Importance of Steric Requirements Relative to Electronic Contributions in Bicycloalkyl-Substituted Titanocene Dichlorides[†]

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A group of bicycloalkyl-substituted titanocene dichlorides was examined by X-ray photoelectron spectroscopy in order to gauge if the rather large steric requirements of these ligands exert greater or lesser impact on the binding energy of the titanium center relative to the electronic effect of alkyl substitution. Simpler model systems were likewise evaluated. X-ray crystallographic data were available for many of the norbornyl-, bornyl-, and pinanyl-fused titanocenes. The solid-state structure of 3 has been established by X-ray crystallographic analysis: space group $C2/c$, $a = 12.456(5)$, $b = 6.695(3)$, $c = 16.591(8)$ Å; $\beta = 98.37(3)°$; $Z = 4$. The structure refined to R and R_w values of 0.067 and 0.079, respectively, with use of 1357 reflections. This information and associated Fenske–Hall calculations revealed that, although heightened levels of ring slippage were in effect, the inductive contributions of substituents directly bonded to the Cp rings dominate over the steric contributions of the space-demanding ligands in controlling the electronic changes at the core titanium atom.

Alkylated η^5-cyclopentadienyl-based ligands are being used with increasing frequency in place of cyclopentadienyl ligands (Cp) because of the often poor solubility of Cp-based metal complexes[1] or because of the desire to control the steric or stereochemical environment about the metal center.[2] The alkylation of a Cp can bring about significant changes in the chemical reactivity of the metal complex,[3] both because of the enhanced inductive electron donation by the alkyl groups to the metal center and of the increased steric demands of the ligand. For example, Ewen has determined that 1,1′-bis(η^5-methylcyclopentadienyl)zirconocene dichloride exhibits higher catalytic activity for Ziegler–Natta polymerization than Cp_2ZrCl_2.[4] For the same reaction, Brintzinger and co-workers have reported that certain trialkylsilyl-substituted cyclopentadienylzirconocenes also function as improved catalysts.[5]

From previous X-ray photoelectron spectroscopy (XPS) studies, the effect of methylation of a cyclopentadienyl ligand on the binding energy of a metal gave evidence of being both predictable and significant. Gassman and co-workers have found that the replacement of hydrogen by methyl on the Cp ligands of titanocene, zirconocene, and hafnocene halides results in a lowering of the metal core orbital binding energies by 0.06–0.08 eV per methyl group.[6] Further, the trialkylsilyl group was discovered to be slightly more electron-donating than methyl.[7] Complete substitution of Cp alkyl groups thus results in nearly a 1-eV change to lower binding energy for the metals; i.e., the metal is reduced. This value is of the same magnitude as that associated with a decrease by one in its oxidation state.[8]

In recent years, the synthesis of a number of bicycloalkyl-fused titanocene dichlorides has been undertaken by the Paquette group for evaluation in various catalytic settings.[9] These metallocenes can be regarded as electronically analogous to bis(1,2-dimethylcyclopentadienyl)titanocene dichlorides. However, we recognized that ligands of the norbornyl, bornyl, and pinanyl type possess greater steric requirements than do methyl groups. Consequently, in an effort to gain insight into the relative importance of electronic and steric contributions as a function of electron density at the titanium center, we have now examined a representative group of this class of metallocenes by XPS.

[†] Dedicated to the memory of Professor Paul G. Gassman.

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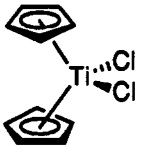
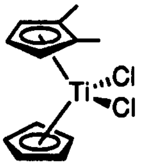
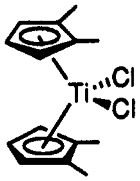
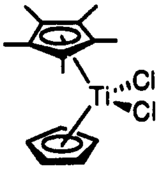
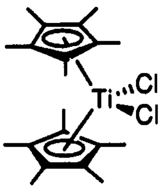
In order to probe the various factors that affect the XPS binding energies, we have also performed nonempirical Fenske–Hall molecular orbital calculations[18] on a number of these systems and on several model titanocene complexes. This molecular orbital method has consistently provided an excellent framework by which to investigate the bonding and orbital energetics of organometallic complexes.[10] These companion calculations are of particular importance since it has been found that as the steric bulk of the bicyclic ligand increases, the distance from the Cp centroid to the metal center increases and the ligand also slips[11] to give unequal bond lengths from each carbon of the Cp ligand to the titanium. These changes are expected to have an impact on the titanium binding energy inasmuch as the charge on the metal center is recognized to be a direct function of the Ti–Cp bond length.[12]

There have been several prior approximate and ab initio theoretical studies of Cp_2MX_2 complexes. These have focused primarily on the bonding, valence orbital energetics, and geometries of these systems.[13] The several goals of the present computational study were (a) to determine how well the XPS results correlate with the Ti (2p) orbital energies that emerge from the electronic structure calculations, (b) to utilize the calculations as a means of discriminating between the electronic and steric influences of the bicycloalkyl ligands upon the Ti (2p) binding energies, and (c) to establish whether these structurally more complex ligands can, in fact, be plausibly approximated by the 1,2-dimethylcyclopentadienide ligand.

Results and Discussion

Synthesis. The structural formulas of the titanocene dichlorides that have been investigated in this study are compiled in Tables 1 and 2. Of these, 1 was purchased commercially (Strem) and 4,[14] 5,[3b,15] and 6–18[9] were prepared by published procedures. The two key reference compounds 2 and 3, syntheses of which had not been previously detailed, were prepared as outlined in Scheme 1.[16] The structural features of 3 in the solid state were determined by X-ray crystallography (Table 3). The relevant bond lengths and bond angles are found in Table 4. These data and the ORTEP diagrams of 3 displayed in Figure 1 immediately call attention to the absence of the same high level of structural distortion present in the more sterically congested analogs 6–18 as detailed elsewhere[9] and summarized below.

Table 1. X-ray Photoelectron Spectroscopic Analyses of Alkylated Cyclopentadienyl Titanocene Dichloride Model Compounds: Titanium ($2p_{3/2}$) and Chlorine ($2p_{3/2}$) Binding Energies

no.	compound	Ti($2p_{3/2}$) (±0.03 eV)	Cl ($2p_{3/2}$) (±0.10 eV)
1		457.09	198.09
2		456.86	198.08
3		456.81	198.15
4		456.72	198.02
5		456.26	197.76

[a] All data were recorded at 50 eV. Typical bandwidth values for full width at half-maximum are 1.87 eV for Ti($2p_{3/2}$) and 1.64 eV for Cl ($2p_{3/2}$).

XPS Studies. In order to gauge the shifts in binding energy of the titanium centers in 1–18 with sufficient accuracy for our purposes, careful control of the XPS experimental parameters was required. This is especially so because the interpretation of shifts in binding energy when dealing with insulating organometallic complexes is complicated by a number of factors, including (1) sample charging during analysis, (2) potential spatial variations in sample charging, (3) influence of final state effects on observed differences in binding energies of different complexes, and (4) influence of changes in structure of the metal complex on binding energy.[17]

The problem of sample charging was addressed by using a polyethylene-coated aluminum support for sample analysis. The polyethylene serves as an internal standard for the calibration of charging by correcting the binding energy of the band of interest by the difference in the observed binding energy value of the C (1s) electron relative to its reference value of 284.60 eV. This approach can be used, with appropriate attention paid to the linearity of the spectrometer, to give reproducible binding energy values within error limits of ±0.03 eV. The magnitude of the change in binding energy due to differential charging across the sample for these complexes was also assessed by multiple analyses of each sample. Differential charging

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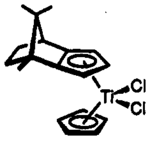
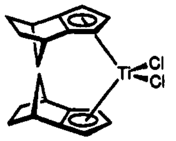
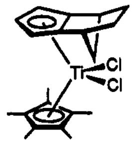
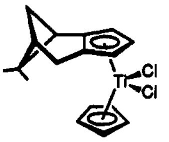
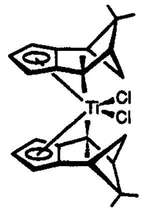
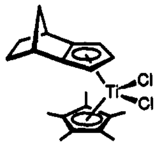
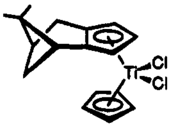
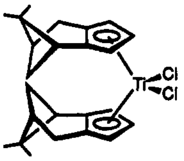
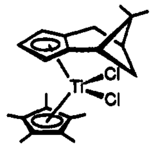
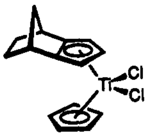
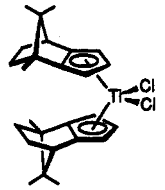
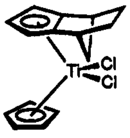
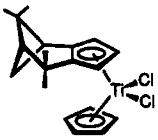
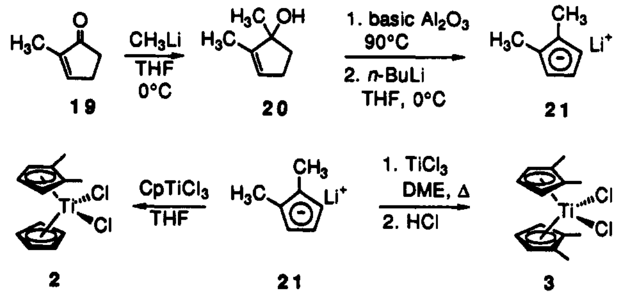
Table 2. X-ray Photoelectron Spectroscopic Analyses of Alkylated Cyclopentadienyl Titanocene Dichloride Compounds: Titanium ($2p_{3/2}$) and Chlorine ($2p_{3/2}$) Binding Energies[a]

1,2-disubstituted				bis(1,2-disubstituted)				Cp*,1,2-disubstituted			
no.	compound	Ti ($2p_{3/2}$) (±0.03 eV)	Cl ($2p_{3/2}$) (±0.10 eV)	no.	compound	Ti ($2p_{3/2}$) (±0.03 eV)	Cl ($2p_{3/2}$) (±0.10 eV)	no.	compound	Ti ($2p_{3/2}$) (±0.03 eV)	Cl ($2p_{3/2}$) (±0.10 eV)
6		456.85	197.92	12		456.61	197.91	16		456.68	198.07
7		456.88	197.84	13		456.60	197.81	17		456.63	198.01
8		456.84	198.02	14		456.54	198.08	18		456.61	197.97
9		456.80	197.95	15		456.50	197.68				
10		456.76	197.81								
11		456.71	197.95								

[a] See footnote to Table 1.

Scheme 1



was not found to play any significant role when analyses are carried out on the polyethylene-coated aluminum supports.

The influence of differences in final state energies on binding energies is typically neglected in other studies. This is a reasonable practice when the structures of the metal complexes studied do not vary appreciably. However, the titanocenes investigated presently differ substantially in the nature of their constituent alicyclic frameworks and the extent to which these building blocks are present. The three categories are defined in Table 2. Nonetheless, we believe that the possibility of final state effects as a major contributor to the differences in binding energies is small, as indicated by the exceptionally good correlation of the calculated ground state core orbital energies and the XPS data (see below).

The XPS binding energies of the Ti ($2p_{3/2}$) and Cl ($2p_{3/2}$) electrons of titanocene dichloride and model alkyl-substituted titanocene dichlorides are contained in Table 1. For the first set of values, the expected trend of greater electron density at the titanium center (lower binding energy) with increasing alkyl substitution of the cyclopentadienyl ligand is followed. The addition of 5 and 10 methyl groups to the cyclopentadienyl ligands as in **4** and **5**, respectively, results in Ti ($2p_{3/2}$) binding energies that are 0.37 and 0.83 eV lower than that found for the unsubstituted complex **1**, consistent with earlier XPS investigations of these compounds.[6] This comparison suggests that the contribution of each methyl substituent has an additive effect resulting in a reduction of the binding energy of the titanium center by approximately 0.08 eV per methyl group.[6] Notwithstanding, model compounds were required that would allow a direct comparison with the various bicycloalkyl-substituted cyclopentadienyltitanocene dichlorides. Usefully, 1,2-dimethyl substitution of the cyclopentadienyl ligand has been found to result in a reduction in the Ti ($2p_{3/2}$) binding energy of **2** relative to **1** by 0.23 eV and a reduction in the Ti ($2p_{3/2}$) binding energy of **3** by 0.28 eV. These binding energies are in accordance with the anticipated additive changes for the Ti ($2p_{3/2}$) electron (0.16 and 0.32 eV, respectively).

Table 3. Experimental Crystallographic Data for 3

formula	$C_{14}H_{18}Cl_2Ti$
fw	305.08
space group	*C*2/*c*
temp, °C	18
cell constants[a]	
a, Å	12.456(5)
b, Å	6.695(3)
c, Å	16.591(8)
β, deg	98.37(3)
cell vol. $Å^3$	1369
formula units/unit cell	4
D_{calc}, g cm^{-3}	1.48
μ_{calc}, cm^{-1}	10.1
diffractometer/scan	Enraf-Nonius CAD4/ω–2θ
radiation, graphite monochromator	Mo Kα (λ = 0.710 73)
max cryst dimens, mm	0.15 × 0.20 × 0.50
scan width	0.80 + 0.35 tan θ
std rflns	136, 228, 425, 423
decay of stds, %	±2
no. of rflns meas	1357
2θ range, deg	$2 \leq 2\theta \leq 50$
range of *hkl*	+14, +7, ±19
no. of rflns obs [$F_o \geq 5\sigma(F_o)$][b]	754
computer programs[c]	SHELX[d]
structure soln	SHELXS[e]
no. of params varied	84
weights	$[s(F_o)^2 + 0.0004F_o^2]^{-1}$
GOF	1.25
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.067
R_w	0.079
largest feature in final diff map	0.5 e^- $Å^{-3}$

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz–polarization. [c] Neutral scattering factors and anomalous dispersion corrections: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149. (Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands). [d] Sheldrick, G. M. SHELX76, a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, England, 1976. [e] Sheldrick, G. M. SHELXS. In *Crystallographic Computing 3*; Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175–189.

Table 4. Bond Distances (Å) and Angles (deg) for 3

Ti–Cl	2.358(2)	Ti–C(1)	2.437(8)
Ti–C(2)	2.461(7)	Ti–C(3)	2.360(7)
Ti–C(4)	2.329(8)	Ti–C(5)	2.377(8)
C(1)–C(2)	1.43(1)	C(1)–C(5)	1.40(1)
C(1)–C(6)	1.48(1)	C(2)–C(3)	1.40(1)
C(2)–C(7)	1.47(1)	C(3)–C(4)	1.40(1)
C(4)–C(5)	1.40(1)	Cent-Ti	2.07
$Cl–Ti–Cl_a$	92.6(1)	C(2)–C(1)–C(5)	106.3(7)
C(2)–C(1)–C(6)	126.8(7)	C(5)–C(1)–C(6)	126.5(8)
C(1)–C(2)–C(3)	107.5(7)	C(1)–C(2)–C(7)	126.1(8)
C(3)–C(2)–C(7)	126.5(8)	C(2)–C(3)–C(4)	109.7(7)
C(3)–C(4)–C(5)	106.4(7)	C(1)–C(5)–C(4)	110.0(8)
$Cent–Ti–Cent_a$	132.7	Cent–Ti–Cl	106.1
$Cent–Ti–Cl_a$	106.0		

The XPS binding energies of the Ti ($2p_{3/2}$) and Cl ($2p_{3/2}$) electrons of the more sterically congested 1,2-dialkyl-substituted titanocene dichlorides are contained in Table 2. The expected value for the Ti ($2p_{3/2}$) electron of the 1,2-dialkylcyclopentadienyl-substituted titanocenes, **6**–**11**, was ~456.9 eV, as all of these compounds are analogous to **2**. While the Ti ($2p_{3/2}$) binding energies of **6**–**8** are in accordance with the expected values, the binding energies of **9**–**11** are significantly lower than that predicted by the simple inductive effect model for 1,2-dialkyl substitution. In these examples, the effect of the sterically demanding ligands on electron density at the titanium center has substantially exceeded the usual limits for bis(1,2-dialkylcyclopentadienyl)titanocene dichlorides. Substitution of the cyclopentadienyl ligands with the equivalent of four methyl groups should result in a Ti ($2p_{3/2}$) binding energy of approximately 456.8 eV. However, **12**–**15** have Ti ($2p_{3/2}$) binding energies of 456.50–456.61 eV. These significant deviations from the simple 0.08 eV/alkyl group rule might have been expected based on the unsymmetrical bonding of the cyclopentadienyl ligand to the titanium center. For each of these 1,2-dialkyl-substituted complexes, the longest metal–ring carbon distance is to the carbons bearing the alkyl substituents and the closest metal–ring carbon distance is to the carbon 1,3-related to the carbons bearing the alkyl substituents (Figure 2). The differences in metal–ring carbon and metal–centroid distances in these complexes can be quite large (metal–Cp centroid distances are in parentheses), *viz.*, from 2.347–2.416 Å (2.06 Å) for **12**[9c] and 2.327–2.480 Å (2.08 Å) for **14**[9a] to 2.30–2.63 Å (2.12 Å) for **13**.[9h] Crystallographic data do not exist for **15**. Even the simple model, bis(1,2-dimethylcyclopentadienyl)titanocene dichloride (**3**), shows quite large differences in the metal–ring carbon and metal–centroid distances with values of 2.329–2.437 Å (2.07 Å). These variances in distances are marked when compared to the metal–ring carbon distances in titanocene dichloride where the distance varies by only 0.05 Å with a range from 2.347 to 2.394 Å (2.06 Å).

This variability in bonding from the metal to the Cp centroid is not isolated to these compounds. Examination of crystallographic data for the model compounds **1**,[18] **4**,[3a] and **5**[15c] finds that the pentamethylcyclopentadienyl ligand is displaced from the titanium center relative to the cyclopentadienyl ligand moving from 2.06 Å to 2.10 Å in **4** (the Cp ligand centroid to metal distance is 2.07 Å) to 2.12 Å in **5**. The variances in distances from the metal–ring carbon for **5** are similar to those of some of the bicycloalkyl titanocenes with a range of 2.34–2.43 Å, while the range for **5** is relatively small (2.39–2.44 Å).

The crystallographic data for two of the pentamethylcyclopentadienyl-substituted complexes of interest, **16**[9e] and **18**,[9i] also reflect quite large deviations from symmetrical bonding for the ligands to the metal center. For **16**, the metal–ring carbon distances for the Cp* (Cp* = η^5-C_5Me_5) ligand range from 2.38 to 2.48 Å with a metal to Cp* centroid distance of 2.10 Å. The 1,2-dialkylcyclopentadienyl ligand metal–ring carbon distance range is quite similar (2.35–2.48 Å) with a metal to Cp centroid distance of 2.09 Å. For **18**, a complex in which the Cp ligands are significantly more sterically demanding, the metal–ring carbon distances for the Cp* ligand range from 2.35 to 2.52 Å with a metal to Cp* centroid distance of 2.10 Å. The 1,2-dialkylcyclopentadienyl ligand metal–ring carbon range is significantly larger (2.31–2.51 Å) with a metal to Cp centroid distance of 2.10 Å.

In general, the more sterically demanding the alkyl substituents on the Cp ligand, the greater the observed deviation from a symmetrical bonding arrangement for the Cp ligand to the metal center. The metal to Cp centroid distance also increases with increasing steric demand of the Cp ligand. The slippage of the cyclopentadienyl ligand from a symmetrical bonding arrangement to an unsymmetrical one or to a localized bonding (η^5 to η^3 or η^1) is well known.[11] The effect of the relatively small slippage observed with these complexes on the electron density at the titanium center is appreciable. The deviations in binding energy from the simple additivity rule are ap-

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(18) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622.

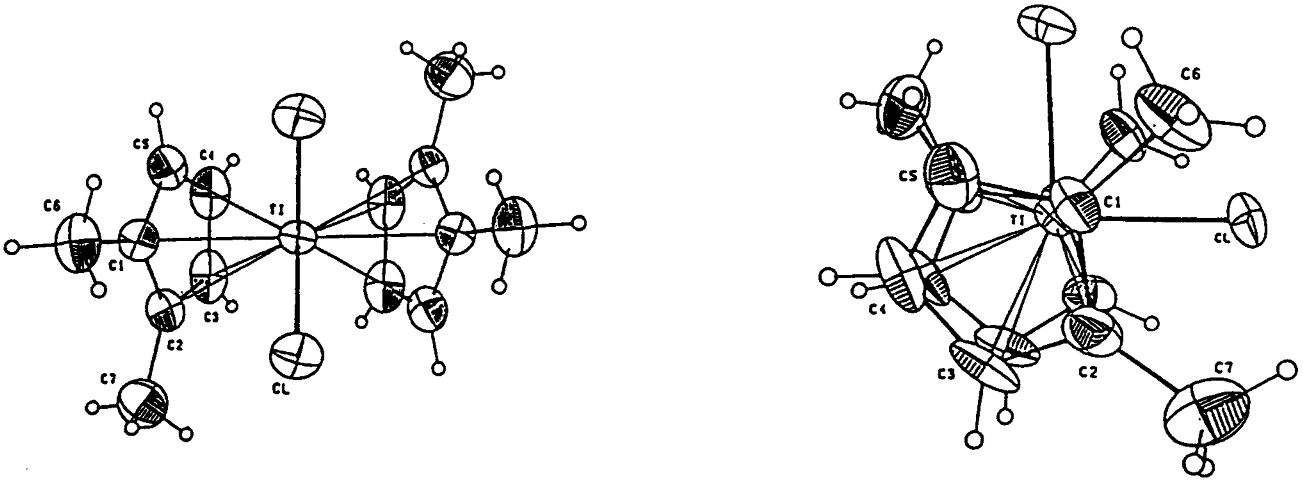

Figure 1. Side (left) and top (right) views of the crystallographically determined molecular structure of **3** as drawn with 50% probability ellipsoids.

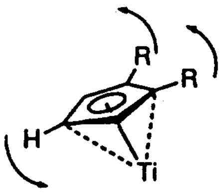

Figure 2. Ring tilt and slippage for 1,2-disubstituted titanocene dichlorides.

proximately 0.2 eV for both the dialkyl- and tetraalkyl-substituted titanocenes (**6–15**) and 0.1 eV for the dialkyl-CpCp* titanocenes (**16–18**). With the observation of consistent and significant departures from symmetrical bonding of the Cp ligands to the titanium center and the deviations in the Ti($2p_{3/2}$) binding energies from the simple additivity model, it became imperative to determine if the measured binding energies were reflecting a change in the electron density of the metal center or possibly a change in the final state energy.

Computational Details. The approximate, nonempirical Fenske–Hall molecular orbital method[19] has been used for all the calculations reported here. Atomic STO basis functions were generated by using the method of Bursten, Jensen, and Fenske.[20] Contracted double-ζ representations were used for the Ti (3d), C (2p), and Cl (3p) atomic orbitals; single-ζ representations were used for the remaining AO's. An exponent of 1.16 was used for the H (1s) AO's. The basis functions for Ti were derived from an atomic calculation on Ti^+, with the 4s and 4p exponents fixed at 2.0. The Ti (2p) AO had an exponent of 8.613 as determined from the atomic calculations.

In the calculations that employed the actual compound geometries, the crystal structure atomic coordinates were used as published with no idealization of geometry. In the cases in which the crystal structure did not include positional data for the hydrogen atoms, the C–H bond lengths of the cyclopentadienyl rings were set at 1.08 Å. In the calculations on model methyl-substituted titanocene dichloride complexes, the Cp_2TiCl_2 framework had an assumed C_{2v} geometry about the Ti atom: Ti–Cp(centroid) = 2.064 Å, Ti–Cl = 2.364 Å, Cp(centroid)–Ti–Cp(centroid) = 131.0°, Cl–Ti–Cl = 94.5°. In these cases, the Cp ligands were based on an idealized D_{5h} structure with C–C = 1.370 Å and C–H = 1.08 Å, and a C(ring)–C(methyl) distance of 1.469 Å was assumed.

In the computational studies, we focused our attention on direct correlations of the Ti (2p) orbital energies with the experimental Ti (2p) core binding energies. In the Fenske–Hall method, core orbitals are not included in the set of variational orbitals used in solving the Hartree–Fock–Roothaan equation. However, the core orbital energies are obtained in a fashion consistent with calculations of the valence molecular orbitals. Most important, the calculated energies of core orbitals within the method explicitly include overlap and charge interactions between same-center core and valence orbitals. Thus, the energies of the core orbitals will reflect variations in the valence electronic structures of the molecules. That such effects are present is evidenced by our observation that no direct correlation exists between the Ti (2p) orbital energy and the calculated Mulliken charge of the Ti atom. Further, because the same Ti (2p) orbital exponent was used in all of the titanocene calculations reported here, the observed changes in calculated Ti (2p) orbital energy are due entirely to changes in the valence electronic structure.

The use of calculations on model complexes affords us the opportunity to explore the relative importance of geometric and substituent effects. The experimental geometries about the Ti atom differ substantially for the various substituted titanocenes. We therefore first investigated whether the variations in the Ti (2p) binding energies could be reproduced by changing only the geometry about the Ti center without explicitly including the electronic effects of alkyl substituents. To this end, calculations were performed on the parent titanocene dichloride[1] in the geometries actually observed for the substituted complexes. The correlation of the experimental Ti (2p) binding energies to the calculated Ti (2p) orbital energies for Cp_2TiCl_2 was extremely poor (R^2 = 0.003), indicating to us that the geometric changes were probably a minor factor in the variation of the binding energies. We therefore anticipated that the inclusion of ring-substituent effects would be essential for correlating the experimental results.

The notion that core binding energies depend principally on the degree of alkyl substitution is in accord with the experimental observations of Gassman et al.[6] and Mach et al.[21] concerning the electronic changes at the metal induced by ring alkylation. In order to test this idea

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(19) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(20) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320.

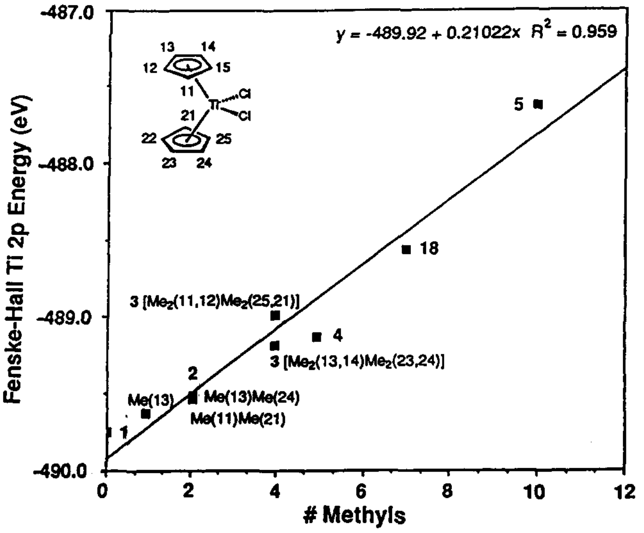

Figure 3. Plot of calculated Ti 2p orbital energy versus the number of methyl groups in a series of complexes ($(\eta^5\text{-}C_5H_{5-m}Me_m)(\eta^5\text{-}C_5H_{5-n}Me_n)TiCl_2$, all calculated in the idealized Cp_2TiCl_2 geometry about the Ti atom.

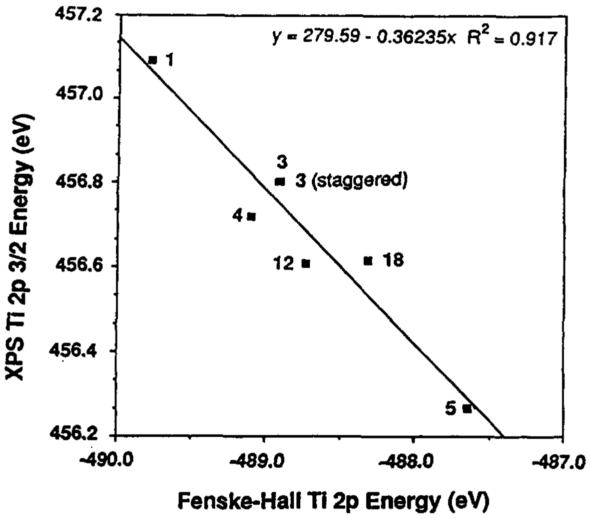

Figure 4. Plot of the experimental Ti $2p_{3/2}$ binding energy versus the calculated Ti 2p orbital energy. The calculations used the crystal structure geometries of the complexes, if known, and included all atoms of the ligands.

further, we performed a series of calculations on model methylated titanocene dichloride complexes $(\eta^5\text{-}C_5H_{5-m}Me_m)(\eta^5\text{-}C_5H_{5-n}Me_n)TiCl_2$ in which the geometry of the Cp_2TiCl_2 fragment was fixed at that of titanocene dichloride. For two of the complexes, $(methylCp)_2TiCl_2$ and **3**, two different sets of substitution sites were chosen in order to test the sensitivity of the results to possible interligand methyl group interactions. The results are summarized in the plot of the calculated Ti (2p) binding energies versus the total number of methyl groups in the complex shown in Figure 3. Note that the calculated Ti (2p) binding energy of complex **2** is virtually the same as that for the two "rotamers" of the $(methylCp)_2$ complex. For this one case, at least, it seems that the Ti (2p) orbital energy is insensitive to whether the methylation occurs entirely on one ring.

The linear correlation of binding energy with the number of methyl substituents in Figure 3 is excellent, indicating that the electronic influence of methyl groups on the Ti center is additive.[22] The slope of the line indicates that each methyl substitution raises the calculated Ti (2p) orbital energy by 0.21 eV, consistent via Koopmans' theorem with the decrease in Ti (2p) binding energy with increased alkylation. We shall discuss the quantitative aspects of this correlation shortly.

Now that the relative influences of geometric and substituent effects were revealed for model complexes, we turned to the XPS results of the complexes containing polycyclic Cp ligands. We were hopeful that the substituent effects of these substituted cyclopentadienyl ligands, such as isodicyclopentadienide, could be approximated by representing the exocyclic portion of the ligand with an appropriate number of methyl groups. Thus, we performed a series of calculations in which the norbornyl, bornyl, and pinanyl ligands were all modeled by 1,2-dimethylcyclopentadienyl. In the model ligand, the exocyclic carbon atoms were left in the same orientation relative to the ring that was found in the true ligands. The two methyl groups were constructed by adding three hydrogen atoms to these carbon atoms. Complexes **1**, **2**, **4**, and **5**, which contain methylated Cp rings and for which XPS Ti (2p) binding energies are known, were also included in this study. A plot of the experimental Ti $(2p_{3/2})$ binding energy versus the calculated Ti (2p) orbital energies for a total of nine complexes reproduced the general trend of decreasing binding energy with increasing alkyl substitution of the Cp ring, although the quantitative correlation is only fair (correlation coefficient $R^2 = 0.77$).

In the above analysis, we also determined the calculated binding energy for **3**, a value that did not correlate well with the other XPS data. This result was intriguing owing to the fact that **3** was the only compound other than **1** for which the *true* geometry was used in its entirety for the calculations. This observation led us to question the validity of using 1,2-dimethylCp as a prototype of the more complex ligands; it seemed to us more reasonable to assume that the results on **3** were more valid than those on the complexes that contained model methylated ligands. For this reason, calculations were undertaken on two of the actual complexes with tricyclic ligands, *viz.*, **12** and **18**. A plot of the experimental Ti $(2p_{3/2})$ binding energy versus the calculated Ti (2p) orbital energies for these two complexes, along with those for **1** and **3**–**5**, is presented in Figure 4. The linear correlation is reasonably good ($R^2 = 0.92$), although it is noted that the points for **12** and **18** lie on opposite sides of the line even though, within experimental error, the two complexes exhibit identical Ti $(2p_{3/2})$ binding energies. Nevertheless, we considered the results in Figure 4 to be encouraging, especially with regard to the general reproduction of alkyl substituent effects on the Ti (2p) binding energy.

The data compiled in Figure 4 indicate that the calculated Ti (2p) orbital energies are ca. 30 eV greater in magnitude than the experimental binding energy. Further, the slope of −0.36 indicates that the variation in the calculated orbital energies is roughly 3 times greater than that of the experimental values. Both of these effects are doubtless due to the choice of a single-ζ, energetically unoptimized Ti (2p) STO. Since the Fenske-Hall method does not yield reliable molecular total energies, we chose basis functions by optimizing the radial fit of the STO to

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[21] (a) Mach, K.; Varga, V.; Antropiusova, H.; Polacek, J. *J. Organomet. Chem.* **1987**, *333*, 205. (b) Mach, K.; Varga, V. *J. Organomet. Chem.* **1988**, *347*, 85. (c) Mach, K.; Antropiusova, H.; Varga, V.; Hanus, V. *J. Organomet. Chem.* **1988**, *358*, 123.

[22] Bursten, B. E.; Green, M. R. *Prog. Inorg. Chem.* **1988**, *36*, 393.

the numerically calculated Herman–Skillman AO.[20] Our experience dictates that using the same Ti (2p) AO for all calculations will give meaningful trends as we proceed through the series, even if the quantitative agreement is not as good as we would have liked.

We can combine the linear relationships of Figures 3 and 4 to correlate the calculated and experimental effects of methylation on the Ti (2p) binding energy. Figure 3 reveals that the calculated Ti (2p) orbital energy decreases by 0.21 eV for each ring methyl substituent. Figure 4 indicates that the experimental binding energy will change 0.36 times the change in the orbital energy. As a consequence, the predicted effect of a single methyl substitution is to lower the Ti ($2p_{3/2}$) binding energy by (0.36)(0.21 eV) = 0.076 eV. Further, the effects of methyl substitution are predicted to be additive. Thus, the replacement of a Cp ligand by a Cp* ligand should lower the Ti ($2p_{3/2}$) binding energy by 5 (0.076 eV) = 0.38 eV. This prediction is in good accord with the results of Gassman et al.,[6] who showed that the Ti ($2p_{3/2}$) binding energy is lowered by 0.3 ± 0.1 eV upon the replacement of a Cp ligand by a Cp* ligand. We therefore believe that the Fenske–Hall calculations correctly model the trends in core binding energies, even though the absolute values of the core orbital energies are inaccurate.

Experimental Section

1,2-Dimethylcyclopentadiene. A solution of 2-methyl-2-cyclopenten-1-one (1.00 g, 10.4 mmol) in 50 mL of THF was cooled to 0 °C and methyllithium (7.0 mL, 1.5 M in ether, 10.5 mmol) was added by syringe. The reaction mixture was stirred for 1 h at 0 °C, warmed to room temperature, quenched 2 h later with 50 mL of ice water, extracted with ether (3 × 100 mL), dried, filtered, and concentrated at room temperature to give **20** as a colorless oil. This material was added to 20 g of basic alumina and treated with 1 mL of quinoline. After standing at room temperature for 4 h, the solid mixture was heated to 90 °C and 15 Torr in a Kugelrohr apparatus. The product was collected at –78 °C to yield the diene as a colorless oily mixture of isomers (0.94 g, 96%).

(η^5-Cyclopentadienyl)(η^5-1,2-dimethylcyclopentadienyl)-dichlorotitanium (2). The above diene mixture was placed in a round-bottomed flask and dissolved in 50 mL of dry THF. The solution was cooled to 0 °C and *n*-butyllithium (6.2 mL, 1.6 M in hexane, 10.0 mmol) was added slowly by syringe. This solution was added to a THF (10 mL) solution of cyclopentadienyltitanium trichloride (1.97 g, 9.0 mmol) via cannula. The mixture, which rapidly turned brick red in color, was concentrated after 4 h leaving a brown residue which was taken up in CH_2Cl_2, filtered through a Celite pad, and concentrated. The resulting solid was sublimed (135–145 °C and 0.01 Torr) to give red microcrystals of **2** (1.82 g, 75%): mp 183–184 °C (dec); ^1H NMR (300 MHz, $CDCl_3$) δ 6.51 (s, 5 H), 6.25 (t, J = 3.0 Hz, 1 H), 6.19 (d, J = 3.0 Hz, 2 H), 2.17 (d, J = 1.5 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 135.4, 120.5, 118.9, 110.1, 14.6; HRMS m/z (M^+) calcd 275.9952, obsd 275.9964. Anal. Calcd for $C_{12}H_{14}C_{12}Ti$: C, 51.92; H, 5.06. Found: C, 52.02; H, 5.09.

Bis(η^5-1,2-dimethylcyclopentadienyl)dichlorotitanium (3). To the diene mixture (4.00 g, 42.5 mmol) in 30 mL of THF was added *n*-butyllithium (28.3 mL, 1.5 M in hexane, 42.5 mmol) via syringe at 0 °C. The ice bath was removed and DME (5 mL) was introduced to dissolve the solids. After 2 h, the solution was added to a slurry of titanium(III) chloride (3.12 g, 20.2 mmol) in 150 mL of DME via cannula. The flask was fitted with a condenser and the mixture was heated to reflux for 24 h, cooled to room temperature, placed in an ice bath, and treated with 50 mL of concentrated HCl. The layers were separated 15 min later and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried, filtered, and concentrated to give a dark red-black residue, which was sublimed at 140–150 °C and 0.01 Torr. Complex **3** was isolated as dark orange crystals (2.86 g, 46%): mp >250 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 6.17 (br s, 6 H), 2.14 (d, J = 0.9 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 133.6, 119.8, 109.5, 14.5; HRMS m/z (M^+) calcd 304.0625, obsd 304.0271. Anal. Calcd for $C_{14}H_{18}C_{12}Ti$: C, 55.12; H, 5.95. Found: C, 55.14; H, 6.00.

X-ray Crystallographic Analysis of 3. An orange single crystal of **3** was mounted in a thin-walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either centric *C*2/*c* or acentric *Cc* from the systematic absences. Successful refinement of the structure was carried out in the centric space group *C*2/*c*. A summary of data collection parameters is given in Table 3.

Least-squares refinement with isotropic thermal parameters led to R = 0.133. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, B = 5.5 Å^2). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.067 and R_w = 0.079. The bond lengths and bond angles are found in Table 4. The final values of the positional parameters are given in the Supplementary Material.

XPS Analyses. The XPS analyses were carried out with a Physical Electronics Industries, Inc., ESCA-Auger Model 550 spectrometer equipped with a Model 15-770 specimen introduction/reaction chamber using Mg Kα radiation. Samples were analyzed on a polyethylene-coated aluminum support allowing an internal calibration against the C (1s) binding energy (284.60 eV) of polyethylene. Instrument linearity was determined prior to each analysis and corrected relative to the binding energies of Au ($4f_{7/2}$) (83.80 eV) and Cu ($2p_{3/2}$) (932.40 eV). Ti ($2p_{3/2}$) binding energy values are ±0.03 eV and Cl ($2p_{3/2}$) binding energy values are ±0.1 eV.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9007132), the Center for Materials Research of The Ohio State University for their financial support of this effort, Professor R. D. Rogers (Northern Illinois University) for the X-ray crystallographic analysis, and the U.S. Department of Education and the Amoco Oil Company for fellowships to M.R.S. C.A.J. is grateful to the Ohio State College of Mathematical and Physical Sciences for financial support.

Supplementary Material Available: Tables of final fractional coordinates, least-squares planes, and thermal parameters for **3** (3 pages). Ordering information is given on any current masthead page.

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