Relative M–X bond dissociation energies in 16-, 17- and 18-electron organotransition-metal complexes (X = halide, H)

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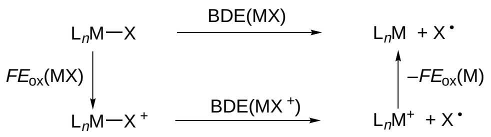
The Fe–halide bonds in Cp*Fe(dppe)X (X = F, Cl, Br, I) complexes are weakened as a consequence of one and two-electron oxidations; the bond weakening decreases in the order F << Cl < Br < I and is much less pronounced for F than the other halides, indicating a pronounced effect of apparent fluoride-to-metal backbonding as a consequence of the removal of electrons.

Knowledge of the nature and energetics of metal–ligand bonding in organotransition-metal complexes is crucial to the understanding of organometallic reactions and catalysis.[1] Recently, the nature of the bonding between organotransition-metal centers and electronegative σ-bonded ligands such as halide, alkoxide, and amido groups has received considerable attention.[2] In addition to forming covalent M–X bonds, these ligands are capable of acting as π donors towards the metal. A ligand p_π to metal d_π electron-pair donation generally serves to destabilize electronically saturated complexes *via* filled–filled repulsive interactions, whereas coordinatively unsaturated species may achieve considerable stabilization through partial π bond formation.[3–9] A substantial line of evidence,[2] including IR ν_{CO} spectroscopy data,[4,5] electrode potentials,[6,10] chemical reactivity,[4,7] and theoretical calculations,[3,4,8] suggests that among the halides, it is the fluoride ligand that is the most efficient electron-pair donor towards the metal.‡

The presence of significant π bonding from halide to metal should be reflected in bond dissociation energy (BDE) changes when this bonding is 'switched on'[3a] by the generation of coordinative unsaturation. To the best of our knowledge, there exist no quantitative data on the homolytic M–X BDEs of metal–halide bonds in closely related pairs of coordinatively saturated (18 electron) and unsaturated (16 electron) species. Here we present the first data concerning the relative M–X bond strengths in 18-, 17- and 16-electron complexes which differ only in their number of valence electrons and thence charge of the central atom. The data establish a pronounced 'fluorine effect', and suggest that a specific electronic or ionic effect of the fluorine is evident already in the 17-electron systems.

Thermochemical cycles that incorporate electrode potential data, introduced by Breslow and Chu,[11] have been frequently used in organic[12] and organometallic[13–15] chemistry to obtain bond-energy data that are not available by direct methods. We have employed this technique to establish a bond-weakening effect of *ca.* 25–33 kJ mol^{-1} when 18-electron metal hydrides were oxidized to their 17-electron cation radicals.[13c,d] Eqn. (1) derived from the thermochemical cycle in Scheme 1, was used to quantify this effect for X = H.

$$\mathrm{BDE(MX)} - \mathrm{BDE(MX^+)} = F[E_{\mathrm{ox}}(\mathrm{MX}) - E_{\mathrm{ox}}(\mathrm{M})] \quad (1)$$



Scheme 1

Scheme 1 is quite general and eqn. (1) can therefore be applied for any other X, and also to evaluate relative BDEs between multiply oxidized species.§ The pertinent 16- and 17-electron species M^+ amd MX^+ are usually so short-lived that electrode potential data, and thereby BDE data, are inaccessible. However, it has been recently demonstrated that the sterically crowded and electron-rich Cp*Fe(dppe) moiety¶ supports metal complexes in a great number of oxidation states, and compounds have been isolated with electron counts ranging from 16 to 19.[16] The persistent 15-electron Cp*Fe(dppe)$^{2+}$ has even been generated in solution.[16d] The Cp*Fe(dppe) derivatives therefore are particularly well suited for the application of thermochemical cycles.

Table 1 summarizes electrochemical data obtained by cyclic voltammetry for the Cp*Fe(dppe)X–Cp*Fe(dppe)X$^+$ and Cp*Fe(dppe)X$^+$–Cp*Fe(dppe)X^{2+} couples for X = H, F, Cl, Br, I. All neutral–monocation redox couples in Table 1 were chemically reversible, near-Nernstian processes (ΔE_p = 67–75 mV). Remarkably, except for X = H, the cation–dication couples were also reversible.

The electrochemical data for these halides constitute the first example of reversible electrode potentials for a complete organometallic L_nMX series (X = F, Cl, Br, I). Interestingly, the reversible oxidation to monocation occurs most readily for the most electronegative halide and becomes progressively more difficult in the series F < Cl < Br < I.[17,18] The trend is the opposite of that predicted on the basis of halide electronegativities alone, and most likely is a manifestation of the importance of apparent π donation from halide to metal. The particularly large jump, > 0.2 V, in the $E°$ value for F relative to Cl and the other halides support the idea that F acts as an exceptionally good donor.‡

The electrochemical data are used in conjunction with eqn. (1) to give the differences in M–X BDEs between Cp*Fe(dppe)X^{n+} complexes when n changes from 0 to 1 to 2. The results are summarized in Table 2. It is important to keep in mind that the data show only the net change in the bond energies caused by oxidation state changes. The data carry no information about

Table 1 Cyclic voltammetry data for the oxidation of Cp*Fe(dppe) derivatives[a]

Compound M	E_1 (M/M$^+$)[b]	E_2 (M$^+$/M^{2+})[b]
Cp*Fe(dppe)[c]	−1.272	−0.290
Cp*Fe(dppe)H	−0.747	0.75[d]
Cp*Fe(dppe)F[e]	−0.824	0.688
Cp*Fe(dppe)Cl	−0.618	0.823
Cp*Fe(dppe)Br	−0.582	0.811
Cp*Fe(dppe)I	−0.540	0.780

[a] THF–0.2 M $NBu_4^+PF_6^-$, T = 20 °C, Pt disk electrode (d = 0.4 mm), voltage sweep rate v = 1.0 s^{-1}. [b] Oxidation potential, V *vs.* $Cp_2Fe–Cp_2Fe^+$. The voltammograms were reversible unless otherwise stated. [c] Measurements were done on Cp*Fe(dppe)$^+PF_6^-$ which, contrary to Cp*Fe(dppe)$^\bullet$, is stable in THF at room temperature. [d] Peak potential for irreversible process. [e] Measurements were performed on Cp*Fe(dppe)F$^{\bullet+}PF_6$ (ref. 19).

Table 2 Relative bond dissociation energies for $\mathrm{Cp^*Fe(dppe)X}^{n+}$ complexes (kJ mol^{-1})[a]

Compound M–X	ΔBDE (MX–MX^+)	ΔBDE (MX^+–MX^{2+})	ΔBDE (MX–MX^{2+})
Cp*Fe(dppe)H	51	100[b]	151[b]
Cp*Fe(dppe)F	43	94	138
Cp*Fe(dppe)Cl	63	107	171
Cp*Fe(dppe)Br	67	106	173
Cp*Fe(dppe)I	71	103	174

[a] Obtained using the data in Table 1 and eqn. (1). [b] Minimum value. The corresponding value for $E_{\mathrm{ox}}(\mathrm{MX}^+–\mathrm{MX}^{2+})$ is a minimum value due to the unknown kinetic potential shift that is imposed by the irreversible nature of this electrode process for X = H.

absolute BDEs. The observed bond energy changes result from the combined σ and π effects.[‡] For all X, overall bond weakening occurs as a consequence of oxidation of the neutral Cp*Fe(dppe)X to their monocations. A further bond weakening, almost twice as large, results when the monocations are oxidized to dications. Thus, the data unambiguously demonstrate that for all X studied, Fe–X bond energies decrease in the order Fe–X > $\mathrm{Fe–X}^{\cdot+}$ > $\mathrm{Fe–X}^{2+}$.

For both oxidation processes, there is a very interesting and obvious trend in the bond activation for the halides. The oxidatively induced bond weakening decreases in the order I > Br > Cl > F and is particularly less pronounced for F than for the other halides. In particular, for the overall two-electron oxidation (which in principle corresponds to the generation of a vacant coordination site) the difference between F and the other halides is > 30 kJ mol^{-1}. It is tempting to attribute this phenomenon to a more efficient donation from F to the metal. This quantity may be viewed as an extra stabilization of the unsaturated 16-electron complex $\mathrm{Cp^*Fe(dppe)X}^{2+}$ that is provided by F, relative to the other halides.

Interestingly, whereas the bond weakening is less pronounced for X = F than for H, a pure σ donor, the opposite is true when Cl, Br and I are compared to H. For a pure σ donor, E_{ox}(MX) should be more positive than for E_{ox}(M) when X is more electronegative than M, and eqn. (1) shows that an oxidation in this case should lead to a weakening of the σ bond. In particular, this situation applies to X = H. For X = F, π donation to the metal is enhanced by the oxidation, and this in part compensates for the σ bond weakening. On the other hand, for X = Cl, Br, and I, a combination of a greater σ bond weakening and a poorer π donation to the metal leads to an overall bond weakening that exceeds even that found for X = H. As noted in the introduction, metal–halide bonding can be rather complex, and we plan to further develop these issues in an extended study that includes theoretical aspects of the Fe–X bonding.[**]

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Notes and References

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[‡] The theoretical results[3b,4,8] imply that π-effects, σ-effects and the ionicity of the M–X bond must all be taken into account when trends in ν_{CO} and other observable parameters are to be explained.

[§] The ΔBDE data obtained from eqn. (1) are in reality free energy based. However, the enthalpic ΔBDE values will be identical to the free-energy ones if ΔS for the top and bottom homolytic processes in Scheme 1 cancel. This will be the case here since M and MX have the same charges and the different X groups are small in comparison to the M fragment. Thus, one might anticipate MX and M to have nearly identical solvation properties. The same applies to MX^+ *vs.* M^+.

[¶] Abbreviations: Cp* = η^5-$\mathrm{C_5Me_5}$; dppe = η^2-$\mathrm{Ph_2PCH_2CH_2PPh_2}$.

[‖] The X-ray crystal structures of $\mathrm{Cp^*Fe(dppe)}^{n+}$ (*n* = 0, 1) have been reported. The cation does not bind THF or counter anion. There was no indication of stabilization by agostic interactions with ligand C–H bonds.[16d]

[**] Preliminary DFT calculations on the halide series indicate that the MX and MX^+ BDEs defined in Scheme 1 include, in addition to the energy necessary to break the M–X bond, a significant component associated with electronic reorganization of the L_nM fragment. However, the reorganization energy barely varies in the halogen series, so that the big jump observed in the ΔBDE values from F to the other halogens is essentially associated with variations on the M–X bond.

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