Direct solution calorimetric measurements of enthalpies of proton and electron transfer reactions for transition metal complexes. Thermochemical study of metal–hydride and metal–metal bond energies ☆

Gabor Kiss, Steven P. Nolan [1], Carl D. Hoff *

Department of Chemistry, University of Miami, Coral Gables, FL 33124, USA

Abstract

Enthalpies of reaction with sodium amalgam, sodium benzophenone ketyl, and metal carbonyl anions of organometallic complexes in THF solution have been measured. Relative to reduction with Na metal, the following enthalpies of reduction (kcal mol^{-1}) are reported: benzophenone = -38.5, $Cr(CO)_2(PEt_3)C_5H_5 = -54.3$, $Cr(CO)_2(PPh_3)C_5H_5 = -59.8$, $1/2[Mo(CO)_3C_5Me_5]_2 = -59.9$, $1/2[W(CO)_3C_5H_5]_2 = -61.7$, $1/2[Mo(CO)_3C_5H_5]_2 = -63.5$, $Cr(CO)_2(P(OMe)_3)C_5H_5 = -64.4$, $1/2[C_5H_5(CO)_3Mo-Cr(CO)_3C_5H_5] = -66.1$, $1/2[Cr(CO)_3C_5H_5]_2 = -68.2$, $Cr(CO)_3C_5Me_5 = -72.3$, $Cr(CO)_3C_5H_5 = -75.6$, $1/2Co_2(CO)_8 = -77.9$. The value for the enthalpy of reduction of benzophenone is 14.5 kcal mol^{-1} more exothermic than recent literature data. The enthalpies of electron transfer and proton transfer between $NaCr(CO)_2C_5H_5$ and other chromium radicals and hydrides have been measured and span about 20 kcal mol^{-1}. These measurements are used in thermochemical cycles to calculate enthalpies of H atom transfer. The role of substituents in determining enthalpies of reaction relevant to electrochemical and pK_a measurement enthalpies of reaction is discussed. The heat of hydrogenation of $Mn_2(CO)_{10}$ has been determined using calorimetrically determined enthalpies of H atom transfer. The heat of hydrogenation, $+4$ kcal mol^{-1} in THF, allows estimation of the Mn–H bond strength = 68 kcal mol^{-1}.

Keywords: Calorimetry; Enthalpy; Proton transfer reactions; Electron transfer reactions; Metal–metal bond energies; Metal hydrides

1. Introduction

The majority of reported organometallic calorimetric studies have focused ont the thermochemical examination of oxidation reactions. Several years ago, the thermochemistry of metal–metal and metal–alkyl complexes [1] was investigated in our laboratory using iodination reactions similar to the earlier solution calorimetric work of Blake [2]. Iodometric titrations have been used by Marks and co-workers [3] to investigate lanthanide and actinide thermochemistry. While this is a very useful approach, in several instances, iodination and other oxidative reactions gave undesirable side

products and could not be used for calorimetric measurements [1]. At that time search for calorimetric techniques relying on reductive rather than oxidative reactions was initiated. In this paper we report results on direct measurements of enthalpies of electron transfer and proton transfer in transition metal systems.

The energetics of organometallic reactions can be studied by a number of physical techniques. Equilibrium spectroscopic techniques, such as those applied by Bor and co-workers [4], have added many valued insights into the factors governing stability of di- and polynuclear metal carbonyls. A requirement which can limit the applicability of equilibrium techniques is that they are restricted to reactions which have measurable equilibrium constants over a suitable temperature range if thermodynamic parameters are to be obtained. Free energy, equilibrium, and kinetic measurements of acid–base proton transfer reactions of metal carbonyl

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hydrides have been studied by Norton and co-workers [5]. A wide range of pK_a values has been determined as a function of the metal and its substituents. Electrochemical measurements on transition metal complexes, including metal dimers and hydrides, have been performed by a number of research groups [6]. In both of these cases the data yield free energies of reaction which cannot be easily resolved into enthalpic and entropic components. Calorimetric measurements can provide direct data on enthalpies of reaction and provide a complementary approach to equilibrium and free energy measurements.

Thermochemical cycles relating acidities, electron affinities and bond strengths have a long history in organic and inorganic thermochemistry. A representative cycle is shown in Eq. (1):

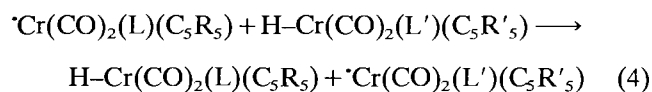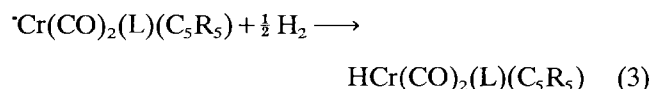$$M–H \xrightarrow{i} M^{\cdot} + H^{\cdot} \xrightarrow{ii} M^{-} + H^{+} \quad (1)$$
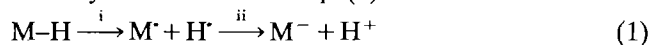
The net reaction in Eq. (1) (corresponding to acid dissociation) is the sum of the first two steps (i: single bond cleavage, ii: electron transfer to M$^{\cdot}$ plus ionization of H$^{\cdot}$). In terms of enthalpies of reaction:

$$\Delta H_{pK_a} = \Delta H_{BDE} + \Delta H_{EA\ metal} + \Delta H_{IP} \quad (2)$$

Cycles of this type have been extensively used in gas phase studies [7]. Tilset and Parker [8] have recently evaluated M–H single bond strengths in solution based on electrochemical and pK_a data. Pugh and Meyer [9] have used related arguments for metal–metal bond strength determinations. Arnett et al. [10] and Bordwell et al. [11] have reported related cycles in organic chemistry.

The chromium centered radicals $^{\cdot}Cr(CO)_2(L)(C_5R_5)$ [12] are stable in solution and provide a basis for detailed analysis of substituent effects on metal complex thermochemistry. In an earlier paper we reported enthalpies of hydrogenation and hydrogen atom transfer as shown in Eqs. (3) and (4) [13].

$$^{\cdot}Cr(CO)_2(L)(C_5R_5) + \tfrac{1}{2} H_2 \longrightarrow$$

$$HCr(CO)_2(L)(C_5R_5) \quad (3)$$

$$^{\cdot}Cr(CO)_2(L)(C_5R_5) + H–Cr(CO)_2(L')(C_5R'_5) \longrightarrow$$

$$H–Cr(CO)_2(L)(C_5R_5) + {}^{\cdot}Cr(CO)_2(L')(C_5R'_5) \quad (4)$$

In this work direct calorimetric measurements of enthalpies of electron transfer and proton transfer are made for a range of transition metal systems. The use of reductive rather than oxidative reactions is well suited to organometallic complexes and provides a new method for investigation of the driving forces governing their reactivity.

2. Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk tube/glove box tech-
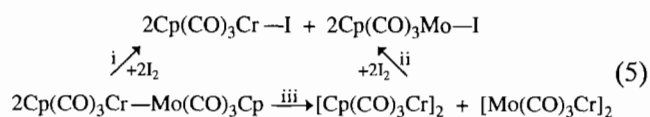
niques. Solvents were purified by distillation from Na$^+$ benzophenone$^-$ under argon into flame dried glassware. IR spectra were recorded on a Perkin-Elmer 1850 FTIR in a sealed liquid cell with Ge windows obtained from Harrick Scientific, Ossining, NY. Use of CaF$_2$ or KBr windows resulted in slow decomposition of some of the highly reactive reagents. Calorimetric measurements were made in stainless steel cells using a Setaram C-60 Calvet calorimeter, or in an all glass Guild isoperibol calorimeter as described in detail elsewhere [1]. Since Na/Hg experiments have not been reported by us before, a typical procedure is described below. All other measurements were made using techniques and methods described in detail previously [1].

2.1. Enthalpy of reaction of Na/Hg with benzophenone

A dilute solution of Na/Hg amalgam (about 1%) was prepared under argon and taken into the glove box. THF was freshly distilled under argon atmosphere from Na$^+$benzophenone$^-$ ketyl into a flame dried Schlenk tube. In the glove box some of the amalgam was transferred to the THF solution. Prior to withdrawing the THF for experiments it was vigorously shaken with the amalgam to insure no water or peroxides were present. The lower chamber of the calorimeter cell was filled with approximately 0.04 g benzophenone that had been purified by vacuum sublimation. The cell was sealed with 2 ml of the Na/Hg amalgam and then about 4 ml of THF was added. The cell was closed in the glove box, and then loaded into the calorimeter. After waiting for thermal equilibration, the calorimetry run was initiated by rotation of the calorimeter. During the reactions, the calorimeter was rotated continuously to insure good mixing of the solution and the amalgam. Data reported is the average of five separate experiments.

3. Results and discussion

The goal of this work was to develop accurate methods for measuring the enthalpies of reduction of organometallic complexes. It originated in efforts to obtain enthalpies of metal–metal metathesis. Madach and Vahrenkamp [14] measured the qualitative equilibrium positions for metal–metal bond metathesis, and found that in most cases a near statistical distribution existed showing little preference for homonuclear or heteronuclear products. For a few complexes, most notably those of the –Cr(CO)$_3$Cp and –Co(CO)$_4$ fragments, however, the heteronuclear products were favored. Attempts to measure quantitatively the enthalpies of these reactions were begun using the scheme illustrated in Eq. (5) for the mixed Cr–Mo complex.

$$2Cp(CO)_3Cr-I + 2Cp(CO)_3Mo-I$$

$$\nearrow^{i}_{+2I_2} \qquad \qquad +2I_2\nwarrow^{ii} \qquad (5)$$

$$2Cp(CO)_3Cr-Mo(CO)_3Cp \xrightarrow{\;iii\;} [Cp(CO)_3Cr]_2 + [Mo(CO)_3Cr]_2$$

If accurate enthalpies of iodination could be measured for the homonuclear (i) and heteronuclear (ii) dimers it would allow determination of the enthalpy of the metal–metal bond metathesis reaction (iii). Unfortunately, it became clear that side products occurred in these reactions, even when using a deficiency of iodine as oxidant.

Since oxidation reactions, such as that shown in Eq. (5) were not successful, a program of reductive calorimetry was begun. Initially this was begun by use of sodium amalgam as reductant. Thus the well known synthetic use of this reagent proceeds as shown in Eq. (6).

$$Cp(CO)_3Cr-Mo(CO)_3Cp \xrightarrow{Na/Hg}$$

$$NaCr(CO)_3Cp + NaMo(CO)_3Cp \quad (6)$$
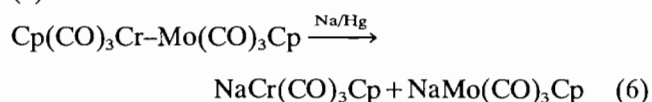
Measurement of the enthalpy of reaction (6), as well as the enthalpy of reduction of $[Cp(CO)_3Cr]_2$ and $[Cp(CO)_3Mo]_2$ would allow evaluation of the metal–metal bond metathesis reaction by a thermochemical cycle similar to that shown in Eq. (5) but with Na/Hg reduction serving to replace oxidation with I_2.

One problem encountered during this work was defining accurately the thermodynamic state of the 'Na/Hg' shown in Eq. (6). The free energies of formation of sodium amalgam are known over a reasonable range [15] and the free energy of reaction (7) is near -19.5 kcal mol^{-1} for a range of sodium concentrations near 1–3%:

$$Na(s) + Hg(l) \longrightarrow Na/Hg(l) \qquad (7)$$
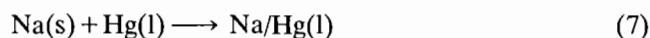
Enthalpies of dilution are small, and *provided the same Na/Hg products were obtained in all reductions*, these would cancel out in any cycle used to calculate the enthalpy of an organometallic reaction. A more significant problem is the visible formation of small amounts of black colloidal Hg. Provided a sufficient amount of Na is present in the amalgam to fully reduce the organometallic complex, formation of soluble Hg complexes can be avoided in most cases. However the enthalpy of formation of the Na/Hg at the end of the reaction could conceivably vary from that calculated based on handbook values. Doubts about the composition of the dark colloidal particles caused us to delay publication of this work until a suitable means of checking the results could be found.

During this time, a report appeared by Stevenson and Hashim on the first measurement of the enthalpy of reduction of benzophenone and related aromatic systems [16]. This work was based on iodination reactions

such as that shown in Eq. (8).

$$2Na^+benzophenone^- + I_2 \longrightarrow$$

$$2NaI + 2benzophenone \quad (8)$$
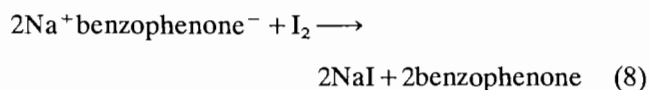
Measurement by Stevenson and Hashim of the enthalpy of reaction (8), and its use in a thermochemical cycle lead to calculation of the enthalpy of reduction of benzophenone by sodium metal is shown in Eq. (9) to be -24.0 ± 1.7 kcal mol^{-1}.

$$Na(solid) + benzophenone(THF) \longrightarrow$$

$$Na^+benzophenone^-(THF) \quad (9)$$
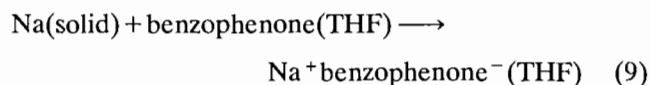
Initial testing of the Na/Hg amalgam technique was performed by direct measurement of the enthalpy of reduction as shown in Eq. (10).

$$Benzophenone(THF) \xrightarrow{Na/Hg}$$

$$Na^+benzophenone^-(THF) \quad (10)$$
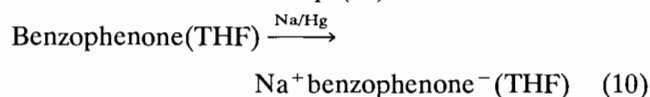
The enthalpy of reaction (10), as measured directly, was -17.9 ± 0.6 kcal mol^{-1}. Combined with an estimate for the enthalpy of formation of Na/Hg [17] of -18.5 kcal mol^{-1}, leads to calculation of a value of -36.4 kcal mol^{-1} for reduction of benzophenone if the more thermochemically active reductant sodium is used as shown in Eq. (9).

The large discrepancy between this result and that of Stevenson and Hashim cast doubt on the amalgam method, and it was abandoned in spite of having made a number of measurements of enthalpies of reduction by it. To avoid the problems of working with Na/Hg, or Na$^+$benzophenone$^-$, metal carbonyl anions were used to measure enthalpies of reduction. As discussed later, the data reported by Stevenson and Hashim appear to be in error, and the earlier amalgam data were in fact correct within experimental error.

This paper describes results of these reductive calorimetric experiments, and illustrate their potential use in calculating thermochemical data. Extension of these techniques as a means to map the thermochemistry of organometallic complexes is in progress.
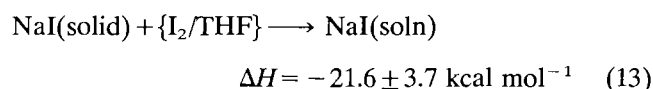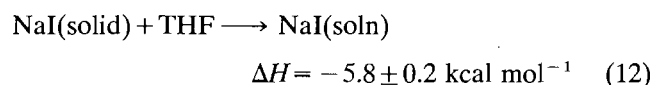
3.1. Revised enthalpy of reduction of benzophenone by sodium

The work of Stevenson and Hashim [16] mentioned earlier reported an experimental value for the enthalpy of reaction (8) of $\Delta H = -102.4\pm2.4$ kcal mol^{-1}. In an attempt to determine the source of error in our Na/Hg reductions mentioned above, the enthalpy of iodination of Na$^+$benzophenone$^-$, reaction (8) was measured and we obtained a value of -72.8 ± 0.6 kcal mol^{-1}. An apparent disagreement of 29.6 kcal mol^{-1} with the reported enthalpy of reaction (8). There was one difference in how the two experiments were per-
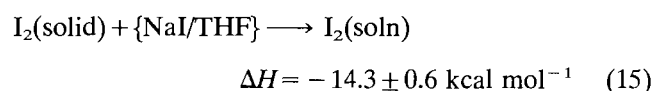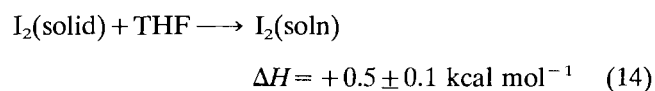
formed. Stevenson and Hashim's measurements [16] were reported by breaking ampoules of Na^+benzophenone$^-$ *into a solution of excess I_2*. Our experiments were done breaking an ampoule of I_2 *into a solution of excess Na^+benzophenone$^-$*. The reason for the differences in the two enthalpies of reaction proved to be the heat of solution of the two moles of NaI generated in the reaction. In the presence of excess I_2, the NaI produced reacts to form equilibrium amounts of NaI_3 [18].

$$NaI(soln) + I_2(soln) \rightleftharpoons NaI_3(soln) \quad (11)$$
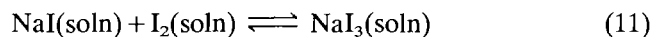
The exothermic nature of formation of the triiodide was verified by two methods. Measurements of the enthalpy of solution of NaI in THF and in I_2/THF, and measurements of the enthalpy of solution of I_2 in THF and in NaI/THF: Measurements were made at concentrations similar to those used in the earlier measurements [16].

$$NaI(solid) + THF \longrightarrow NaI(soln)$$

$$\Delta H = -5.8 \pm 0.2 \text{ kcal mol}^{-1} \quad (12)$$

$$NaI(solid) + \{I_2/THF\} \longrightarrow NaI(soln)$$

$$\Delta H = -21.6 \pm 3.7 \text{ kcal mol}^{-1} \quad (13)$$

The enthalpy of solution of NaI is 15.8 ± 3.9 kcal mol^{-1} more exothermic in the presence of I_2, due to the formation of equilibrium amounts of NaI_3. There was a relatively high experimental error in these measurements due to the slow rate of solution of NaI in THF. Molecular iodine dissolves more rapidly in THF than does NaI. To obtain a more accurate value for the enthalpy of reaction (11), we measured the enthalpy of solution of I_2 in pure THF and in NaI/THF.

$$I_2(solid) + THF \longrightarrow I_2(soln)$$

$$\Delta H = +0.5 \pm 0.1 \text{ kcal mol}^{-1} \quad (14)$$

$$I_2(solid) + \{NaI/THF\} \longrightarrow I_2(soln)$$

$$\Delta H = -14.3 \pm 0.6 \text{ kcal mol}^{-1} \quad (15)$$

Subtraction of Eq. (14) from Eq. (15) yields a value of -14.8 ± 0.7 kcal mol^{-1} for Eq. (11). Since two moles of NaI are produced in Eq. (7), we would predict that there should be a difference of 29.6 ± 1.4 kcal mol^{-1} between our measurement and that of Stevenson and Hashim [16]. That is in agreement with their results and indicates that no errors were made in the calorimetry of Stevenson and Hashim, but that the enthalpy of solution of NaI used did not correspond with that observed in the actual experiment. Due to the equilibrium nature of formation of the triiodide, it would be expected that the enthalpy of solution of NaI in THF would depend strongly on the concentration of free I_2 in solution. Similar effects can occur if differing

amounts of trace water are present and it is always advisable to measure enthalpies of solution under the actual experimental conditions. This is especially true when dealing with ionic complexes in non-aqueous solvents; associative reactions and properties can be sources for large errors. Using thermochemical cycles and data from Stevenson and Hashim we obtain a value of -38.5 ± 0.6 kcal mol^{-1} for the enthalpy of reduction of benzophenone by sodium in THF according to Eq. (9). That value is in reasonable accord with the calculated value based on the Na/Hg method of -36.4 ± 2.6 kcal mol^{-1} and provides a basis for placing organometallic complexes on an absolute scale relative to sodium as discussed in the next section. There does not appear to be any significant intrinsic error in the amalgam method, however the iodination result has greater precision and is in agreement with the reported work [16], once it has been adjusted for the heat of solution of NaI in I_2/THF. In spite of making numerous calorimetric experiments based on amalgam chemistry, other reducing agents discussed below have proven to yield more precise results and this paper will not discuss the amalgam data further except to note that where comparisons could be made it was found to agree within 10% with the other data. The use of sodium amalgam to seal the Calvet cell is a novel approach, and could find use in situations where other reducing agents cannot be utilized.

3.2. Enthalpy of reaction of Na^+benzophenone$^-$ with transition metal carbonyl complexes

Blue solutions of Na^+benzophenone$^-$ react rapidly and quantitatively with metal carbonyl radicals and dimers to generate the corresponding metal carbonyl anions. Experimental enthalpies of reactions such as those shown in Eq. (16) below are collected in Table 1.
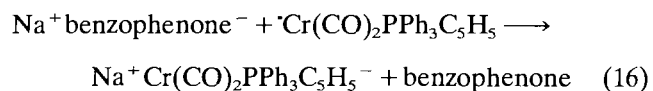
$$Na^+benzophenone^- + {}^{\cdot}Cr(CO)_2PPh_3C_5H_5 \longrightarrow$$

$$Na^+Cr(CO)_2PPh_3C_5H_5{}^- + benzophenone \quad (16)$$

Table 1
Enthalpies of reaction with Na^+benzophenone$^-$: Na^+benzophenone$^- + {}^{\cdot}M \xrightarrow[THF]{30\ ^{\circ}C} Na^+M^- + benzophenone$

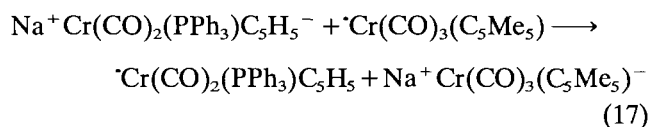| Metal complex	ΔH (kcal mol^{-1})
$Cr(CO)_2(PPh_3)C_5H_5$	-21.3 ± 0.6
$Cr(CO)_2(P(OMe)_3)C_5H_5$	-26.0 ± 0.7
$Cr(CO)_3(C_5Me_5)^a$	-31.9 ± 0.9
$Cr(CO)_3(C_5H_5)^a$	-35.1 ± 0.9
$\frac{1}{2}Co_2(CO)_8{}^b$	-37.4 ± 2.6

^{a} Experimental data is for mixtures of dimer and radical, reported data for enthalpies of dissociation [13] have been used to calculate enthalpy of reduction per mole of monomeric radical.
^{b} Data reported per mole of reaction: $\frac{1}{2}Co_2(CO)_8 + Na^+$benzophenone$^- \rightarrow NaCo(CO)_4$.

In addition to reduction of the chromium centered radicals, reduction of dicobalt octacarbonyl was also measured as shown in Table 1. These data provide relative values for enthalpies of electron transfer in THF and can be placed on an absolute basis relative to Na metal by addition of the value for the enthalpy of reduction of benzophenone by sodium (38.5 ± 0.6 kcal mol^{-1} as discussed above).
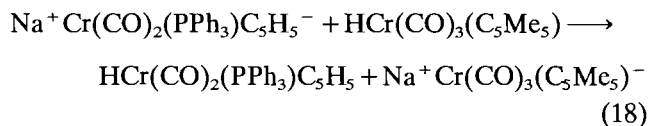
3.3. Enthalpy of reaction of $NaCr(CO)_2(PR_3)C_5H_5$ with transition metal carbonyl complexes

Reduction of Na$^+$benzophenone$^-$ allowed determination of the enthalpy of formation of the chromium centered anions shown in Table 1. Direct reactions of these transition metal anions with other metal radicals were measured as shown in Eq. (17).
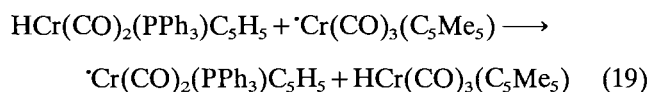
$$Na^+Cr(CO)_2(PPh_3)C_5H_5^- + \cdot Cr(CO)_3(C_5Me_5) \longrightarrow$$

$$\cdot Cr(CO)_2(PPh_3)C_5H_5 + Na^+Cr(CO)_3(C_5Me_5)^-$$
$$(17)$$

The phosphine substituted anion [Cr(CO)$_2$(PPh$_3$)-C$_5$H$_5$]$^-$ was especially useful since the radical produced from it can be quantitatively determined using FT-IR spectroscopy, and shows no tendency towards formation of metal–metal bonded dimers. Enthalpies of electron transfer as shown in Eq. (17) were measured in several combinations between the various Cr centered radicals shown in Table 2. All values refer to the enthalpies of reduction of the free radicals in THF and where necessary have been corrected to adjust for any residual metal–metal bonded complex present. They span a range of over 21 kcal mol^{-1} from Cr(CO)$_2$(PEt$_3$)C$_5$H$_5$ (least stable anion) to Cr(CO)$_3$(C$_5$H$_5$) (most stable anion).

In addition to measuring the enthalpies of electron transfer as shown in Eq. (17), enthalpies of proton transfer were also measured as shown in Eq. (18).

$$Na^+Cr(CO)_2(PPh_3)C_5H_5^- + HCr(CO)_3(C_5Me_5) \longrightarrow$$

$$HCr(CO)_2(PPh_3)C_5H_5 + Na^+Cr(CO)_3(C_5Me_5)^-$$
$$(18)$$

These data are collected in the second column of Table 2. Data are based on reactions of both Na$^+$Cr(CO)$_2$(PPh$_3$)C$_5$H$_5^-$ and Na$^+$Cr(CO)$_2$(PEt$_3$)-C$_5$H$_5^-$ and also span nearly 20 kcal mol^{-1}.

The accuracy of these data can be verified by using the scheme in Eqs. (1) and (2) and calculating enthalpies of hydrogen atom transfer. Subtraction of Eq. (18) (proton transfer) from Eq. (17) (electron transfer) yields directly Eq. (19) (H atom transfer).

$$HCr(CO)_2(PPh_3)C_5H_5 + \cdot Cr(CO)_3(C_5Me_5) \longrightarrow$$

$$\cdot Cr(CO)_2(PPh_3)C_5H_5 + HCr(CO)_3(C_5Me_5) \quad (19)$$

Thus the values reported in the first two columns of Table 2 are used to calculate enthalpies of H atom transfer in the third column. These data have been independently measured, and are shown in parentheses in the third column of Table 2. There is good agreement with previously published experimental measurement of enthalpy of atom transfer [13], giving additional confidence to these measurements.

A second verification route relies on the comparison of relative values in Table 2 to those in Table 1. Electron transfer enthalpies based on the Na$^+$benzophenone$^-$ data in Table 1 show the following stabilities relative to Cr(CO)$_2$(PPh$_3$)C$_5$H$_5$: Cr(CO)$_2$P(OMe)$_3$C$_5$H$_5$ = 4.7 ± 1.3; Cr(CO)$_3$C$_5$Me$_5$ = 10.6 ± 1.5; Cr(CO)$_3$C$_5$H$_5$ = 13.8 ± 1.5. Stabilities relative to Cr(CO)$_2$(PPh$_3$)C$_5$H$_5$ based on data in Table 2 are: Cr(CO)$_2$P(OMe)$_3$C$_5$H$_5$ = 4.6 ± 0.3; Cr(CO)$_3$C$_5$Me$_5$ = 12.5 ± 0.4; Cr(CO)$_3$C$_5$H$_5$ = 15.8 ± 0.5. The values agree and overlap within experimental error. The data for electron transfer in Table 2 are considered by us to be more accurate. They are less exothermic by 21.3 kcal mol^{-1} — the heat of reaction

Table 2
Enthalpies of anion/radical, anion/hydride and radical/hydride reactions (all data in kcal/mol^{-1})

Complex	ΔH e^- *trans* [a]	ΔH H$^+$ *trans* [b]	ΔH H$^\cdot$ *trans* [c]
Cr(CO)$_2$(PEt$_3$)C$_5$H$_5$	0	0	0
Cr(CO)$_2$(PPh$_3$)C$_5$H$_5$	5.5 ± 0.1	5.3 ± 0.3	0.1 ± 0.4
			(0.2 ± 0.4)
Cr(CO)$_2$(P(OMe)$_3$)C$_5$H$_5$	10.1 ± 0.2	6.3 ± 0.6	2.9 ± 0.4
			(3.8 ± 0.8)
Cr(CO)$_3$C$_5$Me$_5$	18.0 ± 0.3	15.3 ± 0.3	2.5 ± 0.4
			(2.7 ± 0.6)
Cr(CO)$_3$C$_5$H$_5$	21.3 ± 0.4	19.7 ± 0.4	1.7 ± 0.6
			(1.6 ± 0.8)

[a] Refers to the enthalpy of electron transfer reaction in solution: NaCr(CO)$_2$(PEt$_3$)C$_5$H$_5$ + $\cdot$Cr$'$ → NaCr$'$ + $\cdot$Cr(CO)$_2$(PEt)$_3$C$_5$H$_5$.
[b] Refers to the enthalpy of proton transfer reaction in solution: NaCr(CO)$_2$(PEt$_3$)C$_5$H$_5$ + HCr$'$ → NaCr$'$ + HCr(CO)$_2$(PEt)$_3$C$_5$H$_5$.
[c] Refers to the enthalpy of hydrogen atom transfer reaction in solution: HCr(CO)$_2$(PEt$_3$)C$_5$H$_5$ + $\cdot$Cr$'$ → HCr$'$ + $\cdot$Cr(CO)$_2$(PEt)$_3$C$_5$H$_5$.
Experimental data taken from Ref. [13]; data shown in parentheses are calculated based on $\Delta H_a - \Delta H_b$.

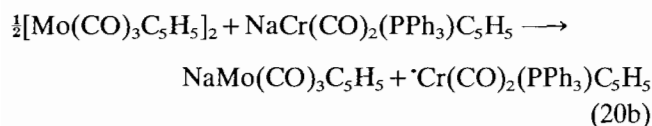of Na^+benzophenone$^-$ with $\cdot Cr(CO)_2(PPh_3)C_5H_5$. Based on this enthalpy, and the 38.5 kcal mol^{-1} enthalpy of formation of Na^+benzophenone$^-$, data for enthalpies of electron transfer are combined in Table 3 for all the complexes studied, relative to elemental Na. To our knowledge this is the first enthalpic data of its type available in organometallic chemistry.
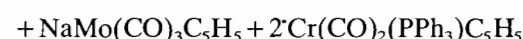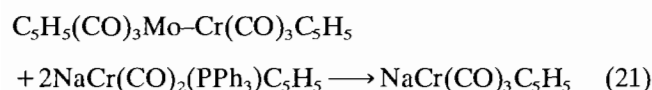
3.4. Enthalpy of metal–metal bond metathesis

The original reason the amalgam work was initiated was to determine enthalpies of metal–metal bond metathesis in metal dimers and clusters. This method is illustrated by Eqs. (19)–(21).

$$\tfrac{1}{2}[Cr(CO)_3C_5H_5]_2 + NaCr(CO)_2(PPh_3)C_5H_5 \longrightarrow$$

$$NaCr(CO)_3C_5H_5 + \cdot Cr(CO)_2(PPh_3)C_5H_5 \tag{20a}$$

$$\Delta H = -8.35 \pm 0.1 \text{ kcal mol}^{-1}$$

$$\tfrac{1}{2}[Mo(CO)_3C_5H_5]_2 + NaCr(CO)_2(PPh_3)C_5H_5 \longrightarrow$$

$$NaMo(CO)_3C_5H_5 + \cdot Cr(CO)_2(PPh_3)C_5H_5 \tag{20b}$$

$$\Delta H = -3.65 \pm 0.1 \text{ kcal mol}^{-1}$$

$$C_5H_5(CO)_3Mo-Cr(CO)_3C_5H_5$$

$$+ 2NaCr(CO)_2(PPh_3)C_5H_5 \longrightarrow NaCr(CO)_3C_5H_5 \tag{21}$$

$$+ NaMo(CO)_3C_5H_5 + 2\cdot Cr(CO)_2(PPh_3)C_5H_5$$
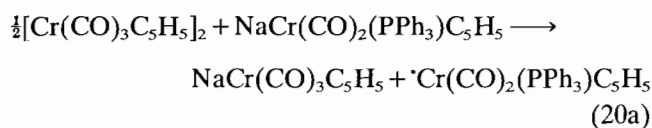
$$\Delta H = -12.5 \pm 0.2 \text{ kcal mol}^{-1}$$

The sum of Eqs. (20a) and (20b) minus Eq. (21) corresponds to the metathesis reaction shown in Eq. (22).

$$\tfrac{1}{2}[Cr(CO)_3C_5H_5]_2 + \tfrac{1}{2}[Mo(CO)_3C_5H_5]_2 \longrightarrow$$

$$C_5H_5(CO)_3Mo-Cr(CO)_3C_5H_5 \tag{22}$$
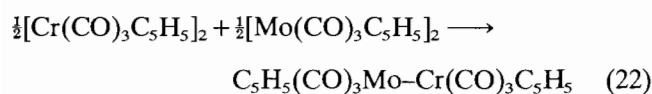
$$\Delta H_{calc} = +0.5 \pm 0.4 \text{ kcal mol}^{-1}$$

The calculated enthalpy of metal–metal metathesis is low in this system, in keeping with the equilibrium studies of Madach and Vahrenkamp which have shown that a number of heteronuclear metal–metal bonded complexes are formed from the homonuclear dimers [14]. The enthalpies of reaction of $[W(CO)_3C_5H_5]_2$ and $[Mo(CO)_3C_5Me_5]_2$ with $NaCr(CO)_2(PPh_3)C_5H_5$ were also measured. Data for reactions involving these complexes are also shown in Table 3. This method can be extended to a wide range of dinuclear and even polynuclear complexes where it may not be possible or practical to measure spectroscopic equilibrium data such as that done by Bor and co-workers [4].

3.5. Heat of hydrogenation of $Mn_2(CO)_{10}$

The stability of the chromium radicals also allows general investigation of hydride transfer reactions such as that shown in Eq. (23).

$$HMn(CO)_5 + \cdot Cr(CO)_2(PPh_3)C_5H_5 \longrightarrow$$

$$HCr(CO)_2(PPh_3)C_5H_5 + \tfrac{1}{2}[Mn(CO)_5]_2 \tag{23}$$
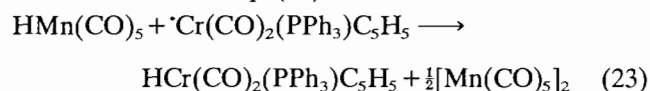
$$\Delta H = -9.7 \pm 0.2 \text{ kcal mol}^{-1}$$

Reaction (23) proceeds quantitatively in solution and provides a basis for determining the heat of hydrogenation of the Mn–Mn dimer. Data on the enthalpy of reaction (24) has been reported earlier [13].

$$\cdot Cr(CO)_2(PPh_3)C_5H_5 + \tfrac{1}{2}H_2 \longrightarrow$$

$$H-Cr(CO)_2(PPh_3)C_5H_5 \tag{24}$$
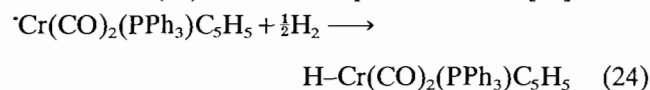
$$\Delta H = -7.7 \pm 1.2 \text{ kcal mol}^{-1}$$

The enthalpies of hydrogenation were measured in toluene solution, however heats of solution largely cancel in these reactions [17]. Assuming only small solvation effects, and subtracting Eq. (23) from Eq. (24) and multiplying by two yields Eq. (25).

$$[Mn(CO)_5]_2 + H_2 \longrightarrow 2H-Mn(CO)_5 \tag{25}$$

The enthalpy of reaction (25) is calculated to be $+4.0 \pm 2.4$ kcal mol^{-1}. This data is in reasonable agreement with the enthalpy of hydrogenation of the manganese dimer determined by equilibrium measurement

Table 3
Enthalpies of reduction (kcal mol^{-1}) for the reaction [a]: Na(solid) + A(THF soln) → Na$^+$[A]$^-$(THF soln)

Compound	ΔH	Compound	ΔH
Na	0	$\tfrac{1}{2}[Mo(CO)_3C_5H_5]_2$	−63.5
Hg(liq) [b]	−18.5	$Cr(CO)_2(P(OMe)_3)C_5H_5$	−64.4
$Ph_2C=O$	−38.5	$Cr(CO)_3C_5Me_5$	−72.3
$Cr(CO)_2(PEt_3)C_5H_5$	−54.3	$\tfrac{1}{2}[C_5H_5(CO)_3Mo-Cr(CO)_3C_5H_5]$	−66.1
$Cr(CO)_2(PPh_3)C_5H_5$	−59.8	$\tfrac{1}{2}[Cr(CO)_3C_5H_5]_2$ [c]	−68.2
$\tfrac{1}{2}[Mo(CO)_3C_5Me_5]_2$	−59.9	$Cr(CO)_3C_5H_5$ [c]	−75.6
$\tfrac{1}{2}[W(CO)_3C_5H_5]_2$	−61.7	$\tfrac{1}{2}Co_2(CO)_8$	−77.9

[a] Errors in absolute values are on the order of 1.5 kcal mol^{-1}. Relative values (see Table 2) may be known to much higher accuracy. For metal–metal bonded dimers designated $\tfrac{1}{2}[M-M]$ the product is the corresponding metal carbonyl anion Na^+M^-.
[b] Product is Na/Hg amalgam [15].
[c] These two values differ by one half the Cr–Cr bond dissociation energy [13] (7.4 kcal mol^{-1}).

in supercritical carbon dioxide [1]. Using a value of 35 kcal mol^{-1} for the Mn–Mn bond strength [2] leads to an estimate of 68 kcal mol^{-1} for the Mn–H bond strength.

As an additional check on this method, we repeated the determination of the enthalpies of hydrogenation of the dimers $[M(CO)_3C_5H_5]_2$ (M = Mo, W), which we had reported earlier [1]. The results agreed within experimental error. A number of qualitative kinetic observations were made during the course of this work. Detailed kinetic studies of these reactions are in progress and will be reported later [17].

3.6. Role of ion pairing and solvent interactions

In the calculated enthalpies of reaction discussed above, ionic complexes did not play a role. For any such complexes undergoing reaction, however, it is to be expected that ion pairing and solvation factors can play a large role in determining reaction energetics. Provided enthalpies of solution are made under identical conditions, these factors will largely cancel provided the end reactions do not involve ions. However, for ionic reactions, that will not be the case. A detailed study of ion pairing and solvation energies is beyond the scope of the paper, however the enthalpy of reaction (26) was measured in THF and acetonitrile to examine just such a thermochemical effect.

$$NaCr(CO)_2(PPh_3)C_5H_5 + HCr(CO)_3(C_5Me_5) \longrightarrow$$

$$HCr(CO)_2(PPh_3)C_5H_5 + NaCr(CO)_3(C_5Me_5)$$
$$(26)$$
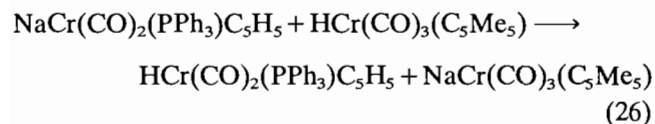
$\Delta H = -9.0 \pm 0.1$ kcal mol^{-1} (in MeCN)
$\Delta H = -10.0 \pm 0.1$ kcal mol^{-1} (in THF)

The relative enthalpies of protonation shift by 1 kcal mol^{-1} in changing solvents. While this is not a large amount, if entropic factors were cancelled, this difference would result in a difference in the relative transition metal hydride acidities of 1.7 pK_a units.

3.7. Comparison between enthalpies of proton transfer and reported pK_a data

The enthalpies of proton transfer, as shown in Table 2, follow the order expected based on donor ability of the ancillary ligands. The acid strength of the Cr–H bond increases in the order $HCr(CO)_2(PEt_3)C_5H_5 <$ $HCr(CO)_2(PPh_3)C_5H_5 < HCr(CO)_2(P(OMe)_3)C_5H_5 <$ $HCr(CO)_3C_5Me_5 < HCr(CO)_3C_5H_5$ and spans about 20

kcal mol^{-1}. The enthalpies of protonation can be used to estimate relative pK_a values if it is assumed that entropies of deprotonation are constant: $HCr(CO)_2$-$(PEt_3)C_5H_5 = 0$; $HCr(CO)_2(PPh_3)C_5H_5 = -4.0$; HCr-$(CO)_2(P(OMe)_3)C_5H_5 = -7.3$; $HCr(CO)_3C_5Me_5 = -13.0$; $HCr(CO)_3C_5H_5 = -15.4$. Due to differences in solvent systems, absolute values in THF are of little utility since most data to date has been reported in acetonitrile. The order of stability is in keeping with the following two observations from the literature [5]. (i) $HMo(CO)_3C_5H_5$ has a pK_a value 3.2 units lower (stronger acid) than $HMo(CO)_3C_5Me_5$ as measured in CH_3CN. This compares favorably to our value for $HCr(CO)_3C_5H_5$ for 2.4 pK_a units more acidic than $HCr(CO)_3C_5Me_5$ in THF. (ii) $HW(CO)_3C_5H_5$ is 10.5 pK_a units more acidic [5] than $HW(CO)_2(PMe_3)C_5H_5$ in CH_3CN which compares to our value that $HCr(CO)_3C_5H_5$ is 15.4 pK_a units more acidic than $HCr(CO)_2(PEt_3)C_5H_5$ in THF. The relatively good agreement with Norton's work on Mo and W gives confidence to our thermodynamic measurements. The role of entropic factors in these relative acidity scales cannot be ignored, and it should be emphasized again that our *estimates* of relative pK_a values are based only on enthalpies of reaction.

3.8. Comparison of enthalpies of electron transfer to reported electrochemical data

The data in Table 3, together with work in progress [17] should provide enthalpy data useful in a number of electrochemical estimations. Electrochemical potentials for reduction of metal–metal dimers have been reported by Dessy et al. [6a].

$$[L_nM]_2 + 2e^- \longrightarrow 2M^- \qquad (27)$$

$Co_2(CO)_8$, -0.9 V; $[Cr(CO)_3C_5H_5]_2$, -1.3 V; $[Mo(CO)_3C_5H_5]_2$, -1.4 V.

According to these data, the most easily reduced transition metal carbonyl is $Co_2(CO)_8$, and $[Mo(CO)_3C_5H_5]_2$ the most difficult. Data in Table 3 indicate that relative enthalpies of reduction follow the same order. The electrochemical data correspond to a free energy difference between $Co_2(CO)_8$ and $[Mo(CO)_3C_5H_5]_2$ of 11.5 kcal mol^{-1}; in reasonable agreement with our value of 14.4 kcal mol^{-1} for the enthalpy of reaction. Assuming that the reported electrochemical data are accurate to 0.1 V (2.3 kcal mol^{-1}), this present agreement is quite good. In view of the direct nature of these measurements they may offer some advantages in determination of true thermodynamic values for enthalpies of electrochemical reactions. Additional work in progress will further define these relationships.

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[1] Spectroscopic evaluation of the equilibrium constant for hydrogenation of $Mn_2(CO)_{10}$ in supercritical CO_2 in the temperature range 165–220 °C yielded an enthalpy of hydrogenation of 8.7 kcal mol^{-1}.

[2] This estimate is based on $Mn_2(CO)_{10}$ from work in Refs. [9] and [20]; it is probably reliable to ± 5 kcal mol^{-1}.

3.9. Factors contributing to M–H bond strengths in H–Cr(CO)₂(PR₃)C₅R₅

In spite of the large differences in enthalpies of proton transfer and electron transfer shown in Table 2, on the order of 20 kcal mol⁻¹, these factors largely cancel in determining metal–hydrogen single bond strengths which span only 3 kcal mol⁻¹ for these complexes. Thus, the relative bond strengths are the result of cancellation of terms roughly an order of magnitude higher. The complex $Cr(CO)_2(P(OMe)_3C_5H_5$ has the strongest Cr–H bond. This is reflected in the relatively low enthalpy of proton transfer in spite of its relatively high value for enthalpy of electron transfer. One advantage of testing this system fully is that all three components of the thermochemical cycle can be accurately measured. In other systems where only two of the three reactions can be measured and the third one must be calculated the thermochemical approach developed here should be applicable.

4. Conclusions

This paper demonstrates the utility of reductive calorimetry in measuring directly enthalpies of reaction in organometallic complexes. These techniques can be used to measure heats of reduction relative to sodium metal. Reaction enthalpy data reported span some 80 kcal mol⁻¹ and are in inverse order to the stability of the anion formed, as shown in Table 3. Detailed calorimetric measurements of proton transfer and electron transfer reactions in a series of chromium carbonyl hydrides and radicals have shown the balance of forces present in determining metal–hydrogen bond strengths. The enthalpy of hydrogenation of dimanganese decacarbonyl (+4 kcal mol⁻¹) has been reported using hydrogen atom transfer thermochemistry. The enthalpy of a metal–metal bond metathesis reaction in which homonuclear Cr–Cr and Mo–Mo complexes react to yield two moles of the heteronuclear Cr–Mo complex has been determined to be nearly thermoneutral based on heats of reduction. Literature data [16] for the enthalpy of formation of Na⁺benxophenone⁻ has been revised to be 14.5 kcal mol⁻¹ more exothermic than reported earlier. These data provide a thermochemical basis for additional thermodynamic, kinetic and electrochemical experiments in progress.

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