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LIGAND REDISTRIBUTION AND CARBONYL INSERTION: THE EFFECT OF COMPETITIVE π-DONATION

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Summary

Electron deficient $CpTiCl_3$ reacts with the bis-alkoxide $CpClTiOCMe_2CMe_2O$ to produce the diolato dimer $(CpTiCl_2)OCMe_2CMe_2O(TiCl_2Cp)$. $CpTiCl_3$ reacts with $Cp_4Ti_4Cl_4(\mu_2\text{-}O)_4$, which also has two oxo ligands on each titanium atom, to produce $[CpTiCl_2]_2O$. These and other redistribution reactions indicate that destabilization results from internal competition for metal *d*-orbitals by strong π-donor (e.g. alkoxide) ligands. Equilibrium constants for the formation of the η^2-acetyl complexes $Cp_2Zr[C(O)Me]X$ by CO insertion into Cp_2ZrMeX decrease in the order X = Me > Cl > OEt. This reflects internal competition of π-donor orbitals on X with the oxygen donor orbital in the η^2-acetyl functionally. The significance of this effect for Fischer-Tropsch syntheses in both homogeneous and heterogeneous media is discussed.

Introduction

We recently presented [1] structural evidence for π-donation by alkoxide and chloride ligands bound to the $CpTi^{3+}$ moiety; alkoxide was by far the more effective π-donor, forming Ti—O bonds as short as 1.75 Å. We now report qualitative thermodynamic results which show dramatically the influence of alkoxide π-donation on chemical reactivity.

Experimental

General

All operations were carried out in a nitrogen filled dry box or using standard Schlenk line techniques. Benzene and THF were vacuum transferred from a solution of sodium benzophenone ketyl; hexane was dried with Na/K alloy. Pinacol, CMe_2OHCMe_2OH, was sublimed at 25°C under vacuum.

* Contribution No. 3527.

Synthetic

$(C_5H_5)\overline{TiCl[OC(CH_3)_2C(CH_3)_2O]}$. This synthesis involves a stepwise procedure planned as follows:

$$\frac{1}{n}[Ti(OEt)_4]_n + HOCMe_2CMe_2OH \rightarrow \underset{\text{(Intermediate 1)}}{\frac{1}{m}[Ti(OCMe_2CMe_2O)_2]_m} + {}_4\ EtOH \qquad (A)$$

$$\frac{1}{m}[Ti(OCMe_2CMe_2O)_2]_m + TiCl_4 \rightarrow \underset{\text{(Intermediate 2)}}{\frac{2}{p}[TiCl_2(OCMe_2CMe_2O)]_p} \qquad (B)$$

$$\frac{1}{p}[TiCl_2(OCMe_2CMe_2O)]_p + TlC_5H_5 \rightarrow \underset{\text{(IIa)}}{C_5H_5\overline{TiCl(OCMe_2CMe_2O)}} + TlCl \qquad (C)$$

Steps A and B of this sequence are based on those employed earlier with 2-methylpentane-2,4-diol [2,3]. Described below are the isolation and ^1H NMR spectroscopic characterization of "intermediate 1" and "intermediate 2" according to these proposed reactions. In each case, however, the complete characterization and the determination of the molecularity of these intermediates was not pursued since only the product of reaction C is of consequence to the work reported here. Such characterization has been completed for the analogous titanium complexes of 2-methylpentane-2,4-diolate [2,3].

a. Intermediate 1, $[Ti(C_6H_{12}O_2)_2]_m$. 1.8 ml $Ti(OEt)_4$ (8.7 mmol) [4] was dissolved in enough benzene to bring the total volume to 10 ml. To this was added, with stirring, 2.08 g pinacol (17.6 mmol), giving immediate dissolution. No heat evolution was observed and some discoloration of the solution occurred. After stirring for $1\frac{1}{2}$ h the solvent was removed and the resulting glassy solid was heated in vacuo at 115°C for 8 h. An NMR ($CDCl_3$) gave a single, broad resonance at δ 1.35 ppm. Yield: 2.0 g (92%). The solid did not melt but darkened above ca. 340°C.

b. Intermediate 2, $[TiCl_2(C_6H_{12}O_2)]_p$. Intermediate 1, $[Ti(C_6H_{12}O_2)_2]_m$ (2.0 g, 7.1 mmol) was placed in 20 ml benzene and the resulting slurry was stirred vigorously at room temperature. To this was added 0.78 ml $TiCl_4$ (7.1 mmol) in 10 ml benzene. Stirring was continued for 2 h and the resulting white solid was filtered from the solution and dried in vacuo after washing with a small portion of benzene. An NMR ($CDCl_3$) gave a sharp singlet at δ 1.59 ppm. Yield: 2.5 g (75%).

c. $(C_5H_5)\overline{TiCl(OCMe_2CMe_2O)}$, IIa. The following synthetic procedure and all subsequent manipulation should be carried out in flamed glassware. This inhibits hydrolysis and dimerization (see below).

$[TiCl_2(OCMe_2CMe_2O)]_p$ (0.90 g, 3.8 mmol) was dissolved in 300 ml DME and the solution cooled to −45°C. $Tl(C_5H_5)$ (1.0 g, 3.8 mmol) was then added at once with stirring. No immediate color change was observed and the solution was held at −45°C for 2 h, after which it was allowed to gradually warm to room temperature overnight. By this time an orange solution had formed along with large amounts of a colorless precipitate (TlCl). The solvent was removed until about 50 ml remained and the colorless solid was filtered away. The filtrate was then taken to dryness to yield an orange solid which was subse-

quently washed with several 20 ml portions of hexane. NMR (δ, ppm) (C_6D_6): 6.21 (s, 5H), 1.30 (s, 6H), 1.00 (s, 6H). Analysis: Found: C, 49.63; H, 6.58; Cl, 13.19. $C_{11}H_{17}O_2ClTi$ Calcd.: C, 49.93; H, 6.48; Cl, 13.40%. Molecular weight (cryoscopic in *p*-dioxane): Found: 275 g/mol. Calcd. (monomer): 264.

The half-life of this monomer (solid state) is ca. $1\frac{1}{2}$ w at room temperature. Only fresh (i.e. $\leq$1 w old) $[TiCl_2OCMe_2CMe_2O]_p$ should be used in this synthesis since the solubility of this compound tends to decrease with time. This synthetic route yielded only trace amounts of $[CpTiCl(OCMe_2CMe_2O)]_2$ (see below) initially but further manipulation (i.e. extractions, etc.) results in decomposition and dimerization. The choice of a polar, coordinating solvent and dilute conditions for the synthesis appears to reduce the yield of dimeric $[CpClTiOCMe_2CMe_2O]_2$ by solvating $[TiCl_2OCMe_2CMe_2O]_p$; THF solvent yields much more of this dimer *. Cp_2TiCl_2 is a common impurity in the synthesis, but its yield is diminished by the low temperature procedure reported here; NaC_5H_5 yields a larger proportion of Cp_2TiCl_2.

$[CpTiClOCMe_2CMe_2O]_2$, IIb. To a solution of 0.45 g $[TiCl_2(OCMe_2CMe_2O)]_p$ (1.9 mmol) in 100 ml DME were slowly added (at 25°C) 0.50 g ($Tl(C_5H_5)$ (1.9 mmol) with vigorous stirring. The solution gradually turned orange and large amounts of a colorless solid formed. After ca. 15 h the solvent was removed under vacuum until the volume was 50 ml, and the solid was filtered away. The filtrate was then taken to dryness, extracted with toluene and filtered again. Finally, the solid was washed with 50 ml of hexane and dried to yield a pale orange solid. NMR (δ, ppm) (C_6D_6): 6.24 (s, 5H), 1.33 (s, 6H), and 1.03 (s, 6H) due to $[CpTiCl(OCMe_2CMe_2O)]_2$. On the upfield side of each of these peaks (i.e. at 6.21, 1.30 and 1.00 ppm) are peaks due to monomeric $CpClTi(OCMe_2CMe_2O)$, IIa. Cp_2TiCl_2 constitutes approximately 15% of the titanium at this point, and can be removed by its low solubility in toluene.

Redissolving the solid in benzene and refluxing for 5 h caused complete conversion of the resonances assigned to the monomer into those of the dimer. Removal of the benzene yielded an orange solid. The molecular weight was determined by freezing point depression in *p*-dioxane to be 530 g/mole (calculated for the dimer: 528). Yield: 35%. The mass spectrum (EI, 70 eV) showed no parent ion ($M^+ = 528$), but showed $(M - C_5H_5)^+$, $(M - Cl)^+$, $(M - O_2C_2Me_4)^+$ and $(M - C_{10}H_{10}Cl)^+$ as well as many fragments also found in the spectrum of IIa; loss of individual methyl groups is not a significant fragmentation process.

Reaction of $CpTiCl_3$ with $(CpTiOCl)_4$. To 24 mg (0.036 mmol) $(CpTiOCl)_4$ [6] in 0.45 ml C_6D_6 was added 20 mg (0.18 mmol) $CpTiCl_3$ (20% excess). These components were shaken to homogeneity in an NMR tube and the ^1H NMR was recorded immediately. The 6.42 ppm resonance characteristic of the titanium tetramer was absent, and a resonance at 6.25 ppm was identified as $(CpTiCl_2)_2O$ by comparison to an authentic sample. A small amount of $CpTiCl_3$ was evident by its resonance at 5.98 ppm (by comparison to a pure sample).

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* We have been unsuccessful in repeating the preparation of $CpTiCl(O_2C_2Me_4)$ according to a recent report [5]. That preparation gives, in our hands, only unreacted starting material (Cp_2TiCl_2). Our product shows inequivalent geminal methyl groups characteristic of a rigid pseudotetrahedral metal center.

Reaction of $CpTiCl_3$ with $CpTiCl(OCMe_2CMe_2O)$. To 25 mg (0.095 mmol) $CpTiCl(OCMe_2CMe_2O)$ in 0.45 ml C_6D_6 was added 25 mg (0.11 mmol, 15% excess) $CpTiCl_3$; within 1 min a fine, bright yellow solid began to precipitate. The NMR tube which contained this mixture was inverted, centrifuged and reinverted for analysis by ^1H NMR. The spectrum of this yellow solution, which showed complete loss of all resonances of $CpTiCl(OCMe_2CMe_2O)$ at 6.21, 1.30 and 1.00 ppm, showed new peaks at 6.23 (5H) and 1.38 ppm (6H) characteristic of $(CpTiCl_2)_2(O_2C_2Me_4)$; these chemical shifts duplicate those of an authentic sample, identified by X-ray crystallography [1]. The low benzene solubility of the product of this reaction is also characteristic of $(CpTiCl_2)_2$-$(O_2C_2Me_4)$. The reaction solution also contained resonances due to the small excess of $CpTiCl_3$ employed. The doubly-bridged dimer $CpClTi(OCMe_2$-$CMe_2O)_2TiClCp$ is also ring-opened by $CpTiCl_3$ to give $(CpCl_2Ti)_2(OCMe_2$-$CMe_2O)$ under these same conditions.

$(C_5H_5)_2Zr(C(O)CH_3)Cl$. A solution of 250 mg $Cp_2ZrMeCl$ [7] was dissolved in ~3 ml toluene. This solution was then stirred under 1 atm CO, with a white precipitate forming within 15 min. Stirring was continued overnight and the mixture was filtered under N_2 and washed with hexane, yielding 200 mg of a dull white powder. NMR (δ, ppm) (C_6D_6): 5.48 (10H), 2.25 (3H). ν(CO) = 1556 cm^{-1} (Nujol).

$(C_5H_5)_2ZrCH_3(OC_2H_5)$. A solution of 25 mg Cp_2ZrMe_2 (0.1 mmol) in C_6D_6 was placed in an NMR tube. To this solution was added 6 μl (0.1 mmol) dry ethanol (from a fresh bottle of anhydrous ethanol), with immediate gas evolution resulting. NMR analysis shows near-quantitative conversion to Cp_2Zr-$(OCH_2CH_3)CH_3$. NMR (δ, ppm) (C_6D_6): 5.75 (s, 10H), 3.83 (q, 2H), 1.00 (t, 3H), 0.32 (s, 3H). The identity of the evolved gas was established as CH_4 by the resonance at 0.12 ppm (identical to authentic dissolved CH_4). Performing the reaction on a larger scale led to the isolation of a clear, light yellow oil with an identical NMR. Sublimation of this oil yields only a colorless oil on the cold finger. The identity of this compound was also established by an independent [8] synthesis (hydrogen transfer) from Cp_2MoH_2 and $Cp_2Zr[C(O)CH_3]CH_3$ under CO.

Competitive carbonylation of Cp_2ZrMe_2 and $Cp_2ZrMeCl$

A C_6D_6 solution consisting of approximately a 3 : 1 mixture of $Cp_2ZrMeCl$ and Cp_2ZrMe_2 was placed in an NMR tube capped with a rubber septum. The solution was frozen with a water ice bath and the NMR tube was evacuated using a syringe needle connected to a vacuum line. The tube was then filled with 1 atm CO (approximately 2 ml gas) and the syringe needle was removed. The NMR tube was allowed to stand with intermittent shaking for about 5 hours. At the end of this period, an observable but not accurately measurable amount of Cp_2ZrMe_2 remained while $Cp_2Zr[C(O)Me]Cl$, $Cp_2ZrMeCl$ and $Cp_2Zr[C(O)Me]Me$ were present in an approximately 2 : 1.3 : 1 ratio. (If excess CO is used, $Cp_2Zr[C(O)Me]Me$ and $Cp_2Zr[C(O)Me]Cl$ are formed almost quantitatively). Additional Cp_2ZrMe_2 was then added to the solution and the system was allowed to equilibrate for 5 h. The final NMR spectrum showed Cp_2ZrMe_2, $Cp_2ZrMeCl$, $Cp_2Zr[C(O)Me]Me$, and $Cp_2Zr[C(O)Me]Cl$ to be present in approximate ratios of 10 : 20 : 10 : 1.

Results and discussion

Redistribution reactions

Ligand redistribution (eq. 1) [9] is a useful synthetic technique when reac-

$$aEX_n + (n - a)EY_n \rightleftharpoons nEX_aY_{n-a} \quad (1)$$

tions are rapid and redistribution is nonrandom, favoring particular mixed complexes. On the other hand, rapid kinetics and statistical redistribution leads to inseparable mixtures. For the representative elements, comproportionation (eq. 1) has been observed [9] to be essentially thermoneutral when the central element E has no empty orbitals (e.g. C), when X and Y possess no filled donor orbitals (e.g. alkyl or aryl), or when X and Y possess filled donor orbitals of comparable availability (X = OMe, Y = OEt). Comproportionation equilibrium constants are rather sensitive probes of these conditions; with E = Si, exchange of halogen with methoxide is nonrandom in favor of mixed species while halide/phenoxide exchange is nearly random [9].

All of these observations are consistent with the idea that relative ligand π-donor capacity is primarily responsible for deviations from thermoneutrality. For example, oxygen lone pairs on phenoxide are less available than on alkoxide due to their delocalization into the phenyl ring. We have cited structural evidence for this same effect [1]. Moreover, the enhanced stability observed for the mixed species EX_aY_{n-a} over the binary precursors EX_n and EY_n may be rationalized by proposing that strong π-donors prefer to become distributed over the maximum number of metal centers; this has the effect of minimizing competition amongst π-donors for the acceptor orbitals available on each central metal, as well as minimizing steric repulsion.

The monocyclopentadienyl Ti^{IV} unit possesses exceptionally high Lewis acidity and therefore provides an optimal setting for demonstrating this preference for "scattering" π-donor ligands among transition metal centers. A wide variety of complexes of the type $CpTi(OR)_{3-n}X_n$ have been prepared [10,11] with n = 1, 2, X = F, Cl, Br, I and R = Et and i-Pr. All were prepared, according to eqs. 2 and 3, which ". . . proceed at room temperature to quantitative

$$CpTiX_3 + 2\ CpTi(OR)_3 \rightarrow 3\ CpTi(OR)_2X \quad (2)$$

$$2\ CpTiX_3 + CpTi(OR)_3 \rightarrow 3\ CpTi(OR)X_2 \quad (3)$$

yields". Even phenoxide will redistribute with chloride to preferentially form $CpTi(OPh)Cl_2$. It is noteworthy that each of these necessarily stepwise reactions must proceed through a mixed complex which is not a final product (i.e. $CpTiX_2OR$ in eq. 2 and $CpTiX(OR)_2$ in eq. 3). Implicit in these reactions are thus the conclusions that the following reactions also proceed to completion.

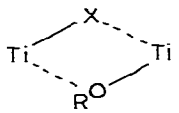
From eq. 2:

$$CpTiX_2OR + CpTi(OR)_3 \rightarrow 2\ CpTi(OR)_2X \quad (4)$$

From eq. 3:

$$CpTiX_3 + CpTi(OR)_2X \rightarrow 2\ CpTi(OR)X_2 \quad (5)$$

Note that these thermodynamic conclusions follow regardless of whether the operative mechanism involves bimolecular ligand exchange, I, or acid catalysis (Scheme 1).



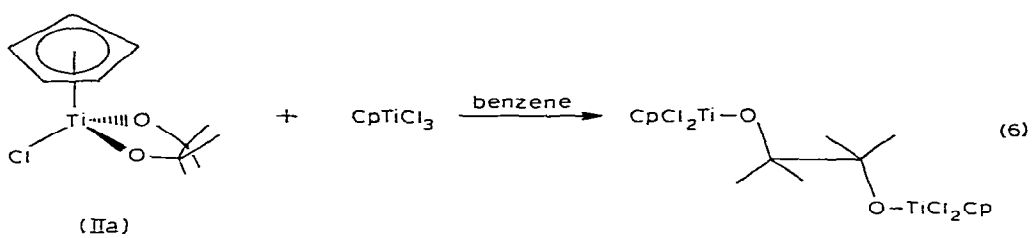
(I)

SCHEME 1

$$CpTi(OR)_3 + HCl \rightarrow CpTi(OR)_2Cl + ROH$$

$$CpTiCl_3 + ROH \rightarrow CpTiCl_2OR + HCl$$

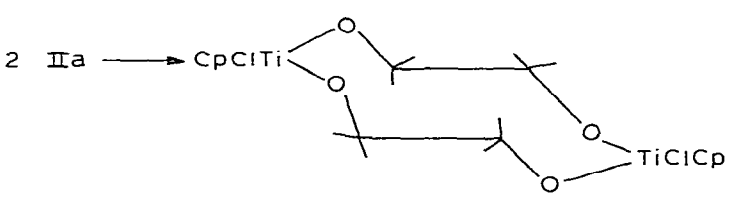
These reactions all proceed with no alteration of the number of moles of material. However, we have found that entropy decreases are readily overcome by the preferential redistribution tendancy of alkoxides. Thus, the pinacolate complex IIa reacts on mixing at 25°C with $CpTiCl_3$ (eq. 6) to produce a bridged



(6)

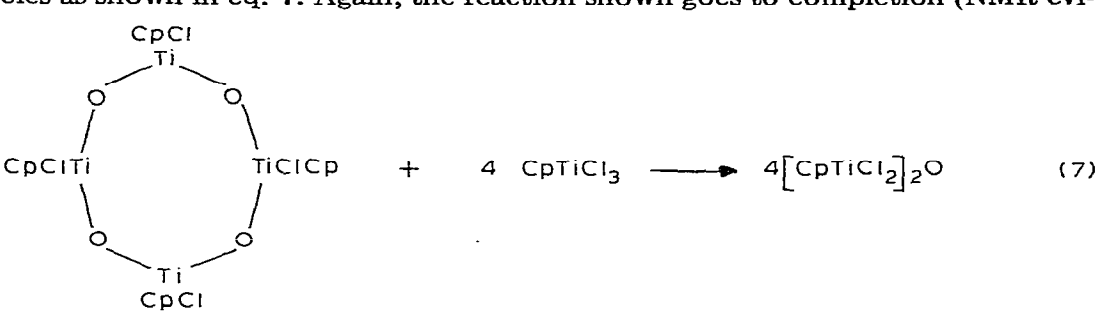
(IIa)

dimer [1]. Complex IIa undergoes oligomerization to IIb on heating in solution. Although IIb has less ring strain than IIa, it too reacts rapidly with $CpTiCl_3$ (2 mol) to give the same singly bridged dimer shown in eq. 6.



(IIb)

We have also observed the conversion of a bis-oxo complex to a monoxo species as shown in eq. 7. Again, the reaction shown goes to completion (NMR evi-



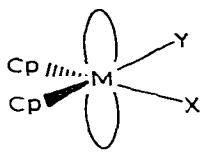
(7)

dence) immediately on mixing in a nonpolar solvent. This reaction converts bent oxo bridges into linear ones.

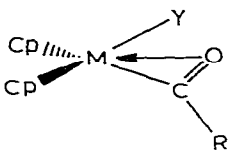
CO insertion reactions

The work of the Floriani [12] and Schwartz [13] groups on CO insertion into the metal—carbon bond of $Cp_2M(Me)X$ species (M = Ti, Zr, Hf; X = CH_3 or halogen) provides crystallographic and spectroscopic parameters on the η^2-C(O)R bonding mode which had been postulated [14,15] as a possible intermediate in the CO insertion reaction [16]. Moreover, the occurrence of this bonding mode among the oxophilic early transition metals provides support for the suggestion [17,18] that this characteristic contributes to the CO hydrogenations observed on these metals.

Group IV complexes of the type Cp_2MXY (X, Y = "one electron donor" ligands) are noteworthy since they establish the 16-electron configuration as not merely accessible, but actually stable for these transition metals; for X = halide or pseudohalide, these complexes resist addition of Lewis bases, in spite of the presence of the accessible LUMO [19] shown in III. In $Cp_2TiCl(OEt)$



(III)



(IV)

[1], this LUMO accepts electron density from one alkoxide lone pair (see Figure 1). When X = alkyl or aryl in III, reaction with CO proceeds rapidly (no intermediate CO adduct has been detected [20]) to the final η^2-acyl product of geometry IV *. Structure IV employs the LUMO of III to form the second bond to the acetyl group; the capacity of IV to bind an additional CO ligand is consequently diminished. Alternatively, IV is an 18-electron complex. Using either formalism, it follows naturally that, even if X and Y in III are both alkyl or aryl groups, CO insertion should proceed selectively in only one M—C bond **. This is observed.

We have observed a more subtle form of internal competition for the LUMO used in binding CO to Cp_2MXY. This effect exists in the form of π bonding by the ligand X in $Cp_2Zr(CH_3)X$. It is reported [12] that $Cp_2Zr(CH_3)_2$ is converted "completely" to the corresponding monoacetyl complex by 1 atm of CO. In C_6D_6 we observe that treatment of $Cp_2Zr(CH_3)Cl$ with 1 atm CO produces the corresponding acetyl complex; resonances of the chloromethyl complex are barely detectable in a single-scan ^1H NMR spectrum. However, it is possible to

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* Since the two most stable empty orbitals of Cp_2TiY^+ (with Y off the idealized C_2 symmetry axis) are localized in the *yz* plane [19], we have drawn IV with L → M donation from the oxygen lone pair. The orbital node makes donation from the filled C=O π bond minimal when the acyl ligand lies in the *yz* plane.

** It is important to correct the early claim [21], which has been cited in later work [22], that $Cp_2Zr(CH_2Ph)_2$ does not insert CO at elevated temperature and pressure. A single CO insertion indeed occurs at 1 atm and 25°C, as reported later [12].

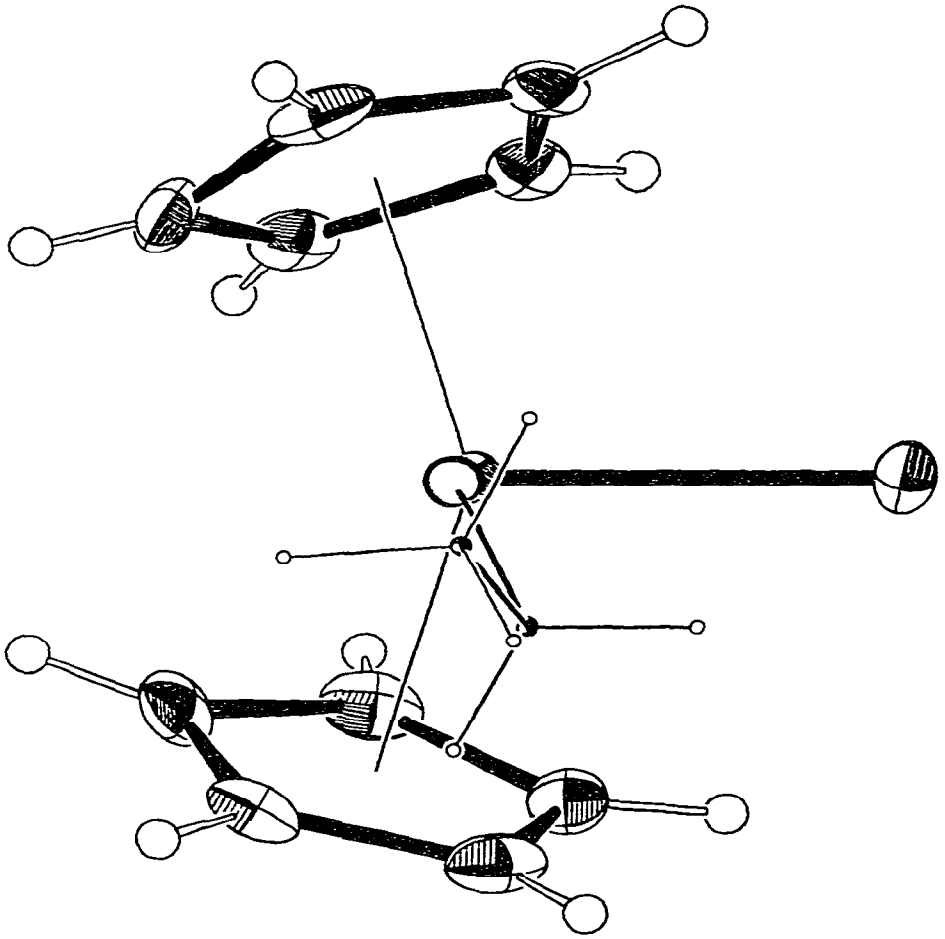


Fig. 1. Molecular structure of $Cp_2TiCl(OCH_2CH_3)$ viewed down the O—Ti bond (atoms of the ethoxy group have been artificially reduced in size for clarity). This Newman projection reveals a rotational conformation which directs one oxygen lone pair towards the metal-based LUMO which lies in the Cl—Ti—O plane (see III).

establish the relative stability of these two acetyl complexes by a direct competition experiment (eq. 8). When complexes Vb and VIa are combined in C_6D_6 under N_2, substantial conversion (>90%) to Va and VIb occurs; this

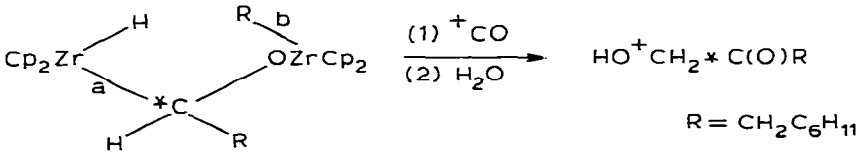
$$\underset{\text{(Vb)}}{Cp_2Zr[C(O)CH_3]Cl} + \underset{\text{(VIa)}}{Cp_2Zr(CH_3)_2} \rightleftharpoons \underset{\text{(Va)}}{Cp_2Zr(CH_3)Cl} + \underset{\text{(VIb)}}{Cp_2Zr[C(O)CH_3]CH_3} \quad (8)$$

equilibrium is established within 0.5 h at 25°C, and has also been approached by combining Va with VIb. The equilibrium constant for eq. 8 equals 20 ± 3 at 25°C in C_6D_6; this value exceeds that calculated solely on the basis of statistics (VIa has two Zr—C bonds). The greater stability of the products in eq. 8 may be attributed to chlorine π-donor stabilization of $Cp_2Zr(CH_3)Cl$ (relative to $Cp_2Zr(CH_3)_2$) and especially to a destabilizing internal competition of Cl and η^2-C(O)Me donor orbitals in $Cp_2Zr[C(O)CH_3]Cl$. Note that electronegativity

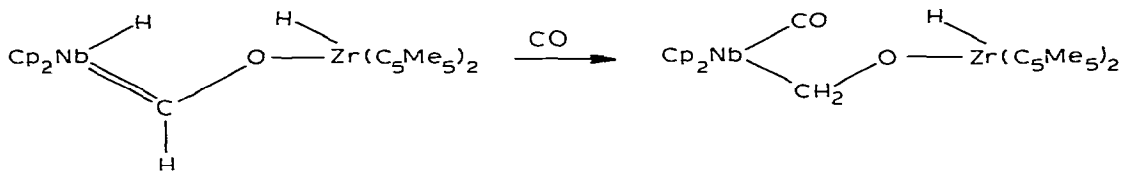
arguments incorrectly predict $Cp_2ZrX[C(O)Me]$ to be more stable when X = Cl than for X = CH_3. It follows that internal L-M donor competition in $Cp_2Zr(OR)[C(O)Me]$ should be maximal, since alkoxide is a much stronger π-donor than chloride [1]. In fact, we find no evidence for CO insertion into $Cp_2Zr(CH_3)OCH_2CH_3$ (2 h at 1 atm and 25°C). Moreover, alcoholysis of $Cp_2Zr[C(O)CH_3]CH_3$ with EtOH also fails to produce the alkoxy acetyl complex, yielding instead $Cp_2Zr(OEt)CH_3$ *.

Catalysts which operate in a homogeneous medium are generally supposed to exhibit product selectivity which is superior to their heterogeneous analogs. Our work suggests two mechanistic bases for the product selectivity exhibited in stoichiometric reactions activated by d^0 Cp_2M fragments. First, the proclivity of early transition metals for binding oxygen ligands (which may be due in large part to the π-donor behavior emphasized here) leads to a selectivity for low molecular weight reduction products (C_1 [18] or C_2 [17]) rather than homologation to long chain hydrocarbons or oxocarbons (e.g. glycerol). In general, the product of the first CO insertion event (into M—H or M—CH_n bonds) terminates the CO reduction to give, respectively, C_1 or C_2 products. The second origin of selectivity derives from the co-ligand (X) effect which we have observed in $Cp_2Zr(X)R$ complexes. Thus, treatment of $Cp_2Zr(X)CH_3$ with synthesis gas may yield a C_2 product via CO insertion when X is a weak π-donor. However, a strong π-donor co-ligand inhibits CO insertion to the point where hydrogenolysis to methane may be the only reaction observed.

We wish to point out several additional examples of this selectivity. In eq. 9 [23] the major product is derived from CO insertion into the Zr—C bond



marked "a", rather than at "b", consistent with alkoxide inhibition of CO insertion. Similarly, $Cp_2ClZrOCH_2ZrClCp_2$ [24] reacts only slowly with CO, suggesting that even a chlorine co-ligand exhibits a perceptible kinetic influence on the Zr—C bond in this dimer. Finally, compound VII [25] reacts with CO (1 atm) to promote metal-to-ligand hydrogen migration, rather than insertion into the Zr—H bond which exists in an oxide environment (<COZr = 166.4° in the related W/Zr dimer [25]).



(1)

(VII)

The co-ligand π-donor effect described here may represent one mechanism

* The relative kinetic stability of this product to further alcoholysis, which is also evident in the ready synthesis of $Cp_2Zr(OEt)CH_3$ from $Cp_2Zr(CH_3)_2$ and EtOH, suggests that alkoxide π-bonding has observable kinetic as well as thermodynamic consequences.

by which a metal oxide matrix (e.g. either Al_2O_3 or ZnO supports or so-called "promoters", Na_2O, K_2O, CaO, BaO, etc.) alters the activity and selectivity of heterogeneous transition metal catalysts [26,27]. Moreover, a matrix of μ_2-O—M′ ligands surrounding a catalytic metal M has a π-donor capacity which may be conveniently varied depending upon the electronegativity of M′ and the presence or absence of unoccupied *d* orbitals on M′.

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