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Electrochemistry of $Ru_2Cp'_2(CO)_4$ and $Ru_2Cp_2(CO)_3(PMe_3)$ and the estimation of $Ru_2(\mu\text{-}H)$ bond dissociation enthalpies☆

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Dedicated to Professor R.J. Angelici on the occasion of his 65th birthday.

Abstract

The oxidation potentials for a series of diruthenium compounds have been measured. The heat of protonation ($-\Delta H_{MHM}$) and oxidation potentials ($E_{1/2}$) for a series of $Ru_2Cp'_2(CO)_4$ ($Cp' = Cp_2$, Cp^*_2, $C_5H_4CH_2C_5H_4$, $(C_5H_4CH_2)_2$, $(C_9H_7)_2$, $C_{10}H_8$, $(HBpz_3)_2$) compounds and $Ru_2Cp_2(CO)_3(PMe_3)$ were used to estimate the homolytic Ru–H–Ru bond dissociation enthalpy (BDEs) using a thermochemical cycle. Poor correlation between $-\Delta H_{MHM}$ and $E_{1/2}$ was observed, as anticipated, due to the effects of the bridging carbonyls on the heats of protonation. There is a correlation between the oxidation potentials and the average ν_{CO} bands for the protonated dimers as both are a measurement of the donor ability of the ligands. The calculated BDE values were also compared with values obtained for mononuclear ruthenium compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemistry; Bridging hydride; Bond dissociation enthalpy; Ruthenium

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1. Introduction

The activation of hydrogen often plays a key role in homogenous and heterogeneous catalysis [1]. Because of this, the thermodynamic properties of transition metal hydrides are of great interest. In many catalytic systems involving metal hydrides, metal–hydrogen bonds are continuously being formed and broken. Understanding the factors that influence metal–hydrogen bond strength will aid in the design of more efficient catalysts. Metal–metal bonded systems are also interesting because they serve as small molecule models of metal surfaces [2]. While many transition metal compounds are known to form terminal hydrides, bridging hydrides are known to form in complexes with more than one metal center. Bond dissociation enthalpy (BDE) estimations can aid in understanding the factors that influence bridging hydride bond strength (Fig. 1).

Previously, BDEs have been calculated for terminal transition metal hydrides [3]. Using the thermochemical cycle (Scheme 1) proposed by Tilset [4], the determination of the BDE required two separate measurements. First, the heat of protonation ($-\Delta H_{MH}$) for the neutral compound was measured using triflic acid in 1,2-dichloroethane (DCE) (Eq. (1)).

$$L_nM + CF_3SO_3H \overset{DCE}{\rightarrow} L_nMH^+ + CF_3SO_3^- \quad (1)$$

Then, the oxidation potential ($E_{1/2}$) for the neutral species was measured by cyclic voltammetry and square wave voltammetry (Eq. (2)). This measurement was straightforward with systems that showed completely reversible oxidation waves.

$$L_nM \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} L_nM^{+\cdot} \quad (2)$$

$$\text{DCE}$$

However, systems with irreversible oxidation required approximation of the $E_{1/2}$ values [3,4]. The combination of these results enabled the calculation of the BDE. The previous study found that for most series of transition

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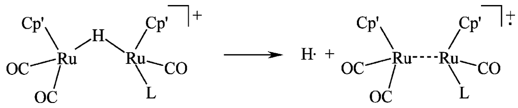
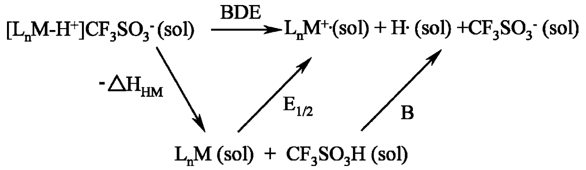


Fig. 1. BDE for a cationic bridging hydride.



Scheme 1. Thermochemical cycle.

metal compounds, the BDE increased with increasing $-\Delta H_{MH}$ values [3]. It was also found that, for compounds with the same ligands, the BDE increased with increasing atomic mass of the metal atom.

There is limited data on the basicities of transition metal complexes containing metal–metal bonds, although a few studies have compared the acidity of these compounds. Bridging hydrides were found to be more acidic than terminal hydrides [5], and replacing CO ligands with phosphites decreased the acidity of bridging hydrides [6]. The basicity of a series of cyclopentadienyl ruthenium carbonyl dimers has been determined [7,8]. The donor ability of the ligands and the bonding of the carbonyl ligands affect the basicity of the ruthenium dimers. Bridging carbonyl ligands greatly reduced the observed basicity.

In this paper, the oxidation potentials for a series of ruthenium dimers are reported. These potentials were measured by cyclic voltammetry using a Pt electrode in DCE solvent. Most of the dimers displayed irreversible oxidation, so approximations of the $E_{1/2}$ values were made. With the oxidation potentials and the previously reported heats of protonation [7,8], the BDEs for the bridging hydrides were estimated. The BDEs for these dimeric species are compared with monomeric ruthenium systems. From this, we compare the influence of ligands on dimeric systems and how bridging hydride BDEs relate to terminal hydrides.

2. Results and discussion

Cyclic voltammetry was used to determine the oxidation potentials for the ruthenium dimers. The potentials reported versus the $Fc^{0/+}$ couple (Table 1) were indirectly obtained by the addition of decamethylferrocene [9]. In accordance with the previous study, data are reported at a scan rate of 0.1 V s^{-1} and the standard relationship between $Fc^{0/+}$ and the saturated calomel reference electrode (SCE) was used to report the oxidation potential versus SCE [3]. The oxidation of $Cp^*_2Ru_2(CO)_4$ showed a quasi-reversible wave followed by a broad irreversible one at 0.534 V versus $Fc^{0/+}$ (Fig. 2). If the potential is switched before the second wave, the first wave was completely reversible (I_r/I_f 0.9 at 100 mV s^{-1}). The oxidation of $(C_5H_4CH_2)_2Ru_2(CO)_4$ showed a quasi-reversible wave followed by a broad irreversible wave at 0.688 V versus $Fc^{0/+}$. A completely reversible wave could not be obtained for this dimer by any means available. The irreversible wave of $Ind_2Ru_2(CO)_4$ (Ind = η^5-C_9H_7) was the only other dimer to display a second oxidation wave which occurred at 1.069 V versus $Fc^{0/+}$. The dimers $Cp_2Ru_2(CO)_4$ and $Tp_2Ru_2(CO)_4$ (Tp = hydrotris(pyrazolyl)borate) showed only one quasi-reversible wave at all scan rates. The remaining compounds in this study displayed one irreversible oxidation.

There are relatively few studies of the electrochemistry of $Cp'_2Ru_2(CO)_4$ compounds. The reported studies of $Cp_2Ru_2(CO)_4$ have focused primarily on the reductive electrochemistry [10]. The electrochemical oxidation of $Cp_2Ru_2(CO)_4$ occurs at 0.37 V versus $Fc^{0/+}$ in THF [11]. The oxidation is irreversible under these conditions, but there are no details as to how many electrons are transferred or what products form. The dimer can be oxidized chemically with two equivalents of Ag^+ and, when done in acetone, yield $CpRu(CO)_2(Me_2CO)^+$ [12]. A thorough investigation of the oxidation of $Tp_2Ru_2(CO)_4$ has been performed [13]. In CH_3CN, the oxidation is irreversible at all scan rates. In methylene chloride, the oxidation is quasi-reversible. In both cases, $Tp_2Ru_2(CO)_4^+$ is proposed as an intermediate. In CH_3CN, this intermediate is further oxidized and then reacts with the solvent to give two equivalents of $TpRu(CO)_2MeCN^+$. This process is much slower in methylene chloride. Only at very high scan rates ($v > 25$ V s^{-1}) was a second irreversible oxidation wave seen which was attributed to the formation of $Tp_2Ru_2(CO)_4^{2+}$. The oxidation of $FvRu_2(CO)_4$ (Fv = $C_{10}H_8$) has been investigated in a variety of coordinating solvents [14]. The oxidation is irreversible and estimated to be a two electron process. The study encountered significant complications due to 'filming' of the electrode.

The iron analogs with Cp and Cp* have been studied in more detail. In coordinating solvents, an ECE mechanism is proposed [15]. In this mechanism a radical cation, $Cp_2Fe_2(CO)_4^+$, is formed. This is quickly attacked by the solvent to yield $Cp_2Fe_2(CO)_4(sol)^+$ which dissociates to give the final oxidation product $CpFe(CO)_2(sol)^+$ and $CpFe(CO)_2$. The $CpFe(CO)_2$ is either oxidized followed by coordination of a solvent molecule to give $CpFe(CO)_2(sol)^+$, or two radicals couple to regenerate the starting material. The electrochemistry of $Cp_2Fe_2(CO)_4$ and $Cp^*_2Fe_2(CO)_4$ in methylene chloride is quite different; two oxidation waves are seen. The first is quasi-reversible and has been determined to be formation of the radical cation,

Table 1
Oxidation potentials, heat of protonation, BDE and average ν_{CO} of ruthenium dimers

Dimer	$E_{1/2}$ [$Fc^{0/+}$] (V)	$E_{1/2}$ [SCE] (V)	$-\Delta H_{MHM}$ (kcal mol^{-1})	BDE (kcal mol^{-1})	Average ν_{CO} (cm^{-1})
Reversible					
$Cp^*_2Ru_2(CO)_4$	−0.046	0.544	19.2 [b]	65.0	2019 [b]
Quasi-reversible					
$Cp_2Ru_2(CO)_4$	0.317	0.907	18.4 [b]	72.6	2046 [b]
$(C_5H_4CH_2)_2Ru_2(CO)_4$	0.304	0.894	16.9 [b]	70.8	2045 [b]
$Tp_2Ru_2(CO)_4$	0.188	0.778	16.6 [b]	67.8	2039 [b]
Irreversible					
$FvRu_2(CO)_4$	0.498	1.088	16.1 [b]	74.5	2055 [b]
$(C_5H_4CH_2C_5H_4)Ru_2(CO)_4$	0.299	0.889	21.0 [b]	74.8	2048 [b]
$Cp_2Ru_2(CO)_3(PMe_3)$	−0.156	0.427	30.0 [a]	73.1	2001 [a]
$Ind_2Ru_2(CO)_4$	0.350	0.940	14.1 [b]	69.1	2046 [b]

[a] Reference [7].
[b] Reference [8].

$Cp'_2Fe_2(CO)_4^+$. This radical cation had been proposed, but it was not characterized until methylene chloride was used as the solvent. The second wave is irreversible due to cleaving the dimer to form $Cp'Fe(CO)_2^+$ which will coordinate the supporting electrolyte anion or any adventitious water.

The Ru dimers seem to follow a mechanism similar to that of the Fe analogs. The first oxidation wave can be attributed to formation of the dimeric radical cation. As seen in Fig. 2, this process is completely reversible if the follow up reactions are slow and/or additional oxidation of the dimer is avoided. At the scan rate required for this study, these two complications could not be avoided in most cases. Even though the potential is switched before any additional dimer oxidation can occur, the first oxidation of $Tp_2Ru_2(CO)_4$ is reported to be quasi-reversible at 1.0 V s^{-1} [13]. Therefore, it is not surprising that the compounds in this study display quasi-reversible and irreversible waves.

By determining the number of electrons transferred during the oxidation of the dimers, additional evidence for the formation of a radical cation can be provided. Chronoamperometry and Eq. (3) [16] were utilized to determine the number of electrons removed during the oxidation of the Cp* dimer. The S_c term is given by the plot of current versus $t^{-1/2}$, as determined by chronoamperometry, where the slope is equal to S_c. Likewise, the S_v term is given by a plot of current versus scan rate$^{1/2}$, as determined by CV. The F term is Faraday's constant, and the k term is $0.4463F^{3/2}(RT)^{-1/2}$. This calculation yielded an n value of 1.05 electrons. An approximation can also be made by comparing the current height of the dimer oxidation to that of a standard. Addition of an equal molar amount of Fc* gave a wave of the same amplitude. This was true for all of the dimers in this study.

$$n = (2FS_v/^{TM^{1/2}}kS_c)^2 \qquad (3)$$

Although $FvRu_2(CO)_4$ is reported to be a two electron process, those studies were done in coordinating solvents [14]. The oxidation potential reported in that study was 0.50 V versus $Fc^{0/+}$, very similar to our

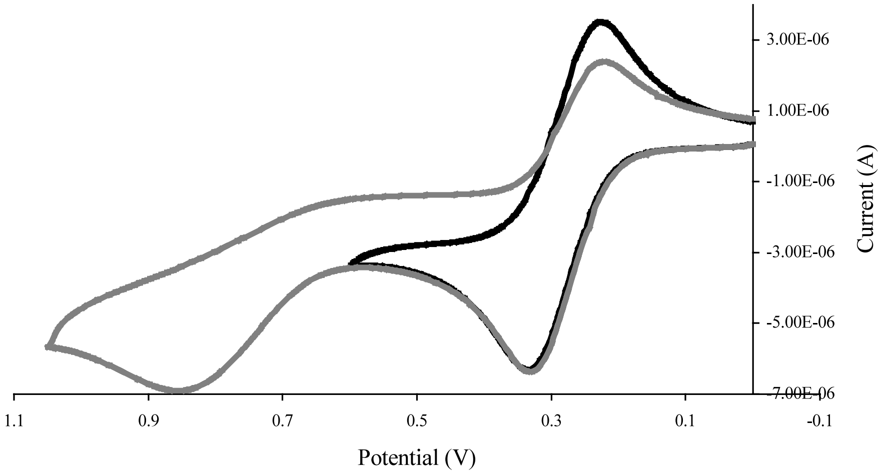


Fig. 2. Oxidation at 100 mV s^{-1} of $Cp^*_2Ru_2(CO)_4$ with different switching potentials.

results. Even though the results are nearly identical, the oxidation in this study is likely to be a one electron process. As mentioned previously, the electrochemistry of $Cp_2Fe_2(CO)_4$ and $Cp^*_2Fe_2(CO)_4$ is different in coordinating and non-coordinating solvents [15]. Coordinating solvents facilitate oxidation of the cation to a dication capable of undergoing follow-up reactions. However, the first oxidation wave occurs at similar potentials in coordinating and non-coordinating solvents. For $Cp_2Fe_2(CO)_4$ the wave in CH_3CN occurs at 0.55 V and the first wave in CH_2Cl_2 occurs at 0.68 V. The potentials are nearly identical for $Cp^*_2Fe_2(CO)_4$, 0.33 V in CH_3CN and 0.34 V in CH_2Cl_2. Therefore, it is not surprising that the oxidation potential determined for $FvRu_2(CO)_4$ in this study should occur at a similar potential to the oxidation in coordinating solvents.

The oxidation potentials reported (Table 1) are $E_{1/2}$ values for the reversible and quasi-reversible systems. Some of the oxidations were irreversible, so approximations were made. The $E_{1/2}$ values can be estimated by finding the potential at 85% of the anodic current [17]. This was done for all of the irreversible systems. The calculation was also performed with the reversible and quasi-reversible systems. The estimated values agreed within ± 0.010 V of the measured values. While this does not prove that this estimation technique is that precise, it does appear that the estimations of $E_{1/2}$ are reasonable.

The oxidation potentials determined in this study display trends related to electronic effects of the ligands. As expected, Cp* is more electron donating than Cp, so the oxidation potential of the Cp* dimer is 0.363 V less positive than that of the Cp dimer. Another example is $Cp_2Ru_2(CO)_3(PMe_3)$; the phosphine ligand is more electron donating than a CO ligand, and, therefore, lowers the oxidation potential by 0.45 V compared with $Cp_2Ru_2(CO)_4$. Conversely, in comparing the Cp dimer with $Ind_2Ru_2(CO)_4$, the oxidation potential only increases by 0.033 V. The donor ability of the Ind ligand versus the Cp ligand has been compared by determination of the heats of protonation of $CpIr(CO)(PPh_3)$ and $IndIr(CO)(PPh_3)$ [18]. The heat of protonation for both compounds is 21.2 kcal mol^{-1}, and given the very small change in the oxidation potential of the Ru dimers it can be assumed that both ligands are similar in electron donating ability. The IR bands of the carbonyl ligands can be a useful means of comparing the electron density at the metal center in a series of compounds. This comparison is complicated in this case by the presence of different isomers, no bridging carbonyls versus two bridging carbonyls, in solution. To avoid this complication, the average ν_{CO} of the $Cp'_2Ru_2(CO)_3LH^+$ has been used [8]. In these compounds, all of the carbonyl ligands are terminal. A plot (Fig. 3) of the previously reported average IR bands versus the oxidation potentials show a reasonable correlation.

The bond dissociation enthalpies of the compounds were calculated based on the previously derived Eq. (4) [3], using the heat of protonation data [7,8] and the

$$\mathrm{BDE(M{-}H^+)} = -\Delta H_{\mathrm{HM}} + 23.06E_{1/2} + 3.3\ \mathrm{kcal\ mol^{-1}} \qquad (4)$$

oxidation potentials versus SCE (Table 1). There is no trend between the oxidation potentials and BDE. The BDE values for the dimers all fall within a fairly narrow range between 65.0 and 74.8 kcal mol^{-1}. The range of BDE values (ca. 10 kcal mol^{-1}) is somewhat lower than the range seen in the heats of protonation for the dimers (16 kcal mol^{-1}). This suggests that the heat of protonation and the oxidation potential of the compound contribute equally to the value of the BDE, as the oxidation potential has a similar variation range (15.2 kcal mol^{-1}).

An estimate of the overall error for the BDE calculation can be determined from the error in ΔH_{MHM} and $E_{1/2}$. The average deviation from the mean reported for the heat of protonation values is no greater than $\pm$ 0.4 kcal mol^{-1} [7,8]. The error associated with the electrochemistry is somewhat more problematic because many of the dimers display irreversible waves. The $E_{1/2}$ values for the irreversible systems could be affected by chemical and/or electrode kinetics [19]. These differences could be 200 mV (4.6 kcal mol^{-1}) or greater [3]. Overall, the uncertainty in the BDE calculations for the irreversible systems will be dominated by the error associated with the electrochemistry. This error somewhat blurs the meaning of the BDE values, but the similarity of all of the BDE values suggests that the approximation is reasonable.

The BDE estimates for these dimeric species are complicated by theoretical structural changes that may occur in forming the diruthenium products (Fig. 1). The first consideration is the degree of Ru–Ru bonding in the protonated dimers. The structures of three protonated dimers have been determined [7,8]. The Ru–H–Ru angle in these three structures are all ca. 120°. This angle implies a ‘closed’ structure that allows close approach of the metal centers and significant overlap between their orbitals [20]. Therefore, removing a hydrogen atom from this system will not require the formation of a metal–metal bond as the two metal centers interact in the protonated dimer. The second consideration is the formation of bridging carbonyls. The spectroelectrochemistry of $Cp_2Fe_2(CO)_4$ shows that there are either bridging or semi-bridging carbonyl ligands in $Cp_2Fe_2(CO)_4^+$ [15]. It is reasonable to anticipate that bridging or semi-bridging carbonyls will be found for some of the oxidized dimers. Since all of the protonated compounds exclusively contain terminal carbonyl ligands, this rearrangement will affect the overall energetics of the system. A future study will

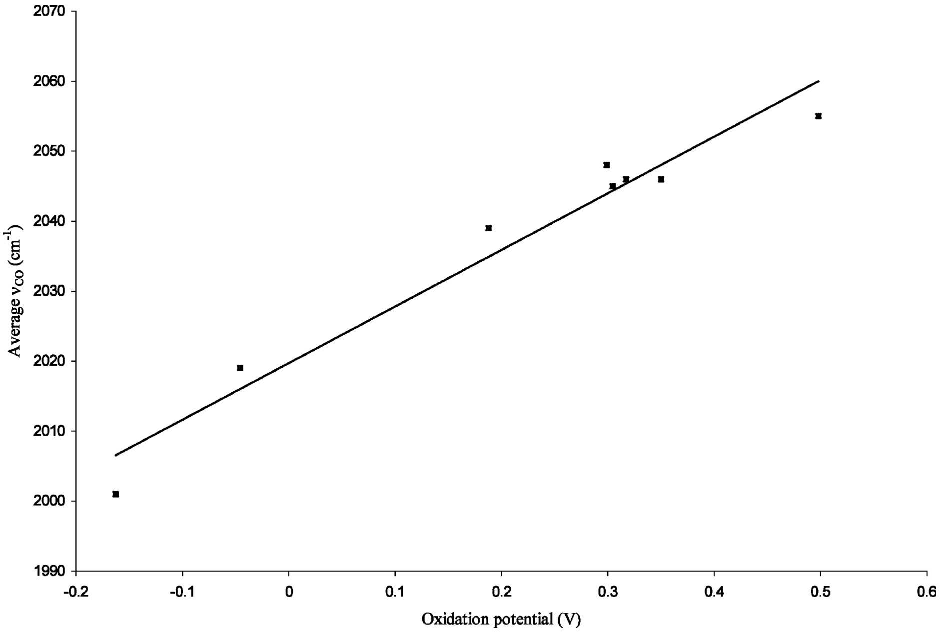


Fig. 3. Comparison of $E_{1/2}$ values of $Cp_2'Ru_2(CO)_3L$ and the average ν_{CO} bands for $Cp_2'Ru_2(CO)_3LH^+$ ($R^2 = 0.9551$).

investigate the spectroelectrochemistry of the dimers known to have bridging carbonyl ligands in solution.

Previous studies of mono-metallic Ru compounds found that the BDEs had a narrower range of 65–70.7 kcal mol^{-1}, a difference of 5.7 kcal mol^{-1} [3,21]. Our values bracket these values for monometallic compounds. While there are subtle differences in BDE values due to ligand effects and metal oxidation states, there does not appear to be a substantial difference when comparing terminal hydride and bridging hydride BDEs. Comparing $Cp_2Ru_2(CO)_4H^+$ with $CpRu(CO)_2H$ is particularly interesting. Using Eq. (5), the BDE of $CpRu(CO)_2H$ was calculated to be 65 kcal mol^{-1} [21]. The BDE of

$$\mathrm{BDE} = 1.37\mathrm{p}K_a + 23.06E^0_{ox} + 58.3 \quad (5)$$

$Cp_2Ru_2(CO)_4H^+$ is estimated to be 7.6 kcal mol^{-1} greater than $CpRu(CO)_2H$, suggesting that it requires more energy to break the terminal Ru–H bond than the bridging Ru–H–Ru.

There are no discernable trends showing the effect of Cp* versus Cp on M–H BDEs. For the series $Cp'Ir(CO)(PR_3)$ (Cp′ = Cp or Cp*, R = Me or Ph), the Cp* compounds were found to be more basic, have less positive oxidation potentials and have lower BDEs then the analogous Cp compounds [3]. The BDE of $Cp^*Cr(CO)_3H$ is slightly higher than that of $CpCr(CO)_3H$, while the opposite ordering was found for the molybdenum analogs [21]. In this study, it seems the Cp dimer has a higher BDE then the Cp* analog. A comparison can also be made between Cp and Tp. In comparing $CpMo(CO)_3H$ and $TpMo(CO)_3H$, the Cp compound has higher wavenumber ν_{CO} in the IR, is more basic and has the higher BDE [4g]. The same trends are also noted for these ruthenium dimers.

Despite the correlation between ligand and steric effects and the oxidation potential, there is no correlation between the heat of protonation (basicity) and the oxidation potentials. A plot of oxidation potential versus heat of protonation shows no discernible trend. This is not surprising as the protonation is affected by the distribution of isomers in the starting compounds [8]. To be protonated, all bridging carbonyls must be converted to terminal. This step will require energy, thus decreasing the measured heat of protonation. Therefore, electronic effects on the heat of protonation are not as well defined in dimeric systems as they are in monomeric systems. Spectroelectrochemical studies have shown that $Cp_2Fe_2(CO)_4^+$ has bridging carbonyl ligands [15]. The ruthenium dimers in this study may not undergo significant structural rearrangement upon oxidation, thus showing a correlation between donor ability and oxidation potential.

Likewise, there was no linear correlation between the BDE and heat of protonation. This is expected, as the BDE depends upon both the $-\Delta H_{MHM}$ and the oxidation potentials. Since there is no trend between the oxidation potential and heat of protonation, there should be no trend between the oxidation potential or heat of protonation and the BDE. For mononuclear systems, a general trend is that the oxidation potential increases as heat of protonation decreases, and that the BDE increases as the heat of protonation increases [3]. Neither of these trends is observed in this study.

3. Experimental

All preparative reactions and purifications were carried out under an atmosphere of argon using standard Schlenk techniques. DCE, HPLC grade from Aldrich, was purified using standard techniques [22] and distilled from P_4O_{10} under argon immediately before use.

The preparation of the ligand precursors, $C_{12}H_{12}$ [23], $C_{11}H_{12}$ [24], and $C_{10}H_{10}$ [25], were carried out according to literature methods. Dicyclopentadiene, pentamethylcyclopentadiene, indene, diphenylacetylene, trimethylphosphine (1.0 M in toluene), and tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) were purchased from Aldrich. Ruthenium dodecacarbonyl, potassium hydrotris-pyrazoylborate, ferrocene, and decamethylferrocene were purchased from Strem. Dicyclopentadiene was cracked over iron filings prior to use [26]. Ferrocene was sublimed prior to use and $Bu_4N^+PF_6^-$ was dried *in vacuo*. All other chemicals were used without additional purification. The dimers $Cp_2Ru_2(CO)_4$ [26], $Cp^*_2Ru_2(CO)_4$ [27], $(C_5H_4CH_2C_5H_4)Ru_2(CO)_4$ [28], $Ind_2Ru_2(CO)_4$ [29], $Tp_2Ru_2(CO)_4$ [30], $(Fv)Ru_2(CO)_4$ [25], $(C_5H_4CH_2)_2Ru_2(CO)_4$ [8], $Cp_2Ru_2(CO)_2(COC_2Ph_2)$ [31] and $Cp_2Ru_2(CO)_3(PMe_3)$ [7] were prepared according to literature methods.

Electrochemical studies were performed utilizing a Cypress Systems, Inc. Omni-101 potentiostat and the accompanying software. Solutions of the analyte were 1.0 mM in 5.00 ml of DCE solvent, and contained 0.1 M $Bu_4N^+PF_6^-$ as the supporting electrolyte. Solutions were purged with argon and stirred prior to studies in order to avoid interference by O_2, and measurements were taken immediately after solution preparation. Scans were made with rates from 50 to 1000 mV s^{-1}, however all oxidation potentials are reported at a scan rate of 100 mV s^{-1}. The 1 mm Pt working electrode was polished with 1 μm diamond paste for 2 min, rinsed with acetone and then polished with 1/4 μm diamond paste for 2 min. Prior to use the electrodes were rinsed thoroughly with DCE. A platinum wire counter electrode was used along with a non-aqueous silver–silver chloride reference electrode.

4. Conclusion

This study investigated the electrochemical oxidation of a series of ruthenium dimers. The dimers undergo a one electron oxidation forming a radical cation. As seen in related iron dimers [15], these radical cations can undergo additional electrochemical and chemical processes. Overall, the oxidation potentials of the dimers tended to follow the ligand donor ability of the various ligands. The oxidation potentials were used to estimate the BDE values for the protonated dimers. The BDE values for the compounds fell within a range of 10 kcal mol^{-1}, which suggests that variations in the heat of protonation and oxidation potentials partially cancel each other out. However, there was no correlation between the heat of protonation and oxidation potentials observed, as was expected due to the effect of carbonyl ligands on the heat of protonation. There was also no correlation between the oxidation potential and the BDE due to the influence of the heat of protonation on the BDE calculation.

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