

Synthesis of $\text{Ti}(\text{OAr-2,6Ph}_2)_2[\text{PhNC}(\text{CH}_2\text{SiMe}_3)=\text{C}(\text{CCH}_2\text{SiMe}_3\text{NPh})\text{NPh}]$ (III). A yellow solution of $\text{Ti}(\text{OAr-2,6Ph}_2)_2(\eta^2\text{-PhNCCH}_2\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)$ (0.5 g) in hexane (20 cm³) was treated with 2 equiv of PhNC. After 6 h, the red supernatant solution was decanted from a few yellow crystals of starting material and allowed to stand, whereupon dark red crystals of $\text{Ti}(\text{OAr-2,6Ph}_2)_2[\text{PhNC}(\text{CH}_2\text{SiMe}_3)=\text{C}(\text{CCH}_2\text{SiMe}_3\text{NPh})\text{NPh}]$ began to form and were finally isolated after a few hours. Cooling of the supernatant solution resulted in the formation of more red crystalline product.

Anal. Calcd for $\text{TiC}_{65}\text{H}_{63}\text{N}_3\text{O}_2\text{Si}_2^{1/2}\text{C}_6\text{H}_{14}$: C, 76.66; H, 6.62; N, 3.94. Found: C, 76.29; H, 6.65; N, 3.66. ¹H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 30 °C): δ -0.73 (s), -0.01 (s, CH_2SiMe_3), 1.30 (d), 2.54 (d, CH_2SiMe_3), 5.68 (d), 6.5-7.1 (m, aromatics), 0.84 (m), 1.18 (m, hexane).

Synthesis of $\text{Ta}(\text{OAr-2,6Me}_2)_3[\text{xyNC}(\text{CH}_2\text{Ph})=\text{C}(\text{CH}_2\text{Ph})\text{Nxy}]$ (IV). Thermolysis of $\text{Ta}(\text{OAr-2,6Me}_2)_3(\eta^2\text{-xyNCCH}_2\text{Ph})_2$ in toluene at 110 °C for 48 h produced the crude product as a yellow oil on removal of solvent. On allowing the oil to stand in contact with hexane, amber crystals of the product suitable for X-ray diffraction studies were obtained. ¹H NMR (C_6D_6 , 30 °C): δ 1.95 (s, OAr-CH_3), 1.96 (s, Nxy-CH_3), 4.07 (s, NCCH_2Ph).

Crystallographic Studies. Five of the six structure determinations were obtained through the Molecular Structure Center of Indiana University⁴¹

while the sixth, that of IIg, was done in house.⁴² Crystal parameters are given in Table VIII. In all structures except III all non-hydrogen atoms were refined anisotropically. For compounds Ia, IIc, and IV the hydrogen atoms were located and refined isotropically while for IIb and IIc they were placed in idealized positions. Further details of the crystallographic studies are contained in the supplementary material.

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Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters and complete bond distances and angles for Ia, Ib, IIc, IIId, III, and IV (80 pages); tables of observed and calculated structure factors (68 pages). Ordering information is given on any current masthead page.

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Hydrogen Atom Abstraction from C-H, P-H, Si-H, and Sn-H Bonds by the Triplet Excited State of the Tetrakis(μ -pyrophosphito)diplatinum(II) Tetraanion. Spectroscopic Observation of the Mixed-Valence Hydride Complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$

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Abstract: Pulse radiolysis of aqueous solutions of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ at pH 4 with added *t*-BuOH gives $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$ via reaction with an electron and a proton. Pulsed-laser photolysis (Nd-YAG at 355 nm) of aqueous solutions of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ with added isopropyl alcohol, phosphorous acid, or hypophosphorous acid also gives $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$ by hydrogen atom abstraction. The mixed-valence hydride is similarly formed in methanolic solutions of (PPN)₄[$\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4$] from added triethylsilane or tributyltin hydride. The intermediacy of the $\text{Me}_2\dot{\text{C}}\text{OH}$ radical is evidenced by the formation of both pinacol and acetone in the photochemically catalyzed dehydrogenation of isopropyl alcohol with $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ in aqueous solution. The other radical, $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$, disproportionates to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}_2^{4-}$ and $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$. The Bu_3Sn radical has been detected by transient difference laser spectroscopy in solutions containing $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ and Bu_3SnH . The quenching rates for hydrogen atom donors with the $^3\text{A}_{2u}$ state of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*}$, as measured by the Stern-Volmer equation, are given and compared.

The tetrakis(μ -pyrophosphito)diplatinum(II) tetraanion continues to be increasingly studied because of reports of the high chemical reactivity of its long-lived triplet ($^3\text{A}_{2u}$) excited state $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*}$. A recent example that has generated interest is the discovery that the complex is a catalyst for the photochemical conversion of isopropyl alcohol into hydrogen and acetone.² A second catalytic application is the use of the complex in the photochemically induced hydrogen atom transfer from isopropyl alcohol to cyclohexene to give acetone and cyclohexane.³ In each case it was suggested that the reaction pathway involved hydrogen

atom transfer from isopropyl alcohol to the $^3\text{A}_{2u}$ state of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*}$, but no supportive evidence was offered in either case. We have now for the first time detected the mixed-valence $\text{Pt}^{\text{II}}\text{Pt}^{\text{III}}$ complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$ in aqueous solutions and have found that the compound is also formed by direct hydrogen atom abstraction from the methine group of isopropyl alcohol.

Although the 1- and 2-electron oxidation of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ is well documented and now relatively well understood,⁴ there has been minimal research on the reduction of this Pt^{II}_2 complex. Two such reports are the 1-electron reduction to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{5-}$ and

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the 2-electron reduction to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{6-}$.^{5,6} As a beginning to understanding the reaction chemistry of these mixed-valence complexes, we have recently found that the 1-electron-oxidized complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{3-}$ undergoes rapid disproportionation to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ and $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{2-}$ but little is yet known of the chemistry of the $\text{Pt}^{\text{I}}\text{Pt}^{\text{II}}$ complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{5-}$. We have now investigated the solution chemistry of this 1-electron-reduced complex because conceptually it can undergo disproportionation to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{6-}$ and $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ or alternatively it can undergo protonation to give the $\text{Pt}^{\text{I}}\text{Pt}^{\text{III}}$ hydride complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$.

Experimental Section

The complex $\text{K}_4[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]\cdot 2\text{H}_2\text{O}$ was prepared by the literature procedure.⁷ The complex $(\text{PPN})_4[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]$ (PPN^+ is bis(triphenylphosphine)nitrogen(1+)) was prepared by mixing aqueous solutions of $\text{K}_4[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]\cdot 2\text{H}_2\text{O}$ and $(\text{PPN})\text{Cl}$ and filtering the precipitated complex from the solution mixture. Water for solutions used in transient difference spectroscopy was passed through a Micropore filtration system, and the methanol used was spectral quality; both fluids were optically transparent under laser photolysis conditions. Phosphorous acid, hypophosphorous acid, triethylsilane, tributyltin hydride, and isopropyl alcohol were commercial samples, which were used without prior purification.

The experimental setup for pulse radiolysis has been described previously.⁸ Electron pulses of 100-ns duration were delivered to samples in a quartz cell having a 2.4-cm optical path length. Absorptions of transient species produced by the pulse were measured by using a conventional xenon lamp, monochromator, and photomultiplier tube assembly, and the signals were digitized by a Biomation 8100 transient recorder. Analysis of the signals was accomplished using an on-line PDP11/70 minicomputer. The absorption of radiation by water produces the primary radicals e_{aq}^- , OH^\cdot , and H^\cdot , with G values of 2.7, 2.7, and 0.55, respectively.⁹ Addition of *tert*-butyl alcohol (approximately 5%) to the aqueous solution removes both OH^\cdot and H^\cdot radicals in reactions that produce the relatively stable *tert*-butyl radical. Thus reduction of an added solute by e_{aq}^- may be observed without complications arising from other, possibly absorbing, species formed from OH^\cdot or H^\cdot radical attack.

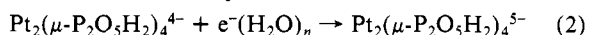
In the photochemical experiments transient species were generated by using the 355-nm third-harmonic, ca. 10-ns, pulses from a Quantel YG481 Nd-YAG laser and were monitored with a conventional xenon lamp, monochromator, photomultiplier arrangement. Digitized signals were passed to a PDP 11/70 computer for analysis. The system has been described more fully elsewhere.⁸

Quenching rates were obtained from data collected at 514 nm on a Spex Fluorolog fluorimeter using 1-cm path length fluorimeter tubes (Spectrocell Corp., Greeland, PA). Emission intensities were collected at 90° to the monochromated exciting light ($\lambda = 368$ nm from a 400-W xenon lamp). Solutions contained $\text{K}_4[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]\cdot 2\text{H}_2\text{O}$ dissolved either in water or in a mixture of water (5%) and the appropriate organic solvent. Buffers (pH 1 or pH 7) were prepared from phosphate mixtures. All solutions were homogeneous; data collection was ceased if the addition of further quencher resulted in cloudiness or separation into phases. Intensity data were analyzed with use of the Stern-Volmer equation (1) for added quencher Q .¹⁰ We have taken τ^0 as 9×10^{-6} s and obtained k_q from the best-fit slope of the data.

$$I_0/I = 1 + k_q\tau^0[Q] \quad (1)$$

Results and Discussion

Transient Difference Spectroscopy. Pulse radiolysis of aqueous solutions (pH 7) of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ ($\lambda_{\text{max}} = 368$ nm), with added *t*-BuOH to remove hydroxyl and hydrogen radicals, gives the mixed-valence $\text{Pt}^{\text{I}}\text{Pt}^{\text{II}}$ complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{5-}$ ($\lambda_{\text{max}} = 420$ nm) (eq 2).⁵ Under these experimental conditions this reduced



complex is relatively stable, as evidenced by the fact that we

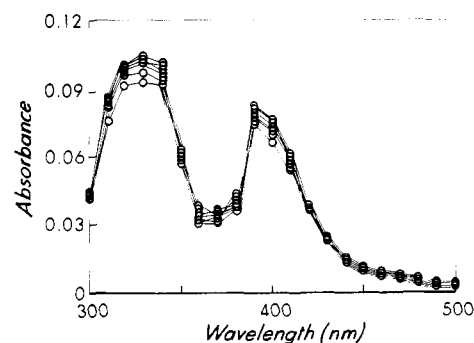


Figure 1. Transient absorption spectra of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$ measured at 0.4, 1.0, 2.2, 3.2, 6.45, and 13.45 μs (A-F; top-bottom traces) after the electron pulse. The solution pH is 4.

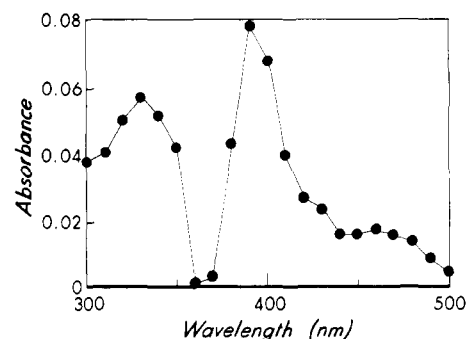
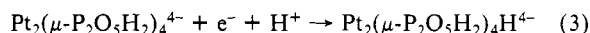


Figure 2. Transient absorption spectrum of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$ obtained by pulsed-laser photolysis (Nd-YAG operating at 355 nm) of an aqueous solution containing $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ and H_3PO_2 . The uncorrected (ground-state bleaching not subtracted) spectrum was measured 13 μs after the pulse.

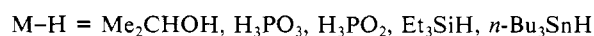
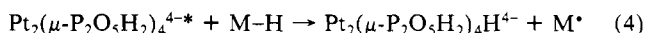
observe only a small amount ($\sim 5\%$) of depletion of this 420-nm band after a time lapse of 20 μs after the electron pulse. Since no new bands occur in the absorption spectrum after this elapsed time, we conclude that the disproportionation reaction of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{5-}$ is considerably slower than that of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{3-}$, which we have previously found to occur with a second-order rate constant of $6.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.⁴

By contrast to solution conditions with pH 7, pulse radiolysis of acidified aqueous solutions (pH 4) of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ with added *t*-BuOH does not give the $\text{Pt}^{\text{I}}\text{Pt}^{\text{II}}$ complex. Instead, we observe the rapid appearance of absorption bands with λ_{max} at 330 and 390 nm on either side of the bleached band of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ at 368 nm (Figure 1).¹¹ These new absorptions are due to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$, which is formed by the addition of both an electron and a proton to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ (eq 3). In step



sequence this reaction may involve hydrogen atom ($\text{H}^+ + e^-$) attack at $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$, or alternatively the pathway may involve protonation of the 1-electron-reduced $\text{Pt}^{\text{I}}\text{Pt}^{\text{II}}$ intermediate $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{5-}$ (by conventional oxidation state terminology, protonation at a metal center is a 2-electron oxidation).

Pulsed-laser photolysis (Nd-YAG operating at 355 nm) of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ in aqueous solution with excess added isopropyl alcohol, phosphorous acid, or hypophosphorous acid or in methanolic solution with the PPN^+ salt of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ and excess triethylsilane or *n*-tributyltin hydride gives the same $\text{Pt}^{\text{I}}\text{Pt}^{\text{III}}$ hydride complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$ as we generated by pulse radiolysis at pH 4 (eq 4). No such reaction occurs with water or methanol



(11) Although we identify $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}^{4-}$ by the presence of absorptions at 330 and 390 nm, the precise λ_{max} value for this complex is difficult to establish because of the overlapping bleaching from the 368-nm band of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$.

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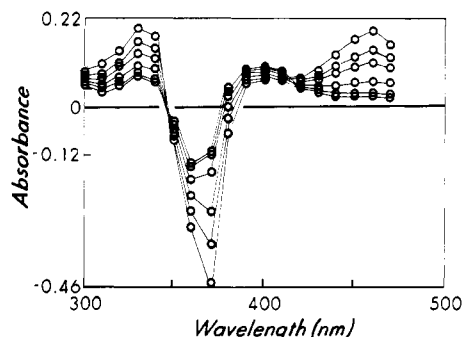


Figure 3. Transient absorption spectra taken 0.4, 1.0, 1.7, 3.2, 6.45, and 13.45 μ s after the pulse (A–F; top–bottom traces) showing the decay of the peaks at 330 and 460 nm due to the $^3A_{2u}$ state of $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and the corresponding residual of the 390-nm band of $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ formed by atom abstraction from Et_3SiH .

itself in the absence of these added hydrogen atom donor reagents. Similarly no hydride formation is observed if phosphoric acid, a compound that differs from phosphorous acid in that it contains no weak P–H bond, is used. The spectral changes diagnostic of the formation of $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ from hypophosphorous acid as the H atom donor are shown in Figure 2. The formation of $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ by the reaction shown in eq 4 is a hydrogen atom abstraction reaction involving cleavage of the C–H, P–H, Si–H, or Sn–H bond by the $^3A_{2u}$ state of $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$. This triplet state, with an electron configuration $\sigma^2(5d_{z^2})\sigma^{*1}(5d_{z^2})\sigma^1(6p_z)$ based on Gray's simplified molecular orbital model,¹² has an unpaired electron in an antibonding frontier orbital ($\sigma^*(5d_{z^2})$) localized in the vacant axial coordination positions. Previously we have found that halocarbons such as aryl bromides react with this $^3A_{2u}$ state by halogen atom (X) transfer from carbon to platinum to give $Pt_2(\mu-P_2O_5H_2)_4X^{4-}$.¹³ It is now clear that this $^3A_{2u}$ state also acts as a reactive free radical for hydrogen atom transfer from carbon, phosphorus, silicon, or tin to platinum. In thermodynamic terms, the reaction does not simply involve the homolysis of an M–H bond and the formation of a Pt–H bond, but an additional driving force to atom transfer is the formation of a partial platinum–platinum bond ($\sigma^2(5d_{z^2})\sigma^{*1}(5d_{z^2})$) in $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$, resulting from the loss of an antibonding electron ($\sigma^2(5d_{z^2})$) from $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$.

The hydride complex $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ is formed directly from the $^3A_{2u}$ state of $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and the added hydrogen atom donor compound M–H. This conclusion comes from a comparison of the decay rates of the absorption bands at 330 and 460 nm and the growth rate of the 390-nm absorption. For spectra collected soon after the laser flash (0.4–13.45 μ s) for the reaction with triethylsilane, we find that the 390-nm absorption due to $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ shows an initial growth that fits to a pseudo-first-order rate plot. Under experimental conditions where the lifetime of the growth of this band is 1.6 μ s, we find that the decay lifetimes of the absorption bands at both 330 and 460 nm are 1.4 μ s, within experimental error of the growth rate of the 390-nm band (Figure 3). From previous work, the $^3A_{2u}$ state of $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ has been found to have absorption bands at 330 and 460 nm;^{4,14} therefore, the lifetime correspondence between the growth of the 390-nm band and the decay of the 460-nm band shows that $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ is formed directly from $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$.

The complex $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ is formed from $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and H_3PO_3 at a rate that is first order in $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and H_3PO_3 for data collected at 390 nm for up to 3 μ s after the flash (Figure 4). When the photoreaction with H_3PO_3 as hydrogen atom donor is followed for a longer period of time (up to 20 μ s), the absorption at 390 nm decreases slowly. The

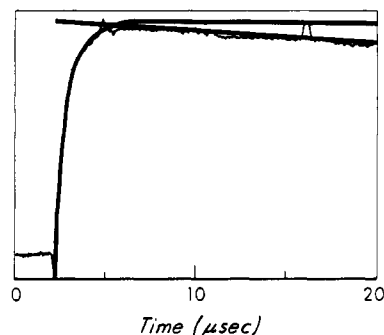


Figure 4. Rapid rise and slow fall of the absorption band at 390 nm due to $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ formed from $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and H_3PO_3 .

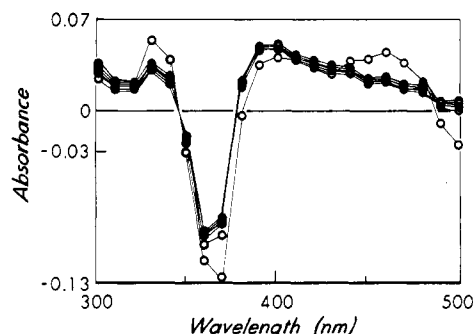
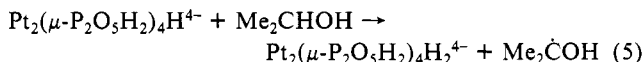


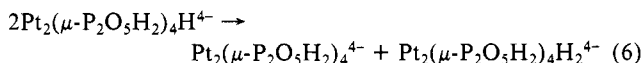
Figure 5. Transient absorption spectrum from the reaction between $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and $n-Bu_3SnH$ measured at 0.1, 0.7, 1.7, 3.2, 7.45, and 1.35 μ s (A–F; top–bottom traces) after the flash showing the band ~ 390 nm assigned to $n-Bu_3Sn^*$.

lifetime for the formation of $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$, obtained by best fit curve routines, is 770 ns.

The complex $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ is a mixed-valent $Pt^{II}Pt^{III}$ ion, and it has been suggested by us in an earlier paper that it will react with isopropyl alcohol to give $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ by hydrogen atom abstraction (eq 5), although no proof was offered



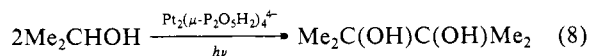
to support this hypothesis. We now find that this suggestion is not correct and that the loss of $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$, formed by photolysis of $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and Me_2CHOH , is due to its disproportionation (eq 6). This conclusion is drawn from the



observation that $Pt_2(\mu-P_2O_5H_2)_4H^{4-}$ decays from solution (equal volumes of water and isopropyl alcohol) by a pathway that follows the second-order rate law (eq 7).

$$\text{rate} = k[Pt_2(\mu-P_2O_5H_2)_4H^{4-}]^2 \quad (7)$$

The atom abstraction reaction shown in eq 4 requires that two radicals are formed as products in the reaction. Photolysis of a mixture of $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ and isopropyl alcohol (M–H = Me_2CHOH) in aqueous solution leads to the formation of hydrogen and acetone. Further examination of the reaction mixture from this photolysis confirms that a second product, obtained in small yield in the reaction, is pinacol.¹⁵ This compound is obtained by the coupling of isopropyl radicals, which have been formed by the abstraction of the methine hydrogen of isopropyl alcohol (eq 8). This result supports our premise that $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$



abstracts the methine hydrogen from Me_2CHOH . Further evidence of the formation of the M^* radicals (eq 4) formed in these

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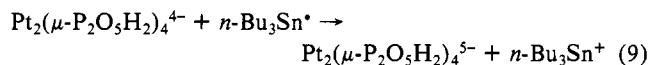
(15) Detected by GLC using a Dexsil 400 column.

Table I. Quenching Rates from Stern–Volmer Plots for the Reaction of Hydrogen Atom Donors with the $^3A_{2u}$ State of $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ at $22 \pm 2^\circ C$

reagent	solvent ^a	max reagent concn, M	rate const ^b (k_q), $M^{-1} s^{-1}$
Me ₂ CHOH	pH 1	0.38	7×10^4
Me ₂ CHOH	pH 7	0.50	2×10^4
Ph ₂ CHOH	water	0.06	8×10^4
PhCH ₂ OH	water	0.02	3×10^6
allyl alcohol	pH 7	0.01	3×10^8
allyl alcohol	methanol	0.29	1×10^6
Ph ₃ CH	DMSO	0.02	2×10^5
Ph ₃ CH	acetone	0.15	3×10^3
2-MeTHF	DMSO	0.02	2×10^5
Et ₃ SiH	methanol	0.09	4×10^5
<i>n</i> -Bu ₃ SnH	DMSO	0.02	2×10^5
H ₃ PO ₃	water	0.06	1×10^4
H ₃ PO ₂	water	0.29	1×10^6
MeCN	methanol	1.68	3×10^4
MeOH, EtOH, DMSO, acetone	water	2.00	$<10^3$

^a All nonaqueous solvents contain 5% water; $[Pt_2(\mu-P_2O_5H_2)_4^{4-}] \sim 10^{-5} M$. ^b A value of $10^3 M^{-1} s^{-1}$ is the lower limit for useful data treatment.

H atom transfers comes from transient difference spectroscopy of the reaction of $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ with *n*-Bu₃SnH. The spectral changes that occur during this reaction show the presence of a transient absorption at low wavelength (~ 300 nm), which is not found with the other hydrogen atom donors (Figure 5). This wavelength maximum corresponds to that previously reported for the tributyltin radical.¹⁶ This absorption band decays with a lifetime of 58 μs , which is the same as the rate of growth of the 420-nm absorption band in the spectrum. Since an absorption maximum at 420 nm corresponds to the formation of $Pt_2(\mu-P_2O_5H_2)_4^{5-}$, these observations can be explained on the basis of a thermal electron-transfer reaction from the *n*-Bu₃Sn[•] radical to $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ (eq 9).



Quenching Studies. The reaction of the $^3A_{2u}$ state of $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ with hydrogen atom donors causes a progressive decrease in the emission intensity at 514 nm as the concentration of hydrogen atom donor is increased. From Stern–Volmer plots

of the intensity data plotted against the quencher concentration $[Q]$, we can obtain quenching rate constants from the slopes of the straight-line plots. The rate constants k_q ($M^{-1} s^{-1}$) are collected in Table I. These data have been obtained either in aqueous solution or in methanol, DMSO, or acetone solvent. None of these fluids caused any significant quenching of the 514-nm emission intensity. Acetonitrile was avoided as a solvent because quenching was observed and also because previous workers had reported obtaining nonreproducible results with this solvent.¹⁷

Our data in Table I show that the quenching rates for hydrogen atom donors range over 5 orders of magnitude and also are solvent dependent. Indeed this marked solvent dependence on the quenching rate constant makes it imperative that rate data be compared under analogous solvent conditions. From the data in Table I, we observe that k_q for triphenylmethane is smaller in acetone solvent than in DMSO and that k_q for allyl alcohol is smaller in methanol than in pH 7 buffer. These comparisons suggest that k_q is larger in solvents of higher dielectric constant. Nevertheless it is clear that other factors are also involved since we observe a smaller quenching rate constant for diphenylcarbinol in aqueous solution than we find for benzyl alcohol in the same solvent.¹⁸

The occurrence of free-radical reactivity from a triplet excited state in a metal complex is conceptually realistic; however, there are very few cases where such chemistry is readily observed.¹⁹ Nevertheless, if comparison is made to the known thermal chemistry of metal-centered radicals, the reactivity of the $^3A_{2u}$ state of $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ correlates with that found for ground-state complexes such as $M(CO)_5$, $M(CO)_5\eta^5L_n$ (L = tertiary phosphine; M = Mn, Re),²⁰ or $Co(CN)_5^{3-}$.²¹

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