

# Alkyl Substituent Effects in the Redox Thermochemistry of Coordination Compounds: Oxidation and Reduction Energetics for Ruthenium Tris( $\beta$ -diketonate) Complexes in Solution and the Gas Phase

Paul Sharpe, N. George Alameddin, and David E. Richardson\*

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

Received June 15, 1994<sup>⊗</sup>

**Abstract:** Alkyl substituent effects in gas-phase and solution redox thermochemistry have been studied for a series of ruthenium coordination complexes. The gas-phase free energies of ionization ( $\Delta G_i^\circ$ ) and electron attachment ( $\Delta G_a^\circ$ ) are compared to electrochemical oxidation and reduction half-wave potentials ( $E_{1/2}$ ) for six ruthenium tris( $\beta$ -diketonate) complexes ( $\text{RuL}_3$ , where  $\text{L} = \text{CH}(\text{COR})_2^-$  and  $\text{R} = \text{methyl, ethyl, } n\text{-propyl, } n\text{-butyl, isopropyl, and } tert\text{-butyl}$ ). Values for  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  were determined from electron-transfer equilibrium measurements by using Fourier transform ion cyclotron resonance mass spectrometry. Substituted benzenes and metallocenes were used as reference compounds. Cyclic voltammetry was used to determine  $E_{1/2}$  values, which were obtained in *N,N*-dimethylformamide and measured relative to the ferrocene/ferrocenium couple. Substitution of methyl with larger substituents results in cathodic shifts in both oxidation and reduction potentials, and the solution data correlate well with the sums of Taft alkyl substituent parameters ( $\sigma_1$ ). Gas-phase cations and anions are stabilized relative to the neutral by larger alkyl substituents, rendering  $\Delta G_i^\circ$  less endoergic and  $\Delta G_a^\circ$  more exoergic as the alkyl group size increases. The trends for solution and gas-phase reduction of the neutral ruthenium(III) complex are therefore reversed. Estimates for the differential solvation free energies for one-electron oxidation ( $\Delta\Delta G_{\text{solv}}^\circ(0/+)$ ) and reduction ( $\Delta\Delta G_{\text{solv}}^\circ(0/-)$ ) are obtained by combining the  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  data with electrochemical  $E_{1/2}$  data. Values of  $\Delta\Delta G_{\text{solv}}^\circ(0/-)$  are less exoergic for complexes with larger alkyl substituents and range from  $-48 \pm 5 \text{ kcal mol}^{-1}$  ( $\text{R} = \text{methyl}$ ) to  $-36 \pm 5 \text{ kcal mol}^{-1}$  ( $\text{R} = tert\text{-butyl}$ ), and these changes in  $\Delta\Delta G_{\text{solv}}^\circ(0/-)$  are identified as the cause of the reversal in the trends for gas-phase and solution reduction free energies. In contrast,  $\Delta\Delta G_{\text{solv}}^\circ(0/+)$  values all fall in the range  $-19$  to  $-16 \text{ kcal mol}^{-1}$  and show no correlation with the size of the alkyl substituents. Analysis of the gas-phase data by a model of substituent effects based on polarizability and inductive contributions of a group shows that alkyl inductive effects are small in these complexes and that relative stabilities of gas-phase ions are primarily due to differences in polarizability of the alkyl substituents  $\text{R}$  on the ligands. A similar analysis for  $\text{R} = \text{CF}_3$  complexes suggests that the substantial effect of that group on gas-phase ionization and electron-attachment energies is almost entirely due to a large inductive effect.

## Introduction

Alkyl substituent effects have been extensively studied for organic compounds in solution, principally through investigations of substituent effects on acidity, basicity, and reactivity at carbon centers.<sup>1</sup> The intrinsic thermodynamic effects of alkyl substituents on acidities and basicities in the absence of solvent have also been investigated through gas-phase ion/molecule equilibrium studies of proton-transfer reactions involving positive and negative ions.<sup>2</sup> It is well known that intrinsic alkyl substituent effects on acidity and basicity revealed in gas-phase investigations are subject to alteration and even reversal of trends when the same reactions are studied in solution.<sup>1,2</sup> In the chemistry of transition metal coordination complexes, electrode

potentials are in many respects as fundamental as acidity and basicity in organic chemistry. Ligand substituents provide a convenient method for altering oxidation–reduction thermochemistry in transition-metal compounds, but few reports comparing intrinsic substituent effects in the gas phase and solution have appeared.<sup>3–5</sup> In this paper we focus on comparisons of ligand alkyl substituent effects in the redox thermochemistry of coordination compounds in the gas phase and solution.

(3) Richardson, D. E.; Ryan, M. F.; Khan, Md. N. I.; Maxwell, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 10482.

(4) (a) Ryan, M. F.; Eyley, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1992**, *114*, 8611. (b) Ryan, M. F.; Richardson, D. E.; Lichtenberger, D. L.; Gruhn, N. *Organometallics* **1994**, *13*, 1190. (c) Ryan, M. F.; Siedle, A. R.; Burk, M. J.; Richardson, D. E. *Organometallics* **1992**, *11*, 4231. (d) Richardson, D. E. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; NATO ASI Series C: Mathematical and Physical Sciences; Kluwer: Dordrecht, The Netherlands 1991; Vol. 367, pp 233–252.

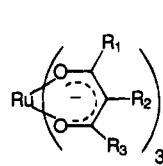
(5) (a) Satsu, Y.; Endo, A.; Shimizu, K.; Sato, G. P.; Ono, K.; Watanabe, I.; Ikeda, S. *Chem. Lett.* **1986**, 585. (b) Matsumura-Inoue, T.; Kuroda, K.; Umezawa, Y.; Achiba, Y. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 857. (c) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928. (d) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowyych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674. (e) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130. Organometallic UV photoelectron spectroscopy studies: (f) Green, J. C. *Struct. Bonding (Berlin)* **1986**, *43*, 37. Organometallic electrochemistry: (g) Kotz, J. C. In *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum Press: New York, 1986.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, November 1, 1994.

(1) Discussions and references for alkyl group effects: (a) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1985; Chapters 8 and 9. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; Chapters 3 and 4.

(2) For example, acidities: (a) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463. (b) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986. (c) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247. Basicities: (d) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445. (e) Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 1240. (f) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Chart 1



R <sub>1</sub> /R <sub>3</sub>	Ligand (R <sub>2</sub> = H)
Me	acetylacetonate
Et	3,5-heptanedionate
<i>n</i> -Pr	4,6-nonanedionate
<i>i</i> -Pr	2,5-dimethyl-3,5-heptanedionate
<i>n</i> -Bu	5,7-undecanedionate
<i>t</i> -Bu	2,2,6,6-tetramethyl-3,5-heptanedionate

We have recently reported<sup>3</sup> intrinsic alkyl substituent effects for a series of alkylnickelocenes via determination of the gas-phase free energies of ionization ( $\Delta G_i^\circ$ ) and electron attachment ( $\Delta G_a^\circ$ ) by using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR). The results show that alkyl groups are not always intrinsically "electron donating" relative to hydrogen in the redox thermochemistry of metal complexes (electron donating here means stabilizing a higher oxidation state relative to a lower one). A simple two-parameter electrostatic model applied to the alkylnickelocene results demonstrates the contributions of alkyl group polarizability and inductive effects in stabilization of the molecular cations and anions relative to the corresponding neutral complexes.<sup>3</sup> Unfortunately, the poor electrochemical reversibility of the nickelocene reduction<sup>6</sup> makes it difficult to obtain accurate solution redox thermochemistry for comparison to the gas-phase results. Thus, the influence of solvation on the trends in the solution redox potentials as a function of alkyl substituent has not been determined for the nickelocene series. In contrast, the compounds investigated in the present study allow a thorough comparative analysis of substituent effects on oxidation and reduction thermochemistry both in solution and in the gas phase.

Transition-metal  $\beta$ -diketonate complexes often exhibit reversible electrochemical behavior,<sup>7,8</sup> and they have therefore been useful parent compounds for investigations of substituent effects in transition-metal redox chemistry. The neutral  $\beta$ -diketonate complexes of ruthenium containing a variety of substituents have electrochemically reversible one-electron oxidation ( $\text{Ru}^{\text{IV/III}}$  or  $+/0$ ) and reduction ( $\text{Ru}^{\text{III/II}}$  or  $0/-$ ) couples,<sup>8</sup> and, in addition, the complexes are volatile and form stable gas-phase molecular cations and anions.<sup>9</sup> We have investigated the compounds shown in Chart 1 in this work. The abbreviations in this paper for the complexes show only the groups attached to the ligand backbone; thus, tris(acetylacetonato)ruthenium(III) is abbreviated  $\text{Ru}(\text{Me},\text{H},\text{Me})_3$ , for example. The  $\text{Ru}(\text{H},\text{H},\text{H})_3$  complex has not been reported and could not be included in the series.

We have determined solution electrochemical oxidation and reduction potentials as well as gas-phase free energies of ionization and electron attachment for the compounds illustrated above. Solvation energetics in one-electron redox couples of these complexes have been deduced by application of thermochemical cycles<sup>10</sup> connecting the gas-phase and solution energetics. Analysis of the data by a simple two-parameter electrostatic model<sup>3,11</sup> has provided an interpretation of the

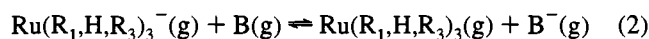
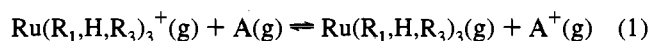
intrinsic roles of polarizability and inductive effects for the alkyl groups in these redox processes.

## Experimental Section

All ruthenium tris( $\beta$ -diketonate) complexes were synthesized by using the "Ruthenium Blue" method of Endo and co-workers.<sup>12</sup> All ligands were commercially available (Lancaster Synthesis) except 2,6-dimethyl-3,5-heptanedione, 4,6-nonanedione, and 5,7-undecanedione ( $\text{R}_1$  and  $\text{R}_3$  in Chart 1 are isopropyl, *n*-propyl, and *n*-butyl, respectively). These ligands were synthesized in good yield by adapting the method reported by Kopecky and co-workers.<sup>13</sup> All ruthenium complexes were purified by column chromatography, using activated alumina and chloroform as eluent. The complexes were further purified by sublimation prior to use. Complexes with bulky alkyl groups on the ligands (*i*-Pr and *t*-Bu) were found to be the most volatile. The complexes  $\text{Ru}(\textit{n}\text{-Pr},\text{H},\textit{n}\text{-Pr})_3$  and  $\text{Ru}(\textit{n}\text{-Bu},\text{H},\textit{n}\text{-Bu})_3$  are viscous oils at room temperature; these compounds were condensed under vacuum onto a cold finger prior to use (130 °C at ca. 100 mTorr).

Cyclic voltammetry<sup>14</sup> was performed with a Princeton Applied Research system (models 173 and 175). A platinum button working electrode and a  $\text{Ag}/\text{AgCl}(\text{satd})$  reference electrode were used. DMF for electrochemical studies was distilled and dried over molecular sieves prior to use. Concentrations of ruthenium tris( $\beta$ -diketonate) complexes and ferrocene were 1–2 mM, and 0.10 M tetraethylammonium perchlorate was used as the supporting electrolyte, except as noted.

Positive and negative ion electron-transfer equilibrium (ETE) studies were performed on a Fourier transform ion cyclotron resonance mass spectrometer.<sup>15</sup> The system used in this work is based on a 3-T superconducting magnet and an Ionspec data station. The use of FT-ICR in the determination of differences in  $\Delta G_i^\circ$  or  $\Delta G_a^\circ$  between two gaseous reactants via ETE measurements has been described in detail elsewhere.<sup>4,16</sup> The present study involved the determination of equilibrium constants for gas-phase reactions of the general types given in eqs 1 and 2, where  $\text{Ru}(\text{R}_1,\text{H},\text{R}_3)_3$  represents a ruthenium tris( $\beta$ -



diketonate) complex and A and B are reference compounds with known  $\Delta G_i^\circ$  or  $\Delta G_a^\circ$  values, respectively. Partial pressures of neutral reactants were established in the  $10^{-7}$ – $10^{-6}$  Torr range, with a total pressure typically from  $0.5 \times 10^{-6}$  to  $3 \times 10^{-6}$  Torr. Pressures for reference compounds were measured with an ion gauge with corrections based on comparisons of the ion gauge to readings of a capacitance manometer in the  $\sim 10^{-5}$  Torr range. The vapor pressures of the ruthenium complexes were not high enough to allow accurate absolute pressure determinations with a capacitance manometer. Therefore, ion gauge readings were used directly with the assumption that the sensitivity of the ion gauge for all of the complexes was constant. This assumption could result in some constant error for all of the free energies derived for the metal complexes, but the accuracy of the relative free energies will not be affected.

(11) Taft, R. W.; Taagepera, M.; Abboud, J. L. M.; Wolf, J. F.; Defrees, D. J.; Hehre, W. J.; Bartmess, J. E.; McIver, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 7765.

(12) Endo, A.; Kajitani, M.; Mukaida, M.; Shimizu, K.; Sato, G. P. *Inorg. Chim. Acta* **1988**, *150*, 25.

(13) Kopecky, K. R.; Nonhebel, D. C.; Morris, G.; Hammond, G. S. *J. Org. Chem.* **1962**, *27*, 1036.

(14) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980.

(15) For reviews of the ion cyclotron resonance technique, see: (a) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316. (b) Gross, M. L.; Rempel, D. L. *Science* **1984**, *226*, 261. (c) Eyler, J. R.; Baykut, G. *Trends Anal. Chem.* **1986**, *5*, 44.

(16) (a) Sharpe, P.; Richardson, D. E. *Coord. Chem. Rev.* **1989**, *93*, 59. (b) Lias, S. G.; Jackson, J. A.; Argentar, H.; Liebman, J. F. *J. Org. Chem.* **1985**, *50*, 333. (c) Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 6027.

(6) Holloway, J. D. L.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 2038.

(7) (a) Vaughn, D. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 1, pp 475–91. (b) Pickett, C. J. *Ibid.*; pp 493–501. (c) Kotz, J. C. In *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum Press: New York, 1986. (d) Bond, A. *Coord. Chem. Rev.* **1984**, *54*, 23. (e) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

(8) (a) Endo, A.; Hoshino, Y.; Hirakata, K.; Takeuchi, Y.; Shimizu, K.; Furushima, Y.; Ikeuchi, H.; Sata, G. P. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 709. (b) Patterson, G. S.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2285.

(9) (a) Sharpe, P.; Eyler, J. R.; Richardson, D. E. *Inorg. Chem.* **1990**, *29*, 2779. (b) Sharpe, P.; Richardson, D. E. *J. Am. Chem. Soc.* **1991**, *113*, 8339. (c) Sharpe, P. Ph.D. Dissertation; University of Florida: Gainesville, FL, 1990.

(10) Richardson, D. E. *Inorg. Chem.* **1990**, *29*, 3213.

The ruthenium complexes were sublimed from a heated solids probe inserted into the high-vacuum chamber. The probe tip was normally situated  $\sim 40$  cm from the ion trap to provide a steady pressure at the trap (confirmed by a reproducible ion intensity over several mass spectra). All flanges and vacuum tubing between the cell region and the external ion gauge head used to monitor pressures in the system were maintained at  $75^\circ\text{C}$  to minimize the pressure gradient from the cell to the gauge head due to condensation of the samples on the vacuum chamber walls. A constant pressure of the complex could be maintained with constant probe temperature ( $35\text{--}100^\circ\text{C}$  depending on the complex) over the time required to obtain equilibrium data in an experiment. The pumping speed on the main vacuum chamber was also reduced as far as possible to reduce pressure gradients in the system without raising the background pressure to unacceptable levels ( $> 10^{-8}$  Torr). Reference compounds were added to required pressures via precision leak valves on the inlet system. The reference compounds chosen were sufficiently volatile to pump quickly out of the system after an ETE experiment in order to confirm that the metal complex pressure had not changed since the beginning of the experiment. Increasing the vacuum system temperature for the less volatile complexes up to  $100^\circ\text{C}$  (the probe temperature) did not have a significant effect on the derived equilibrium constants, so pressure gradients from the ion trap to the ion gauge due to condensation of the complexes on the walls of the vacuum system were not significant under the experimental conditions.

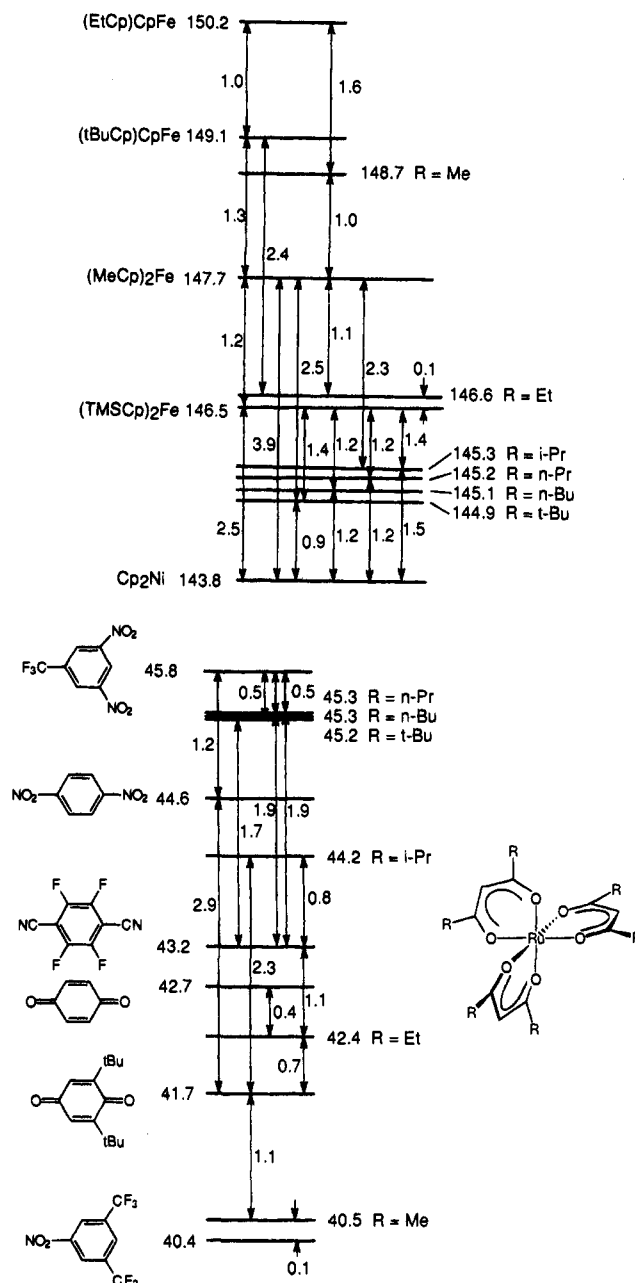
Positive or negative ions were produced by electron impact ionization or low-energy electron capture, and resonance ejection techniques were used to isolate the molecular ions. The ions were trapped in the gas mixture with the ion trap and vacuum system at 350 K, and a set reaction time was allowed prior to detection. The experiment was repeated over incremented reaction times from several hundred milliseconds up to 3–10 s, allowing the time dependence of the ion populations to be monitored. During this time the initial ion intensities were observed to reach and maintain a constant equilibrium ratio. Long reaction times allow many collisions of ions with neutrals ( $\sim 30/s$  at  $10^{-6}$  Torr), and any excess internal energy in the initially formed ions is assumed to be completely dissipated so that derived equilibrium constants ( $K_{\text{et}}$ ) apply to the experimental ion trap temperature of 350 K. A value for  $K_{\text{et}}$  for the reactions in eqs 1 and 2 along with  $\Delta G_i^\circ$  or  $\Delta G_a^\circ$  for the reference compounds yielded  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values for the ruthenium tris( $\beta$ -diketonate) complexes.

ZINDO calculations<sup>17</sup> were performed to give total energies and atomic charge populations for the neutral complex  $\text{Ru}(\text{Me},\text{H},\text{Me})_3$  and its positive and negative ions. Atomic coordinates were taken from the reported crystal structure of the neutral<sup>18</sup> and were assumed to be the same for the ions.

## Results

Results for both the positive and negative ion ETE experiments are displayed in Figure 1 along with the derived values of  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  for the complexes. The arrows denote ETE reactions investigated in this work. Equilibria with at least two different reference compounds were used to establish the position of the new complexes on the ladders. Average values of  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  were obtained by using a weighted average that takes the increasing uncertainty in determined equilibrium constants (eqs 1 and 2) when larger pressure ratios for the neutrals are required (see Appendix).

The  $\Delta G_a^\circ$  values obtained for the ruthenium tris( $\beta$ -diketonate) complexes were determined from reactions with five different reference compounds (Figure 1). The  $\Delta G_a^\circ$  values for most of these compounds have been determined by Kebarle and co-



**Figure 1.** Summary of electron-transfer equilibrium reactions studied with  $\Delta G_{\text{et}}^\circ$ ,  $\Delta G_i^\circ$ , and  $\Delta G_a^\circ$  data ( $\text{kcal mol}^{-1}$ ): (top) ionization ( $\text{RuL}_3 \rightarrow \text{RuL}_3^+ + e$ ), (bottom) electron attachment ( $\text{RuL}_3 + e \rightarrow \text{RuL}_3^-$ ). Numbers next to arrows are experimental  $\Delta G_{\text{et}}^\circ$  values. Numbers next to compounds are  $\Delta G_i^\circ$  and  $-\Delta G_a^\circ$  values for reference compounds (left) and ruthenium tris( $\beta$ -diketonate) complexes (right).

workers,<sup>19</sup> and the reported thermodynamic parameters were used to obtain the values at 350 K. For example, the  $\Delta G_a^\circ$  value for 1,4-dinitrobenzene was reported as  $-44.3 \text{ kcal mol}^{-1}$  at 423 K with  $\Delta S_a^\circ = -4.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ ,<sup>19</sup> which leads to the value of  $\Delta G_a^\circ$  of  $-44.6 \text{ kcal mol}^{-1}$  at 350 K for the present study. 1,4-Dinitrobenzene is itself too involatile to be admitted through the inlet leak valve system and so could not be used readily in reactions with the ruthenium tris( $\beta$ -diketonate) complexes, which also require introduction with a heated solids probe. The values of  $\Delta G_a^\circ$  for 3,5-dinitrobenzotrifluoride

(17) (a) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111. (b) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21. (c) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

(18) Chao, G. K.; Sime, R. L.; Sime, R. J. *Acta Crystallogr.* **1973**, *B29*, 2845.

(19) (a) Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513. (b) Heinis, T.; Chowdhury, S.; Scott, S. L.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 400. (c) Chowdhury, Heinis, T.; Grimsrud, E. P.; Kebarle, P. *J. Phys. Chem.* **1986**, *90*, 2747. (d) Kebarle, P. In *Modern Aspects of Electrochemistry*; Conway, B. E.; Bockris, J. O. M., Eds.; Plenum Press: New York, 1974; No. 9, pp 1–46.

**Table 1.** Gas-Phase  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  Data and Electrochemical Oxidation and Reduction Potentials for Ruthenium Tris( $\beta$ -diketonate) Complexes

complex	$\Delta G_i^\circ$ <sup>a,b</sup>	$-\Delta G_a^\circ$ <sup>a,b</sup>	$E_{1/2}$ vs $Cp_2Fe^{0/+}$ <sup>c</sup>	
			ox. (+/0)	red. (0/-)
Ru(Me,H,Me) <sub>3</sub>	148.7 (6.45)	40.5 (1.76)	0.593	-1.223
Ru(Et,H,Et) <sub>3</sub>	146.6 (6.36)	42.4 (1.84)	0.549	-1.308
Ru( <i>n</i> -Pr,H, <i>n</i> -Pr) <sub>3</sub>	145.2 (6.30)	45.3 (1.96)	0.547	-1.324
Ru( <i>n</i> -Bu,H, <i>n</i> -Bu) <sub>3</sub>	145.1 (6.29)	45.3 (1.96)	0.535	-1.330
Ru( <i>i</i> -Pr,H, <i>i</i> -Pr) <sub>3</sub>	145.3 (6.30)	44.2 (1.92)	0.509	-1.392
Ru( <i>t</i> -Bu,H, <i>t</i> -Bu) <sub>3</sub>	144.9 (6.28)	45.2 (1.96)	0.453	-1.505

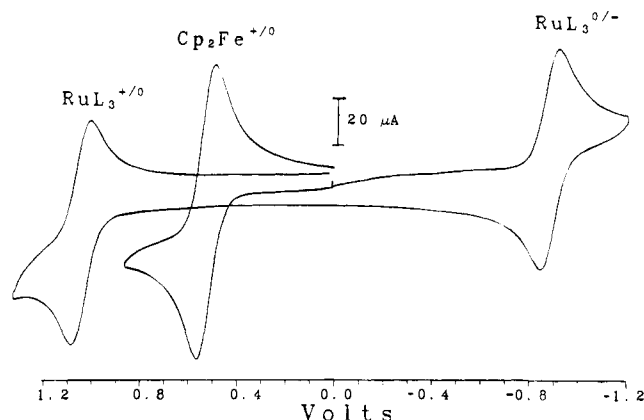
<sup>a</sup> Units are kilocalories per mole. Values in parentheses are in electronvolts. <sup>b</sup> The estimated error in relative values is  $\pm 0.5$  kcal mol<sup>-1</sup>; the estimated error for absolute values is  $\pm 1.5$  kcal mol<sup>-1</sup>. <sup>c</sup> Electrode potential values are in volts; the estimated error is  $\pm 5$  mV.

(-45.8 kcal mol<sup>-1</sup>) and 2,6-di-*tert*-butyl-1,4-benzoquinone (-41.7 kcal mol<sup>-1</sup>) were determined from ETE reactions with 1,4-dinitrobenzene introduced on the heated solids probe. A value for  $\Delta G_a^\circ$  for 2,6-di-*tert*-butyl-1,4-benzoquinone has been reported by Kebarle and co-workers<sup>19</sup> to be -41.4 kcal mol<sup>-1</sup> at 423 K with a value of  $\Delta S_a^\circ$  of -4.6 cal mol<sup>-1</sup> K<sup>-1</sup>. This leads to a value of -41.8 kcal mol<sup>-1</sup> at 350 K, in excellent agreement with the value of -41.7 kcal mol<sup>-1</sup> determined in the present work. 1,4-Dinitrobenzene was also employed as an anchor to establish the free energy of electron attachment of 3,5-dinitrobenzotrifluoride, which proved to be a convenient, volatile reference compound. A value of  $\Delta G_a^\circ$  for 3,5-dinitrobenzotrifluoride has not been previously reported.

All  $\Delta G_i^\circ$  values obtained for the tris( $\beta$ -diketonato)ruthenium(III) complexes were determined relative to four ferrocene derivatives and nickelocene (Figure 1). Ryan et al.<sup>3,4a</sup> recently determined  $\Delta G_i^\circ$  values at 350 K by ETE studies for all of these metallocenes except bis(trimethylsilyl)cyclopentadienyliron ((TMSCp)<sub>2</sub>Fe). The latter compound establishes a useful link from the ferrocenes to nickelocene, and its  $\Delta G_i^\circ$  value at 350 K (146.5 kcal mol<sup>-1</sup>) was determined in this work.

The  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values obtained in this study are presented in Table 1. Errors in the measurements of electron-transfer equilibrium constants produce an estimated  $\pm 0.3$  kcal mol<sup>-1</sup> uncertainty in the individual  $\Delta G_{eq}^\circ$  values (the principal source of error is in pressure determination; the range quoted covers a factor of  $\sim 2.5$  in pressure; see Appendix). Since many of the  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values are anchored to the same reference compound and excellent consistency was observed in the ladders, the estimated error in the relative values for the ruthenium compounds is  $\pm 0.5$  kcal mol<sup>-1</sup>. This estimated error almost certainly accommodates the minor variations expected in ion gauge sensitivity for the various Ru complexes and represents about 10% of the total range of  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values for the complexes. An uncertainty of  $\pm 1.5$  kcal mol<sup>-1</sup> is assigned to absolute values of  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  determined in this study due to the uncertainty in the values of the reference compounds as well as errors in individual ETE measurements.

ETE studies could not be done with two different Ru complexes at the same time since the pressures of the complexes cannot be controlled independently on our system, which has only one solids probe. However, it is possible to introduce two complexes into the system as a mixture on the probe. The relative pressures can be estimated from the initial ion intensities, and the direction of charge transfer can be used to provide conformation of the general trends in the ladders of Figure 1. For example, when Ru(Me,H,Me)<sub>3</sub> and Ru(*t*-Bu,H,*t*-Bu)<sub>3</sub> are introduced together on the probe to yield a  $\sim 2:1$  ratio of partial pressures (Me:*t*-Bu), the direction of charge transfer in both negative and positive ion modes is to the R = *t*-Bu complex,

**Figure 2.** Cyclic voltammogram showing oxidation and reduction of Ru(*i*-Pr,H,*i*-Pr)<sub>3</sub> and ferrocene (internal standard) in DMF (Pt, 0.10 M TEAP, room temperature).

which therefore has the higher electron affinity and lower ionization potential as determined in the ETE experiments.

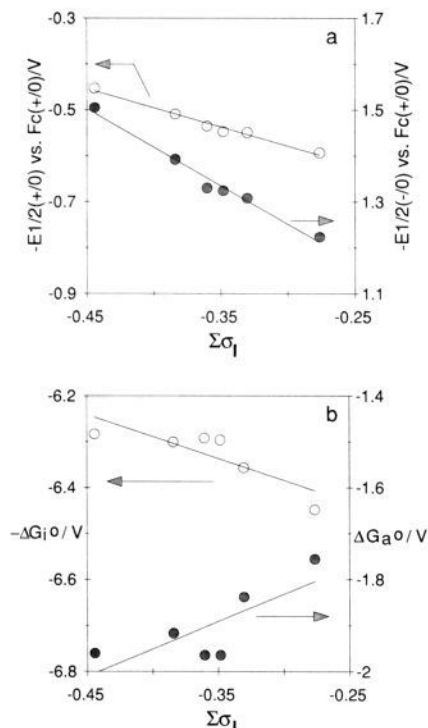
Results obtained from electrochemical oxidation and reduction of the ruthenium tris( $\beta$ -diketonate) complexes are given in Table 1. The values quoted are referenced to the  $Cp_2Fe^{+/0}$  couple, which was used as an internal standard. All oxidations and reductions were carried out in DMF and were found to be reversible in this solvent. Figure 2 shows a typical voltammogram of the oxidation and reduction of Ru(*i*-Pr,H,*i*-Pr)<sub>3</sub>. Preliminary studies also employed acetonitrile as solvent, but reductions of complexes with bulkier ligands were only quasi-reversible in that solvent.

## Discussion

**Electron Affinities and Ionization Energies.** We have previously reported the free energies of electron attachment for a number of transition-metal (acac)<sub>3</sub> and (hfac)<sub>3</sub> (hexafluoroacetylacetonate) complexes, including M = Ru.<sup>9</sup> The value of  $\Delta G_a^\circ$  reported here for Ru(Me,H,Me)<sub>3</sub> (-40.5 kcal mol<sup>-1</sup>) is more exoergic than our previously reported<sup>9</sup> value of -38.7 kcal mol<sup>-1</sup>. We believe the principle source of the difference stems from error in our earlier measurements of the partial pressure of Ru(Me,H,Me)<sub>3</sub> due to its low volatility. In the present study, care was taken to eliminate cold spots on the wall of the high-vacuum chamber between the FT-ICR analysis cell and the ion gauge, thereby ensuring a more uniform pressure throughout the system.

Vertical and estimated adiabatic ionization potentials have been determined for tris( $\beta$ -diketonato)ruthenium(III) complexes from photoelectron spectroscopy studies.<sup>5a</sup> Estimates of the aIP values reported<sup>5a</sup> for Ru(Me,H,Me)<sub>3</sub> (6.50 eV) and Ru(*t*-Bu,H,*t*-Bu)<sub>3</sub> (6.27 eV) are in good agreement with the values of 6.45 and 6.28 eV determined in the present study. It is anticipated that the gas-phase entropies of ionization for these low-spin d<sup>5</sup>-d<sup>4</sup> couples will be small (<4 eu),<sup>20</sup> so it is expected that the free energies of ionization are similar to the energy of ionization and are therefore directly comparable to the photoelectron results.

**Overall Trends in Oxidation and Reduction Energetics.** Trends in gas-phase  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values and solution electrode potentials for the complexes (Table 1) are compared in the plots in Figure 3. To simplify comparisons of the data, the abscissas are all plotted as the free energies of electron attachment to the neutral and cationic complexes (i.e., for  $ML_3^n + e^- \rightleftharpoons ML_3^{n-1}$ ,  $n = 0$  or  $+1$ ), and the axes have the same energy scale (volts relative to  $Fc^{+/0}$  for the solution data and



**Figure 3.** Trends in free energies of oxidation and reduction of ruthenium tris( $\beta$ -diketonate) complexes: (a) gas-phase free energies of ionization ( $\Delta G_i^\circ$ ) and electron attachment ( $\Delta G_a^\circ$ ), (b) electrochemical  $E_{1/2}$  values in DMF relative to the ferrocene/ferrocenium couple. The energies are plotted vs the sums of  $\sigma_1$  alkyl substituent parameters listed by substituent in Table 3.

electronvolts for the gas phase with the electron treated by the ion convention<sup>21</sup>). Both data sets are plotted against the sum of the Taft alkyl substituent parameters ( $\sigma_1$ )<sup>22</sup> per complex. Taft  $\sigma_1$  parameters have previously been shown to be useful in correlating trends in both voltammetry and gas-phase ionization energy data for metal complexes. The  $\sigma_1$  parameters and other related parameters have successfully fit trends in voltammetry data in previous investigations of substituted ruthenium tris( $\beta$ -diketonate) complexes.<sup>8,23</sup> Also, Levitt and Levitt<sup>24</sup> have correlated trends in ionization energies for substituted (benzene)-Cr(CO)<sub>3</sub> derivatives and substituted chromium and copper acetylacetonates with  $\sigma_1$ . In studies of organometallic oxidations, Richardson and co-workers find good  $\sigma_1$  correlations with  $\Delta G_i^\circ$  data for alkylferrocenes and alkylnickelocenes.<sup>3,4</sup> Overall correlations with a parameter such as  $\sigma_1$  are improved by using a restricted range of substituents in the correlations, such as alkyl groups. Levitt and Widing<sup>22</sup> have specifically demonstrated that consistent  $\sigma_1$  values for alkyl groups can be obtained from ionization energy data and acid dissociation constants.

Figure 3a shows that  $\sigma_1$  parameters provide a good fit to the present voltammetry data ( $r = 0.991$  for oxidation and 0.990

for reduction). The larger alkyl groups cause cathodic shifts in electrode potentials relative to  $R = \text{Me}$ , the shifts in the 0/− couples (slope  $-39 \pm 2 \text{ kcal mol}^{-1}$ ) being about twice as large as those for the +/0 couples (slope  $-19 \pm 1 \text{ kcal mol}^{-1}$ ).

The linear fits of the gas-phase  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values (Figure 3b) to  $\sigma_1$  parameters are not as good ( $r = 0.84$  for  $\Delta G_i^\circ$  and 0.79 for  $\Delta G_a^\circ$ ). The poor fits are primarily due to the  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values for Ru(*n*-Pr,H,*n*-Pr)<sub>3</sub> and Ru(*n*-Bu,H,*n*-Bu)<sub>3</sub>. These *n*-Pr and *n*-Bu ligands stabilize both positive and negative forms of the complexes relative to the neutral to a greater extent than predicted by  $\sigma_1$  parameters as applied to the  $\alpha$ -carbon substituted ligands Et, *i*-Pr, and *t*-Bu, but the deviation from the best fit line to the other points cannot reasonably be accounted for by experimental error. A possible explanation for the deviation for the *n*-Pr and *n*-Bu gas-phase complexes is considered later.

In the plots of Figure 3, a negative slope indicates that the higher oxidation state is stabilized relative to the lower as  $\sigma_1$  parameters become more negative. Thus, a negative slope is consistent with the view of alkyl groups as electron donating, with increasing electron donating capacity as the size and number of substituents at the  $\alpha$  carbon increases. Comparing the trends in free energies of ionization (Figure 3b) and oxidation half-wave potentials (Figure 3a), it can be seen that substitution of methyl by larger alkyl groups on the complexes results in less endoergic oxidation in the gas-phase and in solution. In contrast, the trends in gas-phase electron attachment free energies and solution reduction electrode potentials are reversed. Larger alkyl groups render gas-phase reduction more exoergic than for  $R = \text{Me}$  (an "electron-withdrawing" effect), but solution-phase reduction becomes less exoergic for larger groups (the usual electron-donating effect). Traditionally, cathodic shifts caused by alkyl group substitution are discussed in terms of the electron donating effect of alkyl substituents. Clearly, the intrinsic effect of alkyl groups in these redox couples cannot be described as universally electron donating.

In the following sections we analyze the solvation energetics for these couples and consider the intrinsic alkyl effects revealed by the gas-phase data in more detail. Solvation is of course responsible for the reversal in the gas-phase and solution trends for the 0/− couples and therefore obscures the intrinsic effect of alkyl groups when the redox thermochemistry of the complexes is determined in solution.

**Solvation Energetics.** Electrochemical  $E^\circ$  values for oxidation or reduction of a compound can be related to gas-phase free energies of ionization or electron attachment by thermochemical cycles that include the effect of differential solvation free energies for the two members of the couple.<sup>10</sup> Qualitatively, the essentially equal slopes of the Taft  $\sigma_1$  plots for the Ru( $R_1,H,R_3$ )<sub>3</sub><sup>+0</sup> couple in the gas-phase and solution data (Figure 3) show that the change in solvation energy accompanying oxidation is little affected by the type of ligand alkyl substituent. For Ru( $R_1,H,R_3$ )<sub>3</sub><sup>0/−</sup> couples, however, increasing the size of the alkyl substituents causes a significant change in the contribution of solvation to the reduction electrode potential, and this change is the cause of the observed reversal in the gas-phase and solution-phase trends. In this section, we consider quantitative aspects of the different trends for gas-phase and solution energetics.

The relationships between the free energies of ionization and electron attachment of a neutral species and the corresponding electrode potentials are given in eqs 3 and 4. The constant  $C$

$$F(E_{\text{ox}}^\circ + C) = \Delta G_i^\circ + \Delta \Delta G_{\text{solv}}^\circ(0/+)$$
 (3)

$$-F(E_{\text{red}}^\circ + C) = \Delta G_a^\circ + \Delta \Delta G_{\text{solv}}^\circ(0/-)$$
 (4)

(21) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry*; American Institute of Physics: New York, 1988. (b) Sharpe, P.; Richardson, D. E. *Thermochim. Acta* **1992**, *202*, 173.

(22) (a) Levitt, L. S.; Widing, H. F. *Prog. Phys. Org. Chem.* **1976**, *12*, 119–157. (b) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (c) Taft, R. W.; Lewis, I. C. *Tetrahedron* **1959**, *5*, 210.

(23) (a) Handy, R. F.; Lintvedt, R. L. *Inorg. Chem.* **1974**, *13*, 893. (b) Tsiamis, C.; Cambanis, S.; Hadjikostas, C. *Inorg. Chem.* **1987**, *26*, 26. (c) Jannakoudakis, A. D.; Tsiamis, C.; Jannakoudakis, P. D.; Theodoridou, E. *J. Electroanal. Chem.* **1985**, *184*, 123. (d) Tsiamis, C.; Hadjikostas, C. C.; Karageorgiou, S.; Manoussakis, G. *Inorg. Chim. Acta* **1988**, *143*, 17.

(24) (a) Levitt, L. S.; Levitt, B. W. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1907. (b) Levitt, B. W.; Levitt, L. S. *J. Coord. Chem.* **1973**, *3*, 187. (c) Levitt, L. S.; Levitt, B. W. *Tetrahedron* **1975**, *31*, 2355.

**Table 2.** Analysis of Solvation Energetics

complex	$\Delta G_1^\circ + \Delta G_a^\circ$ <sup>a</sup>	$E_{1/2}(\text{ox.}) - E_{1/2}(\text{red.})$ <sup>a</sup>	$\Delta\Delta G_{\text{solv}}^\circ(0/+) + \Delta\Delta G_{\text{solv}}^\circ(0/-)$ <sup>a</sup>	$\Delta\Delta G_{\text{solv}}^\circ(+/0)$ <sup>a,b</sup>	$\Delta\Delta G_{\text{solv}}^\circ(0/-)$ <sup>a,b</sup>
Ru(Me,H,Me) <sub>3</sub>	108.2	41.9	-66.3	-18.6	-47.8
Ru(Et,H,Et) <sub>3</sub>	104.2	42.8	-61.4	-17.5	-43.9
Ru( <i>n</i> -Pr,H, <i>n</i> -Pr) <sub>3</sub>	99.9	43.1	-56.8	-16.1	-40.6
Ru( <i>n</i> -Bu,H, <i>n</i> -Bu) <sub>3</sub>	99.8	43.0	-56.8	-16.3	-40.5
Ru( <i>i</i> -Pr,H, <i>i</i> -Pr) <sub>3</sub>	101.1	43.8	-57.3	-17.1	-40.2
Ru( <i>t</i> -Bu,H, <i>t</i> -Bu) <sub>3</sub>	99.7	45.2	-54.5	-18.0	-36.5

<sup>a</sup> Units are kilocalories per mole. <sup>b</sup> Based on the value of  $E_{1/2} = 0.363$  for Cp<sub>2</sub>Fe<sup>+0</sup> in DMF vs SCE (see text). The estimated error in relative values is  $\pm 1$  kcal mol<sup>-1</sup>; the estimated error for absolute values is  $\pm 5$  kcal mol<sup>-1</sup>.

is the absolute potential for the half-cell reduction reaction occurring at the reference electrode, and  $E_{\text{ox}}^\circ$  and  $E_{\text{red}}^\circ$  are standard oxidation and reduction electrode potentials. The terms  $\Delta\Delta G_{\text{solv}}^\circ(0/+)$  and  $\Delta\Delta G_{\text{solv}}^\circ(0/-)$  are the changes in solvation free energy for oxidation or reduction, respectively, of an electroactive species and will have negative values as a strongly solvated ion is formed upon oxidation or reduction of the neutral complexes (for example, for electrochemical reduction of B,  $\Delta\Delta G_{\text{solv}}^\circ(0/-) = \Delta G_{\text{solv}}^\circ(\text{B}^-) - \Delta G_{\text{solv}}^\circ(\text{B})$ ). Adding eqs 3 and 4 and rearranging leads to eq 5. In eq 5  $\Delta\Delta G_{\text{solv}}^\circ(0/+) +$

$$\Delta\Delta G_{\text{solv}}^\circ(0/+) + \Delta\Delta G_{\text{solv}}^\circ(0/-) = F(E_{\text{ox}}^\circ - E_{\text{red}}^\circ) - (\Delta G_1^\circ + \Delta G_a^\circ) \quad (5)$$

$\Delta\Delta G_{\text{solv}}^\circ(0/-)$  is the sum of the differential solvation energies for the +/0 and 0/- couples, and this quantity does not rely on a knowledge of the absolute potential of the reference electrode. A similar analysis has been applied by Parker<sup>25</sup> for aromatic hydrocarbon radical ions.

Determination of solvation energetics by substituting measured half-wave potentials ( $E_{1/2}$ ) for standard potentials ( $E^\circ$ ) into eqs 3–5 introduces error into derived  $\Delta\Delta G_{\text{solv}}^\circ$  values from several possible sources. Although the approximation  $E_{1/2} \approx E^\circ$  is good when activity coefficients and diffusion coefficients for the oxidized and reduced forms are similar,<sup>14</sup> other contributions to errors are difficult to assess accurately for a given system. A potential problem in equating  $E^\circ$  to  $E_{1/2}$  is the formation of ion-pairs between the supporting electrolyte and the ionic form of the electroactive species.<sup>26</sup> It has been shown that the electrode potential for the reduction of Fe(acac)<sub>3</sub> is shifted toward more anodic potentials by smaller electrolyte cations such as Na<sup>+</sup> and Li<sup>+</sup> compared to tetraethylammonium ion.<sup>26a</sup> In the present study half-wave potentials were measured using 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. We compared electrode potentials measured using TEAP and tetra-*n*-butylammonium hexafluorophosphate, which has a larger cation and a less coordinating anion,<sup>26b</sup> and found no significant shifts in observed  $E_{1/2}$  values for the present complexes. The comparisons indicate that the effect of ion pairing is not likely to be significant in the TEAP/DMF electrolyte. Potentials observed with acetonitrile as solvent were not greatly different from those measured in DMF, suggesting that specific solvent interactions are not present (acetonitrile and DMF have similar dielectric constants (~37 near room temperature) but much different donor properties (Gutman donor numbers 14.1 and 26.6, respectively<sup>26c</sup>)).

Substituting the electrochemical half-wave potentials and gas-phase  $\Delta G_1^\circ$  and  $\Delta G_a^\circ$  values in Table 1 into eq 5 provides estimates of the sum  $\Delta\Delta G_{\text{solv}}^\circ(0/+) + \Delta\Delta G_{\text{solv}}^\circ(0/-)$ . The results are presented in Table 2. The Born charging model<sup>27</sup>

predicts for anions and cations of the same radius that  $\Delta\Delta G_{\text{solv}}^\circ$  for oxidation or reduction is simply half the value of  $\Delta\Delta G_{\text{solv}}^\circ(0/+) + \Delta\Delta G_{\text{solv}}^\circ(0/-)$ . This has been found to be a good approximation for Cp<sub>2</sub>Ni<sup>+0</sup> and Cp<sub>2</sub>Ni<sup>0/-</sup> couples,<sup>3</sup> and Krishtalik<sup>27d</sup> has suggested that the same is true for the Cp<sub>2</sub>Co<sup>+0</sup> and Cp<sub>2</sub>Co<sup>0/-</sup> couples. However, comparison of the data in Figure 3 suggests that this is not the case for the ruthenium tris( $\beta$ -diketonate) complexes as solvation has a dramatically different effect on the trends in the oxidation and reduction energies.

Apportioning the experimental values of  $\Delta\Delta G_{\text{solv}}^\circ(0/+) + \Delta\Delta G_{\text{solv}}^\circ(0/-)$  into the contributions from the individual couples relies on a knowledge of the constant  $C$  in eqs 3 and 4. An analysis of absolute electrode potentials for metal complexes has been given previously<sup>9b,10</sup> and is based on an estimate<sup>28</sup> of the absolute potential of the standard hydrogen electrode as 4.44 V. We ignore the junction potential at the interface of an aqueous reference electrode in a nonaqueous solvent, although comparisons where possible to potentials in water, where no junction potential is present, indicate that the trends as a function of solvent are not unreasonable and the junction potential is relatively small.<sup>29</sup> Using a value of the formal potential of 0.363 V vs SCE for the ferrocene/ferrocenium couple in DMF,<sup>30</sup> which we use as an internal standard, we arrive at  $C = 5.05$  V after correcting for the potential of the Ag/AgCl reference we used. This value, together with the electrochemical data given in Table 1 and eqs 3 and 4, leads to the separation of  $\Delta\Delta G_{\text{solv}}^\circ(0/+) + \Delta\Delta G_{\text{solv}}^\circ(0/-)$  for the complexes.

The resulting differential solvation energies are given in Table 2. The estimated relative errors in these values of differential solvation energy are  $\pm 1$  kcal mol<sup>-1</sup> (based on uncertainties in the relative gas-phase energies and measured electrode potentials that enter into eq 5). The estimated absolute errors in these values ( $\pm 5$  kcal mol<sup>-1</sup>) are however much larger, particularly as a result of the uncertainties in the contributions to the value of  $C$  in eqs 3 and 4. For oxidation of the complexes,  $\Delta\Delta G_{\text{solv}}^\circ(0/+)$  values are all in the range -19 to -16 kcal mol<sup>-1</sup> and show no correlation with the size of the alkyl substituents. For reduction,  $\Delta\Delta G_{\text{solv}}^\circ(-/0)$  values range from -48 to -36 kcal mol<sup>-1</sup>, and are less exoergic for complexes with larger alkyl substituents. A loss of 11 kcal mol<sup>-1</sup> in the exoergic of solvation is observed in  $\Delta\Delta G_{\text{solv}}^\circ(0/-)$  between the Ru(Me,H,Me)<sub>3</sub><sup>0/-</sup> and Ru(*t*-Bu,H,*t*-Bu)<sub>3</sub><sup>0/-</sup> couples. If the solvation energetics were independent of the nature of R for the 0/- couples and the same as for R = Me, the  $E_{1/2}$  of the Ru(*t*-Bu,H,*t*-Bu)<sub>3</sub><sup>0/-</sup> couple would be shifted by almost 0.5 V. This large shift in potential due to a change in

(25) Parker, V. J. *Am. Chem. Soc.* **1976**, *98*, 98.

(26) (a) Kalinowski, M. K.; Cmeil, A. *Inorg. Chim. Acta* **1981**, *49*, 179. (b) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687. (c) Gutman, V. *Coord. Chem. Rev.* **1976**, *18*, 225.

(27) (a) Born, M. *Z. Phys.* **1920**, *1*, 45. (b) Roux, B.; Yu, H.-A.; Karplus, M. *J. Phys. Chem.* **1990**, *94*, 4683. (c) Millen, W. A.; Watts, D. W. *J. Am. Chem. Soc.* **1967**, *89*, 6052. (d) Krishtalik, L. I.; Alpatova, N. M.; Ovsyannikova, E. V. *Electrochim. Acta* **1991**, *36*, 435. (e) Noyes, R. J. *Am. Chem. Soc.* **1962**, *84*, 513.

(28) Trasatti, S. *Pure Appl. Chem.* **1986**, *58*, 955.

(29) Popovych, O. *Crit. Rev. Anal. Chem.* **1970**, *1*, 73.

(30) Sahami, S.; Weaver, M. J. *J. Solution Chem.* **1981**, *10*, 199.

differential solvation energy illustrates the danger of interpreting electrochemical potentials in terms of the molecular properties of the redox couple alone and ignoring the solvation contribution.

For comparison to these data, the value of  $\Delta G_1^\circ$  for ferrocene (153.1 kcal mol<sup>-1</sup>) can be used in eq 3 to obtain a value of  $\Delta\Delta G_{\text{solv}}^\circ(0/+)$  for ferrocene of -37 kcal mol<sup>-1</sup> for DMF as a solvent (see also refs 3 and 4a). Thus, the +/0 couples for the ruthenium  $\beta$ -diketonate complexes have about half the differential solvation energy of the  $\text{Fc}^{+/0}$  couple. The solvation free energies of these metal complexes are significantly less than those of even larger bare metal ions; e.g., the single ion free energy of hydration of  $\text{Cs}^+$  is -66 kcal mol<sup>-1</sup> at 25 °C (using the same free energy of hydration for the proton used for the absolute SHE potential above<sup>28</sup>). The free energy of transfer from water to DMF is small (on the order of -2 kcal mol<sup>-1</sup> for group 1 metal ions). Of course, the bare metal ions form an inner coordination shell of solvent molecules which provide much of the solvation energy (e.g., the  $\Delta H^\circ$  for  $\text{Cs}^+(\text{g}) + 4\text{H}_2\text{O} \rightleftharpoons \text{Cs}(\text{H}_2\text{O})_4^+$  is -48 kcal mol<sup>-1</sup>),<sup>19d</sup> and the complex ions here are coordinatively saturated prior to solvation.

It should be noted that comparisons of solvation energies must be done with care, since a single ion solvation energy (e.g., defined for  $\text{M}^+(\text{g}) \rightleftharpoons \text{M}^+(\text{soln})$ ) is not the same as the differential solvation energy (which corresponds to  $\text{M}^+(\text{g}) + \text{M}(\text{soln}) \rightleftharpoons \text{M}(\text{g}) + \text{M}^+(\text{soln})$ ). These two quantities differ by the solvation energy of the neutral species, a relatively small quantity for atoms that can be estimated by various methods.<sup>27c</sup> For neutral metal complexes, however, the solvation energy of the neutral species could be substantial if specific interactions such as hydrogen bonding are present.

The origin of difference in the magnitudes of differential solvation free energies for the 0/- and +/0 couples is not understood at this time. Despite the experimental evidence to the contrary, ion pairing may be a factor (particularly for the Ru(II) negative ion, which has a more exoergic solvation free energy than the Ru(IV) cation). The similarity of electrode potentials in DMF and acetonitrile with different electrolytes suggests that specific molecular interactions between solvent and the complexes are not critical in the derived solvation energetics. Useful comparisons can be made by comparing the crystallographic radius of ruthenium acetylacetonate ( $\text{Ru}(\text{Me}_3\text{CCH}=\text{C}(\text{Me})_2)_3$ ) with the effective radius ( $r_{\text{eff}}$ ) predicted by the Born model based on derived  $\Delta\Delta G_{\text{solv}}^\circ$  values. An average value of -17.3 kcal mol<sup>-1</sup> for  $\Delta\Delta G_{\text{solv}}^\circ(0/+)$  gives an average  $r_{\text{eff}}$  of ~9.3 Å for all of the cations, which all have comparable  $\Delta\Delta G_{\text{solv}}^\circ(0/+)$  values (the most negative  $\Delta\Delta G_{\text{solv}}^\circ(0/+)$  value is that of  $\text{Ru}(\text{Me}_3\text{CCH}=\text{C}(\text{Me})_2)_3$  and yields  $r_{\text{eff}} = 8.6$  Å). These values can be compared to the crystallographic structure of  $\text{Ru}(\text{Me}_3\text{CCH}=\text{C}(\text{Me})_2)_3$ , in which the distance from the ruthenium atom to the peripheral methyl hydrogens is ~6 Å. The derived thermochemical radii (~9 Å) for the +/0 couples are more consistent with that expected for the larger  $\text{Ru}(t\text{-Bu}_3\text{CCH}=\text{C}(\text{Me})_2)_3^{+/0}$  couple. Ion pairing or specifically stabilizing solvation of the cation by DMF is not consistent with a *larger* deduced thermochemical radius than the maximum structural radius, so the large thermochemical radii for the smaller +/0 couples are not readily explained by experimental artifacts (i.e., ion pairing to the cation would tend to increase the exoergicity of solvation of the ion and thus reduce the thermochemical radius, not increase it).

For negative ions, the  $\Delta\Delta G_{\text{solv}}^\circ(0/-)$  data give values of  $r_{\text{eff}}$  that range from 3.4 Å for  $\text{Ru}(\text{Me}_3\text{CCH}=\text{C}(\text{Me})_2)_3^-$  to 4.5 Å for  $\text{Ru}(t\text{-Bu}_3\text{CCH}=\text{C}(\text{Me})_2)_3^-$ . We have previously speculated<sup>9</sup> that  $r_{\text{eff}}$  values derived from  $\Delta\Delta G_{\text{solv}}^\circ(0/-)$  data for a series of acetylacetonate complexes are smaller than the crystallographic radii due to

**Table 3.** Analysis of Free Energies of Ionization and Electron Attachment for Ruthenium Tris( $\beta$ -diketonate) Complexes

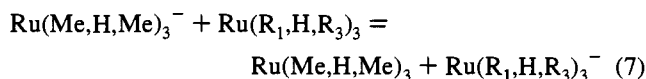
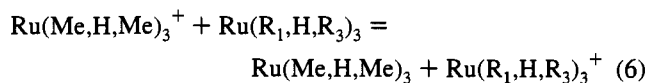
complex	$\Delta G_6^\circ$ <sup>a,b</sup>	$\Delta G_7^\circ$ <sup>a,b</sup>	$\Delta G_{10}^\circ$ <sup>a</sup>	$\Sigma\sigma_f$ <sup>c</sup>	$\Sigma\sigma_a$ <sup>c</sup>	$I^{a,d}$	$P^{a,d}$
$\text{Ru}(\text{Me}_3\text{CCH}=\text{C}(\text{Me})_2)_3$	0.0	0.0	0.0	-0.276	-2.10	0.0	0.0
$\text{Ru}(\text{Et}_3\text{CCH}=\text{C}(\text{Me})_2)_3$	-2.1	-1.9	-0.2	-0.330	-2.94	0.1	2.0
$\text{Ru}(n\text{-Pr}_3\text{CCH}=\text{C}(\text{Me})_2)_3$	-3.5	-4.8	1.3	-0.348	-3.24	-0.6	4.1
$\text{Ru}(n\text{-Bu}_3\text{CCH}=\text{C}(\text{Me})_2)_3$	-3.6	-4.8	1.2	-0.360	-3.42	-0.6	4.2
$\text{Ru}(i\text{-Pr}_3\text{CCH}=\text{C}(\text{Me})_2)_3$	-3.4	-3.7	0.3	-0.384	-3.72	-0.2	3.5
$\text{Ru}(t\text{-Bu}_3\text{CCH}=\text{C}(\text{Me})_2)_3$	-3.8	-4.7	0.9	-0.444	-4.50	-0.5	4.2

<sup>a</sup> Units are in kilocalories per mole. <sup>b</sup> Estimated error in relative values  $\pm 0.7$  kcal mol<sup>-1</sup> based on the estimated relative error in  $\Delta G_6^\circ$  and  $\Delta G_7^\circ$  values ( $\pm 0.5$  kcal mol<sup>-1</sup>). <sup>c</sup> Sums of parameters ( $6\sigma$ ). Parameters from refs 22 and 33. <sup>d</sup> Estimated error  $\pm 0.5$ . The value shown is for the effect of all six R groups on the complex. To obtain the parameter on a per R group basis, this value must be divided by 6.

interpenetration of solvent molecules between the cavities formed by the chelate ligands. This explanation is supported by the lower values of  $|\Delta\Delta G_{\text{solv}}^\circ|$  obtained for complexes with larger alkyl substituents, since steric effects would be expected to hinder solvation for larger R groups by restricting access of solvent to the charged regions of the molecule. However, in view of the less predictable trends in the solvation energetics of the corresponding +/0 couples, this model may obscure other contributions to the total solvation energy.

We now consider other contributions to solvation energies based on a more complete model for electrostatic interactions between a nonspherical molecule and solvent. Assuming no significant difference among the structures of the cationic, neutral, and anionic complexes, the differential solvation free energy results may indicate a significant difference in the distribution of charge in the neutrals, cations, and anions. The Born approach<sup>27</sup> assumes uncharged spheres and charged conducting spheres (monopoles) of uniform charge distribution, but inclusion of multipolar terms is necessary when the molecule does not have a uniform charge distribution. To assess the charge distributions in the  $\text{Ru}(\text{Me}_3\text{CCH}=\text{C}(\text{Me})_2)_3$  neutral complex and its ions, we used the semiempirical ZINDO<sup>17</sup> molecular orbital method. The solvent was modeled in these calculations by a dielectric continuum. The results of the preliminary calculations were not consistent with an explanation of the trend in solvation energetics based on variations in the quadrupolar moments for the nondipolar neutral and ions. Quantitatively, the contributions of the quadrupole term<sup>31</sup> to the calculated solvation energies were not significant (<1 kcal/mol), which is not surprising given the large radii of the complexes. It appears that specific solvent-solute interactions must be considered to rationalize the difference between the solvation energetics of the +/0 and 0/- couples.

**Analysis of Trends in Gas-Phase Data.** The trends in the gas-phase  $\Delta G_1^\circ$  and  $\Delta G_a^\circ$  values for the  $\text{Ru}(\text{R}_1\text{H},\text{R}_3)_3$  complexes are most conveniently considered as shifts relative to  $\text{R}_1$  and  $\text{R}_3 = \text{methyl}$ , as defined by  $\Delta G^\circ$  for the reactions in eqs 6 and 7. Values of  $\Delta G^\circ$  for eqs 6 and 7 ( $\Delta G_6^\circ$  and  $\Delta G_7^\circ$ ) are



given in Table 3. For both eqs 6 and 7 with all species in the gas phase, transferring the *charge* from the  $\text{Ru}(\text{Me}_3\text{CCH}=\text{C}(\text{Me})_2)_3$  complex to the other alkyl complexes is exoergic.

(31) (a) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351. (b) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506.

The  $\Delta G_1^\circ$  data expressed by  $\Delta G_6^\circ$  values can be fit using  $\sigma_1$  parameters with eq 8. The  $\Delta G_a^\circ$  data given by the  $\Delta G_7^\circ$  values are fit by the analogous eq 9. The fits of eqs 8 and 9 are rather poor ( $r = 0.84$  and  $0.79$ , respectively), reflecting the lack of correlation for the *n*-Pr and *n*-Bu cases noted above. In

$$\begin{aligned} \Delta G_6^\circ(\text{Ru}(\text{R}_1, \text{H}, \text{R}_3)_3^{0/+}) &= \rho_+[3\sigma_1(\text{R}_1) + 3\sigma_1(\text{R}_3)] + c = \\ &\rho_+(\sum \sigma_1) + c \\ &= [22(\sum \sigma_1) + 5.1] \text{ kcal mol}^{-1} \quad (8) \end{aligned}$$

$$\begin{aligned} \Delta G_7^\circ(\text{Ru}(\text{R}_1, \text{H}, \text{R}_3)_3^{0/-}) &= \rho_-[3\sigma_1(\text{R}_1) + 3\sigma_1(\text{R}_3)] + c' = \\ &\rho_-(\sum \sigma_1) + c' \\ &= [28(\sum \sigma_1) + 6.6] \text{ kcal mol}^{-1} \quad (9) \end{aligned}$$

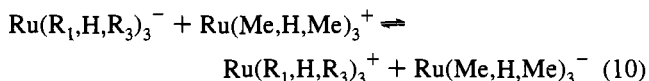
correlations with parameters such as Taft  $\sigma_1$ ,<sup>22</sup> the slope of the regression line is the  $\rho_+$  value, which is a measure of the sensitivity of  $\Delta G_1^\circ$  to alkyl substitution *per substituent* in this case. The value of  $\rho_+$  ( $=22 \pm 7 \text{ kcal mol}^{-1}$ ) in the fit of eq 8 is approximately 45% of that observed for analogous fits to ionizations of 1,1'-alkylferrocenes ( $57 \text{ kcal mol}^{-1}$ ) and 1,1'-dialkylnickelocenes ( $50 \text{ kcal mol}^{-1}$ ),<sup>3,4a</sup> but since  $\text{Ru}(\text{R}_1, \text{H}, \text{R}_3)_3$  complexes have six alkyl substituents (instead of two), the range of observed  $\Delta G_1^\circ$  is slightly greater for a given substituent in the present cases. The value of the constant in eq 8 ( $5.1 \text{ kcal mol}^{-1}$ ) is the expected value of  $\Delta G_6^\circ$  when  $\text{R}_1 = \text{R}_3 = \text{H}$  since  $\sigma_1(\text{H}) = 0$  by definition; therefore, the ionization free energy at 350 K for the unknown  $\text{Ru}(\text{H}, \text{H}, \text{H})_3$  complex is estimated as  $154 \text{ kcal mol}^{-1}$  ( $6.7 \text{ eV}$ ). In a similar manner, the  $\Delta G_a^\circ$  value for  $\text{R}_1 = \text{R}_3 = \text{H}$  is estimated from the constant in eq 9 as  $-34 \text{ kcal mol}^{-1}$ . It should be noted that the effect of  $\text{R} = \text{H}$  compared to  $\text{R} = \text{Me}$  does not always fit a  $\sigma_1$  correlation (especially for electron attachment),<sup>3</sup> so these predictions are not necessarily reliable.

As shown in Figure 3b and Table 3, substitution of larger alkyl groups for the methyl group stabilizes both positive and negative complexes relative to the neutral complex in the gas phase. The gas-phase  $\rho_-$  value for electron attachment from eq 9 is  $28 \pm 11$ , comparable in magnitude with the gas-phase  $\rho_+$  value for ionization ( $22 \pm 7$ ). Alkyl groups, therefore, are not intrinsically electron donating in ruthenium tris( $\beta$ -diketonate) complexes (by electron donating, we mean that a higher oxidation state is more stabilized relative to a lower one as the alkyl group increases in size). The increased stabilization of both positive and negative forms of the complexes relative to the neutral for larger alkyl groups can be attributed to the increasing polarizability of larger alkyl substituents, as discussed below. Furthermore, the amount of stabilization is approximately equal for positive and negative ions as seen by the  $\rho$  values. This result is in contrast to  $\Delta G_1^\circ$  and  $\Delta G_a^\circ$  data obtained for 1,1'-dialkylnickelocenes,<sup>3</sup> which demonstrated that ionization energies were approximately 6 times more sensitive to alkyl substitution than electron attachment energies. Also, studies of gas-phase proton-transfer acidities of various cationic and neutral acids have demonstrated that alkyl groups stabilize positive charge more effectively than negative charge.<sup>1,2</sup> Therefore, the comparable alkyl effects on both the positive and negative ion couples in the present study stand in contrast to most previous comparisons of gas-phase alkyl effects on ion-neutral thermochemistry.

In terms of a classical electrostatic model, the observed trends can be rationalized in terms of a predominant polarizability effect of the substituents and a small, essentially unimportant, inductive effect. Taft et al.<sup>11</sup> proposed a quantitative model to

separate the contributions of polarizability ( $P$ ) and inductive ( $I$ ) effects of substituents based on thermodynamic results from gas-phase proton transfer equilibria. The  $P/I$  model was applied to data obtained for alcohols ROH and their conjugate bases ( $\text{RO}^-$ ) and acids ( $\text{ROH}_2^+$ ). The model was also successful in correlating trends in  $\Delta G_1^\circ$  and  $\Delta G_a^\circ$  for alkylnickelocenes.<sup>3</sup> We have applied the model here to quantify the effects of polarization and induction in the gas-phase ruthenium tris( $\beta$ -diketonate) redox thermodynamics. It should be emphasized that this analysis is *independent* of any previous parameterization scheme for substituent effects.

The  $P/I$  analysis is based on the free energies for the hypothetical reaction given in eq 10. The stabilization due to



polarization of alkyl substituents ( $P$ ), relative to methyl, is assumed to be equal in  $\text{Ru}(\text{R}_1, \text{H}, \text{R}_3)_3^+$  and  $\text{Ru}(\text{R}_1, \text{H}, \text{R}_3)_3^-$ , and therefore, the value of  $\Delta G_{10}^\circ$  depends only on the inductive effect ( $I$ ). With  $I$  and  $P$  positive, the model requires  $-\Delta G_6^\circ = P + I$ ,  $-\Delta G_7^\circ = P - I$ , and  $-\Delta G_{10}^\circ = 2I$ . The results of the analysis are presented in Table 3 (note that the  $P$  and  $I$  values are for the *total* effect of six R groups and must be *divided by 6* to obtain the average contribution *per R group*). In contrast to the cases analyzed earlier<sup>3,11</sup> by the  $P/I$  model, the values of  $\Delta G_{10}^\circ$  for the hypothetical equilibria of eq 10 do not correlate well with  $\sigma_1$  ( $r = 0.4$ ). The extracted values of  $I$  are not significantly different from zero relative to the estimated error in  $I$  ( $\pm 0.5 \text{ kcal mol}^{-1}$ ), and the *stabilizing effect of the larger alkyl groups is primarily due to their greater polarizability* in this model. The  $P$  values are significantly different for Me, Et, and the four others as a group (at the 95% confidence level). There is no significant difference between the  $P$  values for the four Pr and Bu substituents even though a much larger polarizability effect would be expected for, say, *t*-Bu compared to *n*-Pr (see below and the discussion of similar observations in the  $P/I$  analysis of Taft et al.<sup>11</sup>).

The  $P$  values in Table 3 are significantly larger in magnitude than the  $I$  values, again in contrast to previous studies where the magnitudes of  $I$  and  $P$  are comparable (nickelocene redox<sup>3</sup>) or  $I$  is greater than  $P$  (organic acids and bases<sup>11</sup>). The differences in  $P$  values *per group* between  $\text{R} = \text{Me}$  and  $\text{R} = t\text{-Bu}$  are 1.0 and 0.7 for the alkylnickelocenes<sup>3,32</sup> and the  $\text{Ru}(\text{R}, \text{H}, \text{R})_3$  complexes, respectively, indicating a 30% reduction in the polarizability effect for the latter complexes. From a structural point of view, this result is reasonable: the metal- $\alpha$ -carbon distance is  $\sim 4.3 \text{ \AA}$  for the  $\text{Ru}(\text{R}, \text{H}, \text{R})_3$  complexes vs  $\sim 3.3 \text{ \AA}$  for alkylnickelocenes. Precise adherence to the  $1/r^4$  dependence of polarizability effects would not be expected for complexes with such different electronic structures.

Of course, the  $P/I$  model gives no indication about *why* the inductive effect is insignificant in the  $\text{Ru}(\text{R}, \text{H}, \text{R})_3$  complexes compared to the nickelocenes, but it is notable that the parent ligands are quite different in their interaction with the metal centers ( $\pi$  donor Cp vs  $\sigma$  donor acac) and the substituent is one atomic center further removed from the metal in the  $\text{M}(\text{R}, \text{H}, \text{R})_3$  case. The inductive effects of alkyl groups are relatively small in any case,<sup>22</sup> and the correlation of the gas-phase free energies with the inductive parameters  $\sigma_1$  (Figure 3b) is rationalized by the correlation of  $\sigma_1$  with the polarizabilities of alkyl groups.

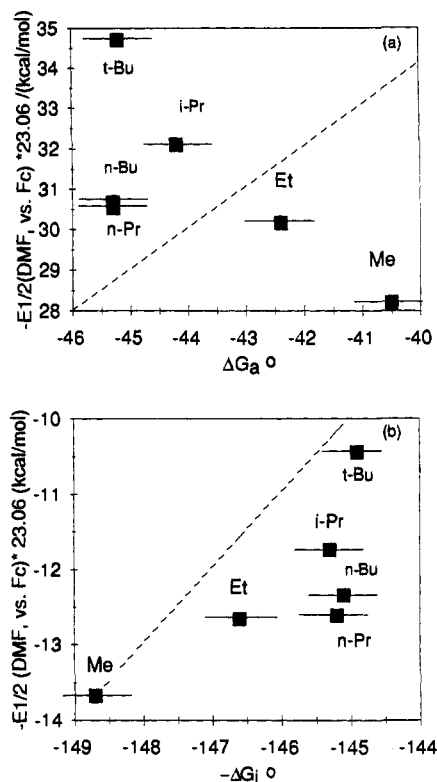
(32) In Table I of ref 3, some of the entries for  $\text{L} = \text{L}' = \text{MeCp}$  should be corrected as follows:  $\Delta G_1^\circ = -4.2$ ;  $\Delta G_a^\circ = -4.9$ ;  $\Sigma I = 2.5$ ;  $\Sigma P = 2.4$ . The resulting  $P$  and  $I$  values for  $\text{R} = \text{Me}$  (per group) are then  $I = 1.3$  and  $P = 1.2$ . The conclusions in ref 3 are not affected by these changes.



Hehre et al.<sup>33</sup> have devised a set of substituent polarizability parameters for substituents ( $\sigma_\alpha$ ) based on theoretical calculations. The sums of the parameters for the alkyl substituents on the ruthenium tris( $\beta$ -diketonate) complexes are given in Table 3. A somewhat better fit to the  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  data is obtained with these parameters ( $r = 0.87$  for  $\Delta G_i^\circ$  and  $r = 0.82$  for  $\Delta G_a^\circ$ ) than with  $\sigma_1$ , although once again the  $\Delta G_i^\circ$  and  $\Delta G_a^\circ$  values obtained for Ru(*n*-Pr,H,*n*-Pr)<sub>3</sub> and Ru(*n*-Bu,H,*n*-Bu)<sub>3</sub> are not fit well by these parameters. Since  $\sigma_1$  and  $\sigma_\alpha$  are strongly correlated for alkyl groups, the fit of ionization or electron attachment data *separately* to either parameter would not support any conclusion on the "origin" of the trends with varying alkyl groups. The *P/I* analysis provides an alternative method for extracting the origin of the trends by *combining* ionization and electron attachment data. As expected, a strong correlation is found between derived *P* values and  $\Sigma\sigma_\alpha$  (Table 3), and the correlation is quite good when the *n*-Pr and *n*-Bu groups are excluded ( $r = 0.98$ ).

**Effects of *n*-Bu and *n*-Pr Substituents.** As is clear from the above discussion and Figure 3, the *n*-Bu and *n*-Pr groups do not affect the redox energetics as expected in the *P/I* analysis or in fits to substituent parameters such as  $\sigma_\alpha$  and  $\sigma_1$ . Plots of the gas-phase energies vs the solution electrode potentials clearly show that the R = *n*-alkyl complexes do not follow the trends established by the more rigid Me, Et, *i*-Pr, and *t*-Bu groups (Figure 4). While the deviations observed might be the result of inaccurate pressure measurements for these two R = *n*-alkyl complexes, the data are also consistent with another explanation based on the conformational flexibility of the longer *n*-alkyl chains. It is probable that the alkyl chains fold back onto the complex to provide additional polarization stabilization of charge buildup upon oxidation or reduction. Such an effect is not evident in solution (note good  $\sigma_1$  fits in Figure 3a), where the solvent dominates the polarization stabilization of charge increase on the complex and the alkyl chains are presumably in an average conformation that resembles that used to establish the  $\sigma_\alpha$  parameters (i.e., "stretched out" away from the metal center).<sup>32</sup> In essence, the less effective intramolecular "solvation" by the conformationally flexible longer chain alkyls present in the gas phase is replaced in solution by the more effective polar solvation shell.

Similar conformational effects can be invoked to explain trends in gas-phase ion thermochemistry for other ions having long chain alkyl substituents. For example, a plot of free energies of proton attachment<sup>21,34</sup> vs  $\sigma_1$  for a series of primary alkylamines also has the *n*-Pr and *n*-Bu cases off the trend line established by the more rigid alkyls, with the *n*-Pr and *n*-Bu amines having a *greater* basicity than expected. Much greater effects due to conformational "wrapping" of long chain substituents are observed for diaminoalkanes, where intramolecular H-bonds contributing an additional  $\sim 20$  kcal/mol to the proton affinity can form by intramolecular ring formation.<sup>35</sup> Evidence for enhanced polarization stabilization by flexible alkyl groups appears in the *P/I* analysis of Taft et al.<sup>11</sup> Clear evidence for intramolecular interactions between a charge center and long *n*-alkyl chains has been presented by Meot-Ner (Mautner), Sieck, and Ausloos in their study of the ionization thermochemistry of normal alkanes.<sup>36</sup>



**Figure 4.** Gas-phase  $\Delta G_a^\circ$  and  $\Delta G_i^\circ$  values vs electrode potentials in DMF for ruthenium tris( $\beta$ -diketonate) complexes: (a) electron attachment (0/− couples), (b) ionization (0/+ couples). The R = *n*-Pr and *n*-Bu complexes have higher electron affinities and lower ionization energies than predicted from the trends for the R = Me, Et, *i*-Pr, and *t*-Bu complexes. On both plots, a dashed line of unity slope is drawn to illustrate the trends that would be observed if the gas-phase and solution energies were directly correlated (i.e., if all couples had the same solvation energy). In (b), the line indicates the expected trend if all couples had the same differential solvation free energies as the R = Me complex. The complete reversal of the trend in (a) from the unity slope of the dashed line to a slope of ca. −1 (for R = Me, Et, *i*-Pr, *t*-Bu) is a consequence of the larger variation of solvation energies as described in the text. The horizontal error lines indicate the estimated relative error for the gas-phase data.

**Trifluoromethyl Substituents.** As reported previously,<sup>9</sup> substituting R = Me with R = CF<sub>3</sub> leads to a large increase in the electron affinity of metal  $\beta$ -diketonate complexes. It is of interest to consider the effects of CF<sub>3</sub> substituents by the same methods used above for alkyl substituents. The effects of CF<sub>3</sub> substitution are much larger than the relatively subtle effects of different alkyl groups, and CF<sub>3</sub> has a large, positive inductive effect and a much smaller polarizability than alkyl groups as seen in the  $\Sigma\sigma_1$  and  $\Sigma\sigma_\alpha$  parameters shown in Table 4. The analysis will therefore provide a check on the general suitability of the *P/I* analysis used above for alkyl groups.

Table 4 presents data on ionization and electron attachment energies for two ruthenium diketonate complexes with R = CF<sub>3</sub> substituents. The  $\Delta G_a^\circ$  value for Ru(CF<sub>3</sub>,H,CF<sub>3</sub>)<sub>3</sub> in Table 4 has been estimated from the ETE value<sup>9a</sup> for Ru(CF<sub>3</sub>,H,CH<sub>3</sub>)<sub>3</sub> assuming that replacement of each Me group by CF<sub>3</sub> produces the same shift in electron affinity (6 kcal mol<sup>−1</sup> per group). Given the close agreement of ETE  $\Delta G_i^\circ$  values and photoelectron ionization potentials noted for the R = alkyl complexes above, the estimated  $\Delta G_i^\circ$  values in Table 4 can be used with some confidence (estimated error  $\pm 5$  kcal mol<sup>−1</sup>).

The results of a *P/I* analysis of the data for R = CF<sub>3</sub> complexes are presented in Table 4. Even noting the possible errors in the estimated ionization and electron attachment energies, it is clear that (a) the CF<sub>3</sub> group exerts most of its

(33) (a) Hehre, W. J.; Pau, C.-P.; Headley, A. D.; Taft, R. W.; Topsom, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 1711. (b) Taft, R. W. *Prog. Phys. Org. Chem.* **1987**, *16*, 1.

(34) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311, 318.

(35) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 2699.

(36) Meot-Ner (Mautner), M.; Sieck, L. W.; Ausloos, P. *J. Am. Chem. Soc.* **1981**, *103*, 5342.

**Table 4.** Data and Substituent Effect Analysis for Ruthenium Tris( $\beta$ -diketonate) Complexes with R = Trifluoromethyl

complex	$\Delta G_1^\circ$ <sup>a,b</sup>	$-\Delta G_a^\circ$ <sup>a</sup>	$\Delta G_6^\circ$ <sup>a</sup>	$\Delta G_7^\circ$ <sup>a</sup>	$\Delta G_{10}^\circ$ <sup>a</sup>	$\Sigma\sigma_1^c$	$\Sigma\sigma_\alpha^c$	$I_{a,d}$	$P_{a,d}$
Ru(CF <sub>3</sub> H,CH <sub>3</sub> ) <sub>3</sub>	169	64 <sup>e</sup>	20.3	-23	43	1.0	-1.8	-22	-0.4
Ru(CF <sub>3</sub> H,CF <sub>3</sub> ) <sub>3</sub>	197 <sup>e</sup>	(88) <sup>f</sup>	48.3	-47	95	2.3	-1.5	-48	1.6

<sup>a</sup> Units are kilocalories per mole. <sup>b</sup> Estimated from adiabatic ionization potentials reported in ref 5a. The estimated error for absolute values is  $\pm 5$  kcal mol<sup>-1</sup>. <sup>c</sup> Sums of parameters ( $6\sigma$ ). Parameters from refs 22 and 33. <sup>d</sup> Estimated error  $\pm 3$ . The value shown is for the effect of all six R groups on the complex. To obtain the parameter on a per R group basis, this value must be divided by 6. <sup>e</sup> Reference 9a. <sup>f</sup> Estimated as described in the text.

influence via the inductive (field) effect in this model and (b) the polarizability contribution is small and on the order of magnitude of that of an alkyl group. This result is in accord with other parameterization schemes and suggests that the *P/I* model provides reasonable insight into the origin of substituent effects in these particular gas-phase redox processes.

When the gas-phase data for the R = CF<sub>3</sub> compounds are combined with those for R = alkyls, the correlation of  $\Delta G_1^\circ$  values with  $\Sigma\sigma_1$  is strong because of the dominance of inductive effects for the two R = CF<sub>3</sub> compounds. The overall correlation of the combined  $\Delta G_a^\circ$  values with  $\Sigma\sigma_1$  is also strong despite the reversal in the plot for the alkyl groups (which cover a narrow range of  $\Sigma\sigma_1$  values, Figure 3b). In contrast, the correlation of the combined  $\Delta G_a^\circ$  or  $\Delta G_1^\circ$  values with  $\Sigma\sigma_\alpha$  is now poor since polarizability has little contribution to the energy trends for the R = CF<sub>3</sub> compounds.

It must be noted that  $\pi$ -resonance effects<sup>22</sup> have not been included but may be important for some substituents since the groups are attached to a planar,  $\pi$ -anion chelating ligand. At this time, an accurate data set for other R groups is not available in the gas-phase ruthenium tris( $\beta$ -diketonate) series, so an analysis involving a wide variety of substituents is not possible.

**Conclusions.** The present work and studies of alkylnickel-ocenes<sup>3</sup> show that the gas-phase electron affinity of metal complexes can be *increased* by larger alkyl substituents. It is now clear that alkyl groups on ligands are not intrinsically electron donating with respect to the gas-phase redox thermochemistry of metal complexes and do not always result in lower electron affinities. The present study has compared R = Me to larger alkyl substituents. The relative effects of R = H and R = Me are not necessarily predictable for the diketonate complexes, since methyl substituents on sp<sup>2</sup> carbon in known cases lower electron affinities relative to hydrogen for organo-metallics and organic compounds.<sup>3,37</sup>

An electrostatic model for the alkyl effects incorporating both inductive and polarization contributions successfully rationalizes the gas-phase trends for the ruthenium  $\beta$ -diketonate complexes. The model analysis suggests that inductive effects are insignificant for these R<sub>1</sub> = R<sub>3</sub> = alkyl substituted complexes, and the gas-phase effects are therefore dominated by the polarizability of the attached group. In contrast, a similar analysis for R = CF<sub>3</sub> complexes suggests that the substantial effect of that group on gas-phase ionization and electron attachment energies is dominated by a large inductive effect. Additional stabilization of charge buildup when the substituent is a conformationally flexible long chain alkyl is suggested by fits of the gas-phase data to  $\sigma_1$  or  $\sigma_\alpha$  parameters and the *P/I* analysis.

Analysis of the solvation energetics for the Ru(R,H,R)<sub>3</sub> one-electron oxidation and reduction couples traces the reversal of trends for gas-phase and solution reductions to the change in differential solvation free energy as a function of the alkyl group. In the reduction of the neutral complex, larger alkyl groups can

be considered to disrupt solvation by restricting solvent access to the charged member of the couple; therefore, the high dielectric solvent is replaced by a low dielectric alkane at the periphery of the complex. This simple rationale does not explain the less exoergic and essentially constant differential solvation free energies for the oxidation couples, however. Despite experimental evidence to the contrary, ion pairing effects cannot be excluded as a possible explanation for the unexpected differences in the reduction and oxidation solution thermochemistry. A more complete model for the solvation thermochemistry would also consider charge distributions and specific solute-solvent interactions in the solvated complexes. A wide variety of sophisticated methods are now available for modeling these effects,<sup>38</sup> and these theoretical approaches may provide quantitative insights into the questions raised by the thermodynamic results described here.

**Acknowledgments.** This work was supported by grants from the National Science Foundation (CHE9008663, CHE9311614). The authors are grateful to M. Zerner and M. Cory for discussions and assistance with the ZINDO calculations. The authors thank J. Miller for the donation of (TMSCp)<sub>2</sub>Fe for use as a reference compound.

## Appendix

Values of  $\Delta G_1^\circ$  and  $\Delta G_a^\circ$  are determined for new compounds by combining data on equilibrium constants for reactions of the type in eqs 1 and 2 with known  $\Delta G_1^\circ$  and  $\Delta G_a^\circ$  values for reference compounds. When an equilibrium constant is large or small, one neutral reactant must have a high partial pressure relative to the other so that the mass spectral intensities of the two ions will be comparable ( $K_{eq} = (I_1P_2)/(I_2P_1)$ , where  $I$  is the mass spectral intensity and  $P_1$  and  $P_2$  are the neutral partial pressures). Since there is an upper limit to total pressures in the FT-ICR experiment, the pressure of one of the gases may be low and comparable to the error in the pressure measurements. It is this limitation on the accuracy of low pressure determinations that limits measurements of equilibrium constants by FT-ICR to approximately the range  $0.001 < K_{eq} < 1000$ . Given the rather small perturbations introduced by varying the alkyl groups, we have used a weighted error analysis in extracting the  $\Delta G_1^\circ$  and  $\Delta G_a^\circ$  values for the ruthenium complexes in this study from equilibria with two or more

(37) (a) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Phys. Chem.* **1982**, *86*, 4873. (b) Janousek, B. K.; Brauman, J. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 2. (c) Heinis, T.; Chowdhury, S.; Scott, S. L.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 400 and references therein.

(38) Some recent references: (a) Gilson, M.; Honig, B. *Proteins* **1988**, *4*, 7. (b) Ford, G. P.; Wang, B. *J. Am. Chem. Soc.* **1992**, *114*, 10563 and references therein. (c) Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1992**, *113*, 8552. (d) J-Charles, A.; Nicholls, A.; Sharp, K.; Honig, B.; Tempczyk, A.; Hendrickson, T. F.; Still, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 1454. (e) Mohan, V.; Davis, M. E.; McCammon, J. A.; Pettitt, B. M. *J. Phys. Chem.* **1992**, *96*, 6428. (f) Bontha, J. R.; Pintauro, P. N. *J. Phys. Chem.* **1992**, *96*, 7778. (g) Lim, C.; Bashford, D.; Karplus, M. *J. Phys. Chem.* **1991**, *95*, 5610. (h) Noodleman, L.; Case, D. A.; Pique, M.; Bashford, D. *Abstracts of Papers*, 203rd ACS National Meeting, 1992; Division of Inorganic Chemistry, American Chemical Society: Washington, DC, 1992; Abstract 596. (i) Karelson, M. M.; Zerner, M. C. *J. Phys. Chem.* **1992**, *96*, 6949. (j) Rauhut, G.; Clark, T.; Steinke, T. *J. Am. Chem. Soc.* **1993**, *115*, 9174.

reference compounds. The method described below weights measurements made with  $P_1 \approx P_2$  (i.e., possible when  $K_{\text{eq}}$  values are near unity) more heavily than those where one pressure is much lower than the other.

The weighted average value and its error for each unknown  $\Delta G_i^\circ$  or  $\Delta G_a^\circ$  value is calculated in two steps. First, multiple determinations of the equilibrium constant with a single reference compound are combined to give a best value for  $\Delta G_{\text{et}}$ . Since the pressure of the neutral compounds is the primary source of experimental error, the error for each equilibrium constant will be pressure dependent. Thus, the error in each  $\Delta G_{\text{et}}$  is given by eq A1 (assuming the errors in the two pressures  $P_1$  and  $P_2$  are independent). From  $\Delta G_{\text{et}} = -RT \ln K_{\text{eq}}$ ,  $\partial \Delta G_{\text{et}} /$

$$\delta \Delta G_{\text{et}} = [(\partial \Delta G_{\text{et}} / \partial P_1)^2 \delta P_1^2 + (\partial \Delta G_{\text{et}} / \partial P_2)^2 \delta P_2^2]^{1/2} \quad (\text{A1})$$

$\partial P_1 = RT/P_1$  and  $\partial \Delta G_{\text{et}} / \partial P_2 = -RT/P_2$ . A typical value for the error in measured pressure,  $\delta P$ , is  $\pm 5 \times 10^{-8}$  Torr. From these results, a weighted average free energy change and the error in this value,  $\langle \Delta G_{\text{et}} \rangle \pm \langle \delta \Delta G_{\text{et}} \rangle$ , is computed by using eqs

A2 and A3, where the summations are over all  $\Delta G_{\text{et}}$  values ( $\Delta G_j$ ) obtained for a single reference compound.

$$\langle \Delta G_{\text{et}} \rangle = \sum (\Delta G_j / \delta \Delta G_j^2) / \sum (1 / \delta \Delta G_j^2) \quad (\text{A2})$$

$$\langle \delta \Delta G_{\text{et}} \rangle = [\sum (1 / \delta \Delta G_j^2)]^{1/2} \quad (\text{A3})$$

Once  $\langle \Delta G_{\text{et}} \rangle \pm \langle \delta \Delta G_{\text{et}} \rangle$  for each reference compound has been found, the derived  $\Delta G_i^\circ$  or  $\Delta G_a^\circ$  value for the new compound is obtained for each reference, and the errors from eq A3 are propagated into the resulting values. The best value for  $\Delta G_i^\circ$  or  $\Delta G_a^\circ$  is finally obtained as a weighted average (by using eq A4) of the values from equilibria with the different reference

$$\langle \Delta G \rangle = \sum (\Delta G_k / \delta \Delta G_k^2) / \sum (1 / \delta \Delta G_k^2) \quad (\text{A4})$$

compounds ( $\Delta G_k$ ). Calculating the weighted average in this way takes into account the higher degree of accuracy inherent in the estimation of smaller free energy changes from equilibrium constants near unity.