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# Computational Study of Methane Activation by $TpRe(CO)_2$ and $CpRe(CO)_2$ with a Stereoelectronic Comparison of Cyclopentadienyl and Scorpionate Ligands

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A computational investigation of metal-based C−H activation with complexes that possess scorpionate (i.e., tris(pyrazolyl)borate) and cyclopentadienyl ligands was reported. The model tris(azo)borate ligand (Tab; $[HB(N{=}NH)_3]^-$) was created as an alternative to the parent tris(pyrazolyl)borate (Tp). The Tab ligand was found to closely reproduce the structure and energetics of Tp in Re-mediated C−H activation of methane. Relative to separated reactants oxidative addition of methane to $CpRe(CO)_2$ was exothermic, while the same transformations with $TpRe(CO)_2$ and $(Tab)Re(CO)_2$ were endothermic. The differences between the Tp and Cp systems were attributed primarily to steric effects. The reactivity differences between Tp and Cp drew attention to how each system would respond, sterically and electronically, to ring substitutions. $TpRe(CO)_3$ complexes consistently had a broader $\nu_{CO}$ (a measure of electronic properties) and cone angle (a measure of steric bulk) range in comparison to $CpRe(CO)_3$ congeners. While Cp was more sensitive to chemical modification on a per substituent basis, Tp was overall more stereoelectronically flexible. Taken together, the results of this research indicated that Tp cannot simply be considered a Cp equivalent and that the reactivity differences for Re(I) are primarily due to steric differences between Tp and Cp.

## Introduction

The central role that the cyclopentadienyl (Cp, $\eta^5$-$C_5H_5$) ligand plays in organometallic chemistry began with the synthesis and characterization of ferrocene in 1951.[1] Cyclopentadienyl is a versatile ligand that can ionically bond with s-block metals as well as covalently bind to p-block elements. For d- and f-block elements, Cp−metal bonding can be ionic, covalent, or, more likely, a combination of these. The location of the metal in the transition or lanthanide/actinide series as well as the formal oxidation state of the metal and the coligands present in the complex determines the precise nature of the Cp−metal bond.[2] Early-transition-metal Cp-containing complexes are used in catalysis for Ziegler−Natta type polymerization of ethylene or propylene.[3] Cyclopentadienyl complexes have also been investigated in C−H activation chemistry, particularly in combination with low-valent late-transition-metal systems, including those that possess Re, W, Rh, and Ir centers.[4] There is evidence that $CpCo^+$ directly involves Cp in the C−H bond activation of methane.[5] However, the Cp ligand typically acts as a "spectator" ligand. Ligand activation is generally more problematic for Cp* (Cp* = pentamethylcyclopentadienyl, $\eta^5$-$C_5Me_5$) complexes, where the pendant methyl groups are particularly susceptible to C−H activation and the formation of so-called "tuck-in" complexes.[6]

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An important research emphasis in organometallic chemistry is the search for new supporting ligation to supplement and improve the workhorses of the field. In this regard, tris(1-pyrazolyl)borate (Tp) and related scorpionate ligands have received considerable interest following the pioneering work of Trofimenko.[7] Some experimental examples of Tp ligands involved in C−H activation include Tp*Ir($C_2H_4$)$_2$ with aromatic substrates, cyclic ethers, and vinyl C−H bonds,[8] Tp*Ir($\eta^4$-1,3-diene) to produce hydrido (1−3-$\eta^3$)-butadienyl species,[9] TpRh(CO)$_2$ and Tp*Rh(CO)$_2$ with methane, [Tp*Ir(PMe$_3$)(Me)(N$_2$)][BAr$_f$] with $C_6H_6$, and Tp*Rh(CN-neopentyl)(R)H with alkanes.[10] Like Cp, Tp affords the potential for systematic manipulation of the steric and electronic profile of the resulting transition-metal complexes through appropriate chemical modification.

Scorpionate ligands are often viewed as Cp equivalents, since both are facially coordinating, six-electron anionic donors. However, more careful consideration of the experimental literature suggests that the situation may not be so straightforward. A recent manuscript specifically highlights the variable donating abilities of Tp and Cp across the transition series.[11] Several researchers have proposed that Tp enforces an octahedral geometry through a combination of steric and electronic preferences. Curtis and co-workers have supported this through the differences in the stabilities of the products of CpMo(CO)$_3^-$ and TpMo(CO)$_3^-$ with acyl halides.[12] Reported Cp/Tp reactivity differences include the observation of oxidative addition by CpRe(L)L′ (L, L′ = CO, PMe$_3$) of C−H bonds.[13] However, Harman et al. have not observed comparable reactivity for Tp congeners of the type {TpRe(CO)(L)} (albeit under disparate reaction conditions).[14] Heinekey and co-workers report that TpIrLH$_3$ exists as a mixed dihydrogen hydride complex, ($\eta^2$-H$_2$)(H), while the Cp analogue is a trihydride.[15] *Five-coordinate* Cp complexes seemingly demonstrate a greater tendency toward oxidative addition reactions than their Tp analogues.

To address issues of Cp versus Tp chemistry with regard to C−H activation, computational studies were carried out to compare the potential energy surfaces for C−H activation of methane by TpRe(CO)$_2$ and CpRe(CO)$_2$. Rhenium was chosen because it provides an example of identical Tp/Cp systems that exhibit disparate reactivity toward C−H bonds.[13,14,16] Additionally, the full tris(1-pyrazolyl)borate ligand and a smaller model (Tab, [HB(N=NH)$_3$]$^-$) were compared for their reactivity differences and similarities, not only to find suitable smaller ligand models for Tp but also to obtain the chemical insight this may impart. Finally, a computational comparison of the stereoelectronic “flexibility” of comparable CpRe and TpRe complexes was undertaken to gauge the response of these functionalities to chemical modification.

## Computational Methods

The Gaussian98 quantum chemistry program package[17] is employed for all ab initio calculations. All calculations utilized the relativistic effective core potentials (ECPs) and attendant valence basis sets of Stevens (SBK).[18] Main-group atoms are described with basis sets of valence double-ζ-plus-polarization (dzp) quality. For transition metals, SBK constitutes a triple-ζ description for the valence $n$d, ($n + 1$)s, and ($n + 1$)p orbitals. This combination of ECPs and basis sets, which we have termed SBK(d), along with other ECP/VBS combinations, has been used in numerous studies on transition-metal complexes and has been found to yield reliable results for the modeling of structural, energetic, and spectroscopic properties when it is used in conjunction with a suitable wave function or density functional method.[19]

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Semiempirical quantum mechanics calculations employed the PM3(tm) Hamiltonian[20] within the Titan[21] and Spartan[22] software. Previous work from our group and others has shown PM3(tm) to be reliable for structural prediction of transition-metal-complex geometries and for identifying trends in CO stretching frequencies among related series of complexes.[23,24]

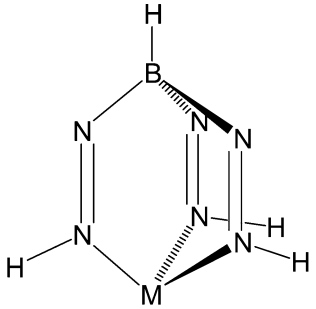
All molecules are fully optimized, with neither geometric nor symmetry constraint. In all cases the electronic state is a singlet and is investigated using restricted density functional formulations. All species are characterized as minima or transition states by calculation of the energy Hessian after successful geometry optimization.

A major difficulty with ab initio or density functional levels of theory to study transition-metal complexes with large Tp ligands is the huge computational time and memory requirement. For the Tp ligand, an increase in effort due to conformational complexity will be mitigated by the rigidity of these chelating ligands. Effective core potentials reduce the number of electrons and thus basis functions, substantially reducing the computational time. However, even with ECPs, the Tp ligand has 244 basis functions with the SBK(d) basis set employed here. Semiempirical quantum mechanics was employed to facilitate calculation of the geometries and vibrational spectra study of very large, and hence experimentally relevant, Cp/TpRe complexes.

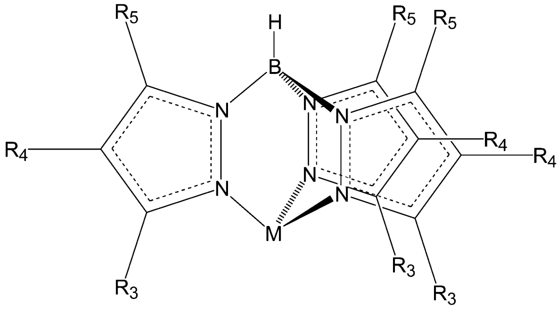
Another solution to the ab initio computational requirements of Tp is to reduce the number of atoms modeled; thus, Tab (Figure 1a) was created. Tab contains significantly fewer basis functions (106 using the basis sets employed in this research) and the same −1 charge as Tp. Therefore, to minimize computational time, Tab was explored as a mimic for the full Tp ligand. An example of the computational time savings is shown in a B3LYP[25] single-point energy calculation with the SBK(d) basis set: Tab takes 1.44 min, while Tp takes 23.8 min for the same calculation on a single processor of an SGI Origin 2000 computer.

## Results and Discussion

**1. Methane Adducts.** There has been considerable experimental[26] and computational[27] interest in weakly bound alkane adducts as intermediates in alkane C−H activation by transition metals. Previous calculations suggest that these adducts play an important role in determining the activity and selectivity of C−H scission.[27,28] The geometries of the LRe(CO)$_2$ (L = Tp, Tab, Cp) methane adducts (Figure 2 and Table 1) are quite interesting and are unlike other characterized methane adducts discussed in the computational literature. The Re···H distances are quite short at about 2.0−2.1 Å, and reasonably large Re−H−C angles of approximately 120° are observed (Table 1). As a comparison, the Ti···H−C fragments of d$^0$-Ti−imido/alkane adducts have an average Ti···H distance of 2.36 Å and a Ti−H−C angle of 107°.[28]



a. Tab



b. Tp

**Figure 1.** The model Tab and full Tp ligand. The 3-, 4-, and 5-positions on the full Tp ligand are denoted.

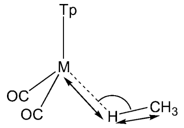


**Figure 2.** Bond lengths and angles of interest for reactants, products, and transition states.

A reduced variational space (RVS[29]) analysis was performed on the Re adducts. An RVS analysis seeks to decompose the total interaction energy between two fragments (methane and the transition-metal complex in this case) into chemically more meaningful contribution. Coulomb-exchange repulsion (CEX) quantifies the repulsion between the occupied molecular orbitals of methane and the complex. Charge transfer (CT) quantifies the energetic stabilization obtained from the transfer of electron density from the occupied orbitals of one fragment to the unoccupied orbitals of the other frag-

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**Table 1. Metric Parameters for Stationary Points in Methane Oxidative Addition**[a]

| | B3LYP/SBK(d) | | |
|---|---|---|---|
| | Cp | Tab | Tp |
| | Adduct | | |
| Re−H | 1.99 | 2.09 | 2.05 |
| C−H | 1.14 | 1.12 | 1.12 |
| Re−H−C | 118.9 | 120.1 | 118.8 |
| | Transition State | | |
| Re−H | 1.69 | 1.68 | 1.67 |
| C−H | 1.50 | 1.70 | 1.72 |
| Re−C | 2.34 | 2.31 | 2.28 |
| C−Re−H | 39.6 | 47.4 | 48.6 |
| | Product | | |
| Re−H | 1.67 | 1.68 | 1.66 |
| C−H | 2.18 | 2.06 | 1.91 |
| Re−C | 2.26 | 2.25 | 2.25 |
| Re−H−C | 70.1 | 73.2 | 77.6 |

[a] Bond lengths are in Å, and bond angles are in degrees.

ment. In comparison with $d^0$ transition-metal adducts the Re complexes have a more destabilizing Coulomb-exchange (CEX) repulsion term that is balanced by a more stabilizing charge transfer ($CT_{MeH\rightarrow Re}$) term. Additionally, $CT_{Re\rightarrow MeH}$ is more stabilizing by about 0.8 kcal mol$^{-1}$ compared with $d^0$-Ti(IV)−imido/alkane adducts. This provides support for the classic Hoffmann−Saillard model[30] of TM⋯H−C bonding (TM = transition metal), since the $CT_{TM\rightarrow RH}$ term describes back-bonding from the metal to the hydrocarbon. Electropositive, $d^0$ transition-metal complexes, such as in the Ti−imido adduct mentioned above, have no available electrons that may participate in metal-to-ligand back-bonding. Thus, $Re^I$−$CH_4$ bonding is stabilized due to d$\pi$ back-bonding, relative to early-transition-metal systems that are $d^0$. In light of the Burgi−Dunitz analysis of Crabtree et al.,[31] it seems reasonable to conclude that the different geometry of the Re−MeH adducts in contrast to their $d^0$ counterparts is a reflection of a stronger metal−substrate interaction and an adduct that is more advanced along the scission reaction coordinate.

**2. Tab versus Tp Reaction Coordinates.** Table 1 shows the bond lengths and angles of interest for Tab and Tp at the B3LYP/SBK(d) level of theory with the SBK(d) valence basis set/effective core potential scheme. Metric data for the CpRe(CO)$_2$ and TpRe(CO)$_2$ fragments are largely unchanged for the various stationary points along their respective reaction coordinate. Furthermore, Tab and Tp have similar geometries. Hence, it is reasonable to assume that the underlying differences in the electronic structures of Tp and Tab are sufficiently small to permit reliable modeling with Tab.

Figure 3 depicts the potential energy surfaces for CpRe(CO)$_2$, TpRe(CO)$_2$, and (Tab)Re(CO)$_2$ at the B3LYP/SBK(d) level of theory. Similar results are obtained at the MP2/SBK(d)//RHF/SBK(d) level of theory. TpRe(CO)$_2$ and (Tab)Re(CO)$_2$ have very similar potential energy surfaces. Both the similar geometries (vide supra) and reaction energetics (Figure 3) indicate that Tab is an effective model for Tp.

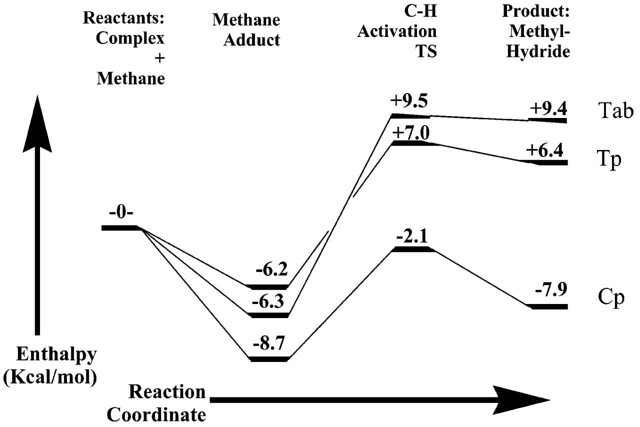
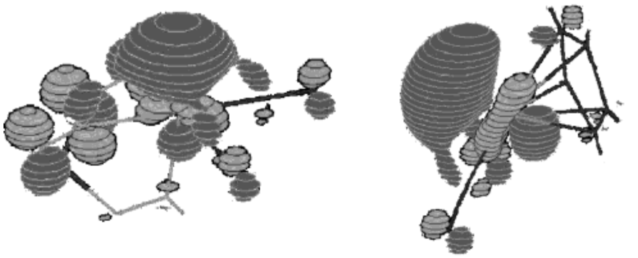
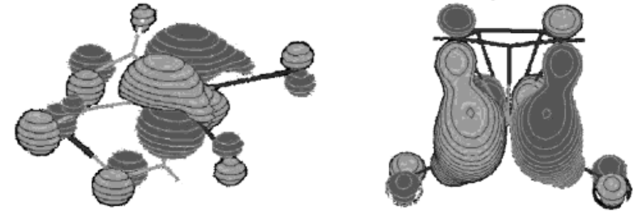


**Figure 3.** Tris(pyrazolyl)borate and Tab vs cyclopentadienyl. Relative enthalpies are determined at the B3LYP/SBK(d) level of theory with zero point and enthalpic corrections to 298.15 K.



A. Tab LUMO B. Cp LUMO



C. Tab HOMO D. Cp HOMO

**Figure 4.** Highest occupied and lowest unoccupied molecular orbitals (B3LYP/SBK(d)) for (Tab)Re(CO)$_2$ and CpRe(CO)$_2$.

**3. Cp versus Tp Reaction Coordinates.** Relative to isolated reactants, methane C−H oxidative addition for TpRe(CO)$_2$ and (Tab)Re(CO)$_2$ is surprisingly endothermic (by 6 and 9 kcal mol$^{-1}$, respectively), while the reaction for CpRe(CO)$_2$ is exothermic by 8 kcal mol$^{-1}$. The enthalpy difference between seven-coordinate TpRe(CO)$_2$(H)(Me) and CpRe(CO)$_2$(H)(Me) complexes is a surprising 14 kcal/mol. These results are consistent with experimentally observed differences in reactivity, and thus, the root causes of this disparity are of interest.

A convincing explanation of such stability trends by Curtis[12] is that Cp has diffuse $\pi$-orbitals that benefit bonding to higher coordination numbers and that the Cp electron cloud is less effective compared with Tp in supporting strong directional character to the frontier orbitals of the CpML$_3$ fragment. These bonding differences were used to explain the relative stabilities of LMo(CO)$_3$(R) and LMo(CO)$_2$(C(O)R) systems, for which L = Tp favors the six-coordinate acyl complex while L = Cp favors the seven-coordinate systems.[12] In contrast, the Tp ligand lacks diffuse $\pi$-orbitals and is effective in promoting directional character to the frontier orbitals due to its strong $\sigma$-donating nature. In accord with Curtis' studies, it is apparent from the orbitals in Figure 4 that the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of

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$CpRe(CO)_2$ are more diffuse (i.e., a greater percentage of these orbitals is delocalized away from the metal) than the corresponding orbitals for $(Tab)Re(CO)_2$.

The present calculations indicate that the difference in reactivity between TpRe and CpRe complexes is due to the intrinsic difference in stability of the oxidative addition products, $LRe(CO)_2(Me)H$ (L = Tp, Cp). This is apparent from Figure 3, which illustrates that there is a significant difference in the oxidative addition potential energy surfaces for the transition states (which are "late" or product-like) as well as the products. In contrast, the formally octahedral methane adducts exhibit a modest difference in energy. For example, the $\Delta\Delta H$ value for Tp versus Cp for the methane adducts is only 2.5 kcal/mol compared with a $\Delta\Delta H$ value of 9.1 kcal/mol for the transition states and 14.3 kcal/mol for the oxidative addition products. The near-zero kinetic barrier for methane elimination from $TpRe(CO)_2(Me)H$ is also suggestive of a lack of even relative metastability for this complex, even if such a species could be made by other synthetic routes. Significant interest has been devoted to the isolation of a transition-metal alkane complex.[32] The computational results suggest that $TpML_2$(alkane) complexes might provide an optimal opportunity to isolate such a system, since oxidative addition is effectively suppressed.

Although the relative donating abilities of Tp and Cp ligands are dependent upon the identity of the transition metal, Tp appears to be more strongly donating than Cp when coordinated to Re.[11] For example, CO stretching frequencies of $TpRe(CO)_3$ and $TpRe(CO)_2(THF)$ are slightly lower than those for $CpRe(CO)_3$ and $CpRe(CO)_2(THF)$.[11] Thus, the energy differences for conversion from five-coordinate $LRe(CO)_2$ to seven-coordinate $LRe(CO)_2(R)H$ (L = Tp, Cp) are not likely to be dictated by the relative Tp/Cp donating abilities. We suggest that the predilection against C−H activation for $TpRe(CO)_2$ is primarily a result of sterics. Analysis of intramolecular differences in the hydrido methyl products highlights the greater steric hindrance for the scorpionate and model scorpionate complexes. The closest H···H contact is 2.2 Å for $Tp(CO)_2(Me)(H)$ and occurs between a methyl hydrogen and a hydrogen on the 3-position of Tp. The distance between the methyl hydrogen and the proton on the bound nitrogen for the Tab analogue is 2.1 Å. The closest contact involving the hydride ligand is 2.5 Å (2.6 Å) with the 3-H. For the Cp-containing product, there is no H···H distance less than 2.7 Å. A search of the Cambridge Structural Database (CSD[33]) indicates that Tp−transition-metal complexes less commonly assume 7-coordination. There are 61 7-coordinate Tp−transition-metal complexes in the CSD (allowing for Tp derivatives). In contrast, Cp commonly forms 7-coordinate complexes. There exist 1122 $CpML_4$ (Cp is assumed to occupy three-coordination sites based on its six-electron donor ability) examples in the CSD, counting derivatives of Cp. For comparison, there are 204 6-coordinate Tp complexes and 1679 6-coordinate Cp complexes in the CSD. Therefore, there would have to be approximately twice as many 7-coordinate Tp complexes to have the same Tp:Cp ratio as the 6-coordinate species.

It is possible that the Tp ligand has a special propensity for octahedral coordination due to polarization of $\sigma$-bonding orbitals; however, this does not explain the energy difference between *five*-coordinate and *seven*-coordinate systems. Further evidence against a special predisposition toward octahedral coordination for Tp-containing complexes is provided by relative acetonitrile exchange rates for $[CpRu(NCMe)_3]^+$ and $[TpRu(NCMe)_3]^+$ complexes. *Dissociative* acetonitrile exchange is approximately 8 orders of magnitude faster for Tp versus Cp.[34] If Tp strongly preferred an octahedral geometry, it might be anticipated that dissociation would be more favorable for the Cp system.

These results seemingly suggest that the different abilities of $TpReL_2$ and $CpReL_2$ systems for the activation of C−H bonds are derived from the different stabilities of the seven-coordinate oxidative addition products, and we suggest that steric differences between Tp and Cp provide the primary driving force for the dissimilar stabilities. That is, seven-coordinate Tp and Tab products that result from oxidative addition suffer from close intramolecular contacts, while the Cp ligand affords a less crowded coordination sphere (see above). As mentioned above, intramolecular H−H contacts between the Re−methyl and Tab ligand are slightly closer than for the Tp system, and in accord with this observation is the somewhat more endothermic oxidative addition of methane to $(Tab)Re(CO)_2$ compared with that to $TpRe(CO)_2$ (Figure 3). It is notable that traditional cone angles might not provide the best indication of steric crowding, since substituents that can significantly alter the cone angle are often remote from the metal center.

**4. $CpRe(CO)_3$ Versus $TpRe(CO)_3$ With Ligand Modifications.** In light of the reactivity differences between $CpRe(CO)_2$ and $TpRe(CO)_2$, the response of Cp and Tp to steric and electronic modification was examined. The study was carried out on $CpRe(CO)_3$ and $TpRe(CO)_3$, because these are stable 18-electron systems.

Tolman[35] used the experimental $A_1$ $\nu_{CO}$ frequency for $Ni(CO)_3L$ complexes to quantify the electronic demand of the coordinated ligand L. This metric is called the Tolman electronic parameter (TEP). Crabtree and coworkers recently used DFT to compute these frequencies and found excellent correlations with Tolman's experimental data (the DFT-based parameter is termed the CEP).[36] Gillespie et al. recently demonstrated that semiempirical quantum mechanics (SEQM) with the PM3(tm) Hamiltonian can reliably be used to determine $\nu_{CO}$ frequencies for $Mo(CO)_5L$, $W(CO)_5L$, $CpRh(CO)L$, and *trans*-$Rh(PR_3)_2(CO)Cl$.[24] This SEQM-based electronic parameter, called SEP, was found to correlate well with both TEP and CEP. SEP allows one to access larger ligand systems due to the SEQM component of the protocol. Therefore, SEQM is used here to compute an electronic parameter for $CpRe(CO)_3$, $TpRe(CO)_3$, and their derivatives. On the basis of previous research in

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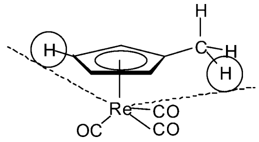

**Figure 5.** Calculation of the Tolman cone angle for $\eta^5$-$C_5H_4Me$. A right-circular cone is constructed around the ligand tangential to the van der Waals radii of the outermost ligand. The interior linear angle, $\theta$, is the cone angle used.

our laboratory,[24] we expect the reliability of the SEP values to be considerably less than approximately ±8 $cm^{-1}$ and the relative accuracy to be less than this value.

To quantify the steric demand of substituted Cp and Tp ligands, a cone angle approach originally reported by White et al. was used.[37] Starting structures were generated from PM3(tm) optimization and were used without modification or sampling of the conformational space of the ligand. Thus, the cone angles reported represent the steric demand of the ligands in the organorhenium environment of interest. Our experience with the PM3(tm) Hamiltonian suggests reliability in the bonds of ±3−5% or less, particularly for organometallics of the heavier transition metals.[23,24]

For the Cp ligand, the five half-cone angles ($\alpha$) were measured from the Cp centroid to the Re to the centers of the five Cp hydrogens. Trigonometry was used to compute the additional angle ($\beta$) from the H center to the Re to the van der Waals radius of the H atom (taken as 1.20 Å). Finally, the cone angle, $\theta$, is given by eq 1.

$$\theta = 2\sum_{i=1}^{5}(\alpha_i + \beta_i) \qquad (1)$$

For a substituted Cp ligand, for example $\eta^5$-$C_5H_4Me$ (Figure 5), there is a choice of which outermost atom to use in the cone angle calculation. Tolman always used the largest cone angle for a given ligand;,[35] therefore, we consistently use the outermost atom that gives rise to the largest cone angle.

Cone angles for the substituted Tp ligands were calculated in an analogous manner. Either the boron atom of Tp or the centroid of coordinated nitrogens can be used in place of the Cp centroid in determining the cone angle. No differences were found in the cone angles using these two different reference points; therefore, the Tp boron atom was used as reference, as it corresponds to a crystallographically identifiable entity.

There were three families of $TpRe(CO)_3$ complexes for which SEP and cone angles were determined: (a) known X-ray crystal structures of Tp complexes, (b) novel Tp complexes with electronically disparate functional groups chosen to identify trends, and (c) monosubstituted Tp complexes with functional groups similar to those found in structurally characterized monosubstituted Cp complexes. The entire list of computational targets is given in the Supporting Information.

Complexes from the Cambridge Crystallographic Database were imported directly into the computational chemistry software in PDB (Protein Databank) format. All other complexes were built within the molecular modeling software, and all complexes were subjected to semiempirical PM3(tm) geometry optimization. The PM3(tm) approach has been shown in previous studies to be reliable for prediction of transition-metal geometries and reproducing trends in $\nu_{CO}$.[24]

Fifty-six Tp ligands (including parent Tp and Tp*; see the Supporting Information) were identified by a search of the CSD to determine what range of CO stretching frequencies (the breathing mode was used to quantify the SEP) and cone angles exist for experimentally known Tp derivatives. These 56 complexes were divided into 10 hetero-scorpionate complexes and 46 homo-scorpionate complexes. The homo-scorpionate complexes included the following fractions: 19 3-R complexes, 2 4-R complexes, 3 3,4-R complexes, 16 3,5-R complexes, 1 4,5-R complex, and 5 3,4,5-R complexes (where R is a substituent).

The calculated SEPs for known Tp ligands ranged from 2115 $cm^{-1}$ for tris(3-2*R*,5*R*-menthylpyrazolyl)Tp to 2150 $cm^{-1}$ for $Tp(CF_3)_2$ (a range of ca. 35 $cm^{-1}$). This compares to an SEP range from 2123 $cm^{-1}$ for tetramethyl-*tert*-butylcyclopentadienyl to 2141 $cm^{-1}$ for $\eta^5$-1,3-bis(pentafluoropentyl)indenylcyclopentadienyl ($\Delta SEP = 18$ $cm^{-1}$) for substituted $CpRe(CO)_3$. The cone angles for $TpRe(CO)_3$ complexes ranged from 211° (parent Tp, $Tp^{4Me}$, and $Tp^{4Br}$) to 292° ($Tp^{iPr,5Me}$ and $Tp^{p\text{-}tBu\text{-}Ph,Me}$), a range of 81°. Cone angles for the experimentally characterized Cp ligands studied range from 140° for Cp and F−Cp to 176° for $C_5Me_4{}^tBu$, a much narrower range of 36°.

While it seems apparent that the Tp ligand is substantially larger than Cp, this is, to our knowledge, the first evidence quantifying the *extent* of its steric variability versus Cp. Previous reports of Cp cone angles range from 116° (based on Zr systems with a Zr−$Cp_{centroid}$ distance of 2.2 Å) to 128° (based on Fe systems with an Fe−$Cp_{centroid}$ distance of 1.73 Å), to 148° (based on Rh(I) and Rh(III) systems).[38] In this work, the Re−$Cp_{centroid}$ distance averages 1.9 Å. Previous reports of Tp cone angles give Tp as 180° for a Mo system and Tp* as 225° for an Fe system.[39]

In light of the calculated reaction coordinate for methane oxidative addition and the CSD search of $CpML_4$ and $TpReL_4$ species, it is possible that the lack of C−H activating ability of $TpRe(CO)_2$ may be substantially steric in origin (see above). The cone angle of $CpRe(CO)_3$ is 140°, as compared to 211° for $TpRe(CO)_3$. Putting these values into the perspective of the original Tolman $Ni(CO)_3(PR_3)$ system: $PPh_3$ has a cone angle of 145°, while $P(mesityl)_3$ has a cone angle of 212°. Thus, the computational study of cone angles supports the suggestion that steric disparity between Tp and Cp derivatives is a major cause of the differences in C−H activation ability.

One hundred and forty-seven novel hetero- and homoscorpionate Tp complexes with highly electron-with-

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drawing and electron-donating groups were chosen to expand the range of SEP and to examine the effects of tris-substitution in comparison to those of bis- and monosubstitution. Twenty-one versions of each complex were built; these were the tris-, bis-, and monosubstituted forms of the 3,4,5-, 3,4-, 3,5-, 4,5-, 3-, 4-, and 5-substituted Tp complexes. The electron-withdrawing groups chosen were F, Br, $NO_2$, and CN. The highest SEP values were produced with substituents in the 3,4,5-, 3,4-, and 3,5-positions. The lowest SEP values were produced when the substituents were in the 5- and 3-positions. The electron-donating groups chosen were Me, $NH_2$, and TMS (TMS = trimethylsilyl). These produced the highest SEP values with substituents in the 4- and 5-positions and the lowest values with substituents in the 3,4,5-, 3,5-, and 3,4-positions.

The calculations indicate that the electron-donating and -withdrawing groups favor different substituent placements upon the Tp framework. The highest overall SEP for the novel Tp complexes was 2155 $cm^{-1}$ for tris-3,4-$NO_2$, and the lowest SEP was 2113 $cm^{-1}$ for tris-3,4,5-TMS. This increases Tp's $\nu_{CO}$ range to 42 $cm^{-1}$. The cone angles ranged from 211° for the parent complex and many of the 4- and/or 5-substituted complexes to 292° for tris-3,4,5-TMS, still a range of 81°. The placement of substituents on all three pyrazolyl rings (the tris form) appears to amplify the SEP ranges vis-à-vis the bis and mono forms. In both the electron-withdrawing and electron-donating complexes, the progression from the mono to the bis to the tris forms involves the expansion of the SEP range at both the high and low ends. For this reason it is suggested that to obtain even larger ranges of electronic diversity in the future only the tris-substituted forms need to be examined. However, the progression from mono to bis complexes for a particular ligand resulted in a larger amplification than did the progression from bis to tris complexes of that ligand.

It was decided that a comparison between monosubstituted $TpRe(CO)_3$ derivatives and monosubstituted $CpRe(CO)_3$ derivatives would give the best measure of each ligand's sensitivity to chemical modification. It was also of interest to study if substitution at the 3-, 4-, or 5-position of the Tp made an appreciable difference upon the steric and electronic properties. It was found, however, that the positioning of the substituent at the 3-, 4-, or 5-position had very little effect on the SEP values. There was, additionally, no significant difference between the SEP of similar monosubstituted TpRe and CpRe complexes (all much less than 1%). This similarity between the mono-Cp and the mono-Tp complexes suggests that the sensitivities of these ligands to steric and electronic manipulation by substituent modification are approximately the same. Upon calculation, the mono-3-substituted Tp derivatives produced SEPs ranging from 2125 $cm^{-1}$ for mono-3-TMS to 2134 $cm^{-1}$ for mono-3-$CF_3$—a 9 $cm^{-1}$ range (the 4- and 5-substituted positions produced smaller ranges), while mono-Cp derivatives had SEPs ranging from 2124 $cm^{-1}$ for mono-COMe to 2136 $cm^{-1}$ for mono-$CF_3$—a 12 $cm^{-1}$ range. The Tp cone angles ranged from 214° for mono-3-F to 239° for mono-3-trityl—a range of 25°. The Cp cone angles ranged from 140° for parent Cp and $CH_4F$ to 159° for $C_5H_4R$ (R = o-tol, mesityl, trityl)—a range of 19°. It was also noted that only the 3-substituted Tp derivatives should be considered when comparing Tp complexes to Cp complexes, because only the 3-substituted position produces cone angles and SEPs substantially different from those of the parent compound.

## Summary and Conclusions

A computational investigation of the bonding, structure, and reactivity of scorpionate and model scorpionate ligands has been reported, as well as the evaluation of the stereoelectronic profile of Tp and Cp ligands with respect to substituent modification. Several conclusions have resulted from this research, the most important of which are summarized below.

(1) The model Tab ligand ($[HB(N{=}NH)_3]^-$) was created as an alternative to the full Tp to reduce the number of basis functions and computational time required for the calculations. The Tab ligand was found to reproduce the potential energy surface of the full Tp ligand in Re-mediated C−H activation of methane. Hence, substantial computational savings can be gained by utilizing the Tab ligand. (2) Neither Tp nor Tab is likely to form a seven-coordinate product. It is apparent that the kinetic barrier to reductive elimination from $TpRe(CO)_2(R)H$ (the microscopic reverse of C−H oxidative addition) is very small and that any $TpReL_2(H)R$ species would not be stable. On the other hand, $CpRe(CO)_2(H)R$ forms a more stable product; there is a 6 kcal $mol^{-1}$ barrier to methane reductive elimination from this species. Additionally, the oxidative addition of methane to $CpRe(CO)_2$ is exothermic, while the same process for $TpRe(CO)_2$ is endothermic. While electronic effects do indeed play some role, in the final analysis perhaps the most satisfying rationalization of Cp/Tp reactivity differences for $TpReL_2$ and $CpReL_2$ fragments lies in the fact that Tp has greater steric hindrance than Cp.

(3) The differences between Tp and Cp drew attention to how each system would respond, sterically and electronically, to substitution. Tp consistently had a broader SEP range (which measures electronic properties) and larger cone angle range (a measure of steric bulk) than Cp. On a per substituent basis Cp was more electronically flexible than Tp. However, overall the Tp platform was more stereoelectronically flexible than Cp. The major advantage of Tp versus Cp ligands with respect to chemical modification may very well lie in the ease of synthesis of derivatives with higher levels of substitution on the pyrazolyl arms.

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**Supporting Information Available:** A table giving the cone angles and semiempirical electronic parameters for tris(1-pyrazolyl)borate and cyclopentadienyl complexes of $Re(CO)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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