

Insertion of a methylene group into the Te–Te bond of $\text{Fe}_2(\text{CO})_6(\mu_2\text{-Te}_2)$

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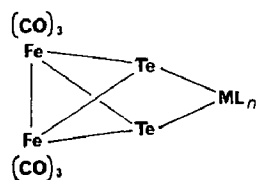
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Abstract

The methylene bridged complex $\text{Fe}_2(\text{CO})_6(\mu\text{-TeCH}_2\text{Te})$ has been prepared from the reaction of $\text{Fe}_2(\text{CO})_6(\mu_2\text{-Te}_2)$ with diazomethane at room temperature and characterized by infrared and NMR spectroscopy, mass spectrometry and elemental analysis.

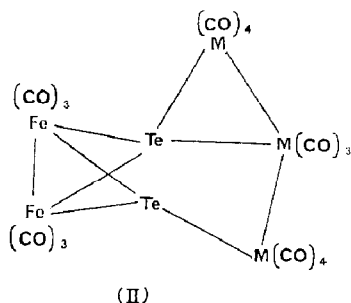
Considerable interest in the synthesis of metal complexes containing bridging methylene groups has been prompted by the possible involvement of methylene groups in carbon monoxide reduction on metal surfaces [1–5]. The use of diazomethane as a source of the methylene group, which permits the insertion of a CH_2 group into a metal–metal bond by a one step mechanism involving donation of the M–M bonding electron pair to the CH_2 of diazomethane and simultaneous loss of N_2 , is one of several routes to methylene bridged complexes [6]. Diorgano ditellurides contain reactive Te–Te bonds across which transition metal substrates and organic moieties are readily added. The reaction of diaryl ditellurides with $\text{Pd}(\text{PPh}_3)_4$ and metal carbonyls usually occurs by cleavage of Te–Te bonds to give products containing bridging or terminal TeAr ligands. However, there are examples of ditellurides which coordinate to metals leaving the Te–Te bond intact [7]. Dialkyl ditellurides have been shown to readily insert CH_2 group into their Te–Te bonds when treated with an excess of diazomethane to form bis(alkyltelluro)methanes [8].

The complexes $\text{E}_2\text{Fe}_2(\text{CO})_6$ (E = S, Se, Te), in which the E_2 ligand symmetrically bridges two $\text{Fe}(\text{CO})_3$ units, readily insert coordinatively unsaturated, low valent metal species into their E–E bonds to form mixed metal complexes $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{ML}_n$ (I) [9,10]. Recently, the addition of polynuclear metal carbonyl

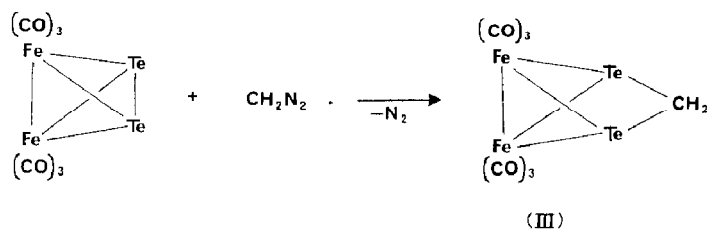


(I)

fragments ' $M_3(CO)_{11}$ ' across the Te-Te bond in $Fe_2Te_2(CO)_6$ to form $Fe_2Te_2(CO)_6M_3(CO)_{11}$ (II) ($M = Ru$ [11], Os [12]) has also been observed. Here, we



report the synthesis and characterisation of the novel $(CO)_6Fe_2(\mu-TeCH_2Te)$ (III), which is formed by the insertion of a methylene group into the Te-Te bond of $Fe_2Te_2(CO)_6$.



A mixture of $Fe_2Te_2(CO)_6$ and diazomethane in diethyl ether solution stirred at room temperature gives almost quantitatively an orange-red compound, identified as $Fe_2(CO)_6(\mu-TeCH_2Te)$ from its infrared, 1H NMR and mass spectral data, and elemental analysis (calculated for $C_7H_2Fe_2O_6Te_2$: C, 15.27; H, 0.36; found C, 15.47; H, 0.34%). The infrared spectrum of III in hexane solution (Fig. 1) shows carbonyl stretching frequencies at 2061 (m), 2022 (s), 1993 (s), 1984 (s) and 1972 (w). The spectrum closely resembles the reported infrared spectrum in the carbonyl region of $Fe_2(CO)_6(\mu-SCH_2S)$, which was originally prepared from $Fe_2(CO)_9$ and 1,3-dithia-5-cycloheptene and structurally characterized by X-ray diffraction techniques [13]. It has also been obtained from the reduction of $Fe_2S_2(CO)_6$ with $LiEt_3BH$, followed by treatment with CH_2I_2 [14]. Recently, the formation of $Fe_2(CO)_6(\mu-SCH_2S)$ as one of the products from the photolytic reaction between $Fe(CO)_5$ and 1,3,5-trithiane has been reported [15]. Interestingly, when $Fe_2(CO)_6(\mu_2-S_2)$ is treated with diazomethane, apart from $Fe_2(CO)_6(\mu-SCH_2S)$, three other compounds, $Fe_2(CO)_6S_2(CH_2)_2$, $Fe_2(CO)_6S_2(CH_2)_3$ and $Fe_2(CO)_6S_2(CH_3)_2$ are also formed [16]. In our reaction of $Fe_2(CO)_6(\mu_2-Te_2)$ with diazomethane, compound III is the sole product. However, we have found that when $Fe_3(CO)_9(\mu_3-Te_2)$ is treated with diazomethane, though compound III is formed as a major product, at least two other compounds, which have not yet been characterised, are also formed in lower yields. The 1H NMR spectrum of III in $CDCl_3$ solution (Fig. 2) shows a singlet at δ 2.2 with ^{125}Te satellites ($^2J(H-Te)$ 24 Hz). The mass spectrum shows a molecular ion peak at m/e 554 and peaks at m/e 526, 498, 470, 442, 414 and 386, corresponding to fragments arising from the successive loss of six carbonyl groups. In terms of the electron counting rules, assuming that each tellurium atom contributes 4 electrons and the $\mu-CH_2$ group contributes 2 electrons, compound III is a 38

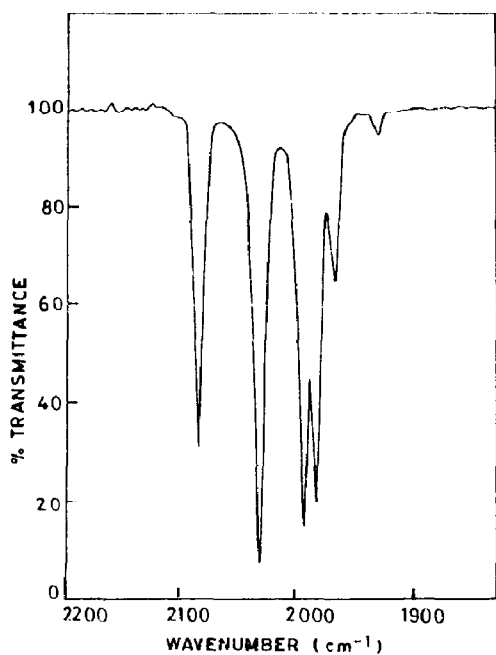


Fig. 1. Infrared spectrum in the carbonyl region of $\text{Fe}_2(\text{CO})_6(\mu\text{-TeCH}_2\text{Te})$ in hexane solution.

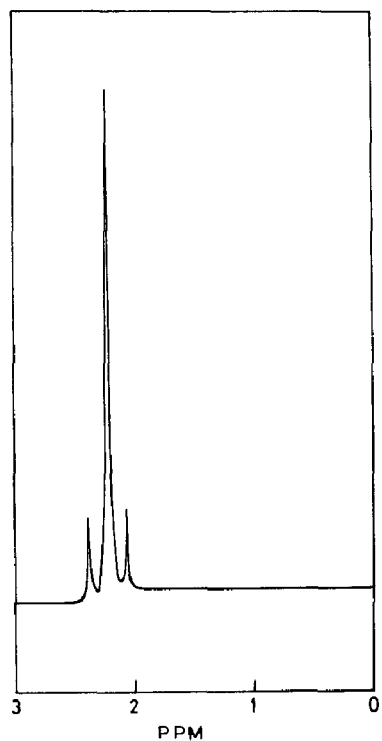


Fig. 2. ¹H NMR spectrum of $\text{Fe}_2(\text{CO})_6(\mu\text{-TeCH}_2\text{Te})$ in CDCl_3 solution (δ , internal Me_4Si).

electron complex, suggesting the presence of a single metal–metal bond, such as that observed in $\text{Fe}_2(\text{CO})_6(\mu\text{-SCH}_2\text{S})$.

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