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Validation of the M−C/H−C Bond Enthalpy Relationship through Application of Density Functional Theory

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Abstract: Density functional theory has been used to calculate H−C and M−C bond dissociation enthalpies in order to evaluate the feasibility of correlating relative M−C bond enthalpies $\Delta H(\mathrm{M-C})_{\mathrm{rel}}$ with H−C bond enthalpies $\Delta H(\mathrm{H-C})$ via computational methods. This approach has been tested against two experimental correlations: a study of (a) $\mathrm{Rh(H)(R)(Tp')(CNCH_2CMe_3)}$ [R = hydrocarbyl, Tp′ = HB(3,5-dimethylpyrazolyl)$_3$] (Wick, D. D.; Jones, W. D. *Organometallics* **1999**, *18*, 495) and (b) $\mathrm{Ti(R)(silox)_2(NHSi}t\mathrm{\text{-}Bu_3)}$ (silox = OSi*t*-Bu$_3$) (Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696). We show that the observation that M−C bond enthalpies increase more rapidly with different substituents than H−C bond enthalpies is reproduced by theory. Quantitative slopes of the correlation lines are reproduced within 4% of the experimental values with a B3PW91 functional and with very similar correlation coefficients. Absolute bond enthalpies are reproduced within 6% for H−C bonds, and relative bond enthalpies for M−C bonds are reproduced within 30 kJ mol^{-1} for Rh−C bonds and within 19 kJ mol^{-1} for Ti−C bonds. Values are also calculated with the BP86 functional.

Introduction

The activation of C−H bonds by metal complexes has long been one of the most important topics in organometallic chemistry.[1−6] Selectivity in the activation of different C−H bonds by a metal fragment is a key factor in determining whether C−H activation can be applied successfully. Considerable effort has been devoted to finding the factors that control the selectivity, including both kinetic and thermodynamic effects.[7,8]

In this paper, we are concerned with the thermodynamics of carbon−metal bond formation and the relationships between bond enthalpies for carbon−metal bonds and those for carbon−hydrogen bonds. Determination of the absolute values of ligand−metal bond enthalpies in polyatomic transition metal complexes is exceptionally difficult and can be achieved only when demanding criteria are met.[9−11] On the other hand, it is sometimes possible to employ kinetic and equilibrium methods to determine free energies for a series of related reactions, for instance involving formation of M−C bonds for a series of hydrocarbyl groups. If it is assumed that entropic factors are constant, bond enthalpies for M−X bonds may be estimated *relative* to a standard (e.g., metal−phenyl). Bryndza et al. were probably the first to notice that such a series of relative M−X bond enthalpies correlates with H−X bond enthalpies.[12] Several such studies of bond energy correlations followed.[13,14]

Two studies of bond energy correlations concentrated on hydrocarbyl systems and presented approximately linear correlations between the M−C and H−C bond dissociation enthalpies. These results made good use of the extensive and accurate data for carbon−hydrogen bond enthalpies. Thus Wick and Jones published correlations between Rh−C bond enthalpies and H−C bond enthalpies of alkanes, alkenes, and benzene for the case of $\mathrm{Rh(H)(R)(Tp')(CNCH_2CMe_3)}$ [R = hydrocarbyl, Tp′ = HB(3,5-dimethylpyrazolyl)$_3$],[15] while Bennett and Wolczanski reported similar studies for Ti−C bonds of $\mathrm{Ti(R)(silox)_2(NHSi}t\mathrm{\text{-}Bu_3)}$ (silox = OSi*t*-Bu$_3$).[16] Both studies reached the remarkable conclusion that metal−carbon bond energies are more sensitive to the hydrocarbyl substituent than the corresponding hydrogen−carbon bond energies. Consequently, the bond energy correlations have a slope that exceeds unity, viz. ca. 1.2 in the rhodium series and ca. 1.1 in the titanium series. The "extra" bond enthalpy of the metal−carbon bonds has a profound effect on the reactivity. Wick and Jones summed it up as follows: "The

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ground state energy differences between alkyl and aryl hydride complexes of rhodium dominate the reactivity. The difference in M−C bond strengths is larger than the corresponding difference in C−H bond strengths giving rise to a strong thermodynamic preference for cleaving strong C−H bonds."

In a recent communication, we showed via a combination of DFT calculations and experiments that the activation of C−H bonds of fluoroarenes by the {CpRe(CO)$_2$} fragment could be highly regioselective.[17] Calculations of the Re−C bond energies and the H−C bond energies for a set of fluorophenyl groups, $C_6F_xH_{5-x}$ ($x = 0-5$), generated a calculated bond energy correlation. This correlation revealed the very strong influence of fluorination of the benzene at the position *ortho* to the metal on the carbon−metal bond energy. In keeping with the calculations, experimental tests demonstrated a clear preference for C−H activation at the position that maximized the number of *ortho*-fluorine substituents. The success of the computational approach opens new possibilities: for instance, can a computational approach be used to calculate new bond enthalpy correlations? If so, it may be possible to determine the variation in slope (sensitivity) with different metal fragments. Alternatively, we may be able to calculate the slope for hydrocarbyl fragments for which there are no experimental data, as for the fluorobenzenes. Before such questions can be answered with confidence, validation of the computational approach is needed. We have therefore carried out a DFT computational study of the bond energy relationships that have been established by Jones and by Wolczanski.

Computational Details

All calculations were performed with the Gaussian 98 set of programs.[18] The transition metal atoms were represented by the relativistic effective core potential (RECP) from the Stuttgart group and their associated basis set,[19] augmented by an f polarization function ($\alpha = 0.5$, Ti; $\alpha = 1.35$, Rh).[20] The chlorine and silicon atoms were represented by RECP from the Stuttgart group and the associated basis set,[21] augmented by a d polarization function ($\alpha = 0.640$, Cl; $\alpha = 0.284$, Si).[22] A 6-31G(d,p) basis set[23] was used for all the remaining atoms of the molecules studied (B, C, H, O, N).

Calculations on the systems for which experimental data are available were performed at the B3PW91[24,25] and BP86[26,27] levels to test the influence of the functional. The choice of the functionals was made with the aim of comparing the performances of hybrid and nonhybrid DFT, using functionals typically considered for transition metal complexes. For systems not available experimentally only B3PW91 calculations were performed. Moreover the calculations for the organic molecules were also performed at the B3PW91 level with cc-pVTZ basis sets.[28]

The actual experimental systems Ti(R)(silox)$_2$(NHSi*t*-Bu$_3$) (silox = OSi*t*-Bu$_3$; R = Ph, vinyl, Me, Et, Pr, *c*-Pr, *c*-Pe, *c*-Bu, Cy, benzyl, CH$_2$SiMe$_3$, Pe = pentyl) were considered in the case of the Wolczanski series along with additional systems (R = Me-allyl, *i*-Pr, *t*-Bu). For the Jones series, the experimental systems Rh(H)(R)(Tp′)(CNCH$_2$CMe$_3$) (Tp′ = HB(3,5-dimethylpyrazolyl)$_3$; R = Ph, *t*-Bu-vinyl, Me, Pe, *c*-Pe, Cy, Me-allyl, mesityl) were modeled by Rh(H)(R)(Tp)(CNCH$_3$) (Tp = HB(pyrazolyl)$_3$), and complexes with additional R groups (R = Me-vinyl, vinyl, Et, Pr, CH$_2$SiMe$_3$, *i*-Pr, *t*-Bu, *c*-Pr, *c*-Bu, allyl, benzyl) were calculated. To have a comparison with the experimental structures determined by X-ray crystallography for Rh(Cl)(R)(Tp′)(CNCH$_2$CMe$_3$) (R = *t*-Bu-vinyl,[15b] *c*-Pr,[29] Pe,[15a] Et,[30] *i*-Pr[29]), the complexes Rh(Cl)(R)(Tp)(CNCH$_3$) (R = *t*-Bu-vinyl, Me-vinyl, vinyl, *c*-Pr, Pe, Et, *i*-Pr) were calculated.

The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum had been reached. The enthalpy values were obtained at $T = 298$ K and $P = 1$ atm within the harmonic approximation as implemented in Gaussian 98. The organic and metal-based radicals needed to obtain the homolytic bond dissociation energies were optimized with the unrestricted DFT formalism.

Bond energy correlations were analyzed with Microcal Origin 6 using unweighted regression tools.[31]

Results

Bond Dissociation Energy in Organic Molecules. Considerable computational effort has been invested in calculating the thermodynamic properties of organic molecules with great accuracy. Correlated methods and large basis sets have been found to be necessary.[32−34] Computations of absolute M−C bond energies are also challenging.[35] Since the functionals of the DFT methods have been implemented so as to fit experimental formation energies, it is not surprising that the DFT calculations can give good results on bond dissociation enthalpies.[36−43] However, the accuracy has been shown to be lower than sophisticated post-HF methods.[44−48] Nevertheless, our purpose is not to obtain the most accurate values for the H−C bond dissociation enthalpies but to obtain a dataset that can be used in conjunction with calculated M−C bond enthalpies where calculations with sophisticated post-HF methods are not possible. Moreover, despite being built upon organic thermochemistry, DFT methods have been shown to yield reliable

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Table 1. Experimental and Calculated Bond Enthalpies of Hydrocarbons R−H (kJ mol^{-1})

R[a]	experimental with standard error	calculated B3PW91	calculated BP86
Ph	473.1 ± 3	455.4	462.7
$H_2C{=}CH$	465.3 ± 3.4	448.6	457.5
Me	438.9 ± 0.4	430.8	441.9
Et	423.0 ± 1.6	410.9	421.4
Pr	423.3 ± 2.1	412	422.5
i-Pr	409.1 ± 2	394.4	403.2
t-Bu	404.3 ± 1.3	381.4	388.9
c-Pr	444.8 ± 1.3	437.5	444.9
c-Bu	403.8 ± 4	398.8	406.8
c-Pe	403.5 ± 2.5	386.6	393
Cy	399.6 ± 4	396.9	405.5
$Ph{-}CH_2$	375.7 ± 1.7	362.0	368.8
$H_2C{=}CH{-}CH_2$	361.9 ± 8.8	349.3	358.5
$H_2C{=}C(Me){-}CH_2$	358.2 ± 4.0	356.6	365.8
CH_2SiMe_3	415.1 ± 4.0	411.7	421.9
Me-vinyl		453.9	462.9
*t*Bu-vinyl		450.0	458.5
Mesityl		361.3	367.9
Pe		411.7	422.1

[a] *c* = cyclo, Pe = pentyl, mesityl = CH_2-(3,5-$C_6H_3Me_2$); other abbreviations are standard.

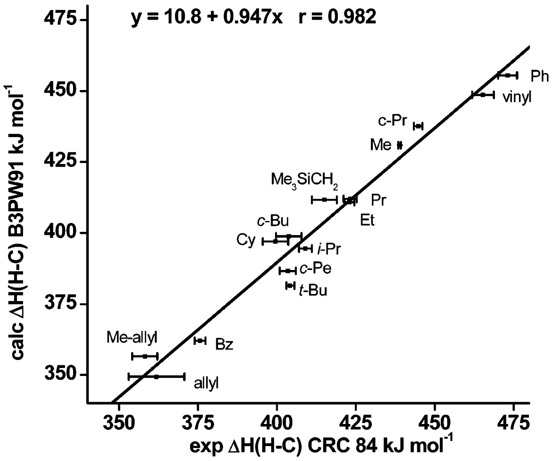

Figure 1. Correlation between calculated and experiment C−H bond enthalpies using B3PW91 functional and CRC Handbook 84th edition, respectively.

results on thermodynamics and kinetics calculations in inorganic and organometallic chemistry.[49−51]

We have considered all the hydrocarbons that have been studied by Jones and Wolzcanski. The H−C bond dissociation enthalpies were taken from the CRC Handbook 84th Edition (CRC 84).[52] We completed this series by including other hydrocarbons related to those of the Jones and Wolzcanski series.

We computed the bond enthalpies at B3PW91/6-31G(d,p) and BP86/6-31G(d,p) levels in order to check the influence of the functional. The results are shown in Table 1 and Figure 1 (B3PW91) and Figure S1 (BP86). The experimental values lie between 350 and 475 kJ mol^{-1} and are given with a standard deviation that is as high as 8 kJ mol^{-1} in the case of the allyl group. Experimental values are greater than the calculated values by a minimum of 1.6 and a maximum of 22.9 kJ mol^{-1}. The quality of the B3PW91 calculation is represented by the least squares linear correlation between the calculated bond enthalpy and the experimental values ($y = 10.8 + 0.947x$ with $r = 0.982$) and by an rms deviation from experiment of 12.5 kJ mol^{-1}. We also tried using the experimental bond enthalpies given by Blanksby and Ellison[53] and by Tsang.[54] They lead to numerical linear equations that are not significantly different. We also tested the cc-pVTZ basis set with the B3PW91 functional for a selection of molecules but obtained no improvement in the results. The BP86 calculations (Table 1) lead to a correlation line ($y = 18.4 + 0.950x$ with $r = 0.978$) and an rms deviation from experiment of 7.2 kJ mol^{-1}. The linear equations above account for calculated and experimental H−C bond enthalpies over a span exceeding 100 kJ mol^{-1}. The slopes are close to 1, and the values for the intercept at $x = 0$ are small. Table 1 shows that the bond enthalpies of a variety of hydrocarbons are reproduced with an accuracy better than 5.6% (B3PW91) or 3.8% (BP86). The largest deviations are found for *t*-Bu.

The trend in C−H bond dissociation enthalpies is well-known, and only a few comments are needed.[55−57] The calculations reproduce the experimental finding that C−H bonds to sp^2 carbon are stronger than bonds to sp^3 carbon. The value of ΔH(Ph−H) is the largest bond enthalpy in the series in accord with experiment, but the B3PW91 value is appreciably less than the experimental value. The hybridization of carbon in cyclopropane lies between sp^2 and sp^3 carbon resulting in a value of ΔH(*c*-Pr−H) intermediate between those of unsaturated and saturated molecules. The bond enthalpies decrease from primary to tertiary carbon (Me−H, Et−H, *i*-Pr−H, *t*-Bu−H), but ΔH(*t*-Bu−H) lies below the correlation line and is significantly underestimated compared to the experimental value. The C−H bond enthalpies in four- to six-membered rings (*c*-Bu−H, *c*-Pe−H, and Cy−H, Pe = pentyl) are calculated to be very similar in agreement with experimental data. The C−H bond enthalpies for toluene (Bz-H), propene (allyl), and 2-methyl propene (Me-allyl-H) form the group with the lowest values due to the stability of the associated conjugated radicals.

Rhodium Series of Wick and Jones. Wick and Jones studied a reaction involving the exchange of ligands via reductive elimination of the molecule R−H and oxidative addition of benzene for the metal fragment RhTp′($CNCH_2CMe_3$) (Scheme 1). They deduced the free energy of the reaction in Scheme 1 from kinetic measurements of the free energies of activation for (a) reductive elimination of benzene, (b) reductive elimination of R−H, and (c) the kinetic selectivity for competitive oxidative addition of R−H and R′−H. The equation shown in Scheme 1 was used to derive the relative Rh−R bond enthalpies, requiring experimental values of the absolute H−C bond enthalpies in the gas phase. They assumed that the entropy and solvation contributions of the two organometallic molecules in the equation are comparable and thus cancel out; a similar assumption was made for the two organic molecules in the

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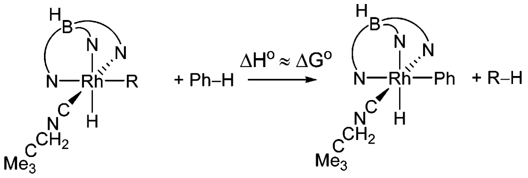
Table 2. Selected DFT Optimized (B3PW91) Geometrical Parameters for $Rh(H)(R)(Tp)(CNCH_3)$ (Distances in Å and Angles in degrees)[a]

R[b]	Rh–R	Rh–N(1)	Rh–N(2)	α	Rh–N(3)	β	Rh–C	γ	Rh–H	δ
Ph	2.032	2.179	2.096	90.6	2.211	96.2	1.877	88.8	1.539	85.7
t-Bu-vinyl	2.014	2.181	2.100	89.7	2.208	93.3	1.874	88.6	1.540	87.3
Me-vinyl	2.010	2.181	2.100	89.4	2.208	93.3	1.874	88.8	1.540	87.0
vinyl	2.007	2.184	2.100	89.4	2.208	93.5	1.876	88.7	1.539	87.0
Me	2.065	2.185	2.103	91.2	2.208	93.6	1.868	87.7	1.543	86.3
Et	2.074	2.198	2.104	90.6	2.206	92.4	1.869	88.7	1.541	88.0
Pr	2.074	2.194	2.104	90.5	2.204	92.3	1.869	88.8	1.543	88.2
Pe	2.074	2.194	2.104	90.5	2.205	92.4	1.869	88.7	1.542	88.0
i-Pr	2.105	2.207	2.113	95.0	2.204	92.4	1.869	87.0	1.542	88.5
t-Bu	2.141	2.213	2.125	94.2	2.228	96.0	1.868	91.3	1.538	86.6
c-Pr	2.047	2.183	2.106	89.7	2.205	92.9	1.870	89.8	1.543	87.5
c-Bu	2.067	2.207	2.114	92.5	2.206	92.6	1.869	89.7	1.547	87.0
c-Pe	2.081	2.202	2.105	90.2	2.227	97.6	1.869	90.0	1.538	84.9
Cy	2.100	2.206	2.107	90.0	2.239	99.3	1.870	89.8	1.536	85.0
CH_2SiMe_3	2.088	2.172	2.107	91.0	2.208	92.4	1.870	89.5	1.542	88.0
allyl	2.091	2.179	2.100	90.0	2.205	91.6	1.873	89.5	1.542	89.0
methallyl	2.096	2.180	2.103	90.5	2.204	91.0	1.871	90.0	1.541	89.6
benzyl	2.095	2.177	2.103	90.9	2.209	90.9	1.872	89.7	1.538	89.5
mesityl	2.095	2.179	2.104	90.8	2.208	90.9	1.871	89.6	1.540	89.5

[a] N(1) is trans to R, N(2) is trans to $CNCH_3$, and N(3) is trans to H. $\alpha = \angle R{-}Rh{-}N(2)$, $\beta = \angle R{-}Rh{-}N(3)$, $\gamma = \angle R{-}Rh{-}C(CNR)$, $\delta = \angle R{-}Rh{-}H$. [b] *c* = cyclo, Pe = pentyl, mesityl = CH_2-(3,5-$C_6H_3Me_2$); other abbreviations are standard.

Scheme 1. Reductive Elimination−Oxidative Addition Reaction of Wick and Jones Showing Their Method of Deriving Relative Bond Enthalpies[a]



$$\Delta H(Rh{-}R)_{rel} = [\Delta H(Rh{-}R) - \Delta H(Rh{-}Ph)] = \Delta H^{o} + [\Delta H(R{-}H) - \Delta H(Ph{-}H)]$$

[a] The dimethyltris(pyrazolyl)borate (Tp′) ligand is abbreviated.

equation. Their values, $\Delta H(Rh{-}C)_{rel}$, were reported relative to the Rh−Ph bond enthalpy.

The system $Rh(H)(R)(Tp')(CNCH_2CMe_3)$ was modeled by replacing the two methyl groups on C3 and C5 of the pyrazolyl rings by H (Tp) and the neopentyl group, CH_2CMe_3, on the isonitrile ligand by a methyl group. The organic ligands in the calculation correspond exactly to those in the experimental systems. We have included a few extra R groups (vinyl, ethyl, propyl, *c*-propyl, *c*-butyl, benzyl) that Wolczanski used so that there is a closer match between the two series and also some other R groups (Me-vinyl, *i*-Pr, *t*-Bu, allyl) in order to test various aspects of the steric strain at rhodium. In our DFT calculations, we calculated the bond dissociation enthalpies from the difference in enthalpy between the two separated radicals and the closed shell molecule.

To validate the computational method, we compare the structure of $Rh(Cl)(R)(Tp')(CNCH_2CMe_3)$ with R = *t*-Bu-vinyl,[15b] *c*-Pr,[29] Pe,[15a] Et,[30] *i*-Pr[29] to the corresponding model Rh(Cl)(R)(Tp)(CNMe) calculated with the B3PW91 functional. There is excellent agreement between the calculated and experimental data for R = *t*-Bu-vinyl, *c*-Pr, and Pe (Table S1 of the Supporting Information), despite the simplification of the Tp and isonitrile ligands. The results for R = ethyl and *i*-propyl are less satisfactory (Table S1) in part due to conformational differences of the R chain with respect to the Tp ligand and some unusual bond lengths seen only for R = Et. The remote substituent on the vinyl does not modify the coordination of the vinyl group or that of the metal fragment (Table S1).

Table 3. Experimental and Calculated Relative (to R = Ph) Rhodium−Carbon Bond Enthalpies for the Jones and Wick System (kJ mol^{-1})[a]

R	$\Delta H(Rh{-}C)_{rel}$ exp	B3PW91	BP86
Ph	0	0	0
t-Bu-vinyl	−30	−0.2	−1.0
Me	−67.3	−50.5	−46.0
Pe	−89	−70.1	−65.9
c-Pe	−117.6	−103.1	−98.9
Cy	−121.3	−96.6	−91.4
methallyl	−147.6	−115.3	−111.4
mesityl	−125.2	−113.3	−112.5
Me-vinyl		1.8	
vinyl		1.4	
Et		−72.5	
Pr		−69.8	
CH_2SiMe_3		−72.4	
i-Pr		−103.6	
t-Bu		−135.7	
c-Pr		−37.2	
c-Bu		−83.2	
allyl		−117.3	
benzyl		−111.1	

[a] Calculations with BP86 are limited to experimental systems.

The geometries of Rh(H)(R)(Tp)(CNMe) are presented in Table 2. As expected the Rh−R distance increases from sp^2 to sp^3 with an intermediate value for *c*-propyl. The Rh−R distance also increases from primary to tertiary carbon. The trans Rh−N bond responds significantly to the Rh−R distances, while the cis Rh−N, Rh−C(CNR), and Rh−H bonds are more constant. There is a variation in the $R{-}Rh{-}L_{cis}$ angles of up to 6°. Although small overall, the changes in the bond lengths and angles around rhodium show that the Rh(H)(Tp)(CNR) fragment adapts itself to the nature of R. However, this responsiveness does not lead to any unusual bonding of the benzyl and the allyl ligands. These two complexes are σ-bonded, and there is neither a trace of an additional interaction with the metal from the π-system nor any indication of partial decoordination of the Tp ligand.

The experimental data and the calculated relative Rh−C bond enthalpies are given in Table 3. The correlation between the experimental relative Rh−C(R) bond enthalpies and the updated

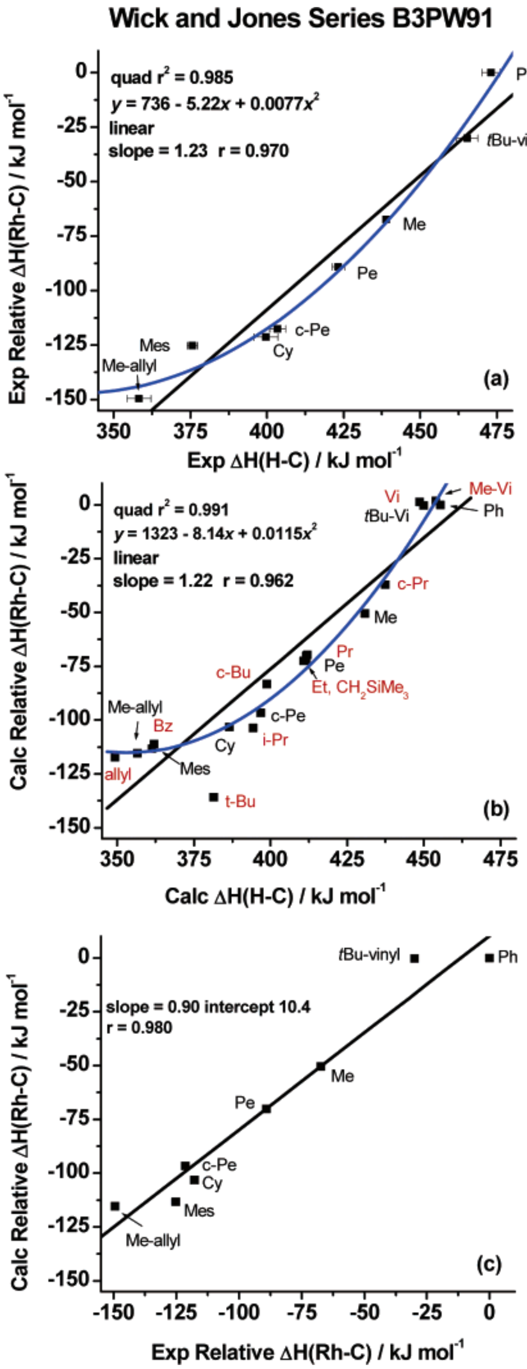


Figure 2. Correlations for the Rh(H)(R)(Tp′)(CNCH$_2$CMe$_3$) (exp) /Rh(H)(R)(Tp)(CNMe) (calc) series with linear (black) and quadratic (blue) fits. (a) Experimental ΔH(Rh−C)$_{rel}$ (relative to phenyl) vs experimental ΔH(H−C). (b) B3PW91 calculated ΔH(Rh−C)$_{rel}$ vs calculated ΔH(H−C); only the substituents used by Jones are included in the calculations of correlations; additional R groups are shown in red. (c) Calculated (B3PW91) ΔH(Rh−C)$_{rel}$ vs experimental ΔH(Rh−C)$_{rel}$.

H−C experimental bond enthalpy values is shown in Figure 2a. Since the experimental H−C bond enthalpies are taken from CRC 84, the original Rh−C/H−C bond enthalpy correlation has been redrawn. We have taken ΔH(Rh−Ph) as reference in accord with Wick and Jones. The least squares line for a linear fit has a slope of 1.23 with $r = 0.970$. The published correlation line, which used the old set of H−C bond enthalpy values, has almost the same slope of 1.22, showing that the updated H−C bond enthalpies have no effect on the results. Following Jones, we have also tried a quadratic fit, leading to an equation $y = 736 - 5.22x + 0.0077x^2$ and to $r^2 = 0.985$. Slopes and correlations are summarized in Table 4.

The corresponding correlations between *calculated* ΔH(Rh−C)$_{rel}$ and *calculated* ΔH(H−C) bond enthalpies are shown in Figure 2b. They have been calculated using only the R groups employed in Jones' original work. The linear fit has a slope of 1.22 with $r = 0.962$. The quadratic fit has $r^2 = 0.991$ and an equation $y = 1323 - 8.14x + 0.0115x^2$. Although these correlations appear to be satisfactory, we note that the bond enthalpy for Rh−*t*-Bu-vinyl is appreciably closer to the Rh−Ph bond enthalpy than in the experimental data. The additional groups all lie close to the line with the exception of *t*-Bu which is below it. When using the BP86 functional, the least squares line has a slope of 1.17 and $r = 0.967$ (Table 4).

A direct comparison of the calculated relative Rh−C bond enthalpies and experimental relative Rh−C bond enthalpies (relative to ΔH(Rh−Ph)), shown in Figure 2c, yields a linear correlation with a slope of 0.90, intercept of 10.4 kJ mol^{-1}, and $r = 0.980$. The calculated bond enthalpies, relative to ΔH(Rh−Ph), are all smaller in magnitude than the experimental values with the largest difference for ΔH(*t*-Bu-vinyl)$_{rel}$. The absolute value calculated for ΔH(Rh−Ph) is 272.7 kJ mol^{-1}. The rms value for the error ΔH(Rh−C)$_{exp}$ − ΔH(Rh−C)$_{calc}$ increases from 21.4 kJ mol^{-1} for B3PW91 to 24.2 kJ mol^{-1} for BP86 (see Figure S2). The correlations also indicate that BP86 results show slightly poorer agreement with experiment than B3PW91.

Titanium Series of Bennett and Wolczanski. Bennett and Wolczanski studied equilibria between Ti(R^1)(silox)$_2$(NHSi*t*-Bu$_3$) and Ti(R^2)(silox)$_2$(NHSi*t*-Bu$_3$) (R^1, R^2 = hydrocarbyl and H, silox = OSi*t*-Bu$_3$) that proceed via reversible 1,2-elimination. The imido complex Ti(silox)$_2$(=NHSi*t*-Bu$_3$) acts as an intermediate as shown in Scheme 2. Bond enthalpies were deduced by means of the equation shown in Scheme 2. DFT calculations have studied the influence of the nature of R−H on the reaction profile.[58] Wolczanski assumed mesityl to have the same bond enthalpy as that of benzyl and neohexyl to have the same value as that of butyl. These authors also assumed that entropy factors were negligible or canceled. We employed DFT calculations to calculate the homolytic bond cleavage of the Ti−C bond with no simplification of the ligands on titanium. We performed calculations for all R groups considered by Wolczanski with the exception of the mesityl and neohexyl groups for which we could not find experimental bond enthalpies for the corresponding hydrocarbons. Whereas Wolczanski used benzyl as a standard, we have taken phenyl to ensure comparability with the Jones series.

The calculated molecular structure is pseudo-tetrahedral (see Table 5 for selected bond lengths and angles). Since the two Ti−O bond lengths are equal within 0.01 Å and the R−Ti−O angles are equal within 3°, average values are given for *r*(Ti−O) and R−Ti−O angles. The geometries could not be compared to the experimental values because the crystals show disorder between OSi and NHSi groups. The methallyl and benzyl ligands coordinate in a pure σ fashion and show no distortion toward an η^3-coordination. For instance, the Ti−C$_\alpha$−C$_\beta$ angle is 109° and 112° for methallyl and benzyl, respectively, and

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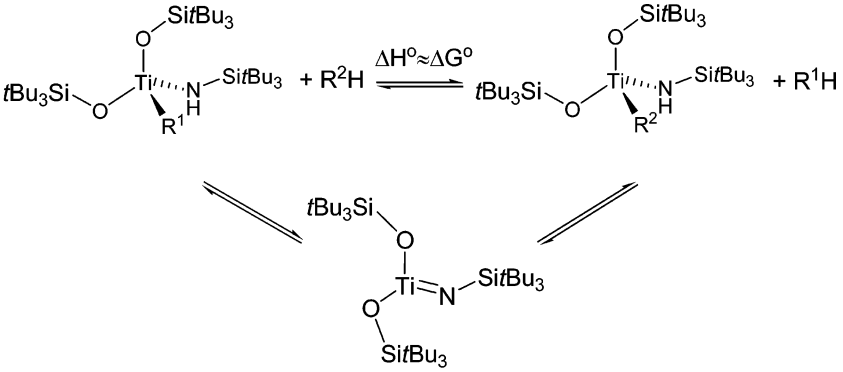
[58] Cundari, T. R.; Klinckman, T. R.; Wolczanski, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 1481.

Table 4. Slope (*s*) and Correlation Coefficients (*r*) for Linear Correlations (*s*/*r* given below)[a]

x	*y*	organic	Jones	Wolczanski
exp/$\Delta H(\mathrm{M-C})_{\mathrm{rel}}$	exp/$\Delta H(\mathrm{H-C})$		1.23/0.970	1.12/0.982[b]
B3PW91/$\Delta H(\mathrm{M-C})_{\mathrm{rel}}$	B3PW91/$\Delta H(\mathrm{H-C})$		1.22/0.962	1.08/0.960[c]
BP86/$\Delta H(\mathrm{M-C})_{\mathrm{rel}}$	BP86/$\Delta H(\mathrm{H-C})$		1.17/0.967	1.04/0.956
exp/$\Delta H(\mathrm{H-C})$	B3PW91/$\Delta H(\mathrm{H-C})$	0.947/0.982		
exp/$\Delta H(\mathrm{H-C})$	BP86/$\Delta H(\mathrm{H-C})$	0.950/0.978		
exp/$\Delta H(\mathrm{M-C})_{\mathrm{rel}}$	B3PW91/$\Delta H(\mathrm{M-C})_{\mathrm{rel}}$		0.90/0.980	0.930/0.989[d]
exp/$\Delta H(\mathrm{M-C})_{\mathrm{rel}}$	BP86/$\Delta H(\mathrm{M-C})_{\mathrm{rel}}$		0.87/0.977	0.903/0.980

[a] Methods and quantities along the *x* and *y* axis for establishing correlations are indicated. [b] 1.31/0.991 are the values when phenyl and benzyl are omitted from the correlations. [c] 1.15/0.955 are the values when phenyl and benzyl are omitted from the correlations. [d] 0.929/0.964 are the values when phenyl and benzyl are omitted from the correlations.

Scheme 2. Wolczanski and Bennett Reaction



$$\Delta H(\mathrm{Ti–R})_{\mathrm{rel}} = [\Delta H(\mathrm{Ti–R}) - \Delta H(\mathrm{Ti–Ph})] = \Delta H^{\mathrm{o}} + [\Delta H(\mathrm{R–H}) - \Delta H(\mathrm{Ph–H})]$$

Table 5. Selected Geometrical Parameters from the DFT Optimized Structures of Ti(R)(silox)$_2$(NHSi*t*-Bu$_3$)[a]

	r(Ti–C)	*r*(Ti–O)$_{\mathrm{av}}$	α	*r*(Ti–N)	*β*	*r*(N–H)
Ph	2.090	1.787	106.0	1.882	106.7	1.020
vinyl	2.074	1.787	106.0	1.883	105.0	1.020
Me	2.084	1.788	105.3	1.885	105.8	1.019
Et	2.088	1.792	105.5	1.889	104.6	1.019
Pr	2.089	1.790	105.5	1.888	104.5	1.020
i-Pr	2.095	1.793	105.0	1.891	104.9	1.020
t-Bu	2.107	1.794	105.1	1.893	105.4	1.021
c-Pr	2.061	1.791	105.6	1.887	105.8	1.019
c-Bu	2.080	1.792	104.4	1.892	107.0	1.020
c-Pe	2.082	1.793	104.8	1.893	106.0	1.021
Cy	2.093	1.793	104.6	1.892	105.9	1.019
methallyl	2.107	1.790	105.6	1.884	104.3	1.019
benzyl	2.113	1.787	106.8	1.884	104.0	1.019
CH$_2$SiMe$_3$	2.082	1.788	107.5	1.888	105.9	1.019

[a] $\alpha = \angle \mathrm{R-Ti-O}$ (averaged), $\beta = \angle \mathrm{R-Ti-N}$ (distances in Å, angles in degrees).

Table 6. Experimental and Calculated Titanium−Carbon Bond Enthalpies for the Ti(R)(silox)$_2$(NHSi*t*-Bu$_3$) (kJ mol^{-1})

	$\Delta H(\mathrm{Ti–C})_{\mathrm{rel}}$		
R	exp	B3PW91	BP86
Ph	0.0	0	0
vinyl	0.6	1.0	2.0
Me	−31.3	−29.8	−27.7
Et	−53.9	−56.9	−56.0
Pr	−55.2	−54.6	−53.3
c-Pr	−20.8	−17.5	−18.7
c-Pe	−80.5	−84.2	−79.4
c-Bu	−70.6	−67.6	−67.6
Cy	−88.2	−74.6	−73.4
Bz	−93.2	−83.2	−83.5
CH$_2$SiMe$_3$	−60.5	−41.0	−40.0
methallyl		−93.7	
i-Pr		−78.6	
t-Bu		−96.4	

there is no shortening of the Ti···C$_\beta$ distance. The most interesting aspect of the geometries is the observation that the calculated range of M—C distance is significantly smaller for the titanium series than that for the rhodium complexes. Furthermore, the distances and angles within the metal fragment hardly vary with R. The R group clearly exerts no influence on the geometry of the Ti fragment as can be understood from the absence of a bond trans to R and the isotropy of a tetrahedral field.

The experimental and calculated bond enthalpies are shown in Table 6. The correlations between the experimental Ti−C and H−C bond enthalpies have been recalculated because of the use of updated experimental H−C bond enthalpies. The results with B3PW91 are shown in Figure 3 with all data points in the correlations, while those in Figure S3 of the Supporting Information exclude the data for the benzyl and phenyl groups from the correlation.

Figure 3a shows a linear correlation between experimental $\Delta H(\mathrm{Ti-C})_{\mathrm{rel}}$ and experimental $\Delta H(\mathrm{H-C})$ with a slope of 1.12 and $r = 0.982$. These values can be compared to Wolczanski's correlation with older H−C bond enthalpy data that had a slope of 1.1 and $r = 0.95$. Wolzcanski tried removal of both the phenyl and the benzyl groups and obtained a slope of 1.36 and $r = 0.995$. The set of points in Figure 2a but with phenyl and benzyl removed and with recent bond enthalpies gives a correlation with a slope of 1.31 ($r = 0.991$) (Figure S3). The modern values of H−C bond enthalpies evidently have little effect on the overall results.

The correlation between the calculated Ti−C bond enthalpies and calculated H−C bond enthalpies gives a correlation with a slope of 1.08 and $r = 0.960$ (Figure 3b), in good agreement

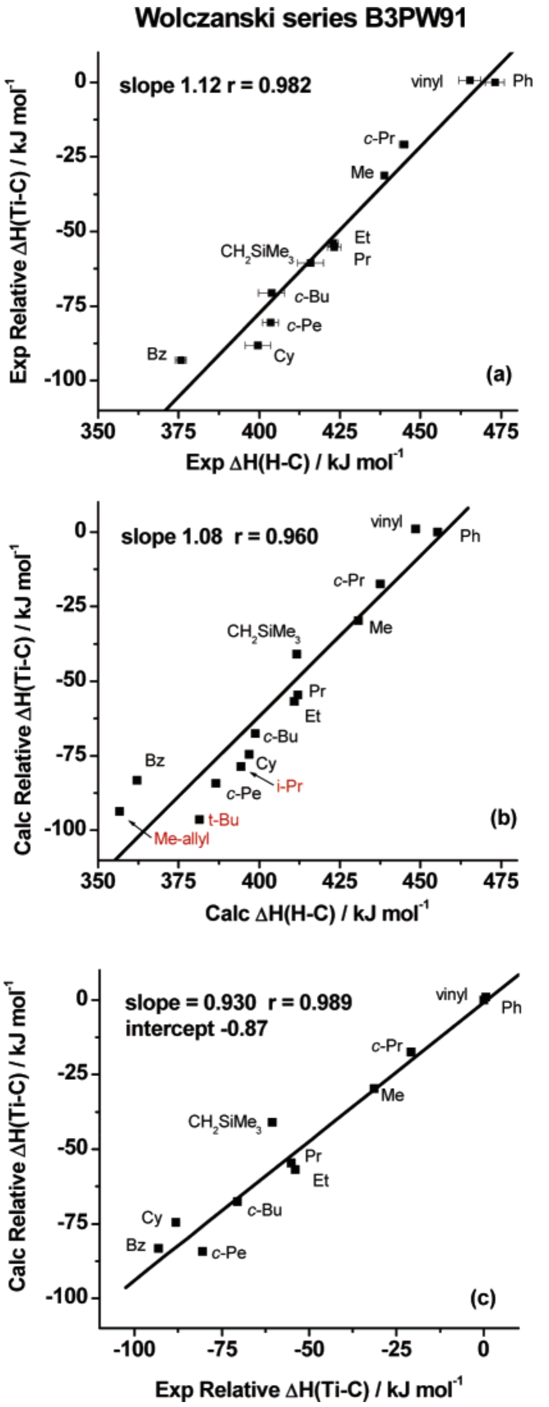


Figure 3. Correlations for Ti(R)(silox)$_2$(NHSi*t*-Bu$_3$). (a) Experimental $\Delta H(\text{Ti}-\text{C})_{\text{rel}}$ (relative to phenyl) vs experimental $\Delta H(\text{H}-\text{C})$. (b) B3PW91 calculated $\Delta H(\text{Ti}-\text{C})_{\text{rel}}$ vs calculated $\Delta H(\text{H}-\text{C})$. The added points shown in red are not included in the correlation. (c) Calculated $\Delta H(\text{Ti}-\text{C})_{\text{rel}}$ vs experimental $\Delta H(\text{Rh}-\text{C})_{\text{rel}}$.

with the experimental values. Omitting phenyl and benzyl in the correlation gives a correlation with a slope of 1.15 and $r = 0.955$, which is significantly different from the values obtained experimentally with the same procedure. However there is no fundamental reason to omit these particular groups.

The correlation between calculated and experimental Ti−C bond enthalpies (Figures 3c) gives a slope of 0.930, intercept $= -0.87$ kJ mol^{-1}, and $r = 0.989$ (without Bz and Ph, slope = 0.929, intercept = 0.26 kJ mol^{-1}, $r = 0.964$). A slope close to unity shows that the calculations provide a good representation of the variations in Ti−C bond dissociation enthalpies, *including those for the phenyl and benzyl groups*. Removal of these groups is not a productive approach in analyzing the computed data. The data in Table 6 show that the calculations of M−C bond enthalpies agree with experiment significantly better than those for the Jones series. Most of the differences are less than 10 kJ mol^{-1}, the only exception being $\Delta H(\text{Ti}-\text{CH}_2\text{SiMe}_3)_{\text{rel}}$ which is overestimated by 19.5 kJ mol^{-1}. The absolute value of $\Delta H(\text{Ti}-\text{Ph})$ was calculated as 260.7 kJ mol^{-1}.

The calculations were also carried out with the BP86 functional on those complexes studied experimentally by Bennett and Wolczanski. Figure S4 shows that the calculated $\Delta H(\text{Ti}-\text{C})_{\text{rel}}$ correlates marginally less well with the calculated $\Delta H(\text{H}-\text{C})$, and furthermore there is a less good match of calculated and experimental $\Delta H(\text{Ti}-\text{C})_{\text{rel}}$. The rms deviation of calculated $\Delta H(\text{Ti}-\text{C})_{\text{rel}}$ from experiment is 8.0 kJ mol^{-1} for B3PW91 and 8.4 kJ mol^{-1} for BP86.

Discussion

Our goal in this study was to discover whether DFT theory could be employed to calculate reliable correlations between $\Delta H(\text{H}-\text{C})$ and relative $\Delta H(\text{M}-\text{C})_{\text{rel}}$ bond enthalpies. If successful, theory could be used to predict such correlations and forecast their impact on thermodynamic preferences and the selectivity of reactions. Such calculated selectivities could inform experiments especially when the energetics of reaction could not be measured.

Correlations. We tested DFT theory against the best available experimental data for correlations, one for a d^0 and one for a d^6 metal, the two series having very different ligand sets. These data sets provide a large range of hydrocarbyl ligands. Our calculated correlations reveal a slope > 1 for the graph of $\Delta H(\text{M}-\text{C})_{\text{rel}}$ vs $\Delta H(\text{H}-\text{C})$ in each case as had been observed by experiment. Furthermore, the agreement between experimental and calculated slopes was remarkable, especially for the rhodium complexes (slopes taken from Table 4: (a) Rh expt 1.23, B3PW91 1.22, BP86 1.17; (b) Ti expt 1.12, B3PW91 1.08, BP86 1.04). The correlation coefficients for theory of 0.956 to 0.967 compare very well to experimental values of 0.970 (Rh) and 0.982(Ti). Our study indicates that the DFT method can be used to evaluate slopes within 4% accuracy for B3PW91 and 8% for BP86. The limiting deviations represent differences in *relative* bond enthalpy of ca. 10 kJ mol^{-1} for B3PW91 and ca. 20 kJ mol^{-1} for BP86 over the full range of hydrocarbyl substituents. While the energetics of individual reactions cannot be calculated with such precision, this work gives confidence that the quantitative trends in the relative energetics can be determined. Our firm conclusion is that the computational method is valid and can be used for prediction.

There has been discussion in the literature whether to merge data for different metals and ligands[12] or whether to treat each metal and ligand set separately.[14] Our findings indicate that merging the data for titanium and rhodium results in a loss of predictive power with a marked reduction in correlation coefficient. At the other extreme, we considered splitting the data into sp^2 and sp^3 carbon-based ligands, or primary, secondary, and tertiary sp^3 ligands. We found that the resulting multiple correlations were also of little use because there were too few members of each family, and new ligands often needed new correlations.

In this paper, we have used theory to extend the range of substituents in both the Rh and Ti series. For rhodium, we find that several additional substituents fit the correlation line including *c*-Pr, *i*-Pr, and even CH_2SiMe_3, but *t*-Bu fits poorly (Figure 2b). For the Ti series, we have added *i*-Pr, *c*-Pe, Me-allyl, and *t*-Bu. The first two fit well; the latter two deviate somewhat more from the calculated correlation line (Figure 3b). Overall, the correlations give confidence that estimates of the relative M−C bond enthalpies for these families of complexes are reliable unless special steric or electronic factors intervene.

We have already reported the application of the method to complexes of the type $ReH(Ar)(Cp)(CO)_2$ for a range of 20 different fluorinated complexes ($Ar = C_6H_{5-x}F_x$, $x = 0-5$).[17,59] We will extend the methodology to new groups of complexes elsewhere.

Bond Enthalpies. As expected, DFT calculations yield quantitative information on the absolute H−C bond enthalpies, which are obtained within ca. 6% for a large variety of R including sp^3 and sp^2 substituents. The calculations with BP86 give marginally poorer correlation coefficients but substantially smaller rms deviations from experiment.

On turning to relative M−C bond enthapies, we find that the relative Rh−C bond enthalpies all lie to one side of the experimental values with the mean difference $[\Delta H_{exp}(Rh-C)_{rel} - \Delta H_{B3PW91}(Rh-C)_{rel}] = -25.1$ and the largest difference −34 kJ mol^{-1}. A likely hypothesis for this discrepancy is that the calculations underestimate the Rh−Ph bond enthalpy. This limitation cannot be attributed to an inadequate geometric representation of the complexes because the calculated structures for Rh(R)(Cl)(Tp)(CNMe) are in good agreement with the experimental geometries of Rh(R)(Cl)(Tp′)(CN*t*Bu). The relative Ti−C bond enthalpies are calculated with much better agreement with experiment (mean difference $[\Delta H_{exp}(Ti-C)_{rel} - \Delta H_{B3PW91}(Ti-C)_{rel}] = -4.2$, largest difference −19 kJ mol^{-1}). The rms deviation is even smaller than that for the organic bond enthalpies. The better quality of the results for the d^0 titanium complexes compared to the d^6 rhodium systems could be attributed in part to a reduced electronic correlation in the former. For the metal systems the B3PW91 calculations give slightly better agreement with experiment than the BP86 results.

Conclusions

Since bond enthalpies play a critical role in the understanding of catalytic and stoichiometric processes in transition metal chemistry, any additional tools for their determination are of great value. By comparison with two established experimental correlations, we have shown in this paper that the concept of correlations between H−C and M−C bond enthalpies is strongly supported by a computational approach with DFT theory and that the quantitative value of the slopes of the correlations can be predicted within 4% (B3PW91) or 8% (BP86). Most importantly, the calculations provide an independent demonstration that M−C bond enthalpies are more sensitive to substituent than C−H bond enthalpies. While absolute bond enthalpies are reproduced within 5% for H−C bonds, the very limited data for *absolute* M−C bond enthalpies do not allow an accurate comparison between experiment and theory. In contrast, this methodology allows the prediction of trends and changes in *relative* bond enthalpy with different substituents. The precision of determination of relative bond enthalpies proved outstanding for a d^0 titanium system, but more caution is needed with a d^6 rhodium system. The method was tested with two functionals, B3PW91 and BP86, and gave satisfactory results with both, though there was a slight preference for the former for the M−C bond enthalpies. While experimental determinations will continue to be preferred to computational determinations of bond energies, it should be recognized that experimental determinations are constrained by a set of serious assumptions that may lead to systematic errors.[9,60] Considering the rarity of determinations of relative metal−carbon bond enthalpies, we believe that theory has great potential in providing data in the many cases for which equilibria suitable for thermochemical evaluation are unavailable.

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Supporting Information Available: Full list of authors for ref 18; correlations with BP86 for calculated and experimental organic bond enthalpies (Figure S1); correlations with BP86 for the rhodium series (Figure S2); correlations with B3PW91 with Bz and Ph excluded for the titanium series (Figure S3); correlations for the titanium series with BP86 (Figure S4); selected geometrical parameters for calculated Rh(Tp)(CNCH3)-(R)(Cl) (R = *t*-Bu-vinyl, Me-vinyl, vinyl, Et, *i*-Pr, *c*-Pr, Pe) at the B3PW91 level (Table S1); Cartesian coordinates and enthalpy for all the structures calculated. This material is available free of charge via the Internet at http://pubs.acs.org.

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