oxidation of 2-propanol occurred, but in a stoichiometric rather than a catalytic manner. A catalytic cycle is not possible, at least on the time scale employed here, because the reoxidation of the dinitrosyl complex designated $[(\text{mixed})Co(NO)_2]^{2+}$ is slow at 70 °C with O_2 as the oxidizing agent.

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Binuclear Platinum(II) Photochemistry. Reactions of Organometallic Hydrides with Electronically Excited Tetrakis(pyrophosphito)diplatinate(II)

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The $d\sigma^*p\sigma$ triplet excited state of $Pt_2(P_2O_5H_2)_4^{4-}$ (Pt_2) abstracts a hydrogen atom from R_3EH (E = Sn, Ge, Si; R = alkyl, phenyl) in acetonitrile solution. The rate constant for H atom transfer decreases according to Sn > Ge ≫ Si. The ultimate product of the reaction, Pt_2H_2, is thermally stable when generated from stannanes or germanes but it decomposes by secondary photoprocesses to H_2 and other Pt_2 complexes. In the case of Si, Pt_2H_2 reacts thermally with other species in the solution, regenerating Pt_2 and forming H_2. For E = Sn or Ge, another reaction product, $Pt_2(ER_3)_2$, is formed by the addition of $R_3E^\bullet$ to Pt_2. Each of these complexes is characterized by a very intense absorption band that is red-shifted with respect to that of Pt_2 (Bu_3Sn, 427 nm; Ph_3Ge, 430 nm) and each exhibits an intense broad emission (Sn, 527 nm; Ge, 531 nm). Photolysis of $Pt_2(ER_3)_2$ yields Pt_2 and $R_3E^\bullet$.

Introduction

The d^8–d^8 binuclear complexes (M_2: M = Rh, Ir, Pt) are known[2-7] to possess $d\sigma^*p\sigma$ triplet excited states ($^3M_2^*$) whose lifetimes are usually long enough to allow bimolecular photochemical reactions to take place. The electron-transfer reactions in which M_2 complexes act as one-electron excited-state reductants have been thoroughly investigated.[2,4-8] However, the M_2 complexes also possess two open axial coordination sites, which make them good candidates for excited-state atom-transfer reactions. This type of reactivity has not been systematically investigated, although a hydrogen atom transfer, $RH + {}^3M_2^* \rightarrow R^\bullet + {}^\bullet M_2H$, was proposed by Roundhill[9] to be a primary process in the Pt_2 photoassisted dehydrogenation of 2-propanol to acetone (Pt_2 = $Pt_2(P_2O_5H_2)_4{}^{4-}$). Recent work in our laboratory has provided support for Roundhill's proposal, and the key intermediate Pt_2H_2 has been characterized.[7,10] Our work also has revealed that excited M_2 complexes can activate other organic substrates, including hydrocarbons (e.g., toluene).[7] Because of its long lifetime (10 μs), high triplet energy (57.7 kcal mol^{-1}),[8,11] and stability, Pt_2 is well suited for photocatalysis.

It is important to explore the reactions of $^3Pt_2^*$ with bonds other than C–H and to understand its atom-transfer reactivity in more detail. For these reasons, the photochemical reactions of Pt_2 with a series of R_3EH (E = Sn, Ge, Si) molecules have been investigated. In the course of this work, some secondary reactions yielding unexpected products were discovered.

Results and Discussion

Reactions with Tributyltin Hydride. An acetonitrile solution of Pt_2 and Bu_3SnH (typically in 4–20-fold excess) turns yellow rapidly under nearly monochromatic 370-nm irradiation. Two products absorbing at 314 and 427 nm are formed (Figure 1). Both products are stable when the irradiation is interrupted.

The absorption band at 314 nm is attributable to Pt_2H_2. The ^{31}P NMR spectrum of Pt_2H_2 (Figure 2) exhibits a triplet (J(P,H) = 7.3 Hz) at δ = 27.9 with two satellites due to ^{31}P–^{195}Pt coupling: ^1J(P,Pt) = 2180 Hz. The absorption band at 314 nm disappears immediately upon exposure of the solution to air. When the solution containing the photoproducts is irradiated at 313 nm, the 314-nm absorption band decreases with concomitant increase of the Pt_2 absorption at 373 nm, whereas the 427-nm band remains unchanged. All these experiments clearly show that the reaction product absorbing at 314 nm is Pt_2H_2.[10]

The ^{31}P NMR spectrum of the 427 nm product (Figure 2) is characteristic of a symmetrical Pt_2X_2 species with equivalent phosphorus atoms. A single peak at 31.1 ppm is present with two small satellites corresponding to ^{31}P–$^{117,118}Sn$ coupling:[12] ^2J(P,Sn) = 69 Hz. Two other satellites are due to ^{31}P–^{195}Pt coupling: ^1J(P,Pt) = 2290 Hz. On the basis of this NMR spectrum, the photoproduct is formulated as $Pt_2(SnBu_3)_2$, with $SnBu_3$ groups coordinated to Pt_2 at axial positions (a Sn–Pt–Pt–Sn unit). The chemical shift and P–Pt coupling are at the upper limits of the ranges typical of axial $Pt^{III}{}_2X_2$ complexes ($18 < \delta < 31$; $2085 < {}^1J(P,Pt) < 2290$ Hz).[13-15]

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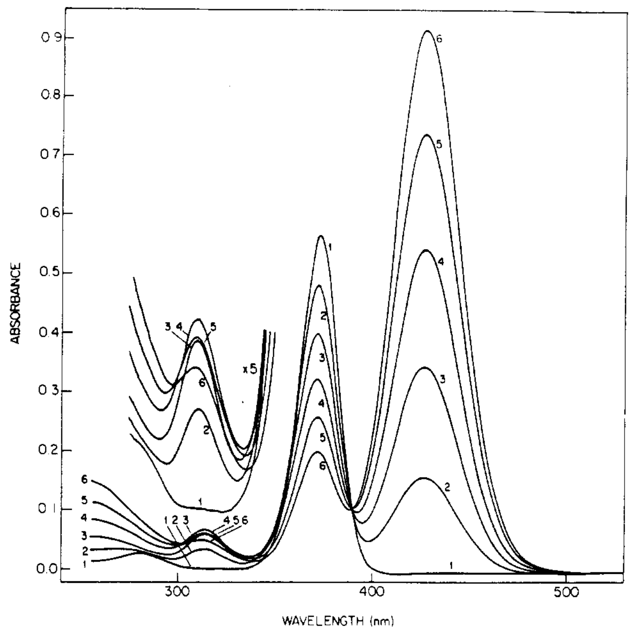

Figure 1. UV-vis spectral changes during 370-nm irradiation of Pt$_2$ and Bu$_3$SnH: 1.45 × 10^{-4} M [Bu$_4$N]$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$]; 1.45 × 10^{-3} M Bu$_3$SnH in CH$_3$CN. Spectra 1-6 were measured after 0, 20, 70, 160, 300, and 500 s, respectively.

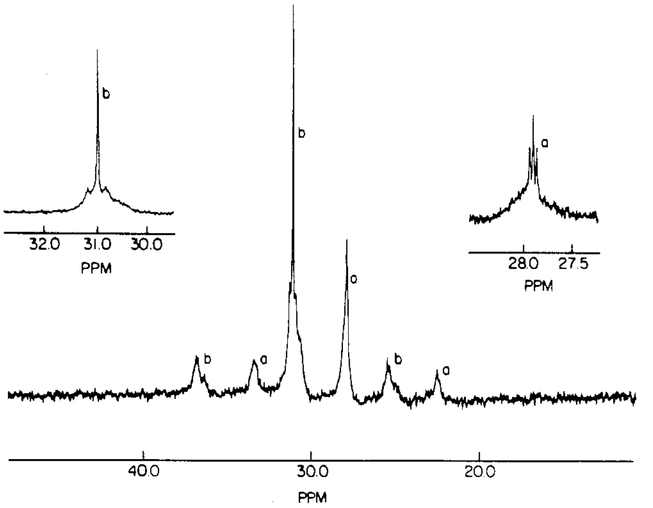

Figure 2. ^{31}P NMR spectrum of a CD$_3$CN solution containing 6.3 × 10^{-3} M [Bu$_4$N]$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$] and 8.7 × 10^{-2} M Bu$_3$SnH that was photolyzed for 4 min: a, Pt$_2$H$_2$; b, Pt$_2$(SnBu$_3$)$_2$. Insets show details of the central peaks.

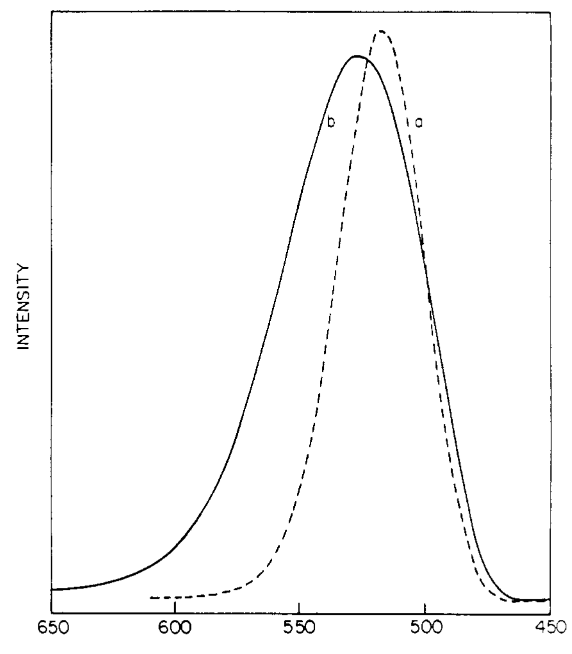

Figure 3. Emission spectra of Pt$_2$ and Pt$_2$(SnBu$_3$)$_2$ measured in acetonitrile solution at room temperature: dashed line (a); 1.5 × 10^{-4} M [Bu$_4$N]$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$] (excitation at 366 nm); solid line (b), 1.2 × 10^{-4} M [Bu$_4$N]$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$] and 8.1 × 10^{-4} M Bu$_3$SnH photolyzed for 19 min at 370 nm before the emission measurement (excitation at 436 nm).

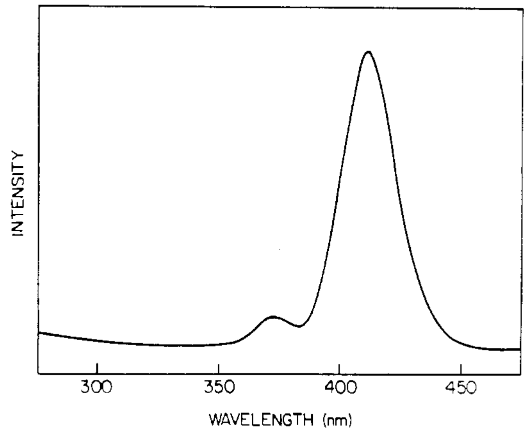

Figure 4. Excitation spectrum monitored at 500 nm of a CH$_3$CN solution containing 1.3 × 10^{-5} M [Bu$_4$N]$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$] and 9.3 × 10^{-3} M Bu$_3$SnH that was photolyzed in a quartz 1-mm capillary for 5 min at 370 nm. (Emission as well as absorption is blue-shifted at 77 K.)

An interesting feature of Pt$_2$(SnBu$_3$)$_2$ is its intense absorption band at 427 nm; the extinction coefficient may be estimated (vide infra) as $\geq$1.41 × 10^5 M^{-1} cm^{-1}, i.e., $\geq$3.8 times the value of the extinction coefficient of the dσ^* → pσ singlet absorption of Pt$_2$. By analogy to other axially coordinated d^7–d^7 complexes, this absorption band is assigned[13,16-18] to a $\sigma \rightarrow$ dσ^* transition. However, due to the strongly reducing Bu$_3$Sn axial ligands, the σ orbital is highly delocalized over the Pt$_2$Sn$_2$ unit.[16] The $\sigma \rightarrow$ dσ^* excitation thus involves a large contribution of LMCT(Sn → Pt), which may explain the unusually high extinction coefficient.[16] An intense absorption band that is red-shifted with respect to that of its parent d^8–d^8 complex has been found[19] in the spectrum of [(CO)$_5$MnRh$_2$(tmb)$_4$Mn(CO)$_5$], a d^7–d^7 complex with axially coordinated Mn(CO)$_5$ groups (tmb = 2,5-dimethyl-2,5-diisocyanohexane). The delocalization of the σ orbital in the Rh$_2$Mn$_2$ complex would be expected to be extensive, and the implied analogy with Pt$_2$Sn$_2$ is not unreasonable.

The Pt$_2$(SnBu$_3$)$_2$ complex also exhibits a strong green emission with a maximum at 527 nm in acetonitrile solution at room temperature. The emission band is broader and the maximum is red-shifted 11 nm relative to that of Pt$_2$ (Figure 3). The emission spectra always were measured in previously photolyzed solutions that contained a small amount of residual Pt$_2$ and an excess of Bu$_3$SnH. However, the broad 427-nm emission was observed only upon excitation at 436 nm, i.e., into the absorption band of Pt$_2$(SnBu$_3$)$_2$. When the complex was excited at 366 nm, only the narrow emission of Pt$_2$ at 516 nm was observed. The emission spectrum of a solution containing Pt$_2$ and an excess of Bu$_3$SnH measured without previous irradiation exhibits only the emission of Pt$_2$ when the solution was excited either at 436 or 366 nm. Moreover, the excitation spectrum of the photolyzed solution (in 1:2 (v/v) CH$_3$CH$_2$CN/2-methyltetrahydrofuran measured in a glass at 77 K) is fairly coincident with its absorption spectrum

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Table I. Rate Constants (k_H)[a] for Hydrogen Atom Transfer Reactions

H atom donor	$^3Pt_2^*$	t-BuO$^\bullet$
Et_3SiH	2.0×10^4	$5.7 \times 10^{6\,b}$
Ph_3SiH	1.6×10^5	$1.1 \times 10^{7\,b}$
Ph_3GeH	2.9×10^7	$8.9 \times 10^{7\,b}$
Ph_3SnH	1.0×10^8	$4.0 \times 10^{8\,b}$
Bu_3SnH	1.2×10^7	$2.2 \times 10^{8\,c}$
Bu_3SnD	6.9×10^6	$1.8 \times 10^{8\,c}$

[a] Rate constants in $M^{-1}\,s^{-1}$. Values for $^3Pt_2^*$ were measured in acetonitrile at 298 K; those for t-BuO$^\bullet$ were measured in 1:2 (v/v) benzene/t-Bu_2O_2. [b] Reference 27; $T = 300$ K. [c] Reference 23; $T = 295$ K.

(Figure 4). It exhibits the intense peak of $Pt_2(SnBu_3)_2$ and a small feature due to Pt_2. It is thus evident that the broad emission at 527 nm corresponds to $Pt_2(SnBu_3)_2$ (with a small contribution from residual Pt_2) and not to an exciplex between $^3Pt_2^*$ and Bu_3SnH. However, the emission of $Pt_2(SnBu_3)_2$ does not possess any of the features characteristic of the triplet → singlet "$d\sigma^*$" emission of Pt_2X_2 complexes, which is observable only in low-temperature glasses and is accompanied by a large Stokes shift.[18] Because the energy of the $\sigma d\sigma^*$ state of $Pt_2(SnBu_3)_2$ is only slightly higher than that of $^3Pt_2^*$ (the $^3(d\sigma^* p\sigma)$ absorption band of Pt_2 peaks[2] at 452 nm), it is possible that the $Pt_2(SnBu_3)_2$ $\sigma d\sigma^*$ state decays by formation of a $^3Pt_2^*(Bu_3Sn^\bullet)_2$ exciplex that is deactivated both radiatively and nonradiatively to $Bu_3Sn^\bullet$ radicals and Pt_2. This interpretation is in accord with the close similarity of the Pt_2 and $Pt_2(SnBu_3)_2$ emission spectra and with the observed photochemistry. When $Pt_2(SnBu_3)_2$ is irradiated at 436 nm, it decomposes rapidly with the regeneration of Pt_2. This is a reaction that is typical of all axial d^7–d^7 M_2X_2 complexes.[17-20] When Pt_2H_2 is present in the solution, it also disappears, probably due to reaction with $Bu_3Sn^\bullet$ radicals that are generated by the photolysis of $Pt_2(SnBu_3)_2$.

Oxidizing agents (e.g., oxygen and p-DBQ = 2,6-di-*tert*-butyl-1,4-benzoquinone) react with $Pt_2(SnBu_3)_2$ to give Pt_2. The presence of p-DBQ$^{\bullet -}$ in the p-DBQ reaction was demonstrated by EPR measurements. (A 3-line signal ($g = 2.003$; $a_H = 0.18$ mT) appears when p-DBQ is added to a previously irradiated solution of Pt_2 and Bu_3SnH.) Although $Pt_2(SnBu_3)_2$ behaves spectroscopically as a d^7–d^7 (formally $Pt^{III}{}_2Sn^{II}{}_2$) species, chemically and photochemically it reacts as $Pt^{II}{}_2Sn^{III}{}_2$, the redox site being the Sn atoms. The $Pt_2(SnBu_3)_2$ thus behaves as a "carrier" of two $Bu_3Sn^\bullet$ radicals, which can be released either thermally by oxidants or photochemically. Analogous behavior of Pt_2H_2 has been observed.[10]

The photochemical[21] reaction of Pt_2 with Bu_3SnH can be summarized as follows:

$$2Pt_2 + Bu_3SnH \xrightarrow{h\nu} Pt_2H_2 + Pt_2(SnBu_3)_2 \qquad (1)$$

The stoichiometry of this reaction was measured by following the decrease of the 373-nm Pt_2 absorption and the increase of the Pt_2H_2 absorption peak upon 370-nm irradiation. The values of $\Delta A_{314}/\Delta A_{373}$ (A_λ is the absorbance at λ) were extrapolated to zero irradiation time to avoid interference from secondary photochemical reactions. An average value of 0.43 was obtained for the usual reaction conditions. At very high (180–200-fold) excesses of Bu_3SnH, values as high as 0.58 were found. As the extinction coefficients of the absorption bands at 373 and 314 nm are virtually the same,[10] the ratio of the absorbance changes is equal to the ratio of concentration changes. Thus one molecule of Pt_2H_2 is formed per two molecules of Pt_2 consumed. The $\Delta A_{427}/\Delta A_{373}$ ratio was found to be 1.9 (extrapolated to zero irradiation time). Assuming the same 2:1 (or lower, due to $Bu_3Sn^\bullet$ recombination) stoichiometry for $Pt_2(SnBu_3)_2$ formation, its extinction coefficient at 427 nm may be estimated to be ≥3.8 times the extinction coefficient of Pt_2 at 373 nm.

The nature of the primary photochemical step was investigated by quenching the $^3Pt_2^*$ lifetime by Bu_3SnH. (Stern–Volmer behavior was found.) The rate constant (k_H) is $1.2 \times 10^7\ M^{-1}\,s^{-1}$. Quenching by Bu_3SnD gives a k_D of $6.9 \times 10^6\ M^{-1}\,s^{-1}$. The H/D kinetic isotope effect is 1.7,[22] which is larger than the value found[23] for the H atom abstraction from Bu_3SnH by t-BuO$^\bullet$ radicals (1.23) but slightly smaller than that for the reactions of Bu_3SnH with alkyl radicals (1.9–2.3).[24] The isotope effect together with the formation of Pt_2H_2 is good evidence that the primary photochemical step in reaction 1 is excited-state hydrogen atom transfer. The $^\bullet Pt_2H$ intermediate abstracts another H atom, thereby producing Pt_2H_2. (Analogous behavior has been found in the reactions of $^3Pt_2^*$ and α(C–H) bonds of alcohols.[7]) The $Bu_3Sn^\bullet$ radicals that are produced in the primary step react with Pt_2 to give $Pt_2(SnBu_3)_2$. The following mechanism (eq 2–5) is proposed:

$$Pt_2 \xrightarrow{h\nu} {}^3Pt_2^* \qquad (2)$$

$$^3Pt_2^* + Bu_3SnH \xrightarrow{k_H} Pt_2H + Bu_3Sn^\bullet \qquad (3)$$

$$Pt_2H + Bu_3SnH \rightarrow Pt_2H_2 + Bu_3Sn^\bullet \qquad (4)$$

$$Pt_2 + 2Bu_3Sn^\bullet \rightarrow Pt_2(SnBu_3)_2 \qquad (5)$$

(We cannot exclude the possibility that the products of reaction 3 also undergo in-cage recombination, thereby producing $Pt_2(H)(SnBu_3)$ species. However, no evidence for this species was found. If it exists, it is rather unstable, either disproportionating to Pt_2H_2 and $Pt_2(SnBu_3)_2$ or reductively eliminating Bu_3SnH.)

Absorption spectra measured during photolysis (Figure 1) reveal secondary photochemical reactions: the Pt_2H_2 band at 314 nm increases at the beginning of the irradiation, then stays constant, and finally decreases and disappears. Also, it is not possible to achieve complete conversion of Pt_2, even by prolonged photolysis.[25] The absorption band of $Pt_2(SnBu_3)_2$ overlaps partially with the Pt_2 band. Thus, after an initial period of photolysis, irradiation in the 370-nm region (which extends from 350 to 390 nm) also excites $Pt_2(SnBu_3)_2$, thereby producing $Bu_3Sn^\bullet$ radicals and Pt_2. The latter species reacts with Pt_2H_2 (vide supra, eq 7):

$$Pt_2(SnBu_3)_2 \xrightarrow{h\nu} Pt_2 + 2Bu_3Sn^\bullet \qquad (6)$$

$$Pt_2H_2 + Bu_3Sn^\bullet \rightarrow H_2 + \text{other products} \qquad (7)$$

The presence of H_2 after the initial stages of photolysis was confirmed by mass spectral analysis.

Triphenyltin hydride, Ph_3SnH, also reacts with Pt_2 photochemically according to eq 1–5. The rate constant (k_H) for the primary H atom transfer (eq 3) is $1.0 \times 10^8\ M^{-1}\,s^{-1}$. This k_H is approximately 8 times larger than that for Bu_3SnH. An analogous increase in the rate constant for H atom abstraction in going from Bu_3SnH to Ph_3SnH was observed in the reaction with *tert*-butyl radicals (7.4×10^5 for Bu_3SnH vs. $3.1 \times 10^6\ M^{-1}\,s^{-1}$ for Ph_3SnH)[26] and with *tert*-butoxy radicals[27] (Table I).

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(21) A thermal reaction between Pt_2 and Bu_3SnH (or other R_3EH species) does not occur on the time scale of the observed photochemistry.

(22) Taking into account the low ν(Sn–H) stretching frequency (1837 cm^{-1} for Me_3SnH: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; pp 380–381), the Sn–H zero-point-energy isotope effect for H atom transfer may be estimated as 3.6, which is much lower than the value for C–H, 6.9 (Melander, L.; Saunders, Jr., W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 4–45, 129–170). The observed Sn–H/D isotope effect accounts for 47% of the zero-point-energy value.

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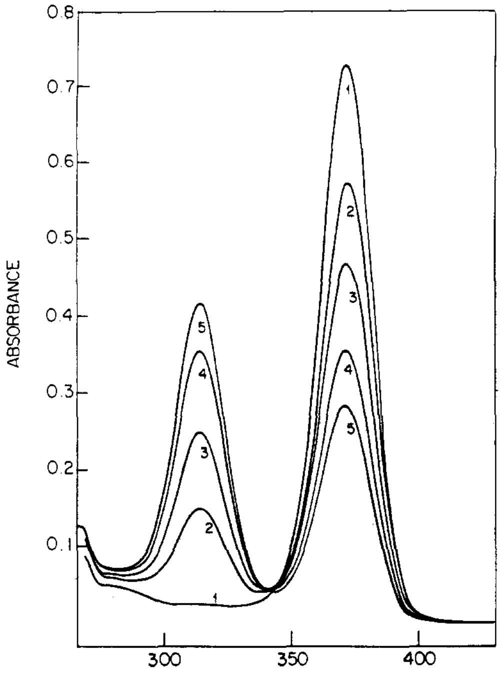

Figure 5. UV-vis spectral changes during 370-nm photolysis of 1.8 × 10^{-4} M $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ and 3.2 × 10^{-1} M Et_3SiH in CH_3CN. Spectra 1-5 were measured after 0, 120, 360, 780, and 1440 s, respectively.

Unlike in the Bu_3SnH reaction, the Pt_2H_2 absorption band at 314 nm increases steadily during irradiation. This is in accord with the observation that the photolysis of $Pt_2(SnPh_3)_2$ at 436 nm causes only a minor decrease in the absorption band of Pt_2H_2; thus, reaction 7 does not take place to a large extent in this case. However, other side reactions must occur during the photolysis of Pt_2 and Ph_3SnH, because clean isosbestic points were not observed.

The spectroscopic properties of $Pt_2(SnPh_3)_2$ are analogous to those of $Pt_2(SnBu_3)_2$. (The spectrum of $Pt_2(SnPh_3)_2$ is characterized by a very strong absorption at 440 nm.) Photolysis at 436 nm only partially regenerates Pt_2, also producing a species that absorbs at ~350 nm.[28] Thermal decomposition of $Pt_2(SnPh_3)_2$ occurs very slowly without regeneration of Pt_2.

Reaction with Triphenylgermane. Photolysis of Pt_2 and Ph_3GeH in acetonitrile solution is analogous to that involving Bu_3SnH. The 373-nm band of Pt_2 decreases, another very intense absorption band at 430 nm attributable to $Pt_2(GePh_3)_2$ increases, and the 314-nm band of Pt_2H_2 exhibits transient behavior. The presence of H_2 after prolonged photolysis was established by mass spectrometry. The mechanism (eq 1-7) proposed for the reaction of Pt_2 with Bu_3SnH applies to Ph_3GeH as well. The rate constant for H atom transfer is 2.9×10^7 M^{-1} s^{-1}.

The $Pt_2(GePh_3)_2$ complex is characterized by a strong absorption at 430 nm and an intense broad emission at 531 nm for 436-nm excitation. It is thermally stable but decomposes to Pt_2 when photolyzed at 436 nm.[28] The Pt_2H_2 is concomitantly destroyed. $Pt_2(GePh_3)_2$ also reacts with oxygen but much more slowly than $Pt_2(SnBu_3)_2$. Its ^{31}P NMR spectrum exhibits a singlet at $\delta = 29.4$ with two satellites: $^1J(P,Pt) = 2250$ Hz. The structure and spectral assignments for $Pt_2(SnBu_3)_2$ are analogous to those for $Pt_2(GePh_3)_2$.

Reactions with Triorganosilanes. Irradiation of Pt_2 with a large (ca. 1000-fold) excess of Et_3SiH or Ph_3SiH produces Pt_2H_2, whose concentration steadily increases during irradiation (Figure 5) until a photostationary state is achieved. (Complete conversion of Pt_2 to Pt_2H_2 was not achieved.) When the irradiation is interrupted, Pt_2H_2 is quantitatively converted back to Pt_2 with production of H_2. (Dihydrogen is formed during irradiation in much higher amounts than in the case of Sn or Ge.) The spectra accompanying both photolytic reactions and back-reactions exhibit the same isosbestic point. However, minor irreversible decomposition takes place during prolonged irradiation (30 min and longer), as only 85–97% of the original Pt_2 is recovered by thermal back-reaction, with the amount depending on the time of the previous photolysis. (The extent of the recovery is larger for Ph_3SiH than Et_3SiH.) The photochemistry of Pt_2 in the presence of triorganosilanes takes place according to eq 8–10. The k_H values are 2.0×10^4 and 1.6×10^5 M^{-1} s^{-1} for Et_3SiH and Ph_3SiH, respectively. Contrary to the case for reactions with Sn and Ge hydrides, no evidence for the formation of $Pt_2(SiR_3)_2$ complexes was found. Owing to their high reactivity, other reactions of $R_3Si^\bullet$ radicals (disproportionation, reaction with a large excess of unreacted R_3SiH, or reaction with the solvent)[29,30] are probably competitive with addition to Pt_2. (By analogy, Pt_2R_2 (R = alkyl or aryl) complexes are not produced either in thermal or photochemical reactions of Pt_2 with RX or RH.[7,9])

$$^3Pt_2^* + R_3SiH \xrightarrow{k_H} Pt_2H + R_3Si^\bullet \quad (8)$$

$$Pt_2H + R_3SiH \rightarrow Pt_2H_2 + R_3Si^\bullet \quad (9)$$

$$Pt_2H_2 \xrightarrow{\text{slow}} Pt_2 + H_2 \quad (10)$$

The thermal decomposition of Pt_2H_2 (eq 10) is a pseudo-first-order process. The rates of formation of Pt_2 and disappearance of Pt_2H_2 are the same. The rate constants are in the range 10^{-4}–10^{-3} s^{-1} for Et_3SiH, depending on the silane concentration and time of the previous photolysis. It appears that Pt_2H_2 reacts with the silanes as well as with other unidentified silicon-containing photolytic products.

Reaction with Triphenylmethane. Neither Pt_2H_2 nor H_2 was observed when acetonitrile solutions containing Pt_2 and a large (>1000-fold) excess of Ph_3CH were irradiated for 2 h at 370 nm. The upper limit for the quenching rate constant is 2×10^4 M^{-1} s^{-1}.

Concluding Remarks

Although the overall mechanisms of the photoreactions between Pt_2 and R_3EH (E = Sn, Ge, Si) depend on E, the primary step in all cases is excited-state H atom transfer:

$$^3Pt_2^* + R_3EH \xrightarrow{k_H} Pt_2H + R_3E^\bullet \quad (11)$$

The rate constants k_H are summarized in Table I and compared with those for H atom abstractions by the t-BuO$^\bullet$ radical. Generally, the reactivity of R_3EH species toward $^3Pt_2^*$ decreases in the same order (Sn > Ge ≫ Si) as the E–H bond energy increases (Sn < Ge < Si).[31] It is surprising that Ph_3CH is inert toward $^3Pt_2^*$, because H atom transfer from this substrate to t-BuO$^\bullet$ occurs with a rate constant (2.6×10^6 M^{-1} s^{-1})[27] comparable to that for the reaction of Et_3SiH (5.7×10^6 M^{-1} s^{-1}). The lack of reactivity with $^3Pt_2^*$ probably is attributable to an

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[28] The photochemical decomposition processes for both $Pt_2(SnPh_3)_2$ and $Pt_2(GePh_3)_2$ are quite complicated. The absorption band of $Pt_2(EPh_3)_2$ (E = Ge, Sn) decreases in intensity and shifts to shorter wavelengths during 436-nm irradiation. Isosbestic points were not observed. The recovery of Pt_2 is only partial (although much higher for $GePh_3$ than for $SnPh_3$), and another species absorbing at ~350 nm forms for $SnPh_3$ and in small amounts also for $GePh_3$. (Photolysis of $Pt_2(SnBu_3)_2$ also leads to a minor product that absorbs at 360–370 nm.) Attack of $R_3E^\bullet$ radicals on the P–O or O–H bonds of $P_2O_5H_2^{2-}$ and/or on Ph_3EH phenyl rings cannot be excluded.[29]

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[30] Armitage, D. A.; Riviere, P.; Riviere-Baudet, M.; Satge, J.; Davies, A. G.; Smith, P. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 2, pp 91–92.

[31] The gas phase (298 K) E–H bond energies of $(CH_3)_3EH$ species have been reported: 90 (Si), 82 (Ge), and 74 kcal mol^{-1} (Sn). Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17–19.

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unfavorable steric factor: the C–H and C–C bonds are much shorter than Si–H and Si–C bonds. The phenyl rings of Ph_3CH thus may interact repulsively with the PO_2H groups of the $P_2O_5H_2^{2-}$ ligands.

Interestingly, the reactivity of ${}^3Pt_2{}^*$ is comparable to that of ${}^3n\pi^*$ excited states of ketones possessing energies similar to ${}^3Pt_2{}^*$ ($E_T = 57.7$ kcal mol^{-1}).[8,11] For example, k_H for the reaction of the ${}^3n\pi^*$ state of benzophenone ($E_T = 69$ kcal mol^{-1})[32] with Bu_3SnH is 4.7×10^7 M^{-1} s^{-1}, whereas for biacetyl ($E_T = 55$ kcal mol^{-1})[32] the rate constant is 1.5×10^7 M^{-1} s^{-1}.[33] The radical-like behavior of the $d\sigma^*p\sigma$ triplet excited state of Pt_2 most likely is attributable to the unpaired electron in $d\sigma^*$, because this electron is strongly localized in the open axial coordination sites.[34] The role of the $d\sigma^*$ electron in the reactions of ${}^3Pt_2{}^*$ apparently is analogous to that of the singly occupied oxo-localized n electron in the ${}^3n\pi^*$ chemistry of organic carbonyl compounds.[32,33]

Experimental Section

Materials. $K_4[Pt_2(P_2O_5H_2)_4]\cdot 3H_2O$ was synthesized according to a standard procedure.[13] (Acetone was not used during the precipitation of the product, as it causes formation of a green impurity.) $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ was prepared from the potassium salt as described previously.[35] All hydrides were obtained from Aldrich except Ph_3GeH and Bu_3SnD (Strem). Fresh samples were used without further purification and were handled under nitrogen. Ph_3CH (Aldrich) was twice recrystallized from ethanol in the presence of charcoal. Tin hydrides were kept cold between experiments. Acetonitrile (Burdick & Jackson high purity solvent) and CD_3CN (Aldrich, Gold Label) were used as obtained; 2-methyltetrahydrofuran (Aldrich) was purified by the ketyl method, whereas propionitrile (Aldrich) was distilled from CaH_2.

Irradiations. Acetonitrile solutions containing $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ (typically $(1.5–2.0) \times 10^{-4}$ M) were degassed by freeze–pump–thawing. Stirred solutions were irradiated in a 10-mm cell, and the absorbance changes were measured in an attached 1-mm cell. A 1000-W Xe–Hg lamp was used as the irradiation source. Irradiations in the 370-nm region were performed by employing a combination of 0–52 cutoff and 7–39 band-pass Corning filters. (The transmittance profile of this filter combination is a nearly symmetrical band with a maximum at 370 nm and a 30-nm fwhm.) Oriel interference filters were used for monochromatic 436- and 313-nm irradiations. NMR samples were prepared by irradiation of the reactants in CD_3CN in 5-mm NMR tubes that were sealed under vacuum. A typical initial Pt_2 concentration for NMR measurements was in the range $(5–8) \times 10^{-3}$ M.

Instrumentation. Cary 17 and HP 8450A instruments were used to record the UV–vis absorption spectra. The emission spectra were obtained as described previously.[3] The excitation spectrum of $Pt_2(SnBu_3)_2$ was measured on a Perkin-Elmer MPF-66 spectrofluorimeter. Quenching experiments employed a Quanta Ray Nd-YAG (8-ns fwhm; 355-nm excitation) laser system.[36] NMR spectra were recorded on a Bruker WM 500-MHz instrument at the Southern California Regional NMR Facility. A Varian E-line Century Series X-band spectrometer was used for the EPR measurements. Dihydrogen was detected by a Du Pont 21 492B mass spectrometer. The gas phase above frozen (77 K) solutions was sampled.

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Spin Cluster Excitations in Ti^{2+}-Doped $MnCl_2$

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Single-crystal absorption spectra of Ti^{2+} as an impurity in $MnCl_2$ were recorded between 1.5 K and room temperature. A particular feature of these spectra is transitions to the low-energy ${}^1E_g$ level of Ti^{2+} in the near-infrared region that are spin-forbidden on the single center. These bands appear entirely as a result of magnetic exchange with the surrounding Mn^{2+} ions. A one-parameter model based on a $Ti^{2+}(Mn^{2+})_6$ spin cluster was used to characterize the spectra. An excellent agreement between theory and experiment was found with a value for the Ti^{2+}–Mn^{2+} exchange parameter of $J = -6.2$ cm^{-1}. The emission spectrum at 45 K was also found to agree with the predictions of the model. The lowest energy ground-state level is described by the function $|15\ 14\rangle$, where 15 is the total spin of Mn^{2+} ions and 14 is the overall spin of the cluster.

1. Introduction

This paper examines the effect of replacing an ion in a magnetic host lattice with another magnetic ion that has a different spin quantum number. The system is a Ti^{2+} impurity in $MnCl_2$. A theoretical treatment based on a $Ti^{2+}(Mn^{2+})_6$ spin cluster is used to provide a quantitative explanation for the anomalous intensities and band shapes of formally forbidden Ti^{2+} spin-flip transitions found in the lowest energy near-infrared spectral region.

Ti^{2+} is the only divalent first-row transition-metal ion which, in fairly strong ligand-field environments, has the pure triplet → singlet absorption transition as the lowest energy one. As a consequence, it is possible to observe sharp line emission from the ${}^1E_g$ excited state to the ${}^3T_{1g}$ ground state when Ti^{2+} is incorporated into $MgCl_2$, by exciting the higher energy spin-allowed bands and allowing the excitation to decay nonradiatively to the ${}^1E_g$ state.[1] However, the complementary absorption bands of this Ti^{2+} spin flip (i.e. ${}^3T_{1g} \rightarrow {}^1E_g$) have never been observed in the spectrum of Ti^{2+} in $MgCl_2$. Even at low temperatures and high concentrations of Ti^{2+},[2,3] these absorption bands have remained elusive, and it has to be concluded that the transition moments are too low to allow observation in absorption. This situation is dramatically reversed, however, when the absorption spectrum of Ti^{2+} in $MnCl_2$ is examined.[4] Here, the low-energy spin-flip transitions are observed as sharp lines with larger ϵ values than those of the

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