solutions of the corresponding hydroquinones (with vastly improved yields) rather than by the literature method: O. Diels and K. Alder, *Chem. Ber.*, **62**, 2337 (1929). Catalytic hydrogenation of **17** (5% Pd C, C_2H_5OH, 1 Torr) furnished **18** quantitatively.

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(21) This subject is to be discussed in more detail separately.

(22) NATO Postdoctoral Fellow with financial support provided by the CNRS.

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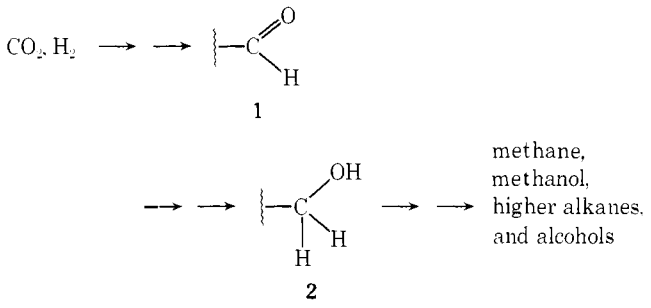
α-Silyloxy and α-Hydroxy Manganese Alkyls. Generation via a New Five-Membered Metallocycle

Sir:

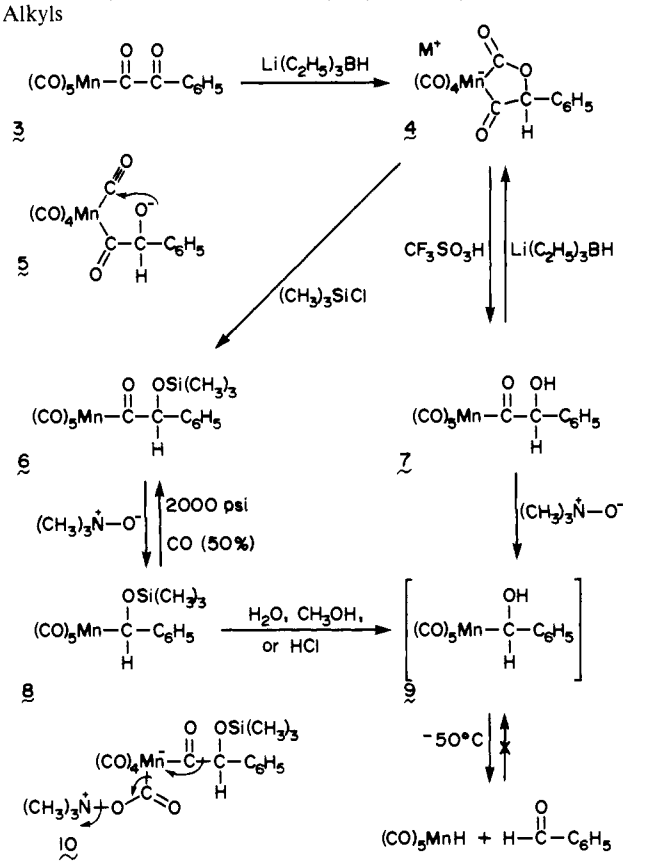
An ongoing research objective in our laboratory has been the generation of ligand types believed to be intermediate in the metal-catalyzed reduction of CO by H_2.[1-3] Since the ultimate reduction products range from methane and methanol to higher alkanes and alcohols (Fischer-Tropsch process),[4,5] there is considerable interest in discerning the factors which control product *selectivity*, and in developing milder and homogeneous catalysts for accomplishing these transformations.[6] Communicated herein are our initial efforts at preparing complexes containing the α-hydroxyalkyl ligand (**2**) and silylated derivatives thereof. α-Hydroxyalkyl **2** has been proposed as a key mechanistic branch point in Fischer-Tropsch reactions,[5,7] and is virtually a required intermediate in the Union Carbide ethylene glycol synthesis.[8] We also wish to report the X-ray structural characterization of a novel metallocyclic system which serves as the fulcrum of our syntheses.



Benzoylformylmanganese pentacarbonyl (**3**, 10 mmol)[1,9] in THF (30 mL) was treated with $Li(C_2H_5)_3BH$ (12 mmol)[10] under nitrogen. Infrared monitoring[11] suggested that an octahedral cis-disubstituted manganese tetracarbonyl product was quantitatively formed. Although we previously reported that $Li(C_2H_5)_3BH$ attacks metal carbonyl acyls at carbon monoxide, yielding kinetically unstable anionic formyl complexes,[2] no characteristic formyl ^1H NMR resonance could be detected, even when this reaction was conducted at −60 °C in a NMR tube.

After 15 min, $PPN^+ Cl^-$ (10 mmol)[12] dissolved in CH_2Cl_2 (50 mL) was added to the reaction mixture. Solvent was removed and the residue extracted with ether (400 mL). Concentration and cooling (0 °C) afforded a yellow precipitate (two crops, 5.73 g, 6.6 mmol, 66%), which could be rendered analytically pure by first washing with cold ether and then extracting into THF. Solvent removal yielded a gold powder (46% overall) for which analytical and spectral data suggested the structure PPN^+-**4** (Scheme I).[13]

Scheme I. Synthetic Routes to α-Silyloxy and α-Hydroxy Manganese Alkyls



The formation of **4** is proposed to occur via intermediate **5**. In light of this unprecedented mode of metallocycle closure, an X-ray crystal structure was undertaken.

Slow recrystallization from ether-hexane afforded suitable air-stable crystals (dec pt 142–144 °C) for study. X-ray data were obtained at −160 ± 5 °C with monochromated Mo Kα (0.71069 Å) radiation on a Syntex $P\bar{1}$ automatic diffractometer. The general techniques employed have been previously described.[14] The unit cell was found to be triclinic, space group $P\bar{1}$ ($Z = 2$), with lattice parameters $a = 10.016$ (4), $b = 15.772$ (5), $c = 15.698$ (4) Å; $\alpha = 86.55$ (3), $\beta = 89.09$ (3), $\gamma = 118.62$ (3)°. Of 5697 reflections with $2\theta < 40°$, 2994 with $I \geq 3\sigma(I)$ were used in the final refinement. All seven phenyl rings were refined as rigid groups (C–C = 1.39 Å, C–H = 1.00 Å). A series of least-squares refinements of positional parameters of all atoms and groups, anisotropic thermal parameters of manganese and phosphorous atoms, and isotropic thermal parameters of all other nonhydrogen atoms converged to $R = 0.055$ and $R_w = 0.058$.[15] A difference Fourier map at this point revealed the location of the proton derived from $Li(C_2H_5)_3BH$, which was included in two further cycles of refinement. A final difference Fourier map showed no peaks larger than 0.4 e/Å. The final standard deviation of an observation of unit weight was 1.28.

The arrangement of ligands about the manganese atom is depicted in Figure 1. The metallocycle is essentially planar, and undergoes clean thermolysis (THF, 65 °C, 6 days) to $PPN[Mn(CO)_5]$, benzaldehyde, and CO.

The metallocycle **4** undergoes two key ring-opening reactions (Scheme I). When in situ prepared Li^+-**4** (1.01 mmol) was treated with $(CH_3)_3SiCl$ (12 mmol), a product formed over a 2-h period. The solvent was removed and the residue column chromatographed (5% EtOAc in hexane). The product eluted rapidly and crystallized upon solvent removal (0.96 mmol, 95% yield, mp 51–53 °C). Based upon micro- and spectral analyses,[16] the silyloxyacyl structure **6** is assigned. This preparation may be executed equally well utilizing

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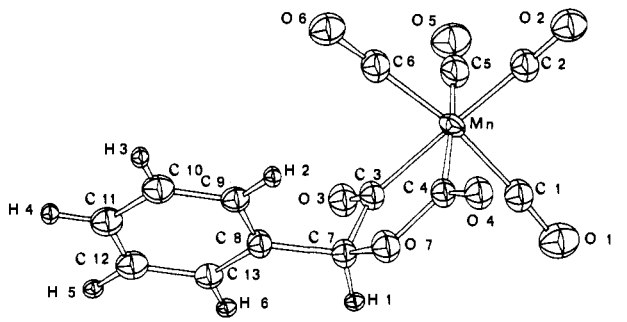

Figure 1. ORTEP drawing of the ligands about one manganese of the unit cell of PPN^+-**4.** The manganese atom is represented by its 50% probability ellipsoid for thermal motion; all other atoms are displayed as spheres based on isotropic thermal motion.

PPN^+-**4,** and the absence of a silyloxycarbene product suggests an operating equilibrium **4** ⇌ **5.**

Treatment of Li^+-**4** or PPN^+-**4** (1.01 mmol) with CF_3SO_3H (1.5–1.8 mmol) afforded the labile hydroxyacyl **7** in quantitative spectroscopic yield. The IR spectrum is nearly coincident with **6** and contains a prominent ν_{O-H}.[17] A broadened ^1H NMR spectrum could also be obtained.[17] Although **7** may be purified to an unstable oil, we have not succeeded in inducing crystallization. Significantly, Li^+-**4** could be re-formed from **7** by deprotonation with $Li(C_2H_5)_3BH$. The –OH group in **7** precludes direct hydroxyacyl synthesis by reaction of $(CO)_5Mn^-$ with an acylating agent. Thus the metallocycle provides a unique entry into the hydroxyacyl system.

Experimentation commenced on methodology for the decarbonylation of **6** and **7.** The anticipated thermal instability of the products led us to investigate *chemical* means for the removal of CO from manganese. Toward this end, **6** (0.29 mmol) in dry $CHCl_3$ (25 mL) was treated with anhydrous $(CH_3)_3N^+$–O^- (0.30 mmol). Reaction occurred over the course of 45 min at 25 °C. After solvent removal and column chromatography of the residue under N_2 (silica gel; 0.5% Et_2O in hexane), a labile oily product was obtained whose spectral[18] and chemical (vide infra) characteristics indicated it to be the silyloxyalkyl **8** (0.25 mmol, 86%). The transformation **6** → **8** is likely to involve the intermediate **10** (Scheme I).[19] Photolysis proved not to be a feasible decarbonylation method, since under the conditions employed (hexane, 0 °C, Hanovia 450-W lamp filtered to 320–360 nm)[20] authentic **8** was decomposed nearly as fast as it was formed from **6.**

At this stage, we sought to determine the effect of an α-oxy substituent on the ability of a metal alkyl to undergo the CO "insertion" reaction. Benzylmanganese pentacarbonyl is reported as inert to carbonylation,[21] and in our hands it remained unreacted after 1 hr under 2000 psi of CO in THF at 25 °C. However, under identical conditions **8** was 50% carbonylated to **6** (11% at 500 psi). Hence the introduction of an α-trimethylsilyloxy substituent dramatically enhances the ability of a benzyl ligand to migrate to coordinated CO.

Efforts were now directed at the generation of α-hydroxyalkyl **9** from precursors **7** and **8.** The attempted protodesilylation of **8** with $(n\text{-}C_4H_9)_4N^+F^-\cdot 3H_2O$ in THF (25 °C) yielded $(n\text{-}C_4H_9)_4N^+Mn(CO)_5^-$ and benzaldehyde instantaneously. These products are the ones that would be expected from a rapid collapse of an alkoxide intermediate generated by fluoride attack upon silicon.[22,23] Thus cleavage conditions which would entail the prior protonation of the ether oxygen were sought. By ^1H NMR, it was observed that the addition of H_2O (−10 °C) or CH_3OH (10 °C) to THF solutions of **8** resulted in the formation of equal amounts of $HMn(CO)_5$ and benzaldehyde (2–3 h; ≥80%) as the only detectable products. These are plausible decomposition products of **9.** In order to maximize the possibility of observing **9,** HCl gas (~2 equiv) was bubbled into a THF-d_8 solution of **8** at −50 °C. Even at this temperature, $HMn(CO)_5$ and benzaldehyde were formed rapidly (<3 min) and without detectable intermediates.[24] Significantly, the *same* products were cleanly generated by reaction of **7** with $(CH_3)_3N^+$–O^- over a 15-min period in CD_2Cl_2 at 25 °C.

The formation of identical products from **7** and **8** under decarbonylating and protodesilylating conditions, respectively, provides good evidence for a common intermediate for which we propose the structure **9.** The kinetic and thermodynamic[23] instability of this species with respect to $HMn(CO)_5$ and benzaldehyde, even at −50 °C, contrasts in two fundamental aspects with the behavior of the presumed intermediate **2** on Fischer–Tropsch type catalysts:[4-8] (a) the generation of aldehydes is not a major process under Fischer–Tropsch conditions[5] (production of formaldehyde is thermodynamically prohibited), and (b) the hydroxyalkyl ligand has a sufficient lifetime to undergo further reactions such as carbonylation or reduction. Hence a fundamental role of the heterogeneous or cluster catalysts able to effect CO reduction must be to alter the reactivity of ligand type **2** vis-à-vis that exhibited by mononuclear **9.** Finally, this study has also demonstrated that an α-oxy substituent can accelerate carbonylation of an alkyl ligand. The preparation of more stable homologues of **9** by variations of the methodology defined herein is under active pursuit.[25]

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Department of Energy, and the National Science Foundation (Instrumentation Grant CHE76-05926), for support of this research. J. C. Selover thanks the IBM Corporation for a fellowship.

Supplementary Material Available: Atomic positions, isotropic and anisotropic temperature factors, bond lengths and bond angles, and calculated and observed structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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(16) Anal. Calcd for $C_{16}H_{15}MnO_7Si$: C, 47.77; H, 3.76; Mn, 13.66. Found: C, 47.59; H, 3.91; Mn, 13.49. IR (cm^{-1}, $CHCl_3$): $\nu_{C\equiv O}$ 2119 (m), 2048 (m, sh), 2020 (vs); $\nu_{C=O}$ 1638 (m). ^{13}C NMR ($CDCl_3$): 285.6, 210.8, 128.4, 127.8,

126.5, 90.1, 1.0 ppm. ^{1}H NMR (CCl_4); δ 7.33 (m, 5 H), 4.68 (s, 1 H), 0.20 (s, 9 H). Mass spectrum: *m/e* 223 (19%, $Mn(CO)_6^+$), 179 (68, $[CH(C_6H_5)(OSi(CH_3)_3)]^+$), 106 (91, $(C_6H_5CHO)^+$), 105 (100, $(C_6H_5CO)^+$).

(17) IR (cm^{-1}, $CHCl_3$): ν_{O-H} 3610–3260 (s, br); $\nu_{C\equiv O}$ 2116 (m), 2052 (m, sh), 2016 (vs); $\nu_{C=O}$ 1639 (m). ^{1}H NMR ($CDCl_3$): δ 7.5 (5 H), 6.2 (1 H), 5.0 (1 H).

(18) IR (cm^{-1}, hexane): 2118 (m), 2024 (vs), 2005 (s). ^{13}C NMR (CD_2Cl_2): 195.9, 129.9, 125.7, 123.0, 74.8, 1.1 ppm. ^{1}H NMR (CD_2Cl_2): δ 7.30 (s, 5 H), 6.07 (s, 1 H), 0.71 (s, 9 H). Mass spectrum: *m/e* 196 (8%, $HMn(CO)_5^+$), 195 (4, $Mn(CO)_5^+$), 179 (12, $[CH(C_6H_5)(OSi(CH_3)_3)]^+$), 106 (100, $(C_6H_5CHO)^+$).

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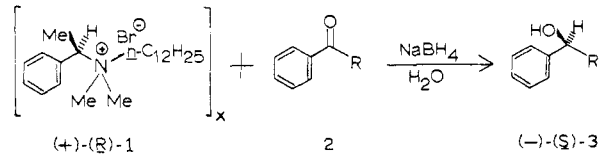
Micelle-Enzyme Analogy: Stereochemical and Substrate Selectivity

Sir:

Stabilizing forces, solution properties, and catalytic activities of aqueous micelles tend to parallel the corresponding characteristics of globular enzymes, thereby constituting the basis of an intriguing and potentially useful analogy.[1-4] The stereochemical component of the analogy, however, is not well established, although aqueous micellar systems have been observed to display manifestations of stereochemical effects consistent with enzymic behavior: the rate and stereochemical course of nitrous acid deamination of 2-aminooctane is significantly affected by micellization;[5a] rapid and selective hydrolyses of enantiomeric *p*-nitrophenyl esters are promoted by nonracemic micelles;[5b] and micelles formed from anionic surfactants materially alter the nonmicellar stereochemistry and hydrolysis rates of water-soluble sulfonates.[5c]

This communication describes some preliminary results which strengthen the micelle-enzyme analogy, for they clearly show the presence of the enzyme characteristics of stereochemical and substrate selectivity in the aqueous micellar system formed from enantiomerically pure (+)-(*R*)-*N*-dodecyl-*N*,*N*-dimethyl-α-phenylethylammonium bromide[6] (**1**) in a way different from previous examples.

Each of the phenyl ketones, **2**, (1×10^{-2} M), solubilized by **1** ($1\text{-}2 \times 10^{-2}$ M), was reduced slowly (~24 h) by the action of sodium borohydride (6×10^{-3} M) at room temperature to the corresponding carbinol, **3**, which was isolated, purified



(+)-(R)-1 2 (−)-(S)-3

(silicic acid chromatography), and identified by comparison with authentic material. Each carbinol was determined to be optically active, and the chiroptical data, which are given in Table I, show micellar **1** to possess the enzymic properties of stereochemical and substrate selectivity.

Stereochemical selectivity is manifest by the fact that the enriched enantiomer of each levorotatory nonracemic carbinol, **3**, possesses the same absolute configuration.[7-9] This suggests that solubilization (binding) of each prochiral ketone by micellar **1** is not only stereochemically ordered (on the time average) but ordered in the same absolute stereochemical sense, favoring reduction at the *re* face of each carbonyl plane. Substrate selectivity is indicated by the dependence of the level of stereoselectivity on the ketonic structure.

While the variation in enantioselectivity among the ketonic substrates is fairly large, ranging over a factor of 12, the absolute levels are all very low. Can such low levels of enantioselectivity have any significance? The fact that each ketone is reduced in the same absolute spatial sense appears to attest to the significance of the results, the low levels not withstanding. Micelles and their surfactant monomers exist in dynamic equilibrium,[4] making it remarkable perhaps that the effects of what must be a net, time-averaged stereochemical ordering in the molecular aggregates can be seen at all. The low levels of enantioselectivity may well be a true reflection of the ability of such dynamic associations to transfer stereochemical influence in the manner required by these experiments. We are, however, continuing to search for combinations of surfactants, substrates, and reactions conditions which will maximize the stereochemical features displayed by the present system.

Table I. Chiroptical Data

R	3, observed			3, maximum				enantioselectivity, % ($[\alpha]/[\alpha]_{max}$)
	$[\alpha]^{22}_D$	*c*	solvent	$[\alpha]_D$	*t*, °C	*c*	solvent	
Me	−0.075 ± 0.038	5.230	benzene	−50.6[a]	27	3.00	toluene	0.14 ± 0.08
Et	−0.200 ± 0.040	5.010	benzene	+40.05[b]	17–20	5.00	benzene	0.50 ± 0.10
Pr^n	−0.723 ± 0.042	4.980	benzene	+43.6[b]	17–20	5.00	benzene	1.66 ± 0.10
Pr^i	−0.194 ± 0.039	5.150	ether	+48.3[c]	23	6.7	ether	0.40 ± 0.08
Bu^t	−0.476 ± 0.048	4.200	acetone	+30.6[d]	23	3.593	acetone	1.56 ± 0.16

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Acknowledgment. We are grateful to the National Institutes of Health for the financial support provided through Grant GM-19335.

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