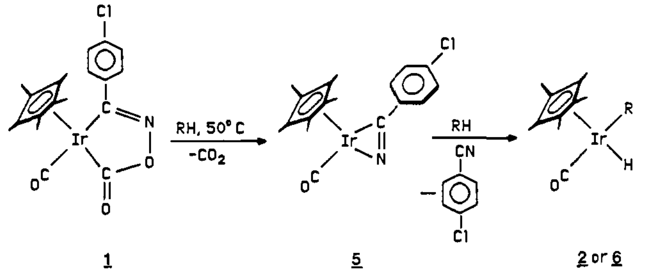
Scheme III



1 **5** **2** or **6**

C$_5$Me$_5$)Ir(CO) into the C–H bonds of benzene;[21] addition of CCl$_4$ converted **2** to the known (η^5-C$_5$Me$_5$)Ir(CO)(Cl)(C$_6$H$_5$)[22,2a] (**3**) in 90.4% overall yield while the known dimer [(η^5-C$_5$Me$_5$)Ir(μ-CO)]$_2$ (**4**),[23] identified by its ^{1}H NMR resonance at 1.58 ppm in C$_6$D$_6$, was produced in 8.6% yield as determined by NMR. When the reaction of **1** was carried out in 100% deuterated benzene and monitored by ^{1}H NMR, two sets of doublets at δ 7.71 (J = 8.3 Hz) and 7.01 (J = 8.3 Hz) appeared;[24] as the reaction proceeded these resonances decreased in intensity as the resonances due to the free p-ClC$_6$H$_4$CN increased. The same intermediate resonances were observed when the reaction was carried out in cyclohexane and the ^{1}H NMR of the reaction products obtained before the reaction had gone to completion, thus suggesting the existence of a common intermediate which is formed before oxidative addition of the solvent occurs. In order to isolate the intermediate, a THF solution of **1** was stirred at 50 °C for 14 h in the dark. Upon removal of the THF under vacuum and extraction of the residue with pentane, a yellow solution was obtained which on cooling afforded a yellow crystalline product in 66% yield. The complex obtained is a side-bonded nitrile complex (η^5-C$_5$Me$_5$)Ir(η^2-NCC$_6$H$_4$Cl)CO[24] (**5**), identified by its characteristic low CN stretching frequency observed at 1781 cm^{-1} in the IR spectrum.[25,26] Complex **5** was also characterized by ^{1}H NMR spectroscopy and complete elemental analyses, and its molecular structure has been determined by a single-crystal X-ray diffraction study.[27] The resonances in the ^{1}H NMR spectrum of **5**[24] coincide with those of the intermediate observed when the thermolysis of **1** was monitored by ^{1}H NMR as described above. In order to confirm that **5** independently activates C–H bonds of hydrocarbons, a 0.07 M solution of **5** in benzene was maintained in the dark at 50 °C for 4 weeks, generating the phenyl hydride product **2** and the dimer **4**, in 76.2% and 18.4% yield, respectively. A mechanism consistent with these observations involves the loss of CO$_2$ from **1** to generate the nitrile complex **5** which at 50 °C is labile and loses the coordinated nitrile to release the metal fragment "(C$_5$Me$_5$)Ir(CO)" which undergoes C–H bond activation (Scheme III). The metallacycle **1** was also found to be very photosensitive; when a sample of **1** was maintained in benzene at 50 °C and photolyzed[28] for 36 h, **2** was obtained in 75.4% yield and **4** in 7.5% yield. The side-bonded nitrile **5** was observed when the ^{1}H NMR spectrum of the reaction mixture was obtained before the reaction had gone to completion, although the steady-state concentration of **5** was low since this compound was particularly photosensitive. When **5** was photolyzed[28] in benzene for 12 h at 50 °C, **2** was obtained in 80.6% yield by ^{1}H NMR; compound **4** was obtained in 4.7% yield. Photolysis of metallacycle **1** in cyclohexane for 13 days under the same conditions yielded the cyclohexylhydride product (η^5-C$_5$Me$_5$)Ir(CO)(H)(C$_6$H$_{11}$) (**6**); addition of CCl$_4$ converted **6** to the known (η^5-C$_5$Me$_5$)Ir(CO)(Cl)(C$_6$H$_{11}$) (**7**)[2a] in 48,6% overall yield. The dimer **4** was obtained in 33.7% yield. When the side-bonded nitrile complex **5** was photolyzed for 24 h in cyclohexane at 50 °C, **6** was obtained which was converted to the chloride derivative to yield **7** in 67.1% overall yield; compound **4** was obtained in 13.1% yield.

The rhodium metallacycle (η^5-C$_5$Me$_5$)(PMe$_3$)Rh[C(p-FC$_6$H$_4$)=NOC(=O)] demonstrates a reactivity similar to that of **1** since the formation of a side-bonded nitrile complex and thermal C–H activation of hydrocarbon solvents are observed. Full details concerning this reaction will be reported shortly.

Acknowledgment. We are grateful to the Office of Naval Research for support of this research and the Johnson-Matthey Corporation for a generous gift of iridium and rhodium chloride. We thank Professor W. A. G. Graham for helpful discussions.

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[21] The reactions were carried out in NMR tubes by using dried and degassed solvents. In a typical experiment, 0.8 mL of reactant solvent was vacuum transferred into 8 mg of the metallacycle **1** and the reactants were maintained at a constant temperature. When the reaction was complete the reactant solvent was removed under vacuum, and deuteriated benzene was then vacuum transferred in and the tube sealed. The alkyl and aryl metal hydrides formed were identified by matching the ^{1}H NMR chemical shifts with the reported values published by other workers or by conversion to the chloro derivatives by addition of CCl$_4$.[2a] Relative yields were measured by ^{1}H NMR integration.

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[24] **5**: IR (Nujol) 1949 (br, ν_{CO}), 1781 (m, ν_{CN}) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 7.72 (d, 2 H, J = 8.3 Hz), 7.01 (d, 2 H, J = 8.3 Hz), 1.69 (s, 15 H).

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[27] Complete details on the X-ray crystal structure of **5** will be given in a full report discussing the reactivity of metallacycles of rhodium and iridium.

[28] Photochemical experiments were carried out using a 100-W tungsten bulb which was supported 6 in. above an oil bath in which the NMR tubes were maintained at constant temperature. The radiated light was contained within the system by aluminum foil and a stream of cold nitrogen gas was used to cool the system to the desired temperature.

On the Difference between Iron–Molybdenum Cofactor of Wild-Type and *nif*V Mutant Molybdenum–Iron Proteins of *Klebsiella pneumoniae*: ENDOR, EXAFS, and EPR Evidence

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Nitrogenase comprises two metalloproteins, the iron protein (Fe protein) and the molybdenum–iron protein (MoFe protein),[2-5] The active site of the enzyme is thought to be associated with the MoFe protein and to include the iron–molybdenum cofactor

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[3] Abbreviations: MoFe, molybdenum–iron; FeMo-co, iron–molybdenum cofactor; *Kp*1, MoFe protein of *K. pneumoniae*; WT, wild type; V$^-$, *nif*V; EXAFS, extended X-ray absorption fine structure; ENDOR, electron nuclear double resonance.

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Table I. Mo EXAFS of WT and *nif*V⁻ *Kp*1[a]

	Mo-S		Mo-Fe		
sample	dist, Å	coord no.	dist, Å	coord no.	
WT	2.369 (12)		2.735 (22)		BFBT
	2.360	4.56 (0.92)	2.702	2.7 (1.23)	FABM
V⁻	2.349 (11)		2.697 (18)		BFBT
	2.352	4.4 (1.6)	2.702	2.8 (2.3)	FABM

[a] Distances and coordination numbers obtained by best fit based on theory (BFBT) and fine adjustment based on models (FABM) methods.[14-16] The *k* ranges used in Fourier filtering and curve fitting are 1-13 and 3-12 Å^{-1}, respectively. Errors are given in parentheses.

(FeMo-co) of approximate composition $\mathrm{MoFe_{6-8}S_{9\pm1}}$. The *nif*V mutant of *Klebsiella pneumoniae* produces mutant MoFe protein that will reduce C_2H_2 in vivo but not N_2.[6,7] The phenotype of the *nif*V mutant is transferred to wild-type (WT) apoprotein upon addition of mutant cofactor,[6] and thus the composition or structure of the mutant cofactor differs from that of the wild type. Chemical analysis shows the *metal* composition of WT and NifV⁻ (V⁻) cofactor to be the same.[7] EXAFS spectroscopic measurements reported here and by others[8] fail to detect a difference in the S and Fe environments of molybdenum. However, endor spectroscopy now provides the first physical evidence of a difference between WT and V⁻ cofactors by showing that the molybdenum site is perturbed in the mutant cofactor.

*Kp*1 exhibits an EPR spectrum derived from the ground-state Kramers' doublet of the $S = {}^3/_2$ molybdenum-iron cofactor.[2,9] The *g* values, the ratio of the $S = {}^3/_2$ zero-field splitting parameters, $\lambda = E/D$, and $g_\perp$ in the $S = {}^3/_2$ representation[11] for this cluster are the same in mutant and wild-type proteins;[10] g'_1 = 4,33; g'_2 = 3.67; g'_3 = 2.02; λ = 0.055; $g_\perp$ = 2.004. From the large pseudonuclear Zeeman effect observed by ENDOR[11] (see below), we find that *D* is the same in mutant and wild-type proteins, D = 12.5 cm^{-1}, and therefore, both *E* and *D* are the same. Since observed changes in *g* values upon binding of substrates and inhibitors show the zero-field splitting parameters to be sensitive measures of the conformational state of the cofactor cluster,[2,12] we may conclude that the overall conformation is the same in wild-type and V⁻ cofactors.

As a major conformational difference seems unlikely, we have examined the local environment of the molybdenum in purified MoFe protein from WT and V⁻ organisms.[9,13] Mo K-edge EXAFS spectroscopy[14-16] gives distances to sulfur and iron that are indistinguishable in the two cases, as are the coordination numbers,[17] Table I, in agreement with the recent EXAFS study of Eidsness et al.[8] The identity of the molybdenum-sulfur and molybdenum-iron distances suggests that the arrangement of iron and sulfur atoms about molybdenum is very similar, if not identical, in WT and mutant cofactors.

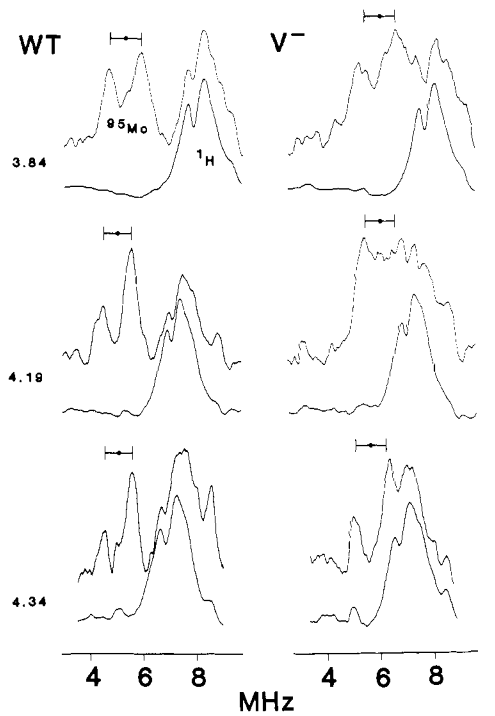

Figure 1. Molybdenum ENDOR of (left) the *Kp*1 wild type (^{100}Mo, 80 mg/mL; ^{95}Mo, 76 mg/mL) and (right) the NifV⁻ *Kp*1 mutant (^{100}Mo, 89 mg/mL; ^{95}Mo, 46 mg/mL). The *g* values and field for each set of paired traces are as listed. The upper spectrum of each pair corresponds to the ^{95}Mo-enriched species and the lower to the analogous ^{100}Mo-enriched protein. Conditions: T = 2 K; microwave frequency, 9.52 GHz; microwave power, 0.2 mW; 100-KHz field modulation 4 G; rf power, 20 W; rf scan rate, 2.5 MHz/s.

By contrast, ^{95}Mo ENDOR studies show a significant difference between the WT and mutant proteins.[18] The molybdenum site of the WT FeMo-co cluster has an appreciable quadrupole interaction, $P_3^{\rm Mo} \sim 1.6$ MHz, and is of rhombic symmetry, $\eta \sim 1$.[11] Data for the NifV⁻ enzyme indicate that $P_3^{\rm Mo}$ is unchanged. This suggests that the overall coordination environment of molybdenum is preserved, in agreement with the EXAFS results. The WT FeMo-co cluster has a small, anisotropic ^{95}Mo hyperfine coupling.[11] ENDOR spectra for the mutant show at most a slight reduction in the ^{95}Mo coupling at g'_3: WT, $A_3^{\rm Mo}$ = 8.3 (5) MHz; NifV⁻, $A_3^{\rm Mo}$ = 7.3 (5) MHz. However, spectra at fields near g'_1 unambiguously demonstrate a significant change in the characteristics of molybdenum (Figure 1). Near g'_1, the enriched samples of WT and NifV⁻ MoFe protein show a doublet associated with transitions between the $m_I = \pm{}^1/_2$ levels of the $I = {}^5/_2$ ^{95}Mo nucleus; the other ("satellite") ^{95}Mo nuclear transitions are not observable at these fields.[11] The doublet splitting, $^2\nu_{\rm Mo}$, is determined by the effective nuclear $\mathbf{g}^{\rm Mo}$ tensor ($h\nu_{\rm Mo} = \beta_{\rm N}|\mathbf{g}^{\rm Mo}\cdot H_0|$), which has a large contribution from the pseudonuclear Zeeman effect. Analysis[11] of this effect gives the zero-field splitting parameter, *D*, noted above to be the same for both proteins. At each observing field in Figure 1, the ^{95}Mo spectra of WT and V⁻ proteins clearly differ. From these and other spectra we estimate the following tensor components: WT, $A_1^{\rm Mo}$ = +4.65 (10) MHz; NifV⁻, $A_1^{\rm Mo}$ = +5.15 (10) MHz.

Thus, the following seem established: (1) the cofactor cluster in *nif*V strains is functionally different from that in the wild-type

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(12) Manuscript in preparation.

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(18) The ENDOR apparatus and acqusition procedure is described in ref 11.

K, pneumoniae.[6] (2) The metal ion composition is unchanged in the V⁻ protein.[6a,7a] (3) EPR spectroscopy shows that the WT and V⁻ cofactors are not distinguished by a major conformational rearrangement. (4) EXAFS shows that the local S and Fe environment of molybdenum is similar, if not identical. (5) ENDOR measurements show the molybdenum site is perturbed in the mutant cofactor. We conclude that the mutant cofactor cluster is not an isomer of the WT, which indicates that it differs by the addition, subtraction, or replacement of a metal–ligand(s). Points (4) and (5) suggest that this difference is most likely due to a change in non-sulfur ligands weakly bound at or near molybdenum, but it could be due to sulfur ligands distant from molybdenum. These possibilities can be tested chemically and spectroscopically. For example, chemical analysis can show whether the sulfur content of mutant cofactor differs from that of WT, and ^{57}Fe ENDOR and Mössbauer studies provide a probe of the iron sites in the cluster.

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Registry No. Nitrogenase iron molybdenum cofactor, 72994-52-6.

Coordinatively Unsaturated Tris(trimethylsilyl)silyl Complexes of Chromium, Manganese, and Iron

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Transition-metal silyl complexes exhibit a limited array of reactivity patterns compared to analogous compounds containing M–C or M–H σ-bonds. The majority of transition-metal silyls are coordinatively saturated and contain carbon monoxide, phosphines, or cyclopentadienyl ancillary ligands.[1] One approach to the design of more reactive silyl complexes is to place the metal in an electron-deficient, low coordination number environment. Use of sterically demanding silyl ligands should allow isolation of low-coordinate silyl complexes which may function as more reactive silylating reagents. Such species may also serve as precursors to conductive metal silicide thin films, which are not easily prepared by direct metal–silicon reactions.[2] Here we report use of the $Si(SiMe_3)_3$ (TTSS) ligand in preparing low coordination number silyl complexes of chromium, manganese, and iron.

First-row transition-metal dichlorides react with 2 equiv of $(THF)_3Li(TTSS)$[3] in ether solvents to afford air- and moisture-sensitive, anionic silyl complexes (eq 1 and 2). Compounds **1–3** are isolated following crystallization from diethyl ether/pentane.

Table I. Data for Silyl Compounds **1–9**

compd	color	yield, %	μ_{eff}, μ_B[a]	dec temp, °C[b]
$Li(THF)_3[(TTSS)_2CrCl]$, **1**	orange	80	6.2[c]	
$Li(DME)_2[(TTSS)_2MnCl]$, **2**	lt yellow	85	5.1[c]	143
$Li(DME)_2[(TTSS)_2FeCl]$, **3**	purple	76	6.3[c]	142
$NEt_4[(TTSS)_2FeCl]$, **4**	purple	62	5.8[d]	148
$NEt_4[(TTSS)FeCl_2(pyr)]$, **5**	orange	62	5.3[d]	119
$NEt_4[(TTSS)_2FeOSO_2CF_3]$, **6**	purple	74	6.1	139
$(TTSS)_2Fe(DME)$, **7**	purple	79	5.7	160
$(TTSS)_2Fe(Et_2O)$, **8**	blue-green	55	5.8	86
$(TTSS)_2Mn(DME)$, **9**	lt yellow	76	5.4	161

[a] Magnetic moments were determined by the Evans Method[9] in benzene, unless otherwise noted. Diamagnetic corrections were not applied. [b] When heated in a sealed capillary, all compounds began to decompose at the temperatures given. [c] Diethyl ether solvent. [d] 1,2-Dimethoxyethane solvent.

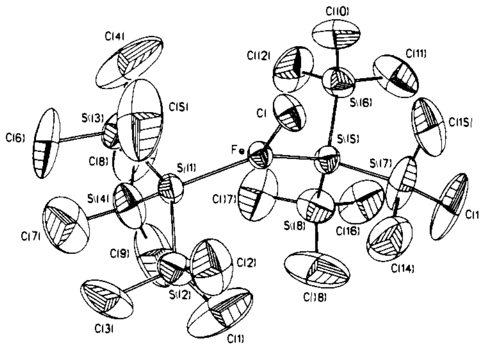

Figure 1. ORTEP view of the anion of **4**. Selected bond distances (Å) and angles (deg): Fe–Cl 2.284 (6), Fe–Si(1) 2.488 (6), Fe–Si(5) 2.491 (6), Si(1)–Si(2) 2.353 (8), Si(1)–Si(3) 2.331 (10), Si(1)–Si(4) 2.303 (10), Si(5)–Si(6) 2.370 (8), Si(5)–Si(7) 2.311 (9), Si(5)–Si(8) 2.331 (11), Cl–Fe–Si(1) 111.7 (2), Cl–Fe–Si(5) 111.1 (2), Si(1)–Fe–Si(5) 136.9 (2), Fe–Si(1)–Si(2) 105.2 (3), Fe–Si(1)–Si(3) 108.4 (3), Fe–Si(1)–Si(4) 121.2 (3), Fe–Si(5)–Si(6) 108.5 (3), Fe–Si(5)–Si(7) 106.0 (3), Fe–Si(5)–Si(8) 120.5 (3).

Orange **1**, which is also obtained from reaction of $CrCl_3$ with 3 equiv of $(THF)_3Li(TTSS)$ (eq 1), is thermally unstable at room temperature but may be stored indefinitely as a solid at −20 °C. Complexes **2** and **3** are stable at room temperature under nitrogen.

$$\begin{tikzcd} CrCl_2\cdot 2THF + 2(THF)_3Li(TTSS) \arrow[dr, "OEt_2"] & \\ & Li(THF)_3[(TTSS)_2CrCl] \quad (1) \\ CrCl_3 + 3(THF)_3Li(TTSS) \arrow[ur, "OEt_2"'] & \end{tikzcd}$$

1

$$MCl_2 + 2(THF)_3Li(TTSS) \xrightarrow{DME} Li(DME)_2[(TTSS)_2MCl] \quad (2)$$

2, M = Mn
3, M = Fe

Paramagnetic silyl complexes are quite rare[1] and to our knowledge do not exist for Cr, Mn, or Fe. These low-coordinate complexes possess large magnetic moments consistent with high-spin electron configurations (see Table I). In toluene at room temperature, the ESR spectrum of **2** exhibits a broad signal with $g = 2.003$ and $a = 1.87 \times 10^{-3}$ cm^{-1}. The compounds in Table I were characterized by infrared spectroscopy and elemental analyses. In some cases, carbon analyses were consistently low and variable;[4] therefore product stoichiometries were confirmed by hydrolysis and ^{1}H NMR integration of the released $HSi(SiMe_3)_3$ and ether against an internal ferrocene standard. Additional characterization is by X-ray crystal structure determination and high-resolution mass spectrometry of related derivatives (vide infra).

[†] University of California at San Diego.

[‡] University of Delaware.

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0002-7863/87/1509-0945$01.50/0