olefins such as bromostyrene. The $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is consumed during this latter reaction, but no organometallic nitrosyl products are formed. Further studies in this regard are currently in progress.

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Registry No. $(\eta^5\text{-}C_5H_5)W(NO)_2H$, 69532-01-0; $(\eta^5\text{-}C_5H_5)W(NO)_2D$, 69532-02-1; $(\eta^5\text{-}C_5H_5)W(NO)_2OSO_2C_6H_4CH_3$, 69532-03-2; $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]BF_4$, 69532-04-3; $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$, 69532-05-4; $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$, 53419-14-0; $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$, 12305-00-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $[(\eta^5\text{-}C_5H_5)W(NO)_2(CO)]PF_6$, 53419-03-7; $Na[AlH_2(OCH_2CH_2OCH_3)_2]$, 22722-98-1; $(C_6H_5)_3CBF_4$, 341-02-6; $HCo(CO)_4$, 16842-03-8; $(\eta^5\text{-}C_5H_5)W(CO)_3H$, 12128-26-6.

References and Notes

(1) Part 7: Kolthammer, B. W. S.; Legzdins, P. *Inorg. Chem.*, in press.
(2) See for example: (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231, and references cited therein. (b) Schunn, R. A. In "The Hydrogen Series"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Vol 1, pp 203–69.
(3) Stewart, R. P., Jr.; Okamoto, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32.
(4) Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1975**, *14*, 1875.
(5) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1977**, *16*, 3173.
(6) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.
(7) Purchased from the Aldrich Chemical Co. as a 70% benzene solution under the trade name Red-al.
(8) Stewart, R. P., Jr.; Moore, G. T. *Inorg. Chem.* **1975**, *14*, 2699.
(9) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Synth.*, **1979**, *19*, 208.
(10) Olah, G. A.; Svoboda, J. J.; Olah, J. A. *Synthesis* **1972**, 544.
(11) (a) Gilmont, P.; Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 238. (b) Edgell, W. F.; Lyford, J. *Inorg. Chem.* **1970**, *9*, 1932.
(12) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, pp 168–69.
(13) Reference 12, pp 156–58.
(14) Barnett, K. W.; Slocum, D. W. *J. Organomet. Chem.* **1972**, *44*, 1.
(15) King, R. B.; Bisnette, M. B. *J. Am. Chem. Soc.* **1963**, *85*, 2527; *Inorg. Chem.* **1964**, *3*, 791.
(16) Cf. the thermal dimerization of $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$: Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
(17) For the first such adduct to be characterized see: McNeese, T. J.; Wreford, S. S.; Foxman, B. M. *J. Chem. Soc., Chem. Commun.* **1978**, 500.
(18) The general features of H^- attack on nitrosyl cations will be discussed in a future publication.
(19) Faller, J. W.; Anderson, A. S.; Chen, C. *J. Chem. Soc. D* **1969**, 719.
(20) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136, and references contained therein.
(21) Labinger, J. A. *Adv. Chem. Ser.* **1978**, *No. 167*, 11.
(22) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022.
(23) Green, M. L. H.; Street, C. N.; Wilkinson, G. *Z. Naturforsch., B* **1959**, *14*, 1595.
(24) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.
(25) Braunstein, P.; Dehand, J.; Munchenbach, B. *J. Organomet. Chem.* **1977**, *124*, 71.
(26) Gladysz, J. A.; Tam. W. *J. Am. Chem. Soc.* **1978**, *100*, 2545, and references contained therein.

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Quantitative Data on Some Oxidative Addition Reactions and on the Lewis Basicity of $Ir^I[(C_6H_5)_3P]_2(CO)Cl$

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A hydrogen-bonding interaction involving a d^8 transition-metal donor is reported and the enthalpy of adduct formation determined. This data coupled with the enthalpy of formation of the SO_2 adduct permits a tentative characterization of this donor in terms of the *E* and *C* model. The donor is contrasted with organic donors. Average metal–halogen bond energies for the Ir(III)–Br and Ir(III)–I bonds in the oxidative addition product of the titled compound are reported.

Introduction

The lone pair of electrons on d^8 rhodium(I) and iridium(I) complexes has given rise to some novel reaction types and to some interesting catalytic systems for small-molecule activation.[1-3] The basicity and nucleophilicity of these Lewis bases are very unusual when compared to those of typical organic donors. Accordingly, considerable effort[1,4-8] has been expended in an attempt to obtain quantitative information to characterize the reactivity of these systems and to provide a theoretical understanding of the reactivity. In this article, we report the first data involving hydrogen bonding to this type of lone pair in $Ir[(C_6H_5)_3P]_2(CO)Cl$ and describe the thermodynamics of a displacement-type reaction that permits a reevaluation of the enthalpy of formation of the SO_2 adduct. The enthalpy of the reaction of this complex with $(CN)_2C{=}C(CN)_2$, I_2, and Br_2 is also reported.

The hydrogen-bonding interaction has a low equilibrium constant and a low enthalpy. A previously described[10,15] GLC technique permits the accurate determination of this enthalpy. A direct determination of the enthalpy of formation of the SO_2 adduct has also been made by using the GLC technique.

Experimental Section

Materials. Chlorocarbonylbis(triphenylphosphine)iridium(I) (t-Ir) and chlorocarbonylbis(tritolylphosphine)iridium(I) (t-Ir′) were prepared by the method of Vrieze et al.[11] Anal. Calcd for $IrCl(CO)[P(C_6H_5)_3]_2$: C, 56.96; H, 3.88; Cl, 4.54. Found: C, 56.96; H, 3.82; Cl, 4.81. Calcd for $IrCl(CO)[P(CH_3C_6H_4)_3]_2$: C, 59.74; H, 4.90; Cl, 4.10. Found: C, 60.00; H, 4.99; Cl, 3.94. 3,3′-Dimethylbiphenyl was prepared by using the method of Kornblum,[12] the clear, colorless distillate boiling at 119 °C at 3 torr being retained. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.71. PCR Inc. 2,2,2-trifluoroethanol (TFE) and Baker Analyzed Reagent benzene were dried over Linde 4A molecular sieves for at least 24 h prior to use. Linde technical grade sulfur dioxide was used as received. The solid support for GLC work was Johns-Manville Chromosorb W, 60–80 mesh, which was acid washed and DMCS treated. Iodine was purified as previously described.

Calorimetry. The basic calorimeter, the procedure for performing the experiments, and analysis of data have been described elsewhere.[13,14] Prior to preparation of the solutions, the solvent was degassed with nitrogen. All solutions were handled in a nitrogen-filled glovebag. The sulfur dioxide adduct of Ir was prepared by saturating the solution for 30 min to ensure complete reaction. The solution was then transferred to the calorimeter and resaturated with a fast

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flow of sulfur dioxide for at least 10 min. The syringe was added and the calorimeter tightly sealed with tape.

Gas-Liquid Chromatography. The gas chromatograph, the procedure for performing the experiments, and analysis of data have been described elsewhere.[10,15] The GLC solution method was used, the acids were injected as dilute helium solutions, and data were analyzed by using the graphical method for analysis of adsorption-dominated data.[15] Enthalpies were determined from equilibrium constants at four or five temperatures over the range of 30–60 °C. Retention times on two solvent columns and three complex-loaded solvents were measured for the calculation of each K.

Results and Discussion

Our goal in this research was to obtain solvent-minimized enthalpies of adduct formation involving a Lewis base with a metal lone pair of electrons. It is of interest to compare this data with enthalpies of adduct formation involving the more typical nonmetal electron-pair donors. For such a comparison to be made, adducts in which the interaction is essentially covalent and others in which it is essentially electrostatic must be investigated.

A quantitative comparison of this donor with typical nonmetallic Lewis bases can be afforded by determining if the enthalpies of adduct formation conform to the reported E and C equation. If they do not conform, this type of lone pair would be unique. If they do conform, the magnitudes of the E_B and C_B parameters would reveal if there were any unique aspects of this chemistry. To obtain E_B and C_B parameters for the metal Lewis base, we must determine the enthalpies of adduct formation of *trans*-$Ir[(C_6H_5)_3P]_2(CO)Cl$ (which we shall abbreviate as t-Ir) with several acids with known E_A and C_A parameters.[14] Substituting experimentally determined, solvation-minimized enthalpies, ΔH, and the E_A and C_A parameters for each acid into

$$-\Delta H = E_AE_B + C_AC_B$$

provides a series of simultaneous equations that can be solved for E_B and C_B. In the case of this donor, complications prevented us from calorimetrically measuring the series of enthalpies needed to characterize the basicity of t-Ir. Complex reactions, other than simple adduct formation, occurred with several acids in the correlation. Furthermore, the enthalpies of adduct formation with all of the hydrogen-bonding acids in the correlation had equilibrium constants that were too low to permit accurate calorimetric or spectrophotometric determination. Sulfur dioxide has been reported to form acid–base adducts reversibly with t-Ir. However, the volatility of SO_2 in stock solutions makes it difficult to accurately determine its concentration in calorimetric runs. Accordingly, the enthalpy of adduct formation with this Lewis acid was determined from the difference in the enthalpy of reaction of t-Ir and the t-Ir–SO_2 adduct with iodine to form the six-coordinate *trans*-$Ir^{III}(CO)[(C_6H_5)_3P]_2I_2Cl$.

$$\text{t-Ir} + I_2 \rightarrow \text{I-Ir-I} \qquad \Delta H = -35.9 \text{ kcal/mol}$$

$$-[\text{t-IrSO}_2 + I_2 \rightarrow \text{I-Ir-I} + SO_2] \qquad \Delta H = +24.6 \text{ kcal/mol}$$

$$\text{t-Ir} + SO_2 \rightarrow \text{t-IrSO}_2 \qquad \Delta H = -11.3 \text{ kcal/mol}$$

An enthalpy of −11.3 kcal/mol results. This value differs[1] from the value of −10.1 kcal/mol reported for the formation of this adduct in chlorobenzene. Attempts were made to determine the enthalpy of formation of the O_2 adduct of *trans*-$IrCO[(C_6H_5)_3P]_2Cl$ by this approach. No reaction occurred in the dark. In light, the O_2 adduct was converted to the iodo complex with a first-order rate constant of $(2.5 \pm 0.5) \times 10^{-6}$ s^{-1}, comparable to that reported (3.5×10^{-6} s^{-1}) for O_2 dissociation.[1]

Literature reports indicated[16] that a GLC technique might be applicable for weakly interacting systems. We have developed a procedure[15] for the accurate determination of enthalpies of adduct formation for solutions of an acid (or base) in the liquid-phase 3,3′-dimethylbiphenyl with a volatile base (or acid). Solubility requirements caused us to use the p-tolyl derivative in these experiments. Within experimental error, the measured enthalpies of formation of the SO_2 adduct of $Ir[(C_6H_5)_3P]_2COCl$ and $Ir[(CH_3C_6H_4)_3P]_2COCl$ are determined to be the same by the two procedures. We shall assume that the p-CH_3 and hydrogen substituents have similar effects (within experimental error) on the Lewis basicity of the iridium center.

Table I. Determined Enthalpies and Associated Reaction

method	reaction[b]	$-\Delta H$, kcal/mol
calorimetric	$\text{t-Ir} + (CN)_2C{=}C(CN)_2 \rightarrow \text{Ir}\cdot(CN)_2C{=}C(CN)_2$	20.6 ± 0.2
calorimetric	$\text{t-Ir} + Br_2 \rightarrow \text{Br-Ir}^{III}\text{-Br}$	52.0 ± 0.4
calorimetric	$\text{t-Ir}\cdot SO_2 + I_2 \rightleftarrows \text{I-Ir}^{III}\text{-I} + SO_2$	24.6 ± 0.1
calorimetric	$\text{t-Ir} + I_2 \rightleftarrows \text{I-Ir}^{III}\text{-I}$	35.9 ± 0.2
GLC	$\text{t-Ir}' + SO_2 \rightleftarrows \text{Ir}'\cdot SO_2$	11.6 ± 0.3[a]
GLC	$\text{t-Ir}' + \text{TFE} \rightleftarrows \text{Ir}'\cdot\text{TFE}$	2.9 ± 0.2[a]

[a] The error limits for the GLC enthalpies are lower limits to the estimated error and are subjective in nature. [b] t-Ir is an abbreviation for $Ir[(C_6H_5)_3P]_2COCl$ and t-Ir′ for $Ir[(CH_3C_6H_4)_3P]_2COCl$. The tolylphosphine derivative was used in the GLC experiments for solubility reasons.

An enthalpy of −2.9 kcal/mol is determined from GLC for the hydrogen-bonding interaction of CF_3CH_2OH with this iridium complex. The infrared spectrum of this system was investigated to determine the nature of the interaction of the alcohol (hydrogen bonding vs. oxidative addition). A weak shifted O–H stretching vibration is found in the adduct at a lower frequency than in the free alcohol ($\Delta\nu_{OH}$ 320 cm^{-1}), supporting a hydrogen-bonding interaction. There are several potential donor centers in the iridium complex capable of undergoing a 3 kcal/mol interaction. Thus, the 3 kcal/mol would constitute an upper limit on the basicity of the metal lone pair. (If another center is coordinating, the metal lone pair is a weaker donor.) The phenyl rings can be eliminated as the donor center in this complex, for a frequency shift of ~70 cm^{-1} would be expected.[17] The large shift observed in ν_{O-H} for an enthalpy of 3 kcal/mol (a shift of less than 100 cm^{-1} is expected for a second-row donor[18]) is in the direction expected for a heavy-metal donor center.[19] Thus, we propose that the hydrogen-bonding interaction involves the lone pair of metal electrons.

The data required to determine the enthalpy for each calorimetric experiment as well as apparent partition coefficients and equilibrium constants required to determine the enthalpy for each GLC experiment are available as supplementary material. The resultant enthalpies calculated from this data are given in Table I.

Even with the indirect calorimetric technique and the GLC procedure, we were thwarted in our attempts to determine enthalpies of adduct formation with other acids whose C/E ratios differed very much from 0.1. In order to compare the basicity of this donor to that of typical nonmetal donors, it is necessary to convert the enthalpies of adduct formation to solvent-minimized data. The calorimetrically determined enthalpy of Ir–SO_2 adduct formation must be corrected for the specific interaction of benzene with SO_2,[20] leading to a solvent-minimized enthalpy of −12.8 kcal/mol. Using benzene E_B and C_B parameters to estimate the 3,3′-dimethylbiphenyl interaction with CF_3CH_2OH leads to a corrected[21] enthalpy of adduct formation of −4.0 kcal/mol for this system.[21] These results clearly indicate that covalency is playing a dominant role in the acid–base interactions involving this metal lone pair. For example, the calculated enthalpies of interaction of

Table II. Predicted Enthalpies of Adduct Formation for Representative Nonmetallic Donors

		$-\Delta H$, kcal/mol	
		SO_2	CF_3-CH_2OH
$(C_2H_5)_2O$	(3.25, 0.963)[a]	3.5	5.2
$(C_2H_5)_2S$	(7.40, 0.339)	6.2	4.7
$(CH_3)_2S$	(7.46, 0.343)	6.3	4.7
$(CH_3)_2Se$	(8.33, 0.217)	6.9	4.7
$[(C_6H_5)_3P]_2Ir(CO)Cl$		12.8	4.0

[a] These are the reported C_B and E_B values of these donors. For SO_2, $C_A = 0.808$ and $E_A = 0.920$ while for TFE, $C_A = 0.461$ and $E_A = 3.881$.

$(C_2H_5)_2O$, $(C_2H_5)_2S$, $(CH_3)_2S$, and $(CH_3)_2Se$ with SO_2 and TFE are reported in Table II.

We note an increasing C_B/E_B ratio with increasing metallic character of the central element in the oxygen-family donor. The donor $(CH_3)_2Se$ has the largest C_B/E_B ratio of any of the donors presently in the correlation. In order to account for the low enthalpy of hydrogen bonding to the iridium complex and the large enthalpy of interaction toward SO_2, covalency (that is, the C_B value) must be even more important and electrostatic binding less important in describing the interaction than in the case of $(CH_3)_2Se$.

Calculation of E_B and C_B values from two enthalpies is very risky.[14] When one attempts this with the solvent-minimized data in Table II, C_B and E_B values of 17 and −0.9, repsectively, arise. These are tentative numbers and should be treated accordingly. Though the potential error is large enough to make the number positive, the negative E_B number is worthy of comment. It could result because the measured SO_2 enthalpy has extra stabilization contained in it from, for example, multiple bonding (sulfur lone pair to metal). If, instead, the reported value truly is a single-bond energy, a new set of transformation constants[14] would have to be applied to all of the reported E and C parameters to make them all positive or zero. The current set would in effect be slightly overestimating the covalent contributions in the context of the electrostatic–covalent model.

The average Ir(III)–I and Ir(III)–Br bond energies can also be calculated from the data obtained. The average bond energy is defined as the average value for the "homolytic" cleavage of the two Ir(III)–X bonds. The value results by combining eq 1–3. The bond energy obtained in this way

$$-[Ir[(C_6H_5)_3P]_2(CO)Cl + X_2 \rightarrow Ir^{III}[(C_6H_5)_3P]_2(CO)ClX_2] \quad (1)$$

$$+[X_2 \rightarrow 2X] \quad (2)$$

$$Ir^{III}[(C_6H_5)_3P]_2(CO)Cl \rightarrow Ir[(C_6H_5)_3P]_2(CO)Cl + 2X \quad (3)$$

refers to the same types of processes occurring in the systems for which average bond energies have been reported. That is, they are not adiabatic bond dissociation energies but incorporate changes in all of the remaining bonds in the molecule after the indicated bond has been broken.

The solvation-minimized enthalpy should be employed for the first reaction described above in calculating bond energies. When 1.4 kcal/mol for the benzene–iodine complex and 0.7 kcal/mol for the benzene–bromine complex are used, solvation-minimized enthalpies of −37.3 and −52.7 kcal/mol result for the oxidative addition reactions with I_2 and Br_2. When values of 45 and 36 kcal/mol for the heat of dissociation of Br_2 and I_2 are used, average bond energies of 49 and 36 kcal/mol result for the Ir–Br and Ir–I bonds. If solvation effects are not canceled out of eq 1, a small error could be introduced in these numbers. The average Ir–Br bond is substantially stronger than the average Ir–I bond in these complexes.

The inductive influence of other ligands coordinated to iridium on these bond strengths and the strengths of other iridium(III)–substituent and rhodium(III)–substituent bonds can be determined by these procedures. The results will be essential to a more complete description of the steps in the catalytic reactions effected by these complexes.

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Registry No. t-Ir, 15318-31-7; t-Ir′, 28195-56-4; t-Ir·SO_2, 59114-13-5; t-Ir′·SO_2, 69745-19-3; Br-Ir^{III}-Br, 69651-17-8; I-Ir^{III}-I, 69651-18-9; Ir·$(CN)_2C{=}C(CN)_2$, 15380-75-3; SO_2, 7446-09-5; CF_3CH_2OH, 75-89-8; $(C_2H_5)_2O$, 60-29-7; $(C_2H_5)_2S$, 352-93-2; $(CH_3)_2S$, 75-18-3; $(CH_3)_2Se$, 593-79-3.

Supplementary Material Available: Tables III and IV containing raw calorimetric and GLC data used to evaluate thermodynamic parameters (3 pages). Ordering information is given on any current masthead.

References and Notes

(1) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968); *Inorg. Chim. Acta*, **5**, 295 (1971).
(2) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968).
(3) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).
(4) W. Strohmeier and R. F. Fleischman, *Z. Naturforsch., B*, **24**, 1217 (1969), and references therein.
(5) B. L. Shaw and R. E. Stainbank, *J. Chem. Soc., Dalton Trans.*, 223 (1972), and references therein.
(6) J. L. McNaughton, C. T. Mortimer, J. Burgess, M. J. Hacker, and R. D. W. Kemmitt, *J. Organomet. Chem.*, **71**, 286 (1974), and references therein.
(7) D. M. Blake and M. Kubota, *Inorg. Chem.*, **9**, 989 (1970), and references therein.
(8) J. P. Collman and C. T. Sears, Jr., *Inorg. Chem.*, **7**, 27 (1968), and references therein.
(9) R. Hoffmann, M. M.-L. Chen, and D. L. Thorn, *Inorg. Chem.*, **16**, 503 (1977).
(10) C. S. Chamberlain and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 6142 (1976).
(11) K. Vrieze, J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Synth.*, **11**, 101 (1968).
(12) N. Kornblum, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 295.
(13) (a) T. D. Epley and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 5770 (1967); (b) M. S. Nozari and R. S. Drago, *ibid.*, **92**, 7086 (1970).
(14) R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973).
(15) C. S. Chamberlain and R. S. Drago, *J. Amer. Chem. Soc.*, in press.
(16) (a) D. E. Martire and P. Riedl, *J. Phys. Chem.*, **72**, 3478 (1968); (b) H. L. Liao and D. E. Martire, *J. Am. Chem. Soc.*, **96**, 2058 (1977).
(17) R. S. Drago, G. C. Vogel and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).
(18) M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **92**, 7086 (1970).
(19) Phosphorus and sulfur donors give rise to a larger $\Delta\nu_{OH}$ value for a given enthalpy than second-row donors. See G. C. Vogel and R. S. Drago, *J. Am. Chem. Soc.*, **92**, 5347 (1970).
(20) R. S. Drago, L. B. Parr, and C. S. Chamberlain, *J. Am. Chem. Soc.*, **99**, 3202 (1977), and references therein. Using reported E and C values, given in this reference and in ref 14, we calculate the C_6H_6–SO_2 interaction as −1.2 kcal/mol^{-1} and the C_6H_6–CF_3CH_2OH interaction as −1.1 kcal/mol^{-1}.
(21) For reasons discussed in the literature,[14] we are not sure that the same solvation correction need be applied to GLC data that is applied to calorimetric data. This coupled with differences in the basicity of benzene and 3,3′-dimethylbiphenyl lead us to believe the value of 4.0 as the solvation-minimized enthalpy could be in error by ~0.5 kcal/mol^{-1}. This potential error in no way affects our qualitative conclusions.
(22) R. S. Drago and D. A. Wenz, *J. Am. Chem. Soc.*, **84**, 526 (1962).