ 73.3 (terminal phosphorus P$_E$), and a doublet of doublets ($J = 42, 23$ Hz) at δ 53.6 (equivalent terminal phosphorus donors P$_T$). The large upfield shift of P$_E$ (relative to **6a**) is consistent with P$_E$ being *trans* to an *N*-phenylthioformimidato ligand rather than a hydride in the coordination sphere,[14] and the major product is assigned as *cis*-Fe(PP$_3$)(SCHNPh)$_2$ (**6b**). The minor product exhibited similar ^{31}P NMR shifts at δ 176.8 (P$_A$, q, $J = 24$ Hz), δ 73.0 (P$_E$, dt, $J = 42, 23$ Hz), and δ 53.7 (P$_T$, dd, $J = 42, 23$ Hz) and is possibly an isomer of **6b**. The ^{1}H NMR spectrum of the dominant product **6b** exhibited the resonances of two nonequivalent thioformimidato protons at δ 9.26 (*trans* to P$_A$) and δ 9.63 (*trans* to P$_E$), while the $^{13}C\{^1H\}$ NMR spectrum exhibited resonances at δ 176.8 and 176.4 for imido carbons *trans* and *cis* to P$_A$, respectively. The high-resolution electrospray mass spectrum showed a single parent ion with a mass of 625.1011 (M − 1)$^+$ (M = **6b**), with no further evidence for the possible structure of the minor product.

The addition of an excess of EtNCS or PhNCO to *cis*-Fe(PP$_3$)(SCHNEt)H(**7a**) and *cis*-Fe(PP$_3$)(OCHNPh)H (**8a**), respectively, results in neither insertion into the second iron-hydride bond nor oligomerization of the substrate. One extra equivalent of the substrate resulted in no reaction, while a large excess only produced previously observed decomposition products for complexes of this type.[14]

Conclusions

Iron dihydrides of the type FeP$_4$H$_2$ react rapidly with PhNCS, EtNCS, and PhNCO, producing stable hydridoiron (η^1-S)-thioformimidates and (η^1-O)-formimidates. In the case of *cis*-Fe(dmpe)$_2$H$_2$ (**1**), *cis* intermediates isomerized to the thermally stable *trans* insertion products at room temperature or below. Evidence from low-temperature spectroscopy of the reactions suggested the initial formation of intermediates that involved bonding of the substrate to the iron center in another mode (η^1-N, η^1-C, or η^2-N, O, or S). The reactivity of each of the substrates PhNCS, EtNCS, and PhNCO was clearly different, and in the presence of excess reagent, products of second insertion *and* dimerization of the thioformimidate or formimidate ligand were characterized.

The tendency for transition metal hydrides to react by insertion of unsaturated substrates is well established through studies by Berke et al.,[34] and metal hydride reactivity has been correlated to the degree of polarization of the transition metal hydride bond (the “hydridicity” of the hydride ligand). The transition metal hydrides which are most reactive toward insertion characteristically contain a hydride disposed *trans* to a strong π-acceptor ligand (e.g., carbonyl, nitrosyl, carbyne),[34] and transition metal hydrides of this type are known to insert aldehydes, ketones, and even imines.

We have clearly established the reactivity of the complexes *cis*-Fe(dmpe)$_2$H$_2$ (**1**) and *cis*-Fe(PP$_3$)H$_2$ (**2**) toward the heteroallenes CO$_2$, COS, CS$_2$,[14] PhNCS, EtNCS, and PhNCO. The propensity of the iron complexes studied in this work to insert heteroallenes places them among the highly reactive metal hydrides. The polarized iron−hydride bond is due to the low electronegativity at the iron center caused by four strongly σ-donating phosphines.[35−37]

Experimental Section

All manipulations were carried out using standard Schlenk, high vacuum, and glovebox techniques. Air-sensitive NMR samples were prepared in a nitrogen- or argon-filled glovebox, with solvent vacuum transferred into an NMR tube fitted with a concentric Teflon valve. Toluene-d_8, tetrahydrofuran-d_8, and benzene-d_6 were dried over sodium/benzophenone and vacuum distilled immediately prior to use. Ether was dried over sodium wire before distillation under nitrogen from sodium/benzophenone. Nitrogen (>99.5%) was used as supplied without

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further purification. Phenyl isothiocyanate and phenyl isocyanate were purchased from Fluka and were washed through silica and deoxygenated prior to use. Ethyl isothiocyanate was purchased from Aldrich Chemical Co. and was deoxygenated prior to use. The syntheses of *cis*-Fe(dmpe)$_2$H$_2$ (**1**)[38,39] and *cis*-Fe(PP$_3$)H$_2$ (**2**)[32] have been described elsewhere.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker DRX400 NMR spectrometer at 400.2, 162.0, and 100.6 MHz, respectively. ^{1}H NMR spectra were referenced to residual toluene-d_7 at δ 2.09, tetrahydrofuran-d_7 at δ 3.58, or benzene-d_5 at δ 7.15; ^{31}P NMR spectra were referenced to external neat trimethyl phosphite at δ 140.85; and ^{13}C NMR spectra were referenced to tetrahydrofuran-d_8 at δ 67.4 or benzene-d_6 at δ 128.0. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer as KBr disks. Electrospray mass spectra were recorded on a Finnigan MAT LCQ mass spectrometer. High-resolution mass spectra were recorded on a Bruker 4.7 T BioApex FTMS fitted with an analytica electrospray source at Monash University, Australia. Elemental analyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

(OC-6-32)-Bis(1,2-bis(dimethylphosphino)ethane)hydrido(*N*-phenylthioformimidato)iron(II), *trans*-Fe(dmpe)$_2$(SCHNPh)H (3a). Phenyl isothiocyanate (11.3 mg, 0.084 mmol) in benzene-d_6 (0.3 mL) was added portionwise at 300 K to an NMR tube containing a solution of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) (30 mg, 0.084 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative formation of **3a**. Removal of solvent and recrystallization of the residue from ether afforded **3a** as an orange-red solid (24 mg, 57%).

Mp >220 °C (dec). HRMS (ES) calcd for C$_{19}$H$_{38}$NP$_4$SFe $(M - 1)^+$: requires 492.1025, found 492.1042. ^{1}H NMR (benzene-d_6, 300 K) δ −24.93 (p, $^2J_{\rm PH} = 50$ Hz, 1H, Fe-*H*), 1.05 (br s, 12H, PC*H*$_3$), 1.40 (m, 4H, PC*H*$_2$), 1.50 (br s, 12H, PC*H*$_3$), 2.25 (m, 4H, PC*H*$_2$), 6.92 (m, 1H, *Ph*$_{\rm para}$), 7.05 (m, 2H, *Ph*$_{\rm meta}$), 7.18 (m, 2H, *Ph*$_{\rm ortho}$) 9.49 (s, 1H, FeSC*H*NPh). ^{31}P{^{1}H} NMR: δ 70.7 (s). ^{13}C{^{1}H} NMR: δ 17.0 (br s, P*C*H$_3$), 24.8 (br s, P*C*H$_3$), 32.4 (s, P*C*H$_2$), 120.5 (s, *Ph*$_{\rm meta}$), 122.0 (s, *Ph*$_{\rm para}$), 129.1 (s, *Ph*$_{\rm ortho}$), 155.4 (s, *Ph*$_{\rm ipso}$), 177.8 (s, FeS*C*HNPh). IR (KBr disk, cm^{-1}): 1590 (ν(C=N)), 1789 (ν(Fe−H)), 2900 (ν(S*CH*NPh)).

Reaction between *cis*-Fe(dmpe)$_2$H$_2$ (1) and Phenyl Isothiocyanate at Lower Temperature. Phenyl isothiocyanate (11.3 mg, 0.084 mmol) in tetrahydrofuran-d_8 (0.3 mL) was added portionwise at 250 K to an NMR tube containing a solution of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) (30 mg, 0.084 mmol) in tetrahydrofuran-d_8 (0.5 mL). NMR spectroscopy indicated the formation of five products in varying amounts, including *trans*-Fe(dmpe)$_2$(SCHNPh)H (**3a**) (approximately 80%) and *cis*-Fe(dmpe)$_2$(SCHNPh)H (**3b**). Upon warming to 280 K, only **3a** and **3b** remained in solution, and further warming to 300 K resulted in quantitative formation of **3a**.

(OC-6-24)-Bis(1,2-bis(dimethylphosphino)ethane)hydrido(*N*-phenylthioformimidato)iron(II), *cis*-Fe(dmpe)$_2$(SCHNPh)H (3b). ^{1}H NMR (tetrahydrofuran-d_8, 260 K): δ −11.46 (ddt, $^2J_{\rm PH} = 64$, 54, 31 Hz, 1H, Fe-*H*), 8.71 (s, 1H, FeSC*H*NPh). ^{31}P{^{1}H} NMR: δ 56.2 (dt, $J = 32$, 21 Hz), 67.6 (ddd, $J = 141$, 41, 21 Hz), 72.6 (ddd, $J = 141$, 41, 32 Hz), 74.6 (dt, $J = 41$, 21 Hz).

(OC-6-12)-Bis(1,2-bis(dimethylphosphino)ethane)bis(*N*-phenylthioformimidato)iron(II), *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (3c). Phenyl isothiocyanate (23 mg, 0.17 mmol) in benzene-d_6 (0.5 mL) was added portionwise at 300 K to an NMR tube containing a solution of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) (30 mg, 0.084 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative formation of **3c** after 3 h. Concentration of the solvent precipitated dark purple crystals of **3c** which were collected and washed with ether to afford **3c** as a dark purple crystalline solid in analytically pure form (22 mg, 42%).

Anal. Calcd for C$_{26}$H$_{44}$N$_2$P$_4$S$_2$Fe: C, 49.68; H, 7.06; N, 4.46. Found: C, 49.9; H, 7.2; N, 4.7. ^{1}H NMR (benzene-d_6, 300 K): δ 1.41 (br s, 24H, PC*H*$_3$), 2.32 (br s, 8H, PC*H*$_2$), 6.91 (m, 6H, *Ph*$_{\rm meta}$ + *Ph*$_{\rm para}$), 7.15 (m, 4H, *Ph*$_{\rm ortho}$), 8.76 (p, $^4J_{\rm PH} = 2$ Hz, 2H, FeSC*H*NPh). ^{31}P{^{1}H} NMR: δ 60.3 (s). ^{13}C{^{1}H} NMR: δ 16.8 (p, $J_{\rm CP} = 7$ Hz, P*C*H$_3$), 31.8 (p, $J_{\rm CP} = 11$ Hz, P*C*H$_2$), 120.4 (s, *Ph*$_{\rm meta}$), 123.0 (s, *Ph*$_{\rm para}$), 129.2 (s, *Ph*$_{\rm ortho}$), 154.1 (s, *Ph*$_{\rm ipso}$), 174.2 (p, $^3J_{\rm CP} = 6$ Hz, FeS*C*HNPh). IR (KBr disk, cm^{-1}): 1593 (ν(C=N)), 2898 (ν(S*CH*NPh)).

Dark brown crystals of **3c** suitable for structure determination by X-ray analysis were grown by slow evaporation of a solution of **3c** in benzene-d_6 at 300 K.

Reaction between *cis*-Fe(dmpe)$_2$H$_2$ (1) and Ethyl Isothiocyanate. Ethyl isothiocyanate (7.3 mg, 0.084 mmol) in benzene-d_6 (0.3 mL) was added portionwise at 300 K to an NMR tube containing a solution of *cis*-Fe(dmpe)$_2$H$_2$ (**1**) (30 mg, 0.084 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative reaction of **1** to form two new products: *trans*-Fe(dmpe)$_2$(SCHNEt)H (**4a**) and *cis*-Fe(dmpe)$_2$(SCHNEt)H (**4b**) in a 1:1.25 ratio. With heat, or on standing, **4a** was formed exclusively within 3 h. Removal of solvent and recrystallization from ether afforded **4a** as a red oil which crystallized on standing (31 mg, 84%).

(OC-6-32)-Bis(1,2-bis(dimethylphosphino)ethane)hydrido(*N*-ethylthioformimidato)iron(II), *trans* -Fe(dmpe)$_2$(SCHNEt)H (4a). Mp 42−45 °C. HRMS (ES) calcd for C$_{15}$H$_{38}$NP$_4$SFe $(M - 1)^+$: requires 444.1025, found 444.1015. ^{1}H NMR (benzene-d_6, 300 K): δ −25.38 (p, $^2J_{\rm PH} = 51$ Hz, 1H, Fe-*H*), 1.10 (br s, 12H, PC*H*$_3$), 1.19 (t, $^3J_{\rm HH} = 8$ Hz, 3H, FeSCHNCH$_2$C*H*$_3$), 1.43 (m, 4H, PC*H*$_2$), 1.54 (br s, 12H, PC*H*$_3$), 2.25 (m, 4H, PC*H*$_2$), 3.37 (q, $^3J_{\rm HH} = 8$ Hz, 2H, FeSCHNC*H*$_2$CH$_3$), 9.03 (s, 1H, FeSC*H*NEt). ^{31}P{^{1}H} NMR: δ 71.3 (s). ^{13}C{^{1}H} NMR: δ 17.0 (m, P*C*H$_3$), 18.0 (s, FeSCHNCH$_2$*C*H$_3$), 24.9 (m, P*C*H$_3$), 32.4 (s, P*C*H$_2$), 55.7 (s, FeSCHN*C*H$_2$CH$_3$), 172.4 (p, $^3J_{\rm CP} = 5$ Hz, FeS*C*HNEt). IR (KBr disk, cm^{-1}): 1540 (ν(C=N)), 1785 (ν(Fe−H)), 2898 (ν(S*CH*NEt)).

(OC-6-24)-Bis(1,2-bis(dimethylphosphino)ethane)hydrido(*N*-ethylthioformimidato)iron(II), *cis*-Fe(dmpe)$_2$(SCHNEt)H (4b). ^{1}H NMR (benzene-d_6, 300 K): δ −11.33 (ddt, $^2J_{\rm PH} = 65$, 55, 32 Hz, 1H, Fe-*H*), 0.68 (m), 0.91 (m), 1.00 (m), 1.19 (t, $^3J_{\rm HH} = 8$ Hz, 3H, FeSCHNCH$_2$C*H*$_3$), 1.30 (m), 1.49 (m), 3.57 (q, $^3J_{\rm HH} = 8$ Hz, 2H, FeSCHNC*H*$_2$CH$_3$), 8.71 (s, 1H, FeSC*H*NEt). ^{31}P{^{1}H} NMR: δ 54.9 (m), 66.5 (ddd, $J = 150$, 41, 22 Hz), 71.0 (ddd, $J = 150$, 41, 32), 73.12 (m). ^{13}C{^{1}H} NMR: δ 15.0−20.0 (m), 18.0 (s, FeSCHNCH$_2$*C*H$_3$), 20.6 (m), 29.4 (m), 33.3 (m), 56.4 (s, FeSCHN*C*H$_2$CH$_3$), 181.7 (s, FeS*C*HNEt).

***trans*-Fe(dmpe)$_2$(SCHN$^+$(Et)C(S)N$^-$(Et))H (4c).** Ethyl isothiocyanate (7.3 mg, 0.084 mmol, 1 equiv) in benzene-d_6 (0.3 mL) was added at 300 K to an NMR tube containing a solution of *trans*-Fe(dmpe)$_2$(SCHNEt)H (**4a**) in benzene-d_6 (0.5 mL) which had been prepared in situ by the reaction between *cis*-Fe(dmpe)$_2$H$_2$ (**1**) (30 mg, 0.084 mmol) and EtNCS (7.3 mg, 0.084 mmol). The reaction mixture was allowed to stand overnight. NMR spectroscopy indicated quantitative reaction of **1** to form *trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (**4c**) and some minor reaction byproducts. Concentration of the solution afforded **4c** as a red crystalline solid which was washed with ether but was not obtained analytically pure (10 mg, 22%).

HRMS (ES) calcd for C$_{18}$H$_{45}$N$_2$P$_4$S$_2$Fe $(M + 1)^+$: requires 533.1324, found 533.1299. ^{1}H NMR (benzene-d_6, 300 K): δ −24.47 (p, $^2J_{\rm PH} = 50$ Hz, 1H, Fe-*H*), 0.98 (br s, 12H, PC*H*$_3$), 1.26 (br s, 12H, PC*H*$_3$), 1.29 (t, $^3J_{\rm HH} = 7$ Hz, 3H, FeSCHN$^+$-CH$_2$C*H*$_3$), 1.35 (m, 4H, PC*H*$_2$), 1.60 (t, $^3J_{\rm HH} = 7$ Hz, 3H, FeSCHN$^+$(Et)C(S)N$^-$CH$_2$C*H*$_3$), 1.85 (m, 4H, PC*H*$_2$), 4.23 (q, $^3J_{\rm HH} = 7$ Hz, 2H, FeSCHN$^+$(Et)C(S)N$^-$C*H*$_2$CH$_3$), 4.69 (q, $^3J_{\rm HH} = 7$ Hz, 2H, FeSCHN$^+$C*H*$_2$CH$_3$) 11.06 (s, 1H, FeSC*H*N). ^{31}P{^{1}H} NMR: δ 68.5 (s). ^{13}C{^{1}H} NMR: δ 12.8 (s, FeSCHN$^+$(Et)-

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$C(S)N^-CH_2CH_3$), 15.5 (m, PCH_3), 16.9 (s, $FeSCHN^+CH_2CH_3$), 24.0 (m, PCH_3), 31.6 (s, PCH_2), 40.4 (s, $FeSCHN^+(Et)C(S)$-$N^-CH_2CH_3$), 49.5 (s, $FeSCHN^+CH_2CH_3$), 169.8 (s, FeS*C*HN), 193.5 (s, $FeSCHN^+(Et)$*C*(S)). IR (KBr disk, cm^{-1}): 984, 1225 (*ν*(C═S)), 1551 (*ν*(C═N)), 1811 (*ν*(Fe−H)), 2900 (*ν*(FeS*CH*N)).

Red crystals of **4c** suitable for structure determination by X-ray analysis were grown at 300 K by slow evaporation of a solution of **4c** in benzene-d_6.

Reaction between *cis*-Fe(dmpe)$_2$H$_2$ (1) and Phenyl Isocyanate. Phenyl isocyanate (18 mg, 0.15 mmol) in benzene-d_6 (0.5 mL) was added portionwise at 300 K to an NMR tube containing a solution of *cis*-$Fe(dmpe)_2H_2$ (**1**) (30 mg, 0.084 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative reaction of **1** to form *trans*-$Fe(dmpe)_2(OCHNPh)H$ (**5a**) and four other products, as well as a red oily precipitate. Filtration, removal of solvent, and recrystallization from ether afforded **5a** as a red solid which could not be separated from other soluble reaction products.

(OC-6-32)-Bis(1,2-bis(dimethylphosphino)ethane)-hydrido(*N*-phenylformimidato)iron(II), *cis*-Fe(dmpe)$_2$-(OCHNPh)H (5a). ^{1}H NMR (benzene-d_6, 300 K): δ −34.31 (p, $^2J_{PH} = 49$ Hz, 1H, Fe-*H*), 1.07 (br s, 12H, PCH_3), 1.39 (br s, 12H, PCH_3), 1.47 (m, 4H, PCH_2), 2.15 (m, 4H, PCH_2), 6.92 (m, 1H, Ph_{para}), 7.02 (m, 2H, Ph_{meta}), 7.26 (m, 2H, Ph_{ortho}), 8.13 (s, 1H, FeOC*H*NPh). ^{31}P{^{1}H} NMR: δ 70.7 (s). ^{13}C{^{1}H} NMR: δ 15.4 (br s, PCH_3), 23.0 (br s, PCH_3), 31.7 (s, PCH_2), 120.0 (s, Ph_{meta}), 121.6 (s, Ph_{para}), 129.0 (s, Ph_{ortho}), 148.7 (s, Ph_{ipso}), 167.8 (s, FeO*C*HNPh). IR (KBr disk, cm^{-1}): 1595 (*ν*(C═N)), 1792 (*ν*(Fe−H)), 2903 (*ν*(O*CH*NPh)). MS *m*/*z* (ES): 476 $(M - 1)^+$, 595 $(M + PhNCO - 1)^+$.

(OC-6-24)-Hydrido(*N*-phenylthioformimidato)(tris(2-dimethylphosphinoethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)-(SCHNPh)H (6a). Phenyl isothiocyanate (7.8 mg, 0.058 mmol) in benzene-d_6 (0.3 mL) was added portionwise at 300 K to an NMR tube containing a solution of *cis*-$Fe(PP_3)H_2$ (**2**) (20 mg, 0.058 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative formation of **6a**. Removal of solvent and recrystallization from ether afforded **6a** as a yellow solid (16 mg, 57%).

Mp 200−205 °C (dec). HRMS (ES) calcd for $C_{19}H_{36}NP_4SFe$ $(M - 1)^+$: requires 490.0868, found 490.0838. ^{1}H NMR (benzene-d_6, 300 K): δ −14.05 (ddt, $J_{PTH} = 66$ Hz, $J_{PAH} = 42$ Hz, $J_{PEH} = 33$ Hz, 1H, Fe-*H*), 0.90−1.15 (m, 12H, $P_A(CH_2CH_2P(CH_3)_2)$, 1.28, 1.57 (2 × m, 2 × 6H, 2 × $P_T(CH_3)$), 1.42 (m, 6H, $P_E(CH_3)_2$), 6.95 (m, 1H, Ph_{para}), 7.15 (m, 2H, Ph_{meta}), 7.23 (m, 2H, Ph_{ortho}), 9.70 (p, $^4J_{PH} = 2.5$ Hz, 1H, FeSC*H*NPh). ^{31}P{^{1}H} NMR: δ 180.4 (dt, $J_{PAPT} = 30$ Hz, $J_{PAPE} = 22$ Hz, 1P, P_A), 62.8 (dd, $J_{P_TP_A} = 30$ Hz, $J_{P_TP_E} = 22$ Hz, 2P, P_T), 60.8 (q, $J = 22$ Hz, 1P, P_E). ^{13}C{^{1}H} NMR: δ 19.3 (m), 20.7 (m), 24.9 (m), 27.3 (m), 30.2 (s), 35.4 (m), 36.3 (m) ($P_A(CH_2CH_2P(CH_3)_2)_3$), 120.8 (Ph_{meta}), 121.8 (Ph_{para}), 129.1 (Ph_{ortho}), 156.3 (Ph_{ipso}), 178.7 (m, FeS*C*HNPh). IR (KBr disk, cm^{-1}): 1494 (*ν*(C═N)), 1802 (*ν*(Fe−H)), 2897 (*ν*(S*CH*NPh)).

Reaction between *cis*-Fe(PP$_3$)(SCHNPh)H (6a) and Excess Phenyl Isothiocyanate. Phenyl isothiocyanate (7.8 mg, 0.058 mmol) in benzene-d_6 (0.3 mL) was added at 300 K to an NMR tube containing a solution of *cis*-$Fe(PP_3)(SCHNPh)H$ (**6a**) in benzene-d_6 (0.5 mL) which had been prepared in situ by the reaction between *cis*-$Fe(PP_3)H_2$ (**2**) (20 mg, 0.058 mmol) and phenyl isothiocyanate (7.8 mg, 0.058 mmol). Over 7 h, **6a** reacted until no ^{31}P-containing material was left in solution. Large amounts of a cream-colored precipitate were formed. The precipitate was collected and washed with ether to afford a cream solid which was only slightly soluble in tetrahydrofuran, forming a red solution. ^{31}P NMR showed the presence of two products in the ratio 2.5:1, and the major product was assigned as *cis*-$Fe(PP_3)(SCHNPh)_2$ (**6b**). The minor product was not further characterized.

(OC-6-23)-Bis(*N*-phenylthioformimidato)(tris(2-dimethylphosphinoethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)-(SCHNPh)$_2$ (6b). HRMS (ES) calcd for $C_{26}H_{41}N_2P_4S_2Fe$ $(M - 1)^+$: requires 625.1011, found 625.1011. ^{1}H NMR (tetrahydrofuran-d_8, 300 K): δ 0.48−2.65 (m, 30H, $P_A(CH_2CH_2P(CH_3)_2)$, 6.80−7.40 (m, 10H, *Ph*), 9.26 (s, 1H, FeSC*H*NPh*(trans to* P_A*)*), 9.63 (s, 1H, FeSC*H*NPh*(trans to* P_E*)*). ^{31}P{^{1}H} NMR: δ 178.4 (dt (apparent q), $J = 23$ Hz, 1P, P_A), 73.3 (dt, $J_{P_EP_T} = 42$ Hz, $J_{P_EP_A} = 23$ Hz, 1P, P_E), 53.6 (dd, $J_{P_TP_E} = 42$ Hz, $J_{P_TP_A} = 23$ Hz, 2P, P_T). ^{13}C{^{1}H} NMR: δ 15.8 (m), 20.7 (m), 21.6 (br s), 26.7 (m), 30.1 (m), 32.5 (m), 35.2 (m) ($P_A(CH_2CH_2P(CH_3)_2)$, 120.8, 120.6, 122.7, 123.2, 127.0, 131.5, 152.3, 155.4 (*Ph*), 176.8 (m, FeS*C*HNPh*(trans to* P_A*)*), 176.4 (m, FeS*C*HNPh*(trans to* P_E*)*). IR (KBr disk, cm^{-1}): 1590 (*ν*(C═N)), 2903 (*ν*(S*CH*NPh)).

(OC-6-24)-Hydrido(*N*-ethylthioformimidato)(tris(2-dimethylphosphinoethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)-(SCHNEt)H (7a). Ethyl isothiocyanate (5 mg, 0.058 mmol) in benzene-d_6 (0.2 mL) was added portionwise at 300 K to an NMR tube containing a solution of *cis*-$Fe(PP_3)H_2$ (**2**) (20 mg, 0.058 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated quantitative formation of **7a**. Removal of solvent and recrystallization from ether afforded **7a** as a bright yellow solid (17 mg, 65%).

Mp 185 °C (dec). HRMS (ES) calcd for $C_{15}H_{36}NP_4SFe$ $(M - 1)^+$: requires 442.0868, found 442.0886. ^{1}H NMR (benzene-d_6, 300 K) δ −13.92 (ddt, $J_{P_TH} = 66$ Hz, $J_{P_AH} = 41$ Hz, $J_{P_EH} = 34$ Hz, 1H, Fe-*H*), 0.95−1.16 (m, 12H, $P_A(CH_2CH_2P(CH_3)_2)$, 1.10 (t, $^3J_{HH} = 7$ Hz, 3H, $FeSCHNCH_2CH_3$), 1.29, 1.59 (2 × m, 2 × 6H, 2 × $P_T(CH_3)$), 1.43 (m, 6H, $P_E(CH_3)_2$), 3.56 (q, $^3J_{HH} = 7$ Hz, 2H, $FeSCHNCH_2CH_3$), 9.31 (br s, 1H, FeSC*H*NEt). ^{31}P{^{1}H} NMR: δ 181.0 (dt, $J_{P_AP_T} = 30$ Hz, $J_{P_AP_E} = 24$ Hz, 1P, P_A), 62.8 (dd, $J_{P_TP_A} = 30$ Hz, $J_{P_TP_E} = 24$ Hz, 2P, P_T), 61.2 (q, $J = 24$ Hz, 1P, P_E). ^{13}C{^{1}H} NMR: δ 18.2 (s, $FeSCHNCH_2CH_3$), 19.3 (m), 20.7 (m), 25.0 (m), 27.4 (m), 30.2 (s), 35.5 (m), 36.3 (m) ($P_A(CH_2CH_2P(CH_3)_2)_3$), 55.8 (s, $FeSCHNCH_2CH_3$), 173.6 (m, FeS*C*HNEt). IR (KBr disk, cm^{-1}): 1543 (*ν*(C═N)), 1803 (*ν*(Fe−H)), 2898 (*ν*(S*CH*NEt)).

(OC-6-24)-Hydrido(*N*-phenylformimidato)(tris(2-dimethylphosphinoethyl)phosphine)iron(II), *cis*-Fe(PP$_3$)-(OCHNPh)H (8a). Phenyl isocyanate (7 mg, 0.058 mmol) in benzene-d_6 (0.3 mL) was added portionwise at 300 K to an NMR tube containing a solution of *cis*-$Fe(PP_3)H_2$ (**2**) (20 mg, 0.058 mmol) in benzene-d_6 (0.5 mL). NMR spectroscopy indicated essentially quantitative formation of **8a**. Removal of solvent and recrystallization from ether afforded **8a** as a bright yellow solid which was not further purified (14 mg, 50%).

Mp 210 °C (dec). ^{1}H NMR (benzene-d_6, 300 K): δ −13.07 (m, 1H, Fe-*H*), 0.90−1.48 (m, 12H, $P_A(CH_2CH_2P(CH_3)_2)$, 1.09, 1.56 (2 × br s, 2 × 6H, 2 × $P_T(CH_3)$), 1.46 (s, 6H, $P_E(CH_3)_2$), 6.94 (m, 1H, Ph_{para}), 7.11−7.23 (m, 4H, $Ph_{ortho} + Ph_{meta}$) 8.81 (s, 1H, FeOC*H*NPh). ^{31}P{^{1}H} NMR: δ 173.3 (dt, $J_{P_AP_T} = 33$ Hz, $J_{P_AP_E} = 23$ Hz, 1P, P_A), 56.2 (dd, $J_{P_TP_A} = 33$ Hz, $J_{P_TP_E} = 23$ Hz, 2P, P_T), 55.1 (q, $J = 23$ Hz, 1P, P_E). ^{13}C{^{1}H} NMR: δ 19.7 (m), 20.5 (m), 25.3 (m), 27.9 (m), 30.2 (s), 35.6 (q, $J = 16$ Hz), 36.9 (dd, $J = 16, 25$ Hz) ($P_A(CH_2CH_2P(CH_3)_2)_3$), 55.8 (s, $FeSCHNCH_2CH_3$), 122.1 ($Ph_{meta} + Ph_{para}$), 128.7 (Ph_{ortho}), 160.6 (Ph_{ipso}), 170.3 (m, FeO*C*HNPh). IR (KBr disk, cm^{-1}): 1571 (*ν*(C═N)), 1794 (*ν*(Fe−H)), 2900 (*ν*(O*CH*NPh)). MS *m*/*z* (ES): 474 $(M - 1)^+$.

X-ray Measurements for *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (3c) and *trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (4c). A summary of crystal data for **3c** and **4c** is given in Table 4.

***trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (3c).** A dark brown bladelike crystal was attached, with Exxon Paratone N, to a short length of fiber supported on a thin piece of copper wire inserted in a copper mounting pin and was quenched in a cold nitrogen gas stream upon mounting on a Bruker SMART 1000 diffractometer equipped with an Oxford Cryosystems Cryostream. Graphite-monochromated Mo Kα radiation was generated from a sealed tube. Cell constants were obtained from a least squares refinement against 916 reflections located in the range $5.15 < 2\theta < 56.29°$. Data were collected at 173(1) K with ω scans to $2\theta = 56.62°$. The intensities of 189 standard reflections recollected at the end of the experiment did not change significantly during the data collection. An empirical correction, determined with SADABS,[40] was applied to the data. The data integration and reduction were undertaken with SAINT and XPREP,[41] and subsequent computations were carried out with the teXsan[42] graphical user interface. The data reduction included the application of Lorentz and polarization corrections. The structure was solved in the space group $P2_1/c$ (No. 14) by direct methods with SIR97[43] and extended and refined with SHELXL-97.[44] The molecule is centered on an inversion site. Most of the non-hydrogen atoms were modeled with anisotropic thermal parameters, and a riding atom model was used for the hydrogen atoms included in the model. The ligand backbone adopted at least two orientations, and the populations of the disordered backbone C(3) and C(4) sites were initially refined and then fixed at 0.5. The disordered atoms were modeled with isotropic temperature factors.

***trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (4c).** A red prismatic crystal was inserted in a glass capillary before mounting on a Bruker SMART 1000 CCD. Graphite-monochromated Mo Kα radiation was generated from a sealed tube. Cell constants were obtained from a least squares refinement against 929 reflections located in the range $4.47 < 2\theta < 51.02°$. Data were collected at 294(2) K with ω scans to $2\theta = 56.74°$. The data integration and reduction were undertaken with SAINT and XPREP,[41] and subsequent computations were carried out with the teXsan[42] graphical user interface. The data reduction included the application of Lorentz and polarization correctionsand a Gaussian absorption correction. The structure was solved in the space group $P\bar{1}$ (No. 2) by direct methods with SIR97[43] and extended and refined with SHELXL-97.[44] The asymmetric unit contained a complex molecule and a highly disordered solvate region. The non-hydrogen atoms of the complex molecule were modeled with anisotropic thermal parameters, and a riding atom model was used for the hydrogen atoms, with the exception of the hydride, which was located and modeled with an isotropic thermal parameter. The disordered solvate molecule region could not be clearly resolved, but is confined to a plane and suggests almost continuous rotational disorder about an axis perpendicular to the solvate molecule plane. Individual solvate molecules could not be discerned. The solvate molecules were assumed to be benzene in at least two overlapping locations, and 12 carbon atoms were assigned to the region with occupancies fixed at 0.25%, i.e., two complex molecules for every benzene molecule. No hydrogen atoms were included in the model for the solvate molecule.

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Supporting Information Available: X-ray crystallographic data files, in CIF format, for *trans*-Fe(dmpe)$_2$(SCHNPh)$_2$ (**3c**) and *trans*-Fe(dmpe)$_2$(SC(H)N$^+$(Et)C(S)N$^-$(Et))H (**4c**) and ^{31}P NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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