# Selectivity and Reactivity in Reactions of Methylaryltitanium(IV) Complexes with Electrophiles

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Methyl or phenyl for halogen-exchange reactions occur between $[TiMe_2(\eta\text{-}C_5H_5)_2]$ or $[TiPh_2(\eta\text{-}C_5H_5)_2]$ with $[TiX_2(\eta\text{-}C_5H_5)_2]$, X = halogen, to give $[TiXMe(\eta\text{-}C_5H_5)_2]$ or $[TiXPh(\eta\text{-}C_5H_5)_2]$, respectively. The reactions are complicated by parallel decomposition of the methyl- or phenyltitanium complexes, which is catalyzed by $[TiX_2(\eta\text{-}C_5H_5)_2]$ or $[TiXR(\eta\text{-}C_5H_5)_2]$. In general, there is little difference in the rates of reaction of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ and $[TiPh_2(\eta\text{-}C_5H_5)_2]$ toward the symmetrization reactions. These reagents also transfer a methyl group or phenyl group to platinum(II) or gold(III), but there are again side reactions. The complex $[TiMePh(\eta\text{-}C_5H_5)_2]$ reacts with electrophiles HCl, HOAc, $HgCl_2$, and MeHgCl to give cleavage of both methyl- and phenyltitanium bonds with little selectivity. In cleavage of $[TiMe(C_6H_4X)(\eta\text{-}C_5H_5)_2]$ there is a correlation of the selectivity for cleavage of the aryl group by electrophiles HCl or $HgCl_2$ with the $\sigma^+$ parameters of substituents X. A mechanism of reaction involving electron transfer from the complex to the electrophile followed by rapid cleavage is tentatively suggested.

## Introduction

In earlier papers, attempts have been made to determine the mechanism of cleavage by electrophiles of the transition-metal–carbon $\sigma$ bond in alkyl and aryl derivatives of platinum(II) and gold(III).[1-3] For tertiary phosphine derivatives of platinum(II), it was found that such reactions gave a rate sequence $[PtMe_2L_2] \gg [PtPh_2L_2]$[1] and that, in *cis*-$[PtMePhL_2]$, the methyl group was cleaved selectively by electrophiles.[3] These results were the opposite of those expected for the classical $S_E2$ mechanism of electrophilic substitution,[4] as found for the gold(III) compounds, and were interpreted in terms of an oxidative addition–reductive elimination sequence.[2,3] This latter mechanism is not possible for alkyl derivatives of titanium(IV), and we have now extended our studies to complexes of structure $[TiR_2(\eta\text{-}C_5H_5)_2]$. We expected that these would show reactivity more like main-group derivatives than like the platinum(II) complexes studied earlier,[1-3] but a much more complex pattern of behavior was actually observed.

## Results

The results of this study fall naturally into three sections. The first two deal with reactions of $[TiR_2(\eta\text{-}C_5H_5)_2]$, R = Me or Ph, with the titanium derivatives $[TiX_2(\eta\text{-}C_5H_5)_2]$ or with platinum or gold derivatives *cis*-$[PtX_2L_2]$ or *cis*-$[AuXMe_2L]$, X = halide and L = tertiary phosphine. In each case, the aim was to examine the relative reactivities of the methyl- and phenyltitanium derivatives and to look for synthetically useful reactions. In the third part, the selectivity of cleavage of methyl or aryl groups from $[TiMeAr(\eta\text{-}C_5H_5)_2]$ was examined.

**Symmetrization Reactions.** These reactions are described by eq 1 and 2 and appear not to have been studied previously.[5-7]

$$[TiMe_2(\eta\text{-}C_5H_5)_2] + [TiX_2(\eta\text{-}C_5H_5)_2] \rightarrow 2[TiXMe(\eta\text{-}C_5H_5)_2] \quad (1)$$

$$[TiPh_2(\eta\text{-}C_5H_5)_2] + [TiX_2(\eta\text{-}C_5H_5)_2] \rightarrow 2[TiXPh(\eta\text{-}C_5H_5)_2] \quad (2)$$

The reactions could be monitored by $^1H$ NMR spectroscopy, since the singlets due to cyclopentadienyl protons of each species were well resolved.[5,6] With the methyl derivatives, the resonances due to methyl groups could also be used. Most reactions were slow, taking several hours to days to reach completion, and yields of product were not quantitative. Complications arose due to decomposition of the dimethyl- or diphenyltitanium(IV) derivative giving methane ($\delta$ 0.23) or benzene ($\delta$ 7.27), respectively, along with unidentified titanium complexes.[8] NMR data for reagents and products are given in Table I. Because of the low rates and side reactions, this is not recommended as a synthetic method for $[TiXMe(\eta\text{-}C_5H_5)_2]$ in most cases.[6] However, a synthesis of $[TiFMe(\eta\text{-}C_5H_5)_2]$ by this method is straightforward and the compound has not been prepared previously. It is readily characterized by the doublet splittings of the methyl and $C_5H_5$ signals in the $^1H$ NMR spectrum due to coupling with the single fluoride. In other cases, the products were identified by comparison of the NMR spectra with those of authentic samples prepared independently.[5-7]

Reactivity comparisons and kinetic studies were severely complicated by the side reactions, but useful data were obtained. NMR samples were made up containing equal concentrations of reagents $[TiMe_2(\eta\text{-}C_5H_5)_2]$ and $[TiX_2(\eta\text{-}C_5H_5)_2]$, and the tubes were sealed and kept at constant temperature. An internal reference, chloroform, was used, and concentrations were determined by comparison of signal intensities with the intensity of the chloroform peak.

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Table I. NMR Data for the Organometallic Complexes[a]

| compound | $\delta(C_5H_5)$[b] | $\delta$(Me)[b] | other |
|---|---|---|---|
| $Ti(OAc)_2(\eta\text{-}C_5H_5)_2$ | 6.46 | | 1.99 (MeCO) |
| $TiF_2(\eta\text{-}C_5H_5)_2$ | 6.44 t | | $^3J$(HF) = 1.7 Hz |
| $TiCl_2(\eta\text{-}C_5H_5)_2$ | 6.57 | | |
| $TiBr_2(\eta\text{-}C_5H_5)_2$ | 6.67 | | |
| $TiI_2(\eta\text{-}C_5H_5)_2$ | 6.81 | | |
| $TiMe_2(\eta\text{-}C_5H_5)_2$ | 6.05 | −0.16 | |
| $TiPh_2(\eta\text{-}C_5H_5)_2$ | 6.19 | | 6.89 (s, Ph) |
| $TiMePh(\eta\text{-}C_5H_5)_2$ | 6.07 | 0.37 | |
| $TiMe(4\text{-}MeOC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.03 | 0.35 | 6.35 (m, $C_6H_4$), 3.60 (MeO) |
| $TiMe(4\text{-}MeC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.00 | 0.37 | 2.14 (MeC) |
| $TiMe(4\text{-}ClC_6H_4)(\eta\text{-}C_5H_5)_2$ | 5.97 | 0.37 | |
| $TiMe(3\text{-}ClC_6H_4)(\eta\text{-}C_5H_5)_2$ | 5.97 | 0.38 | |
| $TiMe(4\text{-}FC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.00[c] | 0.38[c] | |
| $TiMe(3\text{-}FC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.10 | 0.40[c] | |
| $TiFMe(\eta\text{-}C_5H_5)_2$ | 6.12 d | 0.99 d | $^3J$(HF,$C_5H_5$) = 1.5 Hz $^3J$(HF,Me) = 5 Hz |
| $TiClMe(\eta\text{-}C_5H_5)_2$ | 6.25 | 0.85 | |
| $TiBrMe(\eta\text{-}C_5H_5)_2$ | 6.33 | 0.55 | |
| $TiIMe(\eta\text{-}C_5H_5)_2$ | 6.41 | −0.06 | |
| $Ti(OAc)Me(\eta\text{-}C_5H_5)_2$ | 6.13 | 0.84 | 1.74 (MeCO) |
| $TiClPh(\eta\text{-}C_5H_5)_2$ | 6.30 | | 6.87 (br, Ph) |
| $TiCl(4\text{-}MeOC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.42[d] | | |
| $TiCl(4\text{-}MeC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.28 | | |
| $TiCl(4\text{-}ClC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.27 | | |
| $TiCl(3\text{-}ClC_6H_4)(\eta\text{-}C_5H_5)_2$ | 6.27 | | |

[a] Solvent $CDCl_3$. [b] Singlets unless otherwise specified. [c] Impure samples. [d] Solvent acetone-$d_6$.

In the early stages, the reagent concentrations were essentially equal but, in the later stages, the concentration of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ became significantly lower due to the parallel decomposition reaction. Useful kinetic data could not be obtained in these later stages.

Reactions in which disappearance of $[TiX_2(\eta\text{-}C_5H_5)_2]$ was monitored gave good second-order plots (Figure 1), and studies using initial rates showed that reaction rates were first order in each reagent. However, when reactions were monitored by following disappearance of $[TiMe_2(\eta\text{-}C_5H_5)_2]$, second-order plots curved upward and several reactions appeared to follow first-order kinetics. This apparently anomalous behavior was investigated in detail for the system $[TiMe_2(\eta\text{-}C_5H_5)_2]$ with $[TiCl_2(\eta\text{-}C_5H_5)_2]$. The second-order rate constants obtained by monitoring disappearance of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ or $[TiCl_2(\eta\text{-}C_5H_5)_2]$ were $1.2 \times 10^{-3}$ and $7.7 \times 10^{-4}$ L mol$^{-1}$ s$^{-1}$, respectively, at 36 °C, and the difference between these gives the rate constant for the decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ catalyzed by $[TiCl_2(\eta\text{-}C_5H_5)_2]$ as $4.2 \times 10^{-4}$ L mol$^{-1}$ s$^{-1}$. This is clearly a catalyzed decomposition because it does not consume $[TiCl_2(\eta\text{-}C_5H_5)_2]$ but is much faster than decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ in the absence of $[TiCl_2(\eta\text{-}C_5H_5)_2]$.[8] For this uncatalyzed decomposition a first-order rate constant of $2.1 \times 10^{-6}$ s$^{-1}$ was determined by an independent study.[9] There is still a problem in understanding the deviation from second-order kinetics, but this was largely resolved by a study of the decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ catalyzed by $[TiClMe(\eta\text{-}C_5H_5)_2]$. This reaction followed second order kinetics with $k = 2.0 \times 10^{-4}$ L mol$^{-1}$ s$^{-1}$. Very little decomposition of $[TiClMe(\eta\text{-}C_5H_5)_2]$ was observed. Now since 2 molar equiv of $[TiClMe(\eta\text{-}C_5H_5)_2]$ are produced by each $[TiCl_2(\eta\text{-}C_5H_5)_2]$ consumed but the former complex is only half as efficient at catalyzing the decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$, the decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ will appear to be almost independent of concentration of $[TiCl_2(\eta\text{-}C_5H_5)_2]$ for a given kinetic run. Hence the upward slope in the second-order plot is expected. In the early stages it is clear that the

(9) This reaction was followed to low conversion only. If the catalyzed decomposition, as the uncatalyzed reaction, occurs in two distinct stages,[8d] this would correspond to the initial rate only.

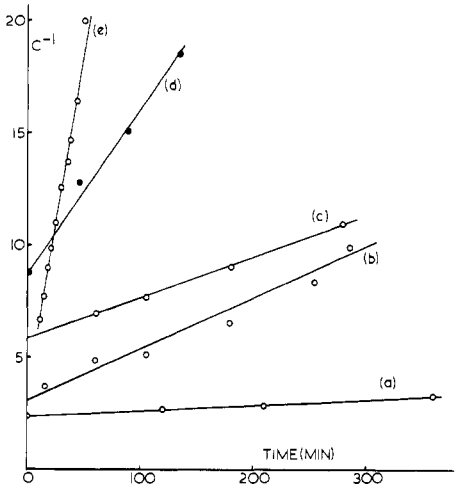


**Figure 1.** Second-order kinetic plots for reactions in $CDCl_3$ at 36 °C, monitored from concentration of dihalobis(cyclopentadienyl)titanium(IV) complex: (a) $[TiCl_2(\eta\text{-}C_5H_5)_2]$ with $[TiMe_2(\eta\text{-}C_5H_5)_2]$; (b) $[TiCl_2(\eta\text{-}C_5H_5)_2]$ with $[TiPh_2(\eta\text{-}C_5H_5)_2]$; (c) $[TiF_2(\eta\text{-}C_5H_5)_2]$ with $[TiMe_2(\eta\text{-}C_5H_5)_2]$; (d) $[TiBr_2(\eta\text{-}C_5H_5)_2]$ with $[TiMe_2(\eta\text{-}C_5H_5)_2]$; (e) $[TiI_2(\eta\text{-}C_5H_5)_2]$ with $[TiPh_2(\eta\text{-}C_5H_5)_2]$. Concentrations are in arbitrary units, and initial concentrations are given in Table II.

symmetrization reaction of eq 1 and the parallel decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ follow the rate laws

$$-\frac{d}{dt}[TiCl_2(\eta\text{-}C_5H_5)_2] = k[TiMe_2(\eta\text{-}C_5H_5)_2][TiCl_2(\eta\text{-}C_5H_5)_2]$$

$$-\frac{d}{dt}[TiMe_2(\eta\text{-}C_5H_5)_2] = (k + k')[TiMe_2(\eta\text{-}C_5H_5)_2][TiCl_2(\eta\text{-}C_5H_5)_2]$$

Here $k$ is the rate constant for the symmetrization reaction and $k'$ is the rate constant for catalyzed decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$.

Very similar effects are seen in reactions of other $[TiX_2(\eta\text{-}C_5H_5)_2]$ reagents with $[TiMe_2(\eta\text{-}C_5H_5)_2]$ or with $[TiPh_2(\eta\text{-}C_5H_5)_2]$, as seen in Table II, which contains a summary of the kinetic data. The following general trends can be observed:

Table II. Second-Order Rate Constants ($k_2$, L mol$^{-1}$ s$^{-1}$) for Reactions of $[TiR_2(\eta\text{-}C_5H_5)_2]$ with $[TiX_2(\eta\text{-}C_5H_5)_2]$ in $CDCl_3$ at 36 °C

| reagents | | | | | |
|---|---|---|---|---|---|
| R | X | $C_0$,[a] L mol$^{-1}$ | $k$,[b] L mol$^{-1}$ s$^{-1}$ | $k + k'$,[c] L mol$^{-1}$ s$^{-1}$ | $k'$,[d] L mol$^{-1}$ s$^{-1}$ |
| Me | F | 0.025 | $2.0 \times 10^{-3}$ | $3.3 \times 10^{-3}$ | $1.3 \times 10^{-3}$ |
| Me | Cl | 0.027 | $7.7 \times 10^{-4}$ | $1.2 \times 10^{-3}$ | $4.2 \times 10^{-4}$ |
| Me | Br | 0.018 | $7.3 \times 10^{-3}$ | $1.8 \times 10^{-2}$ | $1.1 \times 10^{-2}$ |
| Me | I | 0.012 | $4.2 \times 10^{-3}$ | $1.7 \times 10^{-2}$ | $1.3 \times 10^{-2}$ |
| Me | OAc | 0.017 | $3.5 \times 10^{-5}$ | $6.2 \times 10^{-5}$ | $2.7 \times 10^{-5}$ |
| Me | e | 0.085 | | $2.0 \times 10^{-4}$ | |
| Me | f | 0.025 | | $2.1 \times 10^{-6}$ | |
| Ph | F | 0.024 | g | $7.3 \times 10^{-4}$ | |
| Ph | Cl | 0.045 | $2.6 \times 10^{-3}$ | $2.6 \times 10^{-3}$ h | |
| Ph | Br | 0.041 | $1.3 \times 10^{-3}$ | $5.8 \times 10^{-3}$ | $4.5 \times 10^{-3}$ |
| Ph | I | 0.016 | $6.1 \times 10^{-2}$ | $7.0 \times 10^{-2}$ | $0.9 \times 10^{-2}$ |
| Ph | f | 0.025 | | $1.3 \times 10^{-5}$ | |

[a] Initial concentration of each reagent. [b] Rate constant from disappearance of $[TiX_2(\eta\text{-}C_5H_5)_2]$. [c] Rate constant from disappearance of $[TiMe_2(\eta\text{-}C_5H_5)_2]$. [d] Obtained by difference. [e] Reagent $[TiClMe(\eta\text{-}C_5H_5)_2]$. [f] No additive. [g] Small. [h] Poor kinetics, faster in late stages.

1. In general the rate of the symmetrization reaction of eq 1 or 2 parallels the rate of catalyzed decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ or $[TiPh_2(\eta\text{-}C_5H_5)_2]$. This suggests that the reactions leading to methyl or phenyl transfer or to decomposition are related in a mechanistic sense, with a common intermediate or transition state leading to either reaction.

2. The exchange reactions generally are faster for the heavier halide, X, but the trend is not a smooth one. For reactions with $[TiMe_2(\eta\text{-}C_5H_5)_2]$ the rate sequence X = I > Br > F > Cl > OAc is observed (the sequence I > Br was qualitative since rate constants were obtained at different temperatures), and for reactions with $[TiPh_2(\eta\text{-}C_5H_5)_2]$ the rate sequence was X = I > Cl > Br > F.

3. There was no clear trend in the relative reactivity of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ vs. $[TiPh_2(\eta\text{-}C_5H_5)_2]$. With $[TiI_2(\eta\text{-}C_5H_5)_2]$ or $[TiCl_2(\eta\text{-}C_5H_5)_2]$, the phenyl derivative reacted faster but, with $[TiBr_2(\eta\text{-}C_5H_5)_2]$ or $[TiF_2(\eta\text{-}C_5H_5)_2]$, the methyl derivative reacted faster. It is not possible to explain these observations, but it can be concluded that $[TiMe_2(\eta\text{-}C_5H_5)_2]$ and $[TiPh_2(\eta\text{-}C_5H_5)_2]$ are similar in reactivity toward the symmetrization reactions.

**Methylation of Gold and Platinum.** $[TiMe_2(\eta\text{-}C_5H_5)_2]$ acts as a methylating agent toward gold(III) or platinum(II) as shown by reactions 3 and 4.

$$[TiMe_2(\eta\text{-}C_5H_5)_2] + cis\text{-}[AuClMe_2(PPh_3)] \rightarrow [TiClMe(\eta\text{-}C_5H_5)_2] + [AuMe_3(PPh_3)] \quad (3)$$

$$[TiMe_2(\eta\text{-}C_5H_5)_2] + cis\text{-}[PtCl_2(PMePh_2)_2] \rightarrow [TiClMe(\eta\text{-}C_5H_5)_2] + trans\text{-}[PtClMe(PMePh_2)_2] \quad (4)$$

Reaction 3 was complete in about 1 h at 20 °C and was complicated by the slow decomposition of $[AuMe_3(PPh_3)]$ to give ethane and $[AuMe(PPh_3)]$ and by the parallel decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ to give methane. By examining initial rates of reaction at various concentrations of starting materials, it was established that the methyl for chloro-exchange reaction followed second-order kinetics, first order in each reagent. However, the side reactions made it impossible to follow the kinetics for extended periods.

Reaction 4 was much slower, being complete in about 2 weeks at 20 °C. Again significant decomposition of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ occurred to give methane, and meaningful kinetic studies were not possible.

Transfer of methyl groups from $[TiMe_2(\eta\text{-}C_5H_5)_2]$ to *trans*-$[PdCl_2(PMe_3)_2]$ to give *trans*-$[PdClMe(PMe_3)_2]$, using photochemical activation, has been observed previously.[10] The mechanism proposed involved homolysis of TiMe bonds, followed by $S_H2$ displacement of a chlorine radical by a methyl radical from palladium(II). We have confirmed that the thermal reaction of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ with *trans*-$[PdCl_2(PEt_3)_2]$ is slow.

**Synthesis and Reactions of Methylaryltitanium Complexes.** The methylaryltitanium complexes[11] were prepared by reaction of $[TiClMe(\eta\text{-}C_5H_5)_2]$ with the required aryllithium reagent to give $[TiMeAr(\eta\text{-}C_5H_5)_2]$. These syntheses were not straightforward however. Frequently, when excess aryllithium reagent was used, the required product was contaminated with $[TiMe_2(\eta\text{-}C_5H_5)_2]$. It was shown separately that no reaction occurred between $[TiMeAr(\eta\text{-}C_5H_5)_2]$, Ar = aryl, and $[TiClMe(\eta\text{-}C_5H_5)_2]$ so that the byproduct was not formed by a reaction of this kind. It is most probable that exchange occurs between $[TiMeAr(\eta\text{-}C_5H_5)_2]$ and LiAr or LiCl to give methyllithium which then gives $[TiMe_2(\eta\text{-}C_5H_5)_2]$ by reaction with $[TiClMe(\eta\text{-}C_5H_5)_2]$ or $[TiMeAr(\eta\text{-}C_5H_5)_2]$. With use of a stoichiometric quantity of aryllithium, much unchanged $[TiClMe(\eta\text{-}C_5H_5)_2]$ was recovered and separation was difficult. Milder arylating agents failed to react with $[TiClMe(\eta\text{-}C_5H_5)_2]$. Attempted methylation of $[TiClPh(\eta\text{-}C_5H_5)_2]$ was also unsuccessful. In our hands, the amount of impurities formed in the synthesis of $[TiMeAr(\eta\text{-}C_5H_5)_2]$ was not reproducible, and it was necessary to repeat the reactions until a reasonably pure product was obtained. In some cases, for example when Ar = 3- or 4-fluorophenyl, we were unable to prepare samples in pure form despite a large number of attempts. When isolated, the complexes $[TiMeAr(\eta\text{-}C_5H_5)_2]$ were orange solids that were stored in the dark at −78 °C. At room temperature, they decomposed slowly in much the same way that the symmetrical derivatives $[TiMe_2(\eta\text{-}C_5H_5)_2]$ or $[TiPh_2(\eta\text{-}C_5H_5)_2]$ do.[8] They were characterized unambiguously by the $^1H$ NMR spectra, which are given in Table I.

The results of reactions of the complexes $[TiMeAr(\eta\text{-}C_5H_5)_2]$ with the electrophiles anhydrous HCl, acetic acid, mercury(II) chloride, and methylmercury(II) chloride are given in Table III. Before these results are discussed, some experimental aspects need to be mentioned. To determine the selectivity, reactions were carried out with a deficiency of the electrophile at low temperature. In this way, complications due to reaction of, for example, hydrogen chloride with initially formed $[TiClMe(\eta\text{-}C_5H_5)_2]$ or $[TiClAr(\eta\text{-}C_5H_5)_2]$ to give $[TiCl_2(\eta\text{-}C_5H_5)_2]$ were avoided. The product ratio was determined in each case from the intensities of the singlets in the $^1H$ NMR spectra due to the $\eta\text{-}C_5H_5$ groups of each product. These products were synthesized independently in order to confirm the assignments in the NMR spectra. In several cases, $[TiMeAr(\eta\text{-}C_5H_5)_2]$ was shown not to react with $[TiClMe(\eta\text{-}C_5H_5)_2]$ to a measurable extent over a period of several hours. Hence, secondary reactions between starting materials and titanium complex products do not complicate the results shown in Table III. One problem was found in reactions using mercury(II) chloride as electrophile. The initially formed alkyl- or arylmercury(II) chloride acted as an electrophile, though less reactive than mercury(II) chloride itself, and stoichiometries such as shown in eq 5 and 6 were seen.

$$[TiMe_2(\eta\text{-}C_5H_5)_2] + HgCl_2 \rightarrow [TiCl_2(\eta\text{-}C_5H_5)_2] + HgMe_2 \quad (5)$$

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(11) The pentafluorophenyl derivative $[TiMe(C_6F_5)(\eta\text{-}C_5H_5)_2]$ has been reported. Dormond, A.; Dahchour, A. *J. Organomet. Chem.* **1980**, *193*, 321.

$$[TiMePh(\eta\text{-}C_5H_5)_2] + HgCl_2 \rightarrow [TiCl_2(\eta\text{-}C_5H_5)_2] \{+ HgMe_2 + HgMePh + HgPh_2\} \quad (6)$$

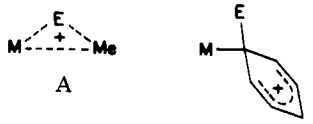
Clearly, the selectivity could not be studied under these conditions. It was therefore necessary to use only $^1/_4$ mol equiv of $HgCl_2$ to obtain the selectivity parameters. We found that the selectivity found in cleavage of $[TiMePh(\eta\text{-}C_5H_5)_2]$ by $HgCl_2$ was almost the same as that for cleavage by MeHgCl. Hence, although the reactivity of the primary product MeHgCl is certainly a complicating factor, we believe that the selectivities for cleavage of methyl- or aryltitanium bonds by $HgCl_2$ are reliable. The data given in Table III for the selectivity are generally obtained only from intensities of NMR signals due to the titanium-containing products. In reactions of $[TiMePh(\eta\text{-}C_5H_5)_2]$ with HCl, the organic products were identified as methane and benzene with no toluene or biphenyl formed, but quantitative analysis was not possible. In reactions with $HgCl_2$ or MeHgCl, the organomercury products were identified by the NMR spectra but no quantitative analyses were made due to experimental problems. The absence of coupling products such as biphenyl or toluene from $[TiMePh(\eta\text{-}C_5H_5)_2]$ rules out reactions involving long-lived alkyl or aryl radicals, but it is known that H abstraction from Ti–Me or Ti–$C_5H_5$ groups is very fast so that a free radical mechanism cannot be eliminated on this basis.[12f]

Both hydrogen chloride and acetic acid gave a slight preference for cleavage of a phenyl group rather than a methyl group from $[TiMePh(\eta\text{-}C_5H_5)_2]$ (Table III), while mercury(II) chloride and methylmercury(II) chloride showed a slight preference for cleavage of a methyl group. We know of no other organometallic system that shows this change in selectivity depending on the electrophile and no other that shows such a slight preference for cleavage of methyl or aryl groups.[1-4,13]

The selectivity correlates roughly with the Hammett $\sigma$ values of the substituents on the aryl group in the complexes $[TiMeAr(\eta\text{-}C_5H_5)_2]$. In reactions with hydrogen chloride the selectivity for aryl cleavage gave the series Ar = 4-$MeOC_6H_6$ > 4-$ClC_6H_4$ > 4-$MeC_6H_4$ > $C_6H_5$ > 3-$ClC_6H_4$ that follows the inverse of the series of Hammett $\sigma$ values with the exception of the derivative with Ar = 4-$ClC_6H_4$. When Ar = 4-$MeOC_6H_4$, the selective cleavage of the aryl group by hydrogen chloride or acetic acid is virtually quantitative, but in other cases only slight differences in selectivity were observed. A more limited series with mercury(II) chloride as electrophile gives the corresponding selectivity series Ar = 4-$MeOC_6H_4$ > 4-$MeC_6H_4$ > $C_6H_5$, as expected from the Hammett $\sigma$ values of the substituents.[14]

## Discussion

This work has shown that the symmetrization reactions of eq 1 and 2 occur at very similar rates and that there is little selectivity in the electrophilic cleavage of a methyl or a phenyl group from $[TiMePh(\eta\text{-}C_5H_5)_2]$ by protic reagents or by mercury(II) chloride. These results are self-consistent and indicate that the methyltitanium(IV) and phenyltitanium(IV) bonds have similar reactivities toward electrophilic reagents as different as HCl, $HgCl_2$, and $[TiCl_2(\eta\text{-}C_5H_5)_2]$. All precedents would indicate that a mechanism involving simple electrophilic attack, but not involving oxidative addition, should lead to selective cleavage of an aryl group.[4] This is also the theoretical prediction since electrophilic attack by $E^+$ should yield intermediates A and B, of which the Wheland intermediate B is expected to be of lower energy since it is resonance stabilized.




A




B

In main-group compounds or late transition-metal complexes, the selective cleavage of a phenyl group from compounds such as $SnMe_3Ph$, HgMePh, or *cis*-$[AuMe_2Ph(PMePh_2)]$ is observed[3,4] and the rate of electrophilic cleavage of the M–R bond is ~500 times greater in $Me_3SnR$ when R = Ph than when R = Me, in accord with the theoretical predictions.[15] However, in several systems involving transition-metal compounds, there is a much lower difference in reactivity between methyl and phenyl derivatives. For example, in cleavage by the $S_E2$ mechanism, a phenyl group, R, is cleaved only 7.4 times fater than a methyl group, R, in reaction of $Hg^{2+}$ with $[CoR(dmgh)_2(H_2O)]$,[16] and a 4-tolyl group, R, is cleaved only twice as fast as a methyl group, R, in reaction of

Table III. Products of Reactions of Electrophiles with $[TiMeAr(\eta\text{-}C_5H_5)_2]$

| reagent (Ar) | electrophile | products (yield, %)[a] |
|---|---|---|
| 4-$MeOC_6H_4$ | HCl | $Cp_2TiClMe$ + $C_6H_5OMe$ (100%) |
| 4-$MeC_6H_4$ | HCl | $Cp_2TiClMe$ + $C_6H_5Me$ (57%)<br>$Cp_2TiCl(C_6H_4Me)$ + $CH_4$ (43%) |
| $C_6H_5$ | HCl | $Cp_2TiClMe$ + $C_6H_6$ (53%)<br>$Cp_2TiCl(C_6H_5)$ + $CH_4$ (47%) |
| 4-$ClC_6H_4$ | HCl | $Cp_2TiClMe$ + $C_6H_5Cl$ (58%)<br>$Cp_2TiCl(C_6H_4Cl)$ + $CH_4$ (42%) |
| 3-$ClC_6H_4$ | HCl | $Cp_2TiClMe$ + $C_6H_5Cl$ (50%)<br>$Cp_2TiCl(C_6H_4Cl)$ + $CH_4$ (50%) |
| 4-$MeOC_6H_4$ | HOAc | $Cp_2Ti(OAc)Me$ + $C_6H_5OMe$ (100%) |
| $C_6H_5$ | HOAc | $Cp_2Ti(OAc)Me$ + $C_6H_6$ (57%)<br>$Cp_2Ti(OAc)C_6H_5$ + $CH_4$ (43%) |
| 4-$MeOC_6H_4$ | $HgCl_2$ | $Cp_2TiClMe$ + 4-$MeOC_6H_4HgCl$ (66%)<br>$Cp_2TiCl(C_6H_4OMe)$ + MeHgCl (34%) |
| 4-$MeC_6H_4$ | $HgCl_2$ | $Cp_2TiClMe$ + 4-$MeC_6H_4HgCl$ (42%)<br>$Cp_2TiCl(C_6H_4Me)$ + MeHgCl (58%) |
| $C_6H_5$ | $HgCl_2$ | $Cp_2TiClMe$ + $C_6H_5HgCl$ (39%)<br>$Cp_2TiClC_6H_5$ + MeHgCl (61%) |
| 4-$ClC_6H_5$ | $HgCl_2$ | $Cp_2TiClMe$ + 4-$ClC_6H_4HgCl$ (~40%)[b]<br>$Cp_2TiCl(C_6H_4Cl)$ + MeHgCl (~60%)[b] |
| $C_6H_5$ | MeHgCl | $Cp_2TiClMe$ + $C_6H_5HgMe$ (40%)<br>$Cp_2TiClC_6H_5$ + $Me_2Hg$ (60%) |

[a] Yields are generally ±2% for Ti complexes. [b] Approximate values; peaks overlap.

(12) The photolysis of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ has been studied by several groups. (a) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299. (b) Samuel, E.; Giannotti, C. *Ibid.* **1976**, *113*, C17. (c) Peng, M.; Brubaker, C. H.; Jr. *Inorg. Chim. Acta* **1978**, *26*, 231. (d) Samuel, E.; Maillard, P.; Giannotti, C. *J. Organomet. Chem.* **1977**, *142*, 289. (e) Bamford, C. H.; Puddephatt, R. J.; Slater, D. M. *Ibid.* **1978**, *159*, C31. (f) van Leeuwen, P. W. N. M.; van der Heijden, H.; Roobeek, C. F.; Frijns, J. H. G. *Ibid.* **1981**, *209*, 169.

(13) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(14) For a good review of Hammett-type correlations in arylmetal complexes, see: Senoff, C. V. *Coord. Chem. Rev.* **1980**, *32*, 111.

(15) Abraham, M. H.; Sedeghat-Herati, M. R. *J. Chem. Soc. Perkin Trans. 2* **1978**, 729.

(16) Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 3166.

$$[FeR(CO)_2(\eta\text{-}C_5H_5)] + 2HgCl_2 \rightleftharpoons [FeR(CO)_2(\eta\text{-}C_5H_5)]^+\cdot[Hg_2Cl_4]^-\cdot \rightarrow \text{products} \quad (7)$$

$$[TiR_2(\eta\text{-}C_5H_5)_2] + [TiX_2(\eta\text{-}C_5H_5)_2] \rightleftharpoons [TiR_2(\eta\text{-}C_5H_5)_2]^+\cdot[TiX_2(\eta\text{-}C_5H_5)_2]^-\cdot$$

$$\swarrow^{(i)} \qquad \downarrow^{(ii)} \quad (8)$$

$$2[TiXR(\eta\text{-}C_5H_5)_2] \qquad [TiX_2(\eta\text{-}C_5H_5)_2] + RH + [Ti(R\text{-}H)(\eta\text{-}C_5H_5)_2]$$

$$[TiR_2(\eta\text{-}C_5H_5)_2] + [TiX_2(\eta\text{-}C_5H_5)_2] \rightleftharpoons (\eta\text{-}C_5H_5)_2Ti\begin{matrix}R\\ \diagup\\ \diagdown\\ X\\ \diagdown\\ \diagup\\ R\end{matrix}Ti(\eta\text{-}C_5H_5)_2 \quad (9)$$

$$\swarrow^{(i)} \qquad \downarrow^{(ii)}$$

$$2[TiXR(\eta\text{-}C_5H_5)_2] \qquad [TiX_2(\eta\text{-}C_5H_5)_2] + RH + [Ti(R\text{-}H)(\eta\text{-}C_5H_5)_2]$$

$[PtI_2(PMe_2Ph)_2]$ with $[PtR_2(1,5\text{-cyclooctadiene})]$.[3] The cleavage of the R–Fe bond in $[FeR(CO)_2(\eta\text{-}C_5H_5)]$ is thought to occur by the $S_E$(oxidative) or electron-transfer mechanism, and the phenyl derivative reacts only 1.4 times faster than the methyl derivative.[17] Finally, in reactions of *cis*-$[PtR_2(PEt_3)_2$ with $H^+$, which probably occur by an $S_E$(oxidative) mechanism, the rate is $10^6$ times greater when R = Me than when R = Ph.[18] The present system, in which $[TiMe_2(\eta\text{-}C_5H_5)_2]$ and $[TiPh_2(\eta\text{-}C_5H_5)_2]$ react at about equal rates with $[TiX_2(\eta\text{-}C_5H_5)_2]$, X = halogen, does not fit the usual reactivity pattern expected for the $S_E2$ mechanism but, in an empirical sense, resembles the $[FeR(CO)_2(\eta\text{-}C_5H_5)]/HgCl_2$ system.[17] Kochi has interpreted this reaction in terms of an electron-transfer mechanism (eq 7).[13,19]

The nature of the final products was very dependent on the nature of the group R. By analogy, the titanium system might react according to eq 8.[20] In (i) the radical pair undergo alkyl for halogen exchange, whereas in (ii) decomposition of the radical cation occurs. If these reactions are competitive, it follows that the rate of phenyl or methyl for halogen exchange and the rate of the catalyzed decomposition of $[TiR_2(\eta\text{-}C_5H_5)_2]$ would be related. Of course, there are other mechanisms such as the $S_E2$ mechanism of eq 9 that could also rationalize this relationship.

All that is needed is an intermediate in which the Ti–R bond is weakened, and then exchange or catalyzed decomposition can follow. The products from the catalyzed decomposition of $[TiR_2(\eta\text{-}C_5H_5)_2]$ are methane when R = Me and benzene when R = Ph, and the titanium products could not be identified. These results parallel those for the uncatalyzed decomposition by either thermal or photochemical activation.[8,12]

This study allows the first correlation of selectivity of aryl or methyl group cleavage in complexes $[L_nMMe(C_6H_4X)]$ as a function of the substituent X. If we define the selectivity for aryl cleavage as $S(Ar) = 100k(Ar)/\{k(Ar) + k(Me)\}$, where $k(Ar)$ is the rate constant for aryl cleavage and $k(Me)$ is the rate constant for methyl cleavage, then a correlation of ln $S(Ar)$ with the substituent constants X can be expected. The results are limited by our failure to synthesize complexes with a very wide range of substituents X but are nevertheless useful. The correlations are rather poor but correlations with substituent constants $\sigma^+$ are considerably better than with $\sigma$. For cleavage by HCl, linear regression analysis of ln $S(Ar)$ vs. $\sigma^+$ gave $\rho = -0.6$ and $r = 0.89$ and for cleavage by $HgCl_2$ analysis gave $\rho = -0.7$ and $r = 0.97$. Generally, the $\rho$ values for ln $k_2$ vs. $\sigma$ correlations of electrophilic cleavage of arylmetal bonds are in the range −2.8 to −6.3,[14] but a much lower value for $\rho$ for the ln $k_3$ vs. $\sigma^+$ correlation for eq 7, R = $C_6H_4X$, of −1.2 was found.[17] The low values of $\rho$ found in the present work could therefore be taken as evidence for the electron-transfer mechanism, but it should be emphasized that the interpretation is not straightforward. For example, if the classical $S_E2$ mechanism operated, an electron-releasing substituent X would activate the aryl group toward electrophilic attack but would also lead to increased electron density in the Ti–Me bond and so also activate this bond. The reaction constant $\rho$ for the selectivity vs. $\sigma^+$ would then be lower than the $\rho$ value for the overall rate constants vs. $\sigma^+$. The absolute rates were too fast for study by techniques available to us.

## Conclusions

We believe that the cleavage of methyl or aryl groups from $[TiR_2(\eta\text{-}C_5H_5)_2]$ does not occur by the classical $S_E2$ mechanism. The evidence comes from the similar rates of reaction of $[TiR_2(\eta\text{-}C_5H_5)_2]$ with $[TiX_2(\eta\text{-}C_5H_5)_2]$ when R = Me or Ph, from the low selectivity observed in reactions of $[TiMePh(\eta\text{-}C_5H_5)_2]$ with electrophiles HCl and $HgCl_2$ and from the low reaction constants, $\rho$, from the Hammett equation in the correlation of selectivity for aryltitanium bond cleavage in reactions of $[TiMe(C_6H_4X)(\eta\text{-}C_5H_5)_2]$ with electrophiles. None of these observations alone is conclusive, but, taken together, they are very difficult to reconcile with the $S_E2$ mechanism.[21] The similarity in many respects to the reactions of $[FeR(CO)_2(\eta\text{-}C_5H_5)]$ with $HgCl_2$ suggests that the electron-transfer mechanism may operate. The $S_E$(oxidative) mechanism is unreasonable for reactions of titanium(IV) complexes, but other mechanisms such as one involving initial interaction of the electrophile with an $\eta\text{-}C_5H_5$ group cannot be eliminated. Taken together with other recent results,[3,22] it is now clear that selectivity results obtained in studies of main-group metal derivatives cannot be

(17) Dizikes, L. J.; Wojcicki, A. *J. Am. Chem. Soc.* **1975**, *97*, 2540; **1977**, *99*, 5304.

(18) Belluco, U.; Croatto, U.; Uguagliati, P.; Pietropaolo, R. *Inorg. Chem.* **1967**, *6*, 718. Belluco, U.; Giustiniani, M.; Graziani, M. *J. Am. Chem. Soc.* **1967**, *89*, 6494.

(19) Wojcicki[17] proposed an $S_E$(oxidative) mechanism for the iron system. This mechanism is not possible for the $d^0$ titanium(IV) system. In the electron-transfer mechanism for Ti(IV) the electron must be removed from a bonding MO since there are no nonbonding d electrons.

(20) The reversible reduction of $[TiCl_2(\eta\text{-}C_5H_5)_2]$ to $[TiCl_2(\eta\text{-}C_5H_5)_2]^-$ is known to be a facile process, but the oxidation potential of $[TiMe_2(\eta\text{-}C_5H_5)_2]$ is not known. (a) Chaloyard, A.; Dormond, A.; Tirouflet, J.; El-Murr, N. *J. Chem. Soc. Chem. Commun.* **1980**, 214. (b) El-Murr, N.; Chaloyard, A.; Tirouflet, J. *Ibid.* **1980**, 446.

(21) It is possible that more than one mechanism is operative. Intuitively, the $S_E2$ mechanism might be expected to be preferred for reactions of HCl, but the electron-transfer mechanism preferred for $[TiCl_2(\eta\text{-}C_5H_5)_2]$. Our evidence does not exclude such possibilities.

(22) Tamaki, A.; Kochi, J. K. *J. Chem. Soc., Dalton Trans.* **1973**, 2620.

carried over to the corresponding transition metal complexes. In transition-metal complexes [$L_nMMePh$], cases are now known where electrophiles give exclusively methylmetal cleavage, exclusively phenylmetal cleavage, and, in the present case, very little selectivity between methyl– and phenyl–metal bond cleavage. No clear pattern of selectivity as a function of transition-metal or supporting ligands is yet apparent, and studies with other transition-metal derivatives are clearly needed.

## Experimental Section

NMR spectra were recorded by using Varian T60 or XL100 spectrometers, and chemical shifts are quoted with respect to $Me_4Si$ reference. All syntheses of organotitanium complexes were carried out under an atmosphere of nitrogen. [$TiMe_2(\eta\text{-}C_5H_5)_2$], [$TiPh_2(\eta\text{-}C_5H_5)_2$], and [$TiClMe(\eta\text{-}C_5H_5)_2$] were prepared by known methods.[5-7] The organotitanium compounds were not sufficiently stable to obtain elemental analyses.

**[$TiMePh(\eta\text{-}C_5H_5)_2$].** A suspension of [$TiClMe(\eta\text{-}C_5H_5)_2$] (1.34 g, 5.9 mmol) in dry ether (30 mL) was cooled to −78 °C. A solution of phenyllithium in benzene/ether (6.5 mL, 1.8 M, 11.7 mmol) was then added dropwise, and the resulting mixture was stirred for 30 min. The reaction mixture was hydrolyzed with saturated aqueous ammonium chloride and allowed to warm to room temperature. The ether layer and washings were separated and dried over $MgSO_4$, and the solvent was evaporated to give an orange oil, which was crystallized by cooling a pentane solution to −78 °C. The product was identified by its $^1H$ NMR spectrum (Table I) and reactions.

Other complexes [$TiMeAr(\eta\text{-}C_5H_5)_2$] were prepared by similar methods. Usually reactions with aryllithium reagents were carried out at temperatures from −20 to 0 °C, rather than at −78 °C as above, but otherwise there were no significant differences in procedure. Yields were in the range 25–70%.

**[$TiMe(O_2CMe)(\eta\text{-}C_5H_5)_2$].** Acetic acid in ether (8 mL, containing 1.40 mmol of HOAc) was added dropwise to a solution of [$TiMe_2(\eta\text{-}C_5H_5)_2$] (0.29 g, 1.39 mmol) in ether cooled to −78 °C. The mixture was stirred for 1 h and allowed to warm to room temperature, and then the solvent was evaporated under vacuum to give the product as an orange oil, which was recrystallized from pentane to give a yellow orange solid, decomp >96 °C.

The complex [$TiPh(O_2CMe)(\eta\text{-}C_5H_5)_2$] was prepared in a similar way.

**[$TiMe_2(\eta\text{-}C_5H_5)_2$] with $HgCl_2$.** Solutions of [$TiMe_2(\eta\text{-}C_5H_5)_2$] (0.252 g, 1.21 mmol) and $HgCl_2$ (0.072 g, 0.26 mmol) in acetone-$d_6$ were cooled to −78 °C, then mixed, allowed to stir at −78 °C for 15 min, and warmed to room temperature. The $^1H$ NMR spectrum showed the presence of [$TiMe_2(\eta\text{-}C_5H_5)_2$], [$TiClMe(\eta\text{-}C_5H_5)_2$], and $HgMe_2$ [$\delta$ 0.18 ($^2J$(HgMe) = 101 Hz)] only. After addition of more $HgCl_2$ in a similar way (total 1.5 mmol), similar NMR analysis showed the presence of [$TiCl_2(\eta\text{-}C_5H_5)_2$], a trace of [$TiClMe(\eta\text{-}C_5H_5)_2$], $HgMe_2$, and HgClMe [$\delta$ 0.94 ($^2J$(HgMe) = 205 Hz)]. Similarly a reaction of [$TiMe_2(\eta\text{-}C_5H_5)_2$] (0.63 mmol) with HgClMe (0.30 mmol) gave unchanged [$TiMe_2(\eta\text{-}C_5H_5)_2$], [$TiClMe(\eta\text{-}C_5H_5)_2$], and $HgMe_2$ as products. A reaction of [$TiPh_2(\eta\text{-}C_5H_5)_2$] with HgClMe gave unchanged starting materials (~70%), [$TiClPh(\eta\text{-}C_5H_5)_2$], and HgMePh [$\delta$(Me) 0.43 ($^2J$(HgMe) = 111 Hz), $\delta$(Ph) 7.20 (s)] (~30%).

**[$TiMe_2(\eta\text{-}C_5H_5)_2$] with [$TiF_2(\eta\text{-}C_5H_5)_2$].** A solution containing [$TiMe_2(\eta\text{-}C_5H_5)_2$] (0.025 M), [$TiF_2(\eta\text{-}C_5H_5)_2$] (0.025 M), and $CHCl_3$ (~0.1 M) in $CDCl_3$ was prepared, placed in an NMR tube, and kept in a bath at 36 °C. The progress of the reaction was monitored by recording $^1H$ NMR spectra at suitable intervals. For kinetics, the peak heights of the resonances due to $\eta\text{-}C_5H_5$ groups of [$TiMe_2(\eta\text{-}C_5H_5)_2$] ($\delta$ 6.04), [$TiF_2(\eta\text{-}C_5H_5)_2$] ($\delta$ 6.44), and [$TiFMe(\eta\text{-}C_5H_5)_2$] ($\delta$ 6.12) were monitored, using $CHCl_3$ as internal reference, as a function of time. In addition a singlet at $\delta$ 0.22 due to methane appeared during the reaction. When the reaction was complete, the product [$TiFMe(\eta\text{-}C_5H_5)_2$] was isolated by evaporation of the solvent. It was a yellow solid, purified by evaporation of an ether solution.

Other symmetrization reactions were monitored in a very similar way.

**[$TiMePh(\eta\text{-}C_5H_5)_2$] with HCl.** A solution of [$TiMePh(\eta\text{-}C_5H_5)_2$] (0.124 g, 0.46 mmol) in ether (5 mL) was cooled to 78 °C, and a solution of anhydrous HCl in ether (0.55 mL, 0.41 M, containing 0.23 mmol of HCl) was added dropwise with stirring. The mixture was allowed to warm to room temperature, and the solvent was evaporated. The mixture was identified as [$TiMePh(\eta\text{-}C_5H_5)_2$], [$TiClMe(\eta\text{-}C_5H_5)_2$], and [$TiClPh(\eta\text{-}C_5H_5)_2$] by the characteristic NMR spectra (Table I) in $CDCl_3$. Integration of the $\eta\text{-}C_5H_5$ NMR signals gave the product composition as [$TiClMe(\eta\text{-}C_5H_5)_2$] (53%) and [$TiClPh(\eta\text{-}C_5H_5)_2$] (47%).

In another experiment, [$TiMePh(\eta\text{-}C_5H_5)_2$] (0.39 mmol) was treated with HCl (0.41 mmol) in a similar way, in a flask fitted with a serum cap. Analysis of the gas phase by GC (molecular sieve 5A column) showed the presence of methane only. The solvent was distilled through the vacuum line and collected. NMR analysis showed the presence of benzene ($\delta$ 7.2) and ether only. The NMR spectrum of the involatile materials showed the presence of [$TiClMe(\eta\text{-}C_5H_5)_2$], [$TiClPh(\eta\text{-}C_5H_5)_2$], and [$TiCl_2(\eta\text{-}C_5H_5)_2$] only (Table I).

Other reactions of methyl aryl complexes with HCl were carried out in a similar way.

**[$TiMePh(\eta\text{-}C_5H_5)_2$] with $HgCl_2$.** A solution of $HgCl_2$ (0.085 g, 0.31 mmol) in acetone-$d_6$ (1 mL) was added to a solution of [$TiMePh(\eta\text{-}C_5H_5)_2$] (0.499 g, 1.85 mmol) in acetone-$d_6$ (2 mL) cooled to −78 °C. NMR analysis of the warmed solution showed the presence of $HgMe_2$, HgMePh, HgClMe, [$TiMePh(\eta\text{-}C_5H_5)_2$], [$TiClMe(\eta\text{-}C_5H_5)_2$] and [$TiClPh(\eta\text{-}C_5H_5)_2$]. The relative intensities of $\eta\text{-}C_5H_5$ resonances due to [$TiClMe(\eta\text{-}C_5H_5)_2$] and [$TiClPh(\eta\text{-}C_5H_5)_2$] was 1:1.56.

In another similar experiment but using a 1:1 mol ratio of reagents, the products were HgClMe, HgMePh, $HgMe_2$, [$TiClPh(\eta\text{-}C_5H_5)_2$], [$TiClMe(\eta\text{-}C_5H_5)_2$], and [$TiCl_2(\eta\text{-}C_5H_5)_2$] as identified by NMR (note that $HgPh_2$ and HgClPh would probably not be detected). The product ratio [$TiClMe(\eta\text{-}C_5H_5)_2$]:[$TiClPh(\eta\text{-}C_5H_5)_2$] was ~1:4 in this case, indicating that the former was more reactive toward further Ti–C bond cleavage.

Other reactions of methyl aryl complexes with $HgCl_2$ were carried out in a similar way.

**[$TiMePh(\eta\text{-}C_5H_5)_2$] with HgClMe.** A solution of HgClMe (0.087 g, 0.35 mmol) in acetone-$d_6$ (1 mL) was added to a solution of [$TiMePh(\eta\text{-}C_5H_5)_2$] (0.169 g, 0.62 mmol) in acetone-$d_6$ (2 mL) cooled to −78 °C. The reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 6 h. Samples were taken occasionally for NMR analysis, which showed the reaction to be still incomplete after this period. Present in the solution were HgClMe, $HgMe_2$, HgMePh, [$TiMePh(\eta\text{-}C_5H_5)_2$], [$TiClMe(\eta\text{-}C_5H_5)_2$], and [$TiClPh(\eta\text{-}C_5H_5)_2$]. In the early stages, analysis showed the ratio of $HgMe_2$:HgMePh to be 1.5:1.

**Registry No.** $Cp_2TiClMe$, 1278-83-7; $Cp_2TiCl(4\text{-}C_6H_4Me)$, 86822-29-9; $Cp_2TiCl(C_6H_5)$, 12663-63-7; $Cp_2TiCp(4\text{-}C_6H_4Cl)$, 86822-30-2; $Cp_2TiCl(3\text{-}C_6H4Cl)$, 86822-41-5; $Cp_2Ti(OAc)Me$, 86822-31-3; $Cp_2Ti(OAc)C_6H_5$, 86822-32-4; $Cp_2TiCl(4\text{-}C_6H_4OMe)$, 86822-33-5; $TiMe(4\text{-}MeOC_6H_4)(\eta\text{-}C_5H_5)a$, 86822-34-6; $TiMe(4\text{-}MeC_6H_4)(\eta\text{-}C_5H_5)_2$, 86822-35-7; $TiMe(C_6H_5)(\eta\text{-}C_5H_5)_2$, 75535-77-2; $TiMe(4\text{-}CpC_6H_4)(\eta\text{-}C_5H_5)_2$, 86822-36-8; $TiMe(3\text{-}ClC_6H_4)(\eta\text{-}C_5H_5)_2$, 86822-37-9; $TiMe_2(\eta\text{-}C_5H_5)_2$, 1271-66-5; $TiPh_2(\eta\text{-}C_5H_5)_2$, 1273-09-2; $TiF_2(\eta\text{-}C_5H_5)_2$, 309-89-7; $TiCl_2(\eta\text{-}C_5H_5)_2$, 1271-19-8; $TiBr_2(\delta\text{-}C_5H_5)_2$, 1293-73-8; $TiI_2(\eta\text{-}C_5H_5)_2$, 12152-92-0; $Ti(OAc)_2(\eta\text{-}C_5H_5)_2$, 1282-51-5; $TiMe(4\text{-}FC_6H_4)(\eta\text{-}C_5H_5)_2$, 86822-38-0; $TiMe(3\text{-}FC_6H_4)(\eta\text{-}C_5H_5)_2$, 86822-39-1; $TiFME(\eta\text{-}C_5H_5)_2$, 86822-40-4; $TiBrMe(\eta\text{-}C_5H_5)_2$, 12153-32-1; $TiIMe(\eta\text{-}C_5H_5)_2$, 12153-38-7; $4\text{-}MeOC_6H_4HgCl$, 3009-79-8; MeHgCl, 115-09-3; $4\text{-}MeC_6H_4HgCl$, 539-43-5; $C_6H_5HgCl$, 100-56-1; $4\text{-}ClC_6H_4HgCl$, 1802-38-6; $C_6H_5HgMe$, 21392-61-0; $Me_2Hg$, 593-74-8.