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Bond energy M–C/H–C correlations: dual theoretical and experimental approach to the sensitivity of M–C bond strength to substituents†

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DFT methods are used to quantify the relationship between M–C and H–C bond energies; for ML$_n$ = Re(η^5-C_5H_5)(CO)$_2$H and fluorinated aryl ligands, theoretical and experimental investigations of *ortho*-fluorine substitution indicate a much larger increase in the M–C than in the H–C bond energy, so stabilising C–H activation products.

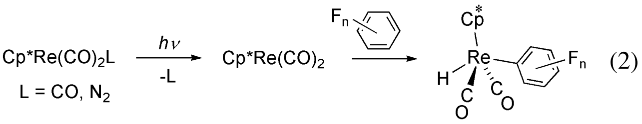
Functionalisation of alkanes or arenes through an oxidative addition/reductive elimination pathway requires the cleavage of the strong C–H bond to give a hydrido–alkyl or a hydrido–aryl intermediate. C–H activation reactions are often very selective for the strongest C–H bonds because of the formation of even stronger metal–carbon bonds.[1] Here we demonstrate the great sensitivity of M–C(aryl) bond dissociation energies (BDE) to fluorine substituents on the bound aryl ring. Moreover, we show that DFT methods offer a predictive way of probing bond energy correlations that is especially valuable considering the dearth of experimental data. BDEs in transition metal complexes are hard to determine by experiment.[2] Often, relative values are obtained for a group of similar complexes through competitive kinetic and/or equilibrium studies [eqn. (1)].

$$L_nM\text{-}X + H\text{-}Y \rightleftharpoons L_nM\text{-}Y + H\text{-}X \qquad (1)$$

Bryndza, Bercaw *et al.*[3] introduced correlations of relative BDE values for L$_n$M–X [Δ*D*(M–X)] with absolute thermochemical BDE values for H–X [*D*(H–X)]. A correlation with slope of 1.0 was obtained for ML$_n$ = Ru(η^5-C_5Me_5)(PMe$_3$)$_2$ and Pt($Ph_2PCH_2CH_2PPh_2$)Me with X = C-, N-, and O-based ligands. The equilibrium constant for eqn.(1) is close to 1.0 and the energies of bonds broken and formed are similar. Bergman, Andersen *et al.* examined NHAr ligands bound to Ni(η^5-C_5Me_5)(PEt$_3$) and found a slope of 1.9.[4] The greater sensitivity of Ni–N bond energies to the aryl substituent was associated with the ionic component of the Ni–N bond.

In the field of C–H bond activation by transition metal complexes, a slope of the Δ*D*(M–C) *vs.* *D*(H–C) line greater than 1.0 has been observed. A good correlation for Δ*D*(Ti–C) *vs.* *D*(H–C) with slope of 1.36 was established for reaction of hydrocarbons with (^{t}Bu$_3$SiO)$_2$Ti(=NSi^{t}Bu$_3$).[5] For Tp′Rh(NC^{t}Bu) [Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate] a plot of Δ*D*(Rh–C) *vs.* *D*(H–C) for R = hydrocarbyl ligands revealed a slope of 1.22.[1] Significant selectivity among these ligands is achieved in bond formation with a strong thermodynamic preference for M–aryl bonds.‡ The trends in metal–carbon bond energies are not well understood and there is great potential for contributions from theory.

Experiments on formation of Rh(η^5-C_5R_5)(PMe$_3$)($C_6H_3F_2$)H with R = H and Me by C–H activation, demonstrated a thermodynamic preference for fluorine to be *ortho* to rhodium.[6] Recently, we have studied the C–H activation reaction of several fluoroarenes by {Re(η^5-C_5Me_5)(CO)$_2$} generated photochemically from Re(η^5-C_5Me_5)(CO)$_3$ and Re(η^5-C_5Me_5)(CO)$_2$(N$_2$) [eqn. (2)].[7] The observed product is either the hydrido-aryl complex or the η^2-arene adduct, depending on the number of F atoms on the phenyl ring. As the number of fluorine substituents increases, the C–H activation product *appears* to become more favoured.



(2)

To gain a better understanding of the reactivity of the fluoroarenes, we have undertaken a systematic study of the hydrido–aryl derivatives for all the possible substitution patterns. The complexes Re(Cp)(CO)$_2$(H)($C_6H_{5-n}F_n$) (n = 0–5, 20 complexes in total, Cp = η^5-C_5H_5, see ESI Table S2†) and associated $C_6H_{6-n}F_n$ were optimised by DFT methods (B3PW91 functional, see ESI†). To estimate the Re–C BDE [*D*(Re–C)] and H–C BDE [*D*(H–C)]), the fragments Re(Cp)(CO)$_2$(H)$^\cdot$ and $C_6H_{5-n}F_n{}^\cdot$ were optimised as spin doublets with unrestricted methods.

In Fig. 1, calculated Δ*D*(Re–C) values (relative to the case n = 0) are plotted against the corresponding calculated *D*(H–C) values. A very good correlation is obtained (r = 0.987) with a slope of 2.25, larger than any observed previously. The method of study has been validated by the agreement between the trends in experimental and calculated BDE (H–C) for a wide range of hydrocarbyl groups and for pentafluorophenyl (see ESI†). For

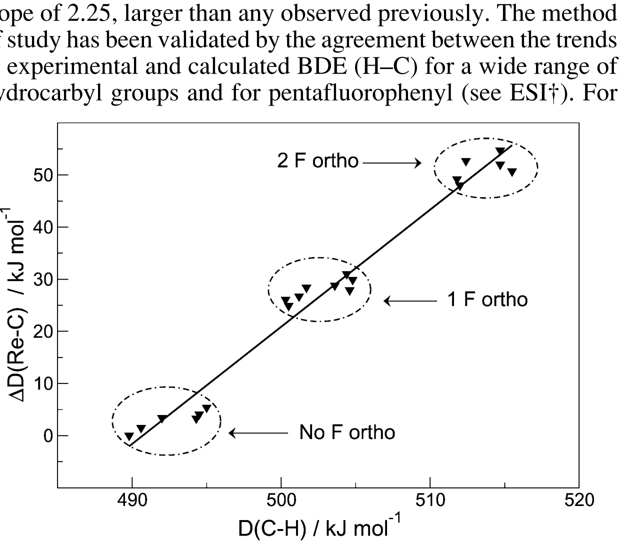


Fig. 1 Plot of bond dissociation energies showing Δ*D*(Re–C) *vs.* *D*(H–C) (kJ mol^{-1}) for Re(Cp)(CO)$_2$(H)($C_6H_{5-n}F_n$) and H–$C_6H_{5-n}F_n$ The value of Δ*D*(Re–C) is taken as zero for n = 0. The slope is 2.25 and the correlation is 0.987.

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† Electronic supplementary information (ESI) available: methods of calculation; Fig. S1: Comparison of calculated and experimental C–H bond dissociation energies for organic molecules; Table S1, comparison of calculated and experimental CO-stretching frequencies; Table S2, total energies, BDE for Re–C and H–C; Table S3, NPA charges *q*(C) and *q*(aryl) for the organic fragments $C_6H_{6-n}F_n$ and the rhenium complexes; preparation and spectroscopic data for Re(η^5-C_5Me_5)(CO)$_2$(2,6-$C_6H_3F_2$)H. See http://www.rsc.org/suppdata/cc/b2/b210036n/

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the organometallic system, the calculations were checked for consistency with crystallographic bond lengths and CO-stretching frequencies (see ESI, Table S1†). We believe that this is the first demonstration of such a correlation of calculated BDE (M–X) with calculated BDE (H–X), a type of correlation that is well established by experiment.

Fig. 1 demonstrates that the position of the fluorine substituents, but not their total number, has a critical influence. Substitution at the *ortho* position increases the energy of the Re–C bond most, resulting in a step pattern. There are three groups of molecules differentiated by the number (0 to 2) of fluorine atoms at the *ortho* position.

Two opposing effects of *ortho*-fluorine substitution are found to be responsible for the slope. The C–H bond increases in strength with F-substitution as a consequence of the destabilising influence of fluorine on the radical $C_6H_{5-n}F_n^{\cdot}$. Thus the *ortho* F-substituted $C_6H_4F^{\cdot}$ is less stable by 10.3 kJ mol^{-1} than the *meta*-substituted isomer. The *para*-substituted species lies only 3.7 kJ mol^{-1} above the *meta*-substituted one (Fig. 2). The F-substituent has a different effect on the Re complexes. The *ortho* F-substituted $Re(Cp)(CO)_2(H)(C_6H_4F)$ is now the most stable system whereas the *meta* and *para* substituted systems follow the energy order of $C_6H_4F^{\cdot}$.

A natural population analysis (NPA)[8] of the total charge distributions, *q*(aryl), on the aryl fragments (sum of all the individual NPA charges for $C_6H_{5-n}F_n$) in the organometallic and organic systems was carried out in order to probe the origin of these results. Like the bond energy, the negative charge on the aryl changes more rapidly in the organometallic than in the organic system.§ A plot (Fig. 3) of Δ*D*(Re–C) as a function of −*q*(aryl) shows a step pattern similar to Fig. 1 indicating that the changes in bond energy are associated with changes in the charge distribution. Furthermore, *ortho* fluorine substitution dominates both the change in bond energy and the change in *q*(aryl). These effects are reminiscent of the increase in bond energy with Pauling electronegativity difference. The importance of the electronegativity difference in influencing the strength of the bond between the two partners has been addressed by Labinger and Bercaw for metal–hydride and metal–alkyl bonds.[9] The increased participation of ionic character in stabilising the M–C bonds agrees with the analysis of their data by Bergman, Andersen and coworkers.[4] Like these authors, we cannot exclude a contribution from π bonding.

In our previous work, we had shown that photolysis of $Re(\eta^5\text{-}C_5Me_5)(CO)_2(N_2)$ in liquid 1,4-difluorobenzene yielded a mixture of $Re(\eta^5\text{-}C_5Me_5)(CO)_2(2,3\text{-}\eta^2\text{-}C_6H_4F_2)$ and the thermodynamically less stable C–H activation product $Re(\eta^5\text{-}C_5Me_5)(CO)_2(2,5\text{-}C_6H_3F_2)H$.[7b] In contrast, the reaction with 2,3,5,6-tetrafluorobenzene yielded only the C–H activation product.[7a] The theoretical results described above led us to predict that the reaction with 1,3-difluorobenzene should yield the 2,6-C–H activation product since this species would benefit from the stabilisation by two *ortho*-fluorines. Accordingly, we irradiated a sample of $Re(\eta^5\text{-}C_5Me_5)(CO)_2(N_2)$ in liquid $1,3\text{-}C_6H_4F_2$. The ^1H and ^{19}F NMR spectra at 253 K showed 85% conversion to a product readily identified as the expected $Re(\eta^5\text{-}C_5Me_5)(CO)_2(2,6\text{-}C_6H_3F_2)H$ (see ESI†). The ^{19}F resonance at low field, *δ* −74.1, is characteristic of fluorines *ortho* to the metal [*cf.* *δ* −83.8 and −122.1 for $Re(\eta^5\text{-}C_5Me_5)(CO)_2(2,5\text{-}C_6H_3F_2)H$]. The IR and mass spectra of the product were also consistent with the identification. It was striking that the η^2-coordination product was not observed.

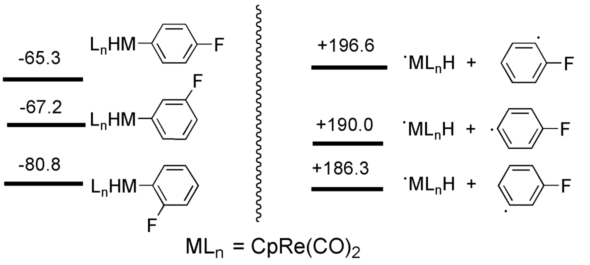

Fig. 2 Influence of site of F substitution on the energies (kJ mol^{-1}) of $Re(Cp)(CO)_2(H)(C_6H_4F)$ (left) and $C_6H_4F^{\cdot}$ (right). The energies are based on ML_n + C_6H_5F as zero. The scales are drawn qualitatively.

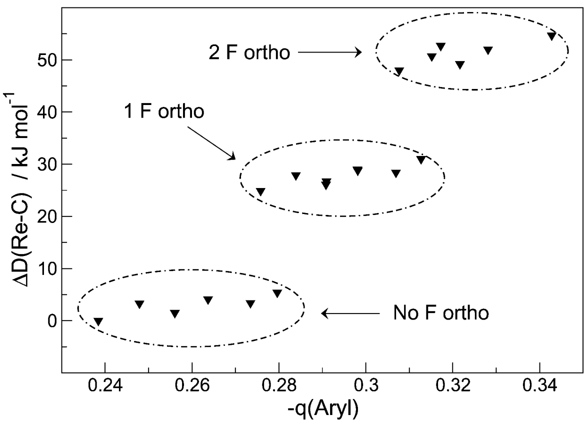

Fig. 3 Relative bond dissociation energies Δ*D*(Re–C) (kJ mol^{-1}) *vs.* total NPA charge on the bound aryl fragment, −*q*(aryl) (see ESI, Table S3†).

Fluorine substituents have been shown to have a much greater influence on a M–aryl bond energy than on the corresponding H–aryl bond energy. The total charge on the aryl fragment appears to be an important factor suggesting that the nature of the metal–ligand fragment, ML_n, may influence the slope. Preliminary calculations with other ML_n fragments in place of d^6 $\{ReCp(CO)_2\}$ reveal similar correlations with slopes varying between 2 and 3.

We have shown that DFT calculations are effective for probing bond energy correlations BDE (M–X) *vs.* BDE (H–X) for X = aryl. When F-substituents are added, H–C bond energies increase, but not nearly as much as the corresponding M–C bond energies. We associate this trend with the observation of C–H bond activation at $\{ReCp^*(CO)_2\}$ with polyfluorinated benzenes but not with benzene.[7,10] The maximum effect calculated for F-substitution is found for two *ortho*-fluorine substituents, leading to the expectation of selective C–H activation that we have confirmed by experiment. The methodology has potential for predictive applications to a wide range of other BDE (M–X) *vs.* BDE (H–X) correlations.

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Notes and references

‡ The contributions of kinetics and thermodynamics to product selectivity are analysed in ref. 1.

§ *q*(aryl) in the organometallic system correlates linearly with *q*(aryl) in the organic molecule (slope = 2.42, *r* = 0.991).

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