Table I. Rate Constants for Methylation of Alkali Dibenzoylmethides by Dimethyl Sulfate at 25 °C

	[MDBM] $\times 10^3$ M	k_2, s^{-1} M^{-1}	k_1, $\times 10^4$, s^{-1}	k_2[MDBM], $\times 10^4$, M^{-1} s^{-1}
KDBM	5.015	0.107	3.22	5.366
NaDBM	5.416	0.052	2.44	2.84

Table II. Calorimetric Heats of Methylation with Methylfluorosulfonate of β-Ketoenolates in Propylene Carbonate and Tetrahydrofuran[a]

Compd[b]	ΔH, kcal/mol[c]	ΔH, kcal/mol[d]
HDBM	No rxn	No rxn
LiDBM	No rxn	−29.6
NaDBM	−26.5 ± 1.1 (98% −O)	−32.2 ± 0.4 (67% −C)
KDBM	−25.8 ± 1.0 (98% −O)	−36.5 ± 0.4
CsDBM	−26.3 ± 0.1	−34.9 ± 1.6
HDPM	No rxn	No rxn
LiDPM	No rxn	−36.5 ± 3.5
NaDPM	−34.7 ± 0.6 (<90% −O)	−36.2 ± 0.8
KDPM	−26.5 ± 1.9 (>90% −O)	− 40.3 ± 0.9 (71% C)
CsDPM	−26.1 ± 0.6 (>90% O)	−40.3 ± 1.4 (83% C)

[a] Concentrations: chelate ≈0.02–0.05 M; $MeSO_3F$ ≈0.00309 M. [b] DBM = dibenzoylmethide; DPM = dipivaloylmethide. [c] In propylene carbonate. [d] In THF.

Points of novelty in the present study are, first, the use of dimethyl sulfate for the rapid in situ formation of the oxosulfonium salt and, second, the kinetic evidence for competition of reaction through it with the normal S_N2 reaction of the sulfate.

In propylene carbonate at 25 °C the potent methylating agent methyl fluorosulfonate[12-15] reacts completely within 2 min[16] with sodium, potassium, and cesium DBM and DPM to produce primarily (90–98%) the oxygen-alkylated product[17] and over 26 kcal/mol of heat. Despite the enormous driving force for the alkylation reaction which is implied by this observation, solutions of both lithium compounds evolved no more heat than did the small background reaction with propylene carbonate under the same conditions during a period of at least a half hour.[18]

Table 11 shows the similar behavior of the lithium chelates and the covalent parent β-diketones, compared with their dramatic difference from the other alkali enolates in propylene carbonate. In contrast, the lithium compounds behave like the other alkali analogues in THF, a solvent which dissociates lithium salts through coordination with the cation. The tabulated results also demonstrate differences in oxygen vs. carbon alkylation as a function of the cation, the anion, and the solvent in conformity with many published observations by other workers.[11,20,21]

The relatively low reactivity of lithium salts compared with those of the other alkali cations has numerous precedents and conforms to their low relative dissociation in dipolar aprotic solvents.[22-25] However, at this point we can only speculate on the thermodynamic or kinetic reasons for it.

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Homogeneous Hydrogenation of Carbon Monoxide

Sir:

We wish to report a homogeneous hydrogenation of carbon monoxide to methane ("methanation"[1]) using $Cp_2Ti(CO)_2$.[2] We also report the serendipitous synthesis and structure of a cluster unprecedented in both cyclopentadienyl chemistry and titanium chemistry.

When a toluene solution of $Cp_2Ti(CO)_2$ is treated with a mixture of hydrogen and carbon monoxide (3:1 mole ratio, total pressure 1 atm at 25 °C) at 150 °C, methane is produced.[3] The solution phase is homogeneous throughout the reaction, and no metal is evident during or after the reaction. When deuterium is used in place of hydrogen, CD_4 is produced; toluene is not detectably deuterated, but some cyclopentadienyl deuteration occurs (infrared evidence). The methanation is not catalytic in titanium, however; methane is produced even under an atmosphere of pure hydrogen (but not under argon). Over a period of 48 h, the color characteristic of $Cp_2Ti(CO)_2$ changes to a royal blue. This blue species is catalytically inactive to a fresh charge of synthesis gas and does not exhibit any infrared bands characteristic of bridging or terminal CO ligands.

We have determined the structure of the intensely blue crystals obtainable from toluene. Using 2730 unique reflections measured with Mo Kα radiation ($2\theta < 50°$), the structure was solved (direct methods) and refined to an agreement factor $R(F)$ of 0.049.[4]

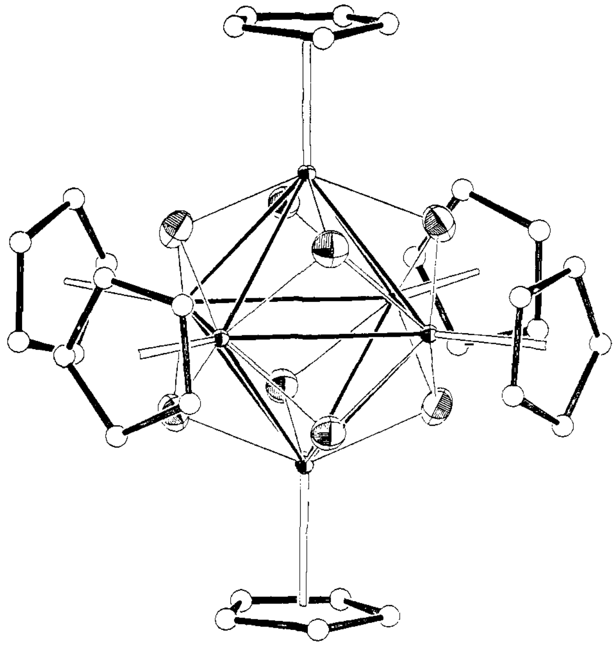


Figure 1. An ORTEP drawing of $Cp_6Ti_6O_8$. A crystallographic mirror plane lies in the vertical direction almost perpendicular to the page. Titanium atoms are shown as small spheres while the ring carbons (open spheres) have been given a *B* (isotropic) of 0.75 Å^2. One metal atom is obscured by a carbon atom. The average Ti–C distance is 2.381 Å (5, 14, 26).

The catalytically inactive species is a regular octahedral cluster of formula $(\eta^5\text{-}C_5H_5)_6Ti_6O_8$ (Figure 1). The seven crystallographically distinct metal–metal distances average 2.891 Å (1, 9, 28).[5] This is the shortest Ti–Ti contact yet observed in a molecular species and may be compared to the 2.951-Å separation found in α-Ti.[6] The planar cyclopentadienyl rings cap all apices of the octahedron, while the eight oxygen atoms occupy all triangular faces. The 14 crystallographically distinct Ti–O distances average to 1.973 Å (3, 7, 15) and indicate a symmetrical μ_3-O functionality. This is, to our knowledge, the first reported Cp_6M_6 cluster. The Ti_6O_8 framework is, however, isostructural with the $Mo_6X_8{}^{4+}$ unit, which has notably shorter (~2.63 Å) metal–metal contacts.[7]

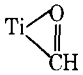
The identification of the bridging groups in $Cp_6Ti_6O_8$ as oxide and not hydroxide follows from the complete absence of an O–H stretching vibration in the infrared, and the single-line proton NMR spectrum (τ 5.92 in toluene-d_8) assigned to the equivalent cyclopentadienyl protons of a diamagnetic molecule.[8] It is also significant that the Ti–O distance observed here is *shorter* than that in $[CpTiOH]_2C_{10}H_8$ (2.05 Å).[9] We assign two infrared absorptions (728 and 598 cm^{-1} in Nujol) as the two allowed (T_{1u}) Ti–O vibrations of the Ti_6O_8 core.[10]

An integral metal oxidation state cannot be identified in $Cp_6Ti_6O_8$; the high symmetry and diamagnetism exclude a localized $Ti^{IV}{}_4Ti^{III}{}_2$ description.[11] This is consistent with the intensity and low energy of the visible absorption; titanium(IV) cyclopentadienyl complexes are normally orange to yellow. Assuming metal–metal bonds of order one and a four-electron count for μ_3-O ligands, the cluster has two electrons in excess of those required by the inert gas formalism.[12]

The favorable thermodynamics of methanation (eq 1) and other reductions of CO[13] are dependent upon the formation of water. In the methanation reaction described here, water, or a protic precursor to it, is presumed to be responsible for formation of $Cp_6Ti_6O_8$. Cyclopentadienyl complexes are generally subject to ring loss by hydrolysis, as observed here.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (1)$$

The present hydrogenation of CO has features in common with that reported recently by Bercaw and his students using zirconium.[14] Both demonstrate the efficacy of early transition elements. The titanium and zirconium catalysts both yield products containing metal–oxygen bonds, consistent with the hard acid behavior of these metals. Note, however, that group 4B metals are not components of typical heterogeneous Fischer–Tropsch catalysts.[13] We wish to suggest that metal–oxygen bonding, either in a π-formyl (I)[15] or a 1,2-(μ_2-CH_nO)



I

$$Ti—CH_nO—Ti$$

II

structure (II; n = 0, 1, 2), is a mechanistic feature critical in activation (toward hydrogen) of CO by early transition metals without the necessity of acidic cocatalysts.[16] Formyl metal complexes are attractive intermediates in catalyzed CO hydrogenation, and it is known[19] that binding of alkali metal cations to carbonyl oxygen promotes the related alkyl carbonyl-to-acyl reaction in $RFe(CO)_4{}^-$.

Formation of intermediates such as I or II requires coordinative unsaturation. Consistent with this hypothesis, CO dissociation appears to be an essential preliminary act in methanation with $Cp_2Ti(CO)_2$. Indeed, methanation with $Cp_2Ti(CO)_2$ also proceeds at 25 °C when photodissociation is effected with UV irradiation.

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Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters (1 page). Ordering information is given on any current masthead page.

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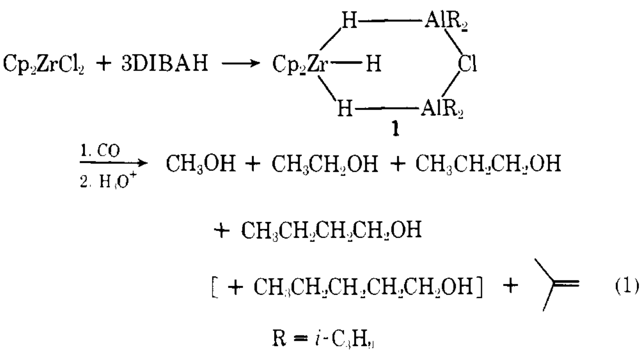
Reduction of Carbon Monoxide to Linear Alcohols by Aluminum Hydrides and Zirconium Complex Catalysts at Room Temperature

Sir:

Current interest in homogeneous analogues of the Fischer-Tropsch process derives from the desire to selectively convert coal, via CO, to hydrocarbon products which can serve as fuels or as feedstocks for other petrochemical processes.[1] Thus far stoichiometric conversion of CO to CH_3OH has been accomplished[2] and reports associated with the catalytic conversion of CO to CH_4[3] or to ethylene glycol[4] have appeared. The Fischer-Tropsch process is especially remarkable, though, in that multicarbon-containing fragments are produced. However, only one report of reductive polymerization of CO, accomplished homogeneously, has yet appeared.[5] All known Fischer-Tropsch-type processes, either heterogeneously or homogeneously accomplished, require elevated temperatures. We have recently found that DIBAH (i-Bu_2AlH) in the presence of Cp_2ZrCl_2 as a catalyst will reduce CO *at room temperature* and 1-4 atm to give, on hydrolysis, a mixture of linear aliphatic alcohols. We wish to report now the results of these studies.

Dissolving Cp_2ZrCl_2 in benzene in the presence of 3 equiv of DIBAH leads to the rapid formation of **1** (and 1 equiv of i-Bu_2AlCl).[6] This complex absorbs approximately 2 equiv of CO (based on Zr) over a period of 24 h (at room temperature) to give a golden yellow solution and to precipitate the Cp_2ZrCl_2 starting material. Addition of 3 equiv more of DIBAH leads to absorption of 2 equiv more of CO; this sequential procedure has been repeated over 10 times with no change in the stoichiometry of CO uptake relative to Zr. ^1H and ^{13}C NMR analysis of the golden yellow oily material obtained on evaporation of volatiles and removal of Cp_2ZrCl_2 indicates that it is a complex mixture of aluminum alkyls (no resonance attributable to a simple aluminum alkoxide is observable in the ^{13}C NMR spectrum).[7] IR (film) analysis indicates the absence of carbonyl absorptions but reveals strong bands attributable to C-O and Al-O-Al units.[8] NMR and VPC analysis of the volatile fraction obtained in this separation indicates that a substantial amount of isobutylene is produced concomitant with CO uptake.[9] It therefore appears that DIBAH can serve as the source of more than one hydride unit in such a CO reduction procedure.[10]

Treatment of the oily product of CO absorption with H_2O/H_2SO_4 yields, as shown by NMR and VPC analyses, methanol, ethanol, propanol, and 1-butanol, with an indication of 1-pentanol. For the mixture of Cp_2ZrCl_2 + 3DIBAH + CO (1 atm), methanol, ethanol, 1-propanol, and 1-butanol were obtained in the molar ratio 1.00:0.12:0.15:0.03 (or, based on CO incorporation, 1.00:0.24:0.45:0.12). That these linear alcohols are derived from CO was easily established using ^{13}CO. Here NMR analysis for CH_3OH showed it to be essentially all $^{13}CH_3OH$.[11] GC/mass spectral analysis confirms this determination for methanol and establishes that the homologous alcohols are formed by incorporating CO into *each carbon unit* of the alkyl chain (reaction 1).

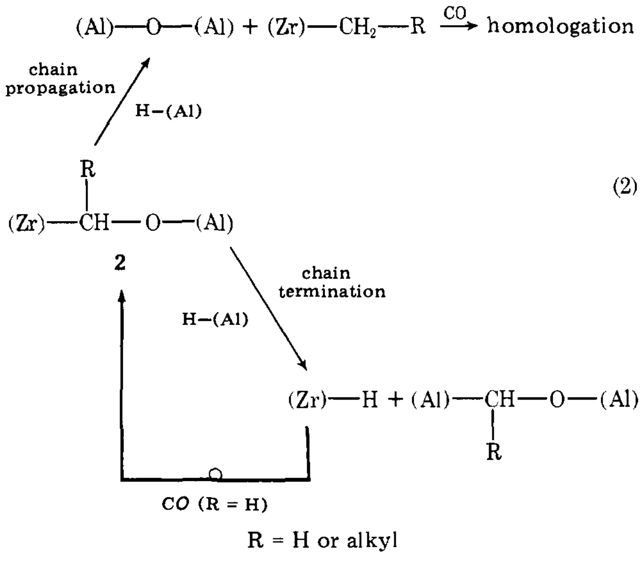


$$Cp_2ZrCl_2 + 3DIBAH \longrightarrow \mathbf{1} \xrightarrow[2.\ H_3O^+]{1.\ CO} CH_3OH + CH_3CH_2OH + CH_3CH_2CH_2OH + CH_3CH_2CH_2CH_2OH\ [+ CH_3CH_2CH_2CH_2CH_2OH] + \quad (1)$$

R = i-C_4H_9

It is important to note that, whereas **1** reacts readily with CO at 1 atm, excess DIBAH retards the uptake of CO (at 1 atm) although, as mentioned, the process done batchwise enables many turnovers based on Zr to be accomplished. In contrast, at 50 psi CO, reduction of CO in the presence of even 30 equiv of DIBAH occurs. Here, methanol, ethanol, 1-propanol, and 1-butanol in the molar ratio of 1.00:0.09:0.05:0.03 were produced (or, based on CO incorporation, 1.00:0.18:0.15:0.12). Intriguingly, distributions of alcohols obtained in these sequences are reminiscent of those observed for linear hydrocarbon products of known Fischer-Tropsch catalytic sequences.[12]

Our results suggest a mechanism in which DIBAH dissociates from **1** to provide a vacant coordination site on Zr. Initial reduction of coordinated CO could occur either by H migration[2] from Zr or by (intramolecular) attack by "external" Al-H.[13] Polymerization of CO may occur via units such as **2**[14] in which chain propagation or termination occurs as shown in reaction 2. Transmetalation of alkyl groups from Zr to Al in exchange for -H has been established[6] and the reduction in this "carbenoid" complex of C-O-Al to H-C by DIBAH is not unreasonable. These results, too, support the contention[3,5] that multinuclear systems may be more useful for reductively *polymerizing* CO than are mononuclear ones. In this regard mixed-metal systems, especially those involving CO coordinators in combination with an oxygen-loving Lewis acid, may prove to be especially effective. Control of product distribution as well as mechanistic details of the fascinating transformation described herein are now under study.



R = H or alkyl

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