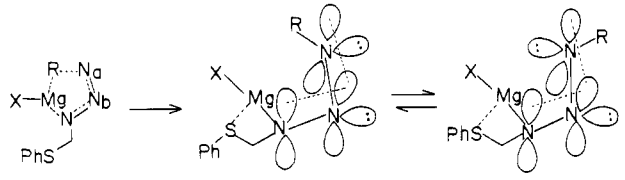
Similarly, cyclohexylmagnesium bromide gave the single acylated triazene **15**[11] (76% isolated yield) if quenched at −78 °C, but if the initial adduct is warmed to 0 °C before quenching with acetic anhydride, only the regioisomeric acyltriazene **16**[11] is isolated (65% yield). In addition to spectroscopic characterization, nucleophilically induced decomposition of crude **15** with tetra-*n*-butylammonium formate in DMF gave a 93% isolated yield (overall from Grignard reagent) of *N*-acetylcyclohexylamine (Scheme I).

The mutually exclusive formation of **15** and **16** under the above conditions suggests two different salts as their precursors. Using the reasonable assumption that the acyl group is transferred with allyl inversion (eq 1) by analogy to the reaction of allylmagnesium halides with carbonyl partners[15] suggests that the precursor of **15** is **14a** and that of **16** is **14b**. To the extent that sulfur stabilizes the magnesium salt by internal ligation, the isomerization of four-membered ring chelate **14a** to six-membered ring chelate **14b** agrees with the thermodynamic bias for the latter.

The exclusive kinetic formation of the thermodynamically less stable magnesium salt is quite striking. Since coordination of the heteroatom to the magnesium of the attacking Grignard reagent cannot account for this observation (vide supra), the explanation must reside in the mechanism of attack of a nucleophile onto an azide function. We believe, as structure **17** represents, that an



17 18 19

incoming nucleophile R and the developing lone pair at N_b are antiperiplanar. Such an attack creates the *cis*-triazene **18**, which would be expected to readily isomerize to *trans*-**19**. This phenomenon begins to emerge as a general principle for nucleophilic addition to heteroatomic unsaturation.[16,17] For example, in the addition of sodium hexamethyldisilazide to benzenediazonium chloride, the kinetic product was exclusively the *cis*-triazene, which subsequently isomerized to the trans compound.[16b] It appears that the bias for the incoming nucleophile and the developing lone pair at the heteroatom to be antiperiplanar dictates the reaction course for azides.

Sulfur also participates in the nucleophilically triggered decomposition of the acylated triazenes. Thus, treating a mixture of **10** and **11** (prepared by quenching the initial adduct at a temperature between 0 and −78 °C) with a variety of nucleophiles such as lithium thiomethoxide in HMPA, potassium superoxide in Me_2SO, tetra-*n*-butylammonium formate in DMF, or potassium hydroxide in Me_2SO led to *N*-phenethylacetamide from **10** according to eq 1 but only recovered **11**. Apparently the process represented in **11** of eq 1 is much less favorable. Attributing the ready decomposition of **10** to activation by sulfur is reinforced by the observation that 1-benzyl-3-methyltriazene and 1-aryl-3-alkyltriazenes are stable to alkali.[18,19] The ability of the lone pairs on heteroatoms to stabilize S_N2 transition states accounts for this effect.

This study revealed that the addition of Grignard reagents to azides proceeds by a stereoelectronically controlled pathway to generate the thermodynamically less stable magnesium salt of the triazene. This observation permitted the development of a successful approach for the amination of alkylmagnesium halides, thereby generalizing the utility of azidomethylphenyl sulfide as a synthon for $^+NH_2$. Further, it appears that the preference for attack on X=Y to occur by the incoming nucleophile and developing lone pair to be antiperiplanar extends to cumulative unsaturation as found in azides.

Acknowledgment. We thank the National Science Foundation and the National Institute of Health, General Medical Sciences, for their generous support of our programs.

Registry No. 1, 77422-70-9; **2**, 84304-06-3; **3**, 84304-07-4; **4**, 52827-27-7; **5**, 17108-22-4; **10**, 84304-09-6; **11**, 84304-10-9; **12**, 877-95-2; **13**, 84304-08-5; phenethyl bromide, 103-63-9; cyclohexyl bromide, 108-85-0; cyclohex-3-en-1-ylmethyl bromide, 34960-41-3; 2-norbornyl bromide, 29342-65-2; 2-(4-methoxyphenyl)ethyl bromide, 14425-64-0; *N*-(2-phenylethyl)benzamide, 3278-14-6; *N*-acetylcyclohexylamine, 1124-53-4; (*N*-cyclohex-3-en-1-ylmethyl)acetamide, 54385-23-8; *exo*-*N*-2-norbornylacetamide, 28607-02-5; *endo*-*N*-2-norbornylacetamide, 56895-94-4; piperonyl chloride, 25054-53-9; Ac_2O, 108-24-7; PhCOCl, 98-88-4.

Supplementary Material Available: Detailed experimental procedure for the preparation of *N*-phenethylacetamide (1 page). Ordering information is given on any current masthead.

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Syntheses, Chemical Properties, and X-ray Crystal Structures of Rhenium Formaldehyde and Thioformaldehyde Complexes

William E. Buhro,[1a,b] Alan T. Patton,[1a,b]
Charles E. Strouse,[1b] and J. A. Gladysz*[1a,b,2]

Departments of Chemistry, University of Utah
Salt Lake City, Utah 84112
and University of California
Los Angeles, California 90024

Fred B. McCormick*[3] and Margaret C. Etter

3M Central Research Laboratories
St. Paul, Minnesota 55101

Received October 22, 1982

The synthesis of transition-metal complexes that contain ligand types which may be transient intermediates in catalytic CO/H_2 reactions has been intensely pursued over the past few years.[4] Recently, a η^2-H_2C=O complex was postulated to be a pivotal intermediate in the partitioning of CO/H_2 between methanol and glycol over homogeneous ruthenium catalysts.[5] Hence we set out to develop a new and potentially general methodology for the synthesis of this scarce[6] class of compounds. In view of current

(1) (a) University of Utah; (b) University of California.

(2) Address correspondence concerning **1** to this author at the University of Utah. Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).

(3) Address correspondence concerning **2** to this author.

(4) This literature is extensive. Some lead reviews are as follows: (a) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (b) Articles contained in "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, D.C., 1981; *ACS Symp. Ser.* No. 152. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (e) Herrmann, W. A. *Ibid.* **1982**, *20*, 159.

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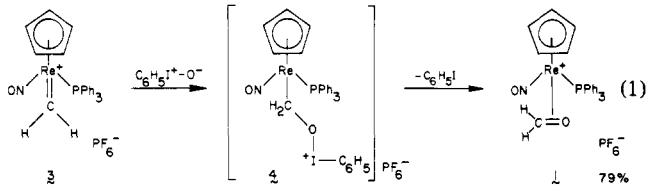
Table I. Spectroscopic Properties of **1** and **2**

	1	**2**
IR (cm^{-1}, CH_2Cl_2)	$\nu_{N\equiv O}$ 1744 s	$\nu_{N\equiv O}$ 1752 s
^1H NMR (δ, acetone-d_6)		
PPh_3	7.76-7.51 (m, 15 H)	7.75-7.44 (m, 15 H)
C_5H_5	6.40 (s, 5 H)	6.41 (d, J_{HP} = 0.8 Hz, 5 H)
$H_2C{=}X$	4.93 (dd, J_{HH} = 16.8 Hz, J_{HP} = 2.3 Hz, 1 H), 4.38, (dd, J_{HH} = 16.8 Hz, J_{HP} = 1.2 Hz, 1 H)	5.08 (m, 1 H), 3.89 (dd, J = 1.5 and 0.8 Hz, 1 H)
^{13}C NMR (ppm)	acetone-d_6	CD_3CN
PPh_3	134.5 (d, $^2J_{CP}$ = 10.8 Hz), 133.7 (s), 130.6 (d, $^3J_{CP}$ = 11.3 Hz), 128.4 (d, $^1J_{CP}$ = 59.7 Hz)	134.7 (d, $^2J_{CP}$ = 9.9 Hz), 133.9 (d, $^4J_{CP}$ = 1.5 Hz), 130.5 (d, $^3J_{CP}$ = 11.5 Hz), 128.7 (d, $^1J_{CP}$ = 61.8 Hz)
C_5H_5	100.4 (s)	100.9 (s)
$H_2C{=}X$	60.6 (s)[a]	30.5 (s)

[a] Gated decoupled spectrum shows J_{CH} of 179 and 184 Hz.

interest in chalcogenide homologues of C_1 oxygenate precursors,[7] the synthesis of η^2-$H_2C{=}S$ complexes[7b-e] was also investigated. In this communication, we report (a) syntheses of the formaldehyde complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (**1**) and the thioformaldehyde complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (**2**), (b) X-ray crystal structures of **1** and **2**, and (c) some basic reactions of **1** and **2**, including their facile reduction to OCH_3 and SCH_3 complexes.

Our strategy for the synthesis of **1** was to treat the electrophilic methylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**3**)[8] with an oxygen nucleophile $X^+\text{–}O^-$. To avoid possible $H_2C{=}O$ displacement, we sought a reagent in which the leaving group X would have minimal nucleophilicity. Reaction of **3** with $(CH_3)_3N^+\text{–}O^-$ did not give tractable products. However, reaction of **3** with $C_6H_5I^+\text{–}O^-$ (CH_2Cl_2, –23 °C, 3 h) gave **1** in 79% crude yield (eq 1). Diffusion crystallization of **1** from CH_2Cl_2/hexane



(1)

gave bronze, air-stable crystals.[9] Spectral properties are summarized in Table I. We envision the conversion **3** → **1** as proceeding via the intermediate **4** (eq 1).

We investigated similar routes for the synthesis of thioformaldehyde complex **2**. The reaction of **3** with $Ph_3P^+\text{–}S^-$ (1 equiv or excess) was rapid at –78 °C. However, inseparable equimolar mixtures of *two* products, **2** and the previously reported[8a] methylidene adduct $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (**5**), were obtained. We ascribed the formation of **5** to the combination

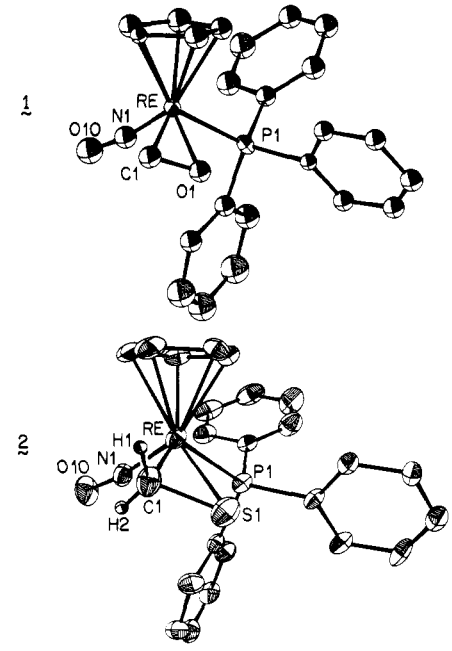


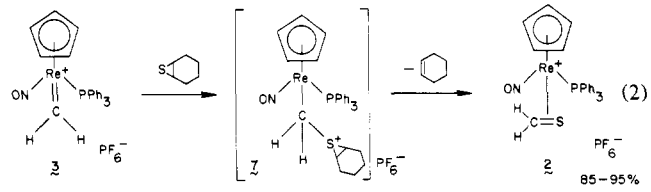
Figure 1. Molecular structures of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (**1**) and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (**2**).

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in **1** and **2**

atoms	**1**	**2**
Bond Lengths (Å)		
Re-C1	2.108 (18)	2.199 (8)
Re-O1, Re-S1	2.036 (11)	2.381 (2)
C1-O1, C1-S1	1.374 (19)	1.742 (9)
Re-N1	1.735 (14)	1.752 (6)
Re-P1	2.455 (4)	2.437 (2)
Re-C_5H_5[a]	2.316	2.292
N1-O10	1.184 (17)	1.171 (8)
Bond Angles (deg)		
Re-C1-O1, Re-C1-S1	67.8 (9)	73.3 (3)
Re-O1-C1, Re-S1-C1	73.5 (9)	62.2 (3)
C1-Re-O1, C1-Re-S1	38.7 (5)	44.5 (2)
N1-Re-P1	88.4 (5)	88.5 (2)
N1-Re-C1	95.9 (7)	90.6 (3)
N1-Re-O1, N1-Re-S1	105.7 (5)	106.5 (2)
P1-Re-C1	116.3 (5)	122.2 (2)
P1-Re-O1, P1-Re-S1	79.1 (3)	80.9 (1)
Re-N1-O10	171.7 (13)	172.5 (7)

[a] Average distance from Re to C_5H_5 carbons.

of unreacted **3** with PPh_3 liberated from intermediate $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SPPh_3)]^+PF_6^-$ (**6**). Fortunately, treatment of **3** with cyclohexene sulfide gave **2** in 85–95% yields after solvent removal and CH_3CN/ether recrystallization.[9] This conversion is envisioned as proceeding via the sulfonium salt **7** (eq 2). We have previously shown that **3** undergoes similar adduct



(2)

formation with acyclic sulfides.[10] Spectroscopic properties of **2** are summarized in Table I.

The diastereotopic $H_2C{=}X$ protons of **1** and **2** have different NMR chemical shifts, as shown in Table I. No coalescence was

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observed upon warming to 100 °C ($CDCl_2CDCl_2$) and 52 °C (acetone-d_6), respectively. Since η^1 and η^2-$H_2C{=}X$ coordination cannot be rigorously distinguished by NMR, we determined the X-ray crystal structures of **1** and **2**.

X-ray data were collected for **1** and **2** at −158 and 25 °C, respectively, as described in the supplementary material. Crystals of **1** belonged to the monoclinic system, space group $P2_1$ (Z = 4), a = 10.113 (3) Å, b = 18.928 (7) Å, c = 13.300 (4) Å, β = 105.03(2)°. Refinement (supplementary material) yielded the structural data in Figure 1 and Table II. Final R indices were R = 0.043 and R_w = 0.052, and the goodness of fit was 1.49. Crystals of **2** belonged to the monoclinic system, space group $P2_1/c$ (Z = 4), a = 9.688 (2) Å, b = 18.536 (4) Å, c = 14.895 (5) Å, β = 103.53 (2)°. Refinement yielded the structural data in Figure 1 and Table II. The final R indices were R = 0.060 and R_w = 0.081, and the goodness of fit was 1.89. In **2**, $H_2C{=}X$ hydrogen atoms were located. Distances and angles (unrefined) are as follows: C1-H1, 1.14 Å; C1-H2, 0.81 Å; H1-C1-H2, 121°; S1-C1-H1, 120°; S1-C1-H2, 108°.

The C-O bond length in **1**, 1.374 (19) Å, is significantly longer than the C=O bond length in free formaldehyde (1.225 Å)[11a] but is slightly shorter than typical C-O single-bond distances (1.41-1.43 Å).[11b] It is close to those found by Berke for $Fe(CO)_2(P(OCH_3)_3)_2(\eta^2\text{-}H_2C{=}O)$ (1.32 (2) Å)[6c,d] and Floriani for $(\eta\text{-}C_5H_5)_2V(\eta^2\text{-}H_2C{=}O)$ (1.353 (10) Å)[6e] but is substantially shorter than that found by Roper for $Os(CO)_2(PPh_3)_2(\eta^2\text{-}H_2C{=}O)$ (1.584 (11) Å).[6a,b]

Complex **2** is the first mononuclear thioformaldehyde complex to be structurally characterized. The C-S bond length, 1.742 (9) Å, is intermediate between that found in $H_2C{=}S$ (1.6108 (9) Å)[12] and typical C-S single bonds (1.80-1.82 Å).[11c] It is significantly shorter than those determined by Adams for a series of triosmium μ_2- and μ_3-thioformaldehyde complexes (1.788 (11)-1.872 (12) Å).[7c-e]

The lengthened $H_2C{=}X$ bonds in **1** and **2** reflect the fact that the $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)^+$ moiety is an extremely good donor. The rhenium HOMO has been shown by Eisenstein[13] to be a d orbital that is bisected by the Re-P bond and perpendicular to the Re-NO bond. Figure 1 shows that **1** and **2** adopt conformations that maximize overlap of the $H_2C{=}X$ π^* orbitals with this HOMO.[14]

The chemistry of **1** and **2** is currently under intensive study. After 19 h at 51 °C in CD_3CN, **1** was converted to a ca. 50:50 mixture of **1** and the nitrile complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3CN)]^+PF_6^-$.[8b] Under identical conditions, **2** showed no sign of reaction. In contrast to other mononuclear η^2-$H_2C{=}X$ complexes,[6,7b] we have not yet obtained well-defined products from reactions of **1** and **2** with electrophiles. However, both **1** and **2** are attacked by nucleophiles. Treatment of **2** with $NaBH_3CN/CH_3OH$ gave, after workup and $CHCl_3$/heptane recrystallization, the thiomethyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_3)$ (**8**)[9] as bright red crystals in 85% yield. Similar conditions converted **1** to a mixture of products. However, **1** and formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$[8a] rapidly reacted at −25 °C to give $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ and methoxide $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$ (**9**)[9] (99% and 74% yields vs. Ph_3SiCH_3 standard). Workup gave spectroscopically pure **9** in 52% yield; deep red crystals were obtained from benzene/hexane. Hydride transfer from a formyl to a formaldehyde ligand is, in our opinion, also a plausible route to catalyst-bound methoxides. Finally, reaction of **1** with PPh_3 gave a μ_2-$H_2C{=}O$ adduct which we assign on the basis of NMR data[9] as the ReOCP regioisomer $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_2PPh_3)]^+PF_6^-$ (**10**). This compound, which can be isolated in 89% yield as orange-red needles, equilibrates to a (84 ± 2):(16 ± 2) **10** ⇌ **1** + PPh_3 mixture in acetone. Facile $\mu_1 \rightleftharpoons \mu_2$ $H_2C{=}O$ equilibria may also be important in catalytic CO reduction.

In summary, the methodology described in this communication should, in view of the increasing numbers of electrophilic alkylidene complexes that are available,[15] allow access to a series of new $H_2C{=}O$ and $H_2C{=}S$ (and possibly RCH=O and RCH=S) complexes. These can be expected to have a rich chemistry which will bear upon important mechanistic issues in transition-metal catalysis.

Acknowledgment. We thank the Department of Energy for support of this research. The crystal structure determination of **1** and FT NMR measurements made use of equipment obtained via NSF departmental instrumentation grants. W.E.B. thanks the Regents of the University of California for a Fellowship.

Registry No. 1, 84369-16-4; **2**, 84369-18-6; **3**, 71763-23-0; **5**, 71763-25-2; **8**, 84369-19-7; **9**, 84369-20-0; **10**, 84369-22-2; $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$, 79919-50-9.

Supplementary Material Available: Spectral,[9] microanalytical,[9] and crystallographic (**1**, **2**)[13] data (85 pages). Ordering information is given on any current masthead page.

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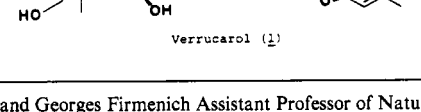
Total Synthesis of (±)-Verrucarol

William R. Roush*[1] and Thomas E. D'Ambra

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received November 5, 1982

The epoxytrichothecenes are a group of secondary fungal metabolites that possess antibiotic, antifungal, antiviral, and/or cytotoxic properties.[2] The fungi responsible for producing these terpenoids (various *Trichothecium*, *Myrothecium*, and *Fusarium* species, among others) have been implicated in a number of diseases of humans, animals, and plants. Certain members of this group, most notably T-2 toxin, nivalenol, and anguidine, have gained considerable notoriety in recent months as a consequence of the "yellow rain" problem.[3] Our interest in these compounds stems from their activity as potent inhibitors of protein synthesis in eucaryotes. For example, the macrocyclic di- and triester derivatives of verrucarol (**1**) possess promising antitumor activity.[2a]



Verrucarol (1)

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