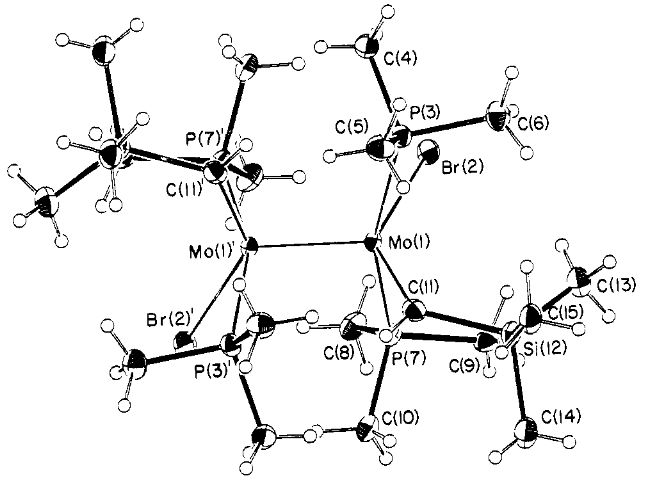

Figure 1. ORTEP view of the $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$ molecule viewed down the C_2 axis of symmetry. Some pertinent bond distances (Å) and angles (deg) are as follows: Mo–Mo = 2.276 (1), Mo–Br = 2.636 (1), Mo(1)–P(3) = 2.535 (2), Mo(1)–P(7) = 2.534 (2), Mo(1)–C(11) = 1.949 (5), Mo–Mo–Br = 116.54 (3), Mo(1)′–Mo(1)–P(3) = 101.54 (4), Mo(1)′–Mo(1)–P(7) = 97.98 (4), Mo(1)′–Mo(1)–C(11) = 109.0 (2), Mo(1)–C(11)–Si(12) = 129.8 (3), Mo(1)–C(11)–H(19) = 120 (3).

I has been characterized by elemental analyses, NMR spectroscopy (^1H, ^{13}C, ^{31}P), and a single-crystal X-ray study.[5] An ORTEP view of the molecule found in the crystal is shown in Figure 1. The molecule has rigorous C_2 symmetry, and the two ends of the molecule are virtually eclipsed, presumably because this minimizes PMe_3–PMe_3 steric repulsions.[6] The solid-state structure is readily reconciled with the observed NMR data and the latter indicate that there is restricted rotation about the Mo–Mo bond.

The Mo–Mo distance of 2.276 (1) Å is indicative of a Mo≡Mo bond,[7] which rather interestingly can be viewed as arising in one of two ways: (i) If the Me_3SiCH ligand is counted as a dianion, then the formal oxidation state for Mo is 3+, giving rise to a d^3–d^3 triple bond of configuration $\sigma^2\pi^4$. (ii) If the Me_3SiCH ligand is viewed as a neutral two-electron donor, the oxidation state of Mo is 1+, giving rise to a d^5–d^5 dimer and a Mo≡Mo bond of configuration $\sigma^2\pi^4\delta^2\delta^{*2}$. However, the two electrons on each molybdenum that might be used to form δ and δ^* Mo–Mo bonds occupy molybdenum d_{xy} orbitals, which have the appropriate symmetry to backbond to the vacant carbon p_z atomic orbitals. The short Mo–C distance, 1.949 (5) Å, and the alignment of the planar Mo–C(H)Si groups provide good evidence for Mo-to-C double bonds.

A number of interesting points emerge: (1) The close relationship between mononuclear and dinuclear chemistry is seen in a comparison of I and II and their respective formation in reactions 1 and 2,[8] respectively. In both I and II, the metal atoms form triple, double, and single bonds and two dative bonds with PMe_3 ligands. The structural analogy between I and $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(Me_2PCH_2CH_2PMe_2)$[9] is most

$$\underset{\mathbf{2}}{W(\equiv CCMe_3)(CH_2CMe_3)_3} + 2PMe_3 \rightarrow \underset{\mathrm{II}}{W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2} + CMe_4 \quad (2)$$

striking: in both molecules, each metal atom is in a distorted square-based pyramidal geometry with the M≡X function occupying the axial position. (2) In I, each molybdenum attains a share of 16 valence electrons, and the Me_3SiCH ligand is not of the "grossly distorted" type of alkylidene ligand commonly observed when an electron-deficient early transition metal shows incipient M–H and M≡CR bond formation.[10] This is quite evident from the relatively small Mo–C–Si angle of 129° and the relatively long Mo–C bond distance 1.949 (5) Å when compared to "distorted" alkylidene ligands bound to tungsten. (3) The remarkably low chemical shift value, δ 14 downfield from Me_4Si, of the Me_3SiCH ligand is reconcilable with its position directly over the Mo≡Mo bond.[11]

Further studies are in progress.[12]

Registry No. I, 83214-27-1; Mo, 7439-98-7.

Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for the $Mo_2Br_2(CHSiMe_3)_2(PMe_3)_4$ molecule (3 pages). Ordering information is given on any current masthead page.

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[5] Anal. Calcd (found): C, 29.00 (29.09); H, 6.81 (6.83); Br, 19.29 (19.30). ^1H NMR (toluene-d_8 solvent, 16 °C) δ 0.80 (s, $SiMe_3$), 1.45 (d, J = 7Hz), 1.55 (d, J = 7Hz, PMe_3, 14.1 (m, =CHSi); $^{13}C\{^1H\}$ NMR δ 283 (m, =CHSi), 17.5 (d, J_{P-C} = 23 Hz, PMe_3), 19.5 (d, J_{P-C} = 24 Hz); (iii) $^{31}P\{^1H\}$ NMR δ −17 and −28 (J = 140 Hz (δ relative to H_3PO_4 external reference)). Crystal data at −165 °C: a = 20.461 (11) Å, b = 9.918 (4) Å, c = 20.468 (11) Å, α = 120.67 (2)°, Z = 4, d_{calcd} = 1.540 g cm^{-3}, and space group $A2/a$. Of the 2802 reflections collected, the 1629 having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. Final residuals are R_F = 0.023 and R_{wF} = 0.027.

[6] The eclipsed conformation is also seen in $Re_2Cl_4(PR_3)_4$ compounds, which have Re≡Re bonds of configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ and has been rationalized in terms of minimizing PR_3–PR_3 steric repulsions (R = Me or Et). See: Cotton, F. A.; Walton, R. A. In "Multiple Bonds between Metal Atoms"; Wiley: New York, **1982**.

[7] For a listing of Mo–Mo distances in compounds containing a central $(Mo\equiv Mo)^{6+}$ unit, see Cotton and Walton in ref 6.

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[12] We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

O-Methylation and O-Protonation of Coordinated Nitric Oxide. Observation of an Anion-Assisted O-H to M-H Tautomerization

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The reactivity of the nitric oxide ligand coordinated to transition metals is varied.[1] Not only is it susceptible to nucleophilic attack in some complexes, but it also reacts with electrophiles in others. Several studies of the reaction of protons with various M–NO groups have resulted in products containing a new N–H bond.[2–4] For instance, treatment of $OsCl(CO)(PPh_3)_2(NO)$ with HCl yields $OsCl_2(CO)(PPh_3)_2(HNO)$,[2] which has been structurally characterized[4] and found to contain an HNO ligand coordinated to the Os via the nitrogen. Until recently studies of the reactions of coordinated NO have been limited to mononuclear complexes. We have undertaken studies of the reactivity of cluster-bound nitrosyl ligands and report here the reactions of $[Ru_3(CO)_{10}(NO)]^-$, **1** (Scheme I), with electrophiles that lead to the first well-defined compounds resulting from O-methylation or O-protonation of coordinated NO.

A 20-mL methylene chloride solution of $PPN[Ru_3(CO)_{10}(NO)]$ (182 mg, 0.158 mmol), prepared by the reaction of $PPNNO_2$ with $Ru_3(CO)_{12}$,[5] was reacted with a stoichiometric amount of $CF_3SO_3CH_3$ at room temperature. The initially deep yellow-green solution became bright lemon yellow upon addition of the CF_3-

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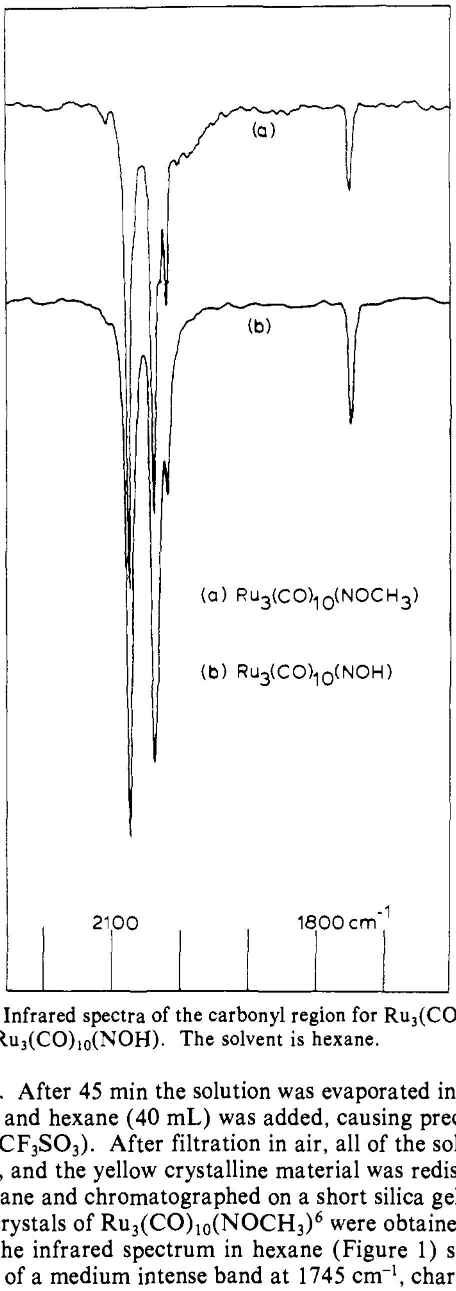

Figure 1. Infrared spectra of the carbonyl region for $Ru_3(CO)_{10}(NOCH_3)$ and $Ru_3(CO)_{10}(NOH)$. The solvent is hexane.

SO_3CH_3. After 45 min the solution was evaporated in vacuo to ~2 mL, and hexane (40 mL) was added, causing precipitation of $PPN(CF_3SO_3)$. After filtration in air, all of the solvent was removed, and the yellow crystalline material was redissolved in pure hexane and chromatographed on a short silica gel column. Yellow crystals of $Ru_3(CO)_{10}(NOCH_3)$[6] were obtained in 66% yield. The infrared spectrum in hexane (Figure 1) shows the presence of a medium intense band at 1745 cm^{-1}, characteristic of a $M_3(\mu_3\text{-CO})$ group. The infrared spectrum in a KBr pellet was similar and allowed the observation of a ν_{C-O} at 1040 (m) cm^{-1} and a ν_{N-O} at 945 (w) cm^{-1} ($\nu_{^{15}N-O}$ 922 cm^{-1}). The ^1H NMR exhibits a singlet due to the methyl group that appears at 3.45 ppm and splits into a doublet when the compound is 90% enriched with ^{15}N ($J_{^{15}N-^1H}$ = 4.4 Hz). The ^{15}N NMR spectrum exhibits a resonance at 285.8 ppm (downfield from NH_3), which is 529 ppm *upfield* from the resonance of $[Ru_3(CO)_{10}(NO)]^-$.

A single-crystal X-ray crystallographic analysis[7] revealed that the product was indeed the O-methylated species containing a $\mu_3\text{-NOCH}_3$ ligand and a μ_3-CO. Figure 2 shows the molecular structure and the atom labels. The cluster lies on a crystallographic mirror plane that passes through C-O-N-Ru-C22-O22-C10-O10. Except for the O-CH_3 group, however, the molecular symmetry closely fits into the point group C_{3v}. The oxygen is tilted toward Ru2 as measured by the Ru2-N-O angle of 117.6 (3)° compared to the Ru1-N-O angle of 132.8 (2)°. One of the hydrogens was located in the final difference Fourier map, and the position of the remaining hydrogen was calculated. Their coordinates are included; however, they were not included in any further structure factor calculations. It is interesting to compare this structure with that of $Fe_3(CO)_{10}[NSi(CH_3)_3]$.[8] The trigonal-bipyramidal $M_3(\mu_3\text{-NR})(\mu_3\text{-CO})$ core is the same, but the orientation of the $M(CO)_3$ groups is different. In $Fe_3(CO)_{10}[NSi(CH_3)_3]$, three of the carbonyls lie in the Fe_3 plane such that the point group of the molecule is C_3 (or C_{3h}, if the triply bridging groups are not included). As is the case with $Fe_3(CO)_{10}[NSi(CH_3)_3]$[9] and related clusters,[10,11] the μ_3-CO of $Ru_3(CO)_{10}(NOCH_3)$ can be replaced by reaction with H_2 to give $H_2Ru_3(CO)_9(NOCH_3)$.[12]

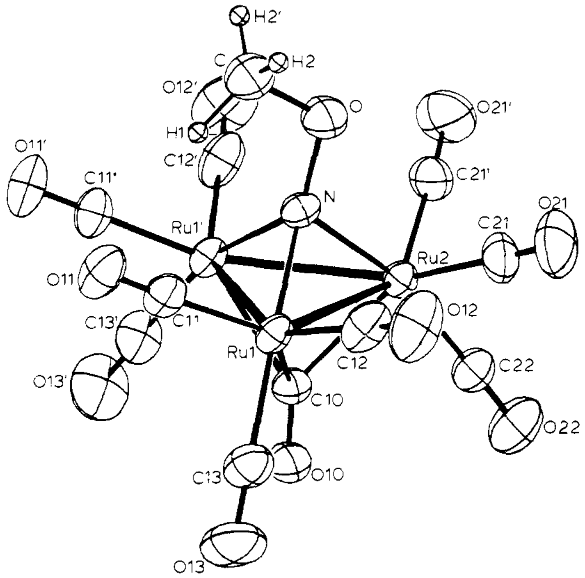

Figure 2. Structure of $Ru_3(CO)_{10}(NOCH_3)$ with the atom labels. Selected distances (Å): Ru1-Ru1', 2.740 (1); Ru1-Ru2, 2.762 (1); Ru1-N, 2.027 (3); Ru2-N, 2.006 (4); N-O, 1.433 (6); C-O, 1.391 (8); Ru1-C10, 2.188 (4); Ru2-C10, 2.150 (6); C10-O10, 1.175 (6); Ru-CO (av), 1.933 (9); C-O (av), 1.13 (1). Selected angles (deg); N-O-C, 112.1 (5); Ru1-N-Ru2, 86.5 (2); Ru1-Ru2-N, 47.1 (1); Ru2-Ru1-C10, 49.8 (2); Ru1-C10-O10, 133.4 (3); N-Ru2-C22, 166.3 (2).

The conversion of the μ_2-NO ligand to a $\mu_3\text{-NOCH}_3$ group is interesting, and we were curious to see if thermolysis would promote formation of $[Ru_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-NO})]^-$ or possibly $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-NO})]^-$. When $PPN[Ru_3(CO)_{10}(NO)]$ (180 mg, 0.156 mmol) was heated in refluxing tetrahydrofuran for 2 h, the red ether-soluble product, tentatively identified as $PPN[Ru_5N(CO)_{14}]$,[13] was isolated in 5% yield. Other examples of the deoxygenation of a nitrosyl ligand forming CO_2 and nitrido clusters have been reported.[14,15]

O-Alkylation of carbonyl ligands has recently been observed to give the COR[16-22] ligand. Commonly, the compounds that have

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[6] IR (ν_{C-O}) 2106 w, 2069 vs, 2032 vs, 2026 m, 2017 s, 1745 m cm^{-1} (hexane), ν_{O-C} 1040 m cm^{-1}, ν_{N-O} 945 w cm^{-1} (KBr); mass spectrum, m/z 602, parent not observed, followed by ten peaks each corresponding to a loss of carbon monoxide. Calcd: C, 21.03; H, 0.48; N, 2.23. Found: C, 21.44; H, 0.49; N, 2.11.

[7] X-ray diffraction data for $Ru_3(CO)_{10}(NOCH_3)$: crystal system orthorhombic; space group *Pnma*; a = 14.775 (4), b = 12.128 (2), c = 9.987 (2) Å; V = 1790 (1) Å^3; Z = 4; absorption coefficient = 24.95 cm^{-1}; diffractometer, Enraf-Nonius CAD4; radiation, graphite monochromatized Mo K_α; scan range = $0° \leq 2\theta \leq 56°$; reflections collected = 2046 unique, 1557 with $F_o > 2.0\ \sigma F_0$; R = 0.025, R_w = 0.035.

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[12] IR (ν_{C-O}) 2115 w, 2078 m, 2057 s, 2049 vs, 2009 s, 2001 vs, 1988 w cm^{-1} (hexane); mass spectrum, m/z 604 (parent), followed by loss of OCH_3 and nine peaks each corresponding to a loss of carbon monoxide; ^1H NMR 3.48 (3 H), -17.18 (2 H) ($CDCl_3$). Anal. Calcd: C, 19.94; H, 0.84; N, 2.32. Found: C, 20.03; H, 0.90; N, 2.34.

[13] IR (ν_{C-O}) 2062 w, 2013 vs, 1999 s, 1958 m, 1819 w cm^{-1} (THF). Anal. Calcd: C, 41.41; H, 2.08; N, 1.93. Found: C, 41.38; H, 2.17; N, 1.91.

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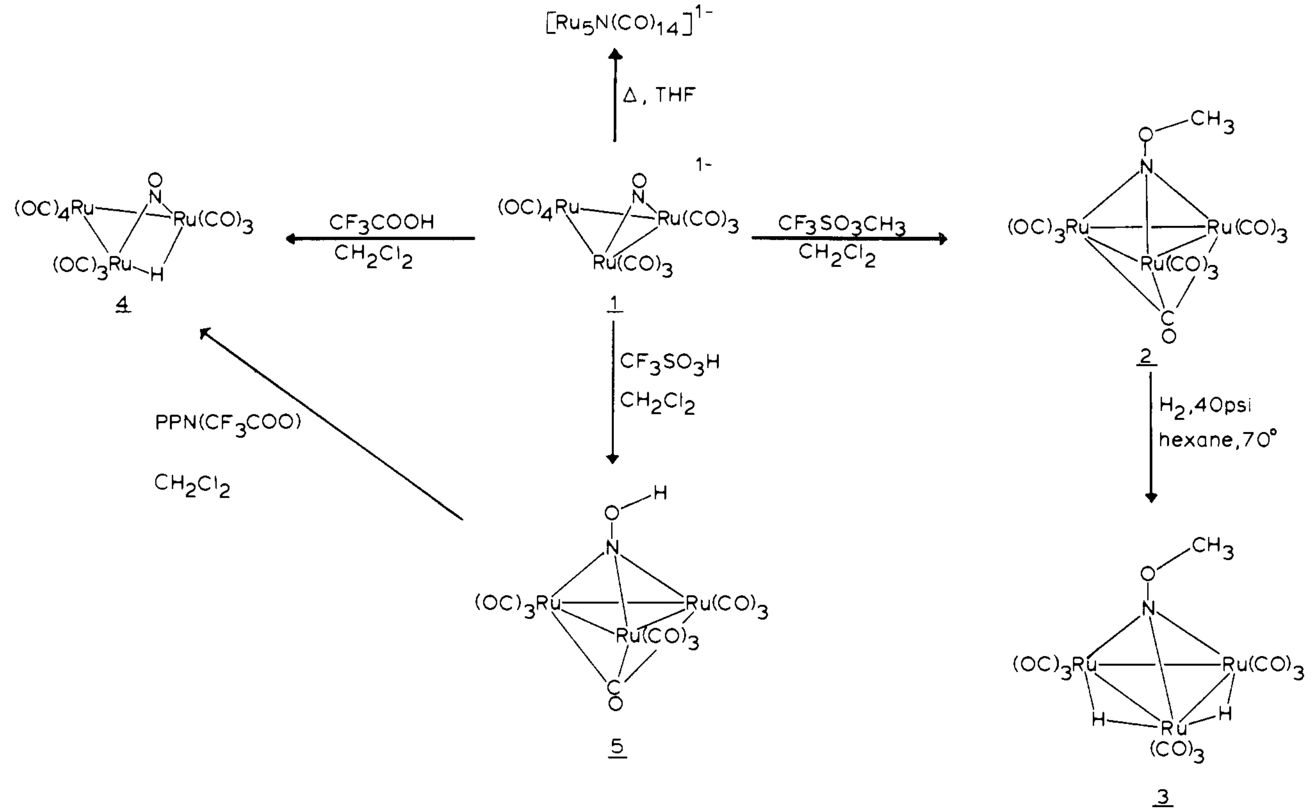
Scheme I



been successfully O-alkylated could also be O-protonated, forming the COH group, which in all cases is unstable except at low temperature.[23-26] We had previously studied[5] the reaction of PPN[$Ru_3(CO)_{10}(NO)$] with CF_3CO_2H in CH_2Cl_2, which gives red $HRu_3(CO)_{10}(NO)$,[27] **4**. When the analogous protonation was conducted with CF_3SO_3H in CH_2Cl_2, the solution turned bright lemon yellow, and the solution infrared spectrum of the product was very similar to that of $Ru_3(CO)_{10}(NOCH_3)$ (Figure 1). Further, a weak absorbance at 3495 cm^{-1} (CH_2Cl_2) is assigned to the ν_{O-H}, and the ν_{N-O} is observed at 1110 cm^{-1} ($\nu_{^{15}N-O}$ 1090 cm^{-1}). A singlet in the ^1H NMR spectrum is found at 8.90 ppm, which compares to 11.25 and 13.2 ppm for the COH in $Co_3(CO)_9(COH)$[24] and $HFe_4(CO)_{12}(COH)$,[26] respectively. The chemical shift of the hydrogen in $HRu_3(CO)_{10}(NO)$ is −11.85 ppm. The ^{15}N NMR spectrum exhibits a resonance at 250.6 ppm, which compares to 807.7 ppm for $HRu_3(CO)_{10}(NO)$. The shift in the nitrogen resonance in going from the μ_2-NO to the μ_3-$NOCH_3$ or μ_3-NOH is substantially larger in magnitude and in the opposite direction of that observed for the unique carbon resonance when converting $[HFe_4(CO)_{13}]^-$ to $HFe_4(CO)_{12}(COCH_3)$ or $HFe_4(CO)_{12}(COH)$.[26] One trend that does seem to be analogous to the carbonyl shifts is that the μ_3-$NOCH_3$ resonance is further downfield than the μ_3-NOH group. Following the same procedure used for the isolation of $Ru_3(CO)_{10}(NOCH_3)$, a yellow hexane solution of $Ru_3(CO)_{10}(NOH)$, **5**, is obtained that cannot be chromatographed and from which a dark yellow oil is obtained upon solvent removal.

The product is assigned a structure analogous to $Ru_3(CO)_{10}(NOCH_3)$. The surprising feature about $Ru_3(CO)_{10}(NOH)$ is not so much that is forms but that it is remarkably stable compared to its carbonyl analogues. At room temperature a CH_2Cl_2 solution of $Ru_3(CO)_{10}(NOH)$ shows no conversion to $HRu_3(CO)_{10}(NO)$ or any other product. The second remarkable feature is the complete selectivity for the two different sites of protonation using the two different strong acids. The major difference between CF_3CO_2H and CF_3SO_3H is the much higher acidity of CF_3SO_3H ($H_0 = -13$)[28] compared to CF_3CO_2H ($H_0 \approx -3$).[29] O-protonation with CF_3CO_2H may simply be thermodynamically unfavorable, which can easily explain the observed selectivity. This statement would require that $Ru_3(CO)_{10}(NOH)$ be a stronger acid than $HRu_3(CO)_{10}(NO)$, which is proven below. The selectivity displayed by CF_3SO_3H must then be related to a higher kinetic barrier for M-protonation compared to O-protonation. There is increasing evidence from detailed studies[30,31] indicating that rates of proton transfer involving M–H groups are slow compared to O–H or N–H groups.

If the above analysis is correct, the result of mixing $Ru_3(CO)_{10}(NOH)$ with $PPN(CF_3CO_2)$ (even with less than 1 equiv) must be the formation of $HRu_3(CO)_{10}(NO)$. *When $Ru_3(CO)_{10}(NOH)$ dissolved in CH_2Cl_2 is mixed with 0.4 equiv of $PPN(CF_3CO)_2$ at room temperature, an instantaneous color change is observed, and the infrared spectrum confirms the presence only of $HRu_3(CO)_{10}(NO)$.* This reaction can be promoted by anions other than $CF_3CO_2^-$. Virtually the identical result obtains upon addition of 0.4 equiv of $PPN(NO_3)$ to a CH_2Cl_2 solution of $Ru_3(CO)_{10}(NOH)$. The relevance of this anion-assisted O–H to M–H tautomerization is not limited to nitrosyl chemistry. Developing a deeper understanding of the acidity of a NOH or a COH group and their interactions with anions may ultimately

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improve our knowledge of support effects in heterogeneous catalysis. Additional studies are in progress to elucidate the details of this tautomerization as well as the reactivity of these new compounds.

Acknowledgment. We gratefully acknowledge the National Science Foundation for support of this work (Grant No. CHE 8106096). R.E.S. thanks the University of Minnesota for an Institute of Technology Corporate Associate fellowship (1980–1982).

Registry No. 1, 79085-63-5; **2**, 83333-39-5; **3**, 83312-29-2; **4**, 73230-19-0; **5**, 83333-40-8; $CF_3SO_3CH_3$, 333-27-7; PPN[$Ru_5N(CO)_{14}$], 83312-28-1; CF_3SO_3H, 1493-13-6.

Supplementary Material Available: List of the atomic coordinates and thermal parameters and the observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Sterochemical Variations in the Cyclocondensation of Aldehydes with Siloxydienes. An Application to the Erythronolide Series

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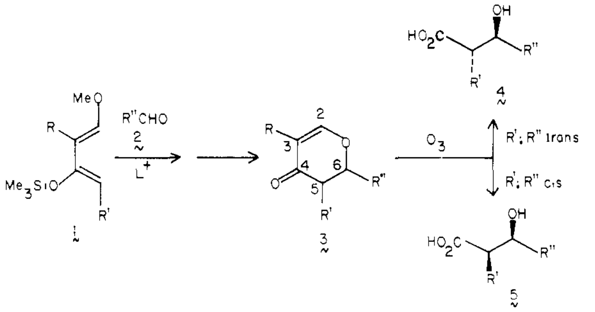
Received June 21, 1982

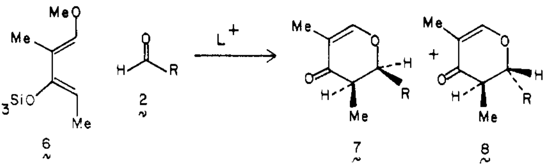
Recently, we reported on the Lewis acid (L^+) catalyzed reactions of aldehydes with siloxydienes.[1] For many applications the value of the reaction will be closely linked to the stereochemical control, which can be exercised at positions 5 and 6 of **3**. Below,

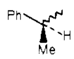


we report that this stereochemical outcome is subject to considerable influence by changing the Lewis acid catalyst. As a result of this finding, solutions to the synthesis of threo- (**4**) and erythro- (**5**) β-hydroxy acids *from the some substrates*, under very simply executed conditions, are now available.

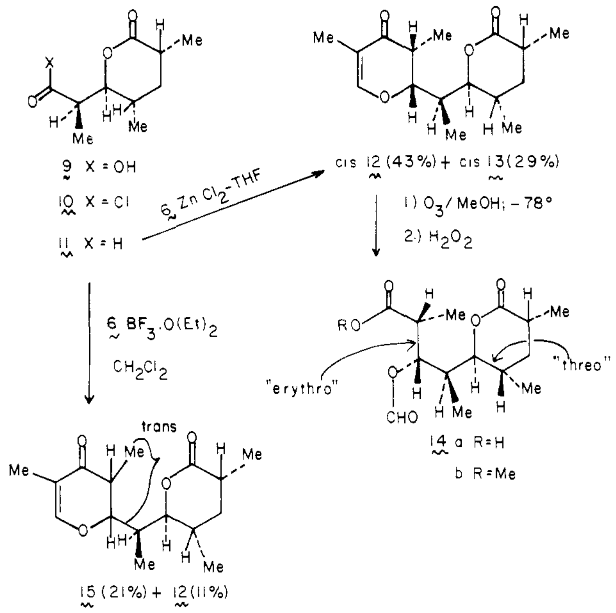
The silyloxydiene **6**[3] was chosen for this study because of its ready availability and stereochemical homogeneity. In examination of its reactions with a range of aldehydes under a wide variety of conditions, an important and remarkable discovery was realized. When the reaction was carried out with $BF_3 \cdot OEt_2$ as the catalyst in methylene chloride (−78 °C), consistent trans (i.e., threo) selectivity was noted as shown in Table I (see entries A).

Table I



	R	method	7, % yield	8, % yield
a	n-C_5H_{11}-	A[4]	21	69
		B[5]	91	2
b	Ph-	A	23	68
		B	78	<2[6]
c		A	17[7]	73[7]
		B	91[8]	<2[6]
d	$Ph(CH_2)_3$-	A	17	64
		B	83	<2[6]
e	$PhCH_2OCH_2$-	A	17	68
		B	66	24

Scheme I



However, when the reaction was carried out in tetrahydrofuran with zinc chloride as the catalyst, virtually complete cis (i.e., erythro) specificity was observed (see entries B). The only departure from this trend is that shown as entry e, method B, wherein cis specificity is eroded. The translatability (by ozonolysis) of dihydro-γ-pyrones to protected Reformatsky-type products of the types **4** and **5** had already been established[1b] and was again exploited in the synthesis of **14**. Application to a more complex setting was undertaken before exploring the mechanistic implications of these observations in detail. Toward that goal we prepared, according to Masamune,[2a,b] the lactonic aldehyde **11** (Scheme I) in two steps from the (Prelog–Djerassi) lactonic acid **9**. It will be recalled[1b] that **9** is prepared by a simple route,[1b] whose first step in the threo selective process shown as entry c, method A. Whereas the synthesis of **9** by our disconnective strategy required access to the threo series, the conversion of **11** → **12** requires fostering of the erythro modality (see arrows in structure

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(1) (a) Danishefsky, S.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.* **1982**, *104*, 358. (b) Danishefsky, S.; Kato, N.; Askin, D; Kerwin, J. F., Jr. *Ibid.* **1982**, *104*, 360. (c) Danishefsky, S.; Kerwin, J. F., Jr. *J. Org. Chem.* **1982**, *47*, 3803. (d) Danishefsky, S.; Kobayashi, S.; Kerwin, J. F., Jr. *Ibid* **1982**, *47*, 1981.

(2) (a) Masamune, S.; Hirama, M.; Mori, S.; Ali, Sk.A.; Garvey, D. S. *J. Am. Chem. Soc.* **1981**, *103*, 1568. (b) Masamune, S. In "Organic Synthesis Today and Tomorrow"; Trost, B. M., Hutchinson, D. R., Ed.; Pergamon Press: New York, 1980; pp 197–215.

(3) Danishefsky, S.; Yan, C.-F.; Singh, R. K.; Gammill, R. B.; McCurry, P. M., Jr.; Fritsch, N.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7001.

(4) Method A: (1) **2** (0.1 M, CH_2Cl_2), **6** (1.1 equiv), $BF_3 \cdot OEt_2$ (1.0 equiv) −78 °C, 1–2 h → aqueous $NaHCO_3$; (2) TFA catalyst (CCl_4) room temperature, 5 min.

(5) Method B: (1) **2** (0.1 M, THF), **6** (2.0 equiv), anhydrous $ZnCl_2$ (1.0 equiv) room temperature, 24–48 h, → aqueous $NaHCO_3$; (2) TFA catalyst (CCl_4), room temperature, 5 min.

(6) None of **8** was detected (NMR, TLC (SiO_2)) in the crude product mixture or isolated upon chromatographic purification.

(7) Only a single diastereomer (Cram adduct) was isolated.