kcal/mol, a value in good agreement with those found for comparable processes involving the triphenylphosphine ligand.[18]

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Supplementary Material Available: Text describing X-ray procedures and tables listing refinement parameters, atomic coordinates, isotropic thermal parameters, anisotropic thermal parameters, H atom coordinates and isotropic displacement parameters, and all bond distances and bond angles (18 pages); a listing of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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Reaction Enthalpies of Atom Transfer to Electronically Excited Tetrakis(pyrophosphito)diplatinate(II)

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The photochemistry of d^8–d^8 binuclear complexes (M_2: M = Pt, Rh, Ir) has been an extremely active area of research.[1] These complexes possess $d\sigma^*p\sigma$ triplet states (M_2^*) that are sufficiently long-lived to undergo bimolecular reactions, such as electron and atom transfer.[1-3] In particular, excited-state atom transfer of these complexes can be an important step in catalytic photoreactions.[1] For example, the tetrakis(pyrophosphito)diplatinate(II) complex, $Pt_2(P_2O_5H_2)_4^{4-}$, catalyzes the photochemical conversion of isopropyl alcohol into hydrogen and acetone.[4]

Although the kinetic behavior of the excited states of these binuclear complexes toward atom and electron transfer has been examined,[1-3] little is known about the thermochemistry of such processes. Herein, we report on the reaction enthalpies of hydrogen and halogen transfer to the excited and ground states of $Pt_2(P_2O_5H_2)_4^{4-}$ (Pt_2). These enthalpies are useful in understanding the atom-transfer reactivity of the excited state of Pt_2 and comparing it to other reactive transition-metal complexes and radicals.

Experimental Section

Materials. $(n\text{-}Bu_4N)_4[Pt_2(P_2O_5H_2)_4]$ was prepared from the potassium salt as described previously.[5] Methanol, CCl_4, and benzene were obtained from J. T. Baker Inc. and used as received. Iodobenzene, benzyl alcohol, isopropyl bromide, and *tert*-butyl bromide were obtained from Aldrich and distilled before use. 2-Hydroxybenzophenone (Aldrich) was recrystallized.

Photoacoustic Calorimetry. The PAC experiment has been previously described.[6] Photoexcitation was conducted at 365 nm (78.4 kcal/mol) by a nitrogen-pumped dye laser on argon-degassed samples at room temperature. The acoustic waves were detected by a PZT transducer (~0.5 MHz). The signal was amplified (Panametrics preamp, Model 5676), digitized (LeCroy 9400), and transferred to a laboratory computer for data analysis. The wave forms were the average of 60–80 laser pulses (<20 μJ). The transducer response function was obtained from photoexcitation of 2-hydroxybenzophenone. The optical densities of the calibration and sample compounds were ~0.8 and were adjusted to be within 1% of each other. Sample absorbances did not change significantly during the experiment. The time resolution of the transducer is approximately 10 ns–5 μs. Heat depositions that occur faster than 10 ns will not be differentiated, whereas those slower than 5 μs will not be detected.

Table I. Experimental PAC Heats of Reaction and Calculated Bond Dissociation Energies of Pt_2X^{a-c}

RX	k_q, $M^{-1}\,s^{-1}$ [d]	$\Delta H_1 + \Delta H_2$	ΔH_2	$D_0(RX)$[e]	$D_0(Pt_2X)$
$C_6H_5CH_2OH$ (1.5 M)	2.5×10^6	32.9 (4.7)[f]	−23.6	81.2 (1.5)	48.3 (4.9)
$(C_4H_9)_3SnH$ (0.2 M)[g]	1.2×10^7	28.2 (1.8)	−28.3	74.0 (2.0)	45.8 (2.7)
CCl_4 (0.05 M)	2.0×10^9	23.5 (1.6)	−33.0	73.1 (1.8)	49.6 (2.4)
$(CH_3)_3CBr$ (0.05 M)	$>10^9$	36.9 (1.3)	−19.6	67.3 (1.7)	31.3 (2.1)
$(CH_3)_2CHBr$ (10.6 M)	1.7×10^8 [h]	35.3 (3.9)	−21.2	68.4 (1.2)	33.1 (4.1)
C_6H_5I (0.063 M)[i]	1.6×10^9	31.4 (3.5)	−25.1	65.4 (2.0)	34.0 (4.0)

[a] In CH_3OH with added substrate RX, at 298 °C. [b] Values are the average of at least five measurements. [c] ΔH and D_0 values in kcal/mol. [d] Values from refs 2 and 3. [e] Values from ref 11. [f] Errors in parentheses are $\pm 1\sigma$. [g] In 1:1 CH_3OH/benzene. [h] Value for $CH_3CH_2CH(CH_3)Br$. [i] See ref 12.

Under reaction conditions where only one heat deposition was observed, $\Delta H = (1 - \alpha)E_{h\nu}$, where $E_{h\nu}$ is the incident laser energy and α is the fraction of the incident photon energy released as heat. In the described experiments, $\Delta H = \Delta H_1$ in the absence of substrate RX and $\Delta H = \Delta H_1 + \Delta H_2$ in the presence of substrate RX. Under reaction conditions where two heat depositions were observed, $\Delta H_a = (1 - \alpha_a)E_{h\nu}$ and $\Delta H_b = -\alpha_b E_{h\nu}$, where α_a and α_b are the fractions of the incident photon energy released as heat in the depositions. The experimental enthalpic, α_a and α_b, and kinetic, $\tau_a \le 10$ ns and τ_b, values were determined by deconvolution of the first 400 points of the acoustic wave forms.[6] In the experiments where 10 μs ≥ $1/(k_q[RX]) \ge 10$ ns, $\Delta H_a = \Delta H_1$ and $\Delta H_b = \Delta H_2$.

Results and Discussion

Photoexcitation (365 nm) of $Pt_2(P_2O_5H_2)_4^{4-}$ (Pt_2) produces the triplet ($^3A_{2u}$) excited state $Pt_2(P_2O_5H_2)_4^{4-*}$ (Pt_2^*) with unit efficiency.[2,3] This highly reactive, long-lived (~10 μs) state undergoes hydrogen and halogen atom transfer reactions with substrates, RX, to yield the radicals $Pt_2(P_2O_5H_2)_4X^{4-}$ (Pt_2X) and $R^\bullet$, shown as follows:

$$Pt_2(P_2O_5H_2)_4^{4-} \xrightarrow[\Delta H_1]{h\nu,\ <10\text{ ns}} Pt_2(P_2O_5H_2)_4^{4-*} \xrightarrow[\Delta H_2,\ \tau_2]{RX} Pt_2(P_2O_5H_2)_4X^{4-} + R^\bullet$$

$$X = H, Cl, Br, I$$

The triplet state Pt_2^* and the radicals Pt_2X have been identified and characterized by transient absorption, resonance Raman, and infrared spectroscopies.[2,3] In addition, the bimolecular rate constants, k_q, for the hydrogen and halogen atom transfer reactions with various substrates RX have also been measured. The radicals Pt_2X are also long-lived (≥10 μs) under the flash photolysis conditions and either disproportionate, atom-abstract from RX, or couple with $R^\bullet$.

The heats of these atom-transfer reaction reactions are determined by time-resolved photoacoustic calorimetry (PAC). PAC measures the volume changes of the system that result primarily from the thermal expansion of the solvent following photoexci-

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tation.[6,7] The amplitude and time evolution of these changes are determined by deconvolution of the experimental acoustic wave forms, as previously described,[6] and yield enthalpic and kinetic information.[8]

Irradiation of Pt_2 in CH_3OH results in a single heat deposition, which reflects the rapid formation of the triplet state Pt_2^*, ΔH_1. The triplet energy of Pt_2^* determined by PAC is 56.5 ± 1.6 kcal/mol, which is in good agreement with previous estimates of 57–58 kcal/mol.[1,6a,9] Irradiation of Pt_2 in CH_3OH with added substrate RX also results in a single heat deposition when $1/(k_q[\mathrm{RX}]) \leq 10$ ns. This deposition reflects both the formation of Pt_2^* *and* the subsequent atom-transfer reaction and yields the atom-transfer-reaction enthalpy from ground state Pt_2, $(\Delta H_1 + \Delta H_2)$. The difference in these values, ΔH_2, is the atom-transfer-reaction enthalpy from the triplet state Pt_2^*. The reaction enthalpies obtained by PAC are given in Table I and, importantly, assume that the radicals Pt_2X and $R^\bullet$ are formed with unit efficiency.[10]

Alternatively, the heat deposition associated with the atom transfer from RX to Pt_2^*, ΔH_2, can be determined directly if the rate of heat deposition is time-resolved by PAC, i.e. $1/(k_q[\mathrm{RX}]) \geq 10$ ns. The lifetimes of Pt_2^*, τ_2, determined by PAC, in the presence of several substrates ($C_6H_5CH_2OH$ (1.5 M), 660 ns; $(C_4H_9)_3SnH$ (0.2 M), 350 ns; CCl_4 (3×10^{-3} M), 305 ns) are in reasonable agreement with those calculated by using the substrate concentrations and literature k_q values,[2,3] $\tau_2(\mathrm{calc}) = 1/k_q[\mathrm{RX}]$. This suggests that the same reaction is being monitored by both flash photolysis and PAC.

The bond dissociation energies of Pt_2X to yield ground-state Pt_2 and $X^\bullet$ radicals, $D_0(Pt_2X)$, are calculated (Table I) from the experimental $(\Delta H_1 + \Delta H_2)$ values, the known bond dissociation energies of RX, $D_0(\mathrm{RX})$,[11] and the relationship

$$D_0(\mathrm{Pt_2X}) = D_0(\mathrm{RX}) - (\Delta H_1 + \Delta H_2)$$

The calculated $D_0(Pt_2X)$ values are the consequence of *two* major structural changes associated with the bond dissociation of Pt_2X: the breaking of both the axial Pt–X bond and the Pt–Pt "single" bond, which is present in Pt_2X but not in Pt_2.[1-3] Assuming the Pt–Pt bond has a "negative" bond dissociation energy of 56.5 kcal/mol, i.e. the triplet energy of Pt_2^*, the energetic consequences of breaking the axial Pt–X bond can be calculated by adding the triplet energy of Pt_2^* to the $D_0(Pt_2X)$ values.[13] The bond dissociation energies for Pt_2X to yield $X^\bullet$ and Pt_2^*, with its intact Pt–Pt "single" bond, are 103, 106, 88.5, and 90.5 kcal/mol, for X = H, Cl, Br, and I, respectively.

The homolytic metal–hydrogen bond energies for a number of transition-metal hydrogen complexes are in the 50–75 kcal/mol range.[14] The M–H bond energies for the $HMn(CO)_5$, $HCo(CO)_4$, $H_2W(Cp)_2$, and $H_2IrCl(CO)(PPh_3)_2$ complexes are reportedly 65, 57, 72.9 (mean), and 60 (mean) kcal/mol, respectively.[14] The $D_0(Pt_2H)$ value, ~47 kcal/mol, is somewhat lower than for other complexes, but it also includes the "negative" bond dissociation energy of the Pt–Pt "single" bond, which is not the case for the other complexes. In this regard, the bond dissociation of Pt_2H_2 to Pt_2H and $H^\bullet$, $D_0(Pt_2X_2)$, might serve as a better comparison in that both Pt_2H_2 and Pt_2H have Pt–Pt "single" bonds. Unfortunately, neither this bond dissociation energy nor the heat of hydrogenation of Pt_2 to Pt_2H_2 has been measured. However, indirect experiments suggest that bond dissociation of Pt_2H_2 is greater than 47 kcal/mol.[15]

It has been previously reported that Pt_2X_2 (X = Cl, Br, I) complexes are easily formed from dihalogen addition to Pt_2 and are quite thermally stable. In contrast, Pt_2H_2 appears to be significantly less stable. The $D_0(Pt_2X)$ values may provide a thermodynamic explanation. Consider the dihalogen or dihydrogen addition reaction to Pt_2

$$\mathrm{Pt_2 + X_2 \rightleftharpoons Pt_2X_2}$$

Assuming that $D_0(Pt_2X) = D_0(Pt_2X_2)$, then the above reaction enthalpy, ΔH_r, is given by

$$\Delta H_r = 2(D_0(\mathrm{Pt_2X})) - D_0(\mathrm{X_2})$$

where $D_0(X_2)$ is the bond dissociation energy of the dihalogen or dihydrogen.[16] The calculated ΔH_r values are 10, −41, −15, and −32 kcal/mol for X = H, Cl, Br, and I. Although the absolute magnitude of these values depends on $D_0(Pt_2X_2)$,[16] the incremental difference between $D_0(Pt_2X)$ and $D_0(Pt_2X_2)$ should be essentially

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(8) In fact, the volume changes result from both the thermal expansion of the solvent and photochemnical reaction volume changes.[6] These two contributions can be separated and analyzed to yield both reaction enthalpy *and* volume information. In these studies, the contribution from photochemical reaction volume changes is considered to be negligible for two reasons: (1) the thermal expansion coefficient of CH_3OH is significant such that this volume contribution should dominate over that from reaction volume changes, and (2) previous work has shown that the formation of Pt_2^* has only a small reaction volume change, and the volume changes of the subsequent atom abstraction reactions should also be small.[6a,22]

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(12) In the iodine abstraction from iodobenzene (0.0625 M) by Pt_2^* in CH_3OH, a slower additional reaction, $\Delta H = -20.4$ kcal/mol, was observed, $\tau = 330$ ns. This reaction may involve the α-hydrogen atom abstraction from CH_3OH by the highly reactive phenyl radical. This reaction is calculated to be exothermic by 17 kcal/mol[11] and estimated to occur with $\tau \geq 30$ ns, which is based on a hydrogen abstraction rate constant, which presumably is lower than that for $(CH_3)_2CHOH$, 1.4×10^6 M^{-1} s^{-1}.[23]

(13) Clearly, the assumption of a "negative" bond dissociation energy of 56.5 kcal/mol is questionable and probably an overestimate. In fact, a better estimate may be the difference between $D_0(Pt_2X)$ and $D_0(Pt_2X_2)$, which assumes the two axial Pt–X bond strengths are equal. However, neither the heats of hydrogenation or halogenation of Pt_2 to Pt_2X_2 nor the $D_0(Pt_2X)$ values are currently available. The "negative" bond dissociation energy of 56.5 kcal/mol is used because it provides a simple enthalpic comparison of the Pt–X bond formed to R–X bond being broken, which has obvious kinetic consequences.

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(15) The Pt–H bond dissociation energy of Pt_2H_2 and consequently the mean bond dissociation energy of Pt_2H_2 are probably significantly larger than 47 kcal/mol, as indicated below. Flash photolysis studies have shown that Pt_2H radicals rapidly disproportionate to yield Pt_2 and Pt_2H_2,[3a] which indicates $\Delta H \geq 0$ for (2), assuming ΔS is negligible. However,

$$\mathrm{Pt_2H \rightleftharpoons Pt_2 + H} \qquad \Delta H \cong 47 \text{ kcal/mol} \tag{1}$$

$$\mathrm{Pt_2 + Pt_2H_2 \rightleftharpoons 2Pt_2H} \qquad \Delta H \geq 0 \text{ kcal/mol} \tag{2}$$

$$\text{net:} \quad \mathrm{Pt_2H_2 \rightleftharpoons Pt_2H + H} \qquad \Delta H \geq 47 \text{ kcal/mol} \tag{3}$$

the Pt–H bond dissociation of Pt_2H_2 is probably significantly less than that observed for Pt_2H to give Pt_2^* and $H^\bullet$, 103 kcal/mol. Flash photolysis studies indicate that Pt_2^*, not Pt_2H, readily abstracts hydrogen atoms from donors such as isopropyl alcohol.[3b] However, Pt_2H does apparently abstract hydrogen atoms from $(C_4H_9)_3SnH$ at an appreciable rate,[2c] which suggests that the Pt–H bond strength may be greater than or similar to that of $(C_4H_9)_3Sn$–H, ~74 kcal/mol.[11c]

(16) $D_0(X_2) = 104, 58, 49.3, 36.5$ for X = H, Cl, Br, I. (a) *CRC Handbook of Chemistry and Physics*, 53rd ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1972. (b) Presumably, $D_0(Pt_2X) \leq D_0(Pt_2X_2)$, with the difference being the Pt–Pt "single" bond strength. Consequently, the heats of halogenation or hydrogenation of Pt_2 to Pt_2X_2 will probably be more exothermic than indicated.

independent of X. Consequently, the relative differences between the ΔH_r values should be meaningful and clearly indicate that the dihalogen adducts should be thermodynamically more stable than the dihydrogen adduct.[17]

Structural data for Pt_2X, as well as for Pt_2X_2 species, indicate that both the Pt–Pt and the Pt–X bond lengths increase in the order Cl < Br < I.[1a] Resonance Raman spectral measurements on Pt_2X ($\sigma^2\sigma^{*1}$) and Pt_2X_2 (σ^2) indicate a decrease in the Pt–Pt and Pt–X vibrational frequencies in the order Cl > Br > I,[1a,18] a trend ascribed to differences in electron donation from the axial ligand X^- in Pt_2X (or Pt_2X_2) into the Pt–Pt $d\sigma^*$ orbital. These results suggest that $D_0(Pt_2X)$ should decrease in the order Cl > Br > I. The experimental PAC results indicate a similar ordering for $D_0(Pt_2X)$, Cl > Br ~ I. The similar calculated bond dissociation energies of Pt_2Br and Pt_2I are somewhat unexpected but perhaps can be explained by competing excited-state processes of Pt_2^*.[10]

The Pt_2^* excited triplet state is one of the most reactive metal-centered radicals toward atom-transfer reactions.[1] The reactions of Pt_2^* are highly exothermic (ΔH_2, Table I), in part because of the extremely strong Pt–X bonds that are formed by Pt_2^*, as indicated earlier. Although factors other than reaction exothermicity are important in determining the absolute rates of atom abstraction, several observations can perhaps be made.

First, Pt_2^*, with its $d\sigma^*$ electron, is electronically similar to alkyl, hydroxyl, or other metal-centered radicals such as $Mn(CO)_5$. However, the reactivities of these species toward atom abstraction can be quite different. These differences can potentially be related to reaction enthalpy or bond strength differences. For example, whereas the rates of hydrogen atom abstraction by Pt_2^*, t-BuO$^•$ radical, and also $n\pi^*$ excited states of ketones are similar, those of other metal-centered radicals are somewhat slower.[1b,19] As indicated earlier, these metal–hydrogen bonds are considerably weaker than the Pt–H and RO–H hydrogen bonds, ~103 kcal/mol.[11,14,20] The significantly faster rate of Cl abstraction from CCl_4 by Pt_2^*, 2×10^9 M^{-1} s^{-1},[2b] than by $CH_3^•$, ~10^3 M^{-1} s^{-1},[21] is possibly related to the difference between the Pt–Cl and the C–Cl bond strengths, 106 and 84.6[9] kcal/mol, respectively.

Second, halogen atom abstraction is apparently faster than hydrogen atom abstraction for a given reaction exothermicity. For example, iodine abstraction from C_6H_5I occurs significantly faster than hydrogen abstraction from $C_6H_5CH_2OH$, although both have similar ΔH_2 values. The faster rates for halogen abstraction may possibly indicate some charge-transfer character in the transition state.

Third, the rate constants for quenching of Pt_2^* by aryl halides (ArX) in methanol are in the order I > Br > Cl.[2b] Although this trend may follow ArX bond strengths as previously suggested, it apparently does not simply follow the reaction exothermicities. The ΔH_2 values for the reaction of Pt_2^* with chloro-, bromo-, and iodobenzene are −10.6, −9.0, and −25.1 kcal/mol, on the basis of the appropriate $D_0(Pt_2X)$ values and the $D_0(RX)$ values of the aryl halides, 95.5 (Cl), 80.6 (Br), and 65.4 (I) kcal/mol.[11]

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(17) Alternatively, the instability of Pt_2H_2 relative to Pt_2X_2 may rather be kinetic in nature. In fact, the hydrogen and halogen adducts may decompose by quite different mechanistic pathways.

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Electrochemical Reduction of Dioxygen in Room-Temperature Imidazolium Chloride–Aluminum Chloride Molten Salts

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Introduction

We report here the voltammetric behavior of dioxygen in a basic, room-temperature chloroaluminate molten salt, 1-ethyl-3-methylimidazolium chloride (ImCl) mixed with $AlCl_3$. Melts composed of mixtures of ImCl and $AlCl_3$ are basic, neutral, or acidic, depending on whether the mole ratio, $AlCl_3$:ImCl, is less than, equal to, or greater than 1, respectively. These melts and the closely related 1-*n*-butylpyridinium chloride–$AlCl_3$ systems have found wide application in studies of the electrochemistry of organic and inorganic species.[1-3] The electrochemistry of O_2 reduction has been the subject of numerous studies in aqueous, nonaqueous, and high-temperature molten salt systems. These have been reviewed in detail by Hoare.[4] To our knowledge, this is the first report of the electrochemistry of O_2 in room-temperature melts.

Experimental Section

ImCl was prepared by a modification of a previously reported procedure.[5] $AlCl_3$ (Fluka) was purified by sublimation. Anhydrous $FeCl_2$ (Alfa Products) was used as received. Melts were prepared by mixing appropriate quantities of ImCl and $AlCl_3$. All manipulations (e.g., preparation of melts, assembling of electrochemical cells) were performed inside a Vacuum Atmospheres Co. drybox, under an atmosphere of purified He.

All electrochemical experiments were performed outside of the drybox, in a gastight, single-compartment cell. The volume of melt used for electrochemical measurements was typically 20 mL. O_2 and Ar were passed through a drying column composed of molecular seives and Drierite, before entering the cell. Gases were introduced into the melt via a gas dispersion tube immersed in the melt and were continuously passed over the melt during measurements.

The working electrodes were glassy carbon (geometric area = 0.071 cm^2) and Pt (geometric area = 0.025 cm^2) disks, obtained from Bioanalytical Systems. The electrodes were polished with 0.25-μm diamond paste (Buehler, Ltd.) on a Nylon buffing pad and were cleaned ultrasonically in 95% ethanol prior to use. The counter electrode was a Pt wire. All potentials were measured with respect to an Al wire immersed in 1.5:1 (mole ratio of $AlCl_3$:ImCl) melt, denoted Al/Al(III). The reference electrode was separated from the working solution by a Vycor frit. All measurements were conducted at the ambient temperature of the laboratory (25 ± 1 °C).

A Princeton Applied Research Model 273 potentiostat controlled by a Digital Equipment Corp. Model PDP-8/e computer was used in all experiments.

Results and Discussion

A typical cyclic staircase voltammogram (CSV), at a glassy-carbon disk electrode, of an O_2-saturated 0.95:1 melt is shown in Figure 1A. Saturation of the melt, as indicated by the constancy of the cathodic peak height (i_{pc}) of the reduction wave with time, required ca. 30 min of vigorous bubbling with dry O_2. O_2 is reduced in a single voltammetric wave with cathodic peak potential $E_{pc} = -0.7$ V vs Al/Al(III). No other redox processes are observed within the electrochemical window of the 0.95:1 melt (+1.0 to −1.8 V). The reduction wave could be eliminated by purging with dry Ar (Figure 1B). No reverse current was observed, following reduction, for sweep rates, v, $5 \le v \le 200$ mV/s. The peak current was a linear function of $v^{1/2}$ but with a positive

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