97375-01-4; **9**, 97375-03-6; **11**, 97375-05-8; **12**, 97375-07-0; **13**, 97375-08-1; A, 12107-38-9; B, 12244-83-6; [$FeCp(CO)_2CH_2OEt$], 12244-98-3; [$FeCp(CO)_2CH_2OC(O)CH_3$], 12244-91-6; [$FeCp(CO)(PMe_2Ph)_2$]$^+$, 83287-98-3; $TlBF_4$, 28625-02-7; PMe_2Ph, 672-66-2; NEt_3, 121-44-8; NC_5H_5, 110-86-1; $P(OMe)_3$, 121-45-9; $S(CH_3)_2$, 75-18-3; $S(CH_3)Ph$, 100-68-5; SPh_2, 139-66-2; $S(C_3H_5)Ph$, 5296-64-0; TlOEt, 20398-06-5; TlOAc, 563-68-8; bicyclo[6.1.0]nonane, 286-60-2; cyclooctene, 931-88-4.

Electron-Promoted C-C Bond Formation. Novel Route to Tetrathiooxalate Derivatives

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Summary: The addition of $NaBH_4$ in THF to [$Fe(\eta^2\text{-}CS_2Me)(CO)_2L_2$]$^+PF_6^-$ (**1b**, L = PPh_3) gave the purple complex $Fe_2(\mu\text{-}\eta^2\text{-}S_2C_2(SMe)_2)(CO)_4(PPh_3)_2$ (**3**, 68%), whereas **1a** (L = PMe_3) under the same conditions afforded $Fe(\eta^2\text{-}HCS_2Me)(CO)_2(PMe_3)_2$ (**2a**). Complex **3** was transformed by exposure to air into a blue derivative, $Fe(\eta^2\text{-}S_2C_2(SMe)_2)(CO)_2PPh_3$ (**4**, 30–48%), the latter reaction being accelerated by the presence of acids, $Na^+PF_6^-$, or H_2O_2. By treatment with sodium amalgam complex **1b** also gave **3** which was transformed in situ into **4**. These reactions are consistent with electron transfer from hydride (or Na/Hg) to **1b**, C–C bond formation of the resulting radical giving **3** and oxidative cleavage of the Fe–Fe bond of **3** to produce **4**. X-ray structure characterizations of **3** and **4** are reported.

Heteroallenes constitute an important class of stable molecules whose activation by metal centers has been investigated extensively.[1,2] This activation is relevant to the synthesis of sulfur-containing organic compounds[3] and the modeling of reduction processes of CO_2,[1,4] especially with respect to C–C bond formation and/or its incorporation into organic substrates.[5] Examples of metal-promoted dimerization of heteroallenes have been reported to date, most of which involve the formation of carbon–heteroatom bonds in the so-called "head-to-tail" mode of coupling.[6]

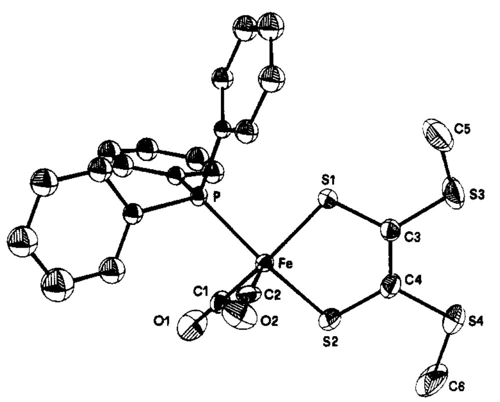
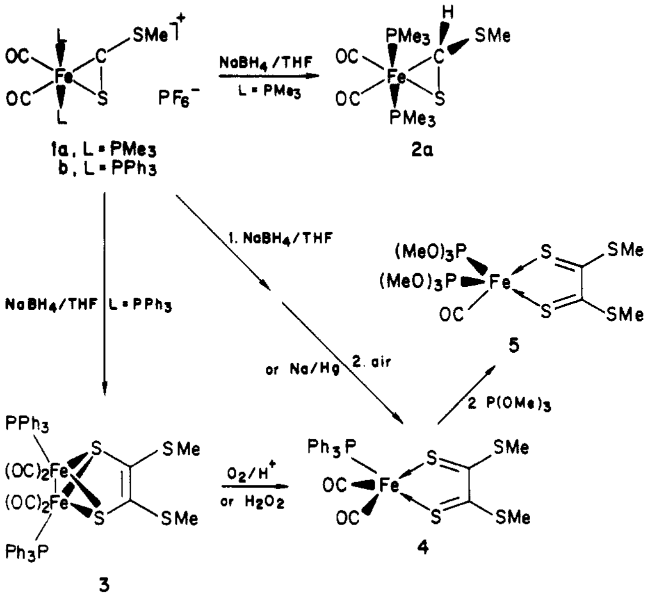


Figure 1. ORTEP view of $Fe(S_2C_2(SMe)_2)(CO)_2(PPh_3)$ (**4**). Selected bond lengths (Å) and angles (deg): Fe–S(1) = 2.163 (3), Fe–S(2) = 2.196 (3), Fe–P = 2.244 (3), S(1)–C(3) = 1.701 (10), S(2)–C(4) = 1.708 (12), C(3)–C(4) = 1.390 (15); S(1)–Fe–S(2) = 87.8 (1), S(1)–C(3)–C(4) = 118.0 (8), S(2)–C(4)–C(3) = 119.2(8).

Scheme I



Only recently have C–C bond formation processes involving heteroallenes been discovered.[7] We now report an interesting example of C–C bond formation with CS_2 as heteroallene which proceeds via electron transfer and leads to the formation of tetrathiooxalate derivatives. The reaction pathway is based on the X-ray structure determination of two key products.

The reaction of borohydride with a [$LnM(\eta^2\text{-}CS_2R)$]$^+$ cation has been shown to proceed in several ways: $Os(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2{}^+$ reacts with $NaBH_4$ to give $Os(H)(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2$[8] while [$N(CH_2CH_2PPh_2)_3Co(\eta^2\text{-}CS_2Me)$]$^+$ under similar conditions leads to SMe group elimination to form the thiocarbonyl ligand in [$N(CH_2CH_2PPh_2)_3Co(CS)$]BPh_4.[9] Recently we observed that

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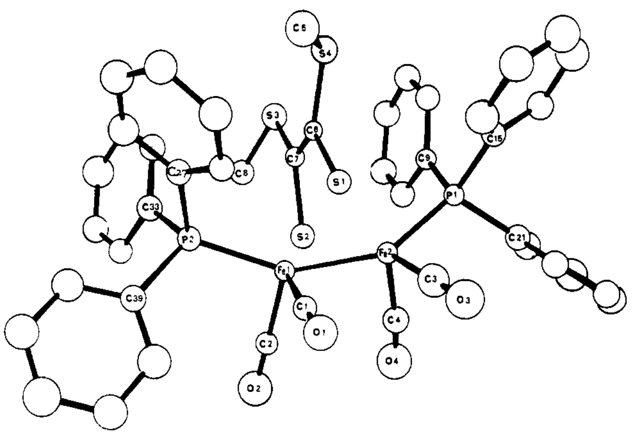


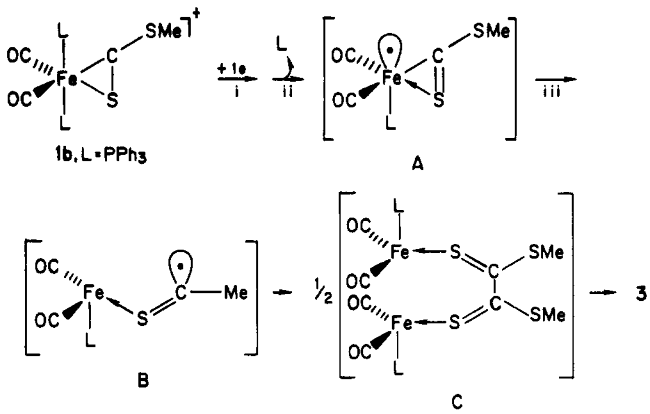
Figure 2. ORTEP view of $Fe_2(S_2C_2(SMe)_2))(CO)_4(PPh_3)_2$ (**3**). Selected bond lengths (Å) and angles (deg): Fe(1)–Fe(2) = 2.525 (2), Fe(1)–S(1) = 2.258 (2), Fe(1)–S(2) = 2.280 (2), Fe(2)–S(1) = 2.276 (2), Fe(2)–S(2) = 2.303 (2), Fe(1)–P(2) = 2.249 (2), Fe(2)–P(1) = 2.256 (2), C(6)–C(7) = 1.303 (8); S(1)–Fe(1)–S(2) = 79.31 (6), S(1)–Fe(2)–S(2) = 78.46 (6) S(1)–C(6)–C(7) = 116.5 (4), S(2)–C(7)–C(6) = 115.8 (5).

$NaBH_4$ reacts with **1a** (L = PMe_3) to give the addition of the hydride to the carbon atom in **2a**[10] (Scheme I); in contrast, the similar reaction with **1b** (L = PPh_3), readily accessible from carbon disulfide,[11] took an unexpected pathway.

The addition of 2 equiv of $NaBH_4$ to a THF solution of **1b** (5 mmol) at room temperature led after 3 h to the formation of a purple product which was transformed in air into a blue complex. The latter was isolated by crystallization from ether–pentane (1:3) in 30% yield; it contained two SMe groups for one PPh_3 ligand[12] and was identified by X-ray analysis[13] as complex **4** (Scheme I). An ORTEP view (Figure 1) indicates that complex **4** contains a coordinated tetrathiooxalate group resulting from the dimerization of the η^2-CS_2R ligand of **1b**.

When the same reaction was interrupted after 2 h, by solvent evaporation, silica gel chromatography under nitrogen of the resulting mixture with THF as eluent afforded small quantities of complex **4** and then, in 64% yield, the previous purple intermediate. This air-sensitive complex, which contained one SMe group per PPh_3 ligand,[15] was identified by an X-ray diffraction study[16] as the bimetallic complex **3** having a bridging tetrathiooxalate group (Scheme I). An ORTEP view of **3** is shown in Figure 2.

Scheme II



Pure complex **3** in solution gave **4** (48 %) on exposure to air in the presence of acid. Complex **4** was further reacted with an excess of $P(OMe_3)$ to give a violet derivative **5** (Scheme I) identified by spectroscopy[17] and corresponding to the displacement of one PPh_3 and one carbonyl ligand by $P(OMe)_3$.

The nature of **3** suggests that the reaction proceeds via an electron transfer from the hydride to complex **1b** which is expected to be more easily reduced than **1a**, due to the weak basicity of PPh_3.

Complex **1b** (0.5 mmol) in THF was then added to 5 mL of 1% sodium amalgam. The reaction solution very quickly, as compared to the previous one with $NaBH_4$, turned purple and then blue. After 1.5 h at room temperature only complex **4** was present, as indicated by chromatography, and it was isolated by crystallization from pentane in 40% yield. The same reaction after 20 min gave a mixture of both complexes, **3** and **4**, which were separated by column chromatography (eluent pentane–ether for **4** and CH_2Cl_2 or THF for **3**) and identified by infrared spectroscopy.[12,15] The easy formation of **3**, following the reduction of **1b**, may be rationalized as occurring through the following steps (Scheme II): (i) transfer of one electron to a metal–ligand σ^* level, (ii) release of the electronic accumulation at the metal (19-electron configuration) by elimination of one L = PPh_3 group, and (iii) homolytic cleavage of the Fe–C bond. Consequently, the intermediate B, with an unpaired electron localized on the carbon atom, represents a good candidate for the dimerization reaction involving a C–C bond formation and leading, via intermediate C, to complex **3**.

The formation of **4** corresponds actually to the loss of one $Fe(CO)_2PPh_3$ group by complex **3**. The reaction takes

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(12) **4**: mp 130–131 °C; IR (Nujol) 2010 (vs), 1950 (vs), 1100 (vs) cm^{-1}; ^{31}P NMR ($CDCl_3$, 309 K, 32.38 MHz) δ 43.35; ^1H NMR ($CDCl_3$, 305 K, 80 MHz) δ 7.66 (m, C_6H_5), 1.55 (s, SMe). Anal. Calcd for $C_{24}H_{21}PO_2S_4Fe$: C, 51.8; H, 3.80; P. 5.56; S, 23.04. Found: C, 52.11; H, 3.83; P, 5.97; S, 22.29.

(13) Crystal data of **4**: $C_{24}H_{21}O_2PS_4Fe$, M_r = 556.51, space group $P2_1/a$, a = 24.143 (6) Å, b = 10.017 (2) Å, c = 10.745 (2) Å, β = 97.38 (2)°, V = 2577.1 Å^3, Z = 4, d_{calcd} = 1.43 g cm^{-3}, μ(Mo Kα) = 9.75 cm^{-1}. The intensities of 5171 reflections were collected up to 2θ = 50° from a crystal of dimensions 0.425 × 0.20 × 0.15 mm using a Philips PW 1100 diffractometer and Mo Kα radiation. The structure was solved by Patterson and Fourier techniques (SHELX76).[14] Least-squares refinement gave the final residues $R(F)$ = 0.084 and $R_w(F)$ = 0.095 for 2440 reflections with $I > 3\sigma(I)$ corrected for decay (28%) and absorption (transmission factors 0.89–0.94). The phenyl rings of the PPh_3 ligand were treated as rigid groups of the D_{6h} symmetry.

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(15) **3**: mp 176–178 °C; IR (Nujol) 1990 (vs), 1950 (s), 1930 (vs), 1910 (m) cm^{-1}; ^{31}P NMR (CD_2Cl_2, 309 K, 32.38 MHz) δ 58.4 (s, PPh_3); ^1H NMR (CD_2Cl_2, 305 K, 80 MHz) δ 7.70, 7.42 (m, C_6H_5), 1.61 (s, SMe). Anal. Calcd for $C_{22}H_{18}O_2P_1S_2Fe$: C, 56.78; H, 3.89; P, 6.65; S, 13.78. Found: C, 56.50; H, 3.75; P, 6.36; S, 13.40.

(16) Crystal data of **3**: $C_{44}H_{36}O_4P_2S_4Fe_2$, M_r = 930.7, triclinic space group $\bar{P}_1$, a = 9.669 (2) Å, b = 13.477 (3) Å, c = 17.323 (3) Å, α = 101.1 (2)°, β = 91.5 (2)°, γ = 110.3 (2)°, Z = 2, μ = 10.13 cm^{-1}. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (λ(Mo Kα) = 0.71069 Å, $2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1, t_{max} = 60 s, no absorption corrections); 7220 reflections whose 3802 with $I > \sigma(I)$. The structure was solved with a Patterson map and several Fourier differences. After isotropic and anisotropic refinements of Fe, S, P, C, O atoms, many hydrogen atoms were found with a Fourier difference. The remaining ones were located manually. The better full-matrix least-squares refinement (x, y, z, and β for non-hydrogen atoms; x, y, z for hydrogen atoms) gives $R_w = [\sum w|F_o - F_c|^2/\sum wF_o^{\,2}]^{1/2}$ = 0.058, and $R = \sum|F_o - F_c|/\sum F_o$ = 0.058 with $1/w = \sigma^2/F = {}^1/_4[\sigma_I^{\,2}/I + (0.04)^2I]$. The scattering factors and f' and f'' values were taken from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974.

(17) **5**: 30% yield; IR (Nujol) 1940 (vs) cm^{-1}; mass spectrum calcd for m/e (M = $C_{11}H_{24}P_2O_7S_4Fe)^+$ 513.923, found m/e 513.925; ^{31}P NMR (CD_2Cl_2, 307 K, 32.38 MHz) δ 5.47 (br, s, $P(OMe)_3$); ^1H NMR ($CDCl_3$, 305 K, 80 MHz) δ 2.97 (t, $P(OMe)_3$, $|J_{PH} + J_{P'H}$ = 11.8 Hz), 2.67 (s, SMe).

place by exposure of a solution of **3** to air but is accelerated by addition of acids, or even $Na^+PF_6^-$ and occurred within seconds when H_2O_2 was added to **3**. During the reduction of **1b** with sodium amalgam, the formation of Na^+ cations may assist the elimination of the $Fe(CO)_2PPh_3$ fragment and accelerate the transformtion **3** → **4**.

The present study suggests that previous examples of C–C bond formation between two metal–heteroallene moieties **7a,b**, which gave rise to the formation of another type of binuclear complex, could also be promoted by a radical process.

Acknowledgment. Thanks are expressed to Dr. H. Le Bozec for helpful discussions and to Mr. D. Masi for technical assistance in the X-ray work.

Registry No. **1b**, 71004-19-8; **3**, 97390-97-1; **4**, 97390-96-0; **5**, 97403-35-5; $NaBH_4$, 16940-66-2; C, 7440-44-0.

Supplementary Material Available: Tables of atomic potential and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Mechanism of CO Insertion into Metal–Oxygen Bonds. Reaction of (DPPE)Pt(OCH_3)R (R = CH_3 or OCH_3) with CO[†]

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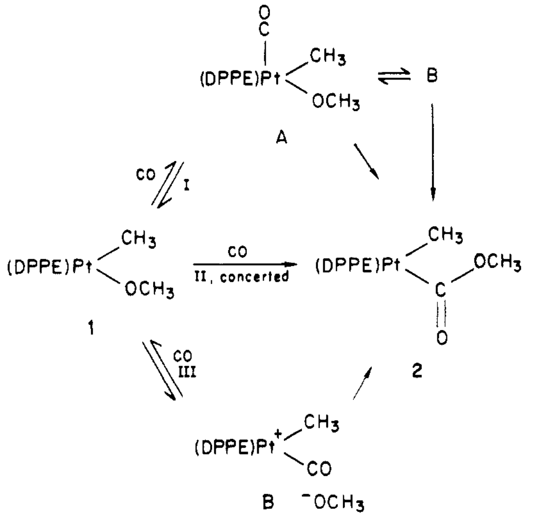
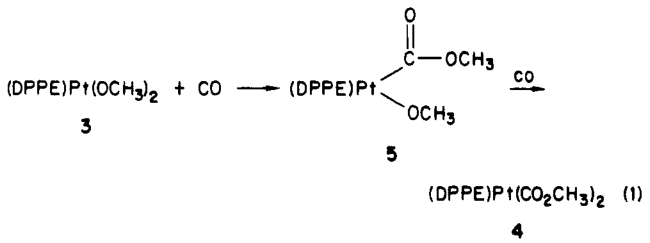
Summary: The carbonylation of (DPPE)$PtCH_3(OCH_3)$, **1** (DPPE = 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$), to yield (DPPE)$PtCH_3(CO_2CH_3)$ is first order in **1** and first order in CO. Low-temperature ^{13}C NMR experiments suggest formation of a five-coordinate CO complex intermediate, and crossover experiments rule out the involvement of dissociated species during this reaction. Similar complex **3**, (DPPE)$Pt(OCH_3)_2$, carbonylates stepwise through (DPPE)$Pt(OCH_3)(CO_2CH_3)$ to ultimately form (DPPE)$Pt(CO_2CH_3)_2$. Similar kinetics and alcohol exchange reactions suggest the carbonylation mechanism is the same one outlined for the methyl methoxide. Low-temperature ^{13}C NMR measurements permit observation and quantification of a five-coordinate CO adduct.

During our investigation of reactions relevant to the palladium-catalyzed carbonylation of alcohols to dialkyl oxalates, we found platinum alkoxide **1** carbonylates to carbomethoxide complex **2**. Similarly, we observed related bis alkoxide **3** reacts with CO to give bis(carbomethoxide) **4** through the intermediacy of complex **5**.[1,2] While carboalkoxide formation from carbonylation of platinum alkoxides has been known for some time,[3] the mechanism has not been explored. We now show the mechanism of carboalkoxide formation for **1** involves inner-sphere insertion of CO into the metal-oxygen bond and most probably proceeds through the formation of a five-coordinate CO complex.

Scheme I



$$(DPPE)PtCH_3(OCH_3) + CO \rightarrow (DPPE)PtCH_3(CO_2CH_3)$$
1 2



$$(DPPE)Pt(OCH_3)_2 + CO \longrightarrow (DPPE)Pt(OCH_3)(CO_2CH_3) \xrightarrow{CO} (DPPE)Pt(CO_2CH_3)_2 \quad (1)$$

Carbonylation of **1** was followed by ^1H and ^{31}P NMR[4] at −20 °C. The reaction is first order in **1** to better than 3 half-lives. With use of CO pressures ranging from 0 to 150 psi, the observed rate was found to be first order in the concentration of CO.[5] This first-order CO dependence suggests this reaction does not proceed by initial dissociation of methoxide; this expectation was confirmed by putting an upper limit on the rate of methanol dissociation from **1** that is 3 orders of magnitude slower than the observed carbonylation rates.[6]

[†] Contribution No. 3562.

(1) Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.*, in press.

(2) Complex **5** was observed during the reaction of **3** and CO which ultimately yields complex **4**. The concentration of **5** is effectively steady state, suggesting it is an intermediate in the production of **4**.

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(4) In a typical experiment, a pressure NMR tube was loaded in a drybox with a THF-d_8 or CD_2Cl_2 solution of **1** and charged to gauge pressures with CO.

(5) The rate of reaction is described by the following relationship: $-d[1]/dt = d[2]/dt = k[1][CO]$ where, in CD_2Cl_2, $k = 4.1 \times 10^{-2}$ s^{-1} mol^{-1} at −20 °C. The concentration of CO in solution was determined by preparing known concentration solutions of ^{13}C-enriched benzaldehyde (90% enrichment in the carbonyl position) and sealing the system with a known pressure of ^{13}CO (also 90% enrichment). The concentration of CO at 1 atm of CO pressure in CD_2Cl_2 is expressed by

$$[CO]_{1\,atm} = 2.75 \times 10^{-6}(T) + 6.45 \times 10^{-3}$$

where [CO] is in molarity and T is in °C over the range of +30 to −80 °C.

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