J. Am. Chem. Soc. 1987, 109, 5233–5235

molecule in the rate-determining step (eq 9) of $O_2$ release provides a rational explanation of the kinetic results. An increase in pH over the course of the reaction accompanies the loss in $O_2$ evolution. This could be due to the protonation of the ligand which decomposes the binuclear structure and produces free Mn(II) in the aqueous phase.

$$[Mn_2^{II}(L)Cl_3] + H_2O_2 \rightleftarrows [Mn_2^{III}(L)(O)Cl_3] + H_2O \quad (8)$$

$$[Mn_2^{III}(L)(O)Cl_3] + H_2O_2 \rightarrow [Mn_2^{II}(L)Cl_3] + H_2O + O_2 \quad (9)$$

The catalytic nature of the above reaction is attributable to the stability of the binuclear manganese site, which is derived from the binucleating ligand structure. In contrast, the series of binuclear Mn(III) and Mn(IV) complexes ($Mn_2^{III}(O)(CH_3CO_2)_2(Pz_3BH)_2$ and $Mn_2^{IV}O_2(bipy)_4$) decomposes $H_2O_2$ in homogeneous solutions by reactions that are stoichiometric at best (Mori, Sheats, and Dismukes, unpublished). This can be explained by the instability of the reduced states toward dissociation of the Mn ions in the absence of a binucleating ligand. Also, mononuclear Mn(II) in solution did not decompose $H_2O_2$ over the same interval, again indicating the need for the redox capacity found in two Mn ions.

The manganese-containing pseudocatalase of *L. plantarum* decomposes $H_2O_2$ by a mechanism that was originally believed to involve the cycling between Mn(III) and Mn(V) oxidation states on a single ion.[2a] Since this earlier report it has been learned that the enzyme contains 2 Mn(III) ions per protein subunit[2b] and that the site is probably binuclear (Fridovich and Beyer, private communication). We suggest that the mechanism of this biological reaction may also involve chemistry which parallels that given in reactions 8 and 9.

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# Dihydridotetrakis(pyrophosphito(2–))diplatinate(III)

**Erica L. Harvey, Albert E. Stiegman, Antonín Vlček, Jr.,[1] and Harry B. Gray***

*Contribution No. 7557 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125.* *Received February 13, 1987*

**Abstract:** The dσ*pσ triplet excited state of $[Pt_2(P_2O_5H_2)_4]^{4-}$ ($Pt_2$) reacts with hydrogen-atom donors to give $Pt_2H_2$. NMR ($^1H$ and $^{31}P$) and IR spectroscopic studies show that $Pt_2H_2$ is an axial dihydride: $^2J_{P-H}$, 11 Hz; $^3J_{P-H}$, 3.7 Hz; $^1J_{Pt-H}$, 884 Hz; $^2J_{Pt-H}$, 103 Hz; $^3J_{H-H}$, 26 Hz; $^2J_{P-O-P}$, >42 Hz; $^1J_{Pt-P}$, 2190 Hz; $^1J_{Pt-Pt}$, ~8000 Hz; ν(Pt–H), 1840 $cm^{-1}$. Reactions of $Pt_2H_2$ include photochemical release of $H_2$, rapid thermal reduction of $O_2$, and thermal reduction of HCl to $H_2$.

Hydrogen-atom transfer has been established as an important reaction pathway for the dσ*pσ triplet excited state of $[Pt_2(P_2O_5H_2)_4]^{4-}$ ($Pt_2$).[2-4] Substrates that serve as H-atom donors include alcohols with α(C–H) bonds[2,3] and triorganosilanes, -germanes, and -stannanes.[4] These substrates all react photochemically with $Pt_2$ upon 370-nm irradiation to produce the same complex,[3] which is characterized by strong absorption at 314 nm. NMR and IR spectroscopic studies reported here show that the common photoproduct is a binuclear platinum(III) dihydride, $[Pt_2(P_2O_5H_2)_4H_2]^{4-}$ ($Pt_2H_2$).

## Experimental Section

The title compound ($Pt_2H_2$) is generated by 370-nm narrow-band irradiation of freeze–pump–thaw degassed acetonitrile solutions of $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ containing the hydrogen-atom donor.[4] The extent of the photoreaction and stability of the photoproduct strongly depend on the nature of the substrate; $Pt_2H_2$ usually decomposes thermally, regenerating $Pt_2$ by reaction with unreacted substrate as well as with other photoproducts. We have found that $Pt_2H_2$ is reasonably stable only when generated by photolysis of either $Bu_3SnH$, $PhCH(OH)CH_2CH_3$, or $PhCH(OH)CH_3$ with $Pt_2$. The latter H donor was used in all experiments described here because conversion of $Pt_2$ to $Pt_2H_2$ at concentrations as high as 0.04 M was achieved (the half-life of $Pt_2H_2$ is at least 1.5 weeks in this case). The alcohols were purchased from Aldrich and distilled before use. Acetonitrile (B and J High Purity Solvent) and $CD_3CN$ (Aldrich Gold Label) were used as received. Both $^1H$ and $^{31}P$ NMR spectra were obtained on a 400-MHz JNM-GX400 FT NMR spectrometer after direct irradiation of a vacuum-sealed 10-mm NMR tube containing $Pt_2$ and $PhCH(OH)CH_3$. The IR spectrum was taken on a Beckman IR 4240; for this experiment the photoproduct was generated in a photolysis cell and transferred to the IR cell in a rigorous $N_2$ atmosphere. A Shimadzu UV-260 spectrometer was used to record the UV–vis absorption spectra. The composition of the atmosphere above the irradiated solutions before and after reaction with HCl and DCl was analyzed by mass spectrometry; the stoichiometry of release of $H_2$ during photolysis of the intermediate was measured by Toepler pumping.

Computer simulations were performed by using the Nicolet NMRSIM program at the Southern California Regional NMR Facility at Caltech. Due to the prohibitive number of spins (10–12) in the actual isotopomers, smaller spin systems (≤ 7) were studied extensively and the results were extrapolated where possible. For example, $J_{P-O-P} > 42$ Hz produces a triplet in the $^1H$ spectrum of an AA′XX′ (A = $^1H$; X = $^{31}P$) spin system and a quintet with the same splitting in the $^1H$ spectrum of an AA′XX′X″X‴ spin system. A reasonable extrapolation is to assume that the $^1H$ spectrum of the actual $AA'XX'X''X'''X''''X'''''X''''''X'''''''$ spin system consists of a nine-line pattern with the same splitting for $J_{P-O-P} > 42$ Hz.

The following set of coupling constants was used, although simulations on the smaller spin systems did not require all the values: $^2J_{P-H}$, 11; $^3J_{P-H}$, 3.7 (also could be $^4J_{P-H}$); $^1J_{Pt-H}$, 884; $^2J_{Pt-H}$, 103; $^3J_{H-H}$, 26; $^2J_{P-O-P}$, 45 (any value >42 Hz gives the same result); $^1J_{Pt-P}$, 2190; $^1J_{Pt-Pt}$, 8000 Hz. All other coupling constants were defined as 0.01 Hz. Very similar systems containing ≤10 spins have been completely simulated;[5] these simulations indicate that P–P couplings occur through the P–Pt–P and P–Pt–Pt–P linkages as well as through the P–O–P linkage. The magnitudes of the P–P couplings other than via the P–O–P bridge could not be determined in the present work, however. All simulations are available as supplementary material.

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(1) Permanent address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Vlašská 9, 11840 Prague, Czechoslovakia.

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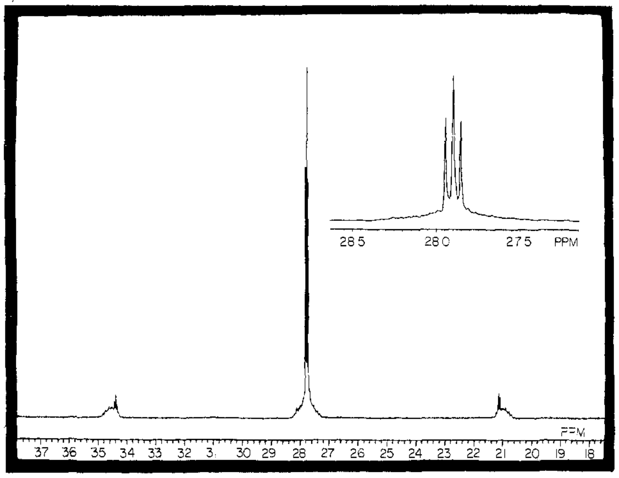

**Figure 1.** $^{31}$P NMR spectrum of the photoproduct generated by 370-nm irradiation (3.5 h) of a 0.043 M $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ and 0.083 M $PhCH(OH)CH_3$ degassed $CD_3CN$ solution.

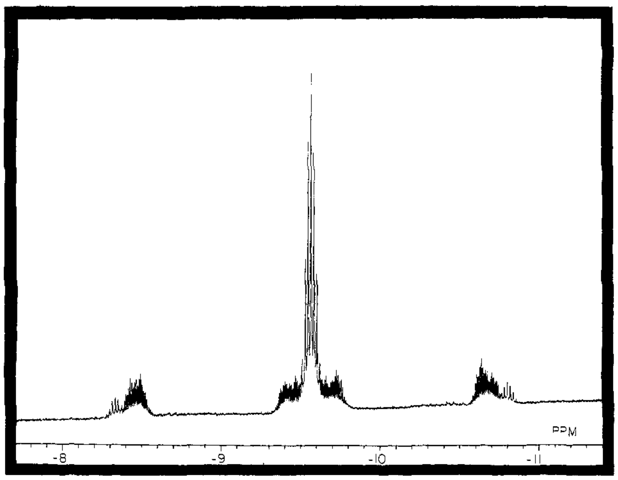

**Figure 2.** $^1$H NMR spectrum of the photoproduct generated by 370-nm irradiation (1.5 h) of a 0.0081 M $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ and 0.016 M $PhCH(OH)CH_3$ degassed $CD_3CN$ solution.

## Results and Discussion

The $^{31}$P NMR spectrum of the 314-nm photoproduct (Figure 1) consists of an apparent triplet at 27.9 ppm with a splitting of 7.4 Hz (vide infra) and $^{195}$Pt satellites ($J_{P-Pt}$ = 2200 Hz) spanning ~100 Hz. The spectra measured at 300 and 230 K are identical. The chemical shift and Pt-P coupling are consistent with known[6] binuclear Pt(III) complexes containing axial ligands: $Pt_2X_2 = [Pt_2(P_2O_5H_2)_4X_2]^{4-}$; X = Cl, Br, I, SCN, $NO_2$. Proton decoupling of the $^{31}$P NMR spectrum collapses the central peaks to a singlet.

The $^1$H NMR spectrum (Figure 2) exhibits a complicated symmetric pattern centered at −9.6 ppm, a chemical shift consistent with the presence of terminal hydrido ligands.[7,8] Analysis of the spectrum suggests an axial structure (H-Pt-Pt-H linkage) in which the presence of chemically equivalent but magnetically inequivalent atoms results in a deceptively simple pattern.[9] Due to the 33.8% natural abundance of NMR-active ($I = {}^1/_2$) $^{195}$Pt (*Pt), the spectrum is further complicated by the presence of three isotopomeric forms of $Pt_2H_2$: H-Pt-Pt-H (44%), H-*Pt-Pt-H (45%), and H-*Pt-*Pt-H (11%).

In the simplest symmetric isotopomer (both Pt nuclei are NMR-inactive), all eight $^{31}$P atoms have the same chemical shift but can couple to one another via the P-O-P bridges, thereby influencing the $^1$H spectrum in a manner dependent on the magnitude of the $^{31}$P-$^{31}$P coupling. The two $^1$H nuclei are similarly chemically equivalent and magnetically inequivalent, so the molecule is an $AA'XX'X''X'''X''''X'''''X''''''X'''''''$ spin system (A, $^1$H; X, $^{31}$P). For large $J_{P-O-P}$, the $^{31}$P nuclei effectively act as an equivalent group to the $^1$H nuclei, splitting their signal into the observed nine-line pattern in the central peak. (Seven lines are clearly visible; the other two are presumably buried under the satellites to either side.) The apparent splitting of 7.3 Hz agrees with that seen in the $^{31}$P NMR spectrum, but simulation of both spectra on analogous systems containing fewer (two or four) $^{31}$P atoms has shown that this splitting is actually the average of the $^{31}$P-$^1$H couplings, $^2J_{P-H}$ = 11.0 and $^3J_{P-H}$ = 3.7 Hz.[10]

The small, finely split satellites at the sides of the central peak in the $^1$H spectrum correspond to $^2J_{Pt-H}$ coupling (103 Hz) in the asymmetric isotopomer (spin system $AA'XX'X''X'''X''''X'''''X''''''X'''''''M$, M = *Pt). The analogous inner part of the more distant peaks corresponds to $^1J_{Pt-H}$ coupling (884 Hz). The apparent doublet character in each of the four multiplets corresponding to the asymmetric molecule is $^1$H-$^1$H coupling (26 Hz); the further fine splitting arises from $^2J_{P-H}$ and $^3J_{P-H}$ couplings. This interpretation is supported by the $^{31}$P-decoupled spectrum, which strongly emphasizes the doublet character of these peaks, by a computer simulation using an $AA'XX'X''X'''M$ system, and by a remarkably accurate first-order hand simulation using the coupling constants reported above.

Using the values of $^2J_{Pt-H}$ and $^1J_{Pt-H}$ obtained in the asymmetric isotopomer to simulate the H-*Pt-*Pt-H $^{31}$P-decoupled $^1$H spectrum produces a four-line pattern with a splitting of 485 Hz between the outer lines and the center for $J_{Pt-Pt}$ > 3000 Hz. In the actual nondecoupled spectrum, the outermost multiplets occur at 485 Hz from the center and show the same pattern and splitting as the central peak, due to the $^{31}$P atoms. The splitting of the inner two lines in the simulated spectrum depends on the value of $J_{Pt-Pt}$; $J_{Pt-Pt} \approx 8000$ Hz reproduces the splitting between two sharp peaks spanning the central singlet in the experimental $^{31}$P-decoupled spectrum and also fits with literature values for Pt-Pt couplings in similar molecules.[5,11] The overall interpretation of the spectrum is supported by the integration; the outer multiplets should account for 27.5% (22% + 5.5%) of the total integrated intensity of the spectrum, and the experimental value is 30%. Both $^{31}$P and $^1$H NMR spectra thus provide good evidence for an axial dihydrido structure ($Pt_2H_2$), which is analogous to other $Pt_2X_2$ complexes.

A medium-intensity IR band at 1840 $cm^{-1}$, corresponding to Pt-H stretching,[12] appears after 370-nm irradiation of an acetonitrile solution of $Pt_2$ with a slight excess of $PhCH(OH)CH_3$. The band disappears when air is allowed into the IR cell. The observed 1840 $cm^{-1}$ Pt-H stretching frequency falls in the terminal M-H range, whereas bridging hydrides are characterized by a much lower Pt-H vibrational frequency.[8,12]

The intense absorption band in the electronic spectrum of $Pt_2H_2$ at 314 nm has an extinction coefficient equal to that of the $d\sigma^* \rightarrow p\sigma$ singlet transition of $Pt_2$ (~$3.7 \times 10^4$ $M^{-1}$ $cm^{-1}$). In analogy to other $Pt_2X_2$ complexes,[6,13] it is assigned to the allowed $\sigma \rightarrow d\sigma^*$ transition[14] of $d^7$-$d^7$ $Pt_2H_2$. Irradiation (313 nm) into the $Pt_2H_2$ $\sigma \rightarrow d\sigma^*$ absorption band quantitatively produces $H_2$ and $Pt_2$. (Photochemical reductive elimination is a general reaction

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[6] Che, C-M.; Butler, L. G.; Grunthaner, P. J.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 4662–4665.

[7] Terminal Pt-H complexes exhibit $^1$H NMR signals at negative $\delta$ values; Pt-H-Pt species usually have $\delta > 0$.[8]

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[9] Becker, E. D., Ed. *High Resolution NMR, 2nd* ed.; Academic: Orlando, FL, 1980; pp 163–167.

[10] The $J_{P-H}$ of 3.7 Hz could arise from coupling via H-Pt-Pt-P ($^3J$) or H-Pt-P-O-P ($^4J$).

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of $d^7$–$d^7$ $M_2X_2$ complexes.[14-16]) Other chemical properties of $Pt_2H_2$ also are consistent with its formulation as a terminal dihydride. It reacts with HCl and DCl to generate $H_2$ and HD, respectively. Dioxygen reacts with $Pt_2H_2$ very rapidly with quantitative regeneration of $Pt_2$. The spectroscopic evidence and the reaction with $H^+$ point to the formal oxidation state assignment $Pt_2^{III}(H^-)_2$, but the $O_2$ chemistry indicates that the molecule also can be viewed as a $Pt_2^{II}(H^\bullet)_2$ species with the redox centers being the hydrido ligands. The $H^\bullet$ groups can be released (and potentially transferred to substrates) either chemically or photochemically in a manner not unlike the alkyl-radical chemistry[17,18] of certain Co(III) complexes.

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**Registry No.** $Pt_2H_2$, 80011-25-2; $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$, 89462-52-2; $Bu_3SnH$, 688-73-3; $PhCH(OH)CH_2CH_3$, 93-54-9; $PhCH(OH)CH_3$, 98-85-1; $H_2$, 1333-74-0; HCl, 7647-01-0; $O_2$, 7782-44-7.

**Supplementary Material Available:** Hand simulation of a satellite arising from the asymmetric isotopomer (spin system AA'XX'X''X'''X''''X'''''X''''''X'''''''M), computer simulations (with parameters) of all three isotopomers on analogous spin systems containing fewer $^{31}P$ nuclei (four to seven spins), and the experimental and simulated $^{31}P$-decoupled $^1H$ spectra (11 pages). Ordering information is given on any current masthead page.

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# Aromatic Nitration with Ion Radical Pairs $[ArH^{\bullet+},NO_2^\bullet]$ as Reactive Intermediates. Time-Resolved Studies of Charge-Transfer Activation of Dialkoxybenzenes

**S. Sankararaman, W. A. Haney, and J. K. Kochi***

*Contribution from the Department of Chemistry, University of Houston, University Park, Houston, Texas 77004.*

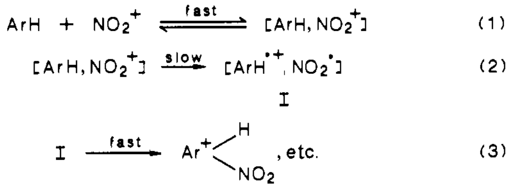
*Received February 3, 1987*

**Abstract:** Aromatic nitrations carried out both under electrophilic conditions and by charge-transfer activation afford the same yields and isomer distributions of nitration products from a common series of aromatic ethers (ArH). Time-resolved spectroscopy establishes the charge-transfer nitration to proceed via the ion radical pair $[ArH^{\bullet+},NO_2^\bullet]$, generated by the deliberate excitation of the electron donor–acceptor or $\pi$ complex of the arene with $C(NO_2)_4$. Laser flash photolysis of the charge-transfer band defines the evolution of the arene cation radical $ArH^{\bullet+}$ and allows its decay kinetics to be delineated in various solvents and with added salts. The internal trapping of $ArH^{\bullet+}$ is examined in the substituted *p*-dimethoxybenzenes $CH_3OC_6H_4OCH_2X$ with X = $CO_2H$, $CO_2^-$, $CO_2Et$, and $CH_2OH$ as the pendant functional groups. The mechanistic relevance of the collapse of $[ArH^{\bullet+},NO_2^\bullet]$ to the Wheland intermediate is discussed in the context of electrophilic aromatic nitrations.

The idea that charge transfer may play a key role in aromatic nitration with nitronium ion was first suggested in 1945 by Kenner,[1] who envisaged an initial step that "involves transference of a $\pi$-electron...". Later Brown[2] postulated charge-transfer complexes as intermediates, and Nagakura[3] provided further theoretical support for one-electron transfer between an aromatic donor (ArH) and an electrophile such as $NO_2^+$. Despite notable elaborations by Pederson,[4] Perrin,[5] Eberson,[6] and others, this formulation has not been widely accepted for nitration and related electrophilic aromatic substitutions.[7]

As broadly conceived, the seminal question focusses on the activation process(es) leading up to the well-established Wheland or $\sigma$-intermediate.[8,9] In the electron-transfer mechanism, the formation of the ion radical I is the distinctive feature, as summarized in Scheme I.[10] Accordingly, the properties and behavior of the intimate ion radical pair I are crucial to establishing its relationship with the numerous facets[11,12] of electrophilic aromatic

**Scheme I**



$$ArH + NO_2^+ \underset{}{\overset{fast}{\rightleftharpoons}} [ArH, NO_2^+] \qquad (1)$$

$$[ArH, NO_2^+] \xrightarrow{slow} \underset{\text{I}}{[ArH^{\bullet+}, NO_2^\bullet]} \qquad (2)$$

$$\text{I} \xrightarrow{fast} Ar^+\!\begin{matrix} H \\ NO_2 \end{matrix}, \text{etc.} \qquad (3)$$

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(10) The brackets denote a loose (encounter) complex or solvent-caged species.

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