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Reduction of Tellurium by $Na_2[Fe(CO)_4]$: Synthesis and Reactivity of $[PPN]_2[Fe_2(CO)_6(Te_2)_2]$

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Summary: $[PPN]_2[Fe_2(CO)_6(Te_2)_2]$ *was synthesized by the direct reaction of* $Na_2Fe(CO)_4$ *with elemental tellurium. Reaction of* $[PPN]_2[Fe_2(CO)_6(Te_2)_2]$ *with iodomethane or diiodomethane yielded* $Fe_2(CO)_6(\mu\text{-}TeMe)_2$*, which was structurally characterized, or the known* $Fe_2(CO)_6(Te)_2(\mu\text{-}CH_2)$*, respectively.*

Introduction

Clusters containing both transition metals and main groups metals have long been an active area of study because of the potential activity of these compounds in catalytic processes as well as their use as precursors to useful solid materials.[1] Work in the chalcogen system has shown that while sulfur and selenium show similar behavior, the reactivity of tellurium is often unique.[2] Iron–tellurium compounds have shown an extremely rich chemistry for quite some time. Several homo- and heterometallic clusters have been prepared using $Fe_3(CO)_9Te_2$[3] and $Fe_2(CO)_6(\mu\text{-}Te_2)$[4] as starting materials.[5] More recently several research groups have investigated the use of the Zintl ion $[Te_4]^{2-}$ in direct reactions with zero or low-valent transition metal compounds to produce clusters. This work has resulted in the synthesis of anions such as $[Pd(Te_4)_2]^{2-}$,[6] $[Fe_2(CO)_6(Te)(Te)_2]^{2-}$,[7] $[Fe_5Te_4(CO)_{14}]^{2-}$, and $[Fe_8Te_{10}(CO)_{20}]^{2-}$.[8] This paper explores an alternative methodology in which highly nucleophilic metal carbonyl anions are used as the reductants to convert main group elements into Zintl ion species. It is intended that the concomitantly formed coordinatively unsaturated transition metal fragments will bond to the Zintl ion species forming new compounds of interesting structure and reactivity. Here we report the reaction of $Na_2Fe(CO)_4\cdot{}^3/_2$ diox (diox = dioxane) with elemental tellurium.

Experimental Section

General Procedures. All reactions and other manipulations were performed with oven-dried Schlenkware using standard techniques on a Schlenk line or in a Vacuum Atmospheres dry box.[9] All solvents were dried and distilled under nitrogen prior to use: THF, ether, and hexane (Na/Ph_2CO); toluene ($LiAlH_4$); dichloromethane (CaH_2). $Na_2Fe(CO)_4\cdot{}^3/_2$ diox,[10] the $Cu(MeCN)_4BF_4$,[11] and the bis(triphenylphosphine)nitrogen(1+) chloride,[12] [PPN]Cl, were prepared according to literature methods. Diiodomethane was distilled from powdered copper. The tellurium (Strem) and the iodomethane (Aldrich) were used without further purification. Solution IR spectra were recorded in 0.1-mm pathlength CaF_2 cells on a Perkin-Elmer Model 1640 FT-IR spectrophotometer. ^1H, ^{13}C, ^{125}Te NMR were all obtained on a Bruker AF 300 spectrometer in either chloroform or THF. Mass spectra were obtained on either a Finnegan 3300 (EI) or a Kratos MS50TC (FABMS). Carbon monoxide analyses were performed using a Rodder Toepler pump.

^{125}Te NMR. All ^{125}Te NMR measurements were made at ambient temperature on a Bruker AF 300 spectrometer operating at 94.693 MHz. A pulse width of 30 ms and a delay of 2 s were used. All spectra were referenced to an external standard of neat Me_2Te ($\delta = 0$). The measurements were made in chloroform with the exception of $[PPN]_2$**[I]** {**[I]** = $[Fe_2(CO)_6(Te_2)_2]$} which was measured in THF due to its reactivity with halogenated solvents.

Synthesis of Na_2[I]. To a Schlenk flask were added 0.50 g (1.44 mmol) of $Na_2Fe(CO)_4\cdot{}^3/_2$ diox, and 0.45 g (3.53 mmol) of tellurium metal. The flask was then charged with 30–40 mL of dry THF and stirred at least 48 h. A small amount of solid material was removed by filtration to yield a deep red solution of Na_2**[I]**. IR (THF, cm^{-1}): 2025 m, 2018 m, 1984 vs, 1945 s.

Metathesis of Na_2[I] with [PPN]Cl. The filtered reaction solution of Na_2**[I]** was stirred over 2–3 g of [PPN]Cl for 12 h to effect the cation exchange. The precipitated salts were removed by filtration resulting in a clear, deep red solution. Removal of the solvent in vacuo gives a dark red powder, $[PPN]_2$**[I]** (0.59 g, 44% based on starting $[Fe(CO)_4]^{2-}$) IR (KBr, cm^{-1}): 2953 m, 2021 m, 2057 m, 2015 s, 1975 s, 1937 s, 1632 s, 1435 m, 1109 s, 745 m, 719 m. FABMS: 727–743 ($[I]^{2-} - 2\,CO$). ^1H NMR (THF-d_8, ppm): 7.8–7.5 (m). ^{13}C NMR (THF-d_8, ppm): 216.9 (s), 134.6 (s), 132 (d, $J_{C-P} = 216.4$ Hz), 129.0 (s), 127.6 (s). All attempts to date to produce X-ray quality crystals have failed due to the reactive nature of this compound.

CO Analysis of $[PPN]_2$[I]. An amount of 0.178 g of $[PPN]_2$**[I]** and 0.85 g of pyridinium tribromide $[C_5H_5NH][Br_3]$ were weighed together into a flask. The flask was then attached to a vacuum line and approximately 25 mL of predried and carefully freeze–thaw degassed dichloromethane was distilled onto the solids at −196 °C. After the flask was sealed, the solvent was thawed and the mixture was heated between 75 and 80 °C for 2–3 h. The reaction mixture was then cooled to −196 °C and the CO collected and quantified utilizing a Toepler pump. Calcd: 3.21×10^{-3} mol CO/g (8.99 wt%) for a formula of $[PPN]_2[Fe_2(CO)_6Te_4]$. Found: 3.19×10^{-3} mol/g (8.94 wt%).

Reaction of Na_2[I] with $Cu(MeCN)_4BF_4$. A solution of Na_2**[I]** in THF was added to solid $[Cu(MeCN)_4]BF_4$ and the resulting mixture was stirred for 2 h at room temperature. The major product was $Fe_2(CO)_6Te_2$ as identified by its IR spectrum.[4] A

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Table I. Crystallographic Data Collection Parameters

compound	II
empirical formula	$Fe_2Te_2C_8O_6H_6$
fw	565.04
crystal system	orthorhombic
space group	*Pmna* (No. 62)
a, Å	20.902(5)
b, Å	10.840(19)
c, Å	6.306(8)
V, Å^3	1428.7(3.7)
Z	4
D(calcd), g cm^{-3}	2.63
μ(Mo Kα), cm^{-1}	60.60
T(max)/*T*(min) (Ψ-scans)	1.00/0.780
λ(Mo Kα), Å	0.7107
T, °C	−80
R, R_w	0.041, 0.067
GOF	2.84

small amount (<5%) of $Fe_3(CO)_9Te_2$ was also present. Yield 0.20 g, 52% based on starting $[Fe(CO)_4]^{2-}$.

Reaction of Na_2[I] with Iodomethane. Excess MeI (0.5 mL, 8.03 mmol) was added dropwise to a solution of Na_2[I] in THF with stirring. The solution immediately changed color from deep red to a red-orange color. After stirring for 1 h the mixture was filtered and the solvent removed in vacuo. Extraction with hexane yielded a solution of $Fe_2(CO)_6(\mu\text{-}TeMe)_2$ (**II**) contaminated with small amounts of the known compounds $Fe_3(CO)_9Te_2$ and $Fe_2(CO)_6Te_2$. These impurities were easily removed by chromatography on Florisil eluting with hexane. The product was isolated as bright red crystals from a concentrated hexane solution cooled to −20 °C (0.22 g, 55% based on starting $[Fe(CO)_4]^{2-}$). IR (hexane, cm^{-1}): 2055 m, 2022 vs, 1985 s, 1981 s, 1970 w. MS (EI, 40eV): 569–559 (M$^+$). ^{1}H NMR (CDCl$_3$, δ, ppm): 2.07 (s). ^{13}C NMR (CDCl$_3$, ppm): 211.9 (s), −17.3 (q, $^1J_{C-H}$ = 143.2 Hz). ^{125}Te NMR (CDCl$_3$, ppm): 20 (q, $^2J_{Te-H}$ = 20.7 Hz).

Reaction of Na_2[I] with Diiodomethane. Following the procedure outlined above for the iodomethane, 1 mL of diiodomethane was added to Na_2[I]. The product was found to be the known $Fe_2(CO)_6Te_2(\mu\text{-}CH_2)$ (**III**) (0.089 g, 23% based on Fe).[13b] IR (hexane, cm^{-1}): 2061 m, 2022 s, 1993 m, 1984 m, 1972 w. MS (EI, 40eV): 554–544 (M$^+$). ^{1}H NMR (CDCl$_3$, δ, ppm): 2.19 (s). ^{13}C NMR (CDCl$_3$, ppm): 211.8 (s), −64.8 (t, $^1J_{C-H}$ = 157.7 Hz). ^{125}Te NMR (CDCl$_3$, ppm): 336 (t, $^2J_{Te-H}$ = 24.9 Hz).

Crystal Structure Determination of II. A red, rod-shaped crystal of approximate dimensions 0.3 × 0.4 × 0.3 mm^3 was selected for the X-ray diffraction study. It was mounted on a glass fiber using epoxy cement. The data were collected on a Rigaku AFC5 four circle automated diffractometer at a temperature of −80 °C. Final unit cell parameters were based on least-squares analysis of 25 carefully centered reflections ($26.9 \leq 2\theta \leq 37.8$). The crystallographic data collection parameters are summarized in Table I. The crystal was shown to be orthorhombic and the space group was chosen as *Pnma* (no. 62) on the basis of the systematic absences and intensity statistics. The data were corrected for absorption (Ψ-scans), Lorentz, and polarization factors. Crystal and instrument stability were checked by measuring three standard reflections every 150 observations. Only small random fluctuations were observed, therefore no decay correction was applied. The analytic form of the scattering factors for the appropriate neutral atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[14] The structure was solved by direct methods using SHELX-86,[15] which located all the non-hydrogen atoms. Refinement was performed using TEXSAN 5.0 structure analysis package.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in calculated positions. Full matrix least squares refinement converged with $R = 0.041$, $R_w = 0.067$, and GOF = 2.84 for 1277 unique reflections with $I > 3\sigma(I)$ and 89 parameters. Final positional and displacement parameters are given in Table II and the bond metricals are found in Table III.

Table II. Positional Parameters and B_{eq} for $Fe_2(CO)_6(\mu\text{-}TeCH_3)_2$

atom	*x*	*y*	*z*	B_{eq}[a]
Te(1)	0.47183(4)	$^1/_4$	0.3390(1)	2.17(4)
Te(2)	0.32187(4)	$^1/_4$	0.4814(1)	2.41(4)
Fe(1)	0.37784(6)	0.1285(1)	0.1889(2)	1.93(6)
O(11)	0.4519(4)	0.0720(8)	−0.191(1)	3.8(4)
O(12)	0.2571(4)	0.0852(9)	−0.029(1)	4.6(4)
O(13)	0.3921(4)	−0.1081(8)	0.415(1)	4.4(4)
C(1)	0.5475(7)	$^1/_4$	0.113(3)	3.3(7)
C(2)	0.2202(7)	$^1/_4$	0.424(3)	3.6(7)
C(11)	0.4232(4)	0.095(1)	−0.043(2)	2.5(4)
C(12)	0.3037(5)	0.102(1)	0.057(2)	3.2(5)
C(13)	0.3873(4)	−0.013(1)	0.329(2)	2.6(4)
H(11)	0.5872	$^1/_4$	0.1929	4.2
H(12)	0.5448	0.1784	0.0327	4.2
H(21)	0.1988	$^1/_4$	0.5601	4.5
H(22)	0.2089	0.3216	0.3497	4.5

[a] $B_{eq} = 8\pi^2/3\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$

Table III. Intramolecular Bond Distances and Angles for $Fe_2(CO)_6(\mu\text{-}TeCH_3)_2$ (II)

Distances (Å)			
Te(1)–Te(2)	3.261(1)	Fe(1)–C(13)	1.78(1)
Te(1)–Fe(1)	2.548(2)	O(11)–C(11)	1.14(1)
Te(1)–C(1)	2.13(2)	O(12)–C(12)	1.13(1)
Te(2)–Fe(1)	2.551(3)	O(13)–C(13)	1.17(1)
Te(2)–C(2)	2.16(1)	C(1)–H(11)	0.972
Fe(1)–Fe(1A)	2.634(5)	C(1)–H(12)	0.927
Fe(1)–C(11)	1.78(1)	C(2)–H(21)	0.970
F(1)–C(12)	1.78(1)	C(2)–H(22)	0.936

Angles (deg)			
Te(2)–Te(1)–Fe(1)	50.28(5)	Fe(1A)–Fe(1)–C(11)	101.8(3)
Te(2)–Te(1)–C(1)	153.9(5)	Fe(1A)–Fe(1)–C(12)	99.3(4)
Fe(1)–Te(1)–Fe(1A)	62.3(1)	Fe(1A)–Fe(1)–C(13)	149.4(3)
Fe(1)–Te(1)–C(1)	108.9(4)	C(11)–Fe(1)–C(12)	92.8(5)
Te(1)–Te(2)–Fe(1)	50.20(4)	C(11)–Fe(1)–C(13)	100.0(5)
Te(1)–Te(2)–C(2)	154.3(5)	C(12)–Fe(1)–C(13)	100.9(5)
Fe(1)–Te(2)–Fe(1A)	62.2(1)	Te(1)–C(1)–H(11)	106.49
Fe(1)–Te(2)–C(2)	109.3(4)	Te(1)–C(1)–H(12)	108.62
Te(1)–Fe(1)–Te(2)	79.52(7)	H(11)–C(1)–H(12)	109.60
Te(1)–Fe(1)–Fe(1A)	58.87(5)	H(12)–C(1)–H(12)	113.66
Te(1)–Fe(1)–C(11)	89.9(3)	Te(2)–C(2)–H(21)	107.81
Te(1)–Fe(1)–C(12)	158.0(4)	Te(2)–C(2)–H(22)	109.48
Te(1)–Fe(1)–C(13)	100.0(3)	H(21)–C(2)–H(22)	108.98
Te(2)–Fe(1)–Fe(1A)	58.92(6)	H(22)–C(2)–H(22)	112.02
Te(2)–Fe(1)–C(11)	160.7(3)	Fe(1)–C(11)–O(11)	179(1)
Te(2)–Fe(1)–C(12)	91.2(4)	Fe(1)–C(12)–O(12)	179(1)
Te(2)–Fe(1)–C(13)	97.8(3)	Fe(1)–C(13)–O(13)	177.2(9)

Results

Crystal and Molecular Structure of II. $Fe_2(CO)_6(\mu\text{-}TeMe)_2$ (**II**) crystallizes in the primitive orthorhombic space group *Pnma* (no. 62). The atomic coordinates and equivalent isotropic displacement parameters are included in Table II and bond metricals can be found in Table III. Figure 1 shows the molecular geometry and the atom labeling scheme. The molecule lies on a mirror plane such that the asymmetric unit contains one $Fe(CO)_3$ fragment and half of each TeMe moiety. The molecules pack into the crystal lattice with no unusually short intermolecular contacts. As Figure 1 shows, **II** exhibits a butterfly

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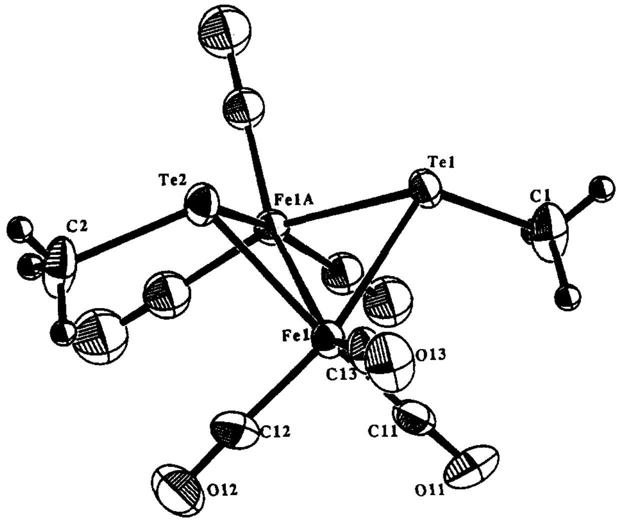

Figure 1. ORTEP representation of $Fe_2(CO)_6(\mu\text{-}TeMe)_2$, (**II**).

Table IV. Comparison of Bond Distances and Angles for II and III

	II	III[13b]
Distances (Å)		
Fe1–(Fe1A or Fe2)	2.634(5)	2.587(2)
Fe1–Te1	2.548(2)	2.551(2)
Fe1–Te2	2.551(3)	2.542(2)
Fe2–Te1		2.546(2)
Fe2–Te2		2.544(2)
Te1–Te2	3.261(1)	3.114(1)
Te1–C1	2.13(2)	2.169(9)
Te2–C1		2.157(12)
Te2–C2	2.16(1)	
Angles (deg)		
Fe1–Te1–(Fe1A or Fe2)	62.3(1)	61.1(1)
Fe1–Te2–(Fe1A or Fe2)	62.2(1)	61.1(1)
dihedral	96.66	90.49

Table V. Multinuclear NMR Data[a]

compound	^{1}H	^{13}C	^{125}Te
$[\mathrm{I}]^{2-}$	NA	216.9	
II	2.07	211.9, −17.4 (J = 143.2)	20 (J = 20.7)
III	2.19	211.8, −64.8 (J = 157.7)	336 (J = 24.9)
Me_2Te	1.59	−20.6 (J = 140.4)	0 (J = 20.5)

[a] Shifts are reported in ppm and coupling constants in hertz. References are ^{1}H, residual chloroform (7.25 ppm); ^{13}C, chloroform solvent (77.0 ppm); ^{125}Te, Me_2Te (0 ppm).

geometry with both the methyl groups in an equatorial position. Comparative bond metricals for **II** and **III** are included in Table IV. Atomic coordinates and anisotropic displacement parameters are included with the supplementary material.

Spectral Features. The infrared spectra in hexane of both **II** and **III** exhibit a band pattern consistent with the presence of a $Fe_2(CO)_6$ moiety. The two lower energy bands that are separated by only 4–8 wavenumbers collapse to a single band in more polar solvents such as toluene or THF. This phenomenon also occurs with $Fe_2(CO)_6Te_2$ making spectral identification of these species slightly ambiguous.

^{1}H, ^{13}C, and ^{125}Te data are summarized in Table V. The ^{1}H NMR spectrum of **II** shows only one signal at 2.07 ppm. This result is consistent with the presence of either only one stereoisomer or rapidly interconverting isomers in solution. The spectrum of **III** shows a singlet at 2.19 ppm. The ^{13}C spectrum of **II** contains two signals at 211.9 and −17.4 ppm which are assigned to the carbonyl carbons and the methyl group, respectively. The ^{1}H-coupled spectrum shows that the methyl signal is a quartet with ${}^{1}J_{C-H}$ = 143.2 Hz. The ^{13}C spectrum of **III** also contained two signals at 211.8 and −64.8 (${}^{1}J_{C-H}$ = 157.7 Hz) ppm. The peak assignments were made in analogous fashion. The ^{125}Te NMR spectrum of **II** shows one signal at 20 ppm which appears as a quartet, ${}^{2}J_{Te-H}$ = 20.7 Hz, when proton coupled. Compound **III** shows one signal at 336 ppm which is a triplet, ${}^{2}J_{Te-H}$ = 24.9 Hz. Compound $[\mathrm{I}]^{2-}$ has a single resonance in the CO region of the ^{13}C spectrum occuring at 216.9 ppm. Unfortunately, to date all attempts at characterizing $[\mathrm{I}]^{2-}$ by ^{125}Te NMR have yielded a very broad feature ranging from approximately −200 to −800 ppm. The cause of this phenomenon has yet to be determined. The same sample gives normal ^{1}H and ^{13}C spectra.

The FABMS of compound **I** shows a series of peaks, centered at 735 amu, from 727 to 743 amu with an isotopic pattern consistent with the presence of an $[Fe_2(CO)_4Te_4]$ fragment. This fragment would correspond to the loss of two carbonyl fragments from the molecular ion. The mass spectrum of **II** exhibits the molecular ion in the range of 559–569 mass units in a pattern that is consistent with the isotopic distribution expected for two tellurium atoms. It also shows peaks that can be associated with the stepwise loss of CO that is characteristic of many cluster compounds as well as peaks corresponding to the loss of one or both methyl fragments. The base peak is the bare Fe_2Te_2 fragment. The mass spectrum of **III** shows similar behavior with stepwise loss of CO but the base peak is the $Fe_2Te_2CH_2$ fragment indicating that the tellurium–carbon bond is more robust in this cluster.

Discussion

Synthesis and Probable Structure of $[PPN]_2[\mathrm{I}]$. The synthesis of $[PPN]_2[\mathrm{I}]$ represents one of the only examples where a nucleophilic metal anion is used as a reducing agent to create Zintl ions directly. It is considerably more common to generate the Zintl ion separately by reduction of the main group element with an alkali metal in a highly polar solvent such as dimethylformamide or ethylenediamine.[6,7] The direct reduction process employed in this work also creates unsaturated transition metal fragments which then react further with both the Zintl ions present and each other to produce mixed metal clusters. This methodology represents a one-step synthesis of cluster species from readily available transition metal anions and the elemental form of the main group element. The exact nature of the initially formed tellurium species in solution is uncertain. If the iron anion and the tellurium are mixed in nearly stoichiometric amounts very little tellurium remains at the end of the reaction; however, the reaction seems to occur faster in the presence of excess tellurium which is easily removed.

The most probable formula for $[PPN]_2[\mathrm{I}]$ is $[PPN]_2[Fe_2(CO)_6(Te_2)_2]$. This formulation is supported by several pieces of experimental evidence. The FABMS shows a complex pattern from 727 to 743 mass units centered at 735 as the most intense. This is consistent with both the molecular mass and the isotope distribution expected for the composition of the anion with the loss of two CO fragments. While FABMS is normally considered to be a soft technique which yields a molecular ion, it should be noted that highly charged organometallic carbonyl compounds fragment extremely easily by the loss of CO under most forms of mass spectrometry. Additionally, decomposition of $[PPN]_2[I]$ with pyridinium tribromide yields 3.19×10^{-3} mol of CO/g of material (8.94 wt %) in excellent agreement with the value expected for $[PPN]_2[Fe_2(CO)_6(Te_2)_2]$, 3.21×10^{-3} mol/g (8.99 wt %). Lastly, the IR pattern is consistent with the presence of a symmetric $Fe_2(CO)_6$ fragment. In a related structure, $[Fe_2(CO)_6(Te)(Te)_2]^{2-}$ reported by Haushalter and co-workers[7] the IR spectrum contains five distinct bands in both the solid state and solution (1995, 1950, 1922, 1898, 1886 cm^{-1}). Compound $[I]^{2-}$ exhibits a simple four-band pattern qualitatively similar to that of **II** and **III**. The simplicity in the infrared pattern is consistent with a symmetric arrangement of the tellurium atoms around the iron fragment. The molecule can be viewed as similar to $[Fe_2(CO)_6(Te)(Te)_2]^{2-}$ with the bridging Te atom replaced by an additional μ^2-η^1-Te_2 fragment. Unfortunately, no structural information is available for this compound. It is extremely sensitive in solution, and all attempts at crystallization have thus far yielded material unsuitable for diffraction studies.

Furthermore, $[PPN]_2[I]$ reacts with oxidizing agents, such as $[Cu(MeCN)_4][BF_4]$, to yield primarily $Fe_2(CO)_6Te_2$. In this process tellurium metal is produced as a byproduct. The reactions with iodomethane and diiodomethane, yielding **II** and **III**, respectively, also produce tellurium metal. The presence of the extruded tellurium in these reactions supports a formula containing a larger tellurium to iron ratio for the starting anion $[I]^{2-}$ than the 1:1 found in **II**, **III**, and $Fe_2(CO)_6Te_2$. In the reaction with alkyl iodides small amounts of the oxidation products are also formed. This is most likely due to the ability of the iodides to act as mild oxidizing agents as well as methylating reagents.

X-ray Structure Determination of II. The Fe–Fe distance in $Fe_2(CO)_6(\mu\text{-}TeMe)_2$ (**II**), 2.634(5) Å, compares well with that in other compounds with $Fe_2(CO)_6$ fragments: 2.614(4) Å in $[Fe_2(CO)_6(\mu\text{-}Te)(\mu\text{-}Te)_2]^{2-}$,[7] 2.607(6) and 2.619(7) Å in $[(MeTeFe_2(CO)_6]_2[TeCH_2Te]$,[17] 2.537(10) Å in $Fe_2(CO)_6(\mu\text{-}SEt)_2$,[18] and 2.575(2) Å in $Fe_2(CO)_6(\mu\text{-}Se_2)$.[19] Likewise the Te–Fe distances, 2.548(2) and 2.551(3) Å, agree well with previously reported values: 2.551(2) and 2.546(2) Å in $Fe_2(CO)_6(Te_2CH_2)$,[13b] 2.53 Å (av) in $Fe_3(CO)_9Te_2$,[20] and 2.572 Å (av) in $[Fe_2(CO)_6(\mu\text{-}Te)(\mu\text{-}Te)_2]^{2-}$.[7] The Te–C distances, 2.16(1) and 2.13(2) Å, are normal and compare well to 2.147 Å in $[PPN][(\mu\text{-}TeMe)\{(\eta^5\text{-}Cp)Mn(CO)_2\}_3]$[21] and 2.169(9) and 2.157(12) Å in $Fe_2(CO)_6(Te_2CH_2)$.[13b] The Te–Te distance, 3.261 Å, is well outside the normal bonding range.

NMR Data. The carbonyl signal in the ^{13}C spectrum of $[PPN]_2[I]$ is shifted in the downfield direction relative to both **II** and **III**, δ = 216.9 ppm versus 211.9 and 211.8 ppm, respectively. However, this shift is smaller than would be expected on moving from a neutral species to a dianion. By comparison, $Fe_3(CO)_{12}$ exhibits a resonance at 212.5 ppm[22] while the corresponding dianion $[Fe_3(CO)_{11}]^{2-}$ appears at 230.7 ppm.[23] The related monoanion, $[HFe_3(CO)_{11}]^-$, shows one room temperature signal at 221.5 ppm.[24] Additionally, deprotonation of $HFe_3(CO)_{10}(COMe)$ causes the carbonyl resonance to shift from 209.9 (av) to 220.1 (av) ppm.[23] The much smaller difference seen between $[PPN]_2[I]$ and **II** or **III** indicates that the charge on $[I]^{2-}$ maybe localized on the terminal tellurium atoms rather than delocalized over the entire cluster. This observation is consistent with the reactivity patterns observed.

One striking spectral difference between **II** and **III** is the value of the carbon–hydrogen coupling constant and the corresponding values for the tellurium–hydrogen coupling constants. Carbon–hydrogen coupling constants have been shown to be related to the amount of s orbital character present in the carbon's hybrid orbitals being used for carbon–hydrogen bonding.[25] Typical average C–H one-bond coupling constants are 125 Hz for sp^3-hybridized carbon and 160 Hz for sp^2 carbon.[26] **II** has a $^1J_{C\text{-}H}$ of 143.2 Hz, which is clearly consistent with a normal sp^3 carbon attached to a heavy main group element. The $^1J_{C\text{-}H}$ of dimethyltellurium was measured as 140.4 Hz while that of iodomethane was reported as 151 Hz.[25] In contrast, the value $^1J_{C\text{-}H}$ = 157.7 Hz for **III** is indicative of substantial sp^2 character at that carbon. For comparison, the $^1J_{C\text{-}H}$ for the ring portion of toluene averages to 155 Hz while the value for the methyl group is 126 Hz.[25] The $^2J_{Te\text{-}H}$ coupling constants also show a similar trend with values of 20.5, 20.7, and 24.9 Hz for dimethyltellurium, **II** and **III**, respectively. These spectral differences indicate that the presence of the two telluriums and the relatively small Te–C–Te angle have introduced substantial sp^2 character into the methylene carbon in **III**.

The ^{125}Te NMR data for **II** and **III** are also deserving of comment. Many tellurium-containing iron carbonyl compounds have their Te NMR shifts grouped into two regions, either very low field (≈1100 ppm) or very high field (≈ −800 ppm) relative to Me_2Te. Rauchfuss and co-workers have put forth an explanation for this rather striking phenomenon. They suggested that the region in which the tellurium signal will be found is determined by the Te–Te distance within the cluster.[27] Those clusters in which the telluriums are close enough to interact directly through space are found at high field and those where the telluriums are isolated from each other resonate at low field. This model seems to fit a large number of the clusters known to date; however, numerous exceptions for other metal systems led Herrmann and co-workers to propose that this interacting/noninteracting model is too simple and that other factors, including those such as the paramagnetic contribution to the shift, must be considered.[28] This analysis involved data from widely different transition metals, so some caution is warranted in making comparisons.

In light of this previous work, it was thought that **II** and **III**, which are very similar structurally, would be ideal compounds to test the predictive power of the interacting/noninteracting model. The major difference between **II** and **III** is the Te–Te distance. In **III** the bridging

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methylene unit forces the Te–Te distance to be 3.114 Å,[13b] within the range necessary for significant through-space interaction. This constraint is absent in **II** and consequently, the Te–Te distance expands to 3.261 Å, well outside the distance associated with significant interactions. If the interacting/noninteracting model were operative, shifts of +1100 and −800 ppm would be predicted for **II** and **III**, respectively. In both cases these values are not observed. The shift δ = 20 ppm observed for **II** indicates that the magnetic environment of the tellurium is similar to that found in Me_2Te. The observed value for **III**, 336 ppm, is qualitatively similar to that found in Ph_2Te_2 (423 ppm)[4] and one of the telluriums in $(\mu, \eta^1{:}\eta^2\ Te_2)[Cp^*Re(CO)_2]_2$ (−200.3 and 434.4 ppm).[29] Both compounds contain ditellurium species with single Te–Te bonds. From our measurements as well as those above it must be concluded that no simple correlation between Te–Te distance and NMR shift exists.

Conclusion

Highly nucleophilic carbonyl anions react with main group elements to form Zintl ion species attached to transition metal carbonyl fragments. The reaction takes place under mild conditions allowing for the isolation of reactive species such as $[Fe_2(CO)_6(Te_2)_2]^{2-}$. This methodology should be applicable to a wide range of transition metal anions and main group elements. Studies on the generality of this synthetic pathway are presently underway.

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Supplementary Material Available: Listings of anisotropic displacement parameters and intermolecular distances for **II** (3 pages). Ordering information is given on any current masthead page.

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