Journal of Organometallic Chemistry, 218 (1981) C57—C61
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

EXPLORATORY ORGANOMETAL-SULFUR CHEMISTRY; SYNTHESES AND UNUSUAL PROPERTIES OF RHENIUM CH_2SR, $CH\overset{+}{S}RR'$, AND $=CHSR]^+$ COMPLEXES

FRED B. McCORMICK and J.A. GLADYSZ**
Department of Chemistry, University of California, Los Angeles, California 90024 (U.S.A.)

(Received June 3rd, 1981)

Summary

The methylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+PF_6^-$ (I) yields kinetically labile sulfonium salts when treated with CH_3SCH_3, $CH_3SCH_2C_6H_5$, and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SCH_3)$ (V); the binuclear adduct formed in the latter case, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)CH_2\}_2S^+CH_3$ (VI), is substantially more stable than the others and undergoes hydride transfer disproportionation to $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHSCH_3)]^+PF_6^-$ (VII) and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (VIII) when heated.

We recently reported the in situ generation [1] and isolation [2] of the first electrophilic methylidene complex, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+PF_6^-$ (I). Catalyst-bound methylidenes have been suggested to play important roles in the synthesis of hydrocarbons from CO/H_2 gas mixtures [3]. Since sulfur poisoning is a ubiquitous problem in catalysis, and mechanisms are generally poorly understood, we have undertaken an exploratory study of the reactions of I and related alkylidenes [5] with organosulfur compounds. In this communication, we report syntheses and representative reactions of a series of compounds containing Re—C—S linkages, including the first bimetallic sulfonium salt, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)CH_2\}_2S^+CH_3PF_6^-$. The presence of the second rhenium in this species dramatically enhances the stability of the ReC—S bonds.

Reaction of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+PF_6^-$ (I, generated in situ in CH_2Cl_2) [1] with CH_3SCH_3 at −78°C gave the sulfonium salt $[(\eta\text{-}C_5H_5)Re(NO)$-

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**Fellow of the Alfred P. Sloan Foundation (1980—1982) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980—1985); after 6/30/82, address correspondence to this author at the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (U.S.A.)

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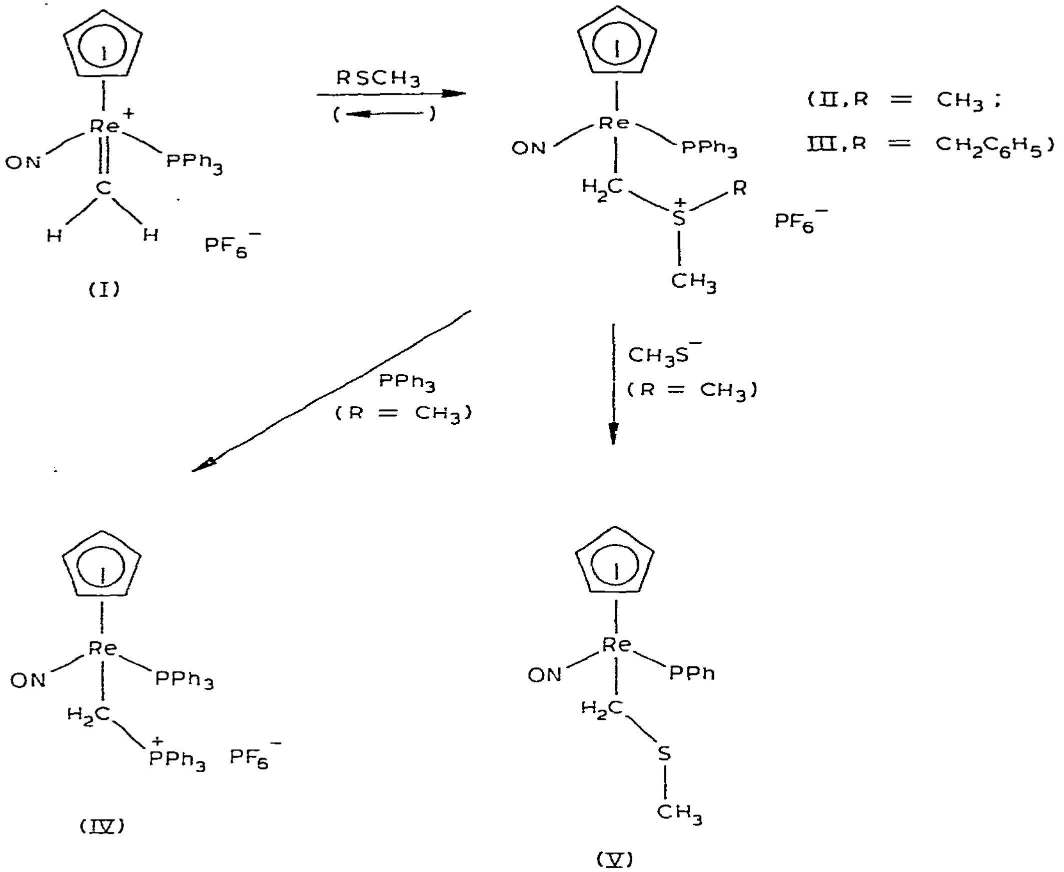
SCHEME 1



(PPh$_3$)CH$_2$S$^+$(CH$_3$)$_2$]PF$_6^-$ (II)* in 90—95% yield after solvent removal and CH$_2$Cl$_2$/hexane recrystallization (Scheme 1). Surprisingly, reaction of I with C$_6$H$_5$CH$_2$SCH$_3$ afforded a much less stable sulfonium salt, [(η-C$_5$H$_5$)Re(NO)-(PPh$_3$)CH$_2$S$^+$(CH$_3$)(CH$_2$C$_6$H$_5$)]PF$_6^-$ (III), which was isolable in crude form but decomposed upon attempted purification. No sulfonium salt could be isolated from the reaction of I with C$_6$H$_5$CH$_2$SCH$_2$C$_6$H$_5$. In these latter two cases, products ultimately obtained were characteristic of the independent decomposition of I [2a,6a]. Ethylidene and benzylidene homologs of I, [(η-C$_5$H$_5$)-Re(NO)(PPh$_3$)(CHR)]$^+$PF$_6^-$ [5], failed to give isolable adducts with CH$_3$SCH$_3$. These data suggested the first step of Scheme 1 to be an equilibrium process, with K_{eq} controlled by the bulk and basicity of the sulfide and the bulk and the electrophilicity of the alkylidene ligand.

The reversibility of sulfonium salt formation was probed by variable temperature ^{1}H NMR and ^{13}C NMR spectroscopy of II. At 27°C in CD$_2$Cl$_2$, only one ^{1}H NMR (200 MHz, δ 2.59 ppm) and one ^{13}C NMR (22.5 MHz,

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*Spectroscopic characterization of new compounds is grouped in the Appendix.

30.1 ppm) resonance were observed for the two diastereotopic methyl groups. Two very broad ^{1}H NMR resonances (δ 4.18 and 3.43 ppm) were observed for the diastereotopic methylene protons. When 1.0 equiv. of CH_3SCH_3 was added to II in CD_2Cl_2, the S-methyl ^{1}H NMR resonances of II and CH_3SCH_3 (δ 2.12 ppm) were replaced by a single absorption at δ 2.35 ppm (12 H). At −40°C, II exhibited two distinct S-methyl ^{13}C NMR resonances (33.9, 27.7 ppm); these coalesced upon warming to 5°C. Low temperature ^{1}H NMR spectra of II showed well defined methylene proton multiplets, but only a single, considerably broadened S-methyl resonance was present at −70°C. These results indicate that the two diastereotopic methyl groups of II are equivalenced by a dissociative mechanism with $\Delta G^{\ddagger}(5°C) \cong 13$ kcal/mol. Considerably higher barriers are found for pyramidal inversion of sulfonium salts [7].

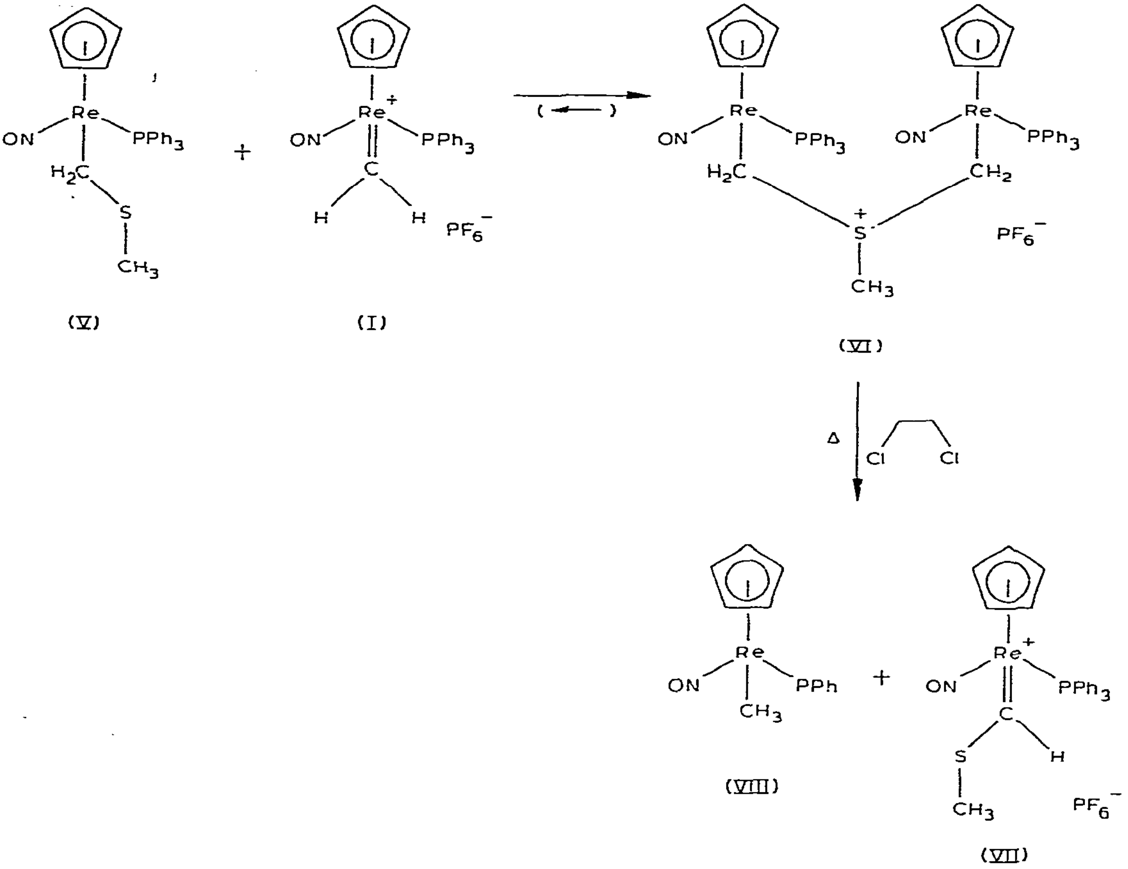
As would be expected from the above observations, nucleophiles were found to effect net displacement of CH_3SCH_3 from II. Thus reaction of II with PPh_3 (CD_3CN, 25°C, 0.5 h) gave the previously reported phosphonium salt $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2{}^+PPh_3)]PF_6^-$ (IV; Scheme 1) [1] in quantitative spectroscopic and 76% isolated yield. Reaction of II with CH_3S^- (THF/CH_3OH, 25°C, 1 h) afforded the methyl thiomethyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SCH_3)$ (V; Scheme 1) in 90—95% yields after solvent removal and recrystallization. Other $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SR)$ complexes have been prepared by this route [6b]. Surprisingly, V could not be cleanly synthesized by the direct reaction of I (generated in situ in CH_2Cl_2) [1] with CH_3S^-; yields varied from fair to zero, and in all cases the major product was the binuclear sulfonium salt $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)CH_2]_2S^+CH_3\,PF_6^-$ (VI). Binuclear complex VI was more conveniently prepared by the alkylation of V with I (89% isolated), as shown in Scheme 2. Both ^{1}H and ^{13}C NMR indicate that VI exists as a ca. 2/1/1 mixture of three diastereomers (two of which are meso) [8].

Additional observations have shown VI to have unusually high thermodynamic stability. For instance, VI did not react with CH_3SCH_3, which implies that conversion to II and V would be energetically uphill. Accordingly, mixture of II and V (CD_3CN, 25°C) resulted in the rapid formation (< 0.25 h) of VI and CH_3SCH_3. Thus V, despite its bulk, binds better to I than CH_3SCH_3.

Although the ReC—S linkage in VI is stronger than in the other sulfonium salts, experiments indicate VI to be in equilibrium with I and V. No deviation from the 2/1/1 equilibrium ratio of diastereomers was observed upon numerous recrystallizations of VI. Addition of PPh_3 to VI rapidly generated ($CDCl_3$, 25°C, < 1 h) V (quantitative by ^{1}H NMR) and IV (90% isolated). Also, when VI was heated in $ClCH_2CH_2Cl$ (83°C, 8 h), methylthiomethylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHSCH_3)]^+PF_6^-$ (VII) and methyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (VIII) [1,2] formed in 82 and 84% isolated yields, respectively (Scheme 2). The former product can be derived by hydride loss from V, and the latter product can be derived by hydride donation to I. Since we have previously shown that I readily abstracts hydride from $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3)$ [1,2], we believe that this observation also reflects the reversibility of the first step of Scheme 2.

The above observations are of particular interest in light of recent work by Helquist [9,10], who has shown the iron complex $[(\eta\text{-}C_5H_5)Fe(CO)_2CH_2S^+(CH_3)_2]$

SCHEME 2



BF_4^- to be an effective reagent for the cyclopropanation of olefins. Our demonstration of CH_3SCH_3 dissociation from II provides explicit precedent for the proposed generation of a highly reactive $[(\eta\text{-}C_5H_5)Fe(CO)_2(CH_2)]^+BF_4^-$ intermediate [11], isolable homologs of which are known to act as cyclopropanating agents [12]. Furthermore, Helquist's observation that $[(\eta\text{-}C_5H_5)\text{-}Fe(CO)_2CH(CH_3)S^+(CH_3)(C_6H_5)]SO_3F^-$ is a much less stable, but considerably more reactive, cyclopropanating agent [10] than $[(\eta\text{-}C_5H_5)Fe(CO)_2CH_2S^+(CH_3)_2$ is consistent with the equilibrium trends noted for the first step of Scheme 1. Unfortunately, the facile dissociation of sulfides from our $[(\eta\text{-}C_5H_5)Re(NO)\text{-}(PPh_3)CH_2S^+RR']$ complexes has thwarted our original objective of studying the stereochemistry of the S-alkylation of V. However, it is significant that sulfur shows a thermodynamic preference for binding to two methylidene carbons; we believe that enhanced basicity of heteroatoms attached to the α-carbon of alkylmetal compounds may be a general phenomenon. We are continuing our study of Re—C—S complexes by the synthesis of new species in which the carbon is in different oxidation states.

Acknowledgement. We are grateful to the Department of Energy for financial support. FT NMR spectrometers utilized were provided by NSF Departmental Instrumentation Grants.

Appendix

(II): ^{1}H NMR (200 MHz, δ (ppm), CD_2Cl_2, 27°C): 7.51—7.32 (m, 15H), 5.28 (s, 5H), 4.18 (br s, 1H), 3.43 (br s, 1H), 2.59 (s, 6H); at −40°C: 7.52—7.30 (m, 15H), 5.26 (s, 5H), 3.87 (br d, $J(^1H—^1H')$ 12.2 Hz, 1H), 3.03 (d of d, $J(^1H'—^1H)$ 12.2 Hz, $J(^1H'—^{31}P)$ 6.8 Hz, 1H); ^{13}C NMR (22.5 MHz, ppm, CD_2Cl_2, 27°C): 91.5 (s), 30.1 (br s), and phenyl carbons; $ReCH_2S$ not observed; at −40°C: 90.8 (s), 34.1 (s). 27. 9 (s), 4.07 (s), and phenyl carbons; IR (cm^{-1}, CH_2Cl_2): $\nu(N{\equiv}O)$ 1657.

(III): ^{1}H NMR (60 MHz, δ (ppm), CD_3CN): 7.50—7.15 (m, 20H), 5.30 (s, 5H), 4.02 (s, 2H), 3.58 (v br s, $ReCH_2$), 2.28 (s, 3H).

(V): ^{1}H NMR (200 MHz, δ (ppm) $CDCl_3$): 7.41—7.26 (m, 15H), 5.05 (s, 5H), 3.30 (d of d, $J(^1H—^1H')$ 10.1 Hz, $J(^1H—^{31}P)$ 7.9 Hz, 1H), 2.93 (d of d, $J(^1H'—^1H)$ 10.1 Hz, $J(^1H'—^{31}P)$ 2.3 Hz), 2.01 (s, 3H); ^{13}C NMR (22.5 MHz, ppm, $CDCl_3$): 89.9 (s), 24.6 (s), −6.1 (s, $ReCH_2$), and phenyl carbons; IR (cm^{-1}, CH_2Cl_2): $\nu(N{\equiv}O)$ 1636.

(VI): ^{1}H NMR (200 MHz, δ (ppm), CD_2Cl_2): 7.47—7.23 (m, 30H), C_5H_5 (ca. 2/1/1, 10H total) at 5.26, 5.22, 5.17, $ReCH_2$ (ca. 0.5/1/0.5/2, 4H total) at 4.13 (d, $J(^1H—^1H)$ 12.8 Hz), 3.81 (d, $J(^1H—^1H)$ 13.1 Hz), 3.51 (d, $J(^1H—^1H)$ 12.8 Hz), 2.97—2.73 (m), and SCH_3 (ca. 1/1, 3H total) at 2.50 (s) and 2.41 (s); ^{13}C NMR (50 MHz, ppm, $CDCl_2CDCl_2$): 91.2, 90.8 (ca. 1/3, C_5H_5), 34.0, 28.0 (ca. 1/1, SCH_3), 12.2, 11.0, 3.9 (ca. 2/1/1, $ReCH_2$); IR (cm^{-1}, CH_2Cl_2): $\nu(N{\equiv}O)$ 1651.

(VII): ^{1}H NMR (200 MHz, δ (ppm), $CDCl_3$): 14.90 (s, 1H), 7.58—7.26 (m, 15H), 5.82 (s, 5H), 2.62 (s, 3H); ^{13}C NMR (22.5 MHz, ppm, $CDCl_3$): 274.4 (s), 96.8 (s), 30.5 (s), and phenyl carbons; IR (cm^{-1}, CH_2Cl_2): $\nu(N{\equiv}O)$ 1717.

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