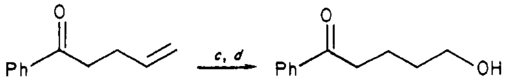
of the ready availability of various kinds of sila functional compounds.[13]

By way of such applications, we present here a few preliminary results of the one-pot transformation of certain terminal olefins to the corresponding anti-Markownikoff alcohols via the hydrosilylation-oxidation sequence, as shown by the following examples (eqs 2-4). Isolated yields based on olefins are given.

$$Br(CH_2)_9CH{=}CH_2 \xrightarrow{a,b} Br(CH_2)_{11}OH \quad 73\% \qquad (2)$$

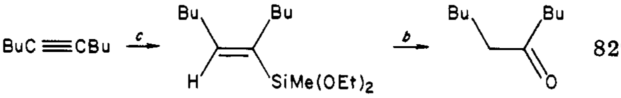
$$MeO_2C(CH_2)_8CH{=}CH_2 \xrightarrow{a,b} MeO_2C(CH_2)_{10}OH \quad 79\% \qquad (3)$$


73% (4)

[a] $HSiMe(OEt)_2$ (1.2 equiv), $RhCl(PPh_3)_3$ (0.5 mol %), 80 °C, 3.5-9 h. [b] 30% H_2O_2 (condition A, see text). [c] $HSiMe(OEt)_2$ (1.2 equiv), $H_2PtCl_6 \cdot 6H_2O$ (0.1 mol %), room temperature, 0.5 h. [d] 30% H_2O_2 (condition C, see text).

The most outstanding feature resides in the simplicity, high regioselectivity, and wide functional group compatibility. First, commercially available, air-stable $HSiMe(OEt)_2$ can be used for the Pt-[14] and Rh-catalyzed[15] hydrosilylation, which proceeds smoothly without solvent under air. Rather, an inert-gas atmosphere should not be employed.[16] This makes the present procedure very simple, in contrast to the existing ones that require special techniques to use air-sensitive metal hydrides.[17] Second, these hydrosilylations introduce a silicon atom, and in turn the hydroxy group, onto the terminal carbon atom exclusively.[18] Third, both the hydrosilylation and the H_2O_2 oxidation are compatible with some functional groups such as halogen, ester, and ketone. Of particular interest is the tolerance of the ketone functionality: none of the hydroboration, hydroalumination, and hydrozirconation reactions are compatible with the ketone group.[17,19] It should be also noted that the isolation of the desired alcohol is quite easy because the byproducts are only water-soluble lower alcohols arising from the other ligands on silicon and inorganic silicic acid derivatives.

Finally, the one-pot procedure is also applicable to the conversion of acetylene to ketone, as shown by eq 5 (see eq 2-4 for conditions). The present method involves the direct conversion of a vinylsilane to the corresponding ketone, not via the traditional epoxidation-acidolysis sequence.[20] Further applications of the present new methodology are currently under investigation.


82%

(5)

Acknowledgment. We thank Shin-etsu Chemical Industrial Co., Ltd., for partial support and a gift of chlorosilanes and Mitsubishi Gas-Chemical Industrial Co., Ltd., for a gift of 90% hydrogen peroxide.

Registry No. n-$C_8H_{17}SiMe(OEt)_2$, 2652-38-2; H_2O_2, 7722-84-1; Ac_2O, 108-24-7; t-BuOOH, 75-91-2; MCPBA, 937-14-4; KF, 7789-23-3; HKF_2, 7789-29-9; $KHCO_3$, 298-14-6; $NaHCO_3$, 144-55-8; K_2CO_3, 584-08-7; n-C_8H_{17}–OH, 111-87-5; n-C_8H_{17}–$Si(OMe)_3$, 3069-40-7; n-C_8H_{17}–$Si(OEt)_3$, 2943-75-1; n-C_8H_{17}–$SiMe_2$(OBu-t), 87261-97-0; n-C_8H_{17}–SiMe(OBu-t)$_2$, 87281-30-9; n-C_8H_{17}–$SiMe_2$(OEt), 87281-31-0; n-C_8H_{17}–$SiMe_2$(OPr-i), 87261-98-1; n-C_8H_{17}–SiMe(OPr-i)$_2$, 87261-99-2; $Br(CH_2)_9CH{=}CH_2$, 7766-50-9; $MeO_2C(CH_2)_8CH{=}CH_2$, 111-81-9; $Br(CH_2)_{11}OH$, 1611-56-9; $MeO_2C(CH_2)_{10}OH$, 24724-07-0; $RhCl(PPh_3)_3$, 14694-95-2; H_2PtCl_6, 16941-12-1; $HSiMe(OEt)_2$, 2031-62-1; *exo*-2-norbornyl–SiMe(OEt)$_2$, 87262-00-8; *endo*-2-norbornyl–SiMe(OEt)$_2$, 87262-01-9; *exo*-norbornanol, 497-37-0; *endo*-norbornanol, 497-36-9; 1-phenyl-4-penten-1-one, 3240-29-7; 5-hydroxy-1-phenyl-1-pentanone, 1011-62-7; dibutylacetylene, 1942-46-7; 5-(5-decenyl)diethoxymethylsilane, 87281-32-1; 5-decanone, 820-29-1.

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[12] We have already developed (i-PrO)$_2$MeSiCH$_2$MgCl as a new nucleophilic hydroxymethylating agent based on the aspects presented here.[1a]

[13] E.g., see: Annual Surveys by Corey, J. Y. *J. Organomet. Chem. Libr.* **1982**, *13*, 1.

[14] Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

[15] Cf.: Chalk, A. J. *J. Organomet. Chem.* **1970**, *21*, 207.

[16] The role of oxygen or hydroperoxide in the $RhCl(PPh_3)_3$-catalyzed hydrosilylation: Kickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308. We have often observed also in the platinum-($H_2PtCl_6 \cdot 6H_2O$) catalyzed hydrosilylation that no reaction starts under an inert-gas atmosphere, but once the reaction mixture is exposed to air for a while, a rapid reaction results. There might be an acceleration effect by oxygen. See also: Harrod, J. F.; Chalk, A. J. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 673-704.

[17] Hydroboration: (a) Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975. Hydroalumination: (b) Sato, F.; Sato, S.; Kodama, H.; Sato, M. *J. Organomet. Chem.* **1977**, *142*, 71.. (c) Isagawa, K.; Tatsumi, K.; Otsuji, Y. *Chem. Lett.* **1977**, 1117. Hydrozirconation: (d) Schwartz J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.

[18] For example, in the hydroboration, appropriate structural modifications are necessary to attain the high regioselectivity.[17a]

[19] Cf.: (a) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1960**, *82*, 681. (b) Brown, H. C.; Karytnyk, W. *Ibid.* **1960**, *82*, 3866.

[20] (a) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080. (b) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *Ibid.* **1977**, *99*, 1993.

Unexpected Rearrangement of the Deprotonation Product of a Thioformic Acid Ester–Hexacarbonyldiiron Complex: Formation of an Exocluster Sulfonium Function†

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Received June 6, 1983

Summary: The carbanion formed by lithium diisopropylamide deprotonation of (μ-SCHSMe)$Fe_2(CO)_6$ undergoes intramolecular nucleophilic attack at iron to give a C–Fe bond with concomitant Fe–S bond cleavage to form a new anion. Alkylation then produces an exocluster sulfonium function. The structure of the alkylation product obtained by reaction with MeI was determined by X-ray crystallography.

In a previous communication[2] we have reported the novel rearrangement of the anion formed by the deprotonation of (μ-CH_2S_2)$Fe_2(CO)_6$, 1 (eq 1). This sequence,

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† Dedicated to Professor Ernst Otto Fischer on the occasion of his 65th birthday on November 10, 1983.

[1] (a) Massachusetts Institute of Technology. (b) University of Alberta. (c) Natural Sciences and Engineering Research Council Postdoctoral Fellow.

[2] Seyferth, D.; Womack, G. B.; Song, L.-C.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 928.

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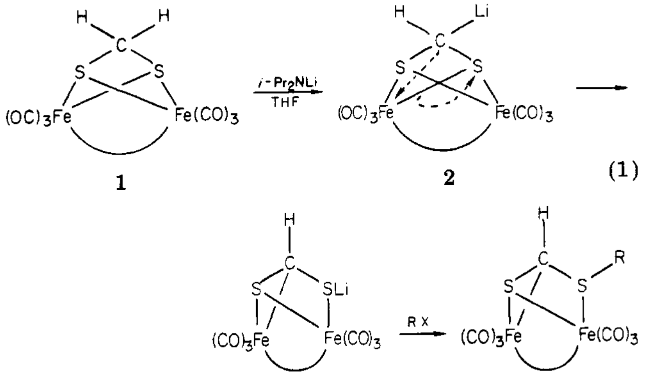
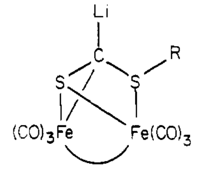
when the electrophile in the last step is varied, represents a general preparation of dithioformic acid ester–hexacarbonyldiiron complexes **4**.



1 **2** (1)

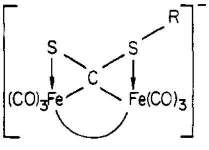
3 **4**

The proton in **4** should be relatively acidic since it is attached to a carbon atom which is bound to two coordinated sulfur atoms. Deprotonation of **4** with lithium diisopropylamide should give **5**, a lithium reagent which



5

might be expected to undergo a rearrangement analogous to that observed with **2**. If intramolecular nucleophilic attack at iron in **5** does take place, then cleavage of an iron–sulfur bond would result. Depending on which Fe–S bond is cleaved, two sulfido anions, **6** or **7** could, in principle, be formed.



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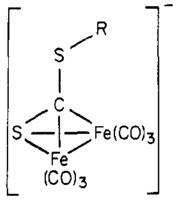
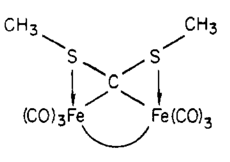
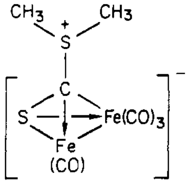


7

In a typical experiment, 1.68 mmol of **4** (R = CH_3), prepared as described previously,[2] in 50 mL of dry tetrahydrofuran (THF) at −78 °C (under nitrogen) was treated with 1.90 mmol of lithium diisopropylamide in 15 mL of THF. The initially red solution of **4** became red-brown. After it had been stirred at −78 °C for 45 min, 16.1 mmol of methyl iodide was added. The reaction mixture was allowed to warm slowly and was stirred at room temperature overnight. Filtration through a pad of silicic acid was followed by evaporation of the filtrate at reduced pressure. The orange solid that remained was purified by column chromatography (silicic acid). Pentane eluted some starting material (11% recovery). Subsequent elution with 1:1 pentane/dichloromethane gave an orange band from which 0.50 g (77% yield) of an air-stable, orange solid, **8**, was isolated.[3] The combustion analysis and the observed molecular ion in the mass spectrum of **8** were in agreement with the $(CH_3)_2S_2CFe_2(CO)_6$ formulation and the S–CH_3 substituents were equivalent in the proton and ^{13}C NMR spectra of **8**. Thus **8** could have either structure **8A** or **8B**. Both structures were without precedent. **8A**



8A



8B

would involve a bridging $(CH_3S)_2C$ carbene ligand, possibly with two S → Fe interactions as shown. **8B** is a sulfur ylide and the negative charge very likely would be delocalized into the $SCFe_2$ cluster. In support of structure **8B**, the electron-impact mass spectrum of **8** showed fragment ions indicative of a Me_2S ligand: 240 ($M^+ - 3CO - Me_2S$), 212 ($M^+ - 4CO - Me_2S$), 184 ($M^+ - 5CO - Me_2S$), and 156 ($CSFe_2^+$).

In other experiments, the anion formed from **4** (R = C_2H_5) also was treated with methyl iodide and that from **4** (R = CH_3) with allyl bromide to give orange, crystalline products of stoichiometry $CH_3(C_2H_5)S_2CFe_2(CO)_6$, mp 73–75 °C, and $CH_3(CH_2{=}CHCH_2)S_2CFe_2(CO)_6$, mp 81–83 °C, respectively. The proton NMR spectrum of the latter showed its allylic protons to be diastereotopic. This would be expected if a $CH_3(CH_2{=}CHCH_2)S^+$ substituent was bonded to a $CSFe_2$ cluster. On the basis of these observations, structure **8B** was favored, but in order to obtain an unambiguous answer to the structural question, a structure determination by X-ray diffraction was undertaken.

$Fe_2(CO)_6(\mu\text{-}\eta^2\text{-}SCSMe_2)$ crystallizes in the space group $P\bar{1}$[4] with $Z = 2$ and cell dimensions $a = 9.585$ (1) Å, $b = 10.276$ (1) Å, $c = 7.601$ (1) Å, $\alpha = 92.18$ (1)°, $\beta = 111.52$ (1)°, $\gamma = 86.94$(1)°, and $V = 695.3$ Å^3. Data were collected on an Enraf-Nonius CAD-4 diffractometer up to $2\theta = 46.0°$ using graphite-monochromated Mo Kα radiation. The structure was solved by Patterson and difference Fourier syntheses and refined by full-matrix least-squares techniques. All hydrogen atoms were located but were not refined; they were input to the least-squares program as fixed contributions in their idealised positions (C–H distances = 0.95 Å). All non-hydrogen atoms were refined anisotropically, and absorption corrections were applied. At the present stage of refinement the conventional crystallographic residuals, R and Rw,[5] are 0.031 and 0.044, respectively, for 2245 unique observed reflections with 172 parameters varied.

The crystal structure determination of the complex unambiguously establishes that methylation has occurred at the alkylated sulfur atom to yield a structure corresponding to **8B** (see Figure 1) and therefore suggests a rearrangement of **5** via the anionic intermediate **7** instead of the alternate route via **6**. The resulting Me_2SCS fragment is bound essentially perpendicular to the Fe–Fe bond and is η^2 coordinated to both iron centers via the "free" C–S end of the ligand to give a quasi-tetrahedral arrangement of the Fe(1), Fe(2), S(2), and C(7) atoms. As can be seen in Figure 1, the molecule possesses almost idealized C_s symmetry in agreement with the ^1H and ^{13}C NMR data; this approximate mirror plane contains the S(1), C(7), and S(2) atoms and bisects the Fe–Fe bond,

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(3) **8**: mp 130 °C dec; IR (CH_2Cl_2) ν(C≡O) 2047 (s), 2003 (s), 1975 (s), 1954 (s), cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (s, SCH_3); ^{13}C NMR (acetone-d_6) δ_C 33.2 (q, J = 144 Hz, SCH_3), 106.7 (s, SCS), 214.0 (s, CO ligands). Anal. Calcd for $C_9H_6O_6S_2Fe_2$: C, 28.01; H, 1.57. Found: C, 28.02; H, 1.67.

(4) The alternate space group $P1$, which would then have two molecules per asymmetric unit, is ruled out owing to the successful refinement of the structure in $P\bar{1}$ with even the methyl hydrogens being located.

(5) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

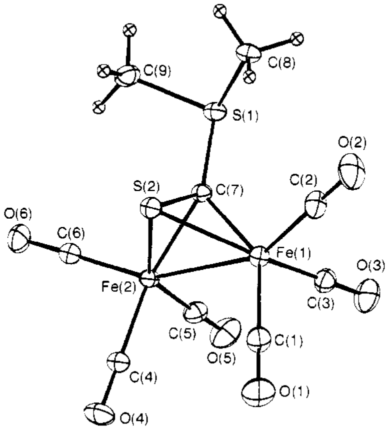

Figure 1. Perspective drawing of (μ-η^2-SCS$(CH_3)_2$)$Fe_2(CO)_6$, 8. Thermal ellipsoids are drawn at the 20% probability level except for hydrogens which are drawn artificially small. Relevant bond parameters are as follows: Fe–Fe = 2.5432 (7) Å, Fe(1)–S(2) = 2.2460 (9) Å, Fe(2)–S(2) = 2.2351 (8) Å, Fe(1)–C(7) = 1.923 (3) Å, Fe(2)–C(7) = 1.921 (3) Å, S(2)–C(7) = 1.734 (3) Å, C(7)–S(1) = 1.730 (3) Å, S(1)–C(Me) = 1.790 Å (mean), Fe–CO = 1.782 Å (mean), C–O = 1.140 Å (mean), S(1)–C(7)–S(2) = 126.9 (2)°.

relating the two tricarbonyliron ends of the complex. All metric parameters are consistent with the observed geometry, and some of the more important of these are given in the figure caption.

Several multinuclear complexes containing the SCX group (X = S, SR, NR, NR_2, OR, etc.) have been structurally characterized[6,7] and are commonly found to exhibit one of two SCX bonding modes; either this group is bound in a side-on manner via the C–S moiety to one metal center[6] or it can bridge the two metals in a cis-dimetalated geometry with the C–S function essentially parallel to the metals and coordinated through sulfur to one metal and through carbon to the other.[7] In these bonding modes the ligands generally function as either two- or three-electron donors depending on the nature of X. The bonding of the $SCSMe_2$ group in the present compound is therefore highly unusual in two important ways; first, in order for the metals to achieve 18-electron configurations, it functions as a six-electron donor and, second, the C–S moiety is bound essentially *perpendicular* to the Fe–Fe bond. This bonding suggests a dipolar ligand formulation as shown in **8B**.

After this structural study was completed, a structurally analogous thioketene complex, $[(C_{10}H_{18}CS)Fe_2(CO)_6]$, was reported by Behrens and co-workers.[8] In this complex the thioketene group is coordinated perpendicular to the Fe–Fe bond through the C–S functionality, much as in our complex. These authors also regard this group as a six-electron donor and formulate an analogous dipolar structure for the ligand.

The present complex $[Fe_2(CO)_6(\mu\text{-}\eta^2\text{-}SCSMe_2)]$, is now only the second known example in which the C–S moiety is bound perpendicular to a metal–metal bond and which functions as a six-electron donor.

Acknowledgment. We are grateful to the National Science Foundation, the Natural Sciences and Engineering Research Council of Canada, and the University of Alberta for support of this work and to Dr. R. G. Ball for X-ray data collection.

Registry No. 4 (R = CH_3), 85534-04-9; 4 (R = C_2H_5), 85534-05-0; 8, 87183-21-9; $CH_3(C_2H_5)S_2CFe_2(CO)6$, 87183-22-0; $CH_3(CH_2{=}CHCH_2)S_2CFe_2(CO)6$, 87183-23-1; Fe, 7439-89-6.

Supplementary Material Available: Tables of positional and thermal parameters, of bond lengths and angles, and of the observed and calculated structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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Radical Trapping by Alkenes as a Route to Organoplatinum(IV) Complexes and as a Test of Mechanism of Oxidative Addition

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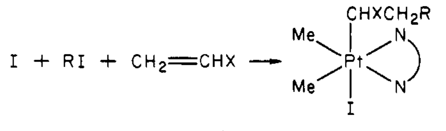
Received August 15, 1983

Summary: Dimethyl(1,10-phenanthroline)platinum(II) reacts with a mixture of RI (R = *i*-Pr or *t*-Bu) and $CH_2{=}CHX$ (X = CN, CHO, C(=O)Me) to give the platinum(IV) complexes $[PtIMe_2(CHXCH_2R)(phen)]$ in good yield. It is shown that the products are formed by a free radical mechanism and that product analysis in such systems can give useful mechanistic data.

Trapping of alkyl radicals by alkenes during oxidative addition has been used as a mechanistic test in several instances, but the method has not been used quantitatively nor has it yielded useful organometallic products.[1] We now report results which show the potential of this trapping procedure for both synthetic and mechanistic applications.

Reaction of $[PtMe_2(1,10\text{-phenanthroline})]$ (I) with *i*-PrI in acetone solution under inert atmosphere gives largely the product of trans oxidative addition $[PtIMe_2(i\text{-Pr})(phen)]$ (II)[2] along with some $[PtI_2Me_2(phen)]$ (III) while the similar reaction of I with *t*-BuI gave only III. In both cases a free radical mechanism was indicated. In the presence of excess of reactive alkenes, new products were formed in high yield according to eq 1 ($\widehat{N\,N}$ = phen).[3,4]



(1)

IVa, X = CN, R = *i*-Pr
b, X = CHO, R = *i*-Pr
c, X = C(=O)Me, R = *i*-Pr
d, X = CN, R = *t*-Bu
e, X = CHO, R = *t*-Bu

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(3) This appears to be the first case in which useful organometallic products have been formed in oxidative addition of a tertiary alkyl halide. Presumably steric effects hinder attack of the *t*-Bu· radical at the metal center. Isolated yields were ~70%.

(4) The reactions were normally carried out in the diffuse daylight. If light was rigorously excluded the reactions occurred much more slowly. The chain reaction (see later) is clearly initiated by a photochemical step, the detailed nature of which is not yet understood.