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Exceptional Sensitivity of Metal−Aryl Bond Energies to *ortho*-Fluorine Substituents: Influence of the Metal, the Coordination Sphere, and the Spectator Ligands on M−C/H−C Bond Energy Correlations

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Abstract: DFT calculations are reported of the energetics of C−H oxidative addition of benzene and fluorinated benzenes, Ar^FH ($Ar^F = C_6F_nH_{5-n}$, $n = 0-5$) at $ZrCp_2$ ($Cp = \eta^5\text{-}C_5H_5$), $TaCp_2H$, $TaCp_2Cl$, WCp_2, $ReCp(CO)_2$, $ReCp(CO)(PH_3)$, $ReCp(PH_3)_2$, $RhCp(PH_3)$, RhCp(CO), $IrCp(PH_3)$, IrCp(CO), $Ni(H_2PCH_2CH_2PH_2)$, $Pt(H_2PCH_2CH_2PH_2)$. The change in M−C bond energy of the products fits a linear function of the number of fluorine substituents, with different coefficients corresponding to *ortho*-, *meta*-, and *para*-fluorine. The values of the *ortho*-coefficient range from 20 to 32 kJ mol^{-1}, greatly exceeding the values for the *meta*- and *para*-coefficients (2.0−4.5 kJ mol^{-1}). Similarly, the H−C bond energies of Ar^FH yield *ortho*- and *para*-coefficients of 10.4 and 3.4 kJ mol^{-1}, respectively, and a negligible *meta*-coefficient. These results indicate a large increase in the M−C bond energy with *ortho*-fluorine substitution on the aryl ring. Plots of D(M−C) vs D(H−C) yield slopes $R^{M-C/H-C}$ that vary from 1.93 to 3.05 with metal fragment, all in excess of values of 1.1−1.3 reported with other hydrocarbyl groups. Replacement of PH_3 by CO decreases $R^{M-C/H-C}$ significantly. For a given ligand set and metals in the same group of the periodic table, the value of $R^{M-C/H-C}$ does not increase with the strength of the M−C bond. Calculations of the charge on the aryl ring show that variations in ionicity of the M−C bonds correlate with variations in M−C bond energy. This strengthening of metal−aryl bonds accounts for numerous experimental results that indicate a preference for *ortho*-fluorine substituents.

Introduction

Bond energies for small molecules provide an accurate and established resource, whereas bond energies of transition metal complexes, D(M−X) are so challenging to determine, that only a very limited number are known.[1] In this paper we use a computational approach to metal−Ar^F ($Ar^F = C_6F_nH_{5-n}$, $n = 0-5$) bond dissociation energies and bond energy correlations[2] in which we address the energetics of C−H oxidative addition of fluorinated benzenes at a wide variety of transition metal fragments. C−H bond activation of benzene derivatives has been studied for a long time,[3] but in the past few years striking advances have been made in *catalytic* activation, especially by borylation[4] and by direct arylation.[5] The range of substituted benzenes has also widened markedly and now includes fluorinated benzenes.[5b−d]

The idea that experimental bond energies of small molecules may correlate with their counterparts in transition metal complexes was first explored by Bryndza, Bercaw, and their collaborators.[2] This concept of a bond energy correlation has the potential to enrich the available data for transition-metal energies, since it should then be possible to predict new D(M−X) values on the basis of the knowledge of small molecules and a few carefully measured examples of D(M−X) that are taken as standards. Bryndza's bond energy correlations

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covered a wide range of X including hydrogen, carbon, oxygen, and nitrogen ligands. Schock and Marks[1b] demonstrated for zirconium that it was more instructive to concentrate on a narrower range of X ligands and later authors confined their correlations to a single donor atom; examples include Ni−N/H−N,[6] Ti−C/H−C,[7] and Rh−C/H−C.[3b,c,8] These studies did not depend on calorimetry to generate absolute bond energies, but instead determined relative bond energies by measurement of equilibrium constants and selected rate constants. The generalization of the findings is, however, limited by the range of compounds that give good equilibria and clean kinetics, so that the number of correlations is very restricted. Because of the small number of systems, it is not straightforward to extend the principles to determine the effect of a change of metal or ancillary ligand.

The developments in computational methods make theoretical estimates of a wide range of bond energies readily accessible. In an earlier paper, we tested DFT methods for bond energy correlations and found that we were able to reproduce most of the features of the experimental bond energy correlations[7,8] for Ti−C/H−C and Rh−C/H−C very accurately.[9] This study served to validate the correlation between the calculated H−C bond energies and the calculated M−C bond energies. Most importantly, we showed that the theoretical methods reproduced the experimental observation that M−C bond energies increase more rapidly with changes in substituent than H−C bond energies, that is the slope of the correlation exceeds unity. Thus, the slope of the correlation, denoted $R^{\mathrm{M-C/H-C}}$ for substituents ranging from benzyl to phenyl is about 1.2 for the rhodium system and about 1.1 for the titanium complexes. The origin of the correlations has been explored by Ziegler.[10] Landis has investigated simple metal hydrides MH_n together with $\mathrm{MH}_{n-1}\mathrm{R}$ (R = hydrocarbyl) and has noted correlations between $D(\mathrm{M-C})$ and $D(\mathrm{H-C})$ as well as between $D(\mathrm{M-C})$ and $D(\mathrm{M-H})$.[11] His values of $R^{\mathrm{M-C/H-C}}$ range from 1.8 for scandium through 1.3 for cobalt, climbing again to 1.5 for copper. Second and third row metals also give substantial variations in $R^{\mathrm{M-C/H-C}}$, but the details are significantly different, especially for the late transition metals. Macgregor et al. have also noted a theoretical correlation for Ru−X/H−X bond energies (X = $\mathrm{CH_3}$, $\mathrm{NH_2}$, OH, F, and $\mathrm{SiH_3}$, $\mathrm{PH_2}$, SH, Cl) in which changes in $D(\mathrm{Ru-X})$ exceed changes in $D(\mathrm{H-X})$[12] and similar effects are calculated for $D(\mathrm{Ru-X})/D(\mathrm{C_{Ar}-X})$.[13]

The observation of slopes $R^{\mathrm{M-C/H-C}} > 1.0$ has an important consequence in the chemical reactivity, as has been explored by Jones et al.[3b,c,8,14] Although stronger C−H bonds may, at first glance, appear harder to activate than weaker C−H bonds, there is almost always a preference to activate the strongest C−H bonds. When converting a rhodium alkyl hydride to a rhodium aryl hydride there is a beneficial stabilization energy that arises from the fact that the difference in bond energy $D(\mathrm{M-C})_{\mathrm{aryl}} - D(\mathrm{M-C})_{\mathrm{alkyl}}$ exceeds the difference $D(\mathrm{H-C})_{\mathrm{aryl}} - D(\mathrm{H-C})_{\mathrm{alkyl}}$; the result is a strong *thermodynamic* preference for activating arene C−H bonds. This trend is the opposite of that for radical formation where the preference is to activate the weaker C−H bond.

Because the C−H bond dissociation energy of $\mathrm{C_6F_5H}$ at 477 kJ $\mathrm{mol^{-1}}$ is 17 kJ $\mathrm{mol^{-1}}$ higher than that of benzene,[15] the M−C bonds of $\mathrm{M-C_6F_5}$ complexes should be stronger than those of analogous $\mathrm{M-C_6H_5}$ complexes by more than 17 kJ $\mathrm{mol^{-1}}$. Indeed, some of the least reactive of metal−carbon σ bonds are found among fluorinated ligands, such as fluoraryl or fluorovinyl, and their inertness has been associated with the exceptionally strong M−C bonds. Thus, migratory insertion of $\mathrm{C_6F_5}$ onto a metal carbonyl group or insertion of an alkene into a $\mathrm{M-C_6F_5}$ bond is observed very rarely, reductive elimination is difficult, and catalytic reactions involving $\mathrm{M-C_6F_5}$ bonds are rarer still;[16] these limitations have inhibited development of organofluorine chemistry through transition metal catalysis.

In our first communication on H−C/M−C bond energy correlations, we reported a computational investigation of the C−H oxidative addition reaction of $\mathrm{Re(\eta^5\text{-}C_5H_5)(CO)_2}$ with $\mathrm{Ar^FH}$ to form $\mathrm{Re(\eta^5\text{-}C_5H_5)(Ar^F)(H)(CO)_2}$, where $\mathrm{Ar^F} = \mathrm{C_6F_nH_{5-n}}$ ($n = 0{-}5$).[17] The resulting M−C/H−C bond energy correlation had an exceptionally steep gradient $R^{\mathrm{M-C/H-C}} = 2.25$ with points falling into three groups according to the number of *ortho*-F substituents. We inferred that the M−C bond energy increases almost as much from $\mathrm{M-C_6H_5}$ to $\mathrm{M-(2,6\text{-}C_6F_2H_3)}$ as from $\mathrm{M-C_6H_5}$ to $\mathrm{M-C_6F_5}$, that is, essentially the full increase in M−C bond energy can be achieved with two *ortho*-fluorine substituents. A natural population analysis indicated that a substantial part of the effect of fluorine substitution was associated with the change in the charge distribution and increased ionic character in the M−C bond, which implies a stronger M−C bond according to the principles of Pauling electronegativity. Similar deductions have been made by several authors for other bond energy correlations.[6,11] Our bond energy correlation led to the prediction that $\mathrm{Re(\eta^5\text{-}C_5H_5)(2,6\text{-}C_6F_2H_3)(H)(CO)_2}$ should be more stable than isomeric arrangements of the fluorine atoms. An experimental test by photochemical reaction of $\mathrm{Re(\eta^5\text{-}C_5Me_5)(CO)_2(N_2)}$ with 1,3-difluorobenzene generated a single product, $\mathrm{Re(\eta^5\text{-}C_5Me_5)(2,6\text{-}C_6F_2H_3)(H)(CO)_2}$, in line with the prediction.[17]

These striking observations leave unanswered the question of whether the effect of fluorine substitution on the aromatic ring can be generalized to other combinations of metals and ancillary ligands, and of whether the value of $R^{\mathrm{M-C/H-C}}$ varies systematically with d-electron configuration. Examples of systematic fluorine substitution of metal−aryl complexes, $\mathrm{M(C_6F_nH_{5-n})}$, are very limited but some striking examples may be found in the thermal reactions of $\mathrm{Rh(\eta^5\text{-}C_5Me_5)(C_6H_5)}$-

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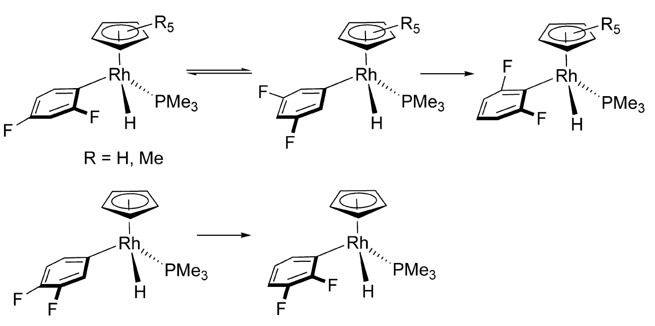
Scheme 1. Thermal Interconversion of Rhodium Fluoroaryl Hydride Complexes showing Preference for F Substituents to be Ortho to Rhodium



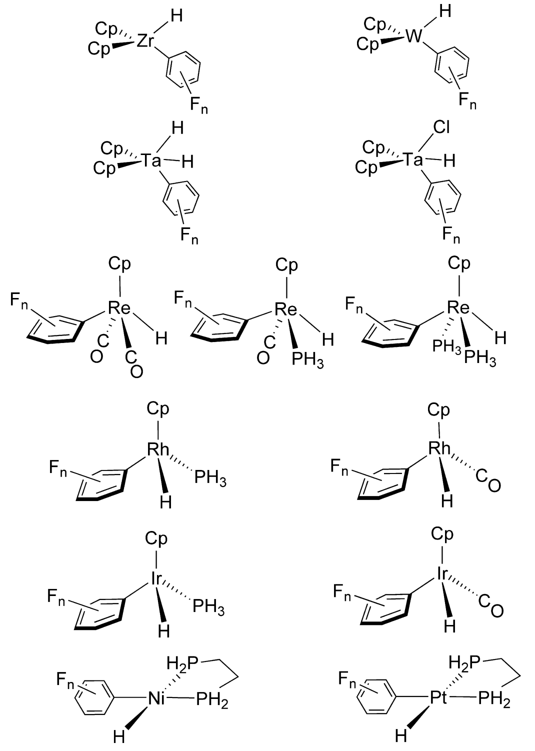
$(H)(PMe_3)$ with $C_6F_nH_{6-n}$.[18] In each case, the thermal reaction of the fluoroaromatic (at 67 °C) yielded the rhodium fluoroaryl hydride. The reactions of fluorobenzene, 1,2-difluorobenzene and 1,4-difluorobenzene each yielded two rotamers of the product $Rh(\eta^5\text{-}C_5Me_5)(Ar^F)(H)(PMe_3)$ with the fluorine substituent ortho to the Rh−C bond. It was also demonstrated that a higher temperature was required to react $Rh(\eta^5\text{-}C_5Me_5)(2,3\text{-}C_6F_2H_3)(H)(PMe_3)$ with benzene than to react the phenyl hydride with 1,2-difluorobenzene. With 1,3-difluorobenzene, all three possible isomers were observed (Scheme 1), but further investigation showed that the 2,4 and 3,5-difluoro isomers of $Rh(\eta^5\text{-}C_5Me_5)(C_6F_2H_3)(H)(PMe_3)$ products were kinetic products that converted to the 2,6-isomer as the thermodynamic product. The photochemical reactions of $Rh(\eta^5\text{-}C_5H_5)(PMe_3)(C_2H_4)$ with the same substrates could be performed at low temperatures allowing the isomerization of $Rh(\eta^5\text{-}C_5H_5)(C_6F_2H_3)(H)(PMe_3)$ to be followed proving conclusively the thermodynamic preference for *ortho*-fluorine substituents.[18] All these observations are in line with stronger M−C bonds on fluorine substituents at the positions ortho to the M−C bond.

In this study, we investigate bond energy correlations for the C−H activation of fluorobenzenes at a wide range of different metal−ligand fragments. Initially, we show that theory can reproduce the established thermodynamic selectivity at $Rh(\eta^5\text{-}C_5Me_5)(PMe_3)$. We proceed to show that the dominant effect of *ortho*-fluorine substitution is common to all the fragments investigated. Moreover, all the bond energy correlations exhibit much larger values of $R^{M-C/H-C}$ than have been documented for other types of substitution at hydrocarbons.

Results

Methodology and Strategy. Accurate calculations of bond dissociation energies can only be performed with high level methods but such calculations are not feasible for molecules which contain transition metals.[19] Large organometallic complexes are best calculated with DFT methods, but their performance in calculating accurate metal−ligand bond dissociation energies is not established. It should be mentioned at this point that absolute experimental values are also not easy to obtain with accuracy since a number of approximations are still used for their determination.[1] Our earlier work has, however, shown that the *trends* are reproduced with considerable accuracy with a functional like B3PW91.[9] The calculated relative C−H bond dissociation enthalpies are in close agreement with experimental values. Likewise, the good agreement between experimental and calculated correlations of relative M−C bond enthalpies $\Delta H(M-C)_{rel}$ with H−C bond enthalpies for Rh−C/H−C and Ti−C/H−C clearly shows that DFT(B3PW91) calculations are reliable reporters for trends and can be used for discussing trends for other transition metal complexes.[7−9] We will apply the same methodology for various transition metal complexes. The selected systems are models for complexes that are known to be able to activate C−H bonds or able to form aryl complexes (Scheme 2). They also represent a wide variety of coordination spheres including $M(\eta^5\text{-}C_5H_5)_2(H)(Ar^F)$, $M(\eta^5\text{-}C_5H_5)_2(H)_2(Ar^F)$, $M(\eta^5\text{-}C_5H_5)(H)(Ar^F)L_2$, $M(\eta^5\text{-}C_5H_5)(H)(Ar^F)L$, and square planar $M(H)(Ar^F)L_2$; they include metals having formal electron counts varying from d^0 to d^8. For all these systems the fluorinated arenes have been investigated to establish the correlation. For most of the metal fragments, all 20 benzenes $C_6F_nH_{6-n}$ were considered that arise when *n* varies from 0 to 5 with all possible regioisomers (see Table 1). Calculations on Ni(dhpe) and Pt(dhpe) (dhpe = $H_2PCH_2CH_2PH_2$) with C_6H_6, C_6F_6 and C_6F_5H have been reported previously.[20]

Scheme 2. Metal−Ar^F Systems under Study ($n = 0-5$, Cp = η^5-C_5H_5)



The bond dissociation energy is defined as the difference in energy between the optimized whole system $ML_nH(Ar^F)$ and the sum of the optimized separated fragments $\bullet ML_nH$ and $\bullet Ar^F$ (see Computational Details). Because we showed in previous work that there is no significant difference in trends when considering bond dissociation energy and bond dissociation enthalpy, we considered bond dissociation energies.[9]

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Table 1. Calculated Bond Dissociation Energies and Relative Bond Dissociation Energies (kJ/mol^{-1}) for Fluorinated Benzenes Ar^F-H and $Rh(\eta^5\text{-}C_5H_5)(H)(Ar^F)(PH_3)$

arene	aryl	$D(H-C)$	$\Delta D(H-C)_{rel}$	$D(Rh-C)$	$\Delta D(Rh-C)_{rel}$
C_6H_6	C_6H_5	489.8	0	256.6	0
C_6FH_5	2-C_6FH_4	500.5	10.7	280.6	24.0
	3-C_6FH_4	490.6	0.8	260.0	3.4
	4-C_6FH_4	494.3	4.5	260.0	3.4
1,2-$C_6F_2H_4$	2,3-$C_6F_2H_3$	500.3	10.5	283.9	27.3
	3,4-$C_6F_2H_3$	494.5	4.7	262.7	6.1
1,3-$C_6F_2H_4$	2,4-$C_6F_2H_3$	504.6	14.8	283.9	27.3
	2,6-$C_6F_2H_3$	512.0	22.2	308.0	51.4
	3,5-$C_6F_2H_3$	492.0	2.2	263.3	6.7
1,4-$C_6F_2H_4$	2,5-$C_6F_2H_3$	501.2	11.4	284.7	28.1
1,2,3-$C_6F_3H_3$	2,3,4-$C_6F_3H_2$	503.6	13.8	286.7	30.1
	3,4,5-$C_6F_3H_2$	495.0	5.2	265.7	9.1
1,2,4-$C_6F_3H_3$	2,3,5-$C_6F_3H_2$	501.7	11.9	288.5	31.9
	2,4,5-$C_6F_3H_2$	504.8	15.0	287.3	30.7
	2,3,6-$C_6F_3H_2$	511.8	22.0	312.1	55.5
1,3,5-$C_6F_3H_3$	2,4,6-$C_6F_3H_2$	515.5	25.7	311.0	54.4
1,2,3,4-$C_6F_4H_2$	2,3,4,5-C_6F_4H	504.4	14.6	290.7	34.1
1,2,4,5-$C_6F_4H_2$	2,3,5,6-C_6F_4H	512.4	22.6	317.6	61.0
1,2,3,5-$C_6F_4H_2$	2,3,4,6-C_6F_4H	514.7	24.9	313.1	56.5
C_6F_5H	C_6F_5	514.7	24.9	319.6	63

Fluorinated Benzenes. The calculated C−H bond dissociation energies (BDEs) of the twenty species $C_6F_nH_{6-n}$ ($n = 0-5$) were listed in an earlier publication[21] and are reproduced in Table 1. The calculated bond dissociation energy for benzene of 489.8 kJ mol^{-1} compares well with the experimental enthalpy of 473.1 kJ mol^{-1}.[15] We showed earlier that the calculated relative H−C enthalpies were in close agreement with experimental relative bond enthalpies for a variety of hydrocarbyls.[9] We are therefore confident that the H−C bond dissociation energies (BDEs) of fluorinated benzenes calculated relative to that for benzene, $\Delta D(H-Ar^F)_{rel}$, give reliable information on the influence of fluorine substituents on H−C BDEs. The values of $\Delta D(H-C)_{rel}$ for fluorinated benzenes shown in Figure 1 display a linear trend with clusters of points in three regions that correspond in increasing order of BDE to zero *ortho*-F, one *ortho*-F, and two *ortho*-F substituents. The data for $\Delta D(H-C)_{rel}$ can be expressed as a linear function shown in eq 1 by multiple regression, where n_{ortho}, n_{meta}, and n_{para} are the numbers of *ortho*-, *meta*-, and *para*-fluorines, and a, b, c, and d are coefficients (eq 1, Figure 1).

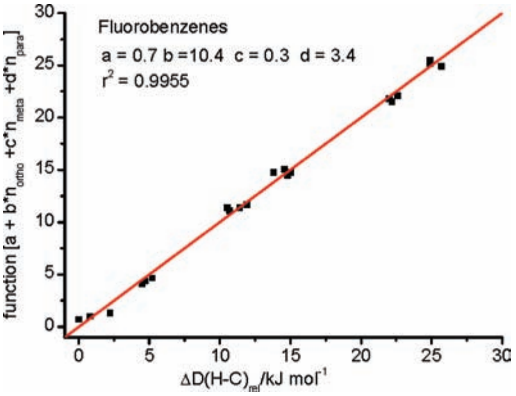


Figure 1. Multiple regression establishing contributions of *ortho*-, *meta*-, and *para*-fluorine substitution to the $H-Ar^F$ bond energies of fluorobenzenes.

$$\Delta D(H-Ar^F)_{rel} = a + bn_{ortho} + cn_{meta} + dn_{para} \text{ kJ mol}^{-1} \tag{1}$$

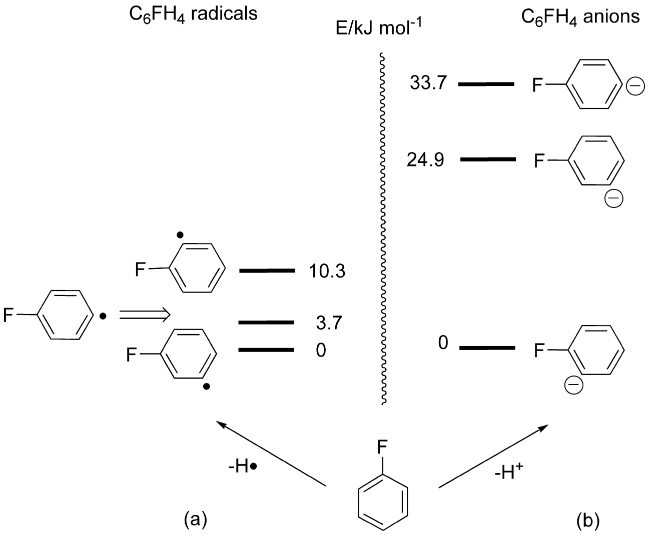
The linear correlation with $r^2 = 0.9955$ gives $a = 0.7 \pm 0.3$, $b = 10.4 \pm 0.2$, $c = 0.3 \pm 0.2$, and $d = 3.4 \pm 0.3$ kJ mol^{-1} (where r is the correlation coefficient). It indicates that substitution by fluorine at any position increases $\Delta D(H-C)_{rel}$ and that the substitution of H by F has an additive influence on the BDE. Introduction of an *ortho*-F has the greatest influence 10.4 ± 0.2 kJ mol^{-1}; a *meta*-fluorine substitution increases the BDE by only 0.3 ± 0.2 kJ mol^{-1} and a *para*-fluorine by 3.4 ± 0.3 kJ mol^{-1}. The H−C bond enthalpies of benzene and pentafluorobenzene differ by 17 kJ mol^{-1} according to experimental results, while the calculated difference is 25 kJ mol^{-1}.[15]

An interpretation of the effect of fluorine can be derived from the C−H BDEs of fluorobenzene. The relative C−H BDEs of the three different C−H bonds in fluorobenzene are fully defined by the relative stability of the three fluorophenyl radicals, because they all derive from fluorobenzene (Scheme 3a). The strongest C−H bond is associated with the least stable radical (radical center ortho to F), while the weakest C−H bond has the radical center meta to F. The π-donating effect of the lone pair of F perpendicular to the benzene ring increases the electron density at the positions ortho and para to F, which energetically disfavors the formation of a radical at these sites. The *ortho*-position is additionally disfavored by direct repulsion between the radical center and the lone pair of F lying in the molecular plane.

$Rh(\eta^5\text{-}C_5H_5)(H)(Ar^F)(PH_3)$. We have selected the rhodium complexes $Rh(\eta^5\text{-}C_5H_5)(H)(Ar^F)(PH_3)$ for detailed analysis because there is more experimental information for these systems than for any other. Because we are interested in trends and not in absolute values, C_5H_5 can be used to model cyclopentadienyl or pentamethylcyclopentadienyl rings and PH_3 can be used as a model of experimental phosphine ligands. It appears from the computational results that there is no interaction between the ligands, suggesting that our simplified systems may not represent the bonding accurately in complexes with very bulky spectator ligands or with ligands that could interact with the fluorinated phenyl group due to their electronic properties.

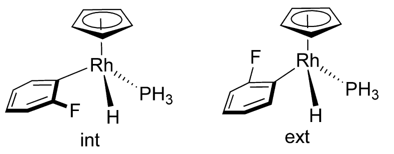
The overall geometry is that of the traditional three-legged piano stool with the aryl ligand parallel (as nearly as possible) to the cyclopentadienyl ring. The Rh−C and Rh−H bonds distances in $Rh(\eta^5\text{-}C_5H_5)(H)(Ar^F)(PH_3)$ are unaffected by the number of fluorines on the aryl ligand. The Rh−C distance is 2.04 Å and the Rh−H distance varies between 1.54 and 1.55 Å for the entire series. The angle $H-Rh-C_{ipso}(Ar)$ averages to 82.2° ± 0.8°. Due to the orientation of the phenyl ring, each of the two positions for the *ortho*- and *meta*-substituents on the phenyl ring are inequivalent because the substituent can lie either toward H or toward PH_3 (labeled int and ext on the diagram below). These results compare fairly well to the experimental structures of the bromide complexes (structures of the hydrides are unavailable). In $Rh(\eta^5\text{-}C_5Me_5)(Br)(Ar^F)(PMe_3)$, the Rh−C bond length is found to be 2.07(1) Å for 2,3-$C_6F_2H_3$, 2.02(2) Å for 2,4-$C_6F_2H_3$ (but 2.076(7) Å for the same compound crystallized in alternative space group), and 2.05(1) Å for 2,4,6-$C_6F_3H_2$.[18] The aryl ring adopts a conformation similar to that of the calculated species although the tilt of 12° of the aryl ring from the $Rh-C_{ipso}$ vector in the direction away from the phosphine ligand is not found in the calculated structure, most probably because of the different nature of the spectator ligands

Scheme 3. Relative Stability of (a) Fluorophenyl Radicals and (b) Fluorophenylanions[a]



[a] Note that both sets derive from fluorobenzene but the two energy scales do not share a common zero of energy.

(H for Br and PH_3 for PMe_3). The presence of two rotamers is also in agreement with the experimental observation. However, the calculated difference in energy between the two rotamers of 7 kJ mol^{-1} (with the most stable isomer having the F pointing toward PH_3) cannot be compared with the experimental difference in energy evaluated by NMR data (almost equienergetic) because of the different nature of the phosphine ligand.



The values of D(M–C) for $Rh(\eta^5\text{-}C_5H_5)(H)(Ar^F)(PH_3)$ were analyzed relative to $D(M-C_6H_5)$ for $Rh(\eta^5\text{-}C_5H_5)(H)(C_6H_5)(PH_3)$ with a similar method to that used for the fluorinated benzenes. The energies of the int and ext rotational isomers (F toward or away from phosphine) were averaged to decrease the bias introduced by the influence of the nature of the phosphine. The calculated BDEs are given in Table 1 and were fitted to eq 2 by multiple regression.

$$\Delta D(\text{M}-\text{C})_{\text{rel}} = a + bn_{\text{ortho}} + cn_{\text{meta}} + dn_{\text{para}} \text{ kJ mol}^{-1} \tag{2}$$

The linear correlation with $r^2 = 0.9972$ gives $a = -1.0 \pm 0.6$, $b = 26.1 \pm 0.4$, $c = 3.8 \pm 0.4$, and $d = 2.5 \pm 0.6$ kJ mol^{-1}. The linear correlation follows the pattern of eq 1, but the value of b is significantly larger than the other values and the values of c and d are close. We tested a fit where we did not separate the effects of *meta*- and *para*-fluorines since their contributions were similar, that is, $c = d$ (eq 3). The regression gave a good fit with $r^2 = 0.9965$ and $a = -1.0 \pm 0.7$, $b = 26.1 \pm 0.4$, and $c = 3.4 \pm 0.3$ (Figure 2). As there was no particular benefit in the fit with four parameters over the one with three parameters, we will only discuss the latter in the present Rh system and in the other complexes studied (Table 2).

$$\Delta D(\text{M}-\text{C})_{\text{rel}} = a + bn_{\text{ortho}} + c(n_{\text{meta}}+n_{\text{para}}) \text{ kJ mol}^{-1} \tag{3}$$

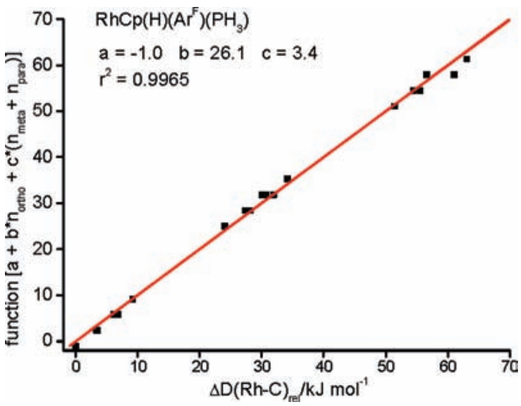


Figure 2. Multiple regression establishing contributions to Rh–C bond dissociation energy from *ortho*- and *meta*/*para*-fluorine substitution for $Rh(\eta^5\text{-}C_5H_5)(H)(Ar^F)(PH_3)$. Contributions of int and ext rotamers are averaged.

The BDE values are clustered in three groups increasing from zero to one to two *ortho*-fluorine substituents on the phenyl ring. Comparison with the values for fluorinated benzenes shows that b has increased by a factor around 2.5, while c (para and meta) remains very close to the contribution of the *para*-substituent in the organic systems. Thus, the M–C BDE is determined principally by b (i.e., by the number of *ortho*-fluorines) and marginally by the *meta*- and *para*-fluorines, resulting in the clusters of points on the correlation line for a given number of *ortho*-fluorines. The fact that *meta*- and *para*-fluorines have similar influences on the $\Delta D(\text{M}-\text{C})_{\text{rel}}$ indicates that electronic effects work differently in the complexes and in the organic fluorinated benzenes.

The variations in the Rh–C bond dissociation energies relative to that of Rh–phenyl ($\Delta D(\text{M}-\text{C})_{\text{rel}}$) are plotted versus the corresponding C–H bond dissociation energies for the fluorinated benzenes ($\Delta D(\text{C}-\text{H})_{\text{rel}}$) in Figure 3. A linear correlation appears with a slope $R^{\text{M}-\text{C/H}-\text{C}}$ of 2.43 ± 0.11 ($r^2 = 0.981$). The 20 values form themselves into three subsets corresponding to zero *ortho*-F (the lowest values for $\Delta D(\text{M}-\text{C})_{\text{rel}}$), to one *ortho*-F, and two *ortho*-F substituents (the highest values for $\Delta D(\text{M}-\text{C})_{\text{rel}}$). This linear correlation is closely related to the multiple regression plots shown in Figures 1 and 2. The implication of $R^{\text{M}-\text{C/H}-\text{C}}$ is that $D(\text{Rh}-\text{C})_{\text{rel}}$ may increase by about 60 kJ mol^{-1} with two *ortho*-fluorine substituents when $D(\text{H}-\text{C})_{\text{rel}}$ rises by only 25 kJ mol^{-1}. The increased dominance of *ortho*-fluorine substitution for the rhodium–carbon bonds can also be seen by comparison of the values of b: for $Rh-Ar^F$ $b = 26.1$ kJ mol^{-1}, while for $H-Ar^F$ $b = 10.4$ kJ mol^{-1}.

Other M(H)(Ar^F)L$_n$ Complexes. Following the results discussed above for $Rh(\eta^5\text{-}C_5H_5)(H)(Ar^F)(PH_3)$, similar calculations were carried out for a variety of other complexes ranging from d^0 $Zr(\eta^5\text{-}C_5H_5)_2(H)(Ar^F)$ to d^8 $M(H)(Ar^F)(dhpe)$ (M = Ni, Pt; dhpe = $H_2PCH_2CH_2PH_2$) (Table 2). The 18-electron d^4 $Re(\eta^5\text{-}C_5H_5)(H)(Ar^F)(CO)_2$ complexes, which were presented in an earlier publication complete the series.[17] The influence of the spectator ligands for a given metal and coordination sphere has been explored by changing PH_3 for CO in the Re, Rh, and Ir complexes because these substitutions correspond to experimentally known complexes. Calculations were carried out for all 20 species $Ar^F = C_6F_nH_{5-n}$ ($n = 0-5$) in the majority of cases, but the parameters were estimated from a smaller sample in four cases.

Structures of M(H)(Ar^F)L$_n$. We consider first the structures of the complexes. The calculated structural features of all

Table 2. Values of $R^{MC/HC}$, D(M−Ph), and a, b, and c (see eq 3)[a]

ML$_n$	$R^{M-C/H-C}$	D(M−Ph) kJ mol^{-1}	a kJ mol^{-1}	b kJ mol^{-1}	c kJ mol^{-1}	b/c
organic H−Ar^F[b]			0.7(3)	10.4(2)	c = 0.3(2) d = 3.4(3)	
$ZrCp_2(H)(Ar^F)$	3.05	283.0	−1.0(4)	32.8(2)	3.3(2)	9.94
$TaCp_2(H)_2(Ar^F)$	2.52	208.5	−0.5(3)	26.9(2)	4.5(2)	5.98
$TaCp_2Cl(H)(Ar^F)$[c]	2.08	122.9	−0.2(3)	23.6(2)	2.9(1)	8.14
$WCp_2(H)(Ar^F)$	2.34	257.7	−0.7(4)	24.9(2)	4.3(2)	5.79
$ReCp(CO)_2(H)(Ar^F)$	2.25	252.0	0.3(4)	24.1(2)	2.0(2)	12.1
$ReCp(CO)(PH_3)(H)(Ar^F)$	2.43	262.5	−0.8(4)	26.0(2)	3.0(2)	8.67
$ReCp(PH_3)_2(H)(Ar^F)$[c]	2.62	266.3	0.1(6)	29.4(4)	4.1(3)	7.17
$RhCp(CO)(H)(Ar^F)$[c]	1.98	256.8	−0.3(4)	22.6(3)	2.5(2)	9.04
$RhCp(PH_3)(H)(Ar^F)$[d]	2.43	252.1	−1.0(7)	26.1(4)	3.4(3)	7.68
$IrCp(CO)(H)(Ar^F)$[c]	1.93	290.8	−0.2(2)	20.0(2)	2.4(1)	8.33
$IrCp(PH_3)(H)(Ar^F)$	2.39	296.4	−0.6(6)	25.6(3)	3.6(3)	7.11
$Pt(dhpe)(H)(Ar^F)$	2.58	313.4	1.8(11)	27.6(6)	4.4(5)	6.27
$Ni(dhpe)(H)(Ar^F)$	2.80	235.7	−0.2(5)	29.8(3)	5.2(2)	5.73

[a] The notation 0.7(3) is used to indicate 0.7 ± 0.3. All the correlation coefficients r^2 are greater than 0.983. [b] The organic system was analyzed via eq 1 with four coefficients. [c] Limited data set: zero F, one *ortho*-F, two *ortho*-F, two *ortho*-F and one *para*, two F *ortho* and two F *meta*, five F. [d] When the regression allowed for independent coefficients for *meta*- and *para*-substituents (eq 2), the following values were obtained: a = −1.0(6), b = 26.1(4), c = 3.8(4), and d = 2.5(6).

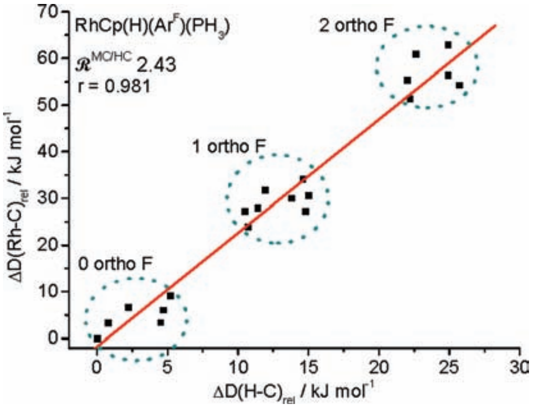
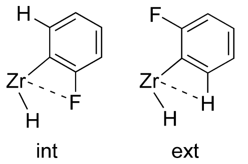


Figure 3. Correlation between the Rh−C bond dissociation energies of Rh(η^5-C_5H_5)(H)(Ar^F)(PH_3) and the H−C bond dissociation energies of fluorobenzenes. The bond energies of int and ext rotamers are averaged. The zero corresponds to the values for H−C_6H_5 and Rh−C_6H_5 bond energies.

systems are in agreement with the experimental structures of related complexes. The metal−carbon (Ar^F) bond length, the metal−hydrogen bond length, and the angle H−M−C$_{ipso}$(Ar^F) are found to be insensitive to the number and position of fluorine substituents on the aryl ring. In Ta(η^5-C_5H_5)$_2$(H)$_2$(Ar^F), the aryl lies in the bisector plane of the two cyclopentadienyl ligands and occupies one of the two outside coordination sites. In this family of complexes, the central hydride and the aryl ligand are forced to be relatively close (the angle H−Ta−C$_{ipso}$ varies from 69.9 to 72.2°), which results in significant energy differences between rotamers with an *ortho*-fluoride substituent pointing toward or away from the central negatively charged hydride. In W(η^5-C_5H_5)$_2$(H)(Ar^F) the aryl group also lies in the bisector plane of the two cyclopentadienyl rings but the angle H−W−C$_{ipso}$ of around 80° leads to smaller differences in energy between rotamers with the *ortho*-fluorine pointing toward or away from the hydride ligand. The iridium complexes have related features to the rhodium complexes previously discussed. The aryl ring lies almost parallel to the cyclopentadienyl ring in the rhenium complexes Re(η^5-C_5H_5)(L)(L′)(H)(Ar^F), as for the rhodium complexes.[21] Consequently, there is only one rotamer when L = L′, but two when L and L′ are different. In the d^8 square planar complexes of nickel and platinum, the aryl ring lies perpendicular to the coordination plane so minimizing steric hindrance and ensuring that there is only one rotamer.

The 16-electron Zr(η^5-C_5H_5)$_2$(H)(Ar^F) complex has an empty coordination site lying in the bisector plane which can lead to additional interaction between the ligand and the metal. This interaction comes exclusively from the *ortho*-H or -F atoms and occurs preferentially inside the H−Zr−Ar angle. Fluorine forms a stronger additional interaction than hydrogen. The ext isomer is more stable than the int isomer by 5 kJ mol^{-1} as a consequence of the repulsions associated with the large number of short internuclear distances when the *ortho*-F is inside the H−Zr−F angle. Thus, the difference in energy between the int and ext rotamers is small for *ortho*-substitution and even smaller for *meta*-substitution, allowing us to average their energies. The formation of an additional bond with a two-electron donor has been considered theoretically,[22] and the preference for inside coordination has been established. In our case, the proximity of the fluorine to the hydride introduces an opposing effect. Similar F-coordination is not applicable to 18-electron species or to 16-electron square planar species because of the absence of available empty d orbitals.



Bond Dissociation Energy for M(H)(Ar^F)L$_n$. Table 2 gives the results of the multiple regression analyses for all M(H)(Ar^F)L$_n$ according to eq 3. The energies of all systems with int and ext isomers were averaged. The complete set of graphs corresponding to Figures 2 and 3 is presented in the Supporting Information. The results are remarkably similar for all metal fragments. In all cases, a is small with a large error, b lies between 20 and 30 kJ mol^{-1} with a small error bar, and c lies between 2.0 and 4.5 kJ mol^{-1}. The behavior of the M−C bond dissociation energies translates into values of $R^{M-C/H-C}$ between 1.93 and 3.05. The values of b/c provide a measure of

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(21) Clot, E.; Oelckers, B.; Klahn, A. H.; Eisenstein, O.; Perutz, R. N. *Dalton Trans.* **2003**, 4065.

(22) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

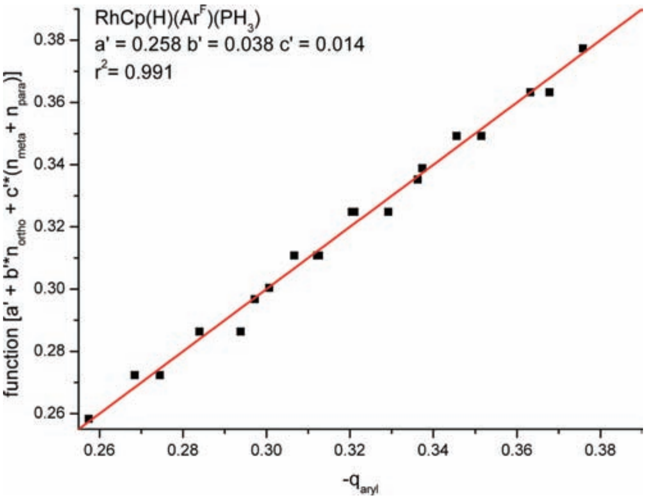

Figure 4. Multiple regression analysis of $-q_{\rm aryl}$, the negative charge on the aryl ring, for Rh(η^5-C_5H_5)(H)(Ar^F)(PH$_3$) calculated by natural bond population analysis. Note that significant increases in the charge result not only from *ortho*-substitution but also from *meta*- and *para*-substitution.

the importance of *ortho*-fluorine substitution compared to *meta*/*para*-substitution and vary from 9.94 for M = Zr(η^5-C_5H_5)$_2$ to 5.73 for Ni(dhpe). We evaluate the results in more detail in the Discussion.

We mentioned in the Introduction that bond energy correlations have been associated with changes in electronegativity of the ligands and, hence, the polarity of the metal–X bonds.[6,11,17] We therefore used natural bond population analysis to estimate the charge on the ipso carbon atom, $q_{\rm ipso}$, and on the whole fluoroaryl ring, $q_{\rm aryl}$. The results on Rh(η^5-C_5H_5)(H)(Ar^F)(PH$_3$) are representative of many of the metal–ligand systems. A multiple regression analysis based on eq 4 (Figure 4)

$$-q_{\rm aryl} = a' + b'n_{\rm ortho} + c'(n_{\rm meta}+n_{\rm para}) \qquad (4)$$

yields $a' = 0.258 \pm 0.002$, $b' = 0.038 \pm 0.001$, and $c' = 0.014 \pm 0.001$, with $r^2 = 0.991$. It is evident that the *ortho*-fluorine substituents exercise the largest effect on $q_{\rm aryl}$, but it does not dominate over the *meta*- and *para*-effects to the extent that is found in the BDEs. As a result, the points are much more evenly distributed in Figure 4 than in Figure 2. In an alternative analysis, we plot $\Delta D_{\rm rel}$(Rh–Ar^F) versus $-q_{\rm aryl}$ and observe a series of steps corresponding to zero, one, or two *ortho*-fluorines (Figure 5). The steps in Figure 5 overlap slightly, whereas the domains shown in Figure 3 are well separated. An analogous plot of $\Delta D_{\rm rel}$(Rh–Ar^F) versus $-q_{\rm ipso}$ yields a substantially different pattern (Figure 6) from that in Figure 5. The value of $-q_{\rm ipso}$ increases substantially with *ortho*-fluorine substitution, and there is also a marked increase with *para*-fluorine substitution, but $-q_{\rm ipso}$ decreases in a regular fashion with *meta*-fluorine substitution. Because *meta*- and *para*-fluorine substitutions have similar effects on the BDEs, we conclude that $q_{\rm aryl}$ acts as a much better guide to the origin of the BDEs than $q_{\rm ipso}$.

We have carried out the same type of analysis on those metal–ligand systems for which we calculated a full set of 20 data points (other than Ir(η^5-C_5H_5)(H)(Ar^F)(PH$_3$)) following eq 4. The resulting multiple regression data are shown in Table 3 and the complete set of graphs are shown in the Supporting Information. The correlation coefficients are satisfactory in all cases except for Zr(η^5-C_5H_5)$_2$(H)(Ar^F). The ratio b'/c', representing the relative importance of *ortho*-fluorine substitution on $q_{\rm aryl}$, varies between 2.2 and 2.8 for the majority of examples but is only 1.6 for the Ta(η^5-C_5H_5)$_2$(H)$_2$(Ar^F) system. The plots of $-q_{\rm aryl}$ versus ΔD(M–Ar^F)$_{\rm rel}$ (Figure 5 and equivalent plots for other metals in the Supporting Information) follow the same pattern for all the metal–ligand systems examined other than Zr(η^5-C_5H_5)$_2$(H)(Ar^F).

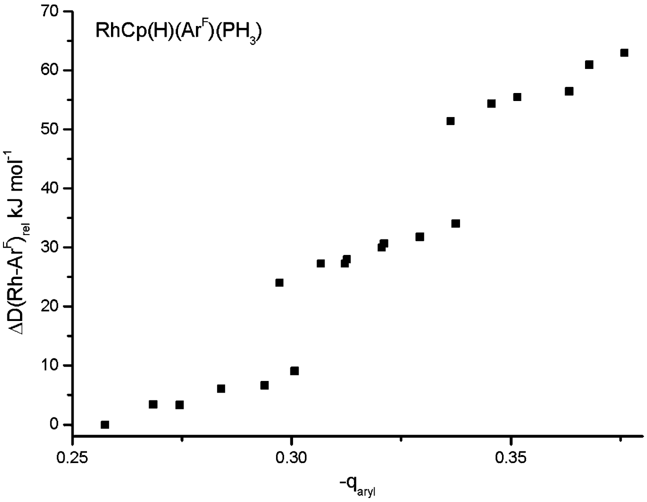

Figure 5. Plot of ΔD(Rh–C)$_{\rm rel}$ vs $-q_{\rm aryl}$, the negative charge on the aryl ring, calculated by natural bond population analysis for Rh(η^5-C_5H_5)(H)(Ar^F)(PH$_3$).

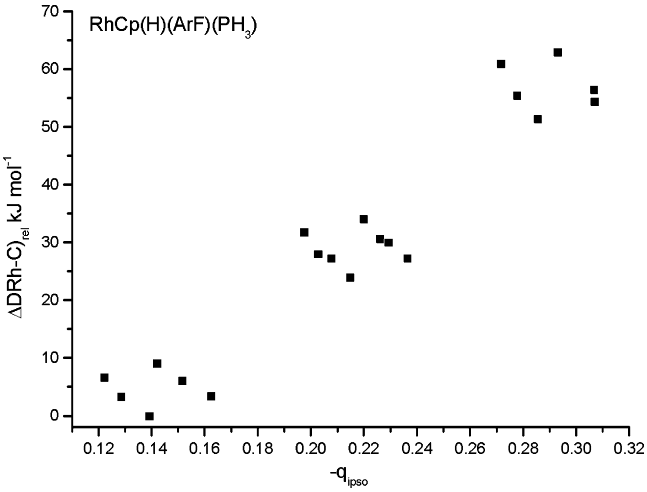

Figure 6. Plot of ΔD(Rh–C)$_{\rm rel}$ vs $-q_{\rm ipso}$ the negative charge on the ipso carbon atom calculated by natural bond population analysis for Rh(η^5-C_5H_5)(H)(Ar^F)(PH$_3$).

Table 3. Results of Multiple Regression on Values of $-q_{\rm aryl}$ According to eq 4

ML$_n$	a'	b'	c'	b'/c'	r^2
organic H–Ar^F	0.121	0.018	0.0074	2.4	0.979
ZrCp$_2$(H)(Ar^F)	0.41	0.057	0.015	3.8	0.854
TaCp$_2$(H)$_2$(Ar^F)	0.399	0.018	0.011	1.6	0.959
WCp$_2$(H)(Ar^F)	0.298	0.029	0.011	2.6	0.982
ReCp(CO)$_2$(H)(Ar^F)	0.241	0.033	0.013	2.5	0.983
ReCp(CO)(PH$_3$)(H)(Ar^F)	0.295	0.026	0.012	2.2	0.973
RhCp(PH$_3$)(H)(Ar^F)	0.258	0.038	0.014	2.7	0.991
Pt(dhpe)(H)(Ar^F)	0.386	0.033	0.012	2.8	0.974
Ni(dhpe)(H)(Ar^F)	0.430	0.037	0.014	2.7	0.988

Discussion

The correlation between M–C and H–C bond energies reveals the same features for all metal fragments. This correlation is therefore valid for a wide variety of electron counts and coordination types at the metal center. In all cases, the slope of the linear correlation lies between two and three showing a marked energetic difference between M−Ar^F regioisomers. In all systems, the number of *ortho*-fluorine atoms is the crucial parameter.

A. Effect of Changes in Spectator Ligands and Metal−Ligand Fragments. Changes in the nature of the spectator ligands affect the value of the slope $R^{M-C/H-C}$ and, hence, the selectivity. Increasing the electron density at the metal by increasing the donating ability of one ligand (Cl vs H or CO vs PH_3) results in an increase of the slope (Table 2). The influence of the spectator ligand depends on the nature of the metal as shown by the increase of $R^{M-C/H-C}$ by 0.56 from Ta(η^5-C_5H_5)$_2$Cl to Ta(η^5-C_5H_5)$_2$H, by 0.2 from Re(η^5-C_5H_5)(CO)$_2$ to Re(η^5-C_5H_5)(CO)(PH_3), by 0.45 from Rh(η^5-C_5H_5)(CO) to Rh(η^5-C_5H_5)(PH_3), and by 0.46 for its iridium analogue. In keeping with these trends, *b* increases by 1.9 kJ mol^{-1} from Re(η^5-C_5H_5)(CO)$_2$ to Re(η^5-C_5H_5)(CO)(PH_3) and by about 3.5 and 5.5 kJ mol^{-1} in the Rh(η^5-C_5H_5) and Ir(η^5-C_5H_5) complexes, respectively.

We now compare fragments with common ligand sets but different metals. Interestingly, the values of the slope $R^{M-C/H-C}$ are almost identical for Rh and Ir despite the intrinsically stronger M−C_6H_5 BDE for the third row metal. The calculated absolute values of the M−C_6H_5 BDE are given for each system in Table 2; in M(η^5-C_5H_5)(PH_3)(H)(C_6H_5), *D*(M−C_6H_5) is larger for M = Ir (296.4 kJ mol^{-1}) than for M = Rh (256.8 kJ mol^{-1}). The situation is even more striking for the d^8 M(dhpe)(H)(Ar^F) complexes (M = Ni, Pt), where greater selectivity is obtained for Ni ($R^{M-C/H-C} = 2.80$ versus $R^{M-C/H-C} = 2.58$ for Pt), even though the M−C_6H_5 BDE is about 80 kJ mol^{-1} lower for M = Ni than for M = Pt. There is, thus, no direct relation between the value of the slope (and hence the selectivity) and the absolute strength of the M−Ar bond.

We also compare other related metal fragments. The values of $R^{M-C/H-C}$ and *b* decrease from d^0 Ta(η^5-C_5H_5)$_2$(H)$_2$(Ar^F) to d^2 W(η^5-C_5H_5)$_2$(H)(Ar^F) by about 0.2 and 4 kJ mol^{-1}, respectively. There is also a decrease from d^4 Re(η^5-C_5H_5)(H)(Ar^F)(L)$_2$ to d^6 Ir(η^5-C_5H_5)(H)(Ar^F)(L). Because of the many factors that can be involved, electronegativity of the metal, ligand field, nature of the ligand, electron count, and so on, we cannot identify the most important factors conclusively, except to note that the ligand effects are larger than the metal effects for the pairs that we have mentioned. Nevertheless, it is interesting to note that the Zr complexes, which introduce additional bonding between the ligand and the metal, are associated with the largest $R^{M-C/H-C}$ value.

B. Origin of the Correlations. An examination of electronic features that might explain the origin of the correlation and the values of the slope has been partially successful. Metal−carbon π-bonding seems to be unimportant since the values of $R^{M-C/H-C}$ do not vary significantly with electron count at the metal. Moreover, substitutions at *para*- and *meta*-positions of the aryl ring have similar effects on the M−C bond energy, whereas π-bonding should make them significantly different.

The best results were obtained by correlating $\Delta D(M-C)_{rel}$ with the total negative charge of the aryl ring, $-q_{aryl}$ (Figure 6 and Table 3). The charge correlations lead us to suggest an interpretation of the results derived from the Pauling's model in which bond energy increases with electronegativity difference, that is, the ionic component of a covalent bond.[23] In modern theory, this approach has been put into practice in particular by Shaik et al.[24,25] The value of *a*′ in Table 3 (see eq 4) is a qualitative measure of the charge on the phenyl ring without fluorine substituents. The value of *a*′ for the organic system is 0.12, while it varies from 0.24 to 0.43 in the metalated systems, showing a substantial accumulation of electron density on the aryl ring upon metalation. The metal−carbon bond is more polar than the H−C bond, as has already been pointed out by Landis.[11] The lower effective electronegativity of the metal fragment with respect to H will increase the weight of the ionic component in the M−Ar^F bond with respect to H−Ar^F. Fluorine substituents increase the polarity of the bond as illustrated by the positive values for *b*′ and *c*′ (Table 3) leading to a more negatively charged aryl ring. This increased bond ionicity leads to a larger value of the BDE. Even though the absolute values of *b*′ and *c*′ are small compared to *a*′, the influence of *ortho*-substitution is clearly stronger than that of *meta*- and *para*-substitution as is illustrated by the values of the ratio *b*′/*c*′.

As a qualitative approach to this problem, we consider the three different anions $[C_6FH_4]^-$ with F ortho, meta, or para to the in-plane lone pair on C. The calculations show that the most stable isomer is the one with F ortho to the anionic center. The *meta*- and *para*-isomers lie at higher energies (24.9 kJ mol^{-1} and 33.7 kJ mol^{-1}, respectively, Scheme 3b) in contrast to the energy pattern found for the radicals. Remarkably, there is a geometrical signature of the preference for the *ortho*-arrangement: the σ lone pair on carbon delocalizes its density into the neighboring σ^*(C−F) orbital, resulting in a lengthening of the C−F bond ortho to the lone pair (1.40 Å vs 1.382 Å and 1.378 Å for meta and para, respectively). The delocalization accounts in part for the *ortho*-effect and is known as hyperconjugation or as negative hyperconjugation. It has been demonstrated that the σ^*(C−F) orbital can accept unshared electron pairs from neighboring atoms if the atomic orbital bearing the electron pair overlaps with the σ^*(C−F) orbital.[26] This effect is important for anions[27] and, thus, for the M−C bond where the anionic contribution is important.

Hyperconjugation has also been reported for radicals,[28] but the effect must be stronger for fluorophenyl anions than for fluorophenyl radicals because our calculations show that the most stable isomer of $[C_6FH_4]^-$ has F ortho to the anionic center while this is not the case for the C_6FH_4 radical. As mentioned in a computational study of the bond dissociation enthalpies in haloethenes,[28] many additional interactions are present in the radical systems. It is not within the scope of this paper to discuss the relative energies of the isomers of C_6FH_4. The stronger hyperconjugation in the case of the anionic system is in line with the closer proximity in energy of the orbital bearing the lone pair and the σ^*(C−F) orbital. The effect of *ortho*-fluorine substitution on the aryl anions is also illustrated by the increased ease of deprotonation (gas-phase CH acidity). The calculated

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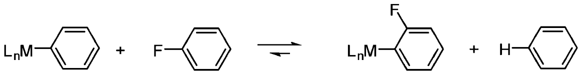
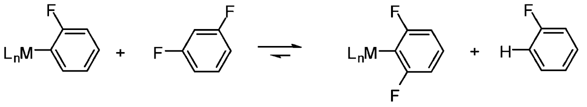
energy of deprotonating benzene is 53 kJ mol^{-1} greater than that of fluorobenzene and 105 kJ mol^{-1} greater than that of 1,3-difluorobenzene.[29]

The interpretation in terms of $-q_{\text{aryl}}$ (eq 4) cannot account entirely for the *ortho*-selectivity, as illustrated by the comparison between the ratio *b*/*c* (Table 2) and the ratio *b*′/*c*′ (Table 3). The former, based on energy increments in the BDE, is significantly more sensitive to *ortho*-fluorine substitution than the latter, based on charge increments on the aryl ring. There are thus factors other than ionicity of the bond that are needed to account for the selectivity for *ortho*-fluorine substitution. In spite of intensive efforts, we have been unable to identify factors that correlate better with the trends in relative bond energy.

C. Comparisons with Experiment. The most satisfactory test of the computational results would be the experimental determination of the slope of the bond energy correlation for metal(fluoroaryl)hydride complexes. A preliminary report of such an experimental determination of the relative Rh−C bond energies for Tp*Rh(CNCH$_2$CMe$_3$)(Ar^F)H (Tp* = tris(3,5-dimethylpyrazolyl)borate) appeared while this paper was being reviewed. When correlated with calculated values of the corresponding H−C bond energies, a slope of the correlation line of 2.38 is obtained in excellent agreement with our calculated values for related systems.[30]

The high values of *b*/*c* (between 5.5 and 12) speak in favor of a strong thermodynamic preference for forming M−Ar^F bonds ortho to fluorine. We can thus anticipate that the following reactions (eqs 5−8) will be exothermic, independently of the nature of M and the ligand set L$_n$.


(5)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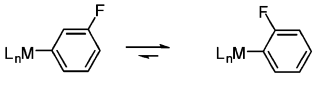
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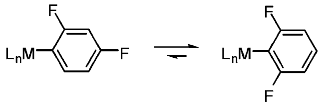
(8)

We now consider the general principle of eqs 5 and 6 that C−H bond activation is more favorable if products are formed with *ortho*-fluorine substituents than without them. This point is illustrated by the reactivity of the Re(η^5-C$_5$H$_5$)(CO)$_2$ and Rh(η^5-C$_5$H$_5$)(PPh$_3$) fragments, where C−H bond activation is conclusive with fluoroaromatics that give *ortho*-substituents but absent for benzene itself.[31,36] It was also demonstrated by the prior calculations on reactions of Ni(dhpe) with benzene vs pentafluorobenzene.[20] Recently, another more complex example has been provided by the reaction of Ni(PEt$_3$)$_2$ with 1,2,4,5-tetrafluorobenzene,[32] in which the C−H activation process has been shown to be reversible, yielding a product with two *ortho*-fluorines. This is a further illustration that fluorine substitution alters the energetics, because C−H activation of benzene is not observed at all. The product evolves to yield the C−F oxidative addition product with one *ortho*-fluorine. The interesting reaction of Co(CH$_3$)(PMe$_3$)$_4$ with pentafluorobenzophenone provides intramolecular competition between C−F and C−H bond activation and results in exclusive C−F bond activation.[33] The authors analyze this reaction with the explicit assumption that the Co−C bond energy is similar regardless of the position of activation, an assumption that is clearly erroneous.

We next consider those cases where there is secure evidence for thermodynamic control of position of substitution. In the case of the reaction of Rh(η^5-C$_5$Me$_5$)(C$_6$H$_5$)(H)(PMe$_3$) with C$_6$F$_n$H$_{6-n}$, the thermodynamic product is always the isomer with the maximum number of fluorine atoms ortho to the Rh−C bond. The same applies to the isomerization of the photochemically generated Rh(η^5-C$_5$H$_5$)(Ar^F)(H)(PMe$_3$) (Scheme 1 and eq 8).[18] The attractive features of this system are that (a) the kinetic products differ from the thermodynamic products; (b) the equilibration occurs after the rate determining step; and (c) the mechanism of equilibration is understood. A further example is furnished by W(η^5-C$_5$Me$_5$)(NO)(CH$_2$CMe$_3$)(Ar^F) formed by thermolysis of W(η^5-C$_5$Me$_5$)(NO)(CH$_2$CMe$_3$)$_2$ with Ar^{F}H (Ar^F = C$_6$FH$_4$, C$_6$F$_2$H$_3$) where strong *ortho*-selectivity is observed. The contrast between the kinetic and thermodynamic selectivity has been demonstrated with the chlorinated analogues and the authors make the reasonable assumption that this conclusion can be extrapolated to the fluorinated molecules.[34] The reaction of [Ir(cyclooctene)(P$_2$Py)]$^+$ (P$_2$Py = 2,6-(CH$_2$P*t*Bu$_2$)$_2$-pyridine) with fluorobenzene shows slight thermodynamic selectivity (2:1, ortho/para) for the *ortho*-regioisomer.[35]

The photochemical reaction of Re(η^5-C$_5$Me$_5$)(CO)$_2$(N$_2$) with fluorobenzenes presents a more complex situation that has been analyzed previously by both experiment and theory.[21] Initial formation of an η^2-arene complex precedes aromatic C−H activation to form the cis hydrido aryl complex (if it occurs at all) and there is a chance for equilibration of regioisomers at this point. The rate determining step, *cis*−*trans*-isomerization, follows C−H activation with the result that there is no chance of equilibration later. The barriers to each step follow the same sequence as the thermodynamic energies of the products, dividing neatly into the three groups for zero, one or two *ortho*-fluorine substituents. Thus, this system has two special features, equilibration prior to the rate determining step and kinetic barriers that follow the thermodynamic order (Hammett principle). At a specific level, we know that 1,4-difluorobenzene reacts with Re(η^5-C$_5$Me$_5$)(CO)$_2$(N$_2$) to form Re(η^5-C$_5$Me$_5$)(CO)$_2$(η^2-C$_6$F$_2$H$_4$) and undergoes ring-whizzing with a low barrier.[36] The reaction with 1,3-difluorobenzene generated a single product, Re(η^5-C$_5$Me$_5$)(2,6-C$_6$F$_2$H$_3$)(H)(CO)$_2$.[17]

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(29) The calculated energies for proton dissociation were as follows: C$_6$H$_6$, 1782.5 kJ mol^{-1}; C$_6$FH$_5$, 1729.8 kJ mol^{-1}; 1,3-C$_6$F$_2$H$_4$, 1677.1 kJ mol^{-1}. In the two last cases, the negative charge lies in the 1-position with fluorine in the 2-position and the 2,6-positions, respectively.

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For the majority of other examples in the literature, we do not know whether the selectivity is thermodynamic or kinetic. Complete selectivity for regioisomers with fluorine ortho to the metal has been observed in the reactions of Ti(CH_2*t*-Bu)(=CH*t*Bu)(PNP) (PNP = N[2-P($CHMe_2$)$_2$-4-methylphenyl]$_2$) with fluorobenzene and 1,2-difluorobenzene to form Ti(Ar^F)(=CH*t*Bu)(PNP) by 1,2−C-H addition at 25 °C. The reaction with 1,3-difluorobenzene generates 2,6 and 2,4-Ti($C_6F_2H_3$) isomers.[37] At much higher temperature β-fluoride elimination occurs to form Ti(F)(=CH*t*Bu)(PNP). In this case, the authors considered the possibility that thermodynamic equilibration occurred via a ring-walking mechanism, but argued that it was unlikely.

Selectivity for activation of C−H bonds ortho to fluorine has also been observed in the reactions of Fe(naphthyl)(H)(dmpe)$_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) with fluorinated benzenes and the reaction of Zr(η^5-C_5Me_5)$_2$$H_2$ with fluorobenzene.[38,39] The reaction of Ir(H)$_5$(P*i*Pr$_3$)$_2$ with 1,3-difluorobenzene yields Ir(H)$_2$(2,6-$C_6F_2H_3$)(P*i*Pr$_3$)$_2$ exclusively, maximizing the number of fluorine substituents.[40] The catalytic cross coupling of alkynes to fluorinated benzenes catalyzed by Ni(COD)$_2$ in the presence of tricyclopentylphosphine also shows selectivity for activation of C−H bonds ortho to fluorine.[41] The direct arylation of fluorinated benzenes catalyzed by palladium complexes involves C−H bond activation and exhibits strong *ortho*-selectivity that has been attributed to changes in C−H acidity.[5c] The same reasoning has been applied to arylation of 1,3-difluorobenzene with copper catalysts.[42] The role of energetics in these cases must await further study but certainly cannot be dismissed.

There is a link between the CH acidity and our own investigation of energetics. We have shown that the energetic preference for *ortho*-fluorine substitution is associated with the increased strength of M−C bonds and that this can be partly attributed to the negative charge on the aryl ring $-q_{\mathrm{aryl}}$ and the ionic character of the metal−carbon bond. The CH acidity is associated with increased stability of the congugate base Ar^- when *ortho*-fluorine substituents are present (see Scheme 3). We have pointed out the relationship of their stabilities to the correlations that we calculated. However, the mechanisms that focus exclusively on CH acidity fail to highlight the most important point, the big increase in the metal−carbon bond energy, *D*(M−C).

The gain in metal−carbon bond energy for metal−aryls with *ortho*-fluorine substituents applies not only to C−H bond activation reactions but to other reactions that make metal−aryl bonds. Examples may be found in the C−F bond activation reactions at Ru(H)$_2$(dmpe)$_2$.[43]

Finally, we turn to the consequences for C−C bond formation of the gain in stability of the metal−aryl product achieved through *ortho*-fluorine substitution. In a catalytic reaction, M−C bond formation is often followed by C−C bond formation and M−C bond cleavage. We have considered three such reactions: insertion of ethylene to form an ethylbenzene, coupling to a phenyl group to form a biphenyl, and insertion of CO to form a benzaldehyde. By consideration of a thermodynamic cycle and calculation of the energies of the isodesmic reaction in eq 9 ($\Delta E = -0.9$, +20.2, and +12.4 kJ mol^{-1} for X = C_2H_5, CHO, and C_6H_5, respectively), we infer that the later steps involving C−C coupling and M−C bond cleavage are less energetically favorable for the *ortho*-fluorinated species in each case (see Supporting Information, Figure S21). The energetic advantage of C−H activation gained through *ortho*-fluorine substituents on the arene may thus be detrimental for further reactions of the metal−aryl complexes.

(9)

Conclusions

In this study, we have shown by DFT calculations that there is a correlation between the M-C and H−C bond dissociation energies in which the organic systems are benzene and fluorinated benzenes $C_6F_nH_{6-n}$ (n = 0−5) and a wide variety of metal fragments which are known to activate C−H bonds. Although fluorine increases the bond energy of an *ortho*-C−H bond, it increases the *ortho*-M−C bond strength even more. It was originally observed for a rhodium complex[18] that fluoro aryl complexes are more stable with *ortho*-fluorine than *para*- or *meta*-fluorine. We infer that this principle is valid for any metal fragment calculated here and presumably for any analog of them. The change in the M−C bond energy of the products is found to fit a linear function of the number of fluorine substituents, with different coefficients corresponding to the *ortho*- and *meta*/*para*-fluorine substituents, respectively. The coefficients represent the contributions of each fluorine substituent to the M−C bond energy directly in kJ mol^{-1}. The *ortho*-coefficient may be as large as 30 kJ mol^{-1}, while the *meta*/*para*-coefficient never exceeds 5 kJ mol^{-1}. The ratio of the values of the *ortho*- and *meta*/*para*-coefficients (*b*/*c*) represents the energetic selectivity for *ortho*-fluorine substitution and varies from about 6−12. The effect of fluorine substitution can also be represented by the slope $R^{\mathrm{M-C/H-C}}$ of the correlation between M−C and H−C bond dissociation energies. R exceeds 1.9 in all cases, which means that there is a large thermodynamic advantage for cleaving the H−C bond ortho to fluorine. Variations between metal ligand centers can be described via changes in the *ortho*-coefficient or changes in $R^{\mathrm{M-C/H-C}}$. The values of $R^{\mathrm{M-C/H-C}}$ vary over a range between 1.9 and 3.05. For a given metal, $R^{\mathrm{M-C/H-C}}$ clearly increases with the electron donating ability of the ligands, but the influence of the ligands is only moderately dependent on the identity of the metal. Surprisingly, for a given ligand set and metals in the same group of the periodic table, $R^{\mathrm{M-C/H-C}}$ does not increase with the strength of the M−C bond. Thus, $R^{\mathrm{M-C/H-C}}$ is similar for Ir and Rh in d^8 M(η^5-C_5H_5)(L) and $R^{\mathrm{M-C/H-C}}$ is larger for Ni than Pt in d^{10} M(dhpe). This study also demonstrates the very large increase in the M−C bond strength on *ortho*-fluorine substitution, while substitution at the *meta*- and *para*-positions has a minor influence.

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There are numerous experiments that support these conclusions even though only a few of them demonstrate relative thermodynamic stability. Even in the case of kinetic control, the Hammett principle often applies so that the kinetic preference follows thermodynamic preference leading to a preferential activation of the C–H bond ortho to the fluorine. Another consequence is that essentially the full gain in M–C bond energy is obtained with two fluorine atoms ortho to the metal. In catalytic processes that involve formation of a metal aryl prior to C–C coupling, this gain in bond energy will be offset by a corresponding loss in the C–C coupling step.

The correlation for the energies is compared to a correlation for the charges calculated by the NBO method. A linear fit similar to that for the M–C bond energy shows that the charge can be expressed as a function of the number of *ortho*-, *meta*-, and *para*-fluorine substituents. It is found that the total charge on the aryl ring varies like the M–C bond energy indicating that the ionicity of the M–C bond is involved in its energetic properties. However, the *ortho*-fluorine dominates the charge correlation less than the energy correlation.

Computational Details. All calculations were performed with the Gaussian03 package[44] of programs with the hybrid B3PW91 functional.[45,46] The metal atoms were represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set,[47] augmented by an *f* polarization function.[48] The phosphorus and chlorine atoms were represented by RECP from the Stuttgart group and the associated basis set,[49] augmented by a *d* polarization function.[50] The remaining atoms were represented by a 6-31G(d,p) basis set.[51] Full optimization of geometry was performed without any constraint, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima.

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Supporting Information Available: Plots corresponding to Figures 2–5 for each metal–ligand system, thermodynamic cycle for eq showing effect of fluorine substitution on C–C coupling, complete author list for Gaussian03 program, and lists of coordinates for all calculated species. This material is available free of charge via the Internet at http://pubs.acs.org.

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