Spies and Angelici[8c] showed that Al_2O_3 deuteriated with D_2O was capable of exchanging with $H_{2,5}$ in 1. The exchange was proposed to be catalyzed by basic oxygen groups on the Al_2O_3 surface.

Relative amounts of $H_{3,4}$ exchange in the differently substituted thiophenes over heterogeneous catalysts are different from the relative rates of exchange in the model complexes 1–4. That is, over HDS catalysts the amounts of $H_{3,4}$ exchange (Chart II) decrease in the order 2,5-DMT > 2-MT > 3-MT > thiophene,[5a,6a] whereas the rates of $H_{3,4}$ exchange in the complexes decrease as thiophene > 2-MT > 3-MT > 2,5-DMT. This difference in trends may be explained by considering that over the catalyst the extent of exchange is dependent not only on the rate of exchange of the absorbed thiophene but also on the amount of the thiophene that is adsorbed. In fact, competitive adsorption studies by Zdrazil[6,21] on $CoMo/Al_2O_3$ give relative adsorption capacities in the order 2,5-DMT (2.5) > 3-MT (~1.7) ≥ 2-MT (1.6) > thiophene (1.0).[22] Thus, the thiophenes with the most methyl groups adsorb to the greatest extent and should therefore have the greatest opportunity to undergo deuterium exchange. And this is the order of exchange that is observed. Thus, the extent of adsorption is more important than the opposing trend which would suggest that the more methyl groups in a π-adsorbed thiophene, the slower its deuterium exchange.

While the model studies presented herein do not prove that deuterium exchange of thiophenes on HDS catalysts proceeds via a π-adsorbed thiophene intermediate, they do provide for the first time experimental results that account for the observed amounts of exchange in the various positions of thiophenes over HDS catalysts. The mechanism of exchange in the model system also suggests that basic sites on the catalyst surface are important in promoting the exchanges; presumably more basic supports than Al_2O_3 would increase the rates of exchange, a possibility that could be examined experimentally.

Acknowledgment. We thank Dr. George H. Spies for many helpful discussions and his initial studies on this project and Dr. R. David Scott for his assistance in setting up the parameters on the NMR for the kinetic runs. A loan of $RuCl_3$ from Johnson Matthey, Inc., is greatly appreciated.

Registry No. 1, 107799-36-0; 2, 107799-38-2; 3, 107799-40-6; 4, 107799-42-8; H_2, 1333-74-0; $CpRu(PPh_3)_2Cl$, 32993-05-8; 2-MT, 554-14-3; 2,5-DMT, 638-02-8; $[CpRu(\eta\text{-}C_6H_6)]PF_6$, 72812-91-0; $[CpRu(NCCH_3)_3]PF_6$, 80049-61-2; $[CpRu(\eta\text{-}2\text{-}MT)]PF_6$, 107799-43-9; $[CpRu(\eta\text{-}C_6H_6)]BF_4$, 91753-79-6; $[CpRu(NCCH_3)_3]BF_4$, 107799-44-0; $[CpRu(\eta\text{-thiophene-}d_4)]PF_6$, 107819-47-6; D_2, 7782-39-0.

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(21) Adsorption studies were accomplished by pulsing the thiophenes and mixtures of thiophenes through a column packed with $CoMo/Al_2O_3$ catalyst at 350 °C under He. Relative adsorptivities were obtained from retention times. See ref 6.

(22) It should be noted that the thiophene adsorption sites in these studies need not be the same sites where deuterium exchange occurs. Thus, the adsorption results may not be related to the deuterium exchange process.

Synthesis, Structure, and Reactivity of the Thioformaldehyde Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$

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Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**2**) and $S{=}PPh_3$ gives a 1:1 mixture of thioformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (**1**) and ylide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (**3**). However, reaction of **2** and cyclohexene sulfide gives **1** (85–95% after recrystallization). An X-ray structure of **1** (crystal data: monoclinic, $P2_1/c$; a = 9.688 (2) Å, b = 18.536 (4) Å, c = 14.895 (s) Å; β = 103.53 (2)°; Z = 4) shows that the $\eta^2\text{-}H_2C{=}S$ ligand adopts a conformation that has significant overlap of its π^* orbital with the rhenium fragment HOMO and its sulfur terminus syn to the PPh_3. Extended Hückel MO calculations on the model compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$ predict a similar conformational energy minimum. Complex **1** is stable in CD_3CN (41 h, 51 °C) but rapidly reacts with PPh_3 (2 equiv) to give **3** (95%) and $S{=}PPh_3$ (88%). Reaction of **1** and $NaBH_3CN$ gives thiomethyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_3)$ (**5**, 85% after recrystallization). The reactivity of **1** is compared to that of formaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$, and the mechanisms of the above reactions are discussed.

Introduction

Thioformaldehyde is the parent member of a rare and unstable class of molecules, thioaldehydes.[2] Thioformaldehyde has been spectroscopically characterized in the gas phase[3] and is found in interstellar space.[4] It has also been the subject of numerous theoretical studies.[5] How-

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ever, to our knowledge thioformaldehyde has not been isolated in a condensed phase. Complexation to a transition metal frequently stabilizes reactive molecules. Hence, ligated $H_2C{=}S$ should be more amenable to direct physical and chemical studies.

Thioformaldehyde is also one of several small sulfur-containing ligands that could plausibly be involved in some metal-catalyzed hydrodesulfurization reactions and sulfur-poisoning processes.[6] Hence, the study of thioformaldehyde complexes may provide insight into the mechanisms of certain catalytic reactions.

Isolable thioformaldehyde complexes were unknown prior to 1977 when Roper reported the synthesis of $Os(CO)_2(PPh_3)_2(\eta^2\text{-}H_2C{=}S)$.[7] Following this landmark discovery, isolable thioformaldehyde complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (1),[8] $(\eta^5\text{-}C_5H_5)M(PMe_3)(\eta^2\text{-}H_2C{=}S)$ (M = Co, Rh),[9] and $Os(NO)(Cl)(PPh_3)_2(\eta^2\text{-}H_2C{=}S)$[10] were reported by ourselves, Werner, and Roper. Syntheses of numerous bridging binuclear and polynuclear thioformaldehyde complexes have also been described.[11-14] In this paper, we give a full account of the synthesis, structure, and reactivity of the rhenium thioformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (1). A portion of this work has been communicated.[8]

Results

Synthesis and Characterization of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (1). In previous work, we have shown that heteronucleophiles (:Nu) readily attack the electrophilic methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (2) to give adducts with a $ReCH_2Nu$ linkage.[15] Hence, we sought a nucleophile that might act as a sulfur-atom donor toward 2. Methylidene complex 2 was generated in situ at −78 °C from $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and $Ph_3C^+PF_6^-$.[15] Subsequent addition of $S{=}PPh_3$ (1 equiv) gave, as assayed by ^1H NMR, a 50:50 mixture of desired thioformaldehyde complex 1 (eq 1) and the known[15] ylide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (3). Complex 3 is readily formed from 2 and PPh_3.

Table I. Summary of Crystallographic Data for $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+ PF_6^-$ (1)

mol formula	$C_{24}H_{22}F_6NOP_2ReS$
mol wt	734.65
cryst system	monoclinic
space group	$P2_1/c$
cell dimens	
a, Å	9.688 (2)
b, Å	18.536 (4)
c, Å	14.895 (5)
β, deg	103.53 (2)
V, Å^3	2600.6 (1)
Z	4
d_{obsd}, g/cm^3	1.85
d_{calcd}, g/cm^3	1.876
cryst dimens, mm	0.44 × 0.20 × 0.08
radiatn, Å	λ(Mo Kα) = 0.710 69
data collectn method	ω–2θ
scan speed, deg/min	30
reflectns measd	$+h,+k,\pm l$
ω-scan width, deg	0.60
bckgd	$^1/_4$ scan after each scan
stds	measured every 2.78 h of X-ray exposure
no. of reflectns measd	7560
data used ($F^2 > 3\sigma(F)^2$)	5440
abs coeff (μ), cm^{-1}	49.94
P factor	0.06
ω-scan rate, deg/min	20 (max), 2.8 (min)
no. of variables	296
$R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$	0.060
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/(\sum w\|F_o\|)^2]^{1/2}$	0.081
goodness of fit	1.887

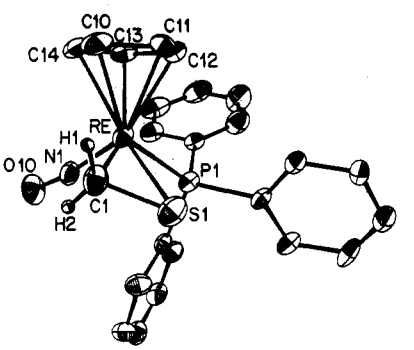
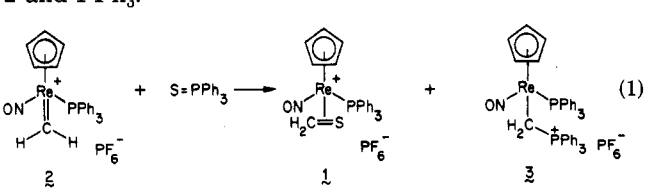


Figure 1. Structure of the cation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (1).



Addition of 2 equiv of $S{=}PPh_3$ to 2 also gave a 50:50 mixture of 1 and 3. However, pure 1 was obtained in 32% yield (64% of theory) by extraction/recrystallization. Note that only 0.5 equiv of $S{=}PPh_3$ is stoichiometrically required for complete reaction.

We sought a sulfur-atom donor that would be more reactive toward 1 than $S{=}PPh_3$ and not liberate a nu-

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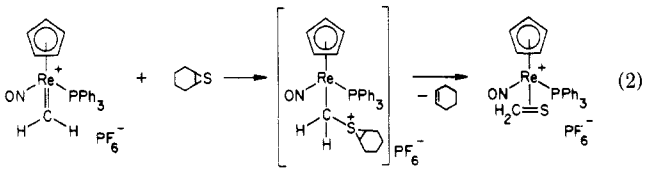
Table II. Atomic Coordinates for Atoms in 1

atom	x	y	z
Re	0.21049 (4)	0.27931 (2)	0.03666 (2)
S1	0.1963 (3)	0.2900 (2)	−0.1246 (2)
P1	0.3335 (2)	0.1687 (1)	0.0135 (2)
P10	0.7856 (3)	0.4239 (2)	0.0806 (2)
O10	−0.0287 (8)	0.1941 (5)	0.0653 (6)
N1	0.0655 (9)	0.2265 (4)	0.0479 (6)
C1	0.0753 (12)	0.3389 (6)	−0.0788 (8)
C10	0.2300 (12)	0.3927 (5)	0.1023 (8)
C11	0.3600 (11)	0.3771 (6)	0.0792 (7)
C12	0.4211 (11)	0.3188 (6)	0.1288 (7)
C13	0.3309 (13)	0.2951 (6)	0.1844 (7)
C14	0.2135 (11)	0.3412 (6)	0.1698 (7)
C121	0.4566 (10)	0.1736 (5)	−0.0605 (6)
C122	0.5400 (11)	0.2341 (5)	−0.0611 (7)
C123	0.6427 (11)	0.2366 (6)	−0.1119 (7)
C124	0.6681 (11)	0.1770 (6)	−0.1602 (7)
C125	0.5861 (11)	0.1153 (6)	−0.1611 (7)
C126	0.4808 (11)	0.1136 (5)	−0.1109 (7)
C131	0.4366 (10)	0.1324 (5)	0.1220 (6)
C132	0.5791 (13)	0.1263 (8)	0.1419 (8)
C133	0.6535 (16)	0.0969 (9)	0.2222 (10)
C134	0.5805 (18)	0.0758 (8)	0.2890 (8)
C135	0.4384 (17)	0.0821 (6)	0.2729 (8)
C136	0.3652 (13)	0.1108 (6)	0.1889 (7)
C141	0.2156 (9)	0.0952 (5)	−0.0326 (6)
C142	0.2487 (11)	0.0248 (6)	−0.0053 (7)
C143	0.1636 (12)	−0.0300 (5)	−0.0445 (7)
C144	0.0483 (13)	−0.0180 (6)	−0.1127 (8)
C145	0.0092 (12)	0.0507 (7)	−0.1434 (8)
C146	0.0925 (12)	0.1087 (6)	−0.1035 (7)
F11	0.721 (1)	0.4214 (5)	0.1656 (6)
F12	0.849 (1)	0.4332 (7)	−0.0066 (8)
F13	0.653 (1)	0.3909 (8)	0.0190 (9)
F14	0.915 (2)	0.4666 (9)	0.1353 (11)
F15	0.694 (2)	0.4888 (10)	0.0436 (10)
F16	0.877 (2)	0.3637 (11)	0.1188 (13)
H1	0.0820	0.4004	−0.0762
H2	0.0000	0.3184	−0.0918

cleophilic byproduct. Accordingly, treatment of **2** with cyclohexene sulfide gave thioformaldehyde complex **1** in 85–95% yields after workup and recrystallization.



(2)

2 **4** **1**

Complex **1** was characterized as summarized in the Experimental Section. Spectroscopic features of a cationic $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)]^+$ complex were evident: IR (cm^{-1}, KBr) $\nu_{N\equiv O}$ 1749 vs; ^1H NMR (δ, acetone-d_6) 6.41 (d, J_{HP} = 0.9 Hz, C_5H_5). The ^1H NMR spectrum of **1** showed well-separated η^2-$H_2C{=}S$ ligand resonances (δ 5.09 and 3.90) and was essentially temperature-independent over the range −68 to 52 °C. The η^2-$H_2C{=}S$ ligand ^{13}C NMR resonance was at 30.5 ppm. We consider this chemical shift to be diagnostic of a η^2-coordination mode, as complexes with η^1-$X_2C{=}S$ ligands commonly exhibit ^{13}C NMR resonances at 180–210 ppm.[16]

Structure of 1. The structure of **1** was further investigated by X-ray crystallography. Yellow-gold prisms of **1** were obtained by vapor diffusion recrystallization using ether/CH_3CN, and X-ray data were obtained under the conditions summarized in Table I. The unit cell was found to be monoclinic, with the lattice parameters given in Table I. Refinement, described in the Experimental Section, included the location of the thioformaldehyde hydrogens from a difference Fourier map. This gave the structure of the cation of **1** shown in Figure 1.

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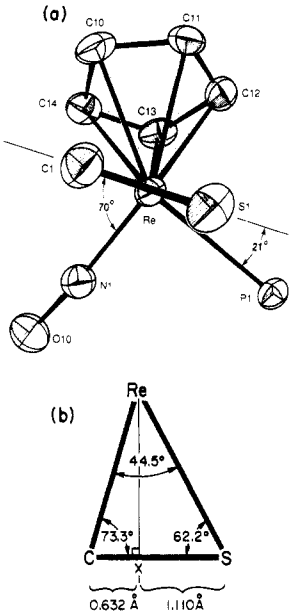


Figure 2. View of the η^2-$H_2C{=}S$ ligand in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (**1**): (a) Newman projection; (b) plane containing Re, C, and S.

Table III. Selected Bond Distances and Angles in 1[a]

from	to	dist, Å
C1	S1	1.742 (9)
C1	Re	2.199 (8)
S1	Re	2.381 (2)
N1	Re	1.752 (6)
P1	Re	2.437 (2)
N1	O10	1.171 (8)
C10	C11	1.411 (11)
C10	C14	1.423 (12)
C10	Re	2.307 (8)
C11	C12	1.363 (12)
C11	Re	2.314 (8)
C12	C13	1.407 (12)
C12	Re	2.296 (8)
C13	C14	1.398 (12)
C13	Re	2.256 (8)
C14	Re	2.285 (7)
C1	H1	1.142
C1	H2	0.805

from	thru	to	angle, deg
S1	C1	Re	77.31 (30)
C1	S1	Re	62.21 (29)
P1	Re	N1	88.45 (21)
P1	Re	S1	80.91 (6)
P1	Re	C1	122.23 (22)
N1	Re	S1	106.54 (23)
N1	Re	C1	90.64 (32)
S1	Re	C1	44.48 (23)
Re	N1	O10	172.48 (67)
C11	C10	C14	106.75 (76)
C12	C11	C10	109.28 (76)
C11	C12	C13	108.38 (75)
C12	C13	C14	108.21 (74)
C13	C14	C10	107.36 (72)
H1	C1	H2	121.43
H1	C1	S1	119.58
H2	C1	S1	108.38
H1	C1	Re	117.11
H2	C1	Re	107.00

[a] See Figure 1 for atomic numbering.

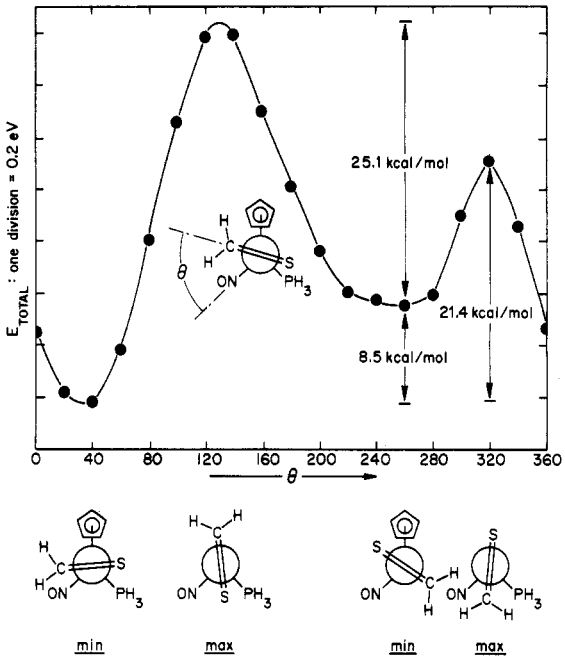


Figure 3. Variation in E_{total} as the η^2-$H_2C{=}S$ ligand is rotated in $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$ (calculated by the extended Hückel method with weighted H_{ij} formula).

Additional views of the η^2-$H_2C{=}S$ ligand are given in Figure 2. Atomic coordinates are listed in Table II, and important bond distances and angles are compiled in Table III. Since thermal parameters, structure factors, and packing diagrams were included in the supplementary material of our communication,[8] they are not republished here.

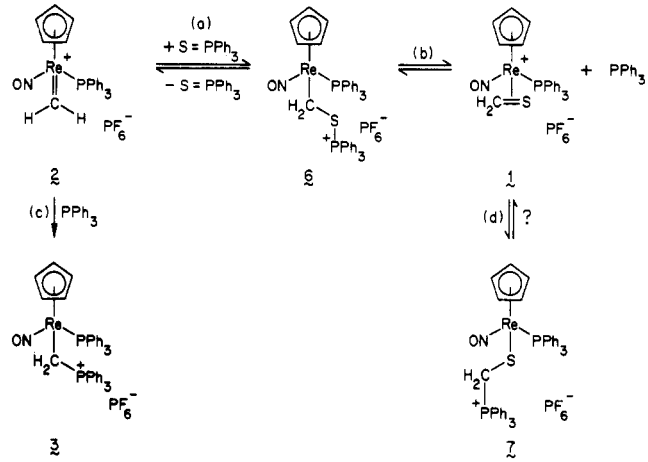
As can be seen in Figure 2a, the η^2-$H_2C{=}S$ ligand is oriented with the sulfur syn to the PPh_3 ligand. The angle of the Re—C=S plane with the Re—P vector is 21°. Figure 2 shows that the η^2-$H_2C{=}S$ ligand is slipped. Consider point X, where the C–S bond intersects the vector drawn from the rhenium perpendicular to the C–S bond. Point X is considerably closer to carbon (0.632 Å) than to sulfur (1.110 Å).

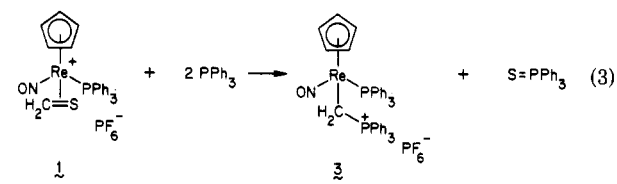
In order to better understand the η^2-$H_2C{=}S$ ligand conformation in 1, extended Hückel MO calculations were conducted on the model compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$ analogously to those previously reported for formaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}O)]^+$.[17] Figure 3 shows the variation in E_{total} as the η^2-$H_2C{=}S$ ligand was rotated. An absolute minimum was found at $\theta = 40°$, and a local minimum, 8.5 kcal/mol higher in energy, was found at $\theta = 260°$. The angle of the Re—C=S plane with the Re—P vector was 50° in the absolute minimum, as compared to 21° in the crystal structure of 1 (Figure 2a).

The calculations also showed that the HOMO of $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$ had in all conformations (θ) a substantial contribution from the two sulfur p orbitals not used in the $H_2C{=}S$ π bond. In the minimum energy η^2-$H_2C{=}S$ conformation ($\theta = 40°$), the third lowest unoccupied orbital was found to have significant $H_2C{=}S$ π^* character. This orbital was localized more on sulfur; coefficients: S, −0.51; C, 0.33. These data will be interpreted in the Discussion.

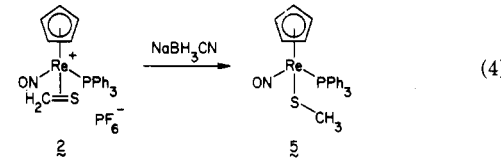
Reactivity of 1. Complex 1 was dissolved in CD_3CN in the presence of an internal standard. After 41 h at 51 °C, no reaction had occurred. Complex 1 was dissolved in acetone and treated with 2 equiv of PPh_3. Subsequently isolated were ylide complex **3** (95%) and $S{=}PPh_3$ (88%), as shown in eq 3. When a similar experiment was conducted with 1 equiv of PPh_3, only half of complex 1 was consumed. No intermediates were detected when these reactions were monitored by ^1H NMR (−73 °C).

Scheme I. Proposed Mechanism for the Interconversion of Complexes 1, 2, and 3





Treatment of 1 with $NaBH_3CN/CH_3OH$ gave thiomethyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_3)$ (**5**) in 85% yield after workup (eq 4). Hence, 1 can also be attacked by nucleophiles at the η^2-$H_2C{=}S$ carbon.



Discussion

Synthesis of 1. Of the two syntheses of thioformaldehyde complex 1 described above, the one that utilizes cyclohexene sulfide (eq 2) is clearly preparatively superior. This reaction is visualized as proceeding via the sulfonium salt **4**, which subsequently extrudes cyclohexene to give 1. We have previously shown that methylidene complex **2** reacts with the acyclic sulfide CH_3SCH_3 to give the sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)_2)]^+PF_6^-$.[18] Other mononuclear η^2-$H_2C{=}S$ complexes have been prepared by H^- attack upon $L_nM(Cl)(CHS)$ precursors,[7] HS^- attack upon $L_nM(I)CH_2I$ precursors,[9] and sulfur oxidation of $L_nM{=}CH_2$ precursors.[10]

The lower yield synthesis of 1 (eq 1) is nonetheless of mechanistic interest. At first glance the chemistry in eq 1 and 3 might seem contradictory. However, these reactions are easily understood in the context of Scheme I. When $S{=}PPh_3$ is added to methylidene complex **2**, the

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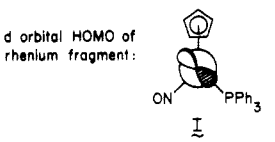
addition product $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SPPh_3)]^+PF_6^-$ (**6**, step a, Scheme I) is likely generated. This species, which cannot be observed by ^1H NMR, eliminates PPh_3 (step b) and gives thioformaldehyde complex **1**. Two factors may be responsible for the formation of co-product **3** in eq 1. First, the overall rate of steps a and b leading to **1** may be slow compared to the scavenging of **2** by PPh_3 (step c). Second, regardless of rates, the independent reaction of **1** and PPh_3 (eq 3) shows that conversion to **3** and $S{=}PPh_3$ is exothermic. Equation 3 requires, however, 2 equiv of PPh_3 to go to completion. Thus, complex **1** cannot be completely consumed under the conditions of eq 1.

Structure of 1. Complex **1** is, to our knowledge, the only structurally characterized η^2-$H_2C{=}S$ complex. The C–S bond length, 1.742 (9) Å, is intermediate between that found in $H_2C{=}S$ (1.6108 (9) Å)[19] and typical C—S single bonds (1.80–1.82 Å).[20] It is significantly shorter than those determined by Adams for a series of triosmium μ_2- and μ_3-η^2-$H_2C{=}S$ complexes (1.788 (11)–1.872 (12) Å).[11] Floriani has found a C—S bond length of 1.762 (4) Å in the vanadium η^2-thiobenzophenone complex $(\eta^5\text{-}C_5H_5)_2V(\eta^2\text{-}Ph_2C{=}S)$,[21] and Mayr and Rheingold have reported a C—S bond length of 1.739 (7) Å in the tungsten η^2-thiobenzaldehyde complex $(\eta^2\text{-}Et_2NCS_2)(\eta^2\text{-}Et_2NCS)W(CO)(\eta^2\text{-}PhCH{=}S)$.[22a] Buchwald has recently determined C–S bond lengths of 1.785 (11) and 1.739 (13) Å in the zirconium η^2-thioacetaldehyde complex $(\eta^5\text{-}C_5H_5)_2Zr(PMe_3)(\eta^2\text{-}CH_3CH{=}S)$.[22b]

The HOMO of the $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ fragment is the d orbital shown in **I**.[17,23] Ideally, the η^2-$H_2C{=}S$



I

ligand in **1** should adopt a conformation that maximizes overlap of this HOMO and the $H_2C{=}S$ π^* acceptor orbital. The experimentally observed 21° angle between the Re—C=S plane and the Re-P vector (Figure 2a) is close to the 0° angle thus expected. Our calculations (Figure 3) find a conformation with a 50° angle between the Re—C=S plane and the Re—P vector to be of lowest energy. We suggest that an additional conformation-determining effect might be derived from the sulfur lone-pair character noted above in the HOMO of $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$. The agreement between theory and experiment for the isostructural η^2-$H_2C{=}O$ complex is slightly better.[17] The observed angle of the Re—C=O plane with the Re—P vector is 15°, and the calculated angle is 30°. In this case, little if any oxygen lone-pair character was found in the HOMO.

Figure 2b shows that the η^2-$H_2C{=}S$ ligand is not bound symmetrically but is "slipped" with rhenium substantially closer to carbon.[24] Consider point X, where the C–S bond

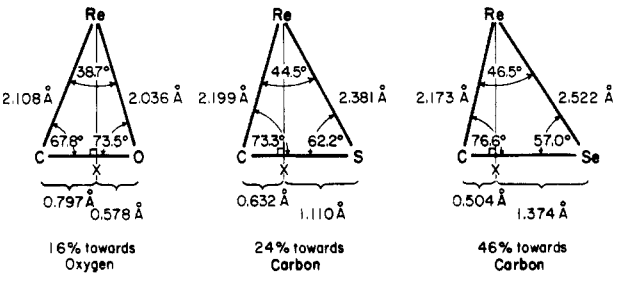


Figure 4. Comparison of the degree of ligand slippage in formaldehyde, thioformaldehyde, and selenoformaldehyde complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}X)]^+$.

intersects the vector drawn from rhenium perpendicular to the C–S bond. For comparison purposes, we define the degree of slippage as the displacement of point X from the midpoint of the C–S bond, *divided* by half the C–S bond length. The η^2-$H_2C{=}S$ slippage in **1** is then 27% (toward *carbon*). In contrast, all structurally characterized formaldehyde complexes show slippage toward oxygen.[8,17,25] As shown in Figure 4, the η^2-$H_2C{=}O$ slippage in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ is 16%.[17] The η^2-$H_2C{=}S$ ligand in **1** is therefore distorted along a reaction coordinate for sulfur-atom abstraction.

Interestingly, the η^2-$H_2C{=}Se$ ligand in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}Se)]^+PF_3^-$ is slipped 46% toward *carbon* (Figure 4).[26] By extrapolation, the η^2-$H_2C{=}Te$ ligand in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}Te)]^+PF_6^-$ should be even more distorted. Several logical synthetic routes to this compound have been unsuccessful.[26]

Reactivity of 1. The η^2-$H_2C{=}O$ ligand in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ is readily displaced by acetonitrile.[17] However, η^2-$H_2C{=}S$ complex **1** is considerably less substitution labile. The $H_2C{=}S$ π orbital has been estimated by ab initio calculations to be 3 eV *higher* in energy than the $H_2C{=}O$ π orbital, and the $H_2C{=}S$ π^* orbital has been estimated to be 2.8 eV *lower* in energy than the $H_2C{=}O$ π^* orbital.[27] On these grounds, thioformaldehyde should be both a better donor and better π-acceptor than formaldehyde, resulting in stronger bonding. A similar conclusion was reached in a recent theoretical study of $(CO)_4Ru(\eta^2\text{-}H_2C{=}X)$ complexes.[28]

Complexes **1** and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ also differ in the regiochemistry of PPh_3 addition to the η^2-$H_2C{=}X$ ligand. Whereas **1** and PPh_3 react to give chemistry derived from PPh_3 attack upon *sulfur* (eq 3), $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ and PPh_3 react to give addition product $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_2PPh_3)]^+PF_6^-$—derived from PPh_3 attack upon *carbon*.[17] Nucleophilic attack upon thiocarbonyl (RR′C=S) sulfur is common and is easily rationalized in terms of hard–soft acid–base theory.[29] In addition, the π^* orbital of free $H_2C{=}S$ is much less localized on carbon

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(24) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (b) A reviewer has commented that since the bonding in the $H_2C{=}X$ complexes in Figure 4 is better described by a three-membered metallacycle than a π adduct, the slippage trend may be viewed as a natural consequence of the atomic covalent radii (O < C < S < Se).
(25) (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Clark, G. R.; Headford, C. E. L.; Marsden, K. Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335. (c) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *Ibid.* **1981**, *219*, 353. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019. (e) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Ibid.* **1985**, *107*, 1985.
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than that of free $H_2C{=}O$.[27] In complex 1, our calculations show the η^2-$H_2C{=}S$ π^* orbital to be more localized on sulfur. The η^2-$H_2C{=}S$ slippage likely enhances this localization. Thus, by analogy to Eisenstein and Hoffmann's analysis of the activation of coordinated olefins to nucleophilic attack by slippage,[24] nucleophilic attack should occur preferentially on η^2-$H_2C{=}S$ sulfur. However, the $NaBH_3CN$ reduction in eq 4 unequivocally shows that 1 can undergo nucleophilic attack at the η^2-$H_2C{=}S$ carbon. Furthermore, none of our data exclude a rapid, reversible addition of PPh_3 to the η^2-$H_2C{=}S$ carbon in 1 to give 7 (Scheme I, step d), or the possibility that 7 may be, *in part*, on the reaction coordinate of eq 3.

Conclusion. In summary, we have developed two new and potentially general strategies for the synthesis of thioformaldehyde complexes. The remarkable facility with which sulfur is introduced and removed from the coordination spheres of 2 and 1 is of potential relevance to hydrodesulfurization and sulfur-poisoning processes. Finally, we have also shown that the chemistry of η^2-$H_2C{=}S$ and η^2-$H_2C{=}O$ ligands differ significantly but in ways that can be rationalized by MO and structural arguments.

Experimental Section

General Data. All reactions were carried out under a dry N_2 atmosphere, but workups were conducted without effort to exclude air. IR spectra were recorded on a Perkin-Elmer 1500 (FT) spectrometer. All ^1H NMR spectra were recorded on modern 200–300-MHz spectrometers and were referenced to $(CH_3)_4Si$. Both ^{13}C and ^{31}P NMR spectra were recorded on Varian 80–200-MHz spectrometers and were referenced to internal $(CH_3)_4Si$ and external H_3PO_4, respectively. Microanalyses were conducted by Galbraith and 3M laboratories.

Solvents were purified as follows: acetone, distilled from $CaSO_4$; CH_2Cl_2, distilled from P_2O_5; ether, distilled from Na/benzophenone; absolute ethanol, used as received; CH_3OH, dried over $CaSO_4$ and purged with N_2; CD_3CN and CD_2Cl_2, vacuum transferred from CaH_2; acetone-d_6, vacuum transferred from $CaSO_4$. Reagent $S{=}PPh_3$ was prepared from PPh_3 and sulfur according to a literature procedure[30] and was recrystallized from hot absolute ethanol. Cyclohexene sulfide (technical grade) and $NaBH_3CN$ (0.1 M in THF) were used as received from Aldrich. Reagents $Ph_3C^+PF_6^-$, PPh_3, and Ph_3SiCH_3 were obtained as described previously.[17]

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (1). A. From Cyclohexene Sulfide. A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.50 g, 0.90 mmol),[15] CH_2Cl_2 (200 mL), and a stir bar. The solution was cooled to −78 °C, and $Ph_3C^+PF_6^-$ (0.40 g, 1.0 mmol) was added with stirring. After 1 h, technical (85%) cyclohexene sulfide (120 μL, 0.96 mmol) was added by syringe. A transient brown color was observed as the drops mixed. The cooling bath was removed, and the reaction was stirred for 1 h. Solvent was then removed by rotary evaporation. This gave a yellow tar that was washed with hexanes and ether to give a mustard yellow solid. This was dissolved in $CHCl_3$ (ca. 5 mL) to give a dark yellow solution that rapidly precipitated fine yellow crystals. These were colloected by filtration and recrystallized by vapor diffusion using acetone/hexanes. This gave yellow prisms of 1 (0.60 g, 0.82 mmol, 91%). **B. From $S{=}PPh_3$.** A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.500 g, 0.896 mmol), CH_2Cl_2 (125 mL), and a stir bar. The solution was cooled to −78 °C, and $Ph_3C^+PF_6^-$ (0.365 g, 0.941 mmol) was added. After 15 min, $S{=}PPh_3$ (0.290 g, 0.986 mmol) was added, and the flask was placed in a −23 °C bath for 1 h. Solvent was removed by rotary evaporation at room temperature, leaving an orange-yellow semisolid residue. The residue was dissolved in a minimum of acetone, and then ether was added. This gave a yellow solid that was collected by filtration and shown to be a 50:50 mixture of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (1) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (3) by ^1H NMR. The yellow solid was triturated with acetone (2 × 5 mL), and the extracts were decanted. The remaining solid (0.322 g) was a 95:5 mixture of 3/1, as assayed by IR. The acetone extracts were combined, and ether was added by vapor diffusion. This gave a yellow-brown solid that was washed with CH_2Cl_2 (2 × 1 mL) and twice recrystallized from CH_2Cl_2/ether. This gave irregular yellow crystals of 1 (0.209 g, 0.285 mmol, 64% of theory), decomp pt 188–190 °C (evacuated capillary). **C. Characterization:** IR (cm^{-1}, KBr) 3127 m, 3079 w, 3060 w, 2971 w, $\nu_{N\equiv O}$ 1749 vs, 1586 w, 1573 w, 1482 m, 1435 s, 1419 m, 1312 w, 1190 w, 1161 w, 1117 w, 1095 s, 1023 w, 998 w, 917 m, 900 m, 879 s, ν_{P-F} 837 vs vbr, 749 s, 707 s, 692 s; ^1H NMR (δ, acetone-d_6) 7.77–7.63 (m, 9 H), 7.54–7.46 (m, 6 H), 6.41 (d, J_{HP} = 0.9 Hz, 5 H), 5.09 (dd, J_{HP} = 1.4 Hz, J_{HH} = 0.9 Hz, 1 H), 3.90 (dd, J_{HP} = 1.7 Hz, J_{HH} = 0.9 Hz, 1 H); $^{13}C\{^1H\}$ NMR (ppm, CD_3CN) PPh_3 at[31] 134.7 (d, J_{CP} = 9.9 Hz, ortho), 133.9 (d, J_{CP} = 1.5 Hz, para), 130.5 (d, J_{CP} = 11.5 Hz, meta), 128.7 (d, J_{CP} = 61.8 Hz, ipso), 100.9 (s, C_5H_5), 30.5 (s, $H_2C{=}S$); $^{31}P\{^1H\}$ NMR (ppm, acetone) 5.59 (s); FAB mass spectrum (8 keV, m/e, relative intensity) 590 (M^+, $^{187}Re^{32}S$, 20), 558 (M^+ − S, 100), 544 (M^+ − CH_2S, 40). Anal. Calcd for $C_{24}H_{22}F_6NOP_2ReS$: C, 39.24; H, 3.02; N, 1.91; P, 8.43. Found: C, 39.41; H, 3.01; N, 2.04; P, 8.23.

Attempted Reaction of 1 with CD_3CN. A 5-mm NMR tube was charged with 1 (0.021 g, 0.029 mmol), Ph_3SiCH_3 standard (0.006 g, 0.022 mol), and CD_3CN (0.500 mL) and was capped with a septum. A reference ^1H NMR spectrum was recorded. The solution (0.056 M in 1) was placed in a 51 ± 1 °C oil bath. After 41 h, no reaction had occurred and ≥98% of 1 remained.

Reaction of 1 with PPh_3. A. A Schlenk flask was charged with 1 (0.200 g, 0.272 mmol), PPh_3 (0.143 , 0.545 mmol), acetone (8 mL), and a stir bar. The reaction was stirred for 2 h. Then CH_2Cl_2 (30 mL) was added to the cloudy orange suspension. This gave a homogeneous solution, and ether was slowly introduced by vapor diffusion. Orange crystals of 3 formed and after 2 days were collected by filtration (0.29 g, 0.258 mmol, 95%). Data for 3: IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1657 s (lit.[15] 1650 cm^{-1}); ^1H NMR (δ, CD_3CN) phenyl protons and 4.68 (s, 5 H), 3.23 (ddd, J_{HH} = 14.0 Hz, J_{HP} = 10.9 Hz, $J_{HP'}$ = 8.1 Hz, 1 H), 2.69 (ddd, J_{HP} = 16.2 Hz, J_{HH} = 14.1 Hz, $J_{HP'}$ = 1.3 Hz, 1 H) (lit.[15] 4.68, 3.23 (ddd, J = 14, 11, 8 Hz), 2.68 ppm (ddd, J = 16, 14, 1 Hz). Solvent was removed from the supernatant by rotary evaporation. This gave a solid residue that was extracted with ether (50 mL). The extract was filtered and concentrated by rotary evaporation to a white solid. The solid was recrystallized from hot absolute ethanol to give $S{=}PPh_3$ (0.070 g, 0.238 mmol, 88%): mp 162 °C; IR (cm^{-1}, KBr) 3050 w, 1478 m, 1433 s, 1307 m, 1178 w, 1158 w, 1098 s, 1067 w, 1024 m, 997 m, 752 m, 745 m, 713 s, 690 s, 635 s, 611 m; $^{31}P\{^1H\}$ NMR (ppm, $CHCl_3$) 43.1 (s) [lit.: mp 161–162 °C;[30] IR (cm^{-1}, KBr)[32] 3050 w, 1470 m, 1428 s, 1300 m, 1173 w, 1150 w, 1095 s, 1062 w, 1019 m, 748 m, 742 m, 710 s, 688 s, 638 s, 611 m; $^{31}P\{^1H\}$ NMR (ppm, $CHCl_3$) 42.6 (s)[33]]. **B.** A 5-mm NMR tube was charged with 1 (0.015 g, 0.020 mmol) and CD_2Cl_2 (0.500 mL) and was capped with a septum and cooled to −78 °C. A solution of PPh_3 (0.005 g, 0.019 mmol) in CD_2Cl_2 (0.100 mL) was added by syringe, and the sample was transferred to a NMR probe that had been pre-equilibrated to −73 °C. A ^1H NMR spectrum was immediately recorded and showed 1 and 3 (68:32) as the only cyclopentadienyl rhenium complexes present. A subsequent spectrum at room temperature showed 1 and 3 in a 50:50 ratio.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_3)$ (5). A Schlenk flask was charged with 1 (0.37 g, 0.50 mmol), CH_3OH (75 mL), and a stir bar. Then a 0.1 M THF solution of $NaBH_3CN$ (5.1 mL, 0.51 mmol) was added to this suspension with stirring. After 20 h, solvent was removed from the homogeneous reaction mixture by rotary evaporation. The resulting orange solid was extracted with $CHCl_3$, leaving a white precipitate. The orange extract was concentrated to ca. 3 mL under a N_2 stream. Heptane was then layered onto this solution. Gradual diffusion gave orange needles and red prisms of 5 (0.28 g, 0.47 mmol, 94%), which were collected by filtration and vacuum dried: mp 213–215 °C dec;

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(31) Assignments of PPh_3 carbons are made as outlined in Table I of ref 17.

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IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1642 s; ^1H NMR (δ, $CDCl_3$) 7.4 (m, 15 H), 5.22 (s, 5 H), 2.42 (s, 3 H); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) PPh_3 at[31] 134.7 (d, J_{CP} = 53.7 Hz, ipso), 133.7 (d, J_{CP} = 10.7 Hz, ortho), 130.3 (d, J_{CP} = 2.4 Hz, para), 128.3 (d, J_{CP} = 10.7 Hz, meta), 91.3 (s, C_5H_5), 27.0 (d, J_{CP} = 8.4 Hz, CH_3); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 19.9 (s); high resolution mass spectrum (m/e), 591.080 71 (M^+; calcd ^{187}Re 591.076 78), 589.067 68 (M^+; calcd ^{185}Re 589.071 78), 329 ($M^+ - PPh_3$), 262 ($^+PPh_3$). Anal. Calcd for $C_{24}H_{23}NOPReS$: C, 48.80; H, 3.92; N, 2.37. Found: C, 48.6; H, 3.8; N, 2.4.

X-ray Crystal Structure of 1. X-ray data were collected as described in Table I on an Enraf-Nonius CAD-4 automated diffractometer. Of 7560 reflections collected with $\theta \leq 30°$, 5440 with $I \geq 3\sigma(I)$ were used in the final refinement. Lorentz and polarization corrections were applied, but absorption corrections (μ = 49.94 cm^{-1}) were not made. The structure solution proceeded smoothly by using standard heavy-atom techniques and was refined by full-matrix least-squares calculations. All calculations were performed on a Vax 11/780 computer with the Enraf-Nonius SDP proram library.[34] All non-hydrogen and non-fluorine atoms were refined with anisotropic Gaussian amplitudes. Anomolous dispersion corrections were applied throughout the refinement. The positions of all non-thioformaldehyde hydrogens were calculated with C-H bond distances set at 0.95 Å and idealized sp^2 geometry. The η^2-H_2C=S thioformaldehyde hydrogens were located from a difference Fourier synthesis. All hydrogen atom contributions were included in structure factor calculations, but their positions were not refined.

MO Calculations. Extended Hückel calculations[35] were conducted with weighted H_{ij} formula. The rhenium and phosphorus atoms of $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$ were assigned idealized octahedral and tetrahedral geometries, respectively. The η^2-H_2C=S carbon and sulfur atoms were assigned bond lengths (below) and angles (below) on the basis of the X-ray crystal structure of 1. The C-Re-S angle was bisected by an axis perpendicular to the Re-P and Re-N vectors. The η^2-H_2C=S ligand was rotated about this axis while the Re-C-S bond distances and angles were held constant. The axis intersected the C-S bond at a distance of 0.837 Å from carbon. The η^2-H_2C=S hydrogen atoms were positioned such that the H-C-H plane was normal to the Re-C-S plane and formed an angle of 157.4° with the C-S vector, thus tilting the hydrogen atoms ca. 23° from ideal sp^2 geometry. Bond lengths used for η^2-H_2C=S were as follows (Å): Re-C, 2.199; Re-S, 2.381; C-S, 1.742; C-H, 1.090. The parameters used for sulfur were as follows: 3s, H_{ii} = -20.00 eV, ζ = 1.817; 3p, H_{ii} = -13.30 eV, ζ = 1.817. The remaining bond lengths and parameters were the same as described previously.[17,36]

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Registry No. 1, 84369-18-6; 2, 71763-23-0; 3, 71763-25-2; 5, 84369-19-7; $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$, 71763-18-3.

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Phosphasilenes: Synthesis and Spectroscopic Characterization

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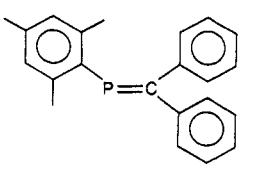
A number of phosphasilenes as representatives of a new class of compounds containing π-bonded silicon is described. Several phosphasilenes ArP=SiR'R'' (**3**, Ar = 2,4,6-tri-*tert*-butylphenyl; R', R'' = phenyl, 2,4,6-trimethylphenyl, 2,4,6-triethylphenyl, 2,4,6-triisopropylphenyl, *tert*-butyl, or certain combinations thereof) were synthesized by the reaction of ArPHLi (**8**) and the corresponding dichlorosilanes R'R''$SiCl_2$ (**4**), followed by elimination of HCl. Depending on R' and R'', several side reactions were encountered; for this reason, and because of the low stability of **3**, their isolation in pure form was not achieved. Compounds **3** were characterized as phosphasilenes by their unique ^{31}P and ^{29}Si NMR data, in particular by the strongly deshielded $\delta(^{29}Si)$ value (148-176 ppm) and the large $^1J(PSi)$ coupling constant (ca. 150 Hz). The (thermal) stability of **3** increases with increasing steric protection. Reactions of **3** with methanol and tellurium are briefly described.

Introduction

Heteroalkenes that contain an element of the third or a higher period in a pπ-hybridized state violate the classical double bond rule[1] which states that such compounds are unstable under ordinary conditions. Indeed, stable derivatives have only been obtained by special precautions, e.g., by resonance stabilization or by steric protection of the double bond.

An early example of the use of steric effects is the stabilization of the P=C unit by a mesityl and two phenyl groups in the phosphaalkene 1.[2] Highly successful was the use of the 2,4,6-tri-*tert*-butylphenyl group that is one of the sterically most demanding groups. It permitted the isolation of the first stable diphosphene **2** by Yoshifuji et al.[3] and has since led to the preparation of a number of compounds with otherwise evasive functionalities[4] as well



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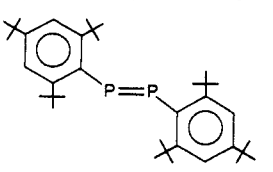

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