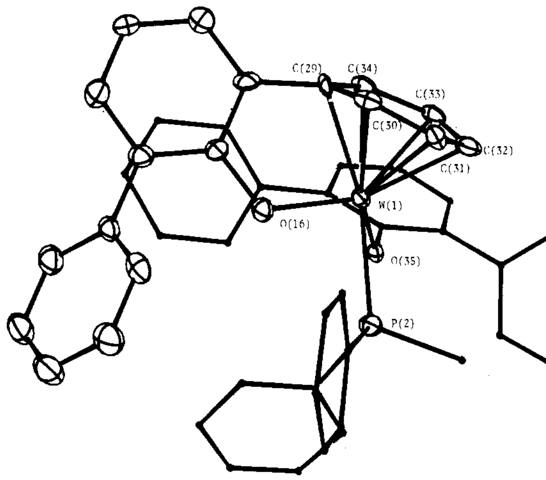

Figure 2. ORTEP view of **2b**. Selected bond distances (Å) and angles (deg): W(1)–P(2) = 2.481 (3), –O(16) = 2.033 (6), –O(35) = 2.001 (6), –C(29) = 2.202 (8), –C(30) = 2.357 (8), –C(31) = 2.292 (a), –C(32) = 2.227 (a), –C(33) = 2.296 (8), –C(34) = 2.286 (a), P(2)–W(1)–O(16) = 79.1 (1), –O(35) = 79.0 (2), O(16)–W(1)–O(35) = 117.1 (2), W(1)–O(16)–C(17) = 117.5 (5), W(1)–O(35)–C(36) = 127.4 (5).

mono-cyclometalated hydride compound that then undergoes a second CH bond activation to generate the observed H_2 gas (Scheme II).[21,22] Addition of the smaller phosphine PMe_2Ph to solutions of **2b** also results in the rapid formation of bis-cyclometalated **1a** along with H_2.

These results taken along with the high thermal stability of the 18-electron complexes W(OAr-2-Ph-6-η^6-C_6H_5)($PMePh_2$)$_2$(H)[8] and W(OAr-2-Ph-6-η^6-C_6H_5)(PMe_2Ph)$_2$(Cl)[23] strongly indicate the lack of facile, direct conversion of an η^6-bound arene group into a σ-bound aryl function via oxidative addition at these W(II) centers. Instead the dislodging of the η^6-arene group appears to be necessary to initiate CH bond activation. Hence in the case of **2b**, steric congestion caused by the added phosphine would displace the η^6-arene leading to a highly reactive "W(OAr)$_2$(PR_3)$_2$" intermediate.[21] Further mechanistic study of this reactivity is underway.

Acknowledgment. We thank the National Science Foundation (Grant CHE-86120643 to I.P.R.) for support of the research. I.P.R. also gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher-Scholar Grant and the Alfred P. Sloan Foundation for a fellowship. J.L.K. gratefully acknowledges the award of a fellowship by Amoco Oil Co.

Supplementary Material Available: Tables of positional parameters, general temperature fractions, bond distances, and bond angles for **1b** and **2b** and also analytical data on intermediates mentioned in text (23 pages); listings of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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[21] The chlorophosphine compounds of W(II) of stoichiometry $WCl_2(PR_3)_4$ have been shown to be highly reactive toward oxidative addition; see: Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808 and references therein.

[22] The double metalation of 2,6-diphenylphenoxide at Ta(III) metal centers has also been demonstrated although no intermediates could be detected; see ref 9b. However, intramolecular oxidative addition of an aliphatic CH bond to Ta(III) has been shown to yield a hydrido–alkyl compound: Lubben, T. V.; Wolczarski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 414.

[23] Formed by the reduction of toluene solutions of W(OAr-2,6-Ph_2)Cl_3 with Na/Hg (4 equiv) in the presence of PMe_2Ph (2 equiv); see supplementary material.

Stereocontrolled Bifacial Complexation of the Isodicyclopentadienyl Ligand to Cyclopentadienyltitanium Dichloride Fragments[1]

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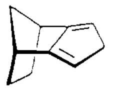
Summary: Reaction of the isodicyclopentadienide anion with (RCp)$TiCl_3$ (R = H, CH_3) and Cp″$TiCl_3$ is shown to proceed under conditions presumed to be kinetically controlled with complete bifacial stereoselectivity depending upon temperature. While endo complexation materializes at −78 °C, exo coordination operates exclusively at room temperature and above, as ascertained by X-ray analysis. The isomeric complexes can also be easily distinguished spectroscopically.

The plane-nonsymmetric nature of isodicyclopentadiene (isodiCp, **1**) has served admirably for examination of the relevance of π-facial selectivity in a wide range of cycloaddition reactions.[2] The remarkable predilection of this system for stereoselective dienophile capture from the sterically more congested endo direction (in the absence of overriding steric effects) is mirrored in its anion (**2**), which captures electrophiles predominantly, if not exclusively, from its endo surface to deliver C_s-symmetric products.[3,4] In a previous paper,[5] we demonstrated that **2** is complexed uniquely from its sterically less crowded exo face when allowed to react with tri- or tetrachloride salts of the group 4 transition metals. The symmetrical complexes represented by **3** (M = Ti, Zr, Hf) result.



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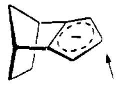

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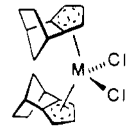

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Like the situation in **1**, the π-facial course of isodicyclopentadienide anion reactions is believed to be governed by a complex interplay of electronic[6] and steric factors.[7] One may immediately inquire whether the crossover in stereoselectivity that materializes in the course of the **2** → **3** conversions, when compared to the reaction

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‡ Faculté des Sciences Dijon.

[1] Part 40 in the series dealing with isodicyclopentadienes and related molecules. (a) For part 39, see: Paquette, L. A.; Gugelchuk, M. *J. Org. Chem.*, in press. (b) For part 38, consult: Paquette, L. A.; Gugelchuk, M.; McLaughlin, M. L. *Ibid.* **1987**, *52*, 4732.

[2] An extensive listing of literature citations can be found in ref 1b.

[3] (a) Paquette, L. A.; Charumilind, P. *J. Am. Chem. Soc.* **1982**, *104*, 3749. (b) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *Ibid.* **1983**, *105*, 3126. (c) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105*, 3136. (d) Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *Ibid.* **1983**, *105*, 7364.

[4] Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.

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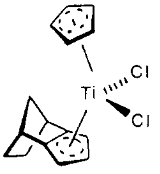
of the former with electrophiles, is kinetically or thermodynamically driven. The isodiCp ligand is relatively large, and its spatial demands are clearly better served by exo complexation. Thus, the thermodynamic bias is clear. In order to address the kinetic aspects of the question, we have more recently examined the stereochemical course of mixed complex formation involving **2** and reagents of the type (RCp)$TiCl_3$. The very striking and unprecedented dependence of product structure on reaction temperature constitutes the subject of this report.

Reaction of $CpTiCl_3$ with isodicyclopentadienyllithium (as the isolated salt or formed in situ) in tetrahydrofuran solution at room temperature for 12 h gave rise after purification to **4** (40%) as the only characterizable product.[8]



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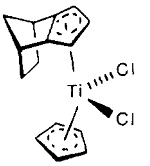

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Although the three-dimensional nature of **4** was conclusively established by X-ray crystallographic analysis, a particularly diagnostic feature of its exo stereochemistry is the appearance of its central and peripheral isodiCp vinylic proton resonances at δ 6.43 (t, J = 2.8 Hz, 1 H) and 6.15 (d, J = 2.8 Hz, 2H), respectively. The identical substance was produced (45% yield) upon heating the thallium salt of **2** with $CpTiCl_3$ in dry benzene for several hours.

In contrast, admixing of the lithium salt of **2** with $CpTiCl_3$ in tetrahydrofuran at −78 °C followed by slow warming to room temperature and stirring for 30 min gave no spectral indication for the formation of **4**. Instead, there was produced somewhat less efficiently (21%) the stereoisomeric endo complex **5**. One striking peculiarity of the stereochemical switchover is a reverse ordering of the isodiCp vinylic proton signals in the ^1H NMR spectrum. Here, the peripheral hydrogens (δ 6.35 (d, J = 2.6 Hz, 2 H) are more deshielded than their central counterpart (δ 6.13 (t, J = 2.6 Hz, 1 H)). These and the other ^1H and ^{13}C NMR features of **5** compare very favorably with those of **7** (see below) for which confirmatory X-ray data are available.

$CH_3CpTiCl_3$ was synthesized by an adaptation of Cardoso's method as detailed for the unsubstituted complex.[9] The methodology offers significantly greater convenience than those reported heretofore.[10] The mixture of isomers obtained in the first step was used without purification in the sequel. The trichloride was isolated in 80% overall yield from methylcyclopentadiene (eq 1).

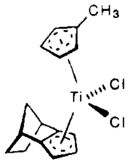
$$H_3CCpLi + ClSi(CH_3)_3 \rightarrow H_3CCpSi(CH_3)_3 \text{ (mixture of isomers)} + LiCl$$

$$H_3CCpSi(CH_3)_3 \xrightarrow{TiCl_4} H_3CCpTiCl_3 + ClSi(CH_3)_3 \qquad (1)$$

The response of the lithium salt of **2** to $CH_3CpTiCl_3$ was equally temperature-sensitive. In boiling tetrahydrofuran, only **6** was obtained [40%; δ 6.38 (t, J = 2.8 Hz, 1 H) and 6.11 (d, J = 2.8 Hz, 2 H)]. Similar treatment under conditions in which the initial reaction temperature of −78 °C was allowed to increase to +25 °C over 14 h led to complex **7** (65%) with very high stereoselectivity and only a trace of **6** (^{13}C NMR). The efficiency of complexation in the case of **2** is worthy of note since reactions of the type

$$Cp'Li + CpTiCl_3 \rightarrow xCpCp'TiCl_2 + yCp_2TiCl_2 + zCp'_2TiCl_2 + LiCl$$

usually lead concomitantly to symmetrical dichloride formation to varying degrees.[11] The structural assignment to **7** was substantiated by X-ray crystallographic analysis. Like **5**, its downfield isodiCp protons appear in the order δ 6.33 (d, J = 2.8 Hz, 2 H) and 6.06 (t, J = 2.8 Hz, 1 H).



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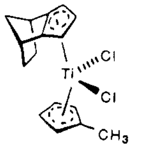

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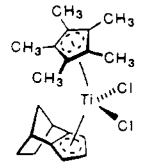

8

The lessened reactivity of (η^5-pentamethylcyclopentadienyl)trichlorotitanium[12] necessitated reflux temperatures (C_6H_6, 12 h) for reaction with isodicyclopentadienylthallium to proceed at a reasonable rate. As anticipated from the earlier observations, only **8** resulted (50%). X-ray analysis confirmed that complexation had occurred above plane, in agreement with the low-field ^1H NMR signals [δ 6.11 (t, J = 2.7 Hz, 1 H), 5.14 (d, J = 2.7 Hz, 2 H)].

The following battery of control experiments were performed. Condensation of isodiCpLi with $CpTiCl_3$ at both 20 °C and the reflux temperature of tetrahydrofuran in the presence of a 10-fold excess of **5** failed to induce isomerization of the latter to **4**. In both instances, a 20:1 mixture of **5** and **4** (the latter resulting from direct complexation) was produced. In a complementary study, **1** was reacted with sodium metal in methanol-*O-d* to effect complete H/D exchange in its cyclopentadiene ring. The extent of labeling was ascertained by conversion to **5**-d_3 and spectroscopic (^1H and ^2H NMR) analysis of this complex. Its deuterium atoms appeared as two broad singlets at δ 6.38 and 6.17 in a 2:1 ratio. When **5**-d_3 was admixed with an equimolar amount of **4** in tetrahydrofuran and maintained either at room temperature (18 h) or at reflux (18 h), no crossover was seen. The ^2H NMR spectrum of reisolated **4** was totally devoid of signals! Admixture of isodiCpLi-d_3 with $CpTiCl_3$ and **5** as described above again showed that no intermediate, side, or decomposition product is involved in converting one material into the other. Consequently, the bifacial complexation so clearly exhibited by **2** does not appear to stem from some isomerization process induced at the more elevated temperatures. Rather, all indicators point to operation of two different kinetically controlled processes that are stereochemically exclusive at the −78 and 25 °C temperature limits.

We have previously given consideration to the possible interplay of those orbital constructs within **2** that could impinge on its capability for achieving stereoelectronic

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[8] All of the new complexes reported herein exhibit IR, 300-MHz ^1H NMR, ^{13}C NMR, mass, and analytical data compatible with their structural assignments.

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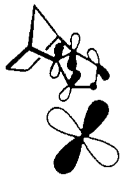
control in these reactions.[13] The model, which is depicted in **9**, visualizes the disrotatory tilting deformations that INDO calculations[14] indicate arise within ψ_1 from σ/π mixing with the neighboring norbornyl framework. To the extent that ψ_1 exerts the more important overlap control, metal ions might well prefer above-plane approach because their d_{z^2}, s, and p_z orbitals (all symmetry related to ψ_1) would be directed to the center of the more electron-rich cyclopentadienide core.

9

10



11

The impact of ψ_1 is not anticipated to be controlling, however, because of its sub-frontier status and the customary greater significance of $d\pi$–ψ_2 interactions relative to those of the d_0–ψ_1 type. Therefore, to the extent that the $p\pi$ orbitals within ψ_2 remain tilted as in **10** (or at least in this manner in the transition state), a large metal atom with diffuse $d\pi$ orbitals could engage in more effective overlap on the endo face as shown in **11**.

Verification of this working hypothesis clearly must await the results of future work. On the other hand, the stereoselectivity crossover as described herein has clearly been defined experimentally. These fascinating findings are presently viewed as an overriding of electronic control (endo directive) by steric considerations when the incoming ligand is sterically bulky. The exclusive formation of **3** conforms to this interpretation, as does the response of a camphor-derived fused cyclopentadiene ligand where the presence of a syn-oriented apical methyl group is adequate to deter the capacity for above-plane complexation.[15]

Acknowledgment. The Ohio State group thanks the National Cancer Institute (Grant CA-12115) for their financial support of this research program.

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The Reactivity of a Terminal Phosphinidene Complex toward Styrenes

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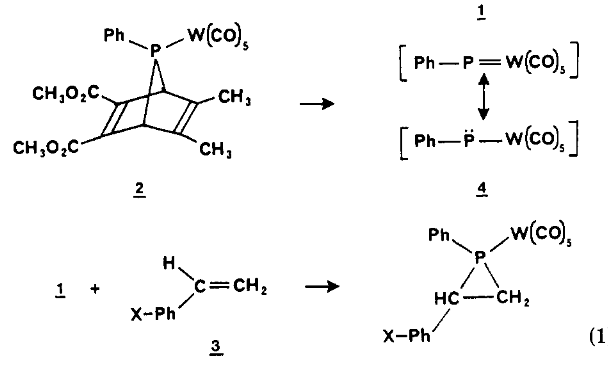
Summary: The Hammett reaction constant for the reaction of the terminal phosphinidene complex [Ph—P=W(CO)$_5$], as generated from the appropriate 7-phosphanorbornadiene complex, toward styrenes is reported and compared to those of "free" carbenes. The mild electrophilicity supports the unencumbered carbene-like nature of the phosphinidene complex and suggests a concerted addition to olefins with a slightly polar transition state.

Mathey's discovery[1] of in situ generation of terminal phosphinidene complexes has resulted in an avalanche of studies that rapidly develop this carbene-like chemistry.[2] Most attention has focussed on the synthetic versatility of the phosphinidene complex.[2] Additional interest centers on the bonding nature between the phosphorus atom and its complexed transition metal.[3] However, in contrast to the broad understanding of carbenic reactivity and selectivity,[4] such characteristics for phosphinidenes are virtually unexplored. Here we report the Hammett reaction constant for the reaction of the terminal phosphinidene complex Ph—P=W(CO)$_5$ (**1**) with olefins to form phosphiranes.

The phosphinidene complex **1** was generated in situ following Mathey's procedure,[5] from the 7-phosphanorbornadiene precursor **2** in toluene at 55 °C with CuCl as catalyst (eq 1), and reacted with an excess of a series of substituted styrenes **3** to form the corresponding phosphiranes; the *p*-phenyl substituents in **3** were OCH$_3$, CH$_3$, Ph, F, Cl, and Br.[6] Relative reaction rates were determined from relative (total) phosphirane product ratios resulting from competitive reactions of **2** with equimolar ratios of substituted and unsubstituted styrenes; two cross checks verified the accuracies of the determined reactivities. The product ratios were determined from integration of the ^{31}P NMR spectra.[7] The obtained selectivities of **1** toward the substituted styrenes are listed in Table I. A plot of the logarithms of the relative reaction rates (selectivities), log k_X/k_H, versus the Brown substituent constant σ^+ results in a linear relationship (Figure 1) and gives a Hammett reaction constant of $\rho = -0.76$ ($r = 0.99$). A similar correlation with σ values is unsatisfactory.



(1)

The Hammett reaction constant of −0.76 supports the singlet electrophilic nature previously assumed[2a,5] for the phosphinidene complex Ph—P=W(CO)$_5$. The mild electrophilicity of **1** suggests a concerted addition to olefins with a slightly polar transition state. The relatively small value of −0.76 also is indicative for the unencumbered carbene-like nature[8] of the phosphinidene complex **1**, thermally generated from the 7-phosphanorbornadiene precursor **2**.

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