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Three Rational Syntheses of New Stable Metal α-Hydroxyalkyl Complexes

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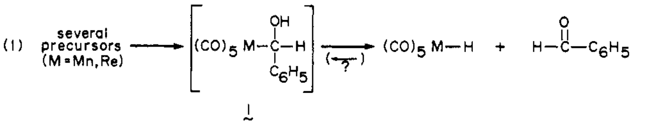
Homogeneous, catalyst-bound α-hydroxyalkyls [$L_nMCH(R)OH$] have been proposed[2–4] as key intermediates in the synthesis of oxygen-containing organic molecules from CO/H_2 gas mixtures.[2–5] Additionally, evidence has been obtained for palladium α-hydroxyethyl intermediates in the Wacker process[6] and for cobalt α-hydroxyalkyl precursors to oxo alcohols.[7] However, isolable metal complexes containing α-hydroxyalkyl ligands are exceedingly scarce.[8] To date, stable examples have been found only with third-row metals which have good donor ligands ((η-C_5H_5)Re(NO)(CO)(CH_2OH), *cis*-$OsH(CH_2OH)(CO)_2[P(C_6H_5)_3]_2$),[8b–d] or where the α-hydoxyalkyl ligand has been substituted with electron-withdrawing groups ((η-C_5H_5)$Fe(CO)_2[C(CF_3)_2OH]$).[8a]

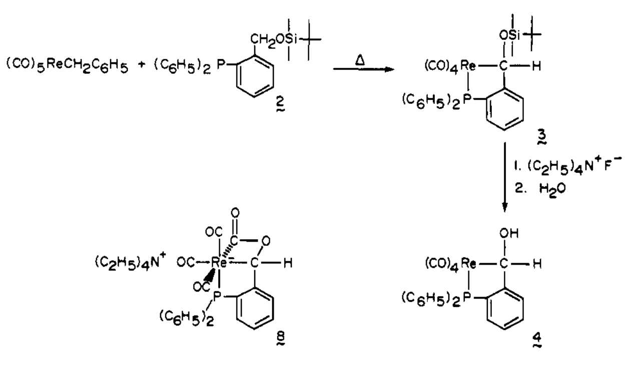
We have previously reported[9] that attempted generation of α-hydroxyalkyls of the formula 1 (eq 1) affords only benzaldehyde and metal hydrides, even at −50 °C. These results, together with the stable complexes mentioned above, suggested to us that metal α-hydroxyalkyls might closely parallel the behavior of hemiacetals and other XCH(R)OH species, which in general rapidly decompose to RCH═O and HX unless (a) X is a very poor leaving group (i.e., −CN), (b) R is a very electronegative group ($-CCl_3$, $-CF_3$), which renders the 1,2 addition of HX to RCH═O thermodynamically more favorable, or (c) X and R are incorporated into a ring, as in certain naturally occuring hemiacetals.[10] Such an analogy would have important implications for the generation and reactivity of catalyst-bound α-hydroxyalkyls. In this communication, we describe the use of strategy c to stabilize the α-hydroxyalkyl system **1** and demonstrate for the first time that $L_nMCH(R)OH$ species can be synthesized from aldehydes and metal hydrides similar to isolable organic XCH(R)OH compounds.



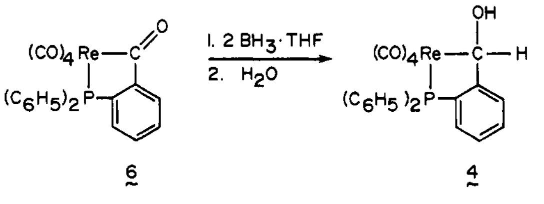
$$\text{(1)}\quad \begin{matrix}\text{several}\\ \text{precursors}\\ (\text{M}=\text{Mn},\text{Re})\end{matrix} \longrightarrow \left[(CO)_5M-\overset{\displaystyle OH}{\underset{\displaystyle C_6H_5}{C}}-H\right] \xrightarrow[(-?-)]{} (CO)_5M-H + H-\overset{\displaystyle O}{\overset{\|}{C}}-C_6H_5$$

1

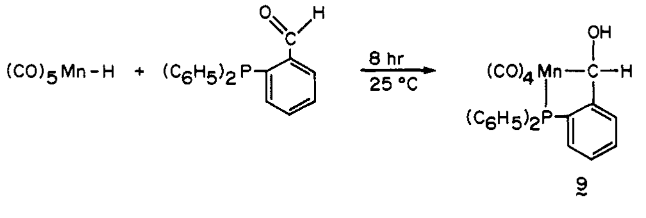
Scheme I. First α-Hydroxyalkyl Synthesis



Scheme II. Second α-Hydroxyalkyl Synthesis



Scheme III. Third α-Hydroxyalkyl Synthesis



For implementation of strategy c, a triarylphosphine ligand was selected for the second link of the α-hydroxyalkyl carbon to the metal. The first successful route began with $(CO)_5ReCH_2C_6H_5$ and the readily prepared phosphine **2** (Scheme I);[11] by use of cyclometalation conditions (octane solvent; 3 h, steam bath, then 2 h, reflux) similar to those reported by Kaesz and McKinney,[13] substitution (replacement of CO by phosphine), rhenium–carbon bond formation, and toluene elimination[14] were accomplished in a single step, affording (after column chromatography and CH_3CN recrystallization) pure **3** in 46% yield. Compound **3** was fully characterized spectroscopically[11b] and displayed the distinguishing low field (δ 6.11) methine ^1H NMR resonance found in $L_nMCH(R)OR'$ compounds.[9,15]

Reaction of **3** with $(C_2H_5)_4N^+F^-\cdot(H_2O)_x$ in acetone/CH_3CN, followed by silica gel filtration, removed the trialkylsilyl protecting group and gave the desired α-hydroxyalkyl **4** (Scheme I) in 77% yield after preparative HPLC.[11b] In contrast to **1**, **4** proved stable to >60 °C. The −OH NMR resonance (δ 3.30, coupled to the methine resonance)[11b] disappeared when **4** (in $CDCl_3$) was treated with D_2O. IR spectra of **4** showed ν_{O-H} (3517 cm^{-1}) to be weak relative to $\nu_{C\equiv O}$. In **4**-d_1, ν_{O-D} was observed at 2603 cm^{-1}. A parent ion was noted in the mass spectrum of **4**.[11b]

Reactions of **4** further support the proposed α-hydroxyalkyl structure. When **4** was treated with 0.06 equiv of CF_3SO_3H in acetone/H_2O, the symmetrical ether $[(CO)_4ReP(C_6H_5)_2(o-$

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(11) (a) Phosphine **2** was synthesized in 90% overall yield by the sequential reaction of $(C_6H_5)_2P(o-C_6H_4CHO)$[12] with $NaBH_4$ and $(CH_3)_2(t-C_4H_9)SiCl$/pyridine. (b) Characterization of **2–5**, **8** and **9** (^1H NMR, ^{13}C NMR, and IR for all cyclometalated complexes; selected mass spectra and microanalyses) is provided in the Supplementary Material.

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$\overline{C_6H_4C}H)]_2O$ (**5**) was isolated (28–36%).[11b] Under slightly different conditions, CF_3SO_3H (0.21 equiv, benzene) effected hydride transfer disproportionation of **4** to the cyclometalated acyl $(CO)_4Re\overline{P(C_6H_5)_2(o\text{-}C_6H_4C}{=}O)$ (**6**, 0.40 equiv) and alkyl $(CO_4)Re\overline{P(C_6H_5)_2(o\text{-}C_6H_4C}H_2)$ (**7**, 0.37 equiv).[16] Similar acid promoted conversion of the α-hydroxyalkyl $(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_2OH)$ to a symmetrical ether has been previously observed by Casey,[8b] and we have noted a related electrophile-induced hydride transfer disproportionation of the methoxyalkyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3)$.[17] Interestingly, workup of the reaction of **3** with $(C_2H_5)_4N^+F^-\cdot(H_2O)_x$ (ca. 0.95 equiv) prior to silica gel filtration afforded the crystalline, fac-substituted anionic tricarbonyl **8** in 93% yield (Scheme I).[11b]

Subsequent to the above isolation of **4**, we were able to detect minor amounts by TLC in other attempted syntheses. By careful optimization of conditions, we obtained **4** in 72% yield by reduction (Scheme II) of **6** with $BH_3\cdot THF$ (2 equiv). Although BH_3 has been previously noted to convert acyl ligands to alkyl ligands,[18] this is the first time that partial reduction of an acyl ligand has been observed.

Efforts to prepare **4** by routes analogous to the reverse of eq 1 were not successful. Substitution of CO in $(CO)_5ReH$ by phosphines is known to occur at erratic rates by free radical chain mechanisms;[19] tractable products did not result from the reaction of $(CO)_5ReH$ with $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$.[12] $(CO)_4LReH$ complexes were obtained from the reactions of $(CO)_5ReH$ with $(C_6H_5)_2P(o\text{-}C_6H_4\overline{CHOCH_2CH_2O})$ and $(C_6H_5)_2P[o\text{-}C_6H_4CH(OCH_3)_2]$. However, we were not able to deprotect the aldehyde functionality once these phosphines were coordinated. Recourse was then made to the more acidic and substitution-labile hydride $(CO)_5MnH$.[19,20] Gratifyingly, its reaction with $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$ gave the manganese α-hydroxyalkyl **9** (Scheme III) in quantitative spectroscopic yield over the course of 8 h at 25 °C.[11b] After column chromatography, **9** was obtained as a stable light yellow powder in 70% yield; spectral properties were very similar to those of **4**.[11b]

The above data, together with our interpretation of the factors contributing to the stability of previously isolated α-hydroxyalkyl complexes, indicate a substantial analogy of organometallic $L_nMCH(R)OH$ with organic $XCH(R)OH$ systems. Hence when the metal is "electron rich" (3rd-row metal and good donor lignds; strategy a), the α-hydroxyalkyl complex is more stable; other thermal reactions may be able to compete with eq 1 type aldehyde extrusion. Furthermore, since the corresponding metal hydride would not be very acidic,[20] such α-hydroxyalkyls should not be kinetically accessible (or only with great difficulty) from aldehydes and L_nMH; rather, alkoxide formation might be the preferred reaction course.[21] First-row transition-metal hydrides tend to be more acidic,[20] but they are also less electron rich. Hence they may react with aldehydes to give small equilibrium quantities of α-hydroxyalkyls (which can be trapped or react further),[7] but strategies b or c must be utilized to obtain isolable species.

The foregoing generalizations should apply equally well to homogeneous catalytic systems and may provide significant insight into catalyst design. Additional properties of the new compounds reported herein will be described in due course.

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Supplementary Material Available: Characterization of **2–5**, **8**, **9** (3 pages). Ordering information is given on any current masthead page.

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(16) Compound **6** has been prepared previously.[13] An authentic sample of **7** was synthesized from commercially available $(C_6H_5)_2P(o\text{-}C_6H_4CH_3)$ using procedures similar to those employed by Kaesz and McKinney for the cyclometalation of $P(o\text{-}C_6H_4CH_3)_3$.[13]

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Efficient and Accurate Calculation of Anion Proton Affinities

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Theoretical investigations of anionic species pose special problems.[1] Since the electron affinities of the corresponding neutral species are often quite low,[2] the extra electron in the anion is only weakly bound. With commonly employed ab initio methods, the HOMO's of anions are often indicated erroneously to have positive energies, i.e., to be unbound.[1] Absurdly negative values for electron affinities are often calculated, especially when electron correlation is not taken into account. Even protonation energies (for which single determinant theory is more appropriate due to conservation of electron pairs) are not predicted well for anions by methods which perform adequately for neutral and positively charged systems.[3] Minimal basis sets, even with "anion optimized" exponents,[4] and double-zeta or split-valence basis sets[5] yield proton affinities (PA's) with unacceptably large errors. These deficiencies are exemplified by the collection of PA data in Table I for a representative set of 19 closed-shell first-row anions. Errors with the STO-3G basis (standard exponents) are 110–230 kcal/mol; the split-valence 4-31G basis set PA's on the average are 31 kcal/mol greater than the experimental values.[2] No significant overall improvement is achieved either by inclusion of polarization functions (d orbitals) in the basis set, e.g., 6-31G*//4-31G, or by correcting for electron correlation, e.g., MP2/6-31G*//4-31G (Table I).[6g] Radom's conclusion, that "near-Hartree-Fock basis sets may be required to provide accurate absolute values of proton affinities",[1a] is discouraging. Consequently, most general theoretical studies on anions have been confined to more limited goals, viz., to obtain structural information[1a,6b] or evaluate stabilization energies through the use of

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