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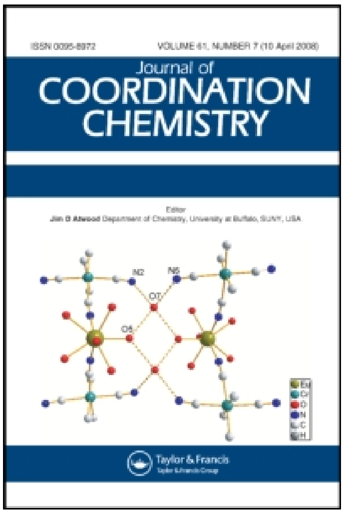

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SUBSTITUENT EFFECTS ON OXIDATIVE ADDITION TO TITANOCENE DICARBONYL COMPLEXES

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SUBSTITUENT EFFECTS ON OXIDATIVE ADDITION TO TITANOCENE DICARBONYL COMPLEXES

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The substituted titanocene dicarbonyl complexes, $Cp_2Ti(CO)_2$, $CpCp^*Ti(CO)_2$, [1]$Cp^*_2Ti(CO)_2$ and $CpCp^{CF_3}Ti(CO)_2$, were reacted with chloroform, yielding the respective titanocene dichloride complexes. The electronic effects of the substituents on the cyclopentadienyl ligands were evaluated by infrared spectroscopy and by X-ray photoelectron spectroscopy (XPS). *Pseudo* first order rate constants were then determined for each of the substituted titanocene dicarbonyl complexes as they reacted with chloroform. No correlation between these electronic effects and the rate constants was possible, however, since the rate constants remained essentially identical regardless of the substituents on the cyclopentadienyl ligands. The reaction of $Cp_2Ti(CO)_2$ with chloroform was also evaluated under normal conditions and exhibited overall first order kinetics, although the rate constant was affected by the chloroform concentration. This suggests a preequilibrium dissociated and reassociation of a carbonyl ligand in the first step in the reaction. Therefore, rather than exhibiting a lack of substituent effects, the rate constants may reflect an adjustment of the preequilibrium position caused by opposing electronic and steric effects imposed by the substituted cyclopentadienyl ligands.

KEYWORDS: titanocene, X-ray photoelectron spectroscopy, kinetics

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has proven to be an exceptionally useful means of identifying the electronic effects imposed on a metal center by its ligands.[2] XPS analysis has been extensively applied to complexes containing substituted cyclopentadienyl ligands, and the electronic effects of a number of substituents have been determined in this manner. Providing that the cyclopentadienyl-metal moiety remains intact throughout a given reaction, the electronic effects of the substituents on the respective reaction rates can then be addressed. We have attempted to explore these electronic effects as they occur in the oxidative addition of an alkyl halide to titanocene dicarbonyl complexes. Deuteriochloroform was chosen as the alkyl halide, since this provided a convenient means of monitoring the reaction

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under *pseudo* first order conditions. The effects of several substituents on this reaction are reported herein.

EXPERIMENTAL

All manipulations of air- and/or moisture-sensitive compounds were performed by using drybox, Schlenk line and vacuum line techniques. Routine ^1H and ^{13}C NMR spectra were recorded on an IBM AC/300 spectrometer. Kinetic measurements by ^1H NMR spectroscopy were carried out on a Nicolet NT-300 spectrometer. Temperatures were determined from $\Delta\upsilon(MeOH)$ (25° and 40°C) and $\Delta(HOCH_2CH_2OH)$ (55°C) and were constant to within ±0.5°C. All NMR samples were prepared in the drybox and the tubes were capped with rubber septa. Infrared spectra were recorded on either a Mattson Polaris^{TM} FT-IR spectrometer or a Beckman 4240 Spectrophotometer. High resolution mass spectra were obtained on an AEI MS30 instrument.

Tetrahydrofuran, hexane, 2,2,4-trimethylpentane and benzene-d_6 were distilled from sodium-benzophenone ketyl under argon and were degassed by several freeze-pump-thaw cycles. Deuteriochloroform was distilled from either phosphorus pentoxide or calcium chloride under argon. Solvents which were used in the drybox were further degassed by several freeze-pump-thaw cycles. Cp_2TiCl_2[1] was purchased from Aldrich Chemical Company. $Cp^*{}_2TiCl_2$,[3] $CpTiCl_3$,[4] $CpCp^*TiCl_2$,[5] and $CpCp^{CF_3}TiCl_2$[6] were made by literature procedures. $Cp_2Ti(CO)_2$ and $Cp^*{}_2Ti(CO)_2$ were also prepared by literature methods[7] with the modification that the products were filtered through celite in place of deactivated alumina.

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Synthesis of $CpCp^*Ti(CO)_2$ (2)

This compound was prepared as for **1**[7] with the modification that activated magnesium powder was used instead of magnesium turnings. Workup as above yielded 66% of **2** as a dark red powder. ^1H NMR (C_6D_6) δ4.57 (s, 5 H), 1.60 (s, 15 H); ^{13}C NMR (C_6D_6) δ104.3 (s), 94.6 (d), 11.7 (q) (CO carbons not observed); IR (KBr) 2968, 2952, 2903, 2854, 1946, 1854, 1486, 1435, 1384, 1263, 1070, 1030, 798 cm^{-1}; Exact mass m/e 304.0948 (Calcd for $C_{17}H_{15}O_2Ti$, 304.0943).

Synthesis of $CpCp^{CF_3}Ti(CO)_2$ (3)

This compound was prepared as for **1**.[7] The complex was extremely water and oxygen sensitive, so workup was carried out in a drybox, rather than on a Schlenk line. The red product, yield 10%, was stored in a dry refrigerator at −30°C for no more than 6 h prior to use in kinetic studies. ^1H NMR (C_6D_6) δ4.84 (m, 2H), 4.54 (s, 5H), 4.20 (m, 2H); ^{13}C NMR (C_6D_6) δ93.48, 93.16, 92.04 (CF_3 carbon not observed); IR (KBr) 3100, 2982, 28971 1979, 1897, 1460, 1315, 1120, 1032, 883, 805 cm^{-1}.

Kinetic Measurements

Pseudo First Order Conditions

0.5 ml of a 8.5×10^{-2} *M* solution of the appropriate titanocene dicarbonyl in deuteriochloroform was placed in an NMR tube. 2,2,4-Trimethylpentane (2 µl) was added as an internal standard. The sample was placed in the probe of the Nicolet NT-300 NMR spectrometer and was equilibrated at the appropriate temperature. Rate contstants were determined by measuring the decrease of the pentamethycyclopentadienyl ligand resonance of **2** and **4** or the cyclopentadienyl ligand resonance of **1** and **3**. Plots of In(A-A∞) were linear for at least three half-lives, and the rate constants were determined from the slope of this line as calculated by least squares methods (See Figure 1 for a representative plot.). Rate constants are reported as the unweighted averages of three experiments, and were measured at three temperatures: 25°, 40° and 55°C.

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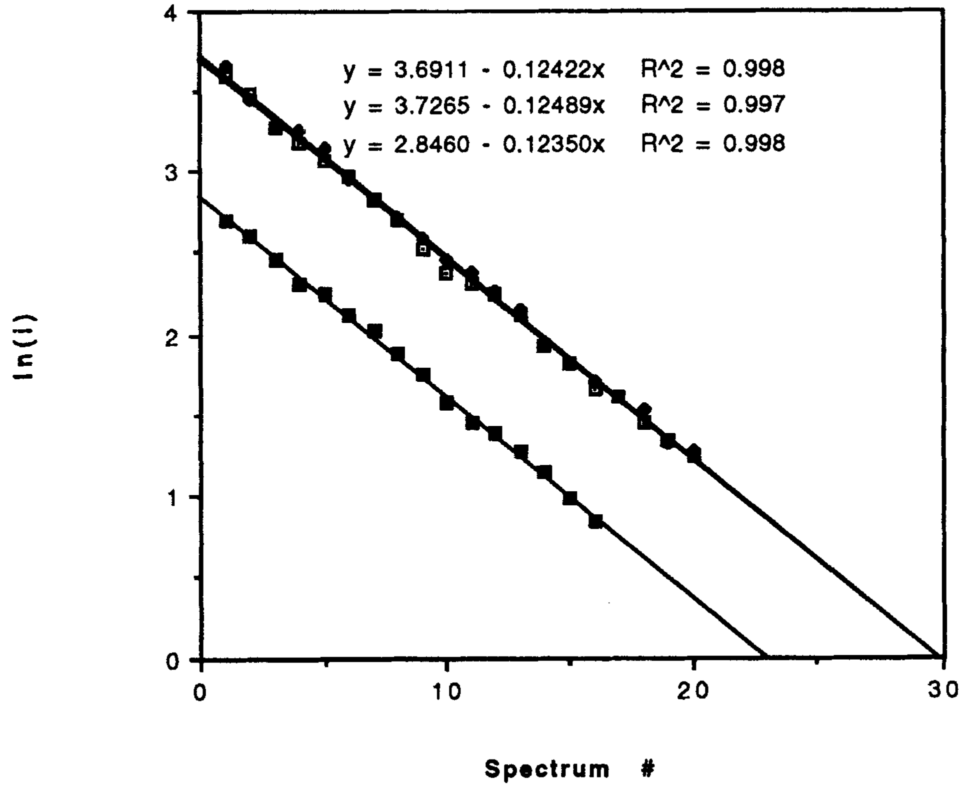

Figure 1 Sample first order plot for the reaction of 1 with deuteriochloroform under *pseudo* first order conditions at 55°C. ^{a}i = integration corrected for infinity point; spectra were taken 15 s apart.

Rate constant dependence on concentration

Rate constants for reactions of **1** with 0.5, 1, 2, 4 and 8 equivalents of deuteriochloroform (based on one chloride per molecule of deuteriochloroform) were obtained at 55°C only. The experiments were run in sets of 3 each, where the reactant (either **1** or deuteriochloroform) which was being maintained at constant concentration was placed in a vial along with 1.5 ml benzene-d_6 and 6 µl 2,2,4-trimethylpentane, and the resulting solution was divided between 3 NMR tubes. The tubes were then capped and maintained in the drybox until needed. Immediately prior to placing each sample in the NMR, the appropriate amount of the missing reactant was added. Rate constants were then obtained as before (See Figure 2 for a representative plot of the decay data and Figure 3 for a representative first order plot.).

RESULTS AND DISCUSSION

Mechanism

Pseudo first order rate constants were obtained for the reactions of four titanocene dicarbonyl complexes, $Cp_2Ti(CO)_2$ (**1**),[1] $CpCp^*Ti(CO)_2$ (**2**), $CpCp^{CF_3}Ti(CO)_2$ (**3**), and $Cp^*_2Ti(CO)_2$ (**4**), with deuteriochloroform. These reactions yielded the respec-

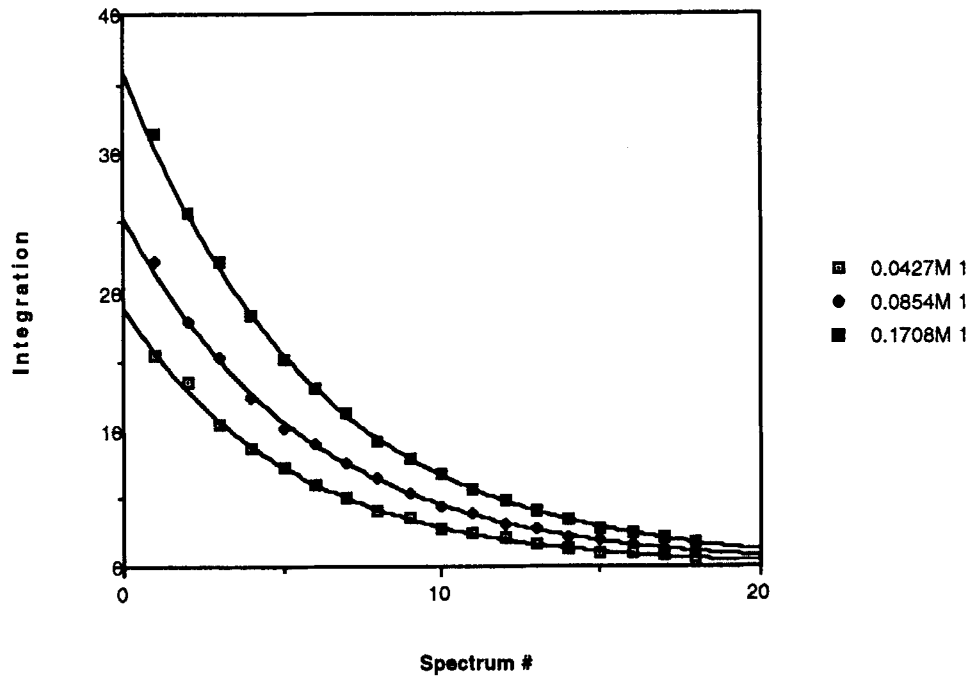

Figure 2 Sample decay plots for the reaction of **1** with 16.94 x 10^{-2} M deuteriochloroform in benzene-d_6 at 55°C.[a] [a]Intergration is corrected for infinity point; spectra were taken 30 s apart.

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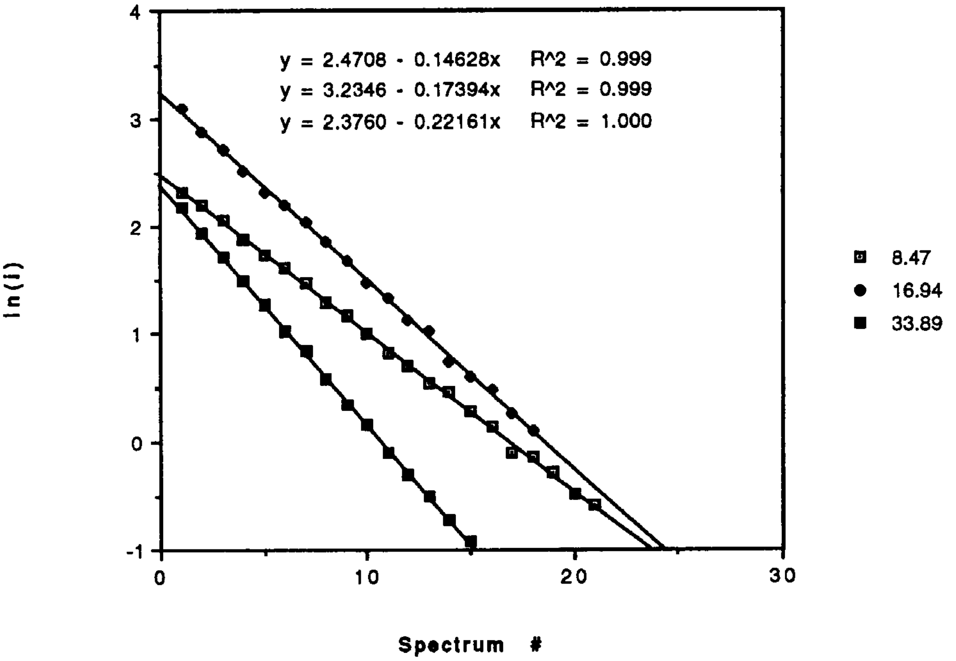

Figure 3 Sample first order plot for the reaction of 1 (8.54×10^{-2} M) with deuteriochloroform ($\times 10^{-2}$ M) at 55°C.[a] [a]i = integration corrected for infinity point; spectra were taken 30 s apart.

tive titanocene dichloride complexes. Loss of the starting complex was monitored by ^{1}H NMR, and the resulting rate constants and activation parameters are given in Table 1. Several intermediates were observed by ^{1}H NMR, in addition to the final product. Peaks corresponding to the proposed chloroform insertion products of type $Cp_2Ti(COCDCl_2)Cl$ were identified by comparison to related complexes. No

Table 1 Kinetic parameters for the oxidative addition of deuteriochloroform to titanocene dicarbonyl complexes **1**–**4**.

cmpd	T (°C) (± 0.5°)	ΔH≠ (kcal mol^{-1})	ΔS≠ (e.u.)	k (s^{-1})	k_{rel} at 40°C
1	25			$(5.29 \pm 0.06) \times 10^{-4}$	
	40	25.5 ± 1.0	12.0 ± 3.1	$(4.34 \pm 0.05) \times 10^{-3}$	2.4
	55			$(3.12 \pm 0.06) \times 10^{-2}$	
2	25			$(5.82 \pm 0.01) \times 10^{-4}$	
	40	26.2 ± 2.0	14.6 ± 6.4	$(4.44 \pm 0.08) \times 10^{-3}$	2.4
	55			$(3.89 \pm 0.03) \times 10^{-2}$	
3	25			$(2.80 \pm 0.03) \times 10^{-4}$	
	40	25.7 ± 0.3	11.5 ± 0.9	$(2.64 \pm 0.22) \times 10^{-3}$	1.4
	55			$(1.70 \pm 0.02) \times 10^{-3}$	
4	25			$(2.45 \pm 0.03) \times 10^{-4}$	
	40	21.9 ± 0.6	-1.3 ± 1.8	$(1.82 \pm 0.02) \times 10^{-3}$	1.0
	55			$(8.22 \pm 0.02) \times 10^{-3}$	

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side reactions or decompositions were observed within the time frame of the experiments.

The reactions of **1** with deuteriochloroform in benzene-d_6 were further examined under nonpseudo first order conditions to determine the dependence of the reaction rate on each component. First order rate constants were obtained and are compiled in Table 2. Titanocene dicarbonyl complexes have been reported to react *via* a dissociative mechanism, wherein the initial, rate determining step in the reaction is loss of a carbonyl ligand. The overall first order rate constants obtained in this reaction are in accordance with rate determining loss of a carbonyl ligand prior to association of the deuteriochloroform.

Although the reaction is apparently first order overall in complex **1**, the mechanism is not simple; the rate constants obtained also clearly show a dependence on the concentration of deuteriochloroform (Figure 4). This situation has also been observed by Basolo[8] during the substitution of one carbonyl ligand on **1** for a phosphine ligand. Overall first order reactions were observed which showed dependences on the concentrations of both **1** and phosphine at (< 0.5 M) concentrations of phosphine. This effect was rationalized as being due to return of the carbonyl ligand in an equilibrium step prior to reaction with the phosphine.

The reaction orders for both **1** and deuteriochloroform were determined by plotting ln(rate) *vs.* ln[reactant]. The order obtained for **1** was 0.919, which is essentially first order, while the deuteriochloroform order was calculated as 0.252 (Figure 5). This low reaction order could reflect the abstraction of multiple chlorines from each chloroform molecule, since the reaction of **1** to **5** proceeds to completion even at a ratio of **1** to chloroform of 2:1. However, the reaction order is more likely indicative of a partial k_{obs} dependence on $k_2[CDCl_3]$ (see equation 1). Assuming that the steady state approximation is valid for the concentrations of CO and Cp_2TiCO, then k_{obs} (equation 2) reflects the microscopic rate constants as shown in equation 3. Thus, a dependence of k_{obs} on $[CDCl_3]$ could be observed at lower deuteriochloroform concentrations and would reach a limit at high concentrations of deuteriochloroform (Figure 6).[8] Under *pseudo* first order conditions for deuteriochloroform, k_{obs} would not reflect changes in the chloroform concentration.

$$Cp_2Ti(CO)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cp_2Ti(CO) + CO \xrightarrow[CDCl_3]{k_2} Cp_2\,Ti(COCDCl_2)Cl \qquad (1)$$

$$d[Cp_2Ti(CO)_2]/dt = -K_{obs}[Cp_2Ti\,(CO)_2] \qquad (2)$$

Table 2 Rate constants determined with varying concentrations of complex 1 and deuteriochloroform in benzene-d_6.

$[CDCl_3]$ ($\times 10^{-2}$ *M*) =	8.47	16.94	33.89
[1]($\times 10^{-2}$ *M*) =		k($\times 10^{-3}$ s^{-1})	
4.27	4.47[a]/4.14[b]	6.08/6.34	6.54/7.18
8.54	5.57[c]/4.82	6.28/5.80	7.51/7.39
17.08	4.77/4.77	6.33/5.61	8.03/8.76

[a]Data corrected for an experimentally determined infinity point. [b]Uncorrected data. [c]The concentration of deuteriochloroform at the start of this experiment was 6.23×10^{-2} *M*.

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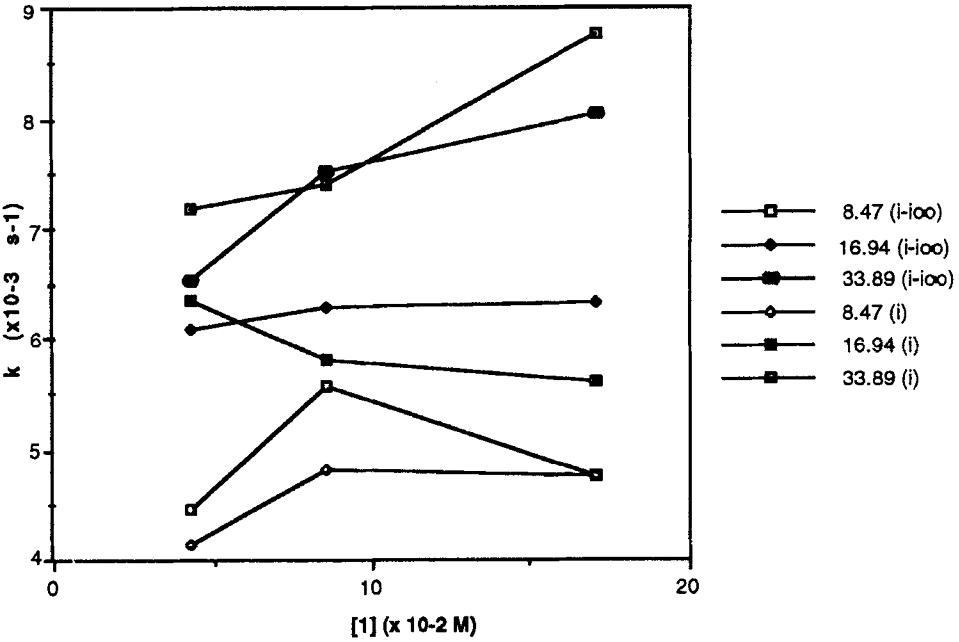

Figure 4 Rate constants determined with varying concentrations of 1 and deuteriochloroform in benzene-d_6.

$$k_{obs} = \frac{k_1k_2[CDCl_3]}{k_{-1}[CO] + k_2[CDCl_3]} \tag{3}$$

The activation parameters (Table 1) are in line with a dissociative mechanism for the reaction of the titanocene dicarbonyl complexes with deuteriochloroform. Very close agreement is observed between the complexes, with the exception of complex **4**. It is interesting that the entropy of activation for the reaction involving **4** is negative, although it is too close to zero to allow meaningful interpretation. Since there is evidence that the general reaction is not a purely first order, dissociative reaction, this negative entropy of activation may be indicative of an associative component.

Substituent Effects

As discussed above, the initial, rate determining step of this reaction appears to be loss of a carbonyl ligand. The rate of the reaction is therefore expected to depend on the ease of Ti-CO bond breaking. The relative strengths of the Ti-CO bonds can be assessed by the carbonyl stretching frequencies for the complexes, as measured by infrared spectroscopy. A shift to higher wavenumbers indicates a weaker Ti-CO bond. The requisite frequencies were obtained for complexes **1**–**4**, and are listed in Table 3. These stretching frequencies indicate that the Ti-CO bond strength increases in the order **3** < **1** < **2** < **4**.

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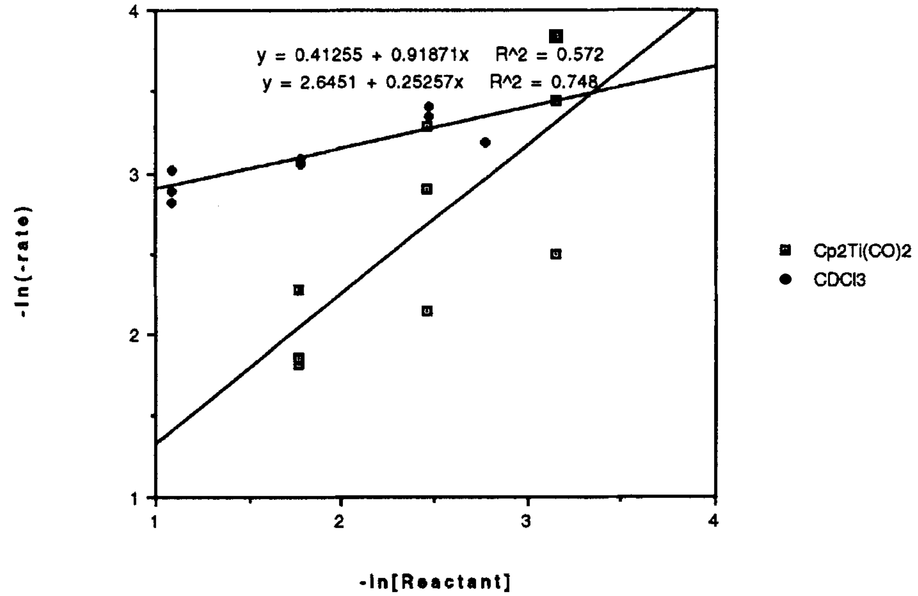

Figure 5 Determination of reactant orders for 1 and deuteriochloroform.

Table 3 Infrared carbonyl stretching frequencies for titanocene dicarbonyl complexes **1–4**, and XPS binding energies for titanocene dichloride complexes **5–8**.[a]

Compound	υCO (cm^{-1})		Ti ($2p_{3/2}$) (± 0.1 ev)
1	1961	1877	
5			456.9
2	1946	1854	
6			456.6
3	1979	1897	
7			457.3
4	1834	1838	
8			456.1

[a] Titanocene dichloride complexes are as follows: Cp_2TiCl_2 (**5**); $CpCp^*TiCl_2$ (**6**); Cp^{CF_3} $CpTiCl_2$ (**7**) and $Cp^*_2TiCl_2$ (**8**).

While carbonyl stretching frequencies reflect the electronic influence of the substituted cyclopentadienyl ligands on the metal, this influence can be more directly measured by XPS. XPS provides information about the effective oxidation state of the metal itself *via* the binding energies of its inner-shell electrons. A large number of substituted cyclopentadienyl ligands in various metal complexes have been analyzed in this manner and consistent electron donating and withdrawing abilities of the substituents have been determined.[2] Binding energies for the respective titanocenes are reported in Table 3; the values given are for the titanocene dichloride complexes, due to the instability of the analogous titanocene dicarbonyl compounds.[9] XPS shows the Cp^{CF_3} ligand to be electron withdrawing, while the methylated cyclopentadienyl ligands are cumulatively electron donating

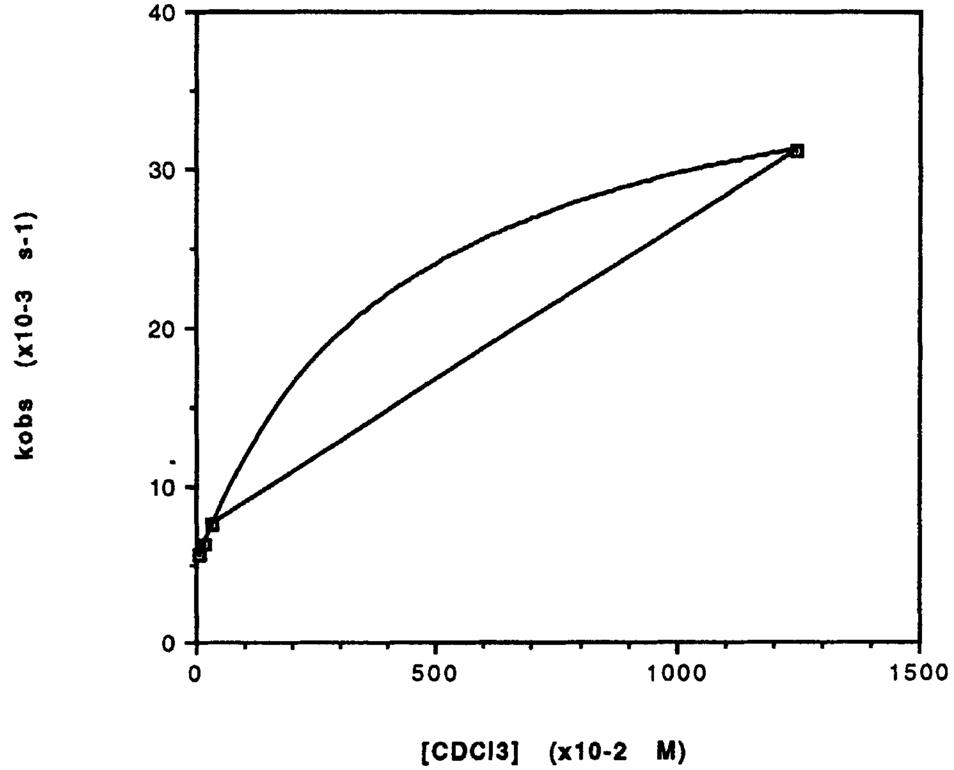

Figure 6 Effect of the deuteriochloroform concentration on k_{obs} for reactions with 8.5×10^{-2} M 1 at 55°C.

(CpCp* < Cp^*_2). These data are in agreement with the infrared stretching frequencies.

Although the electron donating and withdrawing properties of the substituted cyclopentadienyl ligands are clearly observed by XPS and IR, these effects are not readily identifiable in the reaction rates. A comparison of the *pseudo* first order rate constants (Table 1) reveals only a very small difference in rate between the four titanocene dicarbonyl complexes. These rates decrease in the order **1**≈**2** > **3** > **4** with the overall difference between **1** and **4** being less than an order of magnitude. If oxidative addition of deuteriochloroform to complexes **1**–**4** occurred by a simple dissociative mechanism, the XPS and IR data predict that a reaction rate order of **3** > **1** > **2** > **4** would have been observed.

Although the rate differences exhibited by the various complexes are too small to represent a significant trend, it is curious that **1** should react the fastest, while both **3** and **4** are slower. A similar order was observed by Grubbs,[5] wherein the rate for formation of Tebbe's reagent decreased upon substitution at the cyclopentadienyl ligands. This was attributed to a balance between the ligands' effects on the energies of the starting material and the first transition state.

The small relative rate for reaction of **4** *vs* that of **1** with deuteriochloroform (k_{rel}

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at 40°C = 2.4) is also very similar to that found by Basolo[8] for exchange of ^{13}CO by CO in the same complexes (k_{rel} at 45°C = 3.9). This small difference is not in any way typical of titanium complexes. Instead, it was proposed to reflect a damping of the cyclopentadienyl ligands' effects by a preequilibrium dissociation and reassociation of CO prior to attack by the incoming ligand.

Based on Basolo's results,[8] we speculate that the similarity of the rates observed for complexes **1**–**4** is also a consequence of a preequilibrium dissociation and association of a molecule of CO from the titanocene dicarbonyl complexes prior to their reaction with the chloroform, as shown in equation 1. The electron donating ability of the methyl substituents increases the Ti-CO bond strength, thereby decreasing the reaction rate, while the steric congestion imposed by these same substituents may encourage dissociation of the CO and discourage reassociation, thereby increasing the reaction rate. Intramolecular interaction of a methyl substituent on a pentamethylcyclopentadienyl ligand with the titanium center could provide additional stabilization of the mono-carbonyl intermediate. Such a "tuck-in" mechanism may be reflected in the negative entropy of activation observed for complex **4**. However, no analogous effect is identifiable for the other pentamethylcyclopentadienyl-containing species, complex **2**. Conversely, the electron withdrawing CF_3 ligand weakens the Ti-CO bond and encourages CO dissociation, while its steric profile should be too small to encourage CO dissociation or inhibit its reassociation. Therefore, the similar rates observed for complexes **1**–**4** are attributed to the steric and electronic effects opposing each other in this reaction, with the net result being that no significant correlation was observed between the measured electronic effects of the ligands on the titanium and the rate of this reaction.

Acknowledgements

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1. Abbreviations: Cp, cyclopentadienyl anion; Cp*, pentamethylcyclopentadienyl anion; Cp^{CF_3}, trifluoromethylcyclopentadienyl anion.
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