4560 *Inorg. Chem.* **1990**, *29*, 4560-4565

Contribution No. 8116 from the Arnold and Mabel Beckman Laboratories
of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Hydrazido(1–) and 2,2-Dimethylhydrazido(1–) Derivatives of Permethylscandocene. Preparation and Structural Characterization of Their Products from Reactions with Acetonitrile: $(\eta^5\text{-}C_5Me_5)_2\overline{ScN(H)C(CH_3)NN}H_2$ and $(\eta^5\text{-}C_5Me_5)_2\overline{ScN(H)C(CH_3)N}NMe_2$

Pamela J. Shapiro, Lawrence M. Henling, Richard E. Marsh, and John E. Bercaw*

Received March 28, 1990

A rare example of an unsubstituted hydrazido(1–) complex, $Cp^*{}_2ScN(H)NH_2$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$), prepared by reaction of 1 equiv of anhydrous hydrazine with $Cp^*{}_2ScCH_3$, reacts with acetonitrile to form $Cp^*{}_2\overline{ScN(H)C(CH_3)NN}H_2$. The crystal structure of $Cp^*{}_2\overline{ScN(H)C(CH_3)NN}H_2$ (monoclinic system, space group $P2_1/n$ (No. 14), with a = 9.506 (3) Å, b = 14.742 (2) Å, c = 15.609 (2) Å, β = 92.45 (2)°, V = 2187.3 (8) Å^3, Z = 4, and d = 1.177 g·cm^{-3}) reveals a five-membered, nearly planar $[\overline{ScN(H)C(CH_3)NN}H_2]$ ring. The results of a labeling study using $^{15}N{\equiv}CCH_3$ are consistent with a mechanism involving insertion of acetonitrile into the Sc—N bond of $Cp^*{}_2ScNHNH_2$, followed by tautomerization to form $Cp^*{}_2\overline{ScN(H)C(CH_3)NN}H_2$. The closely related compounds $Cp^*{}_2ScN(H)NMe_2$ and $Cp^*{}_2\overline{ScN(H)C(CH_3)N}NMe_2$ also have been prepared by using an analogous reaction pathway, and the structure of the latter has been determined as well (monoclinic system, space group $P2_1/n$ (No. 14), with a = 10.953 (2) Å, b = 19.733 (1) Å, c = 11.441 (1) Å, β = 101.30 (1)°, V = 2424.9 (5) Å^3, Z = 4, and d = 1.138 g·cm^{-3}), revealing a four-membered, nearly planar $[\overline{ScN(H)C(CH_3)N}(NMe_2)]$ ring.

Introduction

Although unsubstituted hydrazido(1–) metal complexes (i.e. $L_nMN(H)NH_2$) are of interest as possible intermediates in the transition-metal-promoted reduction of dinitrogen to hydrazine,[1] they have proven to be somewhat elusive, presumably due to the instability of the highly reducing $N_2H_3^-$ ion.[2] Thus, there are relatively few reported examples of complexes having unsubstituted hydrazido(1–) as a ligand,[3] two of which have been recently confirmed by X-ray structures.[3d] By contrast, there are several examples of fully characterized, substituted hydrazido(1–) species that serve as models for the parent unsubstituted system.[4-6]

We report herein the preparation and characterization of a relatively stable unsubstituted hydrazido(1–) derivative of permethylscandocene, $Cp^*{}_2ScN(H)NH_2$ (**1**) ($Cp^* = (\eta^5\text{-}C_5Me_5)$), the analogous 2,2-dimethyl-substituted hydrazido(1–) derivative, $Cp^*{}_2ScN(H)NMe_2$ (**2**), and some studies of their reactions with acetonitrile.

Results

Scandium hydrazido(1–) complexes were prepared by the method shown in eq 1.

$$Cp^*{}_2ScCH_3 + H_2NNRR' \rightarrow Cp^*{}_2ScN(H)NRR' + CH_4 \quad (1)$$

$$\mathbf{1}, R = R' = H$$

$$\mathbf{2}, R = R' = CH_3$$

Table I. Crystallographic Data for $Cp^*{}_2\overline{ScN(H)C(CH_3)NN}H_2$ (**3**) and for $Cp^*{}_2\overline{ScN(H)C(CH_3)N}NMe_2$ (**4**)

formula	$ScN_3C_{22}H_{36}$	$ScN_3C_{24}H_{40}$
fw	387.50	415.56
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	9.506 (3)	10.953 (2)
b, Å	14.742 (2)	19.733 (1)
c, Å	15.609 (2)	11.441 (1)
V, Å^3	2187.3 (8)	2424.9 (5)
β, deg	92.45 (2)	101.30 (1)
Z	4	4
μ, cm^{-1}	3.54	3.24
λ, Å	0.71073	0.71073
T, K	294	294
final R index ($F_o^2 > 0$); reflns	0.117; 3276	0.064; 2089
final R index [$F_o^2 > 3\sigma(F_o^2)$]; reflns	0.051; 2604	0.0416; 1540
goodness of fit; params; reflns	1.34; 380; 3855	1.78; 253; 2267

Table II. Non-Hydrogen Atom Coordinates and Displacement Parameters for $Cp^*{}_2\overline{ScN(H)C(CH_3)NN}H_2$

atom	10^4x	10^4y	10^4z	10^4U_{eq}[a]
Sc	3113 (0.8)	2326 (0.4)	359 (0.5)	337 (2)
N1	4588 (4)	1152 (3)	65 (2)	421 (11)
N2	4191 (4)	662 (2)	–739 (2)	471 (10)
N3	2168 (4)	1543 (3)	–660 (2)	462 (11)
C1	2925 (5)	914 (3)	–1019 (3)	427 (12)
C2	2421 (10)	438 (6)	–1830 (5)	692 (20)
Cp1	2796 (4)	2455 (3)	1952 (2)	402 (11)
Cp2	1472 (4)	2677 (3)	1552 (2)	425 (11)
Cp3	972 (4)	1890 (3)	1136 (2)	434 (12)
Cp4	1935 (4)	1180 (3)	1284 (2)	407 (11)
Cp5	3068 (4)	1543 (3)	1785 (2)	390 (11)
Cp6	3731 (5)	4001 (2)	383 (3)	438 (12)
Cp7	5007 (4)	3517 (2)	293 (3)	395 (11)
Cp8	4947 (4)	3109 (2)	–519 (3)	394 (11)
Cp9	3641 (5)	3308 (3)	–926 (3)	430 (12)
Cp10	2886 (4)	3845 (2)	–365 (3)	421 (11)
Me1	3658 (8)	3006 (5)	2591 (4)	673 (19)
Me2	644 (7)	3527 (4)	1665 (5)	691 (18)
Me3	–434 (6)	1798 (5)	651 (5)	710 (20)
Me4	1749 (9)	227 (4)	989 (5)	672 (19)
Me5	4299 (7)	1002 (5)	2162 (4)	647 (17)
Me6	3497 (10)	4716 (4)	1045 (5)	726 (20)
Me7	6279 (7)	3554 (6)	904 (5)	746 (19)
Me8	6150 (6)	2660 (4)	–951 (4)	661 (16)
Me9	3249 (10)	3083 (5)	–1833 (4)	743 (21)
Me10	1431 (7)	4241 (5)	–583 (5)	761 (20)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i^*a_j^*)(\vec{a}_i\cdot\vec{a}_j)]$.

Compounds **1** and **2** react with acetonitrile to form the heterometallacycles $Cp^*{}_2\overline{ScN(H)C(CH_3)NN}H_2$ and $Cp^*{}_2\overline{ScN\text{-}}$

---

(1) (a) Henderson, R. A.; Leigh, G. S.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197. (b) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(2) (a) Latham, I. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 399. (b) Clark, C. C. *Hydrazine*; Mathieson Chemical Corp.: MD, 1953; Chapter 1.

(3) (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123-175. (b) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 71. (c) Murray, R. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4557. (d) Schrock, R. R.; Liu, A. H.; O'Regan, M. B.; Finch, W. C.; Payack, J. F. *Inorg. Chem.* **1988**, *27*, 3574.

(4) (a) Carroll, J. A.; Sutton, D.; Cowie, M.; Gauthier, M. D. *J. Chem. Soc., Chem. Commun.* **1979**, 1058. Carroll, J. A.; Sutton, D. *Inorg. Chem.* **1980**, *19*, 3137. (b) Cowie, M.; Gautier, M. D. *Inorg. Chem.* **1980**, *19*, 3142. (c) Chatt, J.; Dilworth, J. R.; Dahlstrom, J. R.; Zubieta, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 786. (d) Dilworth, J. R.; Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Chem. Commun.* **1983**, 1368. (e) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 385.

(5) (a) Barrientos-Penna, C. K.; Campana, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D.; Tracey, A. S. *Inorg. Chem.* **1984**, *23*, 363. (b) Nicholson, T.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 367. (c) Nicholson, T.; Zubieta, J. *Polyhedron* **1988**, *7*, 171.

(6) (a) Fitzroy, M. D.; Frederiksen, J. M.; Murray, K. S.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 3265. (b) Butcher, A. V.; Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 921. (c) Mattes, R.; Scholand, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22* (3), 245.

0020-1669/90/1329-4560$02.50/0

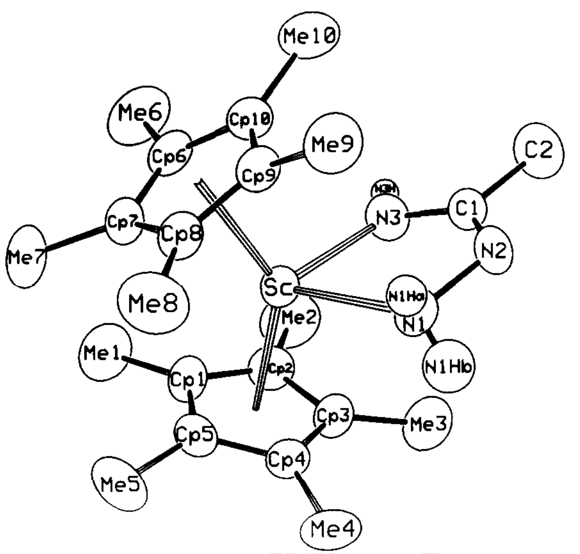


Figure 1. ORTEP drawing of $Cp^*_2ScN(H)C(CH_3)NNH_2$ (3). Thermal ellipsoids are shown at the 50% probability level; methyl hydrogen atoms are omitted for clarity.

Table III. Non-Hydrogen Atom Coordinates and Displacement Parameters for $Cp^*_2ScN(H)C(CH_3)NN(CH_3)_2$

atom	10^4x	10^4y	10^4z	10^4U_{eq}[a]
Sc	8390 (0.7)	1456 (0.4)	7213 (0.7)	390 (2)
Cp1	10255 (4)	2235 (2)	7708 (4)	432 (13)
Cp2	9191 (4)	2629 (2)	7718 (4)	412 (13)
Cp3	8672 (4)	2427 (2)	8689 (4)	427 (13)
Cp4	9391 (5)	1898 (2)	9270 (4)	463 (14)
Cp5	10372 (4)	1778 (2)	8665 (4)	486 (15)
Me1	11218 (4)	2396 (3)	6972 (4)	716 (16)
Me2	8757 (5)	3208 (3)	6898 (4)	703 (16)
Me3	7556 (5)	2759 (2)	9045 (4)	712 (16)
Me4	9265 (5)	1579 (3)	10434 (4)	830 (19)
Me5	11444 (5)	1304 (3)	9107 (4)	841 (18)
Cp6	8881 (4)	1176 (2)	5204 (4)	438 (13)
Cp7	9713 (4)	788 (2)	6021 (4)	465 (14)
Cp8	9013 (4)	318 (2)	6543 (4)	446 (14)
Cp9	7750 (4)	394 (2)	5994 (4)	448 (14)
Cp10	7675 (4)	925 (2)	5171 (4)	438 (14)
Me6	9189 (4)	1714 (3)	4357 (4)	707 (16)
Me7	11110 (4)	744 (3)	6111 (4)	727 (17)
Me8	9544 (5)	-243 (3)	7387 (5)	748 (17)
Me9	6687 (5)	-72 (3)	6089 (4)	673 (16)
Me10	6525 (5)	1124 (3)	4287 (4)	759 (17)
N1	6166 (4)	702 (2)	8743 (4)	775 (15)
N2	6758 (4)	1164 (2)	8055 (4)	583 (13)
N3	6592 (4)	1925 (2)	6619 (4)	632 (14)
C1	6017 (4)	1516 (3)	7230 (6)	664 (20)
C2	4611 (5)	1451 (3)	6998 (6)	1175 (27)
C3	7028 (6)	162 (3)	9191 (5)	890 (20)
C4	5807 (6)	1050 (3)	9755 (6)	1227 (23)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$.

$(H)C(CH_3)NNMe_2$ (eqs 2 and 3), which have been crystallographically characterized. ORTEP drawings of complexes 3 and 4 are shown in Figures 1–3. X-ray crystallographic data are presented in Tables I–V.

$$\underset{1}{Cp^*_2ScN(H)NH_2} + CH_3C{\equiv}N \rightarrow \underset{3}{Cp^*_2ScN(H)C(CH_3)NNH_2} \quad (2)$$

$$\underset{2}{Cp^*_2ScN(H)NMe_2} + CH_3C{\equiv}N \rightarrow \underset{4}{Cp^*_2ScN(H)C(CH_3)NNMe_2} \quad (3)$$

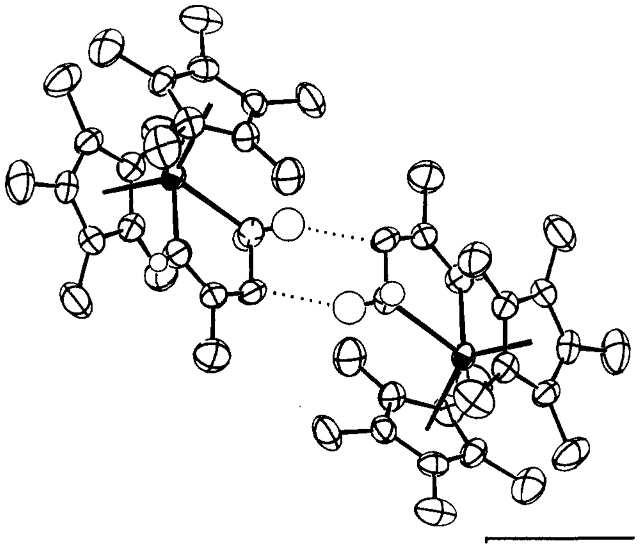


Figure 2. ORTEP drawing of hydrogen-bonded $Cp^*ScN(H)C(CH_3)NNH_2$ pair.

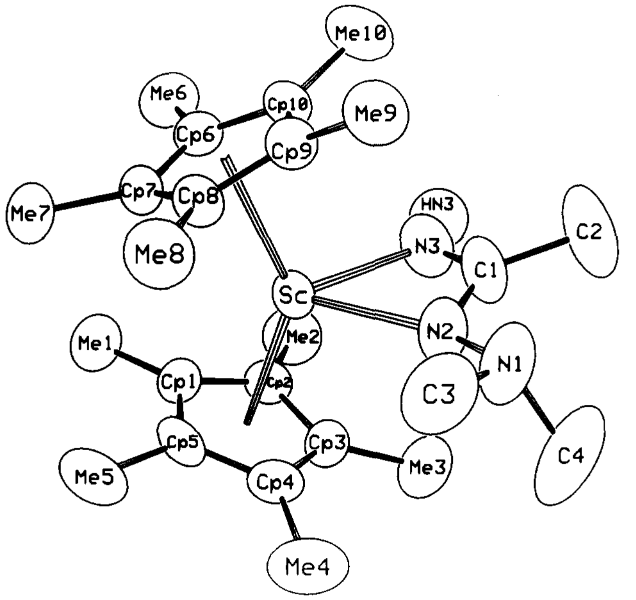


Figure 3. ORTEP drawing of $Cp^*_2ScN(H)C(CH_3)NNMe_2$ (4). Thermal ellipsoids are shown at the 50% probability level; methyl hydrogen atoms are omitted for clarity.

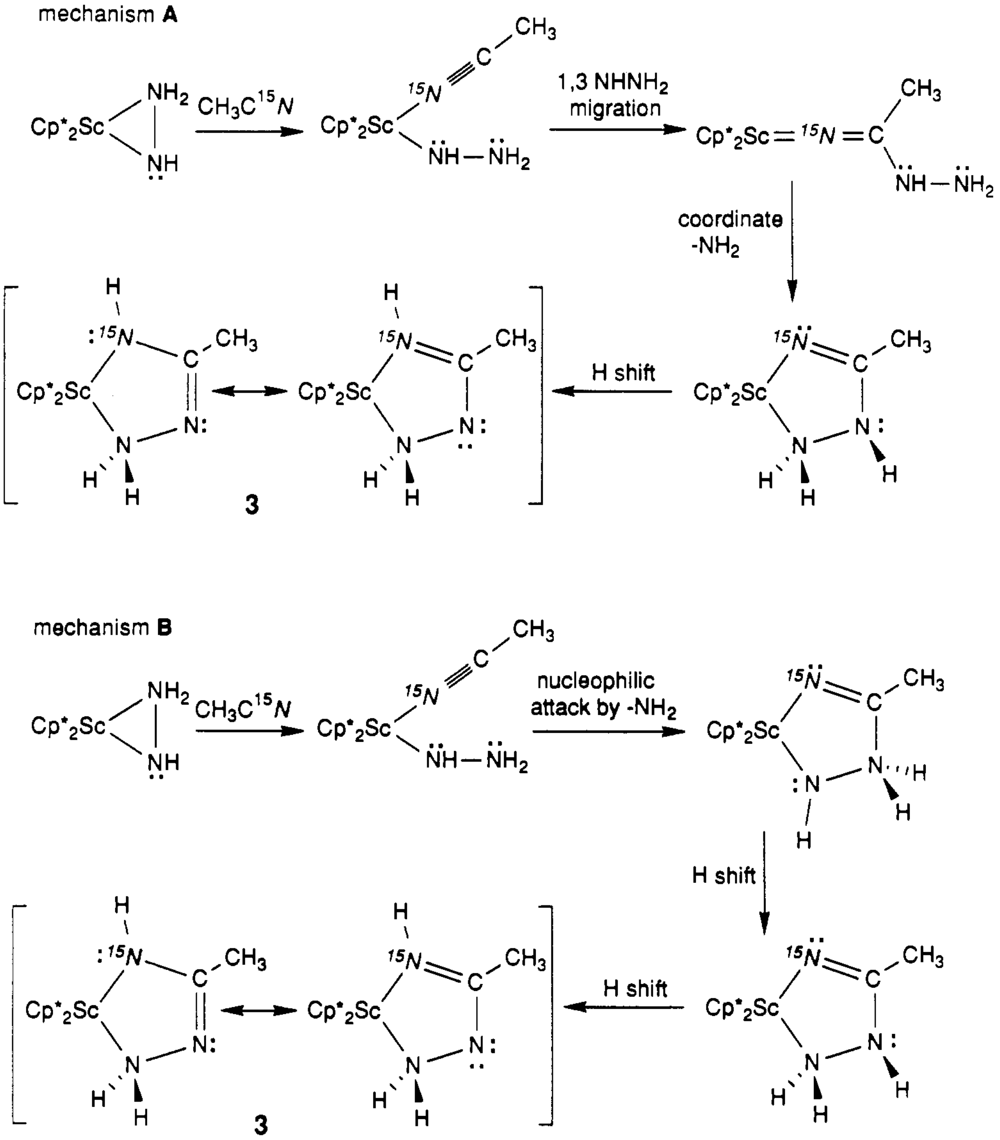
Table IV. Selected Distances and Angles for $Cp^*_2ScN(H)C(CH_3)NNH_2$[a]

Distances, Å			
Sc–Cen1	2.184	N2–C2	2.407 (9)
Sc–Cen2	4.576	N3–C1	1.304 (6)
Sc–N1	2.277 (4)	C1–C2	1.521 (9)
Sc–N3	2.155 (4)	N1···N2$_i$	3.095 (5)
N1–N2	1.494 (5)	N2$_i$···N1HB	2.28 (4)
N2–C1	1.330 (5)		
Angles, deg			
Cen1–Sc–Cen2	162.3	N3–C1–N2	123.9 (4)
N3–Sc–N1	72.4 (1)	C2–C1–N2	115.1 (4)
N2–N1–Sc	112.6 (2)	C2–C1–N3	121.0 (5)
C1–N2–N1	111.3 (3)	N2$_i$···N1HB–N1	153.9 (31)
C1–N3–Sc	118.1 (3)		

[a] A subscript i indicates inversion-related atom.

Labeling studies using $^{15}N{\equiv}CCH_3$ were performed to determine the orientation of the acetonitrile fragment in $Cp^*_2ScN(H)C(CH_3)NNH_2$ (i.e. C2–C1–N2 vs C2–C1–N3, Figure 1) and $Cp^*_2ScN(H)C(CH_3)NNMe_2$ (i.e. C2–C1–N2 vs C2–C1–N3, Figure 3). The latter orientation was found in both cases, and

Scheme I



the mechanistic implications of these results are discussed below.

Discussion

Preparation of $Cp^*_2ScNHNH_2$. Although the reaction between $Cp^*_2ScCH_3$ and 1 equiv of NH_2NH_2 to form $Cp^*_2ScN(H)NH_2$ (**1**) proceeds cleanly (^1H NMR), excess hydrazine protiolytically cleaves the Cp^*–Sc bonds, resulting in decomposition accompanied by loss of Cp^*H (^1H NMR). Compound **1** appears to be indefinitely stable in the solid state at 25 °C, but it decomposes in benzene solution over several days, again with the appearance of free Cp^*H (^1H NMR), likely the result of (sterically hindered, thus slower) intermolecular protiolytic cleavage of Sc–Cp^* bonds by Sc–$N(H)NH_2$. The room-temperature, 400-MHz ^1H NMR spectrum for an unpurified sample of **1** displays an average signal for all three $N(H)NH_2$ protons, which separates into two (still rather broad) signals of 2:1 relative intensity upon cooling to −96 °C. A recrystallized sample, however, displays the two separate hydrazide proton resonances at room temperature. Presumably, trace amounts of residual hydrazine catalyze proton exchange between the two types of hydrazide sites, analogous to the base-catalyzed hydrazide(1−) proton exchange noted earlier for $Cp^*W(CH_3)_3(\eta^2\text{-}N(H)NH_2)$.[3d] Infrared, ^1H NMR, mass spectral, and analytical data for **1** are given in the Experimental Section. The spectral data do not, however, distinguish between the $Cp^*_2Sc(\eta^1\text{-}N(H)NH_2)$ and $Cp^*_2Sc(\eta^2\text{-}N(H)NH_2)$ structures (or some other fluxional alternative with an N–H agostic interaction[7]) for **1**. Due to the novelty of its formulation (particularly so at the time of its first isolation), many attempts were made to obtain crystals of $Cp^*_2ScN(H)NH_2$ suitable for an X-ray structural determination; unfortunately all such attempts have been unsuccessful. In view of the η^2 coordination found by Schrock and co-workers for $[Cp^*W(CH_3)_3(\eta^2\text{-}N(H)NH_2)]^+$ and $Cp^*W(CH_3)_4(\eta^2\text{-}N(H)NH_2)$[3d] and the β C–H agostic structure we have observed for $Cp^*_2ScCH_2CH_3$,[8] we favor the η^2 structure for **1**.

Reaction of $Cp^*_2ScNHNH_2$ with Acetonitrile. Upon addition of excess acetonitrile to **1** in benzene at 25 °C, clear crystals are deposited from solution within minutes. Incorporation of one molecule of acetonitrile into this new compound is indicated by ^1H and ^{13}C NMR data; however, an IR stretch in the region 2100–2300 cm^{-1}, diagnostic of a C≡N group (attributable, for example, to a simple acetonitrile adduct, $Cp^*_2Sc(N\equiv CCH_3)(\eta^1\text{-}N(H)NH_2)$), is absent. Lower frequency vibrations at 1591 and 1607 cm^{-1}, not present for **1**, are observed, however. A single-crystal X-ray structure analysis was then undertaken, and the ORTEP drawing of the molecular structure is shown in Figure 1. As is apparent, the acetonitrile and hydrazido(1−) moieties have combined, forming a five-membered heterometallacycle, $Cp^*_2\overline{ScN(H)C(CH_3)NN}H_2$ (**3**) (eq 2; vide supra).

---

[7] (a) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 3210–3213. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[8] 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*, 203.

Scheme II

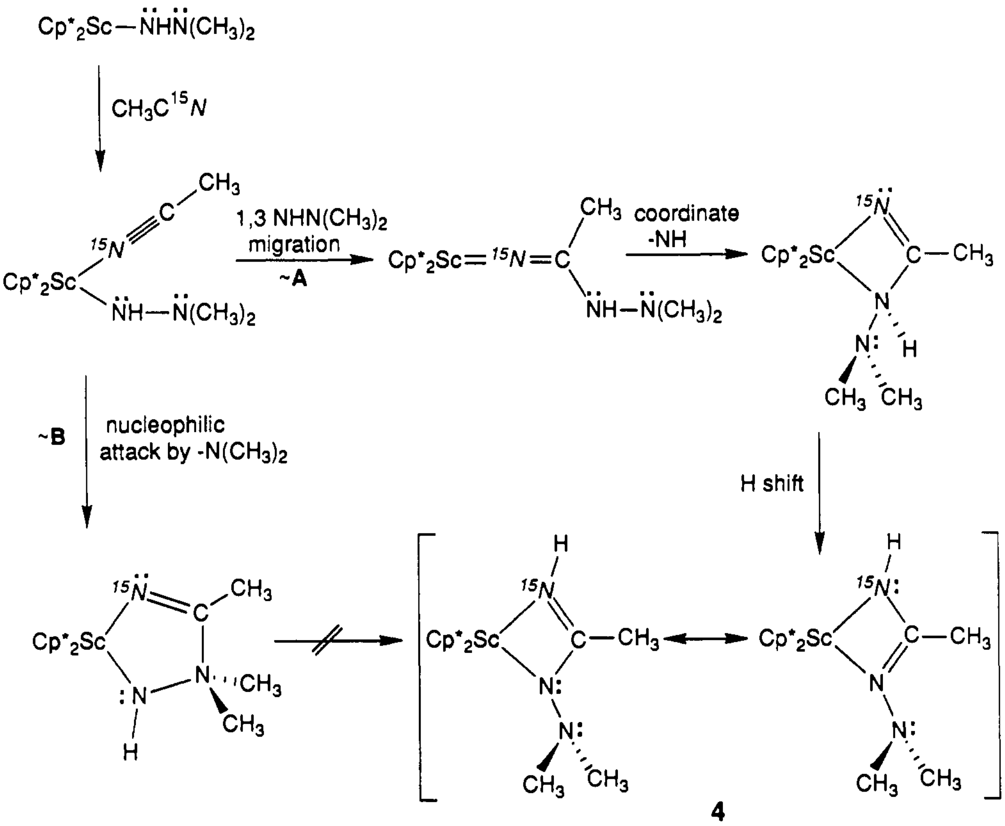


Table V. Selected Distances and Angles for $Cp^*_2\overline{ScN(H)C(CH_3)N}N(CH_3)_2$

	Distances, Å		
Sc–N2	2.264 (4)	N1–C3	1.450 (8)
Sc–N3	2.161 (4)	N1–C4	1.465 (8)
Sc–Cen1	2.233	N2–C1	1.316 (7)
Sc–Cen2	2.231	N3–C1	1.306 (7)
N1–N2	1.439 (6)	C1–C2	1.516 (8)
	Angles, deg		
Cen1–Sc–Cen2	137.8	C3–N1–N2	109.2 (4)
Cen1–Sc–N2	108.5	C4–N1–N2	110.8 (4)
Cen1–Sc–N3	107.4	C4–N1–C3	108.8 (5)
Cen2–Sc–N2	110.6	C1–N2–N1	116.5 (4)
Cen2–Sc–N3	105.6	N3–C1–N2	114.6 (5)
N3–Sc–N2	59.8 (2)	C2–C1–N2	122.8 (5)
Sc–N3–C1	94.2 (3)	C2–C1–N3	122.6 (5)
Sc–N2–C1	89.3 (3)		

The planarity of the ring (to within ±0.12 Å) and nearly equivalent C1–N2 and C1–N3 bond lengths suggest resonance stabilization in the ring, with the two canonical forms shown in Scheme I (vide infra) being the principal contributors. The N1–N2 bond length of 1.483 (5) Å is rather long in comparison with that found for hydrazido(1–) complexes,[4-6] but comparable to that found for N_2H_4.[9]

An interesting feature of the crystal structure is the N1–N1Hb···N2 hydrogen bonding between two centrosymmetrically related molecules, as evidenced by the short *inter*molecular N1–N2 distance (Table IV). An ORTEP drawing showing the hydrogen-bonded pair of molecules is given in Figure 2. Involvement of hydrazide protons in hydrogen bonding has been observed in a variety of metal hydrazide complexes.[3d,4a,c,6a,b]

A labeling experiment carried out with $^{15}N{\equiv}CCH_3$ revealed the acetonitrile nitrogen finally resides at N3, apparent from the sharper proton resonance at δ 3.05 with $^1J_{^{15}N-H} = 70$ Hz attributable to $Cp^*_2\overline{Sc^{15}N(H)C(CH_3)N}NH_2$. Two possible mechanisms for the formation of **3** that are consistent with this result are depicted in Scheme I. Mechanism A involves 1,3-migration of the hydrazide(1–) group to the carbon atom of coordinated acetonitrile, analogous to the reactivity of permethylscandocene alkyl, aryl, and hydride derivatives with nitriles (eq 4),[10] followed by tautomerization to **3**.

$$\begin{gathered} Cp^*_2Sc{-}R + R'C{\equiv}N \rightarrow Cp^*_2Sc{=}N{=}CRR' \\ R = H, CH_3, C_6H_5;\ R' = C_6H_5, CMe_3 \end{gathered} \tag{4}$$

The alternative, mechanism B, involves intramolecular nucleophilic attack by the terminal nitrogen of the hydrazide group at the carbon atom of the coordinated nitrile, a proposal of some merit in light of the generally observed activation of unsaturated ligands toward nucleophilic attack by coordination to an electron-deficient metal.[11] The requirement to move both hydrogens from N2, one to N1 and one to N3, to generate **3** is an unattractive feature of this alternative, however.

Reaction of $Cp^*_2ScNHNMe_2$ with Acetonitrile. To distinguish between the two mechanisms, we examined the reaction of acetonitrile with $Cp^*_2ScN(H)NMe_2$ (**2**). We reasoned that, by replacement of the two hydrogens on the terminal nitrogen of the hydrazide with two methyl groups, formation of a complex analogous to **3** could not occur by mechanism B, since the necessary hydrogen shift would no longer be possible. Reaction of **2** with ^{15}N-labeled acetonitrile resulted in a new species that displayed $^{15}N-^1H$ coupling in the ^1H NMR spectrum (δ 3.9 with $^1J_{^{15}N-H} = 73$ Hz), indicating that a product analogous to **3** had formed. Moreover, infrared data also indicated that the acetonitrile once again had reacted beyond simple adduct formation.

Ultimately, positive structural verification was provided by a single-crystal X-ray analysis for **4** (Figure 3). A four-membered metallacycle is formed in this case (eq 3; vide supra). The smaller ring size adopted by **4** relative to **3** is undoubtedly due to the steric

---

[9] Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 228.

[10] Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

[11] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 7.

bulk of the dimethylamino group, which prevents coordination to the [$Cp^*{}_2Sc$] moiety. Resonance stabilization attributable to the two canonical forms shown for **4** in Scheme II is apparent from the similarity of the two C–N bond lengths (C1–N3 = 1.306 (7) Å; C1–N2 = 1.316 (7) Å). Hydrogen bonding between monomers, analogous to that observed in the solid state for **3**, is not expected and is not observed for **4**.

The implications from the reaction of **2** with acetonitrile (Scheme II) concerning the mechanism for the formation of **3** (mechanism A vs B, Scheme I) are not, however, definitive. Although one may safely infer that mechanism A is plausible, mechanism B is not ruled out conclusively. When the β-nitrogen of the hydrazido(1–) ligand does bear two hydrogens, the reaction with acetonitrile may choose to follow pathway B rather than A.

The balance of evidence does argue for mechanism A, nonetheless. Insertion of a C≡N bond into a scandium–nitrogen bond has been observed before as a competing reaction in the catalytic hydrogenation of *tert*-butyl cyanide to *tert*-butylamine by permethylscandocene hydride.[7] In some related chemistry of amide derivatives of aluminum, nitrile insertion has been observed to occur at the Al–N bond in preference to the Al–C bond.[12] Moreover, the insertion of a nonpolar unsaturated group into a transition-metal–nitrogen bond is a key step in the catalytic hydroamination/cyclization of α,ω-diamino olefins,[13] as well as in the recently reported formation of 2,3-diazametallacyclopentenes from the reaction of $Cp_2Zr(N_2Ph_2)$ with internal alkynes.[14] The tautomerization of the initial product of the nitrile insertion, via a formal 1,3 hydrogen shift (mechanism A, Scheme II), bears some resemblance to the rearrangement that follows insertion of acetonitrile into the Ti–C bond for $Cp^*{}_2Ti(\eta^2\text{-}C_2H_4)$, yielding $Cp^*{}_2TiCH_2CH{=}C(CH_3)NH$.[15]

Conclusions

The modest stability of these hydrazido(1–) derivatives of permethylscandocene, $Cp^*{}_2ScN(H)NH_2$ and $Cp^*{}_2ScN(H)N(CH_3)_2$, may be traced, in part, to the very high reduction potential of these formally Sc(III) complexes, although, in view of the moderate stability of the formally W(VI) complexes [$Cp^*W(CH_3)_3(N(H)NH_2)]^+$ and $Cp^*W(CH_3)_4(N(H)NH_2)$,[3c,d] one may question the premise that the high reduction potential for $[N_2H_3]^-$ is a principal reason for the paucity of examples of stable transition-metal derivatives with the hydrazido(1–) ligand. The susceptibility of the [Sc–Cp*] bonds to protiolytic cleavage limits the stability, especially for $Cp^*{}_2ScN(H)NH_2$, and restricts the types of chemistry that may be explored. For example, reaction with acetone to cleanly yield [$Cp^*{}_2ScN(H)N{=}C(CH_3)_2$] is unlikely, since water (the coproduct) reacts rapidly with all permethylscandocene compounds we have prepared to date. On the other hand, the insertion chemistry observed with acetonitrile is particularly clean and may provide a means to efficiently trap less stable adducts in other systems.

Experimental Section

General Considerations. All manipulations were performed by using glovebox and high-vacuum techniques, as described elsewhere.[16] Argon, hydrogen, and nitrogen were purified by passage over MnO on vermiculite and activated 4-Å molecular sieves. Solvents were dried and purified by prolonged reflux over a suitable drying agent, followed by distillation under an atmosphere of dinitrogen. Ether solvents were stored over sodium benzophenone ketyl; hydrocarbon solvents were stored over titanocene;[17] and methylene chloride and acetonitrile were stored over CaH_2. Anhydrous hydrazine (Aldrich) was transferred to a Kontes Microflex vial with a rotary-type valve and used without prior purification. 1,1-Dimethylhydrazine (Aldrich) was stored over 4-Å molecular sieves in a flask under vacuum and used as received.

NMR spectra were recorded on Varian EM-390 (^1H, 90 MHz), JEOL FX90Q (^1H, 89.56 MHz; ^{13}C, 22.50 MHz), and JEOL GX400Q (^1H, 399.78 MHz) instruments. Infrared spectra were measured as Nujol mulls on KBr plates and recorded on a Beckman IR-4240 spectrometer. Elemental analyses were performed at the Caltech Analytical Laboratory. Mass spectra were obtained from the UC Riverside facility.

$Cp^*{}_2ScCl$ and $Cp^*{}_2ScCH_3$ were prepared as described previously.[10]

$Cp^*{}_2ScNHNH_2$ (1). Method a. $Cp^*{}_2ScCl$ (2.54 g, 7.26 mmol) was dissolved in 40 mL of toluene. A 5.3-mL amount of a 1.5 M $LiCH_3$ solution in diethyl ether (7.95 mmol) was added slowly by syringe to the solution, which was being stirred under argon. After 2 h at room temperature, the volatiles were removed from the reaction mixture under reduced pressure. The residue was washed with 30 mL of petroleum ether, and the resulting solution was filtered. Anhydrous hydrazine (22.5 μL, 7.1 mmol) was syringed into the solution with stirring under argon. The reaction mixture immediately turned from light orange to maroon. After approximately 20 min, the color dissipated and a white precipitate of **1** formed. The precipitate was collected by filtration and dried to yield 1.29 g (51%) of **1**. IR: 3330, 1565, 1012, 712 cm^{-1}. ^1H NMR (toluene-d_8): δ 1.87 (s, $C_5(C\mathit{H}_3)_5$), 2.68 (s, br, $N(H)N\mathit{H}_2$), 2.86 (s, br, $N(\mathit{H})NH_2$). Anal. Calcd for $C_{20}H_{33}N_2Sc$: C, 69.4; H, 9.62; N, 8.09. Found: C, 67.83; H, 9.35; N, 8.08. MW calcd: 345.9. MS largest peak: $m/e = 346$.

Method b. An isolated sample of $Cp^*{}_2ScCH_3$ was used. The reaction with hydrazine was performed under the same conditions as in method a. A 0.837-g amount of $Cp^*{}_2ScCH_3$ (2.54 mmol) afforded 0.518 g of **1** (59%).

$Cp^*{}_2ScNHN(CH_3)_2$ (2). $Cp^*{}_2ScCH_3$ (1.0 g, 3.0 mmol) was dissolved in 30 mL of petroleum ether. 1,1-Dimethylhydrazine, 3.0 mmol, was expanded into a standardized volume connected to a manometer and condensed into the solution at −78 °C. The reaction mixture turned from light orange to bright yellow as it warmed to room temperature. After being stirred for 1 h, the solution was concentrated and cooled to −78 °C to afford yellow crystals of **2**. Yield: 0.45 g (40%). IR: 3175, 2782, 2740, 1208, 1196, 1142, 1080, 1050, 1016, 995, 850, 710, 650, 595, 550, 409 cm^{-1}. ^1H NMR (benzene-d_6): 1.98 (s, $C_5(C\mathit{H}_3)_5$), 2.3 (s, $N(H)N(C\mathit{H}_3)_2$), 4.9 (s, br, $N(\mathit{H})N(CH_3)_2$). ^{13}C NMR (benzene-d_6): δ 119.26 ($\mathit{C}_5(CH_3)_5$), 54.03 ($N(H)N(\mathit{C}H_3)_2$), 11.16 ($C_5(\mathit{C}H_3)_5$). Anal. Calcd for $C_{22}H_{37}N_2Sc$: C, 70.56; H, 9.96; N, 7.48. Found: C, 70.77; H, 9.57; N, 7.25.

$Cp^*{}_2ScN(H)C(CH_3)NNH_2$ (3). Compound **1** (0.79 g, 2.3 mmol) was dissolved in 25 mL of methylene chloride. Acetonitrile, 0.5 mL, was vacuum-transferred to the solution. The reaction was stirred for 30 min at room temperature. The volatiles were removed under vacuum, and the white residue was taken up in 20 mL of petroleum ether as a slurry, which was cooled to −78 °C. The resulting white solid was collected by filtration and dried in vacuo. Yield: 0.54 g (61%). IR: 3370, 3290, 1607, 1591, 1540, 1417, 1355, 1250, 1230, 1156, 720, 550 cm^{-1}. ^1H NMR (benzene-d_6): δ 1.86 (s, $C_5(C\mathit{H}_3)_5$), 1.80 (s, $N(H)C(C\mathit{H}_3)NNH_2$), 3.05 (s, br, $N(\mathit{H})C(CH_3)NNH_2$), 4.04 (s, br, $N(H)C(CH_3)NN\mathit{H}_2$). ^{13}C NMR (benzene-d_6): δ 117.63 ($\mathit{C}_5(CH_3)_5$), 22.64 ($N(H)C(\mathit{C}H_3)NNH_2$), 11.22 ($C_5(\mathit{C}H_3)_5$). Anal. Calcd for $C_{22}H_{36}N_3Sc$: C, 68.19; H, 9.36; N, 10.84. Found: C, 67.84; H, 9.10; N, 10.81.

$Cp^*{}_2ScN(H)C(CH_3)NNMe_2$ (4). Compound **2** (0.145 g, 0.388 mmol) was dissolved in 15 mL of petroleum ether. Acetonitrile, 0.16 mL, was transferred to the solution. The reaction was stirred for 30 min at room temperature. Volatiles were removed under vacuum, the residue was dissolved in 3 mL of pentane, and the mixture was cooled at −78 °C overnight to precipitate a tan powder, which was collected by filtration cold and dried in vacuo. Yield: 0.059 g (39%). IR: 3389, 1650, 1508, 1235, 1192, 1033. ^1H NMR (benzene-d_6): δ 1.92 (s, $(C_5(C\mathit{H}_3)_5)$, 1.92 ($N(H)C(C\mathit{H}_3)NN(CH_3)_2$), 2.4 (s, $N(H)C(CH_3)NN(C\mathit{H}_3)_2$), 3.8 (s, $N(\mathit{H})C(CH_3)NN(CH_3)_2$). ^{13}C NMR (benzene-d_6): δ 118.0 ($\mathit{C}_5(CH_3)_5$), 48.5 ($N(H)C(CH_3)NN(\mathit{C}H_3)_2$), 18.5 ($N(H)C(\mathit{C}H_3)NN(CH_3)_2$), 12.1 ($C_5(\mathit{C}H_3)_5$). Anal. Calcd for $C_{24}H_{39}N_3Sc$: C, 69.5; H, 9.5; N, 10.2. Found: C, 69.3; H, 9.5; N, 9.75.

Structure Determination for $Cp^*{}_2ScN(H)C(CH_3)NNH_2$. A colorless crystal obtained from an NMR tube reaction of $Cp^*{}_2ScNHNH_2$ with CH_3CN in deuteriobenzene was mounted in a thin-walled glass capillary under N_2. The crystal was centered on a CAD-4 diffractometer. Unit cell parameters and an orientation matrix were obtained by a least-squares calculation from the setting angles of 24 reflections. Two quadrants of intensity data out to a 2θ value of 40° and one quadrant of data in the 2θ range 40–50° were collected. No absorption or decay corrections were applied, and the data were reduced to $F_o{}^2$ values and merged to yield the final data set. Systematic absences led to the choice of space

---

[12] Hirabayashi, T.; Itoh, K.; Sakai, S.; Ishii, Y. *J. Organomet. Chem.* **1970**, *21*, 273.

[13] Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109.

[14] Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 894.

[15] Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

[16] Burger, B. J.; Bercaw, J. E. In *New Developments in the Synthesis, Manipulation and Characterization of Organometallic Compounds*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 17–98.

[17] Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

group $P2_1/n$. The coordinates of the scandium atom were obtained from a Patterson map; locations of the other non-hydrogen atoms were determined from successive structure factor-Fourier calculations. Hydrogen atom positions for the methyl groups and for the heterometallacyclic ring were determined from difference maps and were refined along with their isotropic B values. The full least-squares matrix, consisting of coordinates for all of the atoms, anisotropic U_{ij} values for the non-hydrogen atoms, isotropic B values for the hydrogen atoms, an extinction parameter, and a scale factor, contained 380 parameters. A final difference Fourier map showed deviations ranging from −0.61 to 0.63 eÅ^{-3}. The refinement converged with an R factor of 0.117 (0.051 for $F_o^2 > 3\sigma(F_o^2)$) and a goodness of fit of 1.34 for all 3855 reflections.

Structure Determination for $Cp^*_2ScN(H)C(CH_3)NNMe_2$. A colorless crystal grown from a petroleum ether solution of the complex cooled at −60 °C was mounted in a thin-walled glass capillary under N_2. The crystal was centered on a CAD-4 diffractometer. Unit cell parameters and an orientation matrix were obtained by a least-squares calculation from the setting angles of 24 reflections with $35° < 2\theta < 39°$. Two equivalent intensity data sets to a 2θ value of 40° were collected, corrected for absorption (transmission coefficient 0.889–0.956) and a slight decay, reduced to F_o^2 values, and merged to yield the final data set. Systematic absences led to the choice of space group $P2_1/n$. Coordinates of the scandium atom were obtained from a Patterson map; locations of the other non-hydrogen atoms were determined from successive structure factor-Fourier calculations. Hydrogen atom positions were determined from difference maps for the methyl groups and by calculation for the other one. All hydrogen atoms were given isotropic B values 20% greater than that of the attached atom; no hydrogen atom parameters were refined. The full least-squares matrix, consisting of coordinates and anisotropic U_{ij} values for the non-hydrogen atoms and a scale factor, contained 253 parameters. A final difference Fourier map showed deviations ranging from −0.30 to 0.38 eÅ^{-3}. The refinement converged with an R factor of 0.0640 (0.0416 for $F_o^2 > 3\sigma(F_o^2)$) and a goodness of fit of 1.78 for all 2267 reflections.

All calculations were carried out on a VAX 11/750 computer using the CRYM system of programs and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference.[18]

Acknowledgment. This work was supported by grants from the National Science Foundation (Grant No. CHE-8600875), the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER113431), and the Shell Companies Foundation, which are gratefully acknowledged.

Supplementary Material Available: For $(\eta^5\text{-}C_5Me_5)_2ScN(H)C(CH_3)NNH_2$ and $(\eta^5\text{-}C_5Me_5)_2ScN(H)C(CH_3)NNMe_2$, tables of crystal and intensity collection data, complete distances and angles, anisotropic thermal displacement parameters, and hydrogen atom coordinates and displacement parameters (9 pages); tables of observed and calculated structure factors for 3 and 4 (27 pages). Ordering information is given on any current masthead page.

---

(18) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71, 149.

Contribution from the Departments of Organic and Inorganic Chemistry,
University of Sydney, Sydney, NSW, Australia 2006

Synthesis and Structure of $FeCl(C{\equiv}CPh)(DMPE)_2$

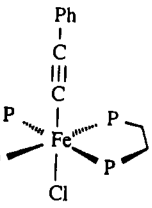
Leslie D. Field,*[†] Adrian V. George,[†] and Trevor W. Hambley[‡]

Received December 27, 1989

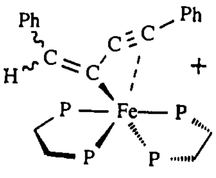
The reaction of $FeCl_2(DMPE)_2$ with phenylacetylene in methanol solution forms three phosphorus-containing products: two complexes, $FeCl(C{\equiv}CPh)(DMPE)_2$ and $[Fe(\eta^3\text{-}C(CHPh)C_2Ph)(DMPE)_2][PF_6]$, and a cyclic diphosphonium salt, $[Me_2PCHPhCH_2P(CH_2CH_2)Me_2][Cl]_2$. Crystals of $FeCl(C{\equiv}CPh)(DMPE)_2$ are monoclinic, space group $P2_1/n$, with a = 9.038 (3) Å, b = 8.852 (2) Å, c = 30.675 (9) Å, β = 96.34 (2)°, Z = 4, and R = 0.042 (2262 F values).

The first metal acetylide complex was isolated in the 1950s, and since that time, a wide variety of alkynyl comlexes of transition metals or metal clusters displaying a range of coordination types have been isolated.[1] The synthesis of such compounds has usually involved the reaction of acetylide salts or Grignard reagents with a metal halide[2] or a metal triflate,[3] though the action of acetylene on a metal halide in the presence of triethylamine and a copper(I) iodide catalyst has also been reported.[4] Aryldiacetylides have been used in the preparation of conjugated poly-yne metal dimers and oligomers,[5] enroute to organic conducting polymers.[6] The formation of metal acetylide complexes indirectly provides one route to vinylidene complexes[1] and may also be used to functionalize alkynes.[7] The vinylidene complexes (formally metal carbenes) were isolated as early as 1966,[8,9] and since then, there has been considerable activity devoted to their study.[10]

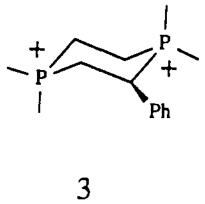
During our investigation of the reaction of acetylenes and acetylides with iron complexes of the type $FeL_2(PP)_2$ [L = H, Cl; PP = $R_2PCH_2CH_2PR_2$; R = $-CH_3$ (DMPE), $-CH_2CH_3$ (DEPE)], we found that phenylacetylene reacted directly with $FeCl_2(PP)_2$ in methanol solvent to give a number of products. With $FeCl_2(DMPE)_2$, phenylacetylene afforded a solid product, which, after recrystallization from ethanol, was identified as the acetylide chloride complex, *trans*-$FeCl(C{\equiv}CPh)(DMPE)_2$ (**1**). Two other products were also isolated from this reaction and identified as the cationic complex **2** (isolated as its $[PF_6^-]$ salt) and the cyclic diphosphonium salt **3**. Bellerby and Mays[9] have previously reported that the reaction of phenylacetylene with $FeCl_2(DEPE)_2$ afforded the vinylidene complex **4b**.



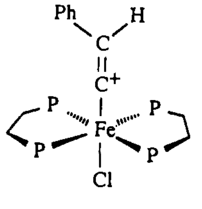
1



2



3



4

a P P = DMPE

b P P = DEPE

[†] Department of Organic Chemistry.

[‡] Department of Inorganic Chemistry.