Supporting Information

Dehydrogenative desulfurization of thiourea derivatives to give carbodiimides, using hydrosilane and an iron complex

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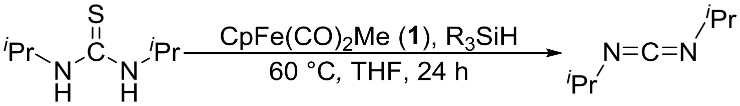
General method for control experiments

THF (3.0 mL), **1** (57.5 mg, 3.0 mmol), ^{i}PrNHC(S)NH^{i}Pr (3.0 mmol), and silane (3.0 mmol) were charged in a Schlenk tube, and the solution was heated at 60 °C for 24 h. 1,3,5-trimethylbenzene (428 μL, 3.0 mmol) was added to the solution as an internal standard and GC-MS spectrum was measured. The amount of ^{i}PrN=C=N^{i}Pr produced was evaluated by relative intensity of signals of the product and the internal standard. These results were shown in Table S2.

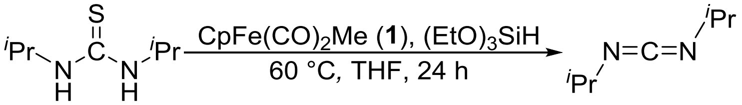
Table S2. Conversion of thiourea into carbodiimide by using various hydrosilanes with the help of 1



Entry	Silane	GC-MS Yield (%)
1	Et_3SiH	34
2	$^nPr_3SiH$	29
3	$^iPr_3SiH$	44
4	$^nBu_3SiH$	24
5	$^tBu_3SiH$	30
6	$(EtO)Me_2SiH$	27
7	$(EtO)_2MeSiH$	31
8	$(EtO)_3SiH$	56
9	$PhMe_2SiH$	20
10	Ph_2MeSiH	29
11	Ph_3SiH	45

THF (3.0 mL), **1** (0.3-9.0 mmol), ^{i}PrNHC(S)NH^{i}Pr (3.0 mmol), and $(EtO)_3SiH$ (1.5-15.0 mmol) were charged in a Schlenk tube, and the solution was heated at 60 °C for 24 h. 1,3,5-trimethylbenzene (428 μL, 3.0 mmol) was added to the solution as an internal standard and GC-MS spectrum was measured. The amount of ^{i}PrN=C=N^{i}Pr produced was evaluated by relative intensity of signals of the product and the internal standard. These results were shown in Table S3.

Table S3. Molar ratio of 1 : ^{i}PrNHC(S)NH^{i}Pr : $(EtO)_3SiH$



Entry	[M] : [S] : [Si][a]	GC-MS Yield (%)[b]	TON
1	1 : 1 : 1	59	-
2	1 : 1 : 2	25	-
3	2 : 1 : 1	76	-
4	2 : 1 : 2	30	-
5	3 : 1 : 1	60	-
6	1 : 2 : 1	20	0.4
7	1 : 2 : 2	29	0.6
8	1 : 2 : 5	22	0.4
9	1 : 10 : 10	10	1.0

[a] Molar ratio of **1** : ^{i}PrNHC(S)NH^{i}Pr : $(EtO)_3SiH$. [b] The values are based on the concentration of ^{i}PrNHC(S)NH^{i}Pr.

Result of X-ray diffraction study of 5.

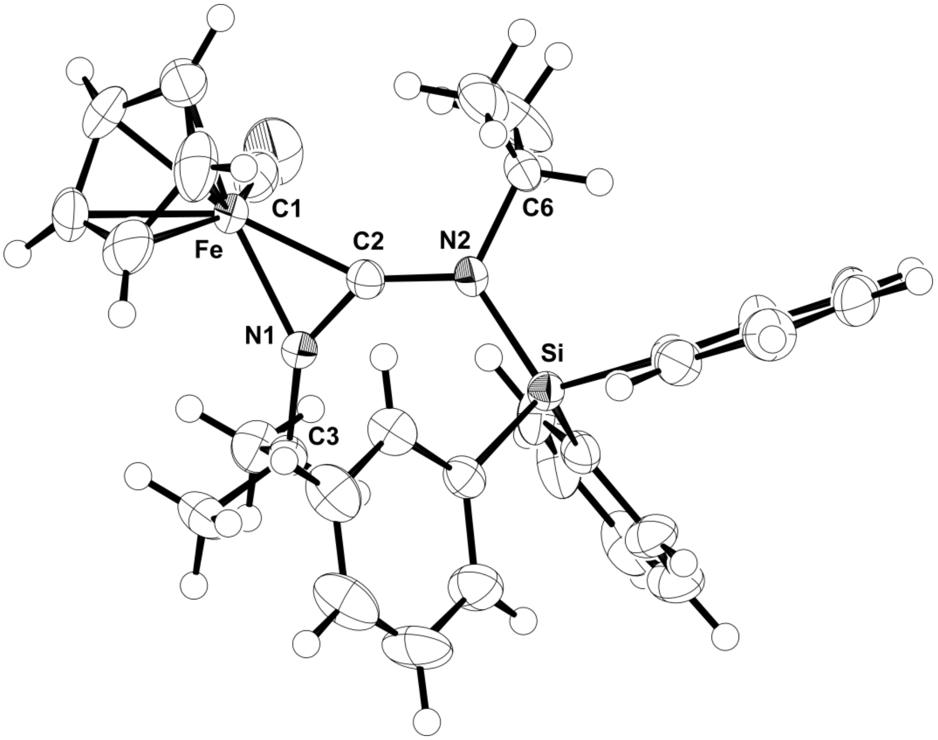


Figure S1. ORTEP drawing of 5 showing the number system.

Table S1. Selected bond distances (Å), angles (°) and a dihedradangle (°).

Fe−C1	1.724(5)	C1−Fe−C2	93.54(18)	C2−N2−C6	116.7(3)
Fe−C2	1.917(4)	C1−Fe−N1	97.61(18)	C2−N2−Si	122.8(3)
Fe−N1	1.937(3)	N1−Fe−C2	38.14(13)	C6−N2−Si	120.5(2)
C2−N1	1.259(4)	Fe−C2−N1	71.8(2)		
C2−N2	1.366(4)	Fe−C2−N2	152.6(3)	N1−Fe−C2−N2	−179.7(7)
N1−C3	1.464(5)	N1−C2−N2	135.6(3)		
N2−C6	1.495(5)	Fe−N1−C2	70.1(2)		
N2−Si	1.761(3)	Fe−N1−C3	141.3(2)		
		C2−N1−C3	143.4(3)		