S-Alkylation of α-Thioether Iron Compounds by $[Ph_3C]^+$ and $[Fe(\eta\text{-}C_5Me_5)(CO)_2(CH_2)]^+$

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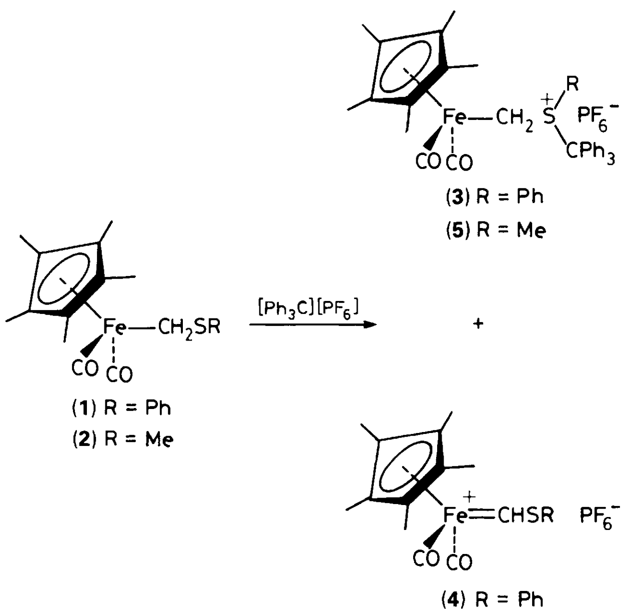
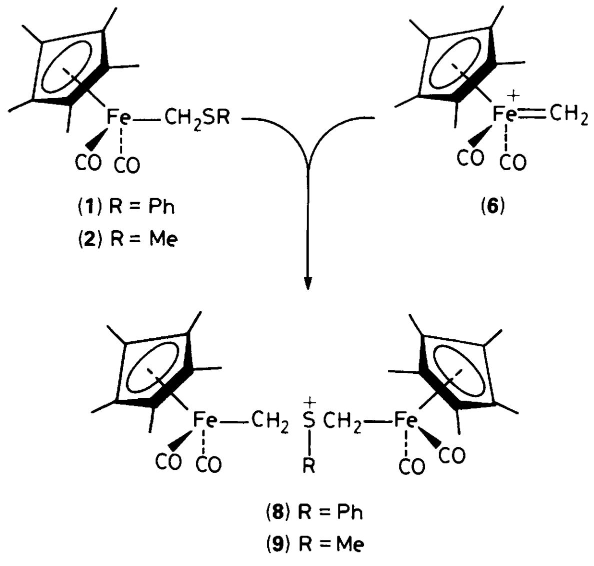
Treatment of the thiomethyl complexes $[Fe(\eta\text{-}C_5Me_5)(CO)_2(CH_2SR)]$ (R = Me or Ph) with $[Ph_3C]^+$ or $[Fe(\eta\text{-}C_5Me_5)(CO)_2(=CH_2)]^+$ results in *S*-alkylation, affording the sulphonium salts $[Fe(\eta\text{-}C_5Me_5)(CO)_2\{CH_2S(R)CPh_3\}]^+$ and $[\{Fe(\eta\text{-}C_5Me_5)(CO)_2CH_2\}_2SR\}]^+$ respectively; the former show promise as agents for methylene transfer to alkenes.

Alkoxy- or alkylthio-alkyl complexes [M–CH(R)ER′; E = O or S] are valuable precursors of carbene complexes.[1] Both the α-hydrogen and the ER′ hetero-group are reactive towards abstracting reagents such as $[Ph_3C]^+$ and, depending on the nature of the ancillary ligands co-ordinated to the metal centre, the reactions have been shown to lead chemospecifically either to the corresponding hetero-substituted carbene complex [M=C(R)ER′] or to the alternative M=CHR species.[1—8] We report here a new pathway for the reaction of thioalkyl complexes with $[Ph_3C]^+$, namely the addition of the latter to sulphur to give sulphonium salts, and the related addition of the methylene complex $[Fe(\eta\text{-}C_5Me_5)(CO)_2(=CH_2)]^+$.

The complexes $[Fe(C_5Me_5)(CO)_2(CH_2SR)]$ [(**1**), R = Ph; (**2**), R = Me]† were prepared in high yield by the reaction of the ferrate $[Fe(C_5Me_5)(CO)_2]^-K^+$ with the appropriate chloromethyl thioether.[9] Treatment of the phenylthiomethyl complex (**1**) with $[Ph_3C][PF_6]$ in dichloromethane leads to the formation in 60:40 ratio of the sulphonium salt $[Fe(C_5Me_5)(CO)_2\{CH_2(SPh)CPh_3\}][PF_6]$ (**3**)† and the phenylthiocarbene complex $[Fe(C_5Me_5)(CO)_2(=CHSPh)][PF_6]$ (**4**) (Scheme 1).† Attempts to separate these products were unsuccessful, but they were readily identified by their characteristic n.m.r. spectra. Monitoring of the reaction by variable temperature n.m.r. spectroscopy revealed that at −40 °C the sulphonium salt (**3**) and the carbene complex (**4**) are produced simultaneously, leading after 3 h at this temperature to the 60:40 mixture, which is retained on warming to room temperature. The concomitant formation of (**3**) and (**4**) indicates that there are two competitive reaction pathways, the $[Ph_3C]^+$ cation acting, unprecedentedly, both as an alkylating agent[10] towards the sulphur atom and as an α-hydride abstractor. This tendency towards $[Ph_3C]^+$ addition, *cf.* alkoxymethyl complexes and $\eta\text{-}C_5H_5$ analogues of the thiomethyl species, can be traced to a combination of the greater stability of sulphonium salts and the increased nucleophilicity of sulphur in the electron-donating $\eta\text{-}C_5Me_5$ system. A still greater tendency is observed for the methylthiomethyl analogue (**2**), which reacts at −80 °C to give only (by n.m.r.) the adduct $[Fe(C_5Me_5)(CO)_2\{CH_2(S\text{-}Me)CPh_3\}][PF_6]$ (**5**),† isolated in 95% yield. Presumably this specificity is a result of an even greater nucleophilicity of sulphur when Ph is replaced by Me.



Scheme 1



Scheme 2

The sulphonium salts (**3**) and (**5**) exhibit excellent methylene transfer[11] properties, indicating that the sulphide group is readily released from its role as a protecting agent for $[Fe(C_5Me_5)(CO)_2(=CH_2)]^+$. Styrene is converted in 80% yield (by g.c.) to phenylcyclopropane upon treatment with (**5**) in refluxing dioxane for 2 hours. The phenyl analogue (**3**) is less effective, giving a 60% yield of the cyclopropane under the same conditions. The full synthetic scope of these reactions is under investigation. The sulphur atoms in (**1**) and (**2**) are also susceptible to electrophilic attack by the methylene ligand in the transient complex $[Fe(C_5Me_5)(CO)_2(=CH_2)]^+$ (**6**). Thus, treatment of a 1:1 mixture of $[Fe(C_5Me_5)(CO)_2(CH_2SR)]$ (**1**) or (**2**) and $[Fe(C_5Me_5)\text{-}$

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† Satisfactory elemental analyses were obtained for compounds (**1**), (**2**), (**5**), (**8**), and (**9**). Selected spectroscopic data: (**1**), ^1H n.m.r. (in C_6D_6): δ 7.48—6.92 (m, 5H, Ph), 2.23 (s, 2H, CH_2), and 1.41 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ n.m.r. (in CD_2Cl_2) δ 218.3 (CO), 146.9 (*ipso* Ph), 128.6 (*ortho* Ph), 124.4 (*meta* Ph), 123.5 (*para* Ph), 96.1 (C_5Me_5), 9.6 ($C_5\mathit{Me}_5$), and 8.5 (CH_2), i.r. (in pentane) 2010, 1957 (s, ν_{CO}) cm^{-1}. (**2**), ^1H n.m.r. (in CD_2Cl_2) δ 2.09 (s, 3H, CH_3), 1.79 (s, 2H, CH_2), and 1.71 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ n.m.r. (in CD_2Cl_2) δ 218.9 (CO), 95.9 (C_5Me_5), 25.4 (CH_3), 16.2 (CH_2), and 9.6 ($C_5\mathit{Me}_5$); i.r. (in pentane) 2000, 1952 (s, ν_{CO}) cm^{-1}. (**3**), ^1H n.m.r. (in CD_2Cl_2); δ 7.59—7.11 (m, Ph and CPh_3), 2.39 (d, 1H, $^2J_{HH}$ 9.8 Hz, CH), 2.31 (d, 1H, $^2J_{HH}$ 9.8 Hz, CH′), and 1.71 (s, 15H, C_5Me_5); ^{13}C n.m.r. (CD_2Cl_2) δ 216.6 (s, CO), 215.9 (s, CO), 147.5 (t, $^2J_{CH}$ 5.5 Hz, *ipso* Ph), 145.1 (t, $^2J_{CH}$ 7.2 Hz, *ipso* $C\mathit{Ph}_3$), 135.6—127.0 (m, Ph and CPh_3), 97.4 (s, C_5Me_5), 82.4 (s, $\mathit{C}Ph_3$), 40.8 (t, $^1J_{CH}$ 153 Hz, CH_2), and 9.6 (q, $^1J_{CH}$ 129 Hz, $C_5\mathit{Me}_5$); i.r. (in CH_2Cl_2) 2000, 1952 (s, ν_{CO}) cm^{-1} (**4**-*cis*, major isomer, 90%); ^1H n.m.r. (in CD_2Cl_2): δ 14.76 (s, ^1H, $C\mathit{H}Ph$), 7.78—7.10 (m, Ph), and 1.95 (s, 15H, C_5Me_5); ^{13}C n.m.r. (in CD_2Cl_2) δ 319.1 (d, $^1J_{CH}$ 151 Hz, $\mathit{C}HPh$), 211.2 (s, CO), 141.0 (br. s, *ipso* Ph), 131.0—126.7 (m, Ph), 104.3 (s, C_5Me_5), and 9.9 (q, $^1J_{CH}$ 129 Hz, $C_5\mathit{Me}_5$); i.r. (in CH_2Cl_2) 2062, 2007 (s, ν_{CO}) cm^{-1}. (**4**-*trans*, minor isomer, 10%); ^1H n.m.r. (in CD_2Cl_2) δ 14.30 (s, 1H, $C\mathit{H}Ph$), 7.78—7.10 (m, Ph), and 1.87 (s, 15H, C_5Me_5); ^{13}C n.m.r. (in CD_2Cl_2): δ 317.0 (d, $^1J_{CH}$ 141 Hz, $\mathit{C}HPh$), 104.5 (s, C_5Me_5), and 9.7 (q, $^1J_{CH}$ 129 Hz, $C_5\mathit{Me}_5$). (**5**), ^1H n.m.r. (in CD_2Cl_2 at −30 °C): δ 7.47 (m, 15H, Ph), 2.22 (s, 3H, CH_3), 1.75 (d, 1H, $^2J_{HH}$ 9.3 Hz, CH), 1.65 (s, 15H, C_5Me_5), and 0.53 (d, 1H, $^2J_{HH}$ 9.3 Hz, CH′); $^{13}C\{^1H\}$ n.m.r. (in CD_2Cl_2): δ 216.8 (CO), 215.6 (CO), 137.0 (br s, *ipso* Ph), 129.7, 129.5, 129.3 (Ph), 97.9 (C_5Me_5), 82.4 ($\mathit{C}Ph_3$), 23.2 (CH_3), 13.2 (CH_2), and 9.4 ($C_5\mathit{Me}_5$); i.r. (KBr, mull) 2005, 1957 (s, ν_{CO}) cm^{-1}. (**8**), ^1H n.m.r. (in CD_2Cl_2): δ 7.60 (m, 5H, Ph), 2.39 (d, 2H, $^2J_{HH}$ 9.7 Hz, CH), 2.29 (d, 2H, $^2J_{HH}$ 9.7 Hz, CH′), and 1.70 (s, 30H, C_5Me_5); ^{13}C n.m.r. (in CD_2Cl_2): δ 216.0 (s, CO), 215.5 (s, CO), 134.6 (d, $^1J_{CH}$ 163 Hz, *para* Ph), 131.4 (d, $^1J_{CH}$ 166 Hz, *ortho* Ph), 131.1 (d, $^1J_{CH}$ 166 Hz, *meta* Ph), 130.0 (s, *ipso* Ph), 97.9 (s, C_5Me_5), 23.3 (t, $^1J_{CH}$ 142 Hz, CH_2), and 9.5 (q, $^1J_{CH}$ 128 Hz, $C_5\mathit{Me}_5$); i.r. (KBr, mull) 1997, 1947 (s, ν_{CO}) cm^{-1}. (**9**), ^1H n.m.r. (in CD_2Cl_2): δ 2.66 (s, 3H, CH_3), 2.16 (d, 2H, $^2J_{HH}$ 9.9 Hz, CH), 1.97 (d, 2H, $^2J_{HH}$ 9.9 Hz, CH′), and 1.78 (s, 30H, C_5Me_5); $^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2): δ 217.3 (CO), 216.9 (CO), 97.7 (C_5Me_5), 32.9 (CH_3), 28.5 (CH_2), and 9.5 ($C_5\mathit{Me}_5$); i.r. (in CH_2Cl_2): 2010, 1952 (s, ν_{CO}) cm^{-1}.

(CO)$_2$(CH$_2$OMe)] (**7**) with one equivalent of $Me_3SiOSO_2CF_3$ [to create (**6**) from (**1**)] affords the binuclear sulphonium salts [{Fe(C$_5$Me$_5$)(CO)$_2$(CH)$_2$}$_2$SR][PF$_6$] [(**8**), R = Ph; (**9**), R = Me]† (Scheme 2). These two species, thermally- and air-stable, are obtained in *ca.* 70% yield, and are novel examples of sulphonium salts disubstituted by first row transition metals. Their formation shows that, despite its great instability,[12] the methylene complex (**6**), when generated under suitable conditions, is an efficient and clean reagent in organometallic syntheses.

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References

1 M. Brookhart and W. B. Studabaker, *Chem. Rev.*, 1987, **87**, 411.

2 M. Brookhart and G. O. Nelson, *J. Am. Chem. Soc.*, 1977, **99**, 6099.

3 A. R. Cutler, *J. Am. Chem. Soc.*, 1979, **101**, 604.

4 T. Bodnar and A. R. Cutler, *J. Organomet. Chem.*, 1981, **213**, C31.

5 A. G. Constable and J. A. Gladysz, *J. Organomet. Chem.*, 1980, **202**, C21.

6 S. E. Kegley, M. Brookhart, and G. R. Husk, *Organometallics*, 1982, **1**, 760.

7 C. Knors, G.-H. Kuo, J. W. Lauher, C. Eigenbrot, and P. Helquist, *Organometallics*, 1987, **6**, 988.

8 V. Guerchais, C. Lapinte, J.-Y. Thépot, and L. Toupet, *Organometallics*, 1988, **7**, 604.

9 C. Roger, M.-J. Tudoret, V. Guerchais, and C. Lapinte, *J. Organomet. Chem.*, 1989, **365**, 347.

10 Alkylation of a vinyl complex by the trityl cation has been reported. G. S. Bodner, D. E. Smith, W. G. Hatton, P. C. Heah, S. Georgiou, A. L. Rheingold, S. J. Geib, J. P. Hutchinson, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1987, **109**, 7688.

11 Alkylidene transfer reactions from sulphonium salts have been described; see E. J. O'Connor, S. Brandt, and P. Helquist, *J. Am. Chem. Soc.*, 1987, **109**, 3739; K. A. M. Kremer and P. Helquist, *J. Organomet. Chem.*, 1985, **285**, 231.

12 V. Guerchais and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1986, 663.