Formation of N-Methylated Cyclic Ligand Systems from Unusual Reactions between Trimethylamine *N*-Oxide and Acetylenes on Fe₃Te₂(CO)₉ and Contrast with Reactions on Fe₃E₂(CO)₉ (E = S, Se)

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Activation of C−H bonds of *N*-methyl groups has been achieved on cluster support. Use of a noncoordinating solvent in the reaction of Me₃NO · 2H₂O, acetylenes, and Fe₃Te₂(CO)₉ leads to activation of *N*-methyl groups of Me₃NO and formation of *N*,*N*-dimethyldihydropyrrole (**1**) and *N*,*N*′-dimethyl-hexahydropyrimidine (**2**) ring systems. The NMe₃ ligand, resulting from TMNO, is retained on the metal cluster due to the absence of a coordinating solvent and reacts with incoming acetylenes. In contrast, activation of the *N*-methyl groups of Me₃NO is not observed in the reaction using Fe₃S₂(CO)₉, which yields complexes with vinylferrocene (**3**) and 1,4-diferrocenylbuta-1,3-diene-2,3-dithio (**4**) units attached to Fe₂S₂(CO)₆. All new compounds have been structurally characterized by single-crystal X-ray diffraction studies.

Introduction

Trimethylamine *N*-oxide (TMNO) has been widely used for the activation of coordinatively saturated metal carbonyl complexes and clusters via oxidative decarbonylation.[1] Traditionally it has been used for the replacement of CO by a donor solvent molecule, which is further replaced by the desired ligand.[2] However, in contrast to the large number of reports on the decarbonylating behavior of TMNO in coordinating solvents such as acetonitrile, little is known about its reactivity in coordinatively "innocent" solvents.[3] We have earlier reported that, in the presence of acetonitrile/TMNO, Fe₃E₂(CO)₉ (E = S, Se, Te) complexes are converted into Fe₂E₂(CO)₆, which can react with coordinatively unsaturated organometallic fragments to form mixed-metal clusters. Thus, the reaction of Fe₃Te₂(CO)₉ with CpMo(CO)₃(C≡CPh) in acetonitrile/TMNO gives a mixed-metal chalcogen cluster with an η¹-acetylide group.[4] Addition of substituted alkynes and of carbenes and alkynyl Fisher carbenes to the E−E′ bonds in Fe₂EE′(CO)₆ also occurs readily

Scheme 1
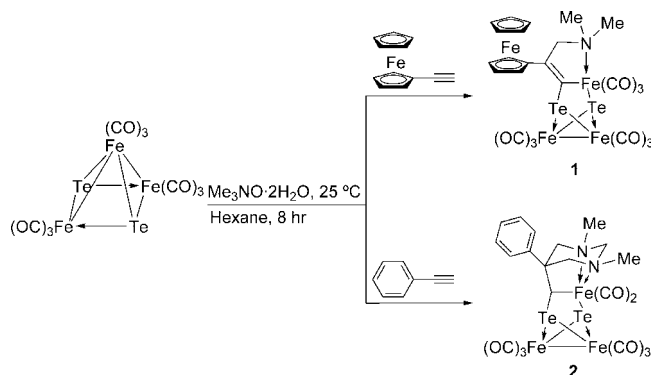
under facile conditions.[5] For instance, a reaction between Fe₂Te₂(CO)₆ and diazomethane results in the insertion of :CH₂ into the Te−Te bond and gives Fe₂(CO)₆(*μ*-TeCH₂Te).[6] In the past, we have used the compounds Fe₃E₂(CO)₉ and Fe₂(CO)₆(*μ*-E₂) (E = S, Se, Te) as supports to carry out numerous types of carbon−carbon bond formations resulting from coupling between metal acetylides.[7] In this paper, we report a novel *N*-methyl activation in a reaction between acetylenes and TMNO · 2H₂O on a Fe₃Te₂(CO)₉ cluster. Also, a contrast in the behavior of Fe₂S₂(CO)₉ is observed in its reaction with ferrocenylacetylene in the presence of TMNO · 2H₂O, where no activation of *N*-methyl groups takes place.

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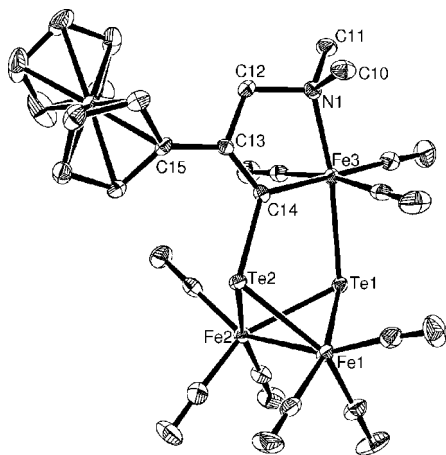
Figure 1. Molecular structure of **1** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.6052(6), Fe(1)−Te(1) = 2.5610(5), Fe(1)−Te(2) = 2.5381(4), Fe(3)−Te(1) = 2.6090(5), Fe(3)−C(14) = 2.008(3), Te(2)−C(14) = 2.136(3), C(13)−C(14) = 1.340(4), Fe(3)−N(1) = 2.092(3); Te(2)−Fe(1)−Te(1) = 83.956(14), Te(2)−Fe(2)−Te(1) = 83.920(14).
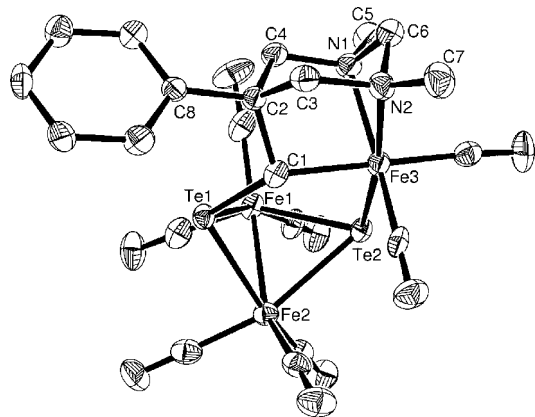

Figure 2. Molecular structure of **2** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.5919(11), Fe(1)−Te(1) = 2.5359(9), Fe(1)−Te(2) = 2.5563(9), Fe(3)−Te(2) = 2.5792(9), Fe(3)−N(1) = 2.085(5), Fe(3)−N(2) = 2.086(5), C(1)−Fe(3) = 2.010(6), C(1)−Te(1) = 2.193(6), C(1)−C(2) = 1.535(7); Te(2)−Fe(1)−Te(1) = 82.95(3), Te(2)−Fe(2)−Te(1) = 82.77(3).

Results and Discussion

Compounds **1** and **2** (Scheme 1) were obtained from a room-temperature reaction of $Fe_3Te_2(CO)_9$, TMNO·$2H_2O$, and ferrocenyl- or phenylacetylene, respectively, in hexane solution. Use of hexane solvent is significant in this reaction, as when acetonitrile or dichloromethane was used, only decomposition resulted.

The IR spectra of both compounds show the presence of a terminal carbonyl stretching pattern typically found in compounds containing the $Fe_2(CO)_6$ moiety. ^1H NMR spectra show signals for *N*-methyl and methylene protons along with signals for Cp protons in **1** and phenyl ring protons in **2**. Crystals of **1** and **2** were grown by slow evaporation of their solutions in hexane/dichloromethane mixtures at 0 °C, and single-crystal X-ray analysis was performed for unambiguous molecular structure determinations. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively.

The structure of **1** consists of a ferra-*N,N*-dimethyldihydro-pyrrole ring containing the ferrocenyl group at the 3-position

Scheme 2.[a]
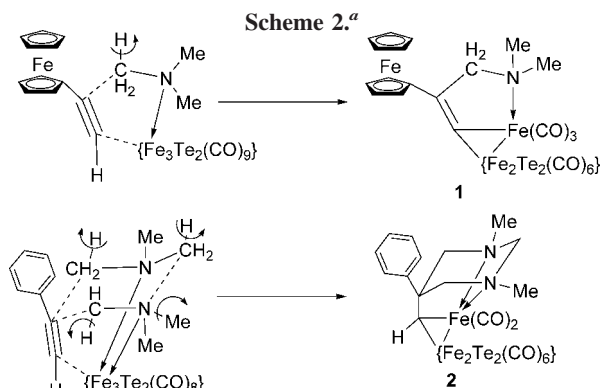
[a] Loss of one H from a methyl group and addition of CH_2NMe_2 group to ferrocenylacetylene on a $Fe_3Te_2(CO)_9$ support results in the formation of **1**. Loss of two H atoms from two methyl groups of one NMe_3 group and loss of one H and a loss of a methyl group from a second NMe_3 and addition of phenylacetylene leads to the formation of the hexahydropyrimidine ring of **2**.

and attached to the wingtip Te atoms of a Fe_2Te_2 butterfly unit. Each iron atom retains the three terminal carbonyls. The pyrrole ring lies approximately perpendicular to the Fe−Fe axis, with the ferrocenyl substituent oriented away from the carbonyl groups of the $Fe_2(CO)_6$ unit. The bond length C(14)−Te(2) = 2.1363(3) Å is similar to the C−Te bond distances in $Fe_2Te_2(CH_2)(CO)_6$ (2.157(12), 2.169(9) Å) reported earlier.[8] The Te−Te distance, Te(1)−Te(2) = 3.4106 Å, is slightly longer than those in complexes of the type $Fe_2Te(X)TeCO)_6$ (X = CH_2, 3.114(1) Å; X = $Fe(CO)_3(PPh_3)$, 3.138(1) Å), indicating a greater opening of the Fe_2Te_2 butterfly unit to accommodate the ferra-*N,N*-dimethylhydropyrrole ring.[8,9] A more open Fe_2Te_2 butterfly unit is also evident from the average Te−Fe−Te bond angles of ca. 84° in **1** and 83° in **2** as compared to average Te−Fe−Te angles in $Fe_2Te(X)TeCO)_6$ complexes reported earlier (X = CH_2, $Fe(CO)_3(PPh_3)$, 75°; X = $Ru_3(CO)_{11}$, 79°).[8−10]

The molecular structure of **2** features an *N,N′*-dimethyl-5-phenylhexahydropyrimidine unit attached to a $Fe_3Te_2(CO)_8CH$ framework. Whereas in **1** the ferra-*N,N*-dimethyldihydropyrrole ring is formally formed by coupling of one trimethylamine with a ferrocenylacetylene molecule, in **2** two trimethylamine ligands from two TMNO groups are incorporated during cyclization and a six-membered ring is formed. The two nitrogen atoms of **2** are attached to the iron cluster by donating their lone pairs to Fe(3). The two N−Fe bond distances in **2**, N(1)−Fe(3) = 2.0854(5) Å and N(2)−Fe(3) = 2.0844(5) Å, are similar to the distance N(1)−Fe(3) = 2.0916(3) Å in **1**. The bond length C(1)−Te(1) = 2.1927(5) Å matches well with those in **1** and $Fe_2Te_2(CH_2)(CO)_6$ reported earlier.[9] The Te−Te distance, Te(1)−Te(2) = 3.3725(5) Å, is also similar to that in **1**, indicative of a similar extent of opening of the Fe_2Te_2 butterfly.

Formation of the new clusters formally involves reaction between one or two molecules of trimethylamine and ferrocenylacetylene or phenylacetylene, respectively, on a ditellurotriiron cluster. It is likely that initially the adduct $[\{Fe_2Te_2(CO)_6\}\{Fe(CO)_3NMe_3\}]$ is formed, in which a ferrocenylacetylene molecule formally inserts between the coordinated trimethylamine and a Te of the $\{Fe_2Te_2(CO)_6\}$ unit

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Scheme 3
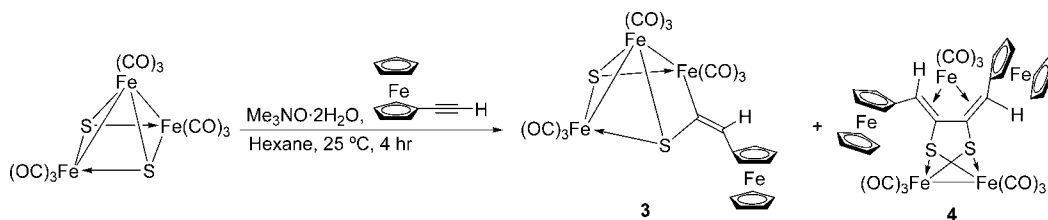
(Scheme 2). In the process, a C−H bond of one methyl group of trimethylamine is activated and transformed into an iminium group, which adds to the α-carbon of the ferrocenylacetylene. In **1**, there is no net loss of carbonyl groups. Although not isolated, a similar type of iminium formation has been invoked in the mechanism proposed for the formation of $[HOs_6(CO)_{17}]^-$ from the reaction of $Os_6(CO)_{18}$ with Me_3NO in a noncoordinating solvent.[3]

Compound **2** can be thought to form by an initial formation of an intermediate, $[\{Fe_2Te_2(CO)_6\}\{Fe(CO)_2(NMe_3)_2\}]$, arising from addition of one trimethylamine and substitution of one carbonyl by a second trimethylamine molecule. A formal addition reaction occurs between one molecule of phenylacetylene and two molecules of trimethylamine. One of the methyl groups from one trimethylamine molecule undergoes conversion to a methylene group, and in the second trimethylamine there is a loss of one methyl group while another methyl group converts to a methylene group (Scheme 2). The square-pyramidal $Fe_3(CO)_9Te_2$ undergoes a structural transformation identical with that observed in **1**.

Although the mechanistic pathway is uncertain at this time, the absence of a coordinating solvent is crucial for the formation of **1** and **2**. Use of a noncoordinating solvent such as hexane ensures that the trimethylamine ligand, originating from TMNO, remains coordinated to the metal and can engage in additions with ferrocenyl- or phenylacetylene on the ditellurotriiron cluster support.

In order to investigate the scope and limitation of using TMNO as a reagent in an innocent solvent in the reaction with chalcogen-bridged clusters, we have looked at the reactions of $Fe_3Se_2(CO)_9$ and $Fe_3S_2(CO)_9$ with ferrocenylacetylene and TMNO. Several compounds were observed in the reaction when

$Fe_3Se_2(CO)_9$ was used; however, none of these were stable enough to enable their isolation and characterization. In contrast, the reaction in which $Fe_3S_2(CO)_9$ was used formed two stable products, compounds **3** and **4** (Scheme 3).

For both compounds the IR spectra showed a carbonyl stretching pattern similar to that seen in the spectra of **1** and **2** and characteristic of a $Fe_2(CO)_6$ unit. ^{1}H NMR spectra of compounds **3** and **4** each show signals for ferrocenyl groups and peaks at δ 6.57 ppm (**3**) and δ 6.53 and 6.61 ppm (**4**) for olefinic protons. Crystals of **3** and **4** were grown by slow evaporation of their solution in hexane/dichloromethane mixtures at 0 °C and single crystal X-ray analysis was performed for unambiguous molecular structure determinations.

The molecular structure of **3**, shown in Figure 3, can be described as consisting of an open butterfly $Fe_2(CO)_6$ unit in which the two S atoms are bridged by a $FcC(H)=CFe(CO)_3$ group. The Fe−Fe (2.579(2), 2.714(2) Å) and Fe−S (2.227(3)− 2.252(3) Å) bond distances of **3** are similar to those observed in $Fe_2(CO)_6(\mu\text{-SXS})$ types of complexes (X = $FcC=CH$, Fe−Fe = 2.4755(12) Å, Fe−S = 2.2658(16)−2.2847(18) Å; $FcC=C(H)C(O)$, Fe−Fe = 2.5077(3) Å, Fe−S = 2.2594(4)− 2.2648(5) Å).[11] The C=C double-bond distance in the vinylidene unit of **3** (1.437(17) Å) is comparable to those in **1** (1.340(4) Å) and other vinylidene complexes (∼1.33 Å).[12]

The structure of **4** differs from that of **3**, in that a $FcC(H)=CC=C(H)Fc$ butadiene unit bridges the two S atoms of a $Fe_2(CO)_6$ unit and is coordinated to a $Fe(CO)_3$ unit in an $\eta^2:\eta^2$ fashion (Figure 4). Structure of **4** can be described as arising from a formal addition of a 1,4-diferrocenylbuta-1,3-diene-2,3-dithiolate to a $Fe_2(CO)_6$ unit. Further, a $Fe(CO)_3$ unit engages in bonding to the two double bonds of the diene unit.

Figure 3. Molecular structure of **3** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.579(2), Fe(2)−Fe(3) = 2.714(2), Fe(3)−C(10) = 1.989(10), S(1)−C(10) = 1.651(14), C(10)−C(11) = 1.437(17), Fe(1)−S(1) = 2.243(3), Fe(1)−S(2) = 2.242(3), Fe(2)−S(1) = 2.250(3), Fe(2)−S(2) = 2.252(3), Fe(3)−S(2) = 2.227(3); S(1)−Fe(2)−S(2) = 85.42(11), C(11)−C(10)−S(1) = 122.2(8), C(11)−C(10)−Fe(3) = 126.3(10).
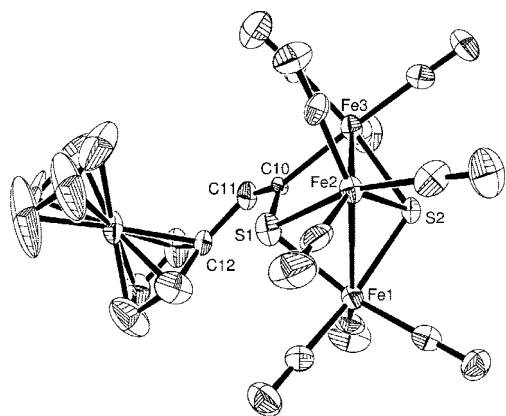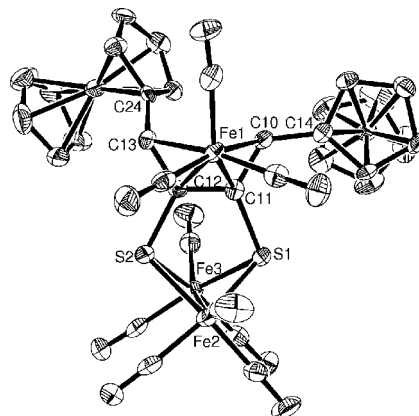

Figure 4. Molecular structure of **4** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(10)−C(14) = 1.465(10), C(10)−C(11) = 1.415(10), C(11)−C(12) = 1.403(9), C(12)−C(13) = 1.428(9), C(13)−C(24) = 1.470(9), S(1)−C(11) = 1.807(7), S(2)−C(12) = 1.794(6), Fe(2)−S(1) = 2.269(2), Fe(3)−S(1) = 2.288(2); S(2)−Fe(2)−S(1) = 80.24(7), C(12)−C(11)−C(10) = 118.7(6), C(11)−C(12)−C(13) = 123.1(6).

Scheme 4
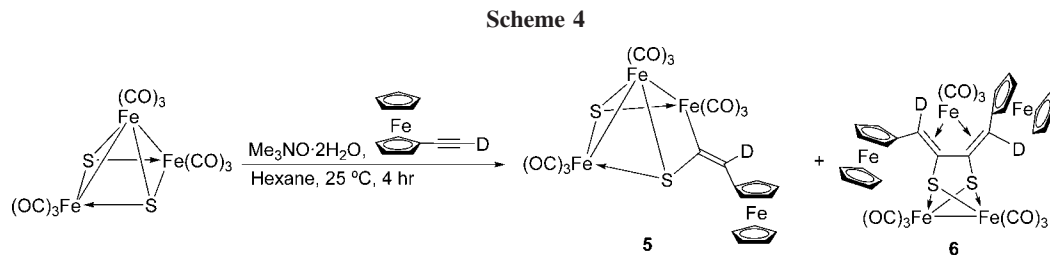
Table 1. Crystal Data and Structure Refinement Parameters for Compounds 1−4

	1	2	3	4
empirical formula	$C_{24}H_{17}Fe_4NO_9Te_2$	$C_{22}H_{20}Cl_2Fe_3N_2O_8Te_2$	$C_{21}H_{10}Fe_4\ O_9S_2$	$C_{33}H_{20}Fe_5O_9S_2$
formula wt	941.99	934.05	693.81	903.86
temp, K	150(2)	150(2)	150(2)	120(2)
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2/c$
a, Å	9.3250(2)	9.8877(2)	13.6715(12)	10.1722(8)
b, Å	15.1222(3)	13.3922(3)	7.1808(5)	12.7137(8)
c, Å	20.0419(4)	22.1362(5)	24.9489(2)	25.4348(16)
α, deg	90	90	90	90
β, deg	90	91.621(2)	94.762(7)	101.025(6)
γ, deg	90	90	90	90
V, Å^3	2826.20(10)	2930.06(11)	2440.8(3)	3228.7(4)
Z	4	4	4	4
D_{calcd}, Mg m^{-3}	2.214	2.117	1.888	1.859
abs coeff, mm^{-1}	4.087	3.646	2.551	2.378
$F(000)$	1792	1784	1376	1808
cryst size, mm	0.38 × 0.33 × 0.31	0.32 × 0.23 × 0.21	0.26 × 0.22 × 0.18	0.27 × 0.21 × 0.18
θ range, deg	2.98−25.00	3.04−24.99	2.95−25.00	3.20−25.00
index ranges	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-16 \leq h \leq 16$	$-12 \leq h \leq 11$
	$-17 \leq k \leq 17$	$-15 \leq k \leq 15$	$-8 \leq k \leq 8$	$-15 \leq k \leq 15$
	$-23 \leq l \leq 23$	$-26 \leq l \leq 26$	$-29 \leq l \leq 29$	$-30 \leq l \leq 30$
no. of collected/unique rflns	24 727/4954	23 848/5135	21 527/4299	20 197/5664
R(int)	0.0261	0.0338	0.1243]	0.0800
no. of data/ restraints/params	4954/0/363	5135/0/354	4299/14/325	5664/0/450
goodness of fit on F^2	1.090	1.113	1.100	0.999
final R indices (I > $2\sigma(I)$)	R1 = 0.0162	R1 = 0.0402	R1 = 0.0774	R1 = 0.0625
	wR2 = 0.0370	wR2 = 0.1041	wR2 = 0.1543	wR2 = 0.1510
R indices (all data)	R1 = 0.0176	R1 = 0.0476	R1 = 0.1424	R1 = 0.0969
	wR2 = 0.0381	wR2 = 0.1108	wR2 = 0.1802	wR2 = 0.1636
largest diff peak and hole, e Å^{-3}	0.740 and −0.257	1.725 and −1.120	2.445 and −0.923	1.308 and −0.754

The bond parameters of $Fe_2(CO)_6S_2$ and the butadiene−$Fe(CO)_3$ unit in **4** are unexceptional. The distance C(11)−C(12) = 1.403(9) Å is also comparable to the corresponding bond in $Fe_2(CO)_6\{\mu\text{-}SC(Fc)\text{=}C(H)S\}$ (1.313(8) Å).[11]

The formation of compound **3** involves a formal hydride shift of ferrocenylacetylene and an insertion of the vinylidene unit :C=C(H)Fc thus formed into a Fe−S bond of $Fe_3S_2(CO)_9$ cluster. We also carried out the reaction using deuterium-labeled ferrocenylacetylene (Scheme 4). The ^{1}H NMR spectra of **5** and **6** showed almost complete disappearances of peaks for the C=C(*H*)Fc and FcC(*H*)CC(*H*)CFc. Their mass spectra showed molecular ion peaks shifted up by one and two units, relative to those of **3** and **4**, respectively, thus confirming that the vinylidene C=C(H)Fc is indeed formed by an intramolecular hydride shift. Although compound **6** can be regarded to formally also be obtained by addition of a second vinylidene unit to **5**, we were unable to effect this transformation on addition of excess ferrocenylacetylene to compound **5**.

Conclusion

The results reported here demonstrate the utility of trimethylamine *N*-oxide as a reagent for addition to unsaturated molecules in a noncoordinating solvent, to form an N-heterocyclic ligand system. Formation of the metalladihydropyrrole and hexahydropyrimidine rings on the telluro−iron carbonyl support is unique and may be prototypical of formation of other

organic molecules arising from addition reactions between trimethylamine *N*-oxide and substituted acetylenes. In contrast, incorporation of an NMe_3 group and *N*-Me activation were not observed in the reaction with the $Fe_3S_2(CO)_9$ cluster, while reaction with $Fe_3Se_2(CO)_9$ did not yield any stable product.

The contrast between reactions of the Te compound from those of the Se- and S-bridged triiron nonacarbonyls is not unexpected and can be ascribed to the much larger difference in the size and basicity of Te as compared with those of its chalcogen congeners.

Experimental Section

General Procedure. Reactions and manipulations were performed using standard Schlenk line techniques under an atmosphere of prepurified argon. Solvents were purified, dried, and distilled under an argon atmosphere prior to use. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrometer as hexane solutions in 0.1 mm path length NaCl cells and NMR spectra on a Varian VXRO-300S spectrometer in $CDCl_3$. Elemental analyses were performed on a Carlo-Erba automatic analyzer. Iron pentacarbonyl and ferrocene were purchased from Fluka and Spectrochem, respectively, and these were used without further purification. Phenylacetylene was purchased from Aldrich and used without further purification. TLC plates were purchased from Merck (20 × 20 cm, silica gel 60 F$_{254}$). Photochemical reactions were carried out using double-walled quartz vessels and a 125 W immersion type mercury lamp manufactured by Applied Photophysics Ltd.

Reaction of Fe₃Te₂(CO)₉, TMNO·2H₂O, and Ferrocenyl- or Phenylacetylene. TMNO·2H₂O (55 mg 0.5 mmol) was added to a round-bottomed side-arm flask containing ferrocenylacetylene (210 mg, 1 mmol) and Fe₃Te₂(CO)₉ (338 mg, 0.5 mmol) in hexane (30 mL). The reaction mixture was stirred at room temperature for 4 h. At the end of the reaction, the reaction mixture was diluted with CH₂Cl₂ and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified through TLC with dichloromethane/petroleum ether (30/70) as eluent to give pure products.

1. Yield: 21%. Anal. Calcd for $C_{24}H_{18}Fe_4NO_9Te_2$: C, 30.60; H, 1.82; N, 1.49. Found: C, 29.54; H, 2.13; N, 1.36. IR (cm⁻¹, ν_{CO}): 2053 (s), 2016 (vs) 1972 (vs), 1956 (s, br). ¹H NMR (CDCl₃): δ 4.33 (s, 5H, η^5-C₅H_5), 4.21−4.43 (m, 4H, η^5-C₅H_4), 3.61 (s, 2H, −CH_2−) 2.37 (s, 6H, CH_3−N). MS (m/z, ES+): 941.8814 (M⁺).

2. Yield: 32%. Anal. Calcd for $C_{21}H_{18}Fe_3N_2O_8Te_2$: C, 29.70; H, 2.14; N, 3.30. Found: C, 28.96; H, 2.73; N, 3.51. IR (cm⁻¹, ν_{CO}): 2047 (s), 2006 (vs), 1989 (vs), 1947 (s). ¹H NMR (CDCl₃): δ 7.31−7.56 (m, 5H, C₆H_5), δ 2.91−3.34 (m, 6H, −CH_2−), 2.29 (s, 6H, CH_3−N). MS (m/z, ES+): 849.1247 (M⁺).

Reaction of Fe₃S₂(CO)₉, TMNO·2H₂O, Ferrocenylacetylene. TMNO·2H₂O (55 mg 0.5 mmol) was added to a round-bottomed side-arm flask containing ferrocenylacetylene (210 mg, 1 mmol) and Fe₃S₂(CO)₉ (242 mg, 0.5 mmol) in hexane (30 mL). The reaction mixture was stirred at room temperature for 4 h. At the end of the reaction, the reaction mixture was diluted with CH₂Cl₂ and filtered through a Celite pad. The filtrate was concentrated and chromatographed on silica gel TLC plates; compounds **3** and **4** were obtained as green and red bands, respectively.

3. Yield: 23%. Anal. Calcd for $C_{21}H_{10}O_9Fe_4S_2$: C, 36.35; H, 1.45; S, 9.24. Found: C, 35.78; H, 2.03; S, 9.54. IR (cm⁻¹, ν_{CO}): 2059 (s), 2021 (vs) 1981 (vs), 1962 (s, br). ¹H NMR (CDCl₃): δ 4.37 (s, 5H, η^5-C₅H_5), 4.24−4.51 (m, 4H, η^5-C₅H_4), 6.57 (s, 1H, FcCH). MS (m/z, ES+): 693.7134 (M⁺).

4. Yield: 19%. Anal. Calcd for $C_{33}H_{20}Fe_5O_9S_2$: C, 43.82; H, 2.23; S, 7.08. Found: C, 43.37; H, 2.70; S, 7.56. IR (cm⁻¹, ν_{CO}): 2080 (s), 2045 (vs), 2009 (vs), 1947 (s). ¹H NMR (CDCl₃): δ 4.27 (s, 5H, η^5-C₅H_5), 4.41 (s, 5H, η^5-C₅H_5), 4.32−4.91 (m, 8H, η^5-C₅H_4), 6.53 (s, 1H, FcCH), 6.61 (s, 1H, FcCH). MS (m/z, ES+): 903.9175 (M⁺).

Preparation of Deuterium-Labeled Ferrocenylacetylene and Its Reaction with Fe₃S₂(CO)₉ and TMNO·2H₂O. A ferrocenylacetylene (210 mg, 1 mmol) solution in THF (20 mL) at −20 °C was treated with n-BuLi (0.7 mL of 1.6 M in hexanes, 1.1 mmol) followed by hydrolysis with D₂O after 30 min. The product was extracted with hexane, and the combined solution was washed with water, dried over Na₂SO₄, and evaporated under reduced pressure to give 185 mg (88%) of ferrocenylacetylene-d. TMNO·2H₂O (55 mg 0.5 mmol) was added to a round-bottomed side-arm flask containing ferrocenylacetylene-d (211 mg, 1 mmol) and Fe₃S₂(CO)₉ (242 mg, 0.5 mmol) in hexane (30 mL). The reaction mixture was stirred at room temperature for 4 h. At the end of the reaction, the reaction mixture was diluted with CH₂Cl₂ and filtered through a

Celite pad. The filtrate was concentrated and chromatographed on silica gel TLC plates; compounds **5** and **6** were obtained as green and red bands, respectively.

5. Yield: 20%. IR (cm⁻¹, ν_{CO}): 2059 (s), 2021 (vs) 1981(vs), 1962 (s, br). ¹H NMR (CDCl₃): δ 4.37 (s, 5H, η^5-C₅H_5), 4.24−4.51 (m, 4H, η^5-C₅H_4). MS (m/z, ES+): 694.7230 (M⁺).

6. Yield: 18%. IR (cm⁻¹, ν_{CO}): 2080 (s), 2045 (vs), 2009 (vs), 1947 (s). ¹H NMR (CDCl₃): δ 4.27 (s, 5H, η^5-C₅H_5), 4.41 (s, 5H, η^5-C₅H_5), 4.32−4.91 (m, 8H, η^5-C₅H_4). MS (m/z, ES+): 905.7090 (M⁺).

Crystal Structure Determination for 1−4. Suitable X-ray-quality crystals of **1**, **2**, and **4** could be grown from a dichloromethane/n-hexane solvent mixture at 0 °C, and X-ray diffraction studies were undertaken. For compound **3**, we were unable to obtain single crystals of sufficiently good quality, and consequently, the data collected and subsequent structure solution are of modest quality. Relevant crystallographic data and details of measurements are given in Table 1. X-ray crystallographic data were collected from single-crystal samples of **1** (0.38 × 0.33 × 0.31 mm³), **2** (0.32 × 0.23 × 0.21 mm³), **3** (0.26 × 0.22 × 0.18 mm³), and **4** (0.27 × 0.21 × 0.18 mm³) mounted on a Oxford Diffraction XCALIBUR-S CCD system equipped with graphite-monochromated Mo Kα radiation (0.710 73 Å). The data were collected by the $\omega-2\theta$ scan mode, and absorption correction was applied by using Multi-Scan. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares against F^2 using SHELXL-97 software.[13] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and refined using a riding model.

Supporting Information Available: CIF files giving crystallographic data (excluding structure factors) for **1−4**. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-661651 (**1**), CCDC-661652 (**2**) CCDC-695954 (**3**) and CCDC-695955 (**4**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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