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Synthesis, Reactivity, and ^{125}Te NMR Studies of $(C_5H_5)RhFe_2Te_2(CO)_x$ (x = 6, 7)

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Received November 5, 1982

The square-pyramidal 50e cluster $Fe_3Te_2(CO)_9$ reacts with $CpRh(CO)_2$ (Cp = η^5-C_5H_5) to give a good yield of the heterometallic 52e cluster $CpRhFe_2Te_2(CO)_7$. This heptacarbonyl undergoes Me_3NO-induced decarbonylation to give two isomers of the hexacarbonyl $CpRhFe_2Te_2(CO)_6$. Recarbonylation of $CpRhFe_2Te_2(CO)_6$ formed the same heptacarbonyl in isomerically pure form. In contrast, addition of PPh_3 to $CpRhFe_2Te_2(CO)_6$ gave two isomers of $CpRhFe_2Te_2(CO)_6PPh_3$ that differ with regard to the placement of the PPh_3 ligand on iron or rhodium. The iron-phosphine adduct undergoes chemically induced decarbonylation to $CpRhFe_2Te_2(CO)_5PPh_3$ while the rhodium-phosphine adduct resists decarbonylation. ^{125}Te NMR spectroscopy has been used for structure elucidation. The 50e (nido) clusters $Fe_3Te_2(CO)_9$, $Fe_3Te_2(CO)_8(PPh_3)$, and $CpMFe_2Te_2(CO)_6$ (two isomers each for M = Co, Rh) all absorb in the range 1123-1081 ppm downfield of Me_2Te. In dramatic contrast, the 52e (arachno) clusters $Fe_3Te_2(CO)_9(PPh_3)$, $CpMFe_2Te_2(CO)$ and $CpRhFe_2Te_2(CO)_6PPh_3$ all absorb in the range −825 to −973 ppm. $PtFe_2Te_2(CO)_6(PPh_3)_2$, which has an arachno-like structure but a nido electron count (50e), absorbs in the arachno range.

Introduction

Bridging nonmetals play a pivotal role in the synthesis and stabilization of many transition-metal cluster compounds.[1] Structural studies have established that nonmetals can span from two to twelve[2] vertices. Reactivity studies have shown that, once assembled, such nonmetal transition-metal clusters are not only very resistant to declusterification but are often coordinatively unsaturated.[3,4]

Table I. Microanalytical Data (Theoretical Values in Parentheses)

compd	% C	% H	% Fe
$CpRhFe_2Te_2(CO)_7$	19.66 (19.72)	0.66 (0.69)	15.17 (15.28)
$CpRhFe_2Te_2(CO)_6$	18.89 (18.79)	0.66 (0.72)	16.01 (15.89)
$CpRhFe_2Te_2(CO)_6PPh_3$ (mixture of isomers)	36.00 (36.09)	2.07 (2.09)	11.81 (11.57)
$CpRhFe_2S_2(CO)_6$	25.46 (25.81)	0.90 (0.98)	21.77 (21.82)
$CpRhFe_2Te_2(CO)_5PPh_3$	36.19 (35.88)	2.14 (2.15)	11.62 (11.92)

We have developed an interest in tellurium-bridged metal carbonyl cluster compounds with recent emphasis on the chemistry $Fe_3Te_2(CO)_9$. This compound can be readily prepared in ca. 90% yield via the reduction of TeO_3^{2-} by $HFe(CO)_4^-$.[5] In contrast to the behavior of its NCH_3, S, and Se analogues, $Fe_3Te_2(CO)_9$ forms adducts with a wide variety of Lewis bases, e.g. NH_3, R_3P, CO, and I^-.[4,6] Furthermore, the Fe_3Te_2 unit is so resistant to declusterification that it can be recovered intact from refluxing neat $P(OCH_3)_3$.[7] In contrast, unbridged clusters like $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ reliably fragment upon treatment with excesses of Lewis bases.[8] In this paper we describe the transmetalation of $Fe_3Te_2(CO)_9$ leading to new clusters whose core stoichiometry is $RhFe_2Te_2$. Mechanistic implications aside, selective and direct transmetalation is a potentially powerful yet obviously simple route to mixed-metal cluster compounds.[9] This method is conceptually distinct from the widely recognized condensation approach[10] since transmetalation preserves the nuclearity of the cluster precursor. In the present case the transmetalated product is of special interest since it, like $Fe_3Te_2(CO)_9$, is effectively coordinatively unsaturated.

This paper describes the utility of ^{125}Te NMR spectroscopy for structural characterization. The $RhFe_2Te_2$ clusters are particularly suitable for this technique for two reasons: first, these clusters undergo a number of relatively subtle structural changes that are difficult to elucidate otherwise and, second, the distinctive nuclear properties of ^{103}Rh (100% naturally abundant, $I = {}^1/_2$) allow us to supplement chemical shift data with J_{RhTe}, thereby strengthening structural assignments. The results on the $RhFe_2Te_2$ system are found to be fully corroborated by the ^{125}Te NMR data obtained for related Fe_2MTe_2 clusters. These results reveal the extraordinary sensitivity of the chemical shift of the bridging tellurium to the metal-metal bonding within the cluster.

Experimental Section

^{125}Te NMR spectra were obtained on $CDCl_3$ solutions at 31.583 or 31.547 MHz on a modified Varian XL-100 spectrometer using an external D_2O lock. Operating parameters included a spectral width of 50 kHz, a pulse width of 25 μs, and a pulse delay of 2 s. To obtain satisfactory spectra, 10^3–10^4 scans were required. All chemical shifts are referenced to neat Me_2Te at 27 °C, upfield being negative. $^{31}P\{^1H\}$ NMR spectra were obtained on the same instrument with 85% H_3PO_4 as the reference. IR spectra were obtained with use of cyclohexane solutions on a Nicolet 7199C FT IR spectrometer. Field desorption mass spectra (FDMS) were run on a Varian 731 spectrometer by Carter Cook. Microanalyses (Table I) were performed by the School of Chemical Sciences analytical laboratory.

Reactions were performed under nitrogen in reagent grade solvents. Thin-layer chromatography was performed on 2 × 10 cm plates cut from sheets of Eastman silica gel coated poly(vinyl chloride). Column chromatography was done with Fisher Florisil. Me_3NO was prepared

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by triply subliming $Me_3NO{\cdot}2H_2O$ (Aldrich) in vacuo at 80 °C. The preparations of $CpRh(CO)_2$,[11] $Fe_3Te_2(CO)_9$,[5] $Fe_3Te_2(CO)_9PPh_3$,[4] $Fe_3Te_2(CO)_8PPh_3$,[4] and $PtFe_2Te_2(CO)_6(PPh_3)_2$[12] are described elsewhere.

$CpRhFe_2Te_2(CO)_7$. $Fe_3Te_2(CO)_9$ (1.1 g, 1.7 mmol) and $CpRh(CO)_2$ (0.40 g, 1.8 mmol) in MeCN (100 mL) were refluxed for 2 h and then evaporated to dryness. The residue was recrystallized from CH_2Cl_2 and MeOH: yield 73% (0.92 g); FDMS m/z 731 (M^+).

$CpRhFe_2Te_2(CO)_6$. Me_3NO (0.027 g, 0.37 mmol) was added to a CH_2Cl_2 (50 mL) solution of $CpRhFe_2Te_2(CO)_7$ (0.23 g, 0.32 mmol). After being stirred 10 min at room temperature, the solution was concentrated to 5–10 mL, and then hexane (~30 mL) was added. Enough CH_2Cl_2 was added to dissolve the crystals that formed. The solution was placed on a Florisil column (80 mL) and eluted with hexane. The red-purple fraction (first band) was evaporated to dryness and then recrystallized from CH_2Cl_2/MeOH: yield 58% (0.15 g); FDMS m/z 703 (M^+); UV–vis (toluene) λ_{max} 395 nm, $\epsilon = 9.75 \times 10^3$ L mol^{-1} cm^{-1}.

Carbonylation of $CpRhFe_2Te_2(CO)_6$. A CH_2Cl_2 (15 mL) solution of $CpRhFe_2Te_2(CO)_6$ (0.050 g) was stirred in an autoclave under 2000 psi of CO. After 1 h at room temperature, a ~1:1 mixture (by TLC using 1:1 benzene/hexane eluent) of hexa- and heptacarbonyl derivatives was obtained. The solution was evaporated to dryness and chromatographed on Florisil (1:1 benzene/hexane eluent). An IR spectrum of the dried residue of the orange fraction (second band) was identical with that of the sample prepared from $CpRh(CO)_2$ and $Fe_3Te_2(CO)_9$.

$CpRhFe_2Te_2(CO)_6PPh_3$. PPh_3 (0.35 g, 1.3 mmol) was added to a CH_2Cl_2 (60 mL) solution of $CpRhFe_2Te_2(CO)_6$ (0.19 g, 0.27 mmol), which was then stirred for 16 h. The resulting mixture was evaporated to dryness, extracted into a mininum of benzene/hexane, and chromatographed on a Florisil column, eluting with 1:1 benzene/hexane. After two minor bands (orange then purple), a third intensely red-orange band was eluted. The dried residue from the third band was recrystallized from CH_2Cl_2/MeOH: yield 71% (0.18 g); FDMS m/z 965 (M^+). The two isomers of $CpRhFe_2Te_2(CO)_6PPh_3$ were separated by using a 40-cm Florisil column (1:1 benzene/hexane eluent). Alternatively the mixture of isomers was reacted with an excess of Me_3NO, which selectively decarbonylated the iron–phosphine isomer. The large difference in polarity between $CpRhFe_2Te_2(CO)_6PPh_3$ and $CpRhFe_2Te_2(CO)_5PPh_3$ permitted easy chromatographic separation of this mixture on Florisil.

$CpRhFe_2Te_2(CO)_5PPh_3$. Excess Me_3NO was added to a CH_2Cl_2 solution of $CpRhFe_2(CO)_6PPh_3$ (iron–phosphine isomer), and the mixture was stirred for 10 min. TLC (1:1 benzene/hexane eluent) showed quantitative conversion to a purple, less polar compound. The solution was filtered through a silica gel plug; then crystals were obtained by adding MeOH and concentrating: FDMS m/z 937 (M^+); UV–vis (toluene) λ_{max} 401 nm.

$CpRhFe_2S_2(CO)_6$. A hexane solution (15 mL) of $CpRh(CO)_2$ (0.11 g, 0.50 mmol) and $Fe_2(S_2)(CO)_6$ (0.17 g, 0.50 mmol) was refluxed for 2 h. The concentrated solution was chromatographed on a Florisil column, and the third band (red-brown) was collected and evaporated. The residue was recrystallized from CH_2Cl_2/CH_3OH: yield 21% (53 mg); FDMS m/z 512 (M^+).

Results and Discussion

Synthesis and Reactivity of $CpRhFe_2Te_2(CO)_7$. $Fe_3Te_2(CO)_9$ was found to react with $CpRh(CO)_2$ (Cp = η^5-C_5H_5) in refluxing CH_3CN to give the transmetalated cluster $CpRhFe_2Te_2(CO)_7$ in 73% yield. The formulation of this new compound is based on microanalytical data and the observation of a molecular ion in its field desorption mass spectrum. Crystals of this compound display a distinctive metallic luster, which is also observed for $Fe_3Te_2(CO)_{10}$.[5] The similarity of these clusters also extends to their ^{125}Te NMR spectroscopy (vide infra). Since the CpRh(CO) and $Fe(CO)_4$ units are electronically equivalent, it follows that the formation of $CpRhFe_2Te_2(CO)_7$ from $Fe_3Te_2(CO)_9$ is equivalent to the addition of a Lewis base to $Fe_3Te_2(CO)_9$.[4] This arises since, in CH_3CN solution, $Fe_3Te_2(CO)_9$ is in equilibrium with $Fe_2(Te_2)(CO)_6$,[12] which in turn reacts with "CpRh(CO)".

Table II. IR Data[a]

compd	ν_{CO}, cm^{-1}
$CpRhFe_2Te_2(CO)_7$	2047 m, 2025 vs, 1981 s, 1972 s
$CpRhFe_2Te_2(CO)_6$	2036 vs, 2009 s, 1984 s, 1968 m, 1951 m
$CpRhFe_2Te_2(CO)_6PPh_3$ ($RhPPh_3$ isomer)	2040 s, 1997 vs, 1974 m, 1951 w, 1938 w
$CpRhFe_2Te_2(CO)_6PPh_3$ ($FePPh_3$ isomer)	2038 m, 2011 vs, 1965 s, 1950 m, 1937 w
$CpRhFe_2Te_2(CO)_5PPh_3$	2025 vs, 1969 sh, 1965 s, 1960 sh, 1922 m
$CpRhFe_2S_2(CO)_6$	2066 w, 2041 s, 1991 m

[a] Cyclohexane solutions.

Table III. ^{125}Te NMR Data ($CDCl_3$ solution)[a]

compd	δ	J, Hz
$Fe_3Te_2(CO)_9$	1123	
$Fe_3Te_2(CO)_9PPh_3$	−887	
	−938	42 (Te–P)
$Fe_3Te_2(CO)_8PPh_3$	1062	
$CpRhFe_2Te_2(CO)_7$[b]	−973	93 (Te–Rh)
$CpRhFe_2Te_2(CO)_6$[c]	1081	
	1109	
$CpRhFe_2Te_2(CO)_6PPh_3$[d,e]	−925	100 (Te–Rh) 21 (Te–P)
	−838	
$PtFe_2Te_2(CO)_6(PPh_3)_2$	−861	561 (Te–Pt)

[a] Positive shifts are downfield of neat Me_2Te. [b] $\delta(^1H)$ 5.66. [c] $\delta(^1H)$ 6.12. [d] $\delta(^{31}P)$ 37.1, $^1J_{PRh}$ = 176 Hz. [e] $\delta(^{31}P)$ 62.3, $^3J_{PRh}$ = 60 Hz, $^2J_{PTe}$ = 56 Hz.

Trimethylamine *N*-oxide effected decarbonylation of the mixed-metal heptacarbonyl cluster to give the purple-black *hexa*carbonyl $CpRhFe_2Te_2(CO)_6$. This compound, like the corresponding *hepta*carbonyl precursor, was characterized by IR spectroscopy (Table II), field desorption mass spectrometry, combustion analyses (Table I), and ^{125}Te NMR spectroscopy (Table III). The decarbonylation of $CpRhFe_2Te_2(CO)_7$ is accompanied by both a color change from orange to brown and a dramatic decrease in chromatographic polarity. This behavior again is completely analogous to the decarbonylation of $Fe_3(\mu_3\text{-}Te)_2(CO)_{10-n}L$.[4] These conversions involve the formation of nido (50e) clusters[13] from arachno (52e) precursors. It is interesting to note that in the nido configuration the mixed-metal cluster exists as two isomers as judged by ^{125}Te NMR spectroscopy. These isomers were not chromatographically separable, and the isomer ratio appeared to be invariant, as judged by IR and ^{125}Te NMR spectroscopy. Thus, they must interconvert readily although at a rate too slow to be measured in our NMR experiments. A similar dynamic process was postulated for $Fe_3(\mu_3\text{-}Te)_2(CO)_{9-n}L_n$[7] and was actually observed for $Os_3(\mu_3\text{-}S)(\mu_3\text{-}NSiMe_3)(CO)_9$.[14]

The reaction of $Fe_2(S_2)(CO)_6$ with $CpRh(CO)_2$ contrasts interestingly with the tellurium cluster chemistry in that we observed only the nido hexacarbonyl $CpRhFe_2S_2(CO)_6$. This observation illustrates the tendency of the μ_3-Te moiety to stabilize more open clusters than found for smaller tethering atoms.

$CpRhFe_2Te_2(CO)_6$ reacted under 2000 psi of CO to re-form the heptacarbonyl derivative, which was spectroscopically indistinguishable from the sample initially prepared from $CpRh(CO)_2$ and $Fe_3Te_2(CO)_9$. The formation of a single isomer from the isomeric nido precursors implies that the thermodynamically most favored heptacarbonyl isomer is that where the "extra" CO is ligated to the rhodium. Different

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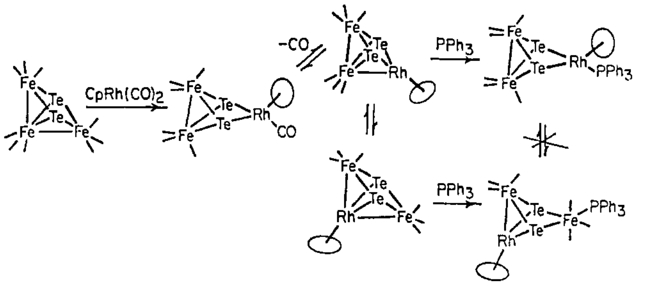
Scheme I



results were obtained for the reaction of the hexacarbonyl precursor with triphenylphosphine.

Reaction of $CpRhFe_2Te_2(CO)_6$ with excess triphenylphosphine at room temperature gave a mixture of *two* chromatographically separable isomers. The ^{31}P NMR spectrum of the reaction mixture revealed that the major isomer had a large J_{PRh} while the minor isomer was characterized by a much smaller J_{PRh} (Table III). These resonances are assigned to the two isomeric clusters of the formula $CpRhFe_2Te_2(CO)_6PPh_3$ (Scheme I). In the major isomer, the phosphine is coordinated to rhodium while the minor isomer is proposed to contain the $Fe(CO)_3PPh_3$ moiety. Upon treatment with Me_3NO, only the $Fe(CO)_3PPh_3$ isomer underwent decarbonylation to give the nido cluster $CpRhFe_2Te_2(CO)_5PPh_3$, which was characterized by FDMS and its electronic absorption spectrum. The nonreactivity of the $CpRhPPh_3$ isomer correlates with the generally observed pattern that a 6-coordinate $Fe(CO)_3$ vertex is particularly resistant to decarbonylation.

^{125}Te NMR Spectroscopy. With the advent of multinuclear NMR spectroscopy, an increasing interest has been shown in the ^{125}Te nucleus.[15,16] This isotope ($I = {}^1/_2$) is 7.3% naturally abundant and is characterized by a relatively high magnetogyric constant. At natural abundance, the ^{125}Te nucleus is approximately 14 times easier to detect than is ^{13}C.[15]

There have been two reports of ^{125}Te NMR studies on transition-metal compounds. The cis and trans isomers of $PtCl_2(Te(CH_2CH_2Ph)_2)_2$ were recently shown to have chemical shifts that differed by 45 ppm.[17] We have previously reported that the ^{125}Te NMR chemical shifts for $Fe_3Te_2(CO)_9$ and $Fe_2Te_2(CO)_6$ differed by 1800 ppm.[5] Thus, it was clear at the inception of the project that, while not necessarily easily correlated, ^{125}Te NMR shifts would be particularly sensitive to subtle structural changes.

The ^{125}Te NMR spectrum of $CpRhFe_2Te_2(CO)_7$ consists of a rhodium-coupled doublet ($J_{RhTe} = 91$ Hz) centered at −973 ppm relative (upfield) to $Te(CH_3)_2$ (Table III). This same isomer of $CpRhFe_2Te_2(CO)_7$ could be prepared via either the transmetalation reaction of $Fe_3Te_2(CO)_9$ or carbonylation of $CpRhFe_2Te_2(CO)_6$. In contrast, the ^{125}Te NMR spectrum of $CpRhFe_2Te_2(CO)_6$ showed signals at 1081 and 1109 ppm downfield of $Te(CH_3)_2$, the intensities being ca. 1:4 in favor of the higher field signal. The ^{125}Te chemical shift change of *2000 ppm* attendant to the interconversion of the hexa- to heptacarbonyl spectacularly illustrates the sensitivity of the chemical shift of the μ_3-Te moiety to the metal–metal bonding in these clusters. Consistent with this, we note that the isomeric PPh_3 adducts of the formula $CpRhFe_2Te_2(CO)_6PPh_3$ again have ^{125}Te NMR shifts very close to that of heptacarbonyl. While the isomeric PPh_3 adducts are characterized by comparable ^{125}Te NMR shifts, they differ appreciably in $|J_{PRh}|$ as determined by ^{31}P NMR spectroscopy. The isomer with the larger $|J_{PRh}|$ of 176 Hz is assumed to possess the PPh_3 coordinated to the RhCp moiety. The other isomer, characterized $|J_{PRh}| = 60$ Hz, must therefore contain the $Fe(CO)_3PPh_3$ group. Furthermore, the ^{125}Te NMR pattern for the Fe–PPh_3 isomer of $[CpRhFe_2Te_2(CO)_6]\cdot PPh_3$ is broad and complex, consistent with the complications associated with slightly nonequivalent Te moieties each of which is coupled to ^{103}Rh and ^{31}P nuclei. On the other hand, the ^{125}Te NMR spectrum of the Rh–PPh_3 isomer is straightforward as it reveals coupling of equivalent Te atoms to both ^{103}Rh and ^{31}P (Figure 1).

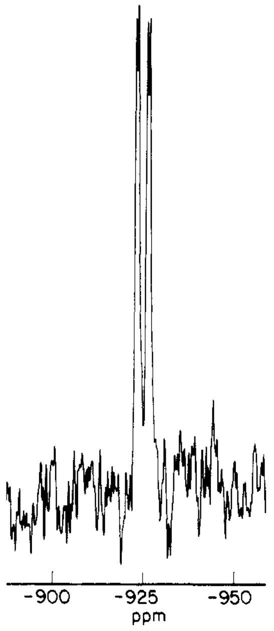


Figure 1. ^{125}Te NMR spectrum of $CpRh(PPh_3)(\mu_3\text{-}Te)_2Fe_2(CO)_6$.

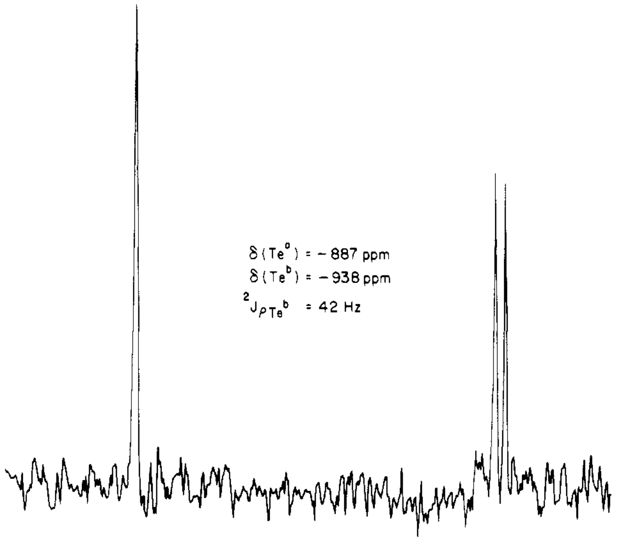


Figure 2. ^{125}Te NMR spectrum of $Fe_3Te_2(CO)_9PPh_3$.

The correlation of ^{125}Te NMR shifts and cluster core structure is strongly supported by studies on related cluster compounds whose structures are well established. $Fe_3Te_2(CO)_9$, a 50 e cluster compound, has a ^{125}Te NMR shift of 1100 ppm downfield of $Te(CH_3)_2$, within 15 ppm of the resonances observed for the $CpRhFe_2Te_2(CO)_6$ isomers. Conversion of $Fe_3Te_2(CO)_9$ to its PPh_3 adduct results in a large upfield shift. Both its chemical shift and the splitting pattern are consistent with the arachno structure for $Fe_3Te_2(CO)_9PPh_3$. This structure, which has been confirmed crystallographically,[4] consists of an $Fe(CO)_3PPh_3$ moiety bridged via two μ_3-Te units

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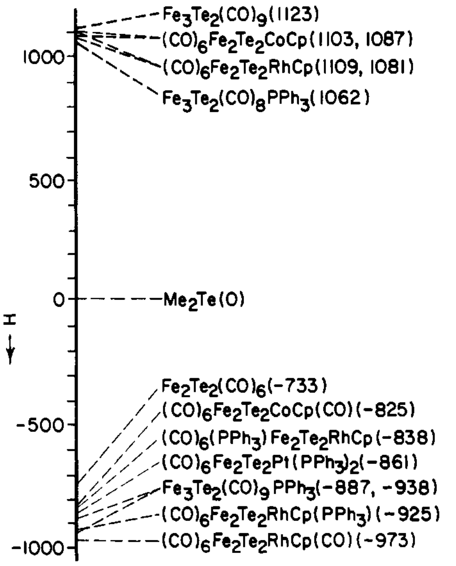
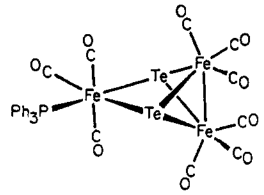
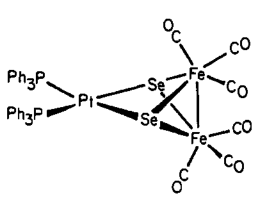


Figure 3. ^{125}Te NMR chemical shift scale for some Te-containing organometallic clusters.

to the $Fe_2(CO)_6$ base. This structure is fully compatible with the ^{125}Te NMR spectrum, which is comprised of a singlet and a ^{31}P-coupled doublet (Figure 2). Decarbonylation of this adduct affords $Fe_3Te_2(CO)_8PPh_3$, whose ^{125}Te NMR shift now lies in the region observed for other nido clusters. From these measurements it is clear that there are two *distinct* chemical shift regions for these nido and arachno M_3Te_2 clusters at 1100 ± 25 and −900 ± 75 ppm, respectively. The observed chemical shift scale is depicted in Figure 3.

The species $PtFe_2Te_2(CO)_6(PPh_3)_2$,[18] like $Fe_3Te_2(CO)_9$, is a 50e cluster compound. On the basis of its electron count alone, a square-pyramidal (nido) structure and a low-field ^{125}Te NMR shift would be anticipated. However, as a consequence of the predilection of platinum(II) for the electron deficient 16e configuration, $Pt(PPh_3)_2$ is *effectively* equivalent to the $Fe(CO)_4$, CpCo(CO), and CpRh(CO) moieties. This assertion is supported by the close structural relationship that exists between $Fe_3Te_2(CO)_9PPh_3$ and $PtFe_2Se_2(CO)_6(PPh_3)_2$[18] (which is completely analogous to $PtFe_2Te_2(CO)_6(PPh_3)_2$).





This structural and electronic equivalence of the arachno (52e) Fe_3Te_2 and MFe_2Te_2 clusters and the 50e $PtFe_2Te_2$ cluster is confirmed by their similar ^{125}Te NMR chemical shifts (Figure 3). This measurement demonstrates that *the observed ^{125}Te NMR shift pattern is a consequence of the number of metal–metal bonds subtended by the tethering Te groups and not the electron count of the cluster.* This conclusion is consistent with the view that the observed ^{125}Te chemical shift pattern results from the magnetic anisotropy associated with the metal–metal bonds.[19]

Conclusions

The conversion of $Fe_3Te_2(CO)_9$ into $CpRhFe_2Te_2(CO)_7$ involves transmetalation concomitant with a nido to arachno cluster expansion. We suggest that the assembly of the Fe_2RhTe_2 clusters proceeds via the 2e oxidative addition of CpRh(CO) across the Te–Te bond of $Fe_2(Te_2)(CO)_6$. A similar process is exemplified by the simple oxidative addition of $PtC_2H_4(PPh_3)_2$ to $Fe_2(Te_2)(CO)_6$ to give $PtFe_2Te_2(CO)_6(PPh_3)_2$.[18] In the event that the incorporated metal fragment can undergo further ligand dissociation and can accommodate a pseudooctahedral coordination geometry, further condensation can occur as observed in the synthesis of the isomeric nido $RhFe_2Te_2$ clusters. The intermediate arachno cluster is readily isolable for $CpRhFe_2Te_2(CO)_7$ whereas for the corresponding sulfide it is unstable with respect to decarbonylation. A particularly important aspect of the conversion of the Fe_3Te_2 cluster to its $CpRhFe_2Te_2$ derivative is that $Fe_3Te_2(CO)_9$ effectively functions as a source of the highly reactive and unstable $Fe_2(Te_2)(CO)_6$ moiety.[5] The implication is that $Fe_3Te_2(CO)_9$ represents a potentially versatile precursor to a number of different clusters containing the $FeTe(CO)_3$ unit.[12]

^{125}Te NMR spectroscopy has proven to be uniquely effective for elucidating structural changes peculiar to the $CpRhFe_2Te_2$ cluster core. While it is logical that a single arachno isomer would obtain for the oxidative addition of $Fe_2(Te_2)(CO)_6$ to "CpRh(CO)", it is not so obvious that the two isomers of $CpRhFe_2Te_2(CO)_6$ would carbonylate to give the same isomer. In contrast, the isomeric triphenylphosphine adducts $CpRhFe_2Te_2(CO)_6PPh_3$ do no readily interconvert, indicative that these are kinetic products.

The distinctive chemical shift patterns observed for the nido and arachno M_3Te_2 clusters (Figure 3) demonstrate the utility of NMR measurements on the cluster core. Similar shift patterns have been observed for related phosphinidine (μ_3-PR) bridged clusters although the $CpRhFe_2Te_2$ system is presently unparalleled for the tractability of its various forms of isomerism. Through comparative studies on the 50e clusters including $PtFe_2Te_2(CO)_6(PPh_3)_2$, we have established that the observed shift patterns are a consequence of metal–metal bonding and *not* core electron count. It follows therefore that the shift pattern reflects the sensitivity of the tethering metalloid (Te) to the considerable anisotropy associated with the metal–metal bonding. In support of this we note that a very similar ^{77}Se NMR chemical shift pattern is observed for $PtFe_2Se_2(CO)_6(PPh_3)_2$ and $Fe_3Se_2(CO)_9$ although the latter, unlike $Fe_3Te_2(CO)_9$, does not form stable Lewis base adducts.[20]

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE 81-06781). We thank Engelhard Industries for a loan of platinum metals and the Selenium-Tellurium Development Association for a gift of tellurium dioxide. We thank Mr. Dennis Warrenfeltz for assistance with the NMR measurements. T.B.R. is a recipient of a Camille and Henry Dreyfus Teacher-Scholar award.

Registry No. $CpRhFe_2Te_2(CO)_7$, 85628-97-3; $Fe_3Te_2(CO)_9$, 22587-70-8; $CpRh(CO)_2$, 12192-97-1; $CpRhFe_2Te_2(CO)_6$, 85612-15-3; Me_3NO, 1184-78-7; $CpRhFe_2Te_2(CO)_6PPh_3$ ($RhPPh_3$ isomer), 85612-16-4; $CpRhFe_2Te_2(CO)_6PPh_3$ ($FePPh_3$ isomer), 85612-17-5; $CpRhFe_2Te_2(CO)_5PPh_3$, 85612-18-6; $CpRhFe_2S_2(CO)_6$, 85612-19-7; $Fe_2(S_2)(CO)_6$, 14243-23-3; $Fe_3Te_2(CO)_9PPh_3$, 80703-13-5; $Fe_3Te_2(CO)_8PPh_3$, 80703-07-7; $HFe_2Te_2(CO)_6(PPh_3)_2$, 76185-29-0; Fe, 7439-89-6; Te, 13494-80-9; Rh, 7440-16-6.

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