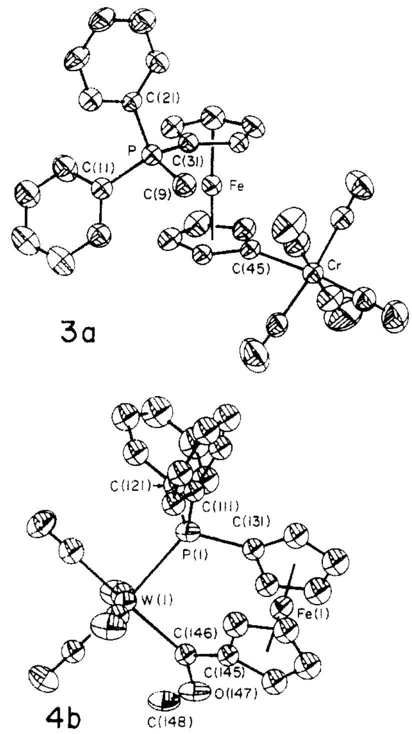
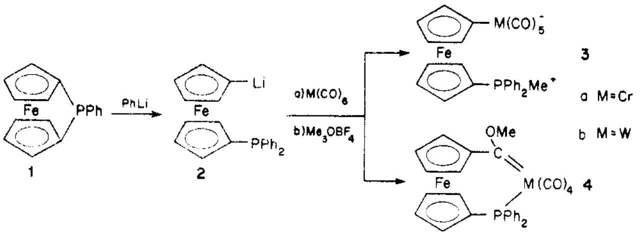


**Figure 1.** Views of **3a** and one molecule of **4b**. Thermal ellipsoids enclose 50% probabilities. Hydrogen atoms have been deleted for clarity.

**Scheme I**



X-ray structures were determined for **3a** and **4b**.[8] Views of **3a** and one of the three crystallographically independent molecules of **4b** are shown in Figure 1.[9] The three molecules of **4b** are structurally similar. Selected distances (Å) for **3a**:[10] Cr–C(45) = 2.149 (5); Cr–C(carbonyls cis to C(45)) = 1.872 (8) (average); Cr–C(carbonyl trans to C(45)) = 1.843 (6); P–C(9) = 1.788 (5); P–C(phenyl) = 1.796 (5) (average); P–C(31) = 1.769 (5). Averaged[9] distances (Å) and angles (deg) for **4b**: W–P = 2.550 (6); W–C(n46) = 2.199 (14); W–C(carbonyl) = 2.017 (23); P–C(phenyl) = 1.839 (14); P–C(n31) = 1.825 (25); C(n45)–C(n46) = 1.49 (2); C(n46)–O(n47) = 1.32(2); O(n47)–C(n48) = 1.44 (2); P–W–C(n46) = 90.7(4); C(n45)–C(n46)–O(n47) = 105.1 (12). The W-carbene carbon and carbene–$C_5H_4$ distances are both in their normal ranges.[3,6,11] The P–C distances are shorter in **3a** than in **4b**.

In view of the result that $Fe(C_5H_5)(C_5H_4PPh_2)$ does not react easily with $M(CO)_6$ at ambient temperature, it is probable that cyclization to give **4** is assisted by formation of the initial acylato complex or a later produced unidentate methyl carbene derivative. The acylato complex is probably the source of **3** via a competitive reaction of the uncomplexed–$PPh_2$ function with $Me_3OBF_4$.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for financial assistance.

**Supplementary Material Available:** Fully labeled thermal ellipsoid diagrams of **3a** and **4b** (Figures 2 and 3) and views of all three independent molecules of **4b** (Figure 4) along with details of structure refinement, tables of crystals data, data collection, positional and thermal parameters, and bond distances and angles, and structure factor listings (92 pages). Ordering information is given on any current masthead page.

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(7) Microanalytical and spectroscopic data for all four compounds are as expected. **4b**: $^{13}C$ NMR 311 ppm (carbene carbon).

(8) Crystals of **3a** are monoclinic of space group $P2_1/n$ with $a$ = 10.809 (2) Å, $b$ = 10.327 (3) Å, $c$ = 22.830 (5) Å, $\beta$ = 90.62 (2)°, $V$ = 2548.2 Å$^3$, $Z$ = 4; present $R_F$ = 0.039 from 2301 observables. Crystals of **4b** are triclinic of space group $P\bar{1}$ with $a$ = 12.259 (3) Å, $b$ = 14.459 (4) Å, $c$ = 23.108 (4) Å, $\alpha$ = 81.19 (2)°, $\beta$ = 75.26 (2)°, $\gamma$ = 78.86 (2)°, $V$ = 3863.1 Å$^3$, $Z$ = 6; present $R_F$ = 0.045 from 6128 observables. Data were collected by $\omega$–$2\theta$ scans on an Enraf-Nonius CAD4F diffractometer, Mo K$\alpha$ radiation (graphite monochromator) with $2\theta_{max}$ = 45° for **3a** and 40° for **4b**.

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## Remarkable Phase-Transfer-Catalyzed Reactions Involving Sulfur

**Howard Alper* and Fazle Sibtain**

*Department of Chemistry, University of Ottawa*
*Ottawa, Ontario, Canada K1N 9B4*

**Frederick W. B. Einstein* and Anthony C. Willis**

*Department of Chemistry, Simon Fraser University*
*Burnaby, British Columbia, Canada V5A 1S6*

*Received November 2, 1984*

*Summary:* An unusual reaction occurs when bromo(pentacarbonyl)manganese is treated with 5 N NaOH, methylene chloride, or 4-methyl-2-pentanone as the organic phase, benzyltriethylammonium chloride as the phase-transfer agent, and elemental sulfur. An X-ray analysis of $[PhCH_2N(C_2H_5)_3^+]_2[(Mn(CO)_3(SCS_3))_2]^{2-}$ confirmed the presence of a perthiocarbonate ligand. Crystal data: triclinic, space group $P\bar{1}$, $a$ = 9.128 (9) Å, $b$ = 9.720 (12) Å, $c$ = 13.308 (6) Å, $V$ = 1050.8 Å$^3$, and $Z$ = 2.

Phase-transfer catalysis is a valuable method for the synthesis of organometallic complexes and for the use of metal compounds as catalysts for a variety of reactions.[1] Recently, the first examples of the phase-transfer-catalyzed desulfurization of organic compounds were described, whereby benzylic mercaptans are converted to hydrocarbons using stoichiometric quantities of triiron dodecacarbonyl.[2] The fate of the sulfur in this reaction was not determined.

$$R_1R_2R_3CSH + Fe_3(CO)_{12} \xrightarrow[60\ °C,\ (C_4H_9)_4N^+HSO_4^-]{5\ N\ NaOH,\ C_6H_6} R_1R_2R_3CH$$

Some interesting complexes have been isolated from the reaction of sulfur with organometallic reagents under ho-

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Table I. Final Atomic Coordinates and Thermal Parameters ($Å^2$) of the Non-Hydrogen Atoms

| atom | $x$ | $y$ | $z$ | $B_{eq}$ or $B$ |
|---|---|---|---|---|
| Mn | 0.67722 (19) | 0.54936 (18) | 0.47090 (13) | 2.85 (10)[a] |
| S(1) | 0.5936 (3) | 0.3386 (3) | 0.4857 (2) | 3.08 (17)[a] |
| S(2) | 0.6348 (4) | 0.3151 (3) | 0.3330 (2) | 3.95 (18)[a] |
| S(3) | 0.6035 (3) | 0.6438 (3) | 0.2949 (2) | 3.58 (18)[a] |
| S(4) | 0.6051 (5) | 0.5083 (4) | 0.1218 (3) | 6.05 (24)[a] |
| C(1) | 0.6132 (12) | 0.4959 (11) | 0.2464 (8) | 3.5 (2) |
| C(11) | 0.7306 (12) | 0.7129 (13) | 0.4570 (8) | 3.4 (3) |
| O(11) | 0.7669 (9) | 0.8204 (8) | 0.4483 (6) | 5.1 (5)[a] |
| C(12) | 0.8680 (14) | 0.4558 (12) | 0.4239 (8) | 3.4 (3) |
| O(12) | 0.9899 (9) | 0.3986 (9) | 0.3914 (6) | 5.9 (5)[a] |
| C(13) | 0.7312 (13) | 0.4727 (13) | 0.6034 (10) | 4.0 (3) |
| O(13) | 0.7734 (9) | 0.4174 (9) | 0.6880 (7) | 5.7 (5)[a] |
| N | 0.7674 (9) | 0.8704 (8) | 0.7907 (6) | 2.59 (17) |
| C(21) | 0.6558 (12) | 0.9039 (11) | 0.8870 (8) | 3.4 (2) |
| C(22) | 0.7133 (11) | 0.9513 (11) | 0.9646 (8) | 3.1 (2) |
| C(23) | 0.6894 (13) | 1.1054 (13) | 0.9511 (9) | 4.8 (3) |
| C(24) | 0.7370 (14) | 1.1528 (14) | 1.0259 (10) | 5.8 (3) |
| C(25) | 0.8043 (14) | 1.0514 (14) | 1.1108 (9) | 5.3 (3) |
| C(26) | 0.8317 (14) | 0.8972 (14) | 1.1269 (10) | 5.8 (3) |
| C(27) | 0.7845 (13) | 0.8521 (12) | 1.0523 (9) | 4.8 (3) |
| C(31) | 0.8205 (12) | 1.0075 (11) | 0.7332 (8) | 3.7 (3) |
| C(32) | 0.9165 (13) | 1.0031 (12) | 0.6314 (8) | 4.5 (3) |
| C(41) | 0.6835 (12) | 0.8300 (11) | 0.7223 (8) | 3.2 (2) |
| C(42) | 0.5573 (12) | 0.9570 (11) | 0.6647 (8) | 3.8 (3) |
| C(51) | 0.9139 (12) | 0.7402 (12) | 0.8283 (8) | 3.7 (3) |
| C(52) | 0.8900 (13) | 0.5849 (13) | 0.8756 (9) | 5.4 (3) |

[a] $B_{eq}$ is the arithmetic mean of the principal axes of the thermal ellipsoid.

mogeneous conditions.[3] We anticipated that the application of phase-transfer catalysis to the chemistry of sulfur may lead to unusual complexes of potential utility as crude oil desulfurization catalysts. This communication reports a truly novel sulfur phase-transfer reaction leading to a polysulfur metal complex.

Gibson and co-workers[4,5] found that bromo(pentacarbonyl)manganese is rapidly converted to the binuclear anion $(CO)_5MnMn(CO)_4Br^-$ (1) using basic phase-transfer conditions. We found that the treatment of the in situ generated 1, formed using methylene chloride as the organic phase and benzyltriethylammonium chloride as the phase-transfer agent, with elemental sulfur at 40 °C for 3 h, afforded complex 2 containing a novel anionic species.

$$BrMn(CO)_5 \xrightarrow[CH_2Cl_2,\ PhCH_2N(C_2H_5)_3{}^+Cl^-]{5\ N\ NaOH}$$

$$\underset{1}{PhCH_2N(C_2H_5)_3{}^+(CO)_5MnMn(CO)_4Br^-} \xrightarrow{S_8}$$

$$\underset{2}{[PhCH_2N(C_2H_5)_3{}^+]_2[(Mn(CO)_3(SCS_3))_2]^{2-}}$$

This reaction can also be effected by using a carbon monoxide rather than a nitrogen atmosphere, the yield being the same in both cases. Besides methylene chloride, 4-methyl-2-pentanone can be employed as the organic phase (reaction time of 30 min at 70 °C). Complex 2 displays three intense terminal metal carbonyl stretching bands in the infrared region at 1993, 1930, and 1912 $cm^{-1}$ (KBr disk). The carbon atom of the SCS unit arises from a carbonyl carbon of the manganese complex and not from the solvent.

An X-ray structure analysis of crystals of 2 was undertaken to unequivocally establish their composition.[6] The unit cell contains discrete triethylbenzylammonium cations and $[(Mn(CO)_3(SCS_3))_2]^{2-}$ anions. Bond lengths and angles in the cation are normal for an organic compound (see

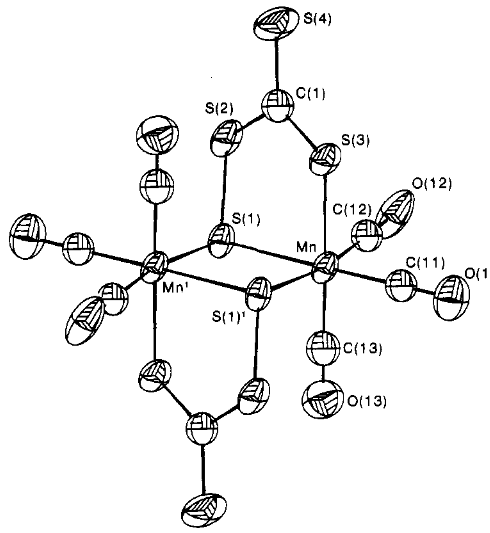

**Figure 1.** SNOOPI diagram of the $[(Mn(CO)_3(CS_3S))_2]^{2-}$ anion. Thermal ellipsoids enclose 50% probabilities. The molecule possesses a crystallographic center of inversion. Selected interatomic distances (Å): Mn–S(1) = 2.365 (4); Mn–S(3) = 2.360 (4); Mn–S(1)$^1$ = 2.381 (4); S(1)–S(2) = 2.070 (4); C(1)–S(2) = 1.743 (10); C(1)–S(3) = 1.720 (10); C(1)–S(4) = 1.638 (11). Selected angles (deg): S(1)–Mn–S(1)$^1$ = 82.20 (14); S(1)–Mn–S(3) = 87.53 (13); Mn–S(1)–Mn$^1$ 97.80 (14).

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[6] Crystals are triclinic of space group $P\bar{1}$ with $a$ = 9.128 (9) Å, $b$ = 9.720 (12) Å, $c$ = 13.308 (6) Å, $\alpha$ = 71.91 (7)°, $\beta$ = 79.97 (6)°, $\gamma$ = 69.86 (9)°, and $V$ = 1050.8 $Å^3$; $C_{34}H_{44}Mn_2N_2O_6S_8$; fw = 943 13, $\rho_{calcd}$ ($Z$ = 2) = 1.490 g $cm^{-3}$. X-ray diffraction intensity data were collected (with some difficulty) on a crystal fragment 0.39 × 0.28 × 0.02 mm on an Enraf-Nonius CAD4F diffractometer employing graphite-monochromatized Mo K$\alpha$ radiation [$\lambda(\alpha_1)$ = 0.709 30 Å]. An absorption correction ($\mu$ = 10.01 $cm^{-1}$) was applied. Of a total of 1684 reflections with $2\theta < 38°$, 1035 were observed [$I > 2.3\sigma(I)$]. The structure was solved by MULTAN, and all non-hydrogen atoms were located by conventional methods. H coordinates were determined geometrically but were not refined. Anisotropic temperature factors were used for Mn, $S_7$ and O atoms and isotropic temperature factors for N and C. Full-matrix refinement (145 variables, observed reflections only) converged to $R_F$ = 0.044 and $R_{wF}$ = 0.044.

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supplementary material). Final atomic coordinates of the non-hydrogen atoms are noted in Table I. The anion is a dimer with a crystallographically imposed center of inversion. The Mn atoms are bridged by the terminal perthio atoms of perthiocarbonate ligands. One of the other terminal atoms of each perthiocarbonate coordinates to an axial site on each Mn to form five-membered SSCSMn chelate rings. Carbonyl ligands complete a distorted octahedral arrangement about each Mn atom. A view of the anion is given in Figure 1. Within the precision of this structure analysis there is no significant difference in the three Mn–S bond lengths (range 2.360 (4)–2.381 (4) Å).

The structures of a few other perthiocarbonates, which do not have carbonyl ligands, have been reported.[7,8] In $[(SCS_3)_2MoS]^{2-}$ and $[(SCS_3)Mo_2S_4(SCS)_3]^{2-}$ the perthiocarbonate is bidentate with the Mo–S (perthio) bond being significantly shorter than the other Mo–S bond to this ligand (ca. 0.06 Å for the former, but only ca. 0.02 Å for the latter).[8] Bond distances within the perthiocarbonate ligand of $[(Mn(CO)_3(SCS_3))_2]^{2-}$ closely parallel those of $[(SCS_3)_2MoS]^{2-}$: the S–S distance is somewhat long, the C–S bond to the uncoordinated S is short, indicating that the double bond is largely localized here and not delocalized into the chelate ring, and the C–S distances within the chelate ring are near equal.

Some comparisons can also be made with perthiolates[9] and $S_4^{2-}$ complexes[10] as they, too, form five-membered chelate rings of the type SS(C or S)S(Metal). In these compounds the metal–S bonds may be near equal[9b,c,10a] or asymmetric,[9a,10b] a feature which is well-known for dithiocarbamates and dithiolates.[11] Perthiolates show shorter C–S bonds within the chelate ring than perthiocarbonates as the double bond is delocalized within the ring. The structure of a copper perthiolate has been reported in which the ligating S atoms bridge metal atoms.[9d]

The following procedure was used: to 3.0 mmol of $Mn(CO)_5Br$ in $CH_2Cl_2$ (50 mL) or 4-methyl-2-pentanone (25 mL) was added an equivalent volume of 5 N NaOH containing benzyltriethylammonium chloride. After the mixture was stirred for 30 min at 40 °C **1** was formed (IR identical with that reported previously),[4] elemental sulfur (0.32 g) was added, and stirring was continued at 40 °C for 3 h ($CH_2Cl_2$) or for 30 min at 70 °C (4-methyl-2-pentanone). The reaction mixture was cooled to room temperature, the phases were separated, and the organic phase was dried ($MgSO_4$). Hexane was added to the organic phase, and orange crystals of **2** were obtained after the solution was stored in a refrigerator; yield 46%. (Anal. Calcd for $C_{34}H_{44}Mn_2N_2O_6S_8$: C, 43.30; H, 4.70; S, 27.20. Found: C, 43.41; H, 4.61; S, 27.33.)

In conclusion, phase-transfer-catalyzed reaction of $Mn_2(CO)_9Br^-$ with sulfur affords a novel class of complexes. The mechanism of this intriguing reaction remains to be determined.

**Acknowledgment.** We are indebted to the Natural Sciences and Engineering Research Council of Canada for support of this work.

**Supplementary Material Available:** A description of the collection of the X-ray diffraction data and refinement of the structure, Figure 2, showing the cation, and tables listing crystal data, data collection and refinement, atomic coordinates and thermal parameters of the hydrogen atoms, interatomic distances and angles, least-squares planes and torsion angles, and observed calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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# Evidence for Intramolecular Pathways in C–C Bond-Forming Reactions Proceeding from Binuclear Iron Complexes[1]

**Govindarajan Sundararajan and**
**Joseph San Filippo, Jr.***

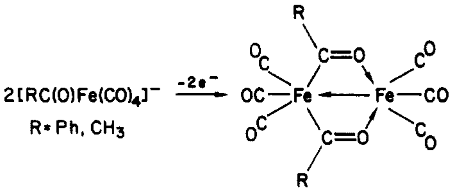
*Department of Chemistry*
*Rutgers, The State University of New Jersey*
*New Brunswick, New Jersey 08903*

*Received July 30, 1984*

*Summary:* Decomposition of the binuclear iron complex **2** (R = *n*-$C_9H_{19}$) in THF or cyclohexane yields three products: *n*-octadecane, 10-nonadecanone, and 10,11-eicosodione. The principal organometallic product is $Fe(CO)_5$. Decomposition obeys first-order kinetics and is characterized by an unusually large, negative entropy of activation, $\Delta S^{\ddagger} = -29$ cal/(mol K) (log $A = 6.07$). The failure to observe any crossover products demonstrates that these decomposition products are produced in processes which do not involve alkyl group scrambling and presumably occur by intramolecular pathways. The reactivity of **2** with methyl iodide and triphenylphosphine has also been briefly examined.

Binuclear complexes would appear to afford an obvious bridge between the chemistry of mononuclear complexes and polynuclear clusters with interest in the latter deriving in part from the suggestion that their chemistry may serve as a model for the study of even more complex multimetal systems such as are found heterogeneous catalysts.[2] In fact, in their extensive studies of the C–C bond-forming reactions of certain simple binuclear organocobalt complexes, Bergman and co-workers demonstrated that the chemistry of these reagents is dominated by intermolecular mononuclear processes.[3-6] We report here the results of our investigation of the ostensibly similar reactions associated with certain binuclear organoiron complexes which, however, appear to occur by *intramolecular* pathways.

Oxidation of acyltetracarbonylferrates by any of several one-electron oxidants yields a neutral complex (eq 1),[7a] the



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[1] Supported by a grant from the NSF, CHE-83-12730.

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