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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Electronic Supplementary Information

1 Methods of Calculation

All calculations were performed with Gaussian 98 within the framework of hybrid DFT (B3PW91). (M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, P. I. Komaromi, G. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 98 (Rev A7); Gaussian, Inc.: Pittsburgh, PA, 1998; A. D. J. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **82**, 284.) The rhenium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group (17 valence electrons) and its associated (8s7p5d)/[6s5p3d] basis set, (D.

Andrae, U. Häussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123) supplemented by an *f* polarization function ($\alpha = 0.869$). A 6-31G(*d,p*) basis set was used for the remaining atoms (P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* 1973, **28**, 213). Optimisations of geometry were performed without any constraint and were followed by analytical computation of the Hessian matrix to confirm the nature of the located extrema as minima on the potential energy surface.

2. Comparison of Calculated and Experimental C-H Bond Dissociation Energies ($kJ.mol^{-1}$) for Organic Molecules

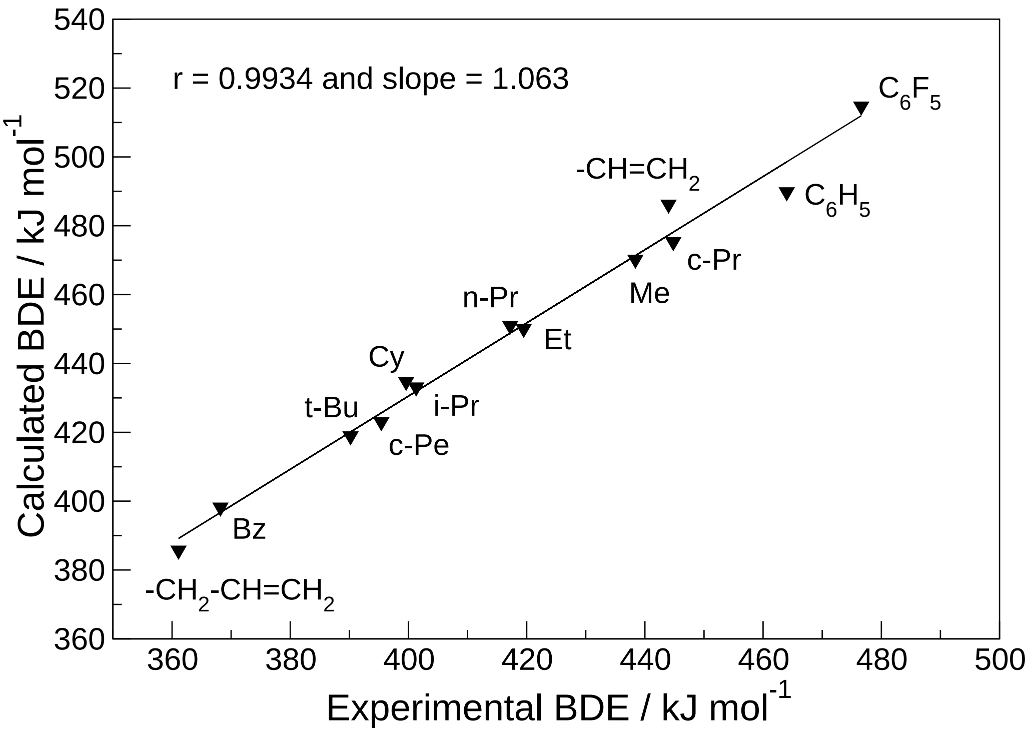

Fig. S1 Comparison of calculated and experimental C-H bond dissociation energies for organic molecules. Experimental values (at 298 K) are taken from the Handbook of Chemistry and Physics, 68th edition (1987).

3. Table S1: Comparison of Experimental and Calculated CO-Stretching Frequencies for $Re(\eta^5\text{-}C_5R_5)(CO)_2(aryl)H$

Aryl	Experiment[a]	Experiment[a]	Theory[b]
	R = Me	R = H	R = H
2,5-$C_6H_3F_2$	1944, 2018[c]		2055, 2116
2,6-$C_6H_3F_2$	1953, 2021		2065, 2118
2,3,5,6-C_6HF_4	1959, 2024[c]	1977, 2040	2069, 2122
C_6F_5	1959, 2024[c]	1978, 2040	2070, 2123

[a] ν/cm^{-1} measured in hexane. [b] Unscaled calculated harmonic frequencies. [c] Data from reference 7.

4. Table S2: Total energies for L_nRe–R, R• and H–R [L_nRe = Re(η^5-C_5H_5)$(CO)_2$(H)] and BDE D(Re-C) and D(H-C). Total energies are in atomic units and BDE values are in kJ mol^{-1}. E[L_nRe•] = –499.070168047 a.u. and E[H•] = –0.5021769355 a.u.

R	L_nReR	R•	R–H	D(Re–C)	D(H–C)
C_6H_5	-730.645511909	-231.479420091	-232.168052261	252.0	489.8
2-C_6H_4F	-829.847619792	-330.672024165	-331.364723327	276.9	500.5
3-C_6H_4F	-829.842440910	-330.675778024	-331.364723327	253.5	490.6
4-C_6H_4F	-829.841725000	-330.674355232	-331.364723327	255.3	494.3
2,6-$C_6H_3F_2$	-929.047805354	-429.863411533	-430.560495708	300.0	512.0
2,5-$C_6H_3F_2$	-929.042550992	-429.866282762	-430.559265311	278.7	501.2
2,3-$C_6H_3F_2$	-929.037528222	-429.861483647	-430.554130193	278.1	500.3
2,4-$C_6H_3F_2$	-929.042962634	-429.866231550	-430.560495708	279.9	504.6
3,5-$C_6H_3F_2$	-929.038410086	-429.871001000	-430.560495708	255.4	492.0
3,4-$C_6H_3F_2$	-929.031369339	-429.863686994	-430.554130193	256.1	494.5
2,3,6-$C_6H_2F_3$	-1028.23582460	-529.051004243	-529.748003217	301.2	511.8
2,4,6-$C_6H_2F_3$	-1028.24215509	-529.056744080	-529.755163380	302.7	515.5
2,3,5-$C_6H_2F_3$	-1028.23188371	-529.054818971	-529.748003217	280.4	501.7
2,3,4-$C_6H_2F_3$	-1028.22580823	-529.048739949	-529.742631247	280.8	503.6
2,4,5-$C_6H_2F_3$	-1028.2309309	-529.053645666	-529.748003217	281.0	504.8
3,4,5-$C_6H_2F_3$	-1028.22015539	-529.051994399	-529.742631247	257.4	495.0
2,3,5,6-C_6HF_4	-1127.42374506	-628.237583567	-628.934836623	304.7	512.4
2,3,4,6-C_6HF_4	-1127.42331737	-628.237429666	-628.935538543	304.0	514.7
2,3,4,5-C_6HF_4	-1127.41320288	-628.235290954	-628.929483074	283.0	504.4
C_6F_5	-1226.60416219	-727.417225353	-728.115344991	306.7	514.7

5. Table S3: NPA charges for the carbon bound to Re, *q(C)*, and for the aryl fragment $C_6H_{5-n}F_n$, *q(aryl)*, in the organic molecules and in the Re complexes.

	organic		**organometallic**	
R	***q(C)***	***q(aryl)***	***q(C)***	***q(aryl)***
C_6H_5	-0.24732	-0.24732	-0.19005	-0.23845
2-C_6H_4F	-0.31844	-0.26201	-0.26930	-0.27579
3-C_6H_4F	-0.23288	-0.25241	-0.18002	-0.25605
4-C_6H_4F	-0.26684	-0.25140	-0.21233	-0.24792
2,6-$C_6H_3F_2$	-0.38803	-0.27667	-0.34575	-0.30769
2,5-$C_6H_3F_2$	-0.30377	-0.26679	-0.25830	-0.29093
2,3-$C_6H_3F_2$	-0.30839	-0.26632	-0.26119	-0.29083
2,4-$C_6H_3F_2$	-0.33732	-0.26583	-0.29054	-0.28390
3,5-$C_6H_3F_2$	-0.21969	-0.25787	-0.17066	-0.27345
3,4-$C_6H_3F_2$	-0.25229	-0.25595	-0.20155	-0.26369
2,3,6-$C_6H_2F_3$	-0.37716	-0.28057	-0.33698	-0.32165
2,4,6-$C_6H_2F_3$	-0.40601	-0.28008	-0.36569	-0.31518
2,3,5-$C_6H_2F_3$	-0.29489	-0.27139	-0.25024	-0.30693
2,3,4-$C_6H_2F_3$	-0.32642	-0.26956	-0.28142	-0.29815
2,4,5-$C_6H_2F_3$	-0.32341	-0.27007	-0.27948	-0.29807
3,4,5-$C_6H_2F_3$	-0.23885	-0.26090	-0.19196	-0.27962
2,3,5,6-C_6HF_4	-0.36762	-0.28505	-0.32962	-0.33672
2,3,4,6-C_6HF_4	-0.39524	-0.28374	-0.35687	-0.32812
2,3,4,5-C_6HF_4	-0.31382	-0.27438	-0.27061	-0.31271
C_6F_5	-0.38601	-0.28809	-0.34926	-0.34277

6. Preparation and Spectroscopic Data for Re(η^5-C_5Me_5)$(CO)_2$(2,6-$C_6H_3F_2$)H

A sample of Re(η^5-C_5Me_5)$(CO)_2(N_2)$ was irradiated for up to 90 min in neat 1,3-$C_6H_4F_2$ in a pyrex NMR tube ($\lambda > 290$ nm) with a medium-pressure Hg arc. The solvent was removed under vacuum and the sample dissolved in hexane (IR spectroscopy), [$^2H_8$]-toluene (NMR spectroscopy), CH_3CN (mass spectrometry).

^{1}H NMR (400 MHz, [$^2H_8$]-toluene, 253 K) δ –8.90 (1H, broad s), 1.66 (15H, s), 6.80 (3H, m). The multiplet was simulated satisfactorily with *g-NMR.*

^{19}F NMR, (376 MHz, [$^2H_8$]-toluene, 253 K) d –74.1 (m).

IR (hexane, ν, cm^{-1}), 2021 (s), 1953 (vs). The IR spectra also showed a small amount of Re(η^5-C_5Me_5)$(CO)_3$ and a product with absorptions at 2003 and 1934 cm^{-1} assigned as Re(η^6-$C_5Me_4CH_2$)$(CO)_2$(2,6-$C_6H_3F_2$) by analogy with previous experiments with pentafluorobenzene.

Mass spectrum, (electrospray, *m/z* –) 489, 491, ($\{M - H^+\}^-$, corresponding to ^{185}Re and ^{187}Re).