Metal Complexes of Sulfur-Containing Ligands. Synthesis and Properties of a Series of Rhenium-Substituted Sulfonium Salts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{–})]_nS^+(CH_3)_{3-n}$ (n = 1–3)

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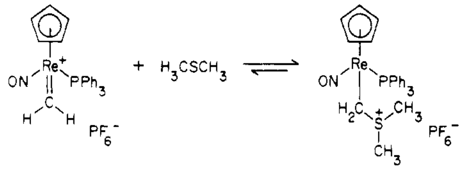
Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**1**, −78 °C) with CH_3SCH_3 gives sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)_2)]^+PF_6^-$ (**2**, 90–95%). Variable-temperature NMR data show that CH_3SCH_3 reversibly gives from **2** with $\Delta G^{\ddagger}_{262}$ = 14.2 kcal/mol and $\Delta G^{\ddagger}_{289}$ = 12.9 kcal/mol. Reaction of **2** with PPh_3 and pyridine give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (**4**, 76%) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\overline{N(CH)_4C}H)]^+PF_6^-$ (**5**), respectively. Reaction of **2** with RS^- gives $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SR)$ (**6**, 79–95%; R = CH_3 (**a**), C_6H_5 (**b**), $CH_2C_6H_5$ (**c**)). Reaction of **1** *or* **2** with **6a** gives binuclear sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{–})]_2S^+CH_3\,PF_6^-$ ($\mathbf{7}^+PF_6^-$, 89–92%) as a 2:1:1 mixture of diastereomers. Treatment of $\mathbf{7}^+PF_6^-$ with NaI/CH_3CN gives $\mathbf{7}^+I^-$, which crystallizes as one diastereomer as shown by X-ray crystallography. Crystal data: orthorhombic, *Pnma*; a = 18.348 (6) Å, b = 20.767 (2) Å, c = 13.944 (2) Å; Z = 4. Reaction of $\mathbf{7}^+PF_6^-$ with PPh_3 gives **4** (90%) and **6a** (71%). Pyrolysis of $\mathbf{7}^+PF_6^-$ (80 °C, 8 h) gives $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**8**, 84%) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHSCH_3)]^+PF_6^-$ (**9**, 82%). Reaction of **1** with Na_2S gives trinuclear sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{–})]_3S^+PF_6^-$ (**10**, 84%). Complex **10** reacts only sluggishly with PPh_3 (65 °C). These reactions show that the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ moiety significantly enhances the basicity of sulfide sulfur atoms that are β to it.

Introduction

The preparation and study of metal complexes of sulfur-containing ligands is of fundamental interest and can also be expected to further understanding of the sulfur poisoning of metal catalysts,[2–5] metal-catalyzed hydrodesulfurization,[3–7] and coal liquefication/gasification chemistry. We have synthesized and extensively examined the physical and chemical properties of rhenium alkylidene complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHR)]^+$.[8] Since coordinated alkylidenes are ubiquitous intermediates in metal-catalyzed reactions,[9] we have undertaken a study of several types of sulfur[10] and other chalcogen[11] derivatives. In this paper, we describe reactions of the methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**1**) with several classes of sulfur nucleophiles. A series of three novel sulfonium salts, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{–})]_nS^+(CH_3)_{3-n}$ (n = 1–3), have been synthesized and their properties and reactivities studied and contrasted. An X-ray crystal structure of the salt with n = 2 is described. A portion of this work has been communicated.[10a]

Results

I. Mononuclear Sulfonium Salts. Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**1**, generated *in situ* in CH_2Cl_2)[8a] with CH_3SCH_3 at −78 °C gave the sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)_2)]^+PF_6^-$ (**2**) in 90–95% yields after workup and recrystallization (eq 1). The structure of this compound followed readily from its spectroscopic properties (Experimental Section). These included two SCH_3 resonances in low-temperature ^1H and ^{13}C NMR spectra, an upfield $ReCH_2S$ ^{13}C NMR resonance (4.1 ppm), and $\eta^5\text{-}C_5H_5$ ^1H (δ 5.25) and ^{13}C (90.8 ppm) NMR resonances. These chemical shifts, and the IR $\nu_{N{\equiv}O}$ at 1657 cm^{-1} (CH_2Cl_2, s), were similar to those found for phosphonium salts derived from the addition of phosphines to **1**.[8a]



(1)

1 2

Reaction of **1** with $C_6H_5CH_2SCH_3$ gave the less stable sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)(CH_2C_6H_5)]^+PF_6^-$ (**3**), which was isolable in crude form but decomposed upon attempted purification. Complex **3** exhibited ^1H NMR properties very similar to **2** (δ, CD_3CN, 60 MHz): 7.50–7.15 (m, $4C_6H_5$), 5.30 (s, C_5H_5), 4.02 (s, $C_6H_5CH_2$), 3.58 (v br s, $ReCH_2S$), 2.28 (s, CH_3). The re-

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[2] (a) Bartholomew, C. H.; Agrawal, P. K.; Katzer, J. R. *Adv. Catal.* **1982**, *31*, 135. (b) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: Orlando, 1984; Chapter 6.

[3] (a) Lesch, D. A.; Richardson, J. W.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569.

[4] (a) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5379. (b) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.

[5] Legzdins, P.; Sânchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525.

[6] Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 3710.

[7] Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6138.

[8] (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *Ibid.* **1982**, *104*, 4865. (c) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *Ibid.* **1983**, *105*, 4958. (d) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *Ibid.* **1983**, *105*, 5804. (e) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *Ibid.* **1983**, *105*, 5811. (f) Kiel, W. A.; Buhro, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879.

[9] See, inter alia: (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983.

[10] (a) McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *218*, C57. (b) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

[11] McCormick, F. B. *Organometallics* **1984**, *3*, 1924.

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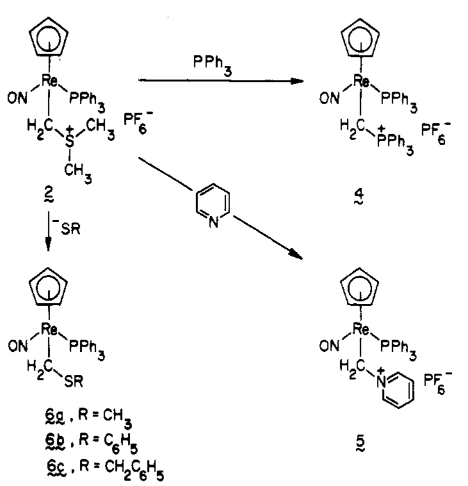
action of 1 with dibenzyl sulfide did not yield a stable sulfonium salt. No evidence for sulfonium salt formation was observed when alkylidene complexes *ac*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHR)]$^+PF_6^-$ (R = C_6H_5, CH_3)[8b,c] were treated with CH_3SCH_3 at room temperature.

The reversibility of eq 1 was probed by variable-temperature ^1H and ^{13}C NMR spectroscopy in CD_2Cl_2. The -41 °C 300-MHz ^1H NMR spectrum of 2 exhibited SCH_3 resonances at δ 2.60 and 2.59 (s). Additional spectra were recorded as the probe temperature was raised in 10 °C increments. At -11 °C, the two SCH_3 resonances coalesced to a broad singlet at δ 2.59. Severe broadening of the two $ReCH_\alpha$ resonances also occurred, and these disappeared into the base line at higher temperatures. From these data, $\Delta G^{\ddagger}_{262}$ = 14.2 kcal/mol was calculated for the process equivalencing the SCH_3 groups.[12] The -27 °C 75-MHz ^{13}C NMR spectrum of 2 exhibited SCH_3 resonances at 34.1 and 28.0 (s) ppm. Additional spectra were recorded as the probe temperature was raised. At 16 °C, the two SCH_3 resonances merged into the base line. At 27 °C, only one SCH_3 resonance was observed (31.0 ppm). From these data, $\Delta G^{\ddagger}_{289}$ = 12.9 kcal/mol was calculated for the process equivalencing the SCH_3 groups.[12]

Since pyramidal inversion barriers in sulfonium salts are generally >25 kcal/mol,[13] a dissociative mechanism was suspected for the above dynamic behavior. Accordingly, when CH_3SCH_3 (1.5 equiv) was added to 2 in CD_2Cl_2 at -37 °C, SCH_3 ^1H NMR resonances (300 MHz) were observed at δ 2.60 (br s, 2, 6 H), and δ 2.06 (s, CH_3SCH_3, 9 H). At or above 12 °C, only a single resonance (δ 2.34) was observed for all 15 SCH_3 protons. At -27 °C, SCH_3 ^{13}C NMR resonances were observed at 17.7 (CH_3SCH_3), 28.0, and 34.1 (2) ppm. At 32 °C, only a single SCH_3 resonance (23.5 ppm) was observed. These data indicate that exchange of the CH_3SCH_3 moiety of 2 with free CH_3SCH_3 is facile.

As would be expected from the above data, nucleophiles readily displaced CH_3SCH_3 from 2. Thus, reaction of 2 with PPh_3 (CH_3CN, 25 °C, 0.5 h) gave the previously reported phosphonium salt [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]$^+PF_6^-$ (4)[8a] in quantitative spectroscopic and 76% isolated yield. In a ^1H NMR monitored experiment, pyridine (1.6 equiv) and 2 reacted (CD_3CN, 25 °C, 0.2 h) to give the previously reported pyridinium salt [(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2\overline{N(CH)_4CH}$)]$^+PF_6^-$ (5)[8a] and CH_3SCH_3. Reaction of 2 with CH_3S^- (THF/CH_3OH, 25 °C, 1 h) gave the (methylthio)methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2SCH_3) (**6a**) in 90-95% yields after workup and recrystallization. Similar reactions of 2 with $C_6H_5S^-$ and $C_6H_5CH_2S^-$ gave (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2SC_6H_5$) (**6b**, 95%) and (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2SCH_2C_6H_5$) (**6c**, 79%), respectively.

II. Polynuclear Sulfonium Salts. Surprisingly, (methylthio)methyl complex **6a** could not be cleanly synthesized by the direct reaction of 1 with CH_3S^-. Yields were at best fair, and in all cases the major product was the binuclear sulfonium salt [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2-)]$_2S^+CH_3PF_6^-$ ($7^+PF_6^-$). Binuclear complex $7^+PF_6^-$ was more conveniently prepared (89-92%, isolated) by reaction of 1 with **6a** as shown in eq 3. Interestingly, $7^+PF_6^-$ was also formed from 1 and CH_3SH (66%, isolated) or CH_3SSCH_3 (51%, isolated). The spectroscopic properties of $7^+PF_6^-$ were similar to those of 2, except that ^1H and ^{13}C NMR showed $7^+PF_6^-$ to exist as a ca. 2:1:1 mixture of three diastereomers. The diastereomer ratio was unaltered by numerous recrystallizations and purification attempts, suggesting eq 3 to be readily reversible. Accordingly, in 70 °C ^1H NMR spectra ($CDCl_2CDCl_2$), $7^+PF_6^-$ exhibited a single broad asymmetric η^5-C_5H_5 resonance.



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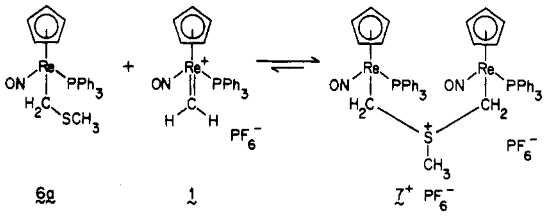
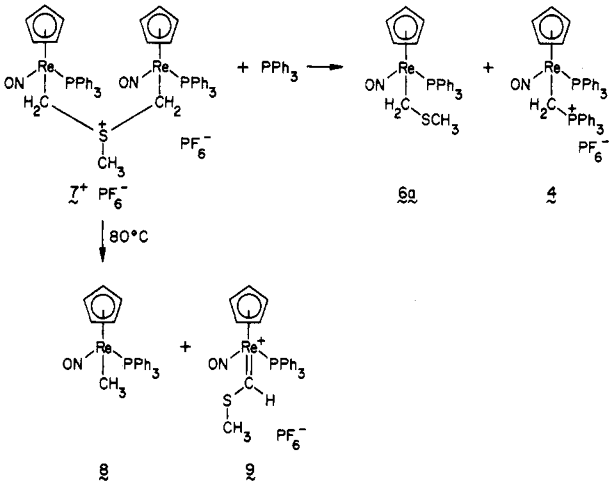


(3)

In a spectroscopically monitored experiment ($CDCl_3$, 25 °C, <1 h), binuclear complex $7^+PF_6^-$ and PPh_3 cleanly reacted to give mononuclear complexes **6a** (71%, isolated) and 4 (90%, isolated), as shown in eq 4. Similarly, addition of excess pyridine to $7^+PF_6^-$ gave **6a** and 5. This reaction, in contrast to that of 2 with pyridine, did not go to completion with only 1.0-2.5 equiv of pyridine. Complex $7^+PF_6^-$ and CH_3SCH_3 did not react, implying that conversion to **6a** and 2 would be energetically uphill. Accordingly, **6a** and 2 cleanly reacted to give $7^+PF_6^-$ and CH_3SCH_3, as shown in eq 5. Reaction of $7^+PF_6^-$ with CH_3S^- gave **6a** (53%, isolated).



(4)

When binuclear complex $7^+PF_6^-$ was heated in $ClCH_2CH_2Cl$ (80 °C, 8 h), methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**8**, 84%, isolated)[8a] and (methylthio)methylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=$CHSCH_3$)]$^+PF_6^-$ (**9**, 82%, isolated) formed as shown in eq

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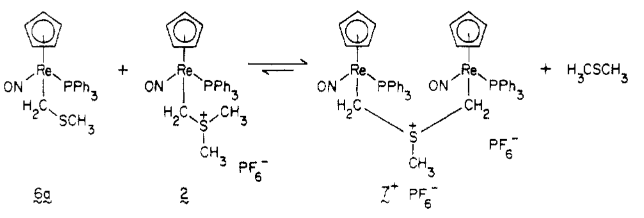
[12] Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

[13] (a) Scartazzini, K.; Mislow, K. *Tetrahedron Lett.* **1967**, 2719. (b) Darwish, D.; Tomilson, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5938. (c) Andersen, K. K.; Cinquini, M.; Papanikolau, N. E. *J. Org. Chem.* **1970**, *35*, 706. (d) Anderson, K. K. In *The Chemistry of the Sulphonium Group*; Striling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; Part 1, pp 255-258.



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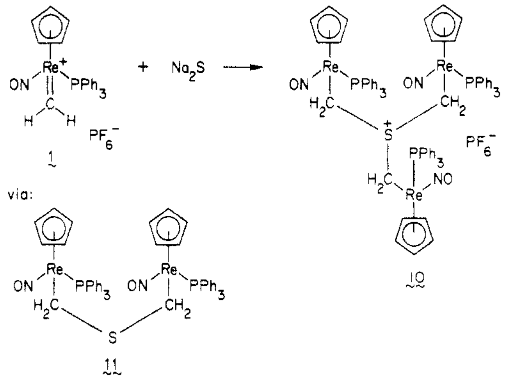
4. Complex **9** can be derived from hydride loss from **6a**, and complex **8** can be derived from hydride attack upon **1**.

When a CH_3CN solution of $7^+PF_6^-$ was treated with NaI, 7^+I^- slowly crystallized as a CH_3CN solvate. Unsolvated 7^+I^- was obtained in 61% yield by subsequent crystallization from acetone/hexanes. Crystals of $7^+I^-\cdot(CH_3CN)_2$ that were suitable for X-ray analysis were grown from warm CH_3CN, and X-ray data were collected under the conditions summarized in Table I.

The unit cell was found to be orthorhombic, with the lattice parameters listed in Table I. Refinement, described in the Experimental Section, yielded the structure shown in Figure 1 for the cationic portion of $7^+I^-\cdot(CH_3CN)_2$. A Newman-type projection is given in Figure 2, and stereoscopic views are included in the supplementary material. Positional parameters, bond distances, and bond angles are given in Tables II, III, and IV, respectively.

Figure 1 shows that $7^+I^-\cdot(CH_3CN)_2$ crystallizes as one of two possible meso diastereomers. A mirror plane passes through C25, S, I, and the two CH_3CN solvate molecules. This requires opposite configurations at the two rhenium atoms. The following torsion angles were calculated: P-Re-C24-S, 166.7°; N1-Re-C24-S, 73.4°; Re-C24′-S-C24, 179.2°. These are conveniently viewed in Figure 2. Additional torsion angles are given in the supplementary material.

Reaction of **1** (generated in situ in CH_2Cl_2) with Na_2S in CH_3OH gave, after workup and recrystallization, the novel trinuclear sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{-})]_3S^+PF_6^-$ (**10**, 84%, isolated), as shown in eq 6. Complex **10** exhibited spectroscopic properties similar to those of **2** and $7^+PF_6^-$ and was, by all criteria, a single diastereomer. In contrast to **2** and $7^+PF_6^-$, **10** reacted only sluggishly with PPh_3 (65 °C, CH_3CN, 0.5 h; >50% of **10** remaining) to yield the phosphonium salt **4** and an unidentified $\eta^5\text{-}C_5H_5$-containing product.



(6)

Table I. Summary of Crystallographic Data for $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{-})]_2S^+CH_3I^-\bullet(CH_3CN)_2$ ($7^+I^-\bullet(CH_3CN)_2$)

formula	$C_{49}H_{47}IN_2O_2P_2Re_2S\cdot 2CH_3CN$
fw	1371.35
cryst system	orthorhombic
space group	*Pnma*
cell dimens (23 °C)	
a, Å	18.348 (6)
b, Å	20.767 (2)
c, Å	13.944 (2)
V, Å^3	5313.1 (3.0)
Z	4
d_{calcd}, g cm^{-3}	1.71
cryst dimens, mm	0.21 × 0.12 × 0.09
radiatn, Å	Mo Kα (λ = 0.71069)
temp of collectn, °C	23
data collectn method	ω-2θ
scan rate, deg min^{-1}	1-20 (variable)
reflectns measd	*h* (0-21), *k* (0-23), *l* (0-15)
scan range, deg	1.0 + 0.350 tan θ
max 2θ, deg	48.0
no. of reflectns between stds	97
total unique data	4133
obsd data, $I > 3\sigma(I)$	2747
no. of variables	333
abs coeff (μ), cm^{-1}	53.3
min transmissn	0.685
av transmissn	0.778
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.038
$R_w = [\sum w_i(\|F_o\| - \|F_c\|)^2/\sum w_i\|F_o\|^2]^{1/2}$	0.052
goodness of fit	1.71
largest shift/error in final cycle	0.15

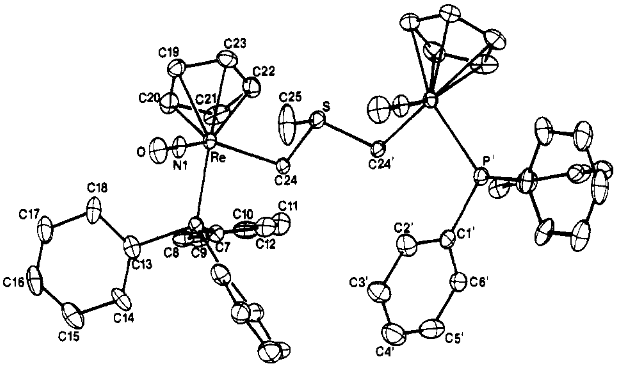


Figure 1. Structure and atomic numbering of the cationic portion of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{-})]_2S^+CH_3I^-\cdot(CH_3CN)_2$ ($7^+I^-\cdot(CH_3CN)_2$). Primed and unprimed atoms are on opposite sides of the symmetry plane.

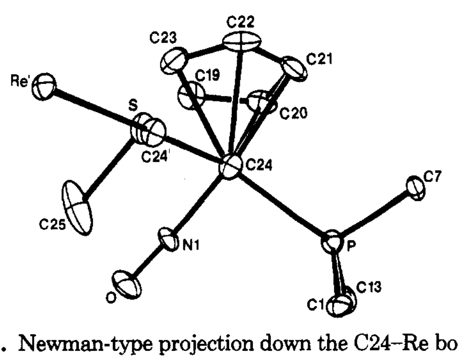


Figure 2. Newman-type projection down the C24-Re bond vector in $7^+I^-\cdot(CH_3CN)_2$.

Discussion

Sulfonium salts that are substituted with a transition metal at an α-carbon, $L_nMCHRS^+R'R''$, are often referred to as sulfur ylide complexes.[14] Previously, most sulfur ylide complexes have been prepared by displacement of an existing ligand by a free sulfur ylide.[14] However, related phosphorus and nitrogen complexes are often synthesized from the corresponding alkylidene complex $L_nM{=}CHR$ (or a precursor) and heteroatom nucleophile.[8a,c,15-17]

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[14] Weber, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 516.

[15] Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

[16] Nakazawa, H.; Johnson, D. L.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1846.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms in $7^+I^- \bullet (CH_3CN)_2$ and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Re	0.37909 (2)	0.91001 (2)	0.44441 (2)	3.028 (7)
I	0.14482 (6)	0.750	0.45288 (7)	4.97 (2)
S	0.3785 (2)	0.750	0.4471 (2)	3.92 (7)
P	0.3430 (1)	0.9566 (1)	0.2978 (2)	3.35 (5)
O	0.5355 (3)	0.9067 (3)	0.3958 (6)	5.7 (2)
N1	0.4725 (4)	0.9083 (3)	0.4135 (6)	3.3 (2)
N2[b]	0.354 (1)	0.750	0.784 (1)	10.4 (6)
N3[b]	0.653 (1)	0.750	0.511 (2)	25 (2)
C1	0.3571 (5)	0.9099 (4)	0.1909 (6)	3.6 (2)
C2	0.4247 (6)	0.8830 (5)	0.1740 (7)	5.0 (2)
C3	0.4416 (6)	0.8486 (6)	0.0936 (8)	5.6 (3)
C4	0.3857 (7)	0.8386 (6)	0.0272 (8)	7.1 (3)
C5	0.3183 (7)	0.8629 (8)	0.0411 (7)	7.2 (4)
C6	0.3047 (7)	0.8969 (5)	0.1219 (8)	5.4 (3)
C7	0.2461 (4)	0.9764 (4)	0.3007 (6)	3.5 (2)
C8	0.2206 (5)	1.0380 (5)	0.3075 (6)	4.3 (2)
C9	0.1482 (6)	1.0507 (5)	0.3239 (7)	5.3 (2)
C10	0.1016 (5)	1.0020 (7)	0.3343 (8)	6.6 (3)
C11	0.1224 (5)	0.9368 (6)	0.327 (1)	6.2 (3)
C12	0.1953 (5)	0.9244 (5)	0.3096 (8)	5.0 (3)
C13	0.3873 (5)	1.0335 (4)	0.2638 (7)	4.2 (2)
C14	0.3915 (6)	1.0529 (5)	0.1700 (8)	5.5 (3)
C15	0.4223 (7)	1.1093 (5)	0.1455 (9)	7.1 (3)
C16	0.4504 (7)	1.1493 (5)	0.215 (1)	7.6 (3)
C17	0.4479 (7)	1.1315 (5)	0.308 (1)	7.2 (3)
C18	0.4166 (6)	1.0723 (5)	0.3347 (9)	5.8 (3)
C19	0.3864 (5)	0.9492 (5)	0.5935 (7)	4.7 (2)
C20	0.3373 (6)	0.9877 (5)	0.5469 (7)	5.1 (2)
C21	0.2783 (5)	0.9470 (7)	0.5269 (7)	6.5 (3)
C22	0.2927 (6)	0.8867 (5)	0.5618 (7)	5.6 (3)
C23	0.3623 (6)	0.8850 (5)	0.6008 (7)	5.2 (3)
C24	0.3465 (5)	0.8189 (4)	0.3801 (6)	3.4 (2)
C25	0.4744 (9)	0.750	0.416 (2)	9.5 (6)
C27[b]	0.2177 (9)	0.750	0.748 (2)	10.1 (7)
C28[b]	0.293 (1)	0.750	0.770 (1)	7.5 (5)
C29[b]	0.667 (1)	0.750	0.329 (2)	11.6 (8)
C30[b]	0.661 (1)	0.750	0.433 (2)	15 (1)

[a] Defined as $(^4/_3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] The solvate atoms are C27–C28–N2 and C29–C30–N3; other atoms are numbered as in Figure 1.

Table III. Bond Distances (Å) in $7^+I^- \bullet (CH_3CN)_2$ with Estimated Standard Deviations in Parentheses

Re–N1	1.767 (6)	C7–C8	1.366 (10)
Re–P	2.357 (2)	C7–C12	1.431 (10)
Re–C19	2.237 (8)	C8–C9	1.374 (11)
Re–C20	2.287 (8)	C9–C10	1.333 (14)
Re–C21	2.309 (8)	C10–C11	1.410 (15)
Re–C22	2.330 (8)	C11–C12	1.386 (11)
Re–C23	2.263 (8)	C13–C14	1.372 (11)
Re–Cp[a]	1.955	C13–C18	1.384 (12)
Re–C24	2.178 (6)	C14–C15	1.345 (12)
S–C24	1.807 (7)	C15–C16	1.38 (2)
S–C25	1.813 (15)	C16–C17	1.346 (14)
N1–O	1.182 (7)	C17–C18	1.406 (12)
P–C1	1.796 (7)	C19–C20	1.369 (12)
P–C7	1.826 (7)	C19–C23	1.409 (13)
P–C13	1.855 (8)	C20–C21	1.400 (13)
C1–C2	1.379 (11)	C21–C22	1.368 (14)
C1–C6	1.388 (11)	C22–C23	1.388 (13)
C2–C3	1.366 (12)	N2–C28[b]	1.13 (2)
C3–C4	1.397 (14)	C27–C28[b]	1.43 (2)
C4–C5	1.349 (14)	N3–C30[b]	1.08 (3)
C5–C6	1.352 (13)	C29–C30[b]	1.46 (3)

[a] Distance from Re to the η^5-C_5H_5 plane. [b] Solvate atoms; other atoms are numbers as in Figure 1.

Table IV. Bond Angles (deg) in $7^+I^- \bullet (CH_3CN)_2$ with Estimated Standard Deviations in Parentheses

P–Re–N1	94.0 (2)	C24–S–C25	101.0 (5)
P–Re–C19	132.4 (3)	P–C1–C2	119.4 (6)
P–Re–C20	99.1 (2)	P–C1–C6	125.4 (6)
P–Re–C21	94.1 (3)	C2–C1–C6	115.2 (7)
P–Re–C22	120.2 (3)	C1–C2–C3	123.8 (8)
P–Re–C23	153.1 (3)	C2–C3–C4	117.1 (9)
P–Re–C24	85.5 (2)	C3–C4–C5	121.4 (9)
N1–Re–C19	100.1 (3)	C4–C5–C6	119.0 (9)
N1–Re–C20	119.5 (3)	C1–C6–C5	123.4 (9)
N1–Re–C21	154.8 (3)	P–C7–C8	123.0 (6)
N1–Re–C22	145.8 (4)	P–C7–C12	117.7 (6)
N1–Re–C23	111.3 (3)	C8–C7–C12	118.6 (7)
N1–Re–C24	98.5 (3)	C7–C8–C9	121.4 (8)
C19–Re–C20	35.2 (3)	C8–C9–C10	119.6 (9)
C19–Re–C21	57.6 (3)	C9–C10–C11	123.2 (8)
C19–Re–C22	57.5 (3)	C10–C11–C12	116.9 (8)
C19–Re–C23	36.5 (3)	C7–C12–C11	120.2 (8)
C19–Re–C24	135.7 (3)	P–C13–C14	121.4 (7)
C20–Re–C21	35.5 (4)	P–C13–C18	119.4 (6)
C20–Re–C22	58.6 (3)	C14–C13–C18	119.2 (8)
C20–Re–C23	60.9 (3)	C13–C14–C15	121 (1)
C20–Re–C24	141.1 (3)	C14–C15–C16	120 (1)
C21–Re–C22	34.3 (4)	C15–C16–C17	119.8 (8)
C21–Re–C23	59.1 (3)	C16–C17–C18	121 (1)
C21–Re–C24	105.9 (4)	C13–C18–C17	118.5 (9)
C22–Re–C23	35.1 (3)	C20–C19–C23	112.3 (8)
C22–Re–C24	85.6 (3)	C19–C20–C21	104.5 (9)
C23–Re–C24	99.2 (3)	C20–C21–C22	109.4 (8)
Re–N1–O	177.9 (6)	C21–C22–C23	109.9 (8)
C1–P–C7	106.3 (4)	C19–C23–C22	103.7 (8)
C1–P–C13	100.9 (4)	Re–C24–S	112.7 (3)
C7–P–C13	103.8 (3)	N2–C28–C27[a]	177 (2)
C24–S–C24′	104.7 (5)	N3–C30–C29[a]	177 (2)

[a] Solvate atoms; other atoms are numbered as in Figure 1.

Equation 1 is, to our knowledge, the only sulfur ylide complex synthesis from an isolable or detectable alkylidene complex. Sulfur ylide complexes have also been prepared by direct or assisted (Ag^+, Tl^+) displacement of halides in halomethyl complexes L_nMCH_2X by sulfides[14,18] and by alkylation of α-(alkylthio)alkyl complexes $L_nMCHRSR'$.[19-21]

The addition of phosphine and amine nucleophiles to alkylidene complexes is an equilibrium process. Several studies have shown that the principal factors influencing K_{eq} are nucleophile basicity, alkylidene complex Lewis acidity, and steric effects.[22] The reaction of methylidene complex **1** and CH_3SCH_3 to give sulfonium salt **2** is clearly reversible, as indicated by the NMR properties of **2** and further suggested by the facile nucleophilic displacement of CH_3SCH_3 from **2** (eq 2). Several K_{eq} trends are evident in our chemistry. First, organic sulfides bulkier than CH_3SCH_3 fail to give stable adducts with **1**. Second, bulkier and less Lewis acidic alkylidene complexes *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHR)]^+PF_6^-$ fail to react with CH_3SCH_3.

However, one K_{eq} trend is to our knowledge without precedent. Equation 5 shows that the basicity of bulky organometallic sulfide **6a** toward **1** is greater than that of CH_3SCH_3! Note also that pyridine (1.6 equiv) completely

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(17) Fischer, H.; Weber, L. *Chem. Ber.* **1984**, *117*, 3340.

(18) (a) Werner, H.; Paul, W.; Feser, R.; Zalk, R.; Thometzek, P. *Chem. Ber.* **1985**, *118*, 261. (b) Bodnar, T. W.; Cutler, A. R. *Organometallics* **1985**, *4*, 1558. (c) Barefield, E. K.; McCarten, P.; Hillhouse, M. C. *Ibid.* **1985**, *4*, 1682.

(19) (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473. (b) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *Ibid.* **1981**, *103*, 1862. (c) O'Connor, E. J.; Helquist, P. *Ibid.* **1982**, *104*, 1869. (d) Kremer, K. A. M. Ph.D. Thesis, SUNY Stony Brook, 1982. (e) O'Connor, E. J. Jr. Ph.D. Thesis, SUNY Stony Brook, 1984.

(20) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.

(21) Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Organometallics* **1985**, *4*, 1178.

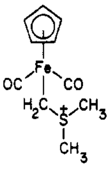
(22) (a) Fischer, H.; Fischer, E. O.; Kreiter, C. G.; Werner, H. *Chem. Ber.* **1974**, *107*, 2459. (b) Fischer, H. *J. Organomet. Chem.* **1979**, *170*, 309. (c) Choi, H. S.; Sweigart, D. A. *Ibid.* **1982**, *228*, 249.

displaces CH_3SCH_3 from **2**, but not **6a** from $\mathbf{7^+}PF_6^-$. Therefore, K_{eq} for eq 3 must be greater than that for eq 1. This suggests that some electronic effect confers enhanced basicity upon the sulfide sulfur atom in **6a**. It is well-known that C_γ of transition-metal allyl complexes, $L_nMCH_2CH{=}CH_2$, is rendered exceptionally nucleophilic via hyperconjugation of the olefin π cloud with the M–C σ bond.[23] We suggest that a similar interaction provides enhanced basicity to heteroatoms with lone electron pairs that are β to transition metals.[23c]

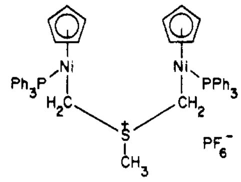
Although K_{eq} for eq 3 is greater than that for eq 1, several observations suggest that eq 3 is readily reversible. First, no deviation from the ca. 2:1:1 mixture of $\mathbf{7^+}PF_6^-$ diastereomers is observed under a variety of recrystallization conditions. Second, the η^5-C_5H_5 ^1H NMR resonances of these diastereomers begin to coalesce at elevated temperatures. Third, PPh_3 converts $\mathbf{7^+}PF_6^-$ to a 1:1 mixture of **6a** and **4** (eq 4). Finally, we have previously reported that methoxymethyl complex $(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3)$ readily transfers an α-hydride to methylidene complex **1** at −78 °C to give methyl complex **8** and methoxymethylidene complex $[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)({=}CHOCH_3)]^+PF_6^-$.[8a] The formation of **8** and (methylthio)methylidene complex **9** from the thermal decomposition of $\mathbf{7^+}PF_6^-$ (eq 4) suggests initial dissociation to (methylthio)methyl complex **6a** and methylidene complex **1**, followed by an analogous hydride transfer. Surprisingly, thiocarbene complexes of the formula $L_nM{=}CHSR$, such as **9**, are relatively uncommon.[20,24]

Although we have not yet been able to cleanly synthesize thioether complex $[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(CH_2{-})]_2S$ (**11**, eq 6), we suggest that the sulfide sulfur in this compound would be even more basic than that in **6a**. As evidence, we note the facile formation of trinuclear sulfonium salt **10** in eq 6. Furthermore, we could not effect any well-defined carbon–sulfur bond cleavage reactions of **10** under conditions where **2** or $\mathbf{7^+}PF_6^-$ would have reacted rapidly. This suggests that K_{eq} for the last step of eq 6 (**11** + **1** → **10**) is larger than that for eq 3. Trinuclear complex **10** is, to our knowledge, the only known example of a α,α',α''-tris-metalated sulfonium salt.

The above data are particularly relevant to recent studies of Helquist and co-workers.[19] They have reported syntheses of the iron sulfonium salts $[(\eta^5$-$C_5H_5)Fe(CO)_2CH_2S(CH_3)_2]^+BF_4^-$ ($\mathbf{12^+}BF_4^-$) and $[(\eta^5$-$C_5H_5)Fe(CO)_2CH_2S(CH_3)_2]^+FSO_3^-$ ($\mathbf{12^+}FSO_3^-$) and an X-ray crystal structure of the latter.[19c,e] They have also shown these compounds to be effective reagents for the cyclopropanation of olefins.[19] Our demonstration of CH_3SCH_3 dissociation from the analogous rhenium complex **2** provides explicit precedent for the proposed equilibrium of $\mathbf{12^+}$ with the highly reactive methylidene complex $[(\eta^5$-$C_5H_5)Fe(CO)_2({=}CH_2)]^+$,[25] isolable analogues of which are known to act as cyclopropanating agents.[26] Helquist and co-workers have also found sulfonium salt $[(\eta^5$-$C_5H_5)Fe(CO)_2CH_2S(CH_3)(C_6H_5)]^+FSO_3^-$, which is an adduct of the bulkier sulfide $CH_3SC_6H_5$ with $[(\eta^5$-$C_5H_5)Fe(CO)_2({=}CH_2)]^+$, to be a much more reactive but less stable cyclopropanating agent than $\mathbf{12^+}$.[19e] Similar observations were made with $[(\eta^5$-$C_5H_5)Fe(CO)_2CH(CH_3)S(CH_3)(C_6H_5)]^+FSO_3^-$, which is a $CH_3SC_6H_5$ adduct of an *ethylidene* complex.[19b,d] These trends are consistent with our K_{eq} data, as sulfide dissociation from these complexes should be more facile than sulfide dissociation from $\mathbf{12^+}$.



$\mathbf{12^+}$



13

A close relative of $\mathbf{7^+}PF_6^-$, binuclear nickel sulfonium salt $[(\eta^5$-$C_5H_5)Ni(PPh_3)(CH_2{-})]_2S^+CH_3\,PF_6^-$ (**13**), has recently been synthesized and structurally characterized by Barefield and co-workers.[21] This complex is a byproduct of the synthesis of mononuclear sulfonium salt $[(\eta^5$-$C_5H_5)Ni(PPh_3)(CH_2S(CH_3)_2)]^+$ from $(\eta^5$-$C_5H_5)Ni(PPh_3)(Cl)$ and $(CH_3)_2S^+CH_2^-$. It was proposed to form via deprotonation of the mononuclear sulfonium salt by $(CH_3)_2S^+CH_2^-$, followed by reaction with additional $(\eta^5$-$C_5H_5)Ni(PPh_3)(Cl)$. Complexes $\mathbf{12^+}FSO_3^-$ and **13** provide valuable structural reference points for $\mathbf{7^+}I^-\cdot(CH_3CN)_2$.

Complex $\mathbf{7^+}I^-\cdot(CH_3CN)_2$ exhibits bond lengths and angles within the $(\eta^5$-$C_5H_5)Re(NO)(PPh_3)$ moiety that are very similar to those found in crystal structures of neutral $(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(X)$ compounds.[8b,27] The sulfonium sulfur is distinctly pyramidal with C–S bond lengths of 1.807 (7), 1.807 (7), and 1.813 (15) Å and C–S–C bond angles (101.0 (5)°, 101.0 (5)°, and 104.7 (5)°) totaling 306.7°. These bond lengths and angles are within experimental error of those found in nickel sulfonium salt **13**.[21] Iron sulfonium salt $\mathbf{12^+}{}^-OSO_2F$ also exhibits very similar C–S bond lengths (1.786 (3), 1.788 (3), and 1.784 (3) Å) and C–S–C bond angles (101.0 (2), 102.2 (2), and 104.9 (2)°).[19c] In typical organic sulfonium salts, C–S bond lengths of 1.78–1.84 Å and C–S–C bond angles of 100–108° are found.[28]

The $M{-}CH_2{-}S$ bond angles in $\mathbf{7^+}I^-\cdot(CH_3CN)_2$, $\mathbf{12^+}FSO_3^-$, and **13** are also quite close (112.7 (3)°, 115.5 (2)°, and 113.6 (7)°). The Re–C_α bond in $\mathbf{7^+}I^-\cdot(CH_3CN)_2$ (2.178 (6) Å) appears slighly shortened from the Re–C_α bonds found in alkyl complexes (−)-(*R*)-$(\eta^5$-$C_kH_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (2.203 (8) Å)[27b] and (*SS*,*RR*)-$(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(CH(CH_2C_6H_5)C_6H_5)$ (2.215 (4) Å).[8a] It is considerably longer than the Re=C double bond in *ac*-$[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$ (1.949 (6) Å).[8b] A similar, slighly shortened Fe–C_α bond was noted in $\mathbf{12^+}FSO_3^-$ and was ascribed to the inductive effect of the sulfonium group and/or a slight contribution by an alkylidene-like resonance form.[19c,e]

Figure 2 shows that the sulfur atom and the second rhenium moiety occupy the sterically least congested site between the small NO and medium-sized η^5-C_5H_5 ligands. The conformation about the C24′–S bond is such that the S–C24 and Re′–C24′ bonds are nearly perfectly antiperiplanar (torsion angle = 179.2°). A similar C_α–Fe Newman

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(23) (a) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K. S.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rusan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. (b) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *Ibid.* **1971**, *93*, 5715. (c) A reviewer has insightfully remarked that since methylidene complex **1** is certainly a poorer Lewis acid than "CH_3^+", the sulfide sulfur of **6a** should logically be more basic than that of CH_3SCH_3.

(24) (a) Battioni, J. P.; Chottard, J. C.; Mansuy, D. *Inorg. Chem.* **1982**, *21*, [illegible]. (b) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1018.

(25) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Nelson, G. O.; Brookhart, M. *Ibid.* **1977**, *99*, 6099.

(26) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *Ibid.* **1982**, *104*, 6119. (c) Casey, C. P.; Miles, W. H.; Tukada, H. *Ibid.* **1985**, *107*, 2924.

(27) (a) Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530. (b) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204. (c) Smith, D. E.; Gladysz, J. A. *Organometallics* **1985**, *4*, 1480.

(28) Perozzi, E. F.; Paul, I. C. In *The Chemistry of the Sulfonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; Part 1, pp 15–77.

projection of $\mathbf{12}^+FSO_3^-$ generated from published atomic coordinates shows a sulfonium ligand orientation essentially identical with that of $\mathbf{7}^+I^-\cdot(CH_3CN)_2$. Consistent with the above reactivity data, molecular models indicate that it should be possible to accommodate only one bulky substituent on sulfur. This, however, does not account for the exceptional stability of **10**. Molecular models show **10** to be very sterically crowded, but this can be relieved somewhat by making the sulfur center more planar. Unfortunately, X-ray quality crystals of this unique complex could not be obtained.

Summary and Relevance to Catalysis. We have developed efficient syntheses of three novel sulfonium salts (**2**, $\mathbf{7}^+X^-$, **10**) of increasing metal nuclearity and contrasted their reactivity. Prior to this study, binuclear and trinuclear complexes of this type were unknown. The $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ substituents exhibit a cumulative stabilizing effect on the sulfonium salts—i.e., the C_α–S bond becomes increasingly difficult to break. This can be attributed to enhanced basicity of sulfide sulfur atoms that are β to $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$.

We propose that this β-basicity enhancement should be general for other transition metals and other heteroatoms. As a consequence, it is tempting to speculate that there may be a cooperative effect in the poisoning of metal catalysts by sulfur- and other heteroatom-containing compounds. Each metal bound to the catalyst poison could make the heteroatom more basic and better able to bind another metal or a ligand of another metal.

Experimental Section

General Data. All reactions were conducted with anhydrous, deoxygenated solvents under a nitrogen atmosphere, unless noted. All reagents were obtained from common commercial suppliers and were used as received.

All NMR spectra were obtained on modern FT spectrometers (80–300 MHz) at ambient probe temperature (unless noted) and were referenced to $(CH_3)_4Si$. IR spectra were recorded on Perkin-Elmer Model 521 or 1500 (FT) spectrometers. Mass spectra were obtained on AEI MS-9 or VG Micromass 7070 spectrometers. Melting points were not corrected. Microanalyses were conducted by Galbraith, Schwarzkopf, and 3M analytical laboratories.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)_2)]^+PF_6^-$ (2). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$[8a] (0.50 g, 0.89 mmol), CH_2Cl_2 (75 mL), and a stir bar and was cooled to −78 °C. Then $Ph_3C^+PF_6^-$ (0.40 g, 10.0 mmol) was added, and the reaction was stirred for 1 h. Then CH_3SCH_3 (100 μL, 1.35 mmol) was added, and the reaction was stirred at −78 °C (15 min) and then allowed to warm to room temperature (ca. 0.5 h). The resulting yellow solution was concentrated under high vacuum to ca. 5 mL. Then hexane (50 mL) was added, and a yellow power precipitated which was collected by filtration and washed with hexanes. Diffusion crystallization of the powder from CH_2Cl_2/hexanes at −20 °C gave **2** (0.64 g, 0.84 mmol, 94%) as yellow plates, mp 123–125 °C dec. Anal. Calcd for $C_{26}H_{28}F_6NOP_2ReS$: C, 40.84; H, 3.69; N, 1.83. Found: C, 41.3; H, 3.8; N, 1.8. ^{1}H NMR (δ, CD_2Cl_2, 27 °C, 200 MHz): 7.51–7.32 (m, PPh_3), 5.28 (s, C_5H_5), 4.18 (v br s, ReCH), 3.43 (v br s, ReCH′), 2.59 (s, $2SCH_3$). ^{1}H NMR (δ, CD_2Cl_2, −41 °C, 300 MHz): 7.50–7.26 (m, PPh_3), 5.21 (s, C_5H_5), 3.81 (br d, J_{HH} = 12.4 Hz, ReCH), 2.97 (dd, J_{HH} = 12.4 Hz, J_{HP} = 7.3 Hz, ReCH′), 2.60 (s, SCH_3), 2.59 (s, SCH_3'). ^{13}C NMR (ppm, CD_2Cl_2, −40 °C, 22.5 MHz): PPh_3 at 133.0 (d, J_{CP} = 54.9, ipso), 132.8 (d, J_{CP} = 9.7), 130.6 (s, p), 128.5 (d, J_{CP} = 9.7 Hz); 90.8 (s, C_5H_5), 34.1 (s, SCH_3), 27.9 (s, $SC'H_3$), 4.1 (br s, $ReCH_2S$). IR (cm^{-1}, CH_2Cl_2): $\nu_{N=O}$ 1657 s.

Reaction of 2 with PPh_3. A 5-mm NMR tube was charged with **2** (0.0115 g, 0.015 mmol) and CD_3CN (600 μL) and was capped with a septum. A ^{1}H NMR spectrum was recorded. Then PPh_3 (0.008 g, 0.031 mmol) was added, and the tube was shaken. After 30 min, a second ^{1}H NMR spectrum was recorded. Complex **2** had been completely converted to $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (**4**, δ 4.68).[8a] The reaction was washed from the tube with a minimum of CH_2Cl_2 and cooled to −20 °C. Ether was allowed to slowly vapor diffuse into the mixture. Orange crystals of **4** formed and were isolated by filtration (0.011 g, 0.011 mmol, 76%).

Reaction of 2 with Pyridine. A 5-mm NMR tube was charged with **2** (0.006 g, 0.0078 mmol) and CD_3CN (400 μL) and was capped with a septum. A ^{1}H NMR spectrum was recorded. Then pyridine (1.0 μL, 0.012 mmol) was added, and the tube was shaken. After 10 min a second ^{1}H NMR spectrum was recorded. Complex **2** had been completely converted to $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\overline{N(CH)_4C}H)]^+PF_6^-$ (**5**, δ 5.17).[8a]

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SCH_3)$ (6a). A Schlenk flask was charged with THF (50 mL), NaH (50% mineral oil dispersion, 0.06 g, 1.25 mmol), and a stir bar. Then excess CH_3SH gas was bubbled through the mixture. The reaction was stirred for 45 min to give a cloudy white suspension. Methanol (2 mL) was added to give a clear, colorless solution. Then **2** (0.30 g, 0.39 mmol) was added, and the reaction was stirred for 2 h. Solvent was removed from the resulting red-orange homogeneous solution by rotary evaporation. this gave an orange solid which was extracted with CH_2Cl_2, leaving a tan insoluble precipitate. Solvent was removed from the extract under a stream of N_2 gas. The resulting orange tar was extracted with ether. The extract was concentrated by slow evaporation and cooled to −20 °C to give orange crystals of **6a** (0.23 g, 0.38 mmol, 97%), mp 190–192 °C dec. Anal. Calcd for $C_{25}H_{25}NOPReS$: C, 49.66; H, 4.17; N, 2.29; S, 5.26; P, 5.15. Found: C, 49.52; H, 4.17; N, 2.32; S, 5.30; P, 5.12. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 7.41–7.26 (m, PPh_3), 5.05 (s, C_5H_5), 3.30 (dd, J_{HH} = 10.1 Hz, J_{HP} = 7.9 Hz, ReCH), 2.93 (dd, J_{HH} = 10.1 Hz, J_{HP} = 2.3 Hz, ReCH′), 2.01 (s, CH_3). ^{13}C NMR (ppm, $CDCl_3$, 22.5 MHz): PPh_3 at 135.4 (d, J_{CP} = 52.5 Hz, ipso), 133.0 (d, J_{CP} = 9.7 Hz), 129.7 (s, p), 127.9 (d, J_{CP} = 9.8 Hz); 89.8 (s, C_5H_5), 24.6 (s, SCH_3), −6.1 (br s, $ReCH_2S$). IR (cm^{-1} CH_2Cl_2): $\nu_{N\equiv O}$ 1636 s.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SC_6H_5)$ (6b). A Schlenk flask was charged with THF (25 mL), NaH (0.035 g, 1.46 mmol), and a stir bar. The suspension was stirred, and C_6H_5SH (380 μL, 0.408 g, 3.71 mmol) was added via syringe. Gas evolution occurred, and a white slurry was obtained. After 30 min, **2** (0.093 g, 0.122 mmol) was added. A pale yellow solution with a suspended white solid resulted. The reaction was stirred overnight and turned deep yellow. Solvent was removed under oil pump vacuum, and the yellow residue was extracted with CH_2Cl_2. The extract was passed through a plug of silica gel. Solvent was removed from the filtrate by rotary evaporation to give an orange powder. The powder was crystallized from CH_2Cl_2/hexanes to give orange plates of $\mathbf{6b}\cdot(CH_2Cl_2)_{0.25}$ (two crops, 0.072 g, 0.105 mol, 86%), mp 191.5–193 °C dec. Anal. Calcd for $C_{30}H_{27}NOPReS\cdot(CH_2Cl_2)_{0.25}$: C, 52.81; H, 4.03; Cl, 2.58. Found: C, 52.98; H, 4.14; Cl, 2.63. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.48–7.41 (m, PPh_3), 7.18–6.95 (m, CC_6H_5), 5.29 (CH_2Cl_2 solvate), 4.95 (s, C_5H_5) 3.57 (dd, J_{HH} = 9.3 Hz, J_{HP} = 7.9 Hz, ReCH), 3.06 (dd, J_{HH} = 9.3 Hz, J_{HP} = 2.2 Hz, ReCH′). ^{13}C NMR (ppm, $CDCl_3$, 75 MHz): PPh_3 at 136.0 (d, J_{CP} = 53.0 Hz, ipso), 133.9 (d, J_{CP} = 10.1 Hz), 130.6 (s, p), 129.0 (d, J_{CP} = 10.0 Hz); SC_6H_5 at 148.8 (s, ipso), 128.5 (s), 125.1 (s), 123.5 (s); 90.5 (s, C_5H_5), −12.1 (d, J_{CP} = 2.8 Hz, $ReCH_2S$). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$, 32 MHz): 23.43 (s). IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1631 s.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SCH_2C_6H_5)$ (6c). A Schlenk flask was charged with THF (30 mL), NaH (0.038 g, 1.58 mmol), and a stir bar. The suspension was stirred, and $C_6H_5CH_2SH$ (390 μL, 0.413 g, 3.33 mmol) was added via syringe. Gas evolution occurred, and a white slurry was obtained. After 30 min, **2** (0.111 g, 0.145 mmol) was added. A pale yellow solution with a suspended white solid resulted. The reaction was stirred overnight and turned orange. Solvent was then removed under oil pump vacuum, and the orange residue was extracted with CH_2Cl_2. The extract was passed through a plug of silica gel, and solvent was removed from the filtrate by rotary evaporation. The resulting solid was recrystallized from ethyl acetate/hexanes to give orange prisms of **6c** (two crops, 0.077 g, 0.113 mmol, 77%), mp 174–175.5 °C dec. Anal. Calcd for $C_{31}H_{29}NOPSRe$: C, 54.69; H, 4.29. Found: C, 54.57; H, 4.12. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.12–7.44 (m, $4C_6H_5$), 4.99 (s, C_5H_5), 3.55 (d, J_{HH} = 13.0 Hz, C_6H_5CH), 3.47 (d, J_{HH} = 13.0 Hz, C_6H_5CH'), 3.22 (dd, J_{HH} = 9.8 Hz, J_{HP} = 7.8 Hz, ReCH), 2.72 (dd, J_{HH} = 9.8 Hz, J_{HP} = 2.6 Hz, ReCH′). ^{13}C NMR (ppm, $CDCl_3$, 75 MHz): PPh_3 at 136.2 (d, J_{CP} = 53.0 Hz, ipso), 133.9 (d, J_{CP} = 11.0 Hz), 130.5 (s, p), 128.7 (d, J = 10.0 Hz); CC_6H_5 at 140.5 (s, ipso), 129.3 (s), 128.3 (s), 126.2 (s); 90.5 (s, C_5H_5), 45.7 (s, $C_6H_5CH_2$), −9.7 (d, J_{CP} = 4.2 Hz, $ReCH_2S$). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$, 32 MHz): 23.63 (s). IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1627 s.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{-})]_2S^+CH_3PF_6^-$ ($7^+PF_6^-$). **A.** A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.0924 g, 0.1654 mmol), CH_2Cl_2 (40 mL), and a stir bar and was cooled to −78 °C. Then $Ph_3C^+PF_6^-$ (0.065 g, 0.162 mmol) was added, and the reaction was stirred for 1 h. Then **6a** (0.100 g, 0.165 mmol) was added, and the reaction was stirred at −78 °C (1.5 h) and then allowed to warm to room temperature (1 h). Solvent was removed from the orange-yellow solution by rotary evaporation. The resulting mustard yellow powder was diffusion crystallized from acetone/hexanes at −20 °C to give $7^+PF_6^-$ (0.193 g, 0.178 mmol, 89%) as orange needles, mp 150–151 °C. **B.** A Schlenk flask was charged with **6a** (0.38 g, 0.64 mmol), CH_2Cl_2 (50 mL), and a stir bar. Then **2** (0.50 g, 0.65 mmol) was added, and the reaction was stirred for 1 h. Solvent was removed from the resulting yellow orange solution by rotary evaporation. This gave an orange tar which was washed with hexanes. The resulting orange solid was diffusion recrystallized from CH_2Cl_2/hexanes at −20 °C to give $7^+PF_6^-\cdot(CH_2Cl_2)_{0.5}$ (0.79 g, 0.59 mmol, 92%) as yellow-orange needles. Anal. Calcd for $C_{49}H_{47}F_6N_2O_2P_3Re_2S\cdot(CH_2Cl_2)_{0.5}$: C, 44.05: H, 3.58; N, 2.08; P, 6.88; S, 2.38. Found: C, 43.77; H, 3.64; N, 2.01; P, 6.84; S, 2.37. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 7.47–7.23 (m, PPh_3); C_5H_5 at 5.26, 5.22, 5.17 (s, 2:1:1); ReCH at 4.13, 3.81, 3.51 (br d, 1:2:1 J_{HH} = 12.8, 13.1, 12.8 Hz); ReCH′ at 2.97–2.73 (m); SCH_3 at 2.50, 2.41 (s, 1:1). ^{13}C NMR (ppm, $CDCl_2CDCl_2$, 50 MHz): PPh_3 carbons at 134.5–128.7; C_5H_5 at 91.2, 90.8 (s, 1:3); SCH_3 at 34.0, 28.0 (s, 1:1), $ReCH_2S$ at 12.2, 11.0, 3.9 (s, 2:1:1). IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1651 s.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{-})]_2S^+CH_3I^-$ (7^+I^-). Complex $7^+PF_6^-$ (0.043 g, 0.033 mmol) was disssolved in CH_3CN (4 mL) without precautions to exclude air. Then NaI (0.20 g, 1.33 mmol) in CH_3CN (1 mL) was added, and the resulting orange solution was kept at room temperature for 72 h. Orange crystals gradually precipitated and were collected by filtration. Diffusion recrystallization from acetone/hexanes at room temperature gave 7^+I^- (0.026 g, 0.020 mmol, 61%) as irregular orange crystals, mp 248–251 °C dec. Anal. Calcd for $C_{49}H_{47}IN_2O_2P_2Re_2S$: C, 45.65; H, 3.67; N, 2.17. Found: C, 45.3; H, 3.8, N, 2.0. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1657 s.

Reaction of $7^+PF_6^-$ with PPh_3. A 5-mm NMR tube was charged with $7^+PF_6^-$ (0.0128 g, 0.0098 mmol) and $CDCl_3$ (600 μL) and was capped with a septum. A ^{1}H NMR spectrum was recorded. Then PPh_3 (0.005 g, 0.019 mmol) was added, and the tube was shaken. After 1 h, a second ^{1}H NMR spectrum was recorded which showed $7^+PF_6^-$ to be consumed and a 1:1 mixture of **4** (δ 4.70) and **6a** (δ 5.05). Solvent was evaporated under a N_2 stream to give a yellow tar. The tar was extracted with ether to give a yellow solution and a bright yellow insoluble solid. The solid was diffusion crystallized from CH_2Cl_2/ether at −20 °C to give **4** (0.0085 g, 0.009 mmol, 90%) as orange needles. The ether extracts were concentrated to an orange tar, which was dissolved in hexanes and filtered. The filtrate was concentrated to ca. 1 mL under a N_2 stream. This was cooled to −20 °C, and orange crystals of **6a** (0.0042 g, 0.007 mmol, 71%) were collected.

Reaction of $7^+PF_6^-$ with Pyridine. A 5-mm NMR tube was charged with $7^+PF_6^-$ (0.0127 g, 0.0097 mmol) and $CDCl_3$ (600 μL) and was capped with a septum. A ^{1}H NMR spectrum was recorded. Then pyridine (2 μL, 0.025 mmol) was added, and the tube was shaken. After 45 min, a second ^{1}H NMR spectrum was recorded with showed $7^+PF_6^-$ to be ca. 50% consumed, and **5** (δ 5.03, 50% of theory) and **6a** (δ 5.07, 50% of theory). A third ^{1}H NMR spectrum was recorded after another 24 h and was unchanged from the second. Then additional pyridine (4 μL, 0.050 mmol) was added, and the remaining $7^+PF_6^-$ was converted to **5** and **6a**. The reaction was concentrated to a yellow oil under a N_2 stream. The oil was washed with ether to give a yellow powder. Subsequent ^{1}H NMR analysis of the powder and washes showed $7^+PF_6^-$ to be the only $\eta^5\text{-}C_5H_5$-containing material.

Reaction of $7^+PF_6^-$ with CH_3SNa. A Schlenk flask was charged with THF (50 mL), NaH (50% mineral oil dispersion, 0.10 g, 2.08 mmol), and a stir bar. Then excess CH_3SH gas was bubbled through this mixture (30 min). Methanol (2 mL; dried over $CaSO_4$ and N_2 purged) was added to give a clear colorless solution. Then $7^+PF_6^-$ (0.293 g, 0.224 mmol) was added, and the reaction was stirred for 3.5 h. The resulting cloudy orange soution was filtered. Solvent was removed from the filtrate by rotary evaporation, giving an orange oil. The oil was extracted with ether, giving an orange solution and a tan-insoluble precipitate. The ether extract was evaporated to an oil which was chromatographed on a short silica gel column using 4:1 (v/v) hexanes/ethyl acetate. The slow moving orange band was collected. Solvent removal under a N_2 stream gave **6a** (0.143 g, 0.242 mmol, 53%) as an orange microcrystalline powder.

Pyrolysis of $7^+PF_6^-$. Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHSCH_3)]^+PF_6^-$ (9). A solution of $7^+PF_6^-$ (0.091 g, 0.070 mmol) in 1,2-dichloroethane (20 mL) was refluxed (ca. 80 °C) for 12 h. Solvent was removed from the dark yellow-brown solution by rotary evaporation. The resulting dark tar was dissolved in a minimum of CH_2Cl_2 and was filtered. Hexane was carefully added to the filtrate such that two layers formed. These were allowed to diffuse together at −20 °C. A dark tar containing yellow needles separated from an orange supernatant. The latter was decanted, and the solvent was removed by rotary evaporation. This gave an orange powder which was dissolved in benzene and filtered through a ca. 0.2-g plug of silica gel. The filtrate was concentrated to ca. 2 mL. Slow diffusion of heptane into this solution gave bright orange crystals (0.033 g, 0.059 mmol, 84%) of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**8**). The tar and yellow needles were dissolved in CH_2Cl_2 and filtered through a ca. 0.2-g plug of silica gel, which removed a dark impurity. Solvent was removed from the yellow filtrate by rotary evaporation. The resulting yellow powder was diffusion crystallized from CH_2Cl_2/hexanes at −20 °C to give $\mathbf{9}\cdot(CH_2Cl_2)_{0.5}$ (0.045 g, 0.057 mmol, 82%) as yellow needles, mp 179–181 °C dec. Anal. Calcd for $C_{25}H_{24}F_6NOP_2ReS\cdot(CH_2Cl_2)_{0.5}$: C, 38.71; H, 3.19; N, 1.77; P, 7.83; S, 4.05. Found: C, 38.64; H, 3.16; N, 1.70; P, 7.83; S, 3.95. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 14.9 (br s, Re=CH), 7.58–7.26 (m, PPh_3), 5.82 (s, C_5H_5), 2.62 (s, CH_3). ^{13}C NMR (ppm, $CDCl_3$, 22.5 MHz): 274.4 (s, Re=C); PPh_3 at 132.9 (d, J_{CP} = 9.8 Hz), 131.8 (s, p), 129.1 (d, J_{CP} = 9.8 Hz), 129.0 (d, J_{CP} = 50.7 Hz, ipso); 96.8 (s, C_5H_5), 30.5 (s, CH_3). IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1717 s.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{-})]_3S^+PF_6^-$ (10). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.05 g, 0.089 mmol), CH_2Cl_2 (15 mL), and a stir bar and was cooled to −78 °C. Then $Ph_3C^+PF_6^-$ (0.04 g, 0.10 mmol) was added, and the reaction was stirred for 1 h. Then anhydrous Na_2S (0.01 g, 0.13 mmol) was added, followed by CH_3OH (10 mL; dried over $CaSO_4$ and N_2 purged). The resulting light tan solution was allowed to gradually warm to room temperature (ca. 1 h). The resulting bright lemon yellow solution was filtered. Solvent was removed from the filtrate by rotary evaporation. The resulting yellow solid was washed with hexanes and extracted with CH_2Cl_2. The extract was separated from a white insoluble material by filtration, and solvent was removed by rotary evaporation. Diffusion crystallization of the residue using 80:20 (v/v) $CHCl_3/CH_2Cl_2$ and heptane at −20 °C gave **10** (0.046 g, 0.025 mmol, 84%) as brittle yellow needles, mp 178–180 °C dec. Anal. Calcd for $C_{72}H_{66}F_6N_3O_3P_4Re_3S$: C, 46.75; H, 3.60; N, 2.27; S, 1.73. Found: C, 46.8; H, 3.7; N, 2.2; S, 2.2. ^{1}H NMR (δ, CD_2Cl_2, 90 MHz): 7.1–7.3 (m, PPh_3), 5.19 (s, C_5H_5), 4.06 (br d, J_{HH} = 12.7 Hz, ReCH), 2.58 (dd, J_{HH} = 12.7 Hz, J_{HP} = 7.6 Hz, ReCH′). ^{13}C NMR (ppm, CD_2Cl_2, 22.5 MHz): PPh_3 at 134.6 (d, J_{CP} = 53.7 Hz, ipso), 133.6 (d, J_{CP} = 9.8 Hz), 130.9 (s, p), 128.9 (d, J_{CP} = 11.0 Hz); 91.6 (s, C_5H_5), 10.1 (s, $ReCH_2S$). IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1653 s.

X-ray Crystal Structure of $7^+I^-\cdot(CH_3CN)_2$. Complex 7^+I^- was dissolved in a minimum of hot CH_3CN. The saturated solution was allowed to cool to room temperature and was left undisturbed for several days. The resulting orange prisims were solvated and began to lose the solvate within several hours after separation from the mother liquor. An orange crystal was removed from the mother liquor and immediately mounted in a sealed glass capillary for data collection. The crystal was found to be orthorhombic by the Enraf-Nonius CAD4 SDP peak search, centering, and indexing programs and by a Delauney reduction calculation.[29] Unit-cell measurements were made and refined for 25 reflections in the range $10 < \theta < 15°$. The crystal and intensity measurement parameters obtained are summarized in Table I. Background counts were measured at both ends of the scan range with the use of a ω–2θ scan, equal at each side to one-fourth of the scan range of the peak. As a check on crystal stability, three check reflections were monitored and these showed significant decay (7.5%). Therefore, a linear decay correction was applied.

Lorentz and polarization corrections were applied.[29] An empirical absorption correction based on a series of ψ scans was applied to the data.[30] Relative transmission coefficients ranged from 0.685 to 0.882 with an average value of 0.778.

The structure was solved by the Patterson heavy-atom method which revealed the position of the rhenium atom. The remaining non-hydrogen atoms and the two molecules of acetonitrile were located in succeeding difference Fourier syntheses. Positions of hydrogens on the phenyl and cyclopentadienyl rings were calculated and added to the structure factor calculations, but their positions were not refined. Because the software used handled a maximum of seven scattering factor tables, the hydrogen atoms were included as $^1/_6$ occupancy carbons with fixed B values of 5.0. The four highest peaks in the final difference map (0.7–1.0 e/Å^3) were in the vicinity of the rhenium atom (ca. 1.2 Å). The values of the atomic scattering factors were taken from the usual tabulation, and the effects of anomalous dispersion were included.[31] The R factors for the final refinement were $R = 0.038$ and $R_w = 0.052$.[32]

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Registry No. 2, 80136-84-1; 4, 71763-25-2; 5, 71763-30-9; 6a, 80136-87-4; 6b, 102920-58-1; 6c, 102920-59-2; $7^+PF_6^-$, 80136-89-6; 7^+I^-, 102920-60-5; $7^+I^-\cdot(CH_3CN)_2$, 102920-61-6; 8, 71763-18-3; 9, 80136-91-0; 10, 102940-14-7; $Ph_3C^+PF_6^-$, 437-17-2; CH_3SCH_3, 75-18-3; CH_3SH, 74-93-1; C_6H_5SH, 108-98-5; $C_6H_5CH_2SH$, 100-53-8.

Supplementary Material Available: Stereoscopic views of and tables of crystallographic data (temperature factors and torsion angles) for $7^+I^-\cdot(CH_3CN)_2$ (7 pages); a table of structure factors for $7^+I^-\cdot(CH_3CN)_2$ (9 pages). Ordering information is given on any current masthead page.

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(29) The intensity data were processed as described in *CAD4 and SDP Users Manual*; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/\text{NPI})(C - 2B)$, where $K = 20.17 \times$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in net intensity is given by $\sigma^2(I) = (K/\text{NPI})[C + 4B + (pI)]$ where p is a factor used to downweight intense reflections.

(30) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallog., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968,** *A24,* 351.

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A, 2.2C, and 2.3.1.

(32) The function minimized is $\sum w_i||F_o| - |F_c||^2$ where $w = 1/\sigma^2(F_o)$. The weighted and unweighted residuals are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$.

Cationic Molybdenum(IV)- and Tungsten(IV)-Iridium(III) Complexes with Hydride and η^5:η^1-Cyclopentadienyl Bridging Ligands. Syntheses and X-ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4))IrH(PMePh_2)_2][BPh_4]$ (M = Mo and W)

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Cations of the type $[IrH_2(\text{solvent})_2L_2]^+$ (1; L = tertiary phosphine) react readily with the hydrido complexes $[MH_2(\eta^5\text{-}C_5H_5)_2]$ (M = W (3) and M = Mo (4)) to afford the dihydrido η^5:η^1-cyclopentadienyl-bridged complexes $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}H)_2(\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4))IrHL_2]^+$ (6, M = W, and 7, M = Mo). The structures of complex cations 6 and 7 in solutions were unambiguously established by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The X-ray crystal structures of the $[BPh_4]^-$ salts of cations 6c and 7c (L = $PMePh_2$) were determined. The two compounds are isomorphous and belong to space group Cc; unit-cell dimensions: a = 10.736 (1) Å, b = 18.872 (2) Å, c = 26.060 (2) Å, β = 101.43 (1)°, V = 5175 (1) Å^3, and Z = 4 for [6c][BPh$_4$] and a = 10.724 (2) Å, b = 18.834 (2) Å, c = 26.091 (3) Å, β = 101.44 (3)°, V = 5165 (2) Å^3, and Z = 4 for [7c][BPh$_4$]. The structures were refined to R = 0.045 and 0.052, respectively. The hydride ligands in [6c][BPh$_4$] were located and refined by least squares. The geometries of the two cations are similar; the interesting difference being the metal–metal distance (W–Ir = 2.706 (1) and Mo–Ir = 2.641 (1) Å). The reaction of 3 with $[IrH_2(\text{acetone})_2(PCy_3)_2]^+$ (1e), however, follows a different well-defined stoichiometry giving 6e, $[WH_3(\eta^5\text{-}C_5H_5)_2]^+$ (11), and $[IrH_5(PCy_3)_2]$ (13e).

Introduction

The "Lewis acid/Lewis base" coupling reaction has proved to be a very successful approach to the synthesis of heterometallic hydrido-bridged complexes[1] (eq 1). (Usually the acceptor is a cationic solvento complex). The application of this reaction has been extensively investigated in this laboratory.[1–4]

$$\underset{\text{“Lewis base”}}{L_mMH_x} + \underset{\text{“Lewis acid”}}{L'_nM'} \rightarrow \underset{x\,=\,1\text{–}3}{L_mM(\mu\text{-}H)_xM'L'_n} \quad (1)$$

In many cases the product isolated from this type of reaction is not that expected on the basis of eq 1 as, during

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(1) Venanzi, L. M. *Coord. Chem. Rev.* **1982,** *43,* 251.

(2) Naegeli, R.; Togni, A.; Venanzi, L. M.; Albinati, A. *Organometallics* **1983,** *2,* 926.

(3) Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M.; Albinati, A. *J. Am. Chem. Soc.* **1982,** *104,* 6825.

(4) Lehner, H.; Matt, D.; Togni, A.; Thouvenot, R.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1984,** *23,* 4254.

0276-7333/86/2305-1785$01.50/0