is V shaped (C–C–C = 146°) and bridges the Mo–Mo bond; it may be considered to form one olefin–metal bond to each molybdenum atom.

The structure of the binuclear palladium complex **5** is very different from that of Cotton's Mo_2 compound. It is not only that the C–C–C angle is much smaller but also, more important, that the bonding mode of the C_3H_4 moiety is not of the same type. As far as we know, there is precedent for the σ-alkyl-plus-π-allyl function of the C_3H_4 group only in two other complexes, namely, $Fe_2(CO)_6L(C_3H_4)$ (L = CO and PPh_3)[14] and $(C_5H_5)_2Ru_2(CO)_3(C_3H_4)$.[15] The iron complexes differ from the Pd_2 compound **5** insofar as in both $Fe_2(CO)_7(C_3H_4)$ and $Fe_2(CO)_6PPh_3(C_3H_4)$ a M–M bond is still present. However, it is worth noting that the structural data for the bridging allyl ligand in **5** (C–C = 1.41 and 1.47 Å, C–C–C = 116.4°) and in $Fe_2(CO)_6PPh_3(C_3H_4)$ (C–C = 1.41 and 1.45 ± 0.02 Å, C–C–C = 116 ± 1.3°)[14] are very similar.

Experimental Section

NMR spectra were recorded on a Varian T 60 and mass spectra on a Varian MAT CH 7. All experiments were carried out under purified nitrogen. The synthesis of $C_5H_5(P\text{-}i\text{-}Pr_3)Pd(\eta^1,\eta^3\text{-}C_3H_4)Pd(P\text{-}i\text{-}Pr_3)Cl$ (**2**) has been described previously.[5]

Preparation of $C_5H_5(P\text{-}i\text{-}Pr_3)Pd(\eta^1,\eta^3\text{-}C_3H_4)Pd(P\text{-}i\text{-}Pr_3)Br$ (5). $(\mu\text{-}C_5H_5)(\mu\text{-}Br)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**4**) (0.55 g, 0.81 mmol)[6] was dissolved in toluene (10 mL), and allene was bubbled through the solution for 30 min. An orange-red solution and a flocky precipitate resulted which was removed by filtration. The solution was concentrated in vacuo, and pentane was added. After the solution was left standing at 0 °C, orange-red crystals of **5** were formed which were washed with pentane and dried in vacuo: yield 0.3 g (53%); mp 86 °C; mass spectrum (70 eV), *m/e* 717 (32%, M^+), 451 (56, $M^+ - PdP\text{-}i\text{-}Pr_3$), 426 (98, $Pd(P\text{-}i\text{-}Pr_3)_2^+$), 371 (95, $C_5H_5Pd(C_3H_4)P\text{-}i\text{-}Pr_3^+$), 266 (100, $PdP\text{-}i\text{-}Pr_3^+$).

Anal. Calcd for $(C_5H_5)(C_3H_4)Pd_2(P\text{-}i\text{-}Pr_3)_2Br$: C, 43.47; H, 7.20; Pd, 29.62. Found: C, 43.15; H, 7.08; Pd, 29.90.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and BASF and DEGUSSA for gifts of chemicals. We also thank Miss Dr. G. Lange for the mass spectrum, Mrs. E. Ullrich for the elemental analysis, and Dr. U. Schubert, Munich, for valuable discussions.

Registry No. 4, 57622-82-9; **5**, 80048-98-2; allene, 463-49-0.

Supplementary Material Available: Table V, structure factors as observed and calculated for $C_5H_5(P\text{-}i\text{-}Pr_3)Pd(\eta^1,\eta^3\text{-}C_3H_4)Pd(P\text{-}i\text{-}Pr_3)Br$ (9 pages). Ordering information is given on any current masthead page.

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The Reactivity of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ toward Lewis Bases. 1

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The compound $Fe_3(\mu_3\text{-}Te)_2(CO)_9$, **1**, reacts with a range of Lewis bases, L, to form adducts $Fe_3(\mu_3\text{-}Te)_2(CO)_9L$ where L = PPh_3, *t*-BuNC, CO, and amines. Spectroscopic evidence indicates that, contrary to previous suggestions, the base is bound to an iron center and *not* to the tellurium atoms. X-ray crystallography of the PPh_3 adduct proves this point: the structure consists of an isosceles triangle of iron atoms tethered by capping μ_3-Te atoms. The basal $Fe_2(CO)_6$ unit contains a Fe–Fe bond while the apical $Fe(CO)_3PPh_3$ is octahedral, two coordination sites being occupied by the bridging tellurium atoms. We suggest that in **1** the μ_3-Te moieties are constrained to acute (strained) ~60° Fe–Te–Fe angles which are fixed by Fe–Fe bonding. Upon adduct formation, one Fe–Fe vector elongates by 1.4 Å and one pair of the acute Fe–Te–Fe angles opens up to 98°. As such, **1** represents an unusual example of a strained metal cluster compound and the difference in its chemical behavior relative to the analogous but less strained $Fe_3(\mu_3\text{-}E)_2(CO)_9$ (E = S, Se) can thus be understood. Treatment of **1** with potentially chelating bis(tertiary phosphines) demonstrates that **1** is effectively coordinatively unsaturated with respect to only one base addition: in this way monodentate derivatives of $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) were prepared. For $Ph_2PCH_2CH_2PPh_2$(dppe), the chelate-bridged bis cluster compound $[Fe_3(\mu_3\text{-}Te)_2(CO)_9]_2$(dppe) was isolated and characterized.

Introduction

Tellurium-containing transition metal clusters have been little studied[1-8] as they are few in number and they have been assumed to be chemically analogous to the more numerous sulfur and selenium derivatives. Certain characteristics of tellurium suggest, however, that the chemistry of its transition metal clusters may prove distinctive. First, tellurium has a relatively large covalent radius (1.36 Å); therefore one might expect geometrical differences between tellurium-bridged clusters and those containing sulfur and

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[1] $Fe_3(\mu_3\text{-}Te)_2(CO)_9$: Hieber, W.; Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91.

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[3] $Co_2Fe(\mu_3\text{-}Te)(CO)_9$: Strouse, C. E.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6032.

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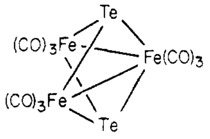
[8] The second paper in this series will describe the stereochemistry of substituted derivatives of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$.

selenium. Additionally, since tellurium enjoys an extensive coordination chemistry of its own,[9] this Lewis acidity could be manifested in its transition metal derivatives.

With the objective of evaluating the influence of tellurium on the reactivity of its transition metal clusters, we chose to first reexamine the behavior of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$, **1**, toward Lewis bases. Compound **1** is known to undergo substitution by Lewis bases via second-order kinetics[10-15] (first order in cluster and first order in Lewis base) and in some cases unstable intermediates of the formula $Fe_3(\mu_3\text{-}Te)_2(CO)_9L$ could be isolated in such reactions, eq 1.



1

$$Fe_3Te_2(CO)_9 \underset{-L}{\overset{+L}{\rightleftharpoons}} Fe_3Te_2(CO)_9L \xrightarrow{-CO} Fe_3Te_2(CO)_8L \quad (1)$$

Interestingly the sulfur and selenium analogues of $Fe_3Te_2(CO)_9$ undergo substitution primarily via a first-order, presumably dissociative, process.[12] The difference in kinetic behavior between the tellurium-containing cluster and the analogous clusters of S and Se was attributed to the Lewis acidity of Te, and on the basis of a variety of circumstantial evidence, the suggestion has been repeatedly advanced that in these adducts the Lewis base was in fact bound to the nonmetal component of the cluster.[10-15] Adduct formation by metal cluster compounds is unusual,[16-19] and thus we investigated this system in order to clarify the nature and scope of this reaction and to determine the role of the tellurium atoms in these processes.

Experimental Section

^1H NMR spectra were obtained on a Varian EM-390 spectrometer using Me_4Si as an internal reference. ^{31}P and ^{125}Te NMR spectra were obtained on a modified Varian XL-100 spectrometer with proton decoupling and using an external D_2O lock with 85% H_3PO_4 and Me_2Te (neat), respectively, as external references. All NMR samples were $CDCl_3$ solutions. IR spectra were obtained on a Perkin-Elmer 599B spectrophotometer on cyclohexane solutions. UV-visible spectra were recorded with a Varian Cary 219 spectrophotometer on toluene solutions. Field desorption mass spectra were run on a Varian 731 spectrometer by Mr. Carter Cook. Microanalyses were performed by the School of Chemical Sciences analytical laboratory.

Reactions were performed under nitrogen in reagent grade solvents. Ligands were obtained from commercial sources and used without further purification. Compounds **1** and **2c** were prepared as previously described.[7]

$Fe_3Te_2(CO)_9PPh_3$ (2a). Compound 1 (1.0 g, 1.5 mmol) and PPh_3 (5.0 g, 19 mmol) were dissolved in benzene (50 mL) and stirred 5 min at room temperature. After being concentrated, the resulting solution was chromatographed on a 2 × 40 cm Bio-Beads SX-4 column. The dark red fraction was eluted with benzene, evaporated to dryness, and recrystallized from CH_2Cl_2/MeOH; yield 0.87 g (62%). Anal. Calcd for $C_{27}Fe_3H_{15}O_9PTe_2$: C, 34.61; H, 1.61; Fe, 17.88; P, 3.30. Found: C, 34.82; H, 1.33; Fe, 17.66; P, 3.45.

$Fe_3Te_2(CO)_9$(*t*-BuNC), 2b. *tert*-Butyl isocyanide (150 μL) was added to a stirred solution of 1 (0.5 g, 0.74 mmol) in CH_2Cl_2 (25 mL). After 1 min the solution was diluted with MeOH and concentrated to afford crystals which were washed with 95% EtOH; yield 0.43 g (77%). Anal. Calcd for $C_{14}Fe_3H_9NO_9Te_2$: C, 22.18; H, 1.19, Fe, 22.09; N, 1.85. Found C, 22.58; H, 1.04; Fe, 21.93; N, 1.88.

$Fe_3Te_2(CO)_8PPh_3$, 3a. Compound 1 (0.715 g, 1.06 mmol) and PPh_3 (0.276 g, 1.06 mmol) were dissolved in 150 mL of CH_2Cl_2. After being refluxed for 18 h, the solution was evaporated to dryness. The residue was dissolved in hexanes (150 mL), and the solution was refluxed for 30 min, filtered through a 2-cm plug of silica gel, and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/MeOH, giving 0.81 g of black crystals (84%). Anal. Calcd for $C_{26}Fe_3H_{15}O_8PTe_2$: C, 34.35; H, 1.66; Fe, 18.43; P, 3.41. Found: C, 34.27; H, 1.67; Fe, 18.43; P, 3.32.

The Reaction of $Fe_3E_2(CO)_9$ (E = S, Se) and PPh_3. $Fe_3Se_2(CO)_9$ (58 mg, 0.10 mmol) and PPh_3 (130 mg, 0.50 mmol) were stirred in CH_2Cl_2 (5 mL) at 25 °C. TLC on silica gel indicated that a small amount of $Fe_3Se_2(CO)_8PPh_3$ had formed after 1 h. After 48 h, $Fe_3Se_2(CO)_8PPh_3$ was the predominant iron complex in solution. Under the same conditions $Fe_3S_2(CO)_9$ did not react with the PPh_3 in 6 h and $Fe_3Te_2(CO)_9$ was quantitatively converted to $Fe_3Te_2(CO)_9PPh_3$.

Reaction of 1 with Nitrogenous Bases. Addition of neat nitrogenous bases (NH_3, 1-MeIm, and 4-Mepy) to CH_2Cl_2 solutions of 1 resulted in a rapid color change to orange. Dilution of these solutions with hexane, followed by concentration with a stream of N_2 or NH_3 (for the NH_3 adduct), gave red brown microcrystalline precipitates which upon storage evolved the free amine. Attempted TLC of any of these compounds resulted in their decomposition.

$Fe_3Te_2(CO)_9$(dppm), 4a. Bis(diphenylphosphino)methane (0.20 g, 0.53 mmol) was added to a CH_2Cl_2 solution (50 mL) of 1 (0.34 g, 0.5 mmol). After being refluxed for 5 min, the solution was concentrated and chromatographed on a silica gel column. Crystals were obtained from benzene/hexane. Anal. Calcd for $C_{34}Fe_3H_{22}O_9P_2Te_2$: C, 38.56; H, 2.08; Fe, 15.83; P, 5.86. Found: C, 38.42; H, 1.99; Fe, 15.73; P, 5.97.

$Fe_3Te_2(CO)_9$(dppe), 4b. Compound 1 (0.135 g, 0.20 mmol) was added to a stirred solution of dppe (0.24 g, 0.6 mmol) in CH_2Cl_2 (10 mL). After 5 min TLC (silica gel/1:1 benzene/hexane) indicated complete conversion to the desired product. The compound was stable in solution for several hours at 25 °C; however, attempted purification (crystallization or preparative chromatography under an inert atmosphere) was unsuccessful.

$Fe_3Te_2(CO)_9$(dppeS), 4b-S. To the above prepared solution of $Fe_3Te_2(CO)_9$(dppe) was added a large excess of sulfur (~50 mg). After being stirred 15 min the solution was evaporated to dryness and the resulting solid was chromatographed on a silica gel column with CH_2Cl_2. The red-orange fraction was collected, and crystals were obtained by adding hexane and concentrating to a small volume. Anal. Calcd for $C_{35}Fe_3H_{24}O_9P_2STe_2$: C, 38.03; Fe, 15.16; H, 2.19; P, 5.60. Found: C, 37.61; H, 2.25; Fe, 13.85; P, 6.54.

$[Fe_3Te_2(CO)_9]_2$(dppe), 4c. Compound 1 (0.17 g, 0.25 mmol) and dppe (0.040 g, 0.10 mmol) were dissolved in CH_2Cl_2 (15 mL). After being stirred 5 h at 25 °C, the solution was filtered through silica gel and diluted with MeOH. Concentration to a small volume produced a brown solid which was recrystallized twice from CH_2Cl_2/MeOH; yield 0.138 g (80%). Anal. Calcd for $C_{44}Fe_6H_{24}O_{18}P_2Te_4$: C, 30.23; H, 1.38; Fe, 19.17; P, 3.54. Found: C, 30.18; H, 1.36; Fe, 18.58; P, 3.96.

$Fe_3Te_2(CO)_9$(dppp), 4d. Equimolar amounts of 1 and 1,3-bis(diphenylphosphino)propane were dissolved in CH_2Cl_2 and refluxed for 5 min. The resulting solution was evaporated to

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dryness, and the solid obtained was recrystallized in benzene/hexane. TLC indicated the presence of some starting material. In addition to TLC, the identity of this compound was verified by IR and ^{31}P NMR.

$Fe_3Te_2(CO)_7(dppm)$, 5a. This compound was prepared by heating **4a** in refluxing benzene for 30 min and was crystallized from $CH_2Cl_2/MeOH$. Anal. Calcd for $C_{32}H_{22}Fe_3O_7P_2Te_2$: C, 38.32; H, 2.20; Fe, 16.70; P, 6.19. Found: C, 38.21; H, 2.33; Fe, 15.53; P, 6.2.

Crystallography. X-ray crystallography was performed as a commercial service by Dr. C. S. Day of Crystalytics Co.

Dark red single crystals of $Fe_3Te_2(CO)_9PPh_3$ were grown from CH_2Cl_2/hexanes at −20 °C. A 0.50 × 0.60 × 0.38 mm crystal was mounted on a 0.15-mm diameter glass fiber. The crystals are triclinic $P\bar{1}—C_i^1$ (No. 2),[20] with $a = 9.891$ (3) Å, $b = 12.140$ (3) Å, $c = 13.571$ (3) Å, $\alpha = 100.59$ (2)°, $\beta = 89.75$ (2)°, $\gamma = 105.49$ (2)°, and $Z = 2$ at 20 ± 1 °C. Intensity measurements were made on a computer controlled four-circle Nicolet autodiffractometer using 0.90° wide ω scans and graphite-monochromated Mo $K\bar{\alpha}$ radiation. A total of 7095 independent reflections having $2\theta < 55.0°$ were measured in two concentric shells of increasing 2θ. A scanning rate of 6.0°/min was employed for the scan between ω settings 0.45° above and below the calculated $K\bar{\alpha}$ doublet value ($\lambda_{K\bar{\alpha}}$ = 0.71073 Å) for those reflections having $3.0° < 2\theta < 43.0°$, and a scanning rate of 4.0°/min was used for those reflections having $43.0° < 2\theta < 55.0°$. Six standard reflections measured every 400 reflections as a monitor for possible disalignment and/or deterioration of the crystal gave no indication of either. Before applying standard Lorentz and polarization corrections, we corrected the intensity data empirically for absorption effects using ψ scans for seven reflections having 2θ values between 8° and 36°.

The three iron and two tellurium atoms were located by direct methods, and the remaining nonhydrogen atoms were located by using standard difference Fourier techniques. Isotropic unit-weighted full-matrix least-squares refinement for the nonhydrogen atoms gave R_1(unweighted, based on F) = 0.072 and R_2(weighted) = 0.073; anisotropic[22] refinement converged to $R_1 = 0.029$ and $R_2 = 0.033$ for 3220 reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. These and all other subsequent structure factor calculations employed an anomalous dispersion correction to the scattering factors of the iron, phosphorus, and tellurium atoms.[23] The final cycles of empirically weighted[25] full-matrix least-squares refinement which employed anisotropic thermal parameters[22] for all nonhydrogen atoms converged to $R_1 = 0.029$[26] and $R_2 = 0.039$[27] for 6007 independent reflections having $2\theta \leq 55°$ and $I > 3\sigma(I)$. During the final cycle of refinement, no parameter shifted by more than $0.62\sigma_p$, with the average shift being less than $0.05\sigma_p$, where σ_p is the estimated standard deviation of the parameter.

Results

We found that compound **1** readily reacted with a wide variety of Lewis bases to form orange adducts many of which are easily obtained in crystalline form. Our objective in this study was to define the nature of this adduct formation via a combined spectroscopic and structural study and to explore the scope and synthetic utility of this reaction. For measurement purposes we focused most of our attention on spectroscopically visible ligands such as phosphines (^{31}P NMR) and isocyanides (IR).

Table I. IR Data (cm^{-1}, Cyclohexane Solution)

compd	ν_{CO}
$Fe_3Te_2(CO)_9$, **1**	2046 vs, 2025 vs, 2004 s, 1992 w(br)
$Fe_3Te_2(CO)_9PPh_3$, **2a**	2060 w, 2041 s, 2016 vs, 1992.5 w, 1981 vs, 1968 w
$Fe_3Te_2(CO)_9$*t*-BuNC, **2b**	2070 w, 2044 vs, 2028 vs, 2020 m, 2007 s, 1990 m, 1983.5 vs, 1970 m, 1958 w, (ν_{NC} 2167)
$Fe_3Te_2(CO)_{10}$, **2c**	2102 w, 2052 s, 2045 s, 2033 w, 2014 m, 1993 m, 1981 w, 1968.5 w
$Fe_3Te_2(CO)_8PPh_3$, **3a**	2053 m, 2015 s, 1992 s (br), 1942 w
$Fe_3Te_2(CO)_9(dppm)$, **4a**	2062 w, 2040 s, 2016 vs, 1989.5 m, 1980 s, 1967.5 w(br)
$Fe_3Te_2(CO)_9(dppe)$, **4b**	2066 w, 2041 s, 2015 s, 1995 m, 1982.5 s, 1969 m, 1956 w
$Fe_3Te_2(CO)_9(dppeS)$, **4b-S**	2042 s, 2016 vs, 1994 w, 1983 s, 1970 w
$[Fe_3Te_2(CO)_9]_2(dppe)$, **4c**	2042 s, 2016 vs, 1991 w, 1984 s, 1971 w
$Fe_3Te_2(CO)_9(dppp)$, **4d**	2059 w, 2041 s, 2016 s, 1993.5 m, 1989.5 s, 1982.5 s, 1970 w(br)
$Fe_3Te_2(CO)_7(dppm)$, **5a**	2042 s, 1986.5 vs, 1981 s(sh), 1965 w, 1945.5 w, 1939 w

Table II. $^{31}P\{^1H\}$ NMR Data

compd	$\delta(^{31}P)^a$	J_{PX}, Hz
2a	41.9	42 (X = Te), 120^c
3a	68.0	*b*
4a	35.7, −31.4	89 (X = P′), 48 (X = Te)
4b	42.1, −12.9	37 (X = P′), *b*
4b-S	42.7, 39.8	48 (X = P′), *b*
4c	40.3	*b*
4d	33.5, −23.0	44 (X = Te)
5a	49.7, 43.4	63.6 (X = P′), 27 (X = Te)

^{a} Positive chemical shifts are downfield of our 85% H_3PO_4 standard. ^{b} J_{PTe} was ill-defined. ^{c} Unassigned—intensity is ~25% of the Te satellites.

Table III. Field Desorption Mass Spectral Results

compd	*m/e*(calcd)	*m/e*(obsd) (approx rel intensity)	assign
2a	936	936 (80%)	M^+
		908 (20%)	$M^+ - CO$
2b	758	758 (50%)	M^+
		730 (50%)	$M^+ - CO$
4a	1059	1059 (33%)	M^+
		1031 (33%)	$M^+ - CO$
		1003 (33%)	$M^+ - 2CO$
4b-S	1105	1105 (40%)	M^+
		1077 (60%)	$M^+ - CO$
4c	1748	1692 (100%)	$M^+ - 2CO$
5a	1003	1003 (100%)	M^+

Adduct Formation with Unidentate Ligands. Addition of an excess of triphenylphosphine to a CH_2Cl_2 solution of **1** caused a rapid color change to the orange characteristic of the adduct. The product of this reaction, $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$, **2a**, was isolated in high yield and characterized by IR, field desorption mass spectrometry[28] (FDMS), combustion analysis, and ^{31}P NMR (Tables I–III). The ^{31}P NMR measurement showed only one resonance downfield of free ligand flanked by two sets of

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(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

(21) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1967; Vol. II, pp 302–5.

(22) The anisotropic thermal parameter is of the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

(23) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1967; Vol. IV, pp 149–50.

(24) The weighting scheme used in the least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ is defined as $w = 1/\sigma_F^2$.

(25) For empirical weights: $\Delta_F = \sum_o^3 a_n|F_o|^n = a_o + a_1|F_o| + a_2|F_o|^2 + a_3|F_o|^3$ with the a_n being coefficients from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_o^3 a_n|F_o|^n$. In this case: $a_o = 0.886$, $a_1 = 4.28 \times 10^{-3}$, $a_2 = 1.60 \times 10^{-4}$, and $a_3 = -1.52 \times 10^{-7}$.

(26) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

(27) $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2\}^{1/2}$.

(28) Beckey, H. D.; Schulten, H. R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 403.

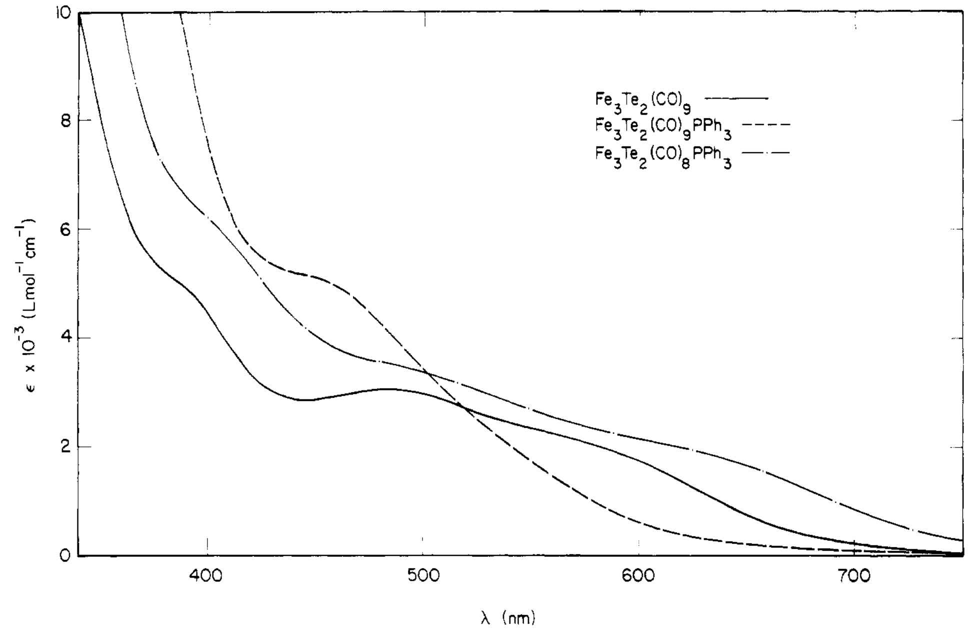

Figure 1. Electronic absorption spectra of **1**, **2a**, and **3a** in toluene at 30 °C.

satellites, one of which we assign to $^2J_{\mathrm{Te,P(trans)}}$. The small value of this coupling constant is inconsistent with direct binding of the PPh_3 to Te.[6] As previously mentioned, adduct formation is accompanied by a dramatic change in the optical absorption spectrum (Figure 1). In view of the prevailing theoretical assumptions[29] that in complexes of this type both the HOMO and LUMO are metal–metal bonding or antibonding in character, such a dramatic shift in the optical spectrum suggests that a change in metal framework had occurred. This view was supported by the X-ray crystal structure analysis.

These adducts are intermediates in the formation of substituted derivatives[10–12] of **1**; thus we found that $Fe_3(\mu_3\text{-}Te)_2(CO)_8PPh_3$, **3a**, was formed in good yield when **2a** was heated in hexane. The black color of **3a**, or more specifically its optical spectrum, closely resembles that for **1** (Figure 1). This finding supports the notion that the HOMO and LUMO of these compounds are primarily metallic in character and are not particularly sensitive to substituent effects. The ^{31}P NMR shift for **3a** is different from **2a** and displays ^{125}Te satellites (as shoulders) of similar magnitude as found for **2a**. From the practical perspective, not only the color and IR spectroscopy differentiate the substituted derivatives of **1** from the adducts but also thin-layer chromatography on silica gel is conventient for the analysis of mixtures **1**, **2a**, and **3a**. The stereochemistry of compounds of the formula $Fe_3(\mu_3\text{-}E)_2(CO)_8L$ has previously been studied by ^{13}C NMR spectroscopy.[6,14]

The reaction of **1** with *t*-BuNC was especially facile. The solution IR (Table II) of the product, $Fe_3(\mu_3\text{-}Te)_2(CO)_9(t\text{-}BuNC)$, **2b**, showed that ν_{CN} shifted to lower frequency upon coordination, indicating that this ligand is functioning as a net π acceptor, in accord with the base binding at an iron center.

The parent compound, **1**, is prepared in good yield via the reduction of TeO_3^{2-} by a basic aqueous solution of $Fe(CO)_5$. As originally described,[1] this synthesis affords primarily **1** and a small amount of the more fragile $Fe_2(\mu\text{-}Te_2)(CO)_6$.[7] We recently reported that a modified procedure for the same reaction affords a good yield of $Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$,[7] **2c**, which, on the basis of spectral comparisons, is analogous to **2a** and **2b**. Consistent with its coordinative saturation, orange solutions of **2c** do not react with a large excess of PPh_3. Thus **2c** resembles most other metal carbonyl clusters in being exchange inert. Since **2c** does not form upon reaction of **1** with $Fe(CO)_5$ in neutral or basic solution, this CO adduct must be an intermediate in the traditional synthetic procedure for **1**.[1]

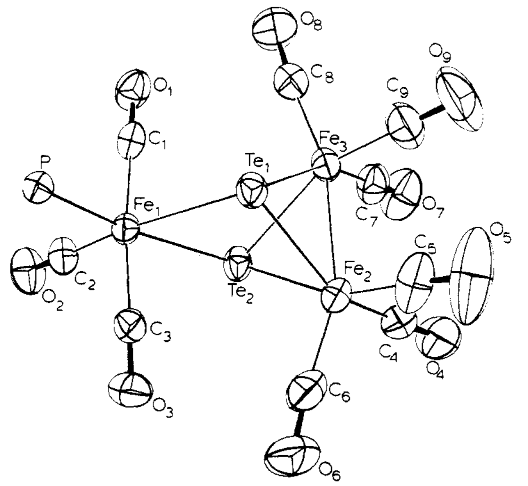

Figure 2. ORTEP plot of the metal coordination spheres of the $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$ molecule with thermal ellipsoids drawn at the 50% probability level.

Compound **1** quickly reacted with classical nitrogenous bases, ammonia, 1-methylimidazole, and 4-methylpyridine, to form orange adducts. Attempted chromatography of any of these adducts caused reversion to **1** or its substituted analogues. In the case of ammonia, adduct formation was reversed simply by purging with argon or stirring in vacuo. By monitoring the ammonolysis and its reversal using optical spectroscopy, we demonstrated that each cycle was not completely reversible but was accompanied by a steady change in the spectrum of the nonadduct form. Adduct formation by incremental addition of 4-methylpyridine to **1** was monitored spectrophotometrically and an isosbestic point at 492 nm was observed. The formation constant for $Fe_3Te_2(CO)_9(pyMe)$ was estimated to be 50 M^{-1} in toluene at 27 °C.

Description of the Structure of $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$. As depicted in Figure 2, the structure of **2a**

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[29] Tyler, D. R.; Gray, H. B. *J. Amer. Chem. Soc.* **1978**, *100*, 7888.

Table IV. Bond Lengths and Selected Nonbonded Contacts Involving Nonhydrogen Atoms in Crystalline $Fe_3Te_2(CO)_9(P(C_6H_5)_3)^a$

type^b	length, Å	type^b	length, Å
Te_1-Fe_1	2.657 (1)	C_{a1}-C_{a2}	1.397 (6)
Te_2-Fe_1	2.668 (1)	C_{a1}-C_{a6}	1.395 (6)
		C_{a2}-C_{a3}	1.401 (7)
Te_1-Fe_2	2.565 (1)	C_{a3}-C_{a4}	1.378 (8)
Te_1-Fe_3	2.577 (1)	C_{a4}-C_{a5}	1.393 (9)
Te_2-Fe_2	2.575 (1)	C_{a5}-C_{a6}	1.396 (6)
Te_2-Fe_3	2.567 (1)	C_{b1}-C_{b2}	1.401 (6)
		C_{b1}-C_{b6}	1.392 (6)
$Te_1 \cdots Te_2$	3.138 (1)	C_{b2}-C_{b3}	1.392 (7)
		C_{b3}-C_{b4}	1.390 (8)
Fe_2-Fe_3	2.585 (1)	C_{b4}-C_{b5}	1.386 (8)
		C_{b5}-C_{b6}	1.402 (7)
$Fe_1 \cdots Fe_2$	3.947 (1)	C_{c1}-C_{c2}	1.410 (6)
$Fe_1 \cdots Fe_3$	3.939 (1)	C_{c1}-C_{c6}	1.395 (6)
		C_{c1}-C_{c3}	1.389 (7)
Fe_1-P	2.297 (1)	C_{c3}-C_{c4}	1.392 (8)
		C_{c4}-C_{c5}	1.377 (8)
Fe_1-C_1	1.815 (4)	C_{c5}-C_{c6}	1.405 (8)
Fe_1-C_2	1.805 (4)		
Fe_1-C_3	1.822 (4)	O_1-C_1	1.131 (5)
Fe_2-C_4	1.777 (5)	O_2-C_2	1.125 (6)
Fe_2-C_5	1.789 (6)	O_3-C_3	1.127 (5)
Fe_2-C_6	1.782 (7)	O_4-C_4	1.133 (7)
Fe_3-C_7	1.781 (5)	O_5-C_5	1.145 (9)
Fe_3-C_8	1.786 (5)	O_6-C_6	1.134 (10)
Fe_3-C_9	1.785 (5)	O_7-C_7	1.143 (7)
		O_8-C_8	1.139 (7)
P-C_{a1}	1.830 (4)	O_9-C_9	1.132 (7)
P-C_{b1}	1.838 (4)		
P-C_{c1}			

^{a} The numbers in parentheses are the estimated standard deviations in the last significant digit. ^{b} Atoms are labeled in agreement with the figures.

consists of an isosceles triangle of iron atoms with the short edge representing the 2.585 (1)-Å Fe–Fe bond. The basal $Fe_2Te_2(CO)_6$ unit resembles that found for $Fe_2(\mu\text{-}Se_2)(CO)_6$ with the distorted octahedral geometry of each iron being defined by three carbonyls, two bridging tellurium atoms, and the metal–metal bond. The unique iron appears to be conventionally octahedral with the two pseudohalide (one electron donor) tellurium atoms and the triphenylphosphine meridionally disposed. The observed geometry is that which would result from the addition occurring from the sterically most accessible direction. The Fe–C distances (Table IV) for the carbonyls clearly indicate that Fe(1) has a higher oxidation state than Fe(2) and Fe(3): this is also consistent with the view that the tellurium atoms are functioning as one electron donor (pseudohalides) toward the unique iron.

We attribute the unusual reactivity of 1 to the energy inherent in its four acute Fe–Te–Fe angles and for this reason the geometry about the tellurium atoms deserves special comment. In **2a**, the angles (Table V) Fe(2)–Te(1)–Fe(3) and Fe(2)–Te(2)–Fe(3) are 60.3° which can be compared with the M–Te–M angles of 63.6° found in $Co_2Fe(\mu_3\text{-}Te)(CO)_9$.[3] In keeping with the 18-electron rule each tellurium functions as a three-electron bridge along the metal–metal bonded edge in **2a** while for 1 the EAN rule requires that the three-electron bridges occur across the *open* iron–iron edge (vide infra). The four Fe(1)–Te–Fe(2) and the Fe(1)–Te–Fe(3) angles in 2 average 97.8°. We assume that the *two* small triangular faces (Fe(2)–Te–Fe(3)) in **2a** are geometrically similar to the *four* small triangular faces in 1;[30] *thus the conversion of 1 to the adduct is accompanied by the opening of two Fe–Te–Fe angles.* In the language of Wade's rules,[31] adduct formation involves the conversion of a five-vertex-seven-electron pr, nido cluster to a five-vertex-eight-electron pr, arachno cluster.

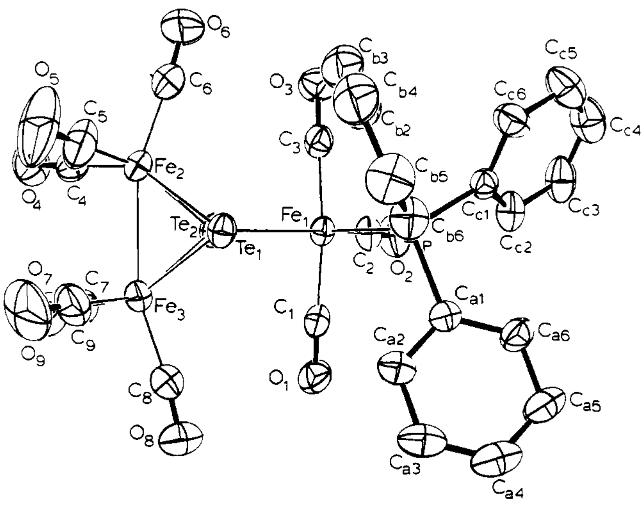
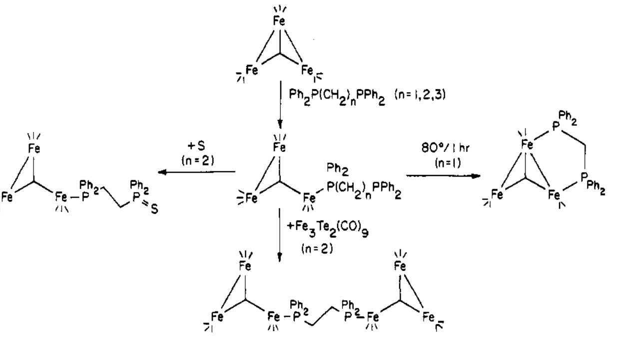
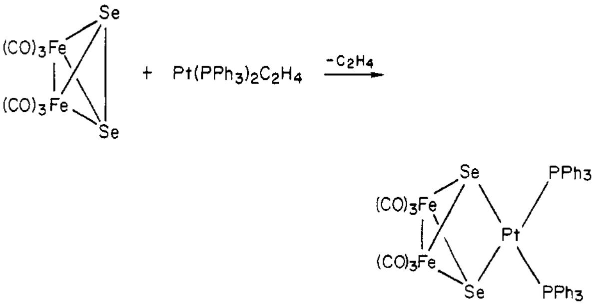


Figure 3. ORTEP plot of the nonhydrogen atoms of the $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$ molecule with thermal ellipsoids drawn at the 50% probability level.

Scheme I



A top view of the molecule (Figure 3) shows the Te atoms to be significantly displaced toward the base of the triiron isosceles triangle. This perspective suggests an alternative view of **2a** as being derived from the addition of a 16-electron $Fe(CO)_3PPh_3$ unit to the Te–Te bond of $Fe_2(\mu\text{-}Te_2)(CO)_6$.[7] For this reason this structure bears a strong resemblance to that of the crystallographically characterized $PtFe_2(\mu_3\text{-}Se)_2(CO)_6(PPh_3)_2$ prepared according to eq 2.[6] The similarity between the adducts



(2)

derived from 1 and our previously reported $PtFe_2(\mu_3\text{-}E)_2(CO)_6(PPh_3)_2$ includes their electronic absorption

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[30] The structure of $Fe_3Te_2(CO)_7(PPh_3)_2$ has been determined and will be described in a future publication.

[31] Wade, K. *Adv. Inorg. Radiochem.* **1976**, *18*, 1.

[32] Monodentate dppe: Keiter, R. L.; Sun, Y. Y.; Brodack, J. W.; Cary, L. W. *J. Am. Chem. Soc.* **1979**, *101*, 2638 and references therein.

Table V. Bond Angles Involving Nonhydrogen Atoms in Crystalline $Fe_3Te_2(CO)_9(P(C_6H_5)_3)$[a]

type[b]	angle, deg	type[b]	angle, deg
$Fe_1Te_1Fe_2$	98.19 (2)	$Te_1Fe_1Te_2$	72.21 (2)
$Fe_1Te_1Fe_3$	97.62 (2)	$Te_1Fe_2Te_2$	75.25 (2)
$Fe_1Te_2Fe_2$	97.66 (2)	$Te_1Fe_3Te_2$	75.17 (2)
$Fe_1Te_2Fe_3$	97.59 (2)		
		$Te_1Fe_2Fe_3$	60.06 (2)
$Fe_2Te_1Fe_3$	60.35 (2)	$Te_2Fe_2Fe_3$	59.67 (2)
$Fe_2Te_2Fe_3$	60.36 (2)	$Te_1Fe_3Fe_2$	59.59 (2)
		$Te_2Fe_3Fe_2$	59.97 (2)
Te_1Fe_1P	93.74 (3)		
$Te_1Fe_1C_1$	88.2 (1)	$Te_1Fe_2C_4$	151.4 (2)
$Te_1Fe_1C_2$	167.5 (1)	$Te_1Fe_2C_5$	89.4 (2)
$Te_1Fe_1C_3$	89.4 (1)	$Te_1Fe_2C_6$	108.8 (2)
Te_2Fe_1P	165.88 (3)	$Te_2Fe_2C_4$	94.1 (2)
$Te_2Fe_1C_1$	86.8 (1)	$Te_2Fe_2C_5$	159.5 (2)
$Te_2Fe_1C_2$	95.4 (1)	$Te_2Fe_2C_6$	101.1 (2)
$Te_2Fe_1C_3$	86.7 (1)	$Fe_3Fe_2C_4$	91.5 (2)
PFe_1C_1	94.4 (1)	$Fe_3Fe_2C_5$	101.0 (2)
PFe_1C_2	98.7 (1)	$Fe_3Fe_2C_6$	158.8 (2)
PFe_1C_3	91.9 (1)	$C_4Fe_2C_5$	93.2 (3)
$C_1Fe_1C_2$	89.5 (2)	$C_4Fe_2C_6$	99.3 (3)
$C_1Fe_1C_3$	173.4 (2)	$C_5Fe_2C_6$	96.6 (3)
$C_2Fe_1C_3$	91.5 (2)		
		$Te_1Fe_3C_7$	158.4 (2)
Fe_1PC_{a1}	115.2 (1)	$Te_1Fe_3C_8$	103.6 (2)
Fe_1PC_{b1}	115.2 (1)	$Te_1Fe_3C_9$	90.2 (2)
Fe_1PC_{c1}	112.7 (1)	$Te_2Fe_3C_7$	90.8 (2)
$C_{a1}PC_{b1}$	102.3 (2)	$Te_2Fe_3C_8$	109.3 (2)
$C_{a1}PC_{c1}$	104.7 (2)	$Te_2Fe_3C_9$	152.3 (2)
$C_{b1}PC_{c1}$	105.5 (2)	$Fe_2Fe_3C_7$	99.3 (2)
		$Fe_2Fe_3C_8$	160.9 (2)
$Fe_1C_1O_1$	177.7 (4)	$Fe_2Fe_3C_9$	92.4 (2)
$Fe_1C_2O_2$	178.8 (4)	$C_7Fe_3C_8$	96.5 (2)
$Fe_1C_3O_3$	177.9 (4)	$C_7Fe_3C_9$	95.4 (3)
$Fe_2C_4O_4$	177.6 (5)	$C_8Fe_3C_9$	96.8 (3)
$Fe_2C_5O_5$	177.9 (6)	$PC_{b1}C_{b2}$	119.5 (3)
$Fe_2C_6O_6$	175.0 (7)	$PC_{b1}C_{b6}$	121.4 (3)
$Fe_3C_7O_7$	179.3 (5)	$C_{b2}C_{b1}C_{b6}$	119.1 (4)
$Fe_3C_8O_8$	174.9 (5)	$C_{b1}C_{b2}C_{b3}$	120.6 (4)
$Fe_3C_9O_9$	179.2 (6)	$C_{b2}C_{b3}C_{b4}$	120.3 (5)
		$C_{b3}C_{b4}C_{b5}$	119.4 (5)
$PC_{a1}C_{a2}$	117.6 (3)	$C_{b4}C_{b5}C_{b6}$	120.8 (5)
$PC_{a1}C_{a6}$	122.5 (3)	$C_{b5}C_{b6}C_{b1}$	119.9 (4)
$C_{a2}C_{a1}C_{a6}$	119.9 (4)		
$C_{a1}C_{a2}C_{a3}$	119.4 (4)	$PC_{c1}C_{c2}$	118.4 (3)
$C_{a2}C_{a3}C_{a4}$	120.1 (5)	$PC_{c1}C_{c6}$	121.8 (3)
$C_{a3}C_{a4}C_{a5}$	121.0 (5)	$C_{c2}C_{c1}C_{c6}$	119.8 (4)
$C_{a4}C_{a5}C_{a6}$	119.0 (5)	$C_{c1}C_{c2}C_{c3}$	119.3 (4)
$C_{a5}C_{a6}C_{a1}$	120.5 (4)	$C_{c2}C_{c3}C_{c4}$	120.6 (5)
		$C_{c3}C_{c4}C_{c5}$	120.4 (6)
		$C_{c4}C_{c5}C_{c6}$	119.9 (5)
		$C_{c5}C_{c6}C_{c1}$	120.0 (5)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with the figures.

spectra and their ^{77}Se and ^{125}Te NMR behavior.[6]

Adducts of Ditertiary Phosphines. Evidence presented so far indicates that 1 is coordinatively unsaturated to the extent that it can bind a *single* electron pair ligand and thereafter behaves like the more conventional variety of exchange inert, closed-shell metal carbonyl cluster compounds. This pattern extends to the reactivity of 1 toward chelating ligands (Scheme I). The ditertiary phosphines were chosen for these experiments since their ^{31}P NMR behavior is sensitive to their mode of coordination.[32]

Treatment of 1 with 1 equiv of dppm (dppm = bis(diphenylphosphino)methane) effected clean conversion to the $Fe_3(\mu_3\text{-}Te)_2(CO)_9(dppm)$ (**4a**) which was isolated as thermally and aerobically robust orange crystals. Field desorption mass spectrometry confirmed the formulation of **4a** but also revealed the presence of some $Fe_3Te_2(CO)_n(dppm)$ (n = 7, 8) which are apparently formed in the ionization/volatilization process in the probe. Of crucial importance is the ^{31}P NMR of **4a** which clearly demonstrated the presence of two nonequivalent, strongly coupled phosphorus moieties whose resonance frequencies were consistent with one being coordinated and one being pendant (Figure 4). When incorporated in bi- or trimetallic complexes, dppm generally functions as a bridging ligand, $Fe_2(CO)_7(dppm)$[33] being a prime example. The synthesis of **4a** demonstrates that 1 is kinetically labile with respect to *only one* ligand addition.

Table VI. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $Fe_3(\mu_3\text{-}Te)_2(CO)_9(P(C_6H_5)_3)$[a]

atom type[b]	10^4x	10^4y	10^4z
Te_1	2825.5 (2)	2770.9 (2)	3027.5 (2)
Te_2	810.9 (3)	617.6 (2)	3734.2 (2)
Fe_1	142.7 (5)	1817.1 (4)	2437.9 (4)
Fe_2	2699.3 (6)	2296.0 (5)	4796.6 (4)
Fe_3	3405.4 (6)	908.0 (5)	3328.0 (4)
P	114.8 (9)	3140.1 (8)	1431.0 (7)
O_1	1014 (4)	175 (3)	852 (2)
O_2	−2753 (3)	360 (3)	2028 (3)
O_3	−709 (4)	3282 (3)	4179 (3)
O_4	3195 (5)	932 (4)	6243 (3)
O_5	5385 (6)	4051 (5)	5386 (5)
O_6	1015 (7)	3589 (7)	6040 (4)
O_7	3598 (5)	−954 (3)	4369 (3)
O_8	3687 (5)	−366 (5)	1324 (3)
O_9	6368 (4)	2177 (5)	3647 (5)
C_1	707 (4)	820 (3)	1462 (3)
C_2	−1646 (4)	929 (4)	2188 (3)
C_3	−357 (4)	2732 (4)	3519 (3)
C_4	2978 (5)	1444 (5)	5670 (3)
C_5	4343 (7)	3365 (5)	5138 (4)
C_6	1638 (7)	3089 (6)	5519 (4)
C_7	3515 (5)	−225 (4)	3966 (4)
C_8	3520 (5)	136 (5)	2090 (4)
C_9	5221 (5)	1677 (5)	3524 (5)
C_{a1}	556 (4)	2724 (3)	129 (3)
C_{a2}	1816 (4)	2421 (4)	−35 (3)
C_{a3}	2224 (5)	2147 (4)	−1020 (4)
C_{a4}	1372 (7)	2152 (4)	−1819 (4)
C_{a5}	106 (6)	2441 (4)	−1666 (3)
C_{a6}	−290 (5)	2738 (4)	−685 (3)
C_{b1}	1365 (4)	4581 (3)	1825 (3)
C_{b2}	1392 (5)	5177 (4)	3141 (4)
C_{b3}	2362 (6)	6250 (4)	3141 (4)
C_{b4}	3312 (5)	6747 (4)	2484 (4)
C_{b5}	3286 (6)	6163 (4)	1502 (4)
C_{b6}	2307 (5)	5086 (4)	1164 (3)
C_{c1}	−1605 (4)	3416 (3)	1339 (3)
C_{c2}	−2754 (4)	2483 (4)	912 (3)
C_{c3}	−4077 (5)	2667 (5)	860 (4)
C_{c4}	−4273 (5)	3759 (5)	1230 (5)
C_{c5}	−3156 (6)	4675 (5)	1646 (5)
C_{c6}	−1808 (5)	4510 (4)	1701 (4)

[a] The numbers in parentheses are the estimated standard deviation in the last significant digit. [b] Atoms are labeled in agreement with Figures 2 and 3.

We can be certain that no thermodynamic effects prevent the diphosphine in **4a** from functioning as a bidentate ligand since **4a** is easily converted to $Fe_3(\mu_3\text{-}Te)_2(CO)_7(dppm)$, **5a**, upon heating in benzene. The inequivalence of the two phosphorus atoms (^{31}P NMR) in **5a** is consistent with the structure shown in the scheme, this geometry being dictated by the geometric preference of dppm for metal–metal distances of 2.7–3.2 Åa.[34] Qualitative ex-

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(33) Cotton, F. A.; Hunter, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 4422.

(34) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2501.

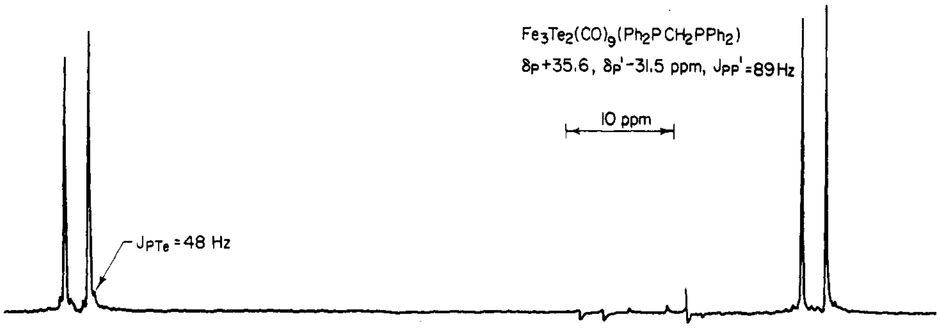


Figure 4. 40.5-MHz proton-decoupled ^{31}P NMR spectrum of $Fe_3(\mu_3\text{-}Te)_2(CO)_9(dppm)$.

periments demonstrate that the disubstituted character of **5a** does not impede further adduct formation.[8]

The reaction of **1** with 1 equiv of dppe (dppe = 1,2-bis(diphenylphosphino)ethane) gave two chromatographically distinct orange products. We found that **1** and excess dppe favored the less polar and smaller (by gel permeation chromatography) of the two adducts which, on the basis of ^{31}P NMR (Table II) and IR (Table I), is $Fe(\mu_3\text{-}Te)_2(CO)_9(dppe)$,[32] **4b**. Treatment of **4b** with sulfur afforded the corresponding monosulfide which was definitively characterized by IR and more importantly by ^{31}P NMR. The field desorption mass spectrum of the sulfide of **4b** (**4b**-S) gave a molecular ion corresponding to $Fe_3Te_2(CO)_8PPh_2CH_2CH_2PPh_2S$, indicating that decarbonylation had occurred in the volatization/ionization of this relatively heavy molecule. The reaction of dppe with 2 equiv of **1** afforded the bis cluster compound $[Fe_3(\mu_3\text{-}Te)_2(CO)_9](dppe)$,[35,36] **4c**, which corresponded to the other component of the 1:1 reaction of dppe with **1**. ^{31}P NMR spectrometry demonstrated the equivalence of the (coordinated) phosphorus atoms in **4c**, and this singlet is flanked by distinct shoulders attributable to ^{125}Te satellites. As expected, the FDMS of **4c** showed a molecular ion for the twice decarbonylated compound. Unlike **4b**, **4c** proved to be sufficiently robust to isolate as a microcrystalline product in good yield.

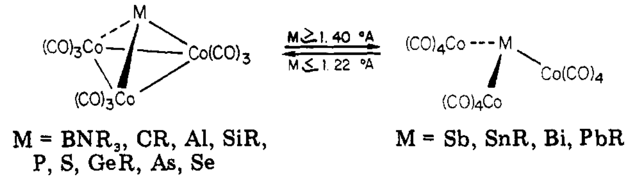
The compound $Fe_3(\mu_3\text{-}Te)_2(CO)_9(dppp)$ (dppp = 1,3-bis(diphenylphosphino)propane) was not isolated in pure form. Its ^{31}P NMR demonstrated that here again only one donor was coordinated; in this case, however, no PP' coupling was observed.

Discussion

Two aspects of the reactivity of **1** require comment: the reason for the reactivity difference between **1** and its S and Se analogues and a mechanistic rationale consistent with our synthetic and structural results.

The structural chemistry of tetrahedral transition metal-nonmetal cluster compounds (TMNMCs) has been thoroughly and systematically examined by Dahl, Schmid, and their co-workers. Schmid has focused on elucidating the structural trends in the electron precise tricobalt carbonyl TMNMCs as a function of the covalent radius of the tethering nonmetal.[37] As summarized in his recent review, the principal result is that the tricobalt assembly adopts a closed, nonacarbonyl structure when the covalent radius of the nonmetal is 1.22 Å (Ge)[38] or less. However, when the capping nonmetal assumes the covalent radius of 1.40 Å (Sb) or greater, these compounds adopt the open dodecacarbonyl structure with *no* cobalt-cobalt bonds (Scheme II. Inasmuch as the covalent radius of Te is 1.36 Å, $Co_3(\mu_3\text{-}Te)(CO)_9$ represents a missing link in Schmid's analysis. This compound has resisted synthesis apparently as a result of combined steric and electronic factors. While $Co_3(\mu_3\text{-}Te)(CO)_9$ is not known, the electron precise 48-electron cluster, $FeCo_2(\mu_3\text{-}Te)(CO)_9$ has been prepared in 30% yield[3] and is quite stable, suggesting that the upper limit for the closed tricobalt cluster is larger than previously appreciated.

Scheme II



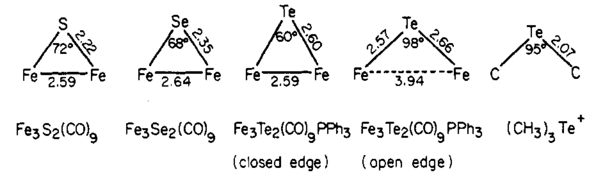


Figure 5. Selected structural parameters for compound **2a** and related species.

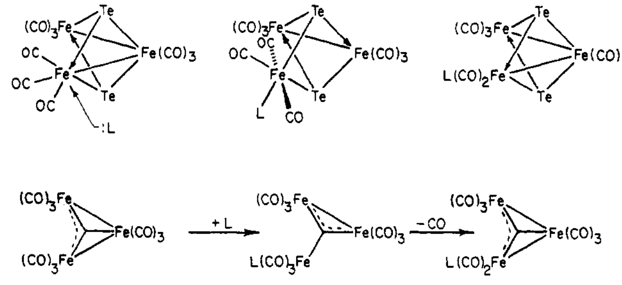


Figure 6. The stereochemistry of adduct formation by $Fe_3(\mu_3\text{-}Te)_2(CO)_9$.

It appears that tellurium occupies a borderline position in TMNMCs. Consistent with this thesis, the recently reported $Fe_2(\mu\text{-}Te_2)(CO)_6$ is unstable thermally due to ring strain,[7] but its more open derivative $Fe_2Pt(\mu_3\text{-}Te)_2(CO)_6(PPh_3)_2$ is quite robust.[6] Compound **1** is both synthetically[7] and topologically related to $Fe_2(\mu\text{-}Te_2)(CO)_6$ via the addition of a $Fe(CO)_3$ fragment to a $FeTe_2$ face. It follows, therefore, that **1** should be subject to considerably more strain in the Fe-E-Fe angle than its S and Se analogues. Figure 5 illustrates the progressive tightening of the M-E-M angle as a function of E. For comparison, uncon-

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(35) Dppe-bridged complexes: Mawby, R. J.; Morris, D.; Thorsteinson, E. M.; Basolo, F. *Inorg. Chem.* **1966**, *5*, 27.

(36) Dppe bridged complexes: Keiter, R. L.; Kaiser, S. L.; Hansen, N. P.; Brodack, J. W.; Cary, L. W. *Inorg. Chem.* **1981**, *20*, 283 and references therein.

(37) Schmid, G. *Angew, Chem., Int. Ed. Engl.* **1978**, *17*, 392.

(38) The semiopen (arachno) cluster $CH_3GeCo_3(CO)_{11}$ has been isolated as an intermediate in the synthesis of $CH_3GeCo_3(CO)_9$: Etzrodt, G.; Schmid, G. *J. Organomet. Chem.* **1979**, *169*, 259.

strained approximately sp^3-hybridized divalent Te assumes a 95° C–Te–C angle in $[(CH_3)_3Te]I$.[39]

An operational mechanism for the formation of the adducts has been formulated which involves only modest rearrangement of the starting structure and which is consistent with the stereochemistry of both the adduct and the substitution product. Attack at an open face of 1 would place the addend on a basal iron meridional with respect to the tellurium atoms and would induce the tautomerization of the Fe–Fe and the Fe–Te bonding arrangement. This tautomerization involves loss of one Fe–Fe bond and a formal shift in the orientation of the tellurium lone pairs (Figure 6). Reversal of this process with explusion of a CO (which is also meridional with respect to the Te atoms) completes the cycle and affords the basally substituted derivative of 1 (e.g., **3a**). An alternative mechanism would involve attack by the ligand at the apical, seven-coordinated iron; however, this mechanism requires considerably more rearrangement of the cluster.

It is important to note that the reactivity associated with each ~60° M–Te–M angle is not independent since 1 binds *only one* donor which in turn opens only one of the two pairs of acute Fe–Te–Fe angles. Were there any tendency to bind an additional ligand to afford the open cluster, e.g., $Fe_3(\mu_3\text{-}Te)_2(CO)_9L_2$, one would expect this to occur in the derivatives which contain monodentate di(tertiary phosphine) ligands.

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Supplementary Material Available: A full crystallographic report including tables of positional and thermal parameters (34 pages). Ordering information is given on any masthead page.

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Chelate-Assisted Oxidative Addition of Functionalized Phosphines to Iridium(I)

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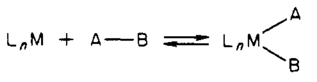
This paper is concerned with an evaluation of the factors which influence the facility of the oxidative addition of chelating substrates. Spectrophotometrically we determined the [Ir(III)]/[Ir(I)] ratios resulting from the oxidative addition of C_6H_5XH and $o\text{-}Ph_2PC_6H_4XH$ (X = O, CO_2) to *trans*-$IrCl(CO)(EPh_3)_2$ (E = P, 1; E = As, 2). The measured [Ir(III)]/[Ir(I)] ratios for the chelating substrates were 10^3–10^4 greater than those for the nonchelating substrates. While benzaldehyde does not detectably add to 1, $o\text{-}Ph_2PC_6H_4CHO$ (PCHO) does so quantitatively ($K \simeq 5 \times 10^4$) affording a stable acyl hydride, $IrH(PCO)Cl(CO)(PPh_3)$. Related stable acyl hydrides prepared in this way are $IrH(PCO)Cl(CO)(PCHO)$, $IrH(PCO)Cl(CO)(AsPh_3)$, $IrH(AsCO)Cl(CO)(AsPh_3)$, and $IrH(PCO(CHO))Cl(CO)(PPh_3)$, the last compound being derived from (phenylphosphino)dibenzaldehyde ($P(CHO)_2$). Equilibrium measurements using 1, 2, PCHO, and the analogous arsine, AsCHO, established a strong dependence of the facility of the oxidative addition on the nature of the ancillary donor ligands. An attempted synthesis of a nonchelated acyl hydride from the reaction of "$IrH(CO)(PPh_3)_2$" and PhCOCl gave only 1 and PhCHO. This result establishes that the differing facilities for oxidative addition of PhCHO and PCHO to 1 is a thermodynamic and not a kinetic effect. The single-crystal X-ray diffraction study of PCHO itself revealed an unexceptional structure which closely resembles that of PPh_3. $o\text{-}Ph_2PC_6H_4CHO$ crystallizes in the triclinic space group $C_i^1\text{-}P\bar{1}$ with cell dimensions of $a = 10.663$ (3) Å, $b = 11.065$ (3) Å, $c = 8.585$ (2) Å, $\alpha = 103.20$ (2)°, $\beta = 105.95$ (2)°, $\gamma = 118.67$ (2)°, $V = 772.8$ (3) Å^3, and $Z = 2$.

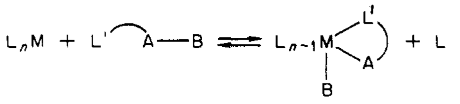
Introduction

The oxidative addition reaction is of great importance in inorganic and organometallic chemistry.[1a] Traditionally, this process involves the formal addition of two one-electron fragments to a single metal center[1b,2] (eq 1)



$$L_nM + A\text{—}B \rightleftharpoons L_nM\begin{matrix}A\\B\end{matrix} \quad (1)$$

although several variations on this theme exist including addition to bimetallic complexes,[3-5] one-electron oxidative addition,[2] and oxidative elimination.[6] An alternative mode of addition is that involving chelating substrates where the addend fragments occupy three (or more) coordination sites in the product (eq 2). This last process can be considered a special case of the cyclometalation reaction.[7-9]



(2)

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