

Thermodynamic Acidities and Homolytic Metal–Hydrogen Bond Energies of Group 8 Protonated Decamethylmetallocenes Cp^*_2MH^+ ($\text{M}=\text{Ru}, \text{Os}$)

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The first thermodynamic acidities and homolytic metal–hydrogen bond dissociation energies (BDE) of metal-protonated metallocenes in solution are reported. The $\text{p}K_{\text{a}}$ of $\text{Cp}^*_2\text{OsH}^+$ in acetonitrile has been determined as 9.9 ± 0.1 from proton-transfer equilibrium measurements. For $\text{Cp}^*_2\text{RuH}^+$, the $\text{p}K_{\text{a}}$ has been estimated as 4.3 on the assumption that $\text{p}K_{\text{a}}$ differences in acetonitrile are straightforwardly related to differences in the reported heats of protonation of Cp^*_2Os and Cp^*_2Ru in 1,2-dichloroethane. The $\text{p}K_{\text{a}}$ data are used in conjunction with reversible oxidation potential data for the metallocenes to obtain metal–hydrogen BDE values of 284 kJ mol^{-1} for $\text{Cp}^*_2\text{RuH}^+$ and 298 kJ mol^{-1} for $\text{Cp}^*_2\text{OsH}^+$, respectively. The BDE value for $\text{Cp}^*_2\text{RuH}^+$ is essentially equal to that of Cp_2RuH^+ in the gas phase.

The metal–hydrogen bond remains one of the most important ‘functional groups’ in organotransition-metal chemistry. Metal hydrides are commonly involved in stoichiometric and catalytic reactions of great industrial importance.^{1–3} Knowledge about the metal–hydrogen bond strengths are of crucial importance when such processes are to be understood in detail.^{4–8} The metal–hydrogen bond can be envisioned to undergo cleavage either homolytically [eqn. (1)] or heterolytically [eqns. (2) and (3)].

The energy changes of reactions 1 and 2 are available from the metal–hydride homolytic bond dissociation energy (BDE, defined in enthalpy terms) and $\text{p}K_{\text{a}}$, respectively.



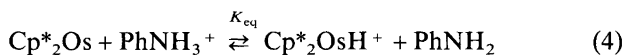
Solution BDE^{4–13} and $\text{p}K_{\text{a}}$ ^{4,11,12,14–20} data for a variety of metal hydrides, as well as heat of protonation data for a series of neutral complexes,^{21–26} have now been accumulated, and allow for systematic trends arising from differences in the nature of the metal and ancillary ligands to be assessed to some extent.

The decamethylmetallocenes Cp^*_2Ru and Cp^*_2Os ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) are known to undergo protonation at the metal to give the cationic hydride complexes $\text{Cp}^*_2\text{RuH}^+$ and $\text{Cp}^*_2\text{OsH}^+$, respectively.²⁷ Angelici and coworkers have reported the heats of protonation (ΔH_{HM}) of the two metallocenes by trifluoromethanesulfonic acid in 1,2-dichloroethane (DCE).²¹ The heats of protonation were $\Delta H_{\text{HM}} = -79.5 \text{ kJ mol}^{-1}$ for Cp^*_2Ru and $-111.3 \text{ kJ mol}^{-1}$ for Cp^*_2Os . The 32 kJ mol^{-1} difference between the two translates into the Os complex being more basic than the Ru one by 5.5 $\text{p}K_{\text{a}}$ units in DCE. As a solvent, DCE offers a clear advantage when such measurements are performed because of its low basicity. This allows for the existence of species more acidic than those that are stable in another solvent commonly used for organometallic compounds, acetonitrile.²⁴ Until now, $\text{p}K_{\text{a}}(\text{MH})$ (acetonitrile) and ΔH_{MH} (DCE) data have not both been available for one single compound. As a result of this lack of a common anchoring point, the large body of available ΔH_{MH} (DCE) data has not yet been firmly related to the $\text{p}K_{\text{a}}$ (acetonitrile) scale, which has been commonly used for the investigation of metal–hydride acidity.^{11,12,14–16} In this paper we provide solution (acetonitrile) $\text{p}K_{\text{a}}$ and BDE data for $\text{Cp}^*_2\text{RuH}^+$ and $\text{Cp}^*_2\text{OsH}^+$.

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Results and discussion

Acidity measurements. The pK_a of $\text{Cp}^*_2\text{OsH}^+$ was determined by measurement of proton-transfer equilibria between Cp^*_2Os and $\text{PhNH}_3^+\text{BF}_4^-$ ($pK_a = 10.6$)²⁸ in acetonitrile [eqn. (4)].



The equilibrium constant was determined from the integrated signal intensities in ^1H NMR spectra in acetonitrile- d_3 . Separate resonances were observed for Cp^*_2Os and $\text{Cp}^*_2\text{OsH}^+$, whereas the resonances due to PhNH_2 and PhNH_3^+ could not be distinguished due to rapid amine proton exchange.[†] The proton-transfer equilibrium constant was estimated making the assumption that $[\text{PhNH}_2] = [\text{Cp}^*_2\text{OsH}^+]$ from the overall mass balance, and resulted in $pK_a(\text{Cp}^*_2\text{OsH}^+) = 9.9 \pm 0.1$ (three measurements, one standard deviation). These results are consistent with a report³⁰ that triethylamine (pK_a 18.5 in acetonitrile)²⁸ and pyridine (pK_a 12.3),²⁸ but not diphenylamine (acetonitrile pK_a not available; expected to be considerably less basic than aniline) causes the deprotonation of $\text{Cp}^*_2\text{OsH}^+$ in dichloromethane.

We anticipated, on the basis of Angelici's work,²¹ that Cp^*_2Ru (5–6 pK_a units less basic than Cp^*_2Os) would not be sufficiently basic for acid/base equilibria to be investigated in acetonitrile. [Norton and co-workers found that $\text{Co}(\text{CO})_4\text{H}$, with pK_a 8.3 in acetonitrile, underwent partial deprotonation in the absence of added bases even in carefully dried acetonitrile].¹⁵ This assumption was corroborated by experiments, and it was seen that not even $p\text{-CF}_3\text{C}_6\text{H}_4\text{NH}_3^+\text{BF}_4^-$ ($pK_a = 8.6$)¹⁵ caused detectable protonation of the substrate. In order to arrive at a reasonable value for the pK_a of $\text{Cp}^*_2\text{RuH}^+$, we relate the pK_a difference in acetonitrile (ΔpK_a) for Cp^*_2Os and Cp^*_2Ru to the difference in heat of protonation in DCE ($\Delta\Delta H_{\text{HM}}$) through $pK_a = -\Delta\Delta H_{\text{HM}}/2.301RT$, or $\Delta pK_a = -\Delta\Delta H_{\text{HM}}/5.70 \text{ kJ mol}^{-1}$ at 25°C. It is an underlying assumption that $\Delta\Delta S_{\text{HM}} = 0$ and that ion-pairing effects play no role or are comparable for the two compounds. The estimated pK_a for $\text{Cp}^*_2\text{RuH}^+$ is then 4.3.[‡]

Determination of M–H bond dissociation energies. Thermochemical cycles of the type that was first introduced by

[†] This suggests that proton transfer to/from the metal centers occurs relatively slowly, whereas proton transfer between nitrogen atoms takes place rapidly, in accord with previous observations.²⁹

[‡] Rottink and Angelici have found²⁴ that a nicely correlated plot of pK_a data for a series of nitrogen bases in acetonitrile vs. ΔH for protonation of the same nitrogen bases in DCE has a slope of 1.52 rather than the theoretically expected slope of 1.36. The source of this deviation is not known; however, if this empirical correlation is used, the pK_a for $\text{Cp}^*_2\text{RuH}^+$ is predicted to be $(9.9 - 7.6/1.52) = 4.9$. The change in the predicted pK_a for $\text{Cp}^*_2\text{RuH}^+$ is therefore small (0.6 pK_a units) due to the modest differences in heats of protonation of Cp^*_2Ru and Cp^*_2Os .

Breslow³¹ employing electrode potential data have found widespread use for the indirect determination of thermochemical data that are not available by more direct methods.^{32–34} Equation (5) shows the relationship between the BDE and pK_a of a cationic metal hydride MH^+ , when the oxidation potential of the metal hydride conjugate base is known.^{10–12,35}

$$\text{BDE}(\text{MH}^+) = 5.70pK_a(\text{MH}^+) + 96.48E_{\text{ox}}(\text{M}) + C \quad (5)$$

The magnitude of the constant term C depends on the particular solvent and reference electrode used for the measurements and equals 249 kJ mol^{-1} when measurements are performed in acetonitrile with the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ (Fc) couple as the reference.¹⁰ The value for C has been obtained by two different methods and gives results that agree well with data obtained by other techniques when reversible electrode potentials are available.¹⁰

Figure 1 shows cyclic voltammograms for the oxidation of Cp^*_2Ru and Cp^*_2Os (1.0 mM) in acetonitrile/0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$ at a voltage sweep rate $\nu = 1.0 \text{ V s}^{-1}$ (25°C, $d = 0.6 \text{ mm}$ Pt disc electrode). The voltammograms establish that compounds Cp^*_2Ru and Cp^*_2Os undergo oxidations at $E = 0.122$ and -0.055 V vs. Fc , respectively. (It has previously been reported that the reversible, one-electron oxidations occur at 0.55 V vs. SCE for Cp^*_2Ru ³⁶ and at 0.46 V vs. SCE for Cp^*_2Os ,³⁷ both in dichloromethane). The reversible potentials are taken as the midpoints between the cathodic and anodic peak potentials. Repeated measurements on independently prepared solutions were reproducible to within $\pm 2 \text{ mV}$. A close inspection of the CV trace for Cp^*_2Ru

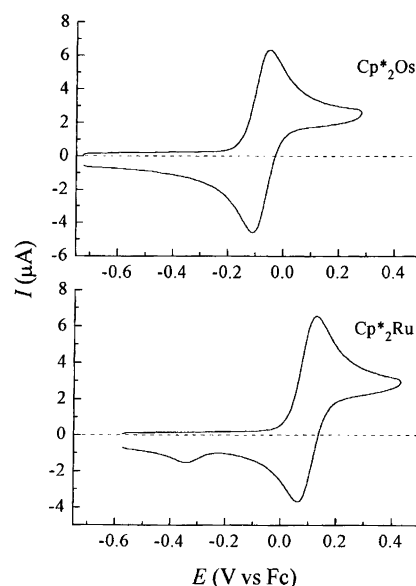
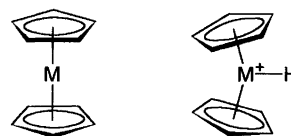


Fig. 1. Cyclic voltammograms for the oxidation of Cp^*_2Ru and Cp^*_2Os . Experimental conditions: 1.0 mM substrate in acetonitrile/0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$, Pt disc electrode ($d = 0.6 \text{ mm}$), voltage sweep rate $\nu = 1.0 \text{ V s}^{-1}$, 25°C.

reveals that the electrode reaction is not fully reversible in the chemical sense. A minor, cathodic wave is seen at $E = -0.38$ V vs. Fc on the reverse scan. The relative intensity of this wave was greater at $v = 0.1$ V s⁻¹, supporting the notion that the wave is caused by a product arising from a relatively slow (on the measurement time scale) reaction of Cp*₂Ru⁺ in acetonitrile. The nature of this process has not been further investigated, but we suspect that the product may be Cp*₂Ru(NCMe)²⁺, produced either by solvent-assisted³⁸ oxidation or disproportionation of the cation radical. The product wave was not detected in dichloromethane. No analogous wave was seen during the oxidation of Cp*₂Os, even at sweep rates as low as 0.1 V s⁻¹.

The BDE(MH⁺) data can now be determined from eqn. (5) for M = Cp*₂Ru (284 kJ mol⁻¹) and Cp*₂Os (298 kJ mol⁻¹). Table 1 summarizes the heat of protonation, pK_a(MH⁺), E_{ox}(M), and BDE(MH⁺) data.

A few estimates of M–H BDEs are available for organoruthenium hydrides. Using the thermochemical cycle [eqn. (5)] we have earlier estimated the Ru–H BDE for CpRu(CO)₂H to be 272 kJ mol⁻¹,¹⁰ estimates of Ru–H BDEs for CpRu(PR₃)₂(H)₂⁺ derivatives depend on assumptions made for conversions of pK_a data from one solvent to the other but fall in the approximate range 300–320 kJ mol⁻¹.^{13,19} The gas-phase Ru–H BDE of the unmethylated ruthenocene hydride Cp₂RuH⁺ has been estimated first as 331 ± 21 kJ mol⁻¹ by ion-cyclotron resonance measurements,³⁹ but was later refined to 271 ± 21 kJ mol⁻¹.⁷ Gas-phase and solution-phase BDE data for organic compounds RH are usually quite similar, since solvation enthalpies of RH and R⁺ species tend to cancel and the enthalpy of solvation of H⁺ amounts to only ca. 4 kJ mol⁻¹.⁴⁰ We therefore conclude that because bond-energy differences are well within the experimental uncertainties, the Ru–H BDE of Cp₂RuH⁺ is not significantly different from that of Cp*₂RuH⁺. It has been previously seen that permethylation of the Cp ring leads to a slight increase in Cr–H BDEs from CpCr(CO)₃H (257 kJ mol⁻¹) to Cp*Cr(CO)₃H (261 kJ mol⁻¹).⁹ One might have anticipated a somewhat destabilizing effect arising from permethylation of ruthenocene because protonation at the metal center forces a bending of the planar neutral sandwich complex to give a 'bent sandwich' cation (Scheme 1). The permethylation of the ring would introduce a steric repulsion disfavoring the bent structure. However, the experimental data suggest that this is not the case. Steric repulsions were previously seen¹² to de-



Scheme 1

stabilize considerably the M–H bonds in Tp*M(CO)₃H relative to TpM(CO)₃H (M = Mo, W; Tp = hydridotris(pyrazolyl)borate; Tp* = hydridotris(3,5-dimethylpyrazolyl)borate).

In summary, we have reported the first pK_a and BDE data for protonated metallocenes in solution. These data will serve as an anchor for the determination of absolute BDE values for a number of metal hydrides for which heat of protonation data are already available.⁴¹

Experimental

All manipulations involving organometallic compounds were carried out under an atmosphere of purified nitrogen or argon. Acetonitrile was distilled first from P₂O₅ and then from CaH₂, and acetonitrile-*d*₃ was freshly distilled from CaH₂. Acetonitrile containing 0.1 M Bu₄N⁺PF₆⁻ as the supporting electrolyte was used as solvent for the electrochemical measurements and was passed through a column of active neutral alumina before use to remove water and protic impurities. The electrolyte was freed of air by purging with solvent-saturated, purified argon, and all measurements were carried out under a blanket of solvent-saturated argon.

Electrochemical measurements were performed with an EG&G-PAR model 273 potentiostat/galvanostat driven by an external HP 3314A sweep generator. The signals were fed to a Nicolet 310 digital oscilloscope and processed by an on-line personal computer. The working electrode was a Pt disc electrode ($d = 0.6$ mm), the counter-electrode was a Pt wire, and the Ag wire reference electrode assembly was filled with acetonitrile/0.01 M AgNO₃/0.1 M Bu₄N⁺PF₆⁻. The reference electrode was calibrated against Cp₂Fe, which is also used as the reference in this work. The positive-feedback *iR* compensation circuitry of the potentiostat was employed; the separation of anodic and cathodic peaks for the Cp₂Fe oxidation was 59–61 mV in acetonitrile at a voltage scan rate $v = 1.0$ V s⁻¹.

Table 1. Thermodynamic data for some metallocene derivatives.

MH ⁺	–ΔH(MH ⁺)/kJ mol ⁻¹	pK _a (MH ⁺)	E _{ox} (M)/V vs. Fc	BDE(MH ⁺)/kJ mol ⁻¹
Cp* ₂ RuH ⁺	79.5	4.3	0.122 ^a	284
Cp* ₂ OsH ⁺	111.3	9.9	–0.055 ^b	298
Cp ₂ RuH ⁺				271 ^a

^a Gas-phase measurements from Ref. 7.

^1H NMR spectra were recorded on a Varian-Gemini 200 instrument. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standard ($\delta = 1.93$ for acetonitrile- d_3).

Cp^*_2Ru and Cp^*_2Os were kindly provided by Professor Angelici. $\text{PhNH}_3^+\text{BF}_4^-$ was prepared from freshly distilled PhNH_2 and $\text{HBF}_4\cdot\text{Et}_2\text{O}$ in ether.

*Determination of the pK_a of Cp^*_2Os in acetonitrile- d_3 .* A solution of $\text{PhNH}_3^+\text{BF}_4^-$ (ca. 1 mg) and Cp^*_2Os (3–4 mg; saturated solution) in acetonitrile- d_3 (1 mL) was filtered through celite and transferred to an NMR tube which was equipped with a ground-glass joint. The tube was attached to the vacuum line and sealed under vacuum. The ^1H NMR spectrum showed that the proton-transfer equilibrium [eqn. (4)] was established, and the pK_a of $\text{Cp}^*_2\text{OsH}^+$ was determined from eqn. (6).

$$\Delta pK_a = pK_a(\text{MH}^+) - pK_a(\text{baseH}^+) = \log\left(\frac{[\text{base}][\text{MH}^+]}{[\text{baseH}^+][\text{M}]}\right) \quad (6)$$

Separate signals due to Cp^*_2Os ($\delta = 1.60$, Cp^*) and $\text{Cp}^*_2\text{OsH}^+$ ($\delta = 1.96$, Cp^* ; -15.5 , OsH) were observed. Owing to rapid proton transfer involving PhNH_2 and PhNH_3^+ , an averaged spectrum was observed. The assumption was made that $[\text{PhNH}_2] = [\text{Cp}^*_2\text{OsH}^+]$. Measurements on three independently prepared solutions resulted in $\Delta pK_a = 0.7 \pm 0.1$. Taking $pK_a(\text{PhNH}_3^+) = 10.6$ (Ref. 6) results in $pK_a(\text{Cp}^*_2\text{OsH}^+) = 9.9 \pm 0.1$.

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Note added in proof. The interpretation of the minor peak in the cyclic voltammogram of Cp^*_2Ru as arising from the reduction of $\text{Cp}^*_2\text{Ru}(\text{NCMe})^{2+}$ has been confirmed by a recent report on the electrochemistry of Cp^*_2Ru and analogues.⁴²

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