resulting exciplex does not have a charge distribution which would encourage α-proton transfer from the amine radical-cation center.[19]

Although these results dramatically illustrate the different acceptor orbital locations of n,π^* and π,π^* triplets, it is difficult to assess the individual k_{CT} values quantitatively. Since there apparently is a nearly 50:50 mixture of n,π^* and π,π^* triplets in **1-V**,[11] the actual rate constant for a π,π^* triplet is $\sim 1 \times 10^9$ s^{-1}. This value is comparable to that in δ-(dialkylamino)valerophenones,[9] an interesting and somewhat surprising fact. Although in both cases there are four connecting atoms between the nitrogen donor and the excited acceptor, the conformational preferences of the ester group[20] might have been expected to destabilize a cyclic conformation such as pictured in the scheme.

In summary, the specific probe afforded by intramolecular bifunctional photochemistry reveals that there is a vast difference between n,π^* and π,π^* triplets in the position at which donor orbitals can feel sufficient overlap for rapid electron-transfer interactions. More generally, these results strongly support the concept of HOMO and LUMO orbital overlap in electron-transfer reactions. We are currently studying internal quenching in other amino ketones to assess the generality of these conclusions.

Acknowledgment. This work was generously supported by NSF Grant CHE-79-10831.

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Photoinduced Elimination of H_2 from $[Pt_2H_3(dppm)_2]PF_6$ and $[Pt_2H_2Cl(dppm)_2]PF_6$[†]

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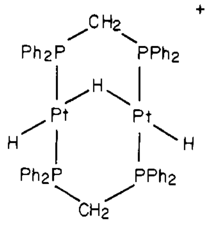
Photolysis of *monomeric* di- and polyhydride transition-metal complexes has generally been found to give elimination of H_2 as the dominant photoreaction.[1-3] The question arises as to whether or not H_2 elimination will occur from *di-and polynuclear* hydride complexes in which the hydride ligands are bound to different metals or bridge two or more metal centers. Such dinuclear elimination reactions could be important in solar energy conversion schemes using soluble complexes for producing H_2 from H_2O.[4-6] The few polynuclear hydridocarbonyl cluster complexes which have had their photochemistry examined do not show H_2 loss but instead either CO loss or metal–metal bond cleavage.[7-10] In search of such H_2 elimination reactions we have examined the dinuclear hydride complexes $[Pt_2H_3(dppm)_2]PF_6$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) and $[Pt_2H_2Cl(dppm)_2]PF_6$ (**2**), both of which have been well characterized by Brown, Puddephatt, and co-workers.[11-13] The studies reported herein show that both of these complexes readily lose H_2 upon photolysis and demonstrate the feasibility of such reaction from di- and polynuclear hydride complexes.[14]



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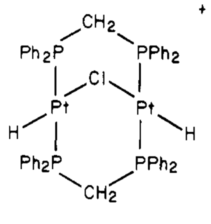

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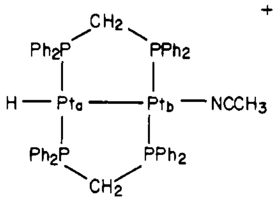
Degassed acetonitrile solutions of **1** show little or no decomposition upon prolonged heating at 80 °C, but photolysis ($\lambda \geq 300$ nm) of thoroughly degassed CH_3CN solutions of $[Pt_2H_3(dppm)_2]PF_6$ gives visible gas evolution and a rapid change from colorless to red. The UV-VIS spectral changes which occur are shown in Figure 1, and the maintenance of the isosbestic points at 337 and 372 nm indicates a clean conversion to products. The red color arises as a result of the weak visible absorption by the photoproduct (ϵ_{450} 130 M^{-1} cm^{-1}). One mole of H_2 per mole of complex irradiated is rapidly evolved ($\sim$30 min), although prolonged photolysis (>48 h) leads to secondary photochemical reactions and further slow evolution of H_2. A total of 1.42 mol of H_2 were evolved in one 66-h experiment. Concentration and cooling of CH_3CN solutions irradiated to the point of evolution of 1 mol of H_2 give a red solid which has been characterized as $[Pt_2H(CH_3CN)(dppm)_2]PF_6$.[15] The reaction shown in eq 1 is

$$[Pt_2H_3(dppm)_2]^+ + CH_3CN \xrightarrow{h\nu} H_2 + [Pt_2H(CH_3CN)(dppm)_2]^+ \quad (1)$$

thus indicated and spectroscopic data imply structure **3** for the photoproduct. The IR spectrum of **3** shows a ν_{Pt-H} vibration at



3

2033 cm^{-1}, indicative of a terminal rather than bridging hydride, and a weak ν_{CN} stretch at 2258 cm^{-1}. The hydride resonance in the ^1H NMR spectrum of **3** in CD_3CN solution appears at δ -8.9 as a pseudoquintet due to coupling to the four ^{31}P nuclei ($^2J_{P-H}$, $^3J_{P-H}$ = 9 Hz) with two sets of $^1/_4$ intensity satellites from coupling to the two inequivalent ^{195}Pt atoms ($^1J_{Pt_a-H}$ = 975 Hz; $^2J_{Pt_b-H}$ = 73 Hz). As Puddephatt has shown,[16-18] this satellite pattern is

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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(14) Photoinduced elimination of H_2 from *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma,\eta\text{-}C_5H_4)_2]$ and from $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ has also been implicated but few details were given. The mechanism suggested for the latter involved an intermediate with both hydrides on one metal as the light-absorbing species from which H_2 loss occurred (Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J., *J. Chem. Soc., Dalton Trans.* **1980**, 29).

(15) Anal. Calcd. for $C_{52}H_{48}F_6N_1P_5Pt_2$: C, 46.39; H, 3.57. Found: C, 46.01, H, 3.59 (Schwarzkopf Microanalytical Laboratory). IR (CH_3CN): ν_{Pt-H} = 2033 cm^{-1}; $\nu_{C\equiv N}$ (KBr) = 2258 cm^{-1}.

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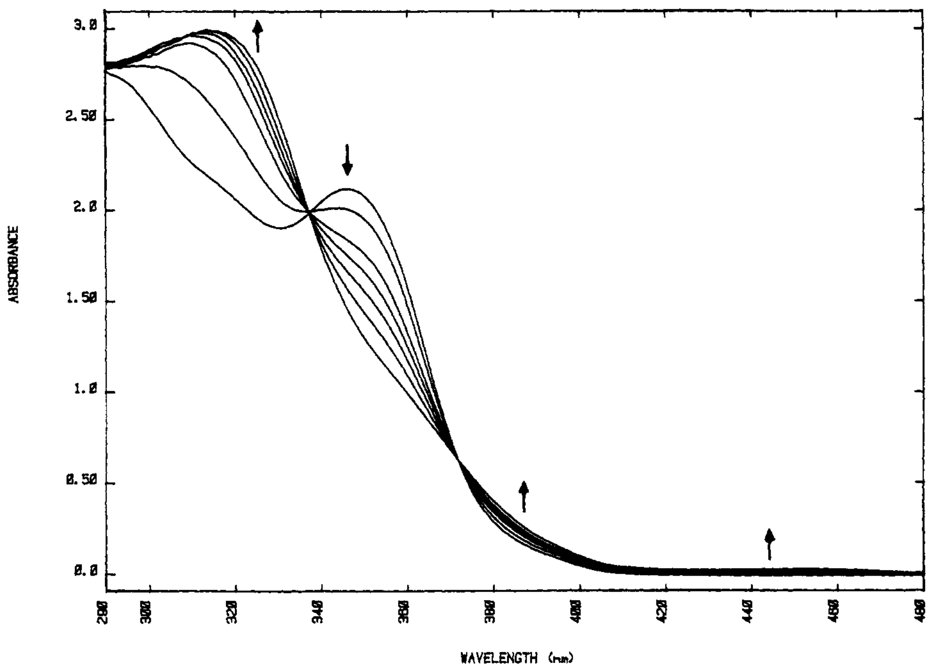


Figure 1. UV-visible spectral changes during 366-nm photolysis of a CH_3CN solution of $[Pt_2H_3(dppm)_2]PF_6$. The arrows indicate the direction of the spectral changes after beginning photolysis, and the spectra were successively recorded after 0, 0.5, 1, 1.5, 2, 3, and 5 min of total irradiation time.

characteristic of a terminal hydride, whereas a 1:8:18:8:1 quintet pattern is expected for a bridging hydride. This ^1H NMR resonance pattern is similar to that observed for $[Pt_2H(CO)(dppm)_2]PF_6$[17] and $[Pt_2H(dppm)_3]PF_6$[18] which have structures analogous to that proposed for **3**. The ^1H NMR spectrum of **3** also shows a singlet at δ 1.95 due to the methyl group of the CH_3CN ligand. The $[Pt_2H(CH_3CN)(dppm)_2]^+$ photoproduct reacts with CO and H_2, both at 25 °C and 1-atm pressure, to, respectively, yield $[Pt_2H(CO)(dppm)_2]^+$[17,19] and $[Pt_2H_3(dppm)_2]^+$, providing further support for the proposed structure and also suggesting a rich derivative chemistry for this complex.

Photolysis of **1** in THF and acetone solutions gives similar results although the photoproducts, which are presumably analogous to **3**, are not as completely characterized. The spectral properties of the red solid isolated from photolysis of THF solutions of **1** are consistent with the formulation $[Pt_2H(THF)(dppm)_2]PF_6$.[20] ^1H NMR monitoring of photolysis of **1** in CD_2Cl_2 solutions showed the formation of $[Pt_2HCl_2(dppm)_2]^+$ (δ -12 (m)[11]) and $[Pt_2H_2Cl(dppm)_2]^+$ (δ -17 (m)[11]) in an approximate 7:3 ratio.

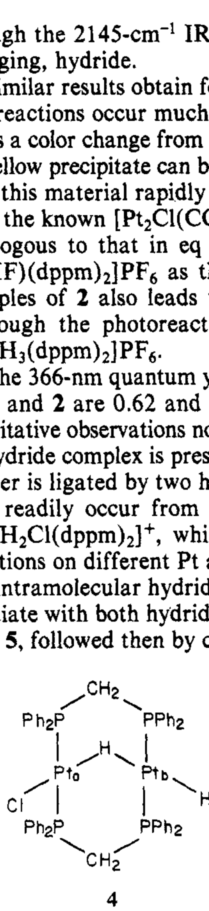
H_2 loss also occurs when **1** is irradiated in the solid state. White solid samples of **1** in vacuo or under N_2 rapidly turn red upon exposure to sunlight, fluorescent room light, or UV irradiation ($\lambda \geq 300$ nm). Mass spectral analysis of gases above irradiated solid samples showed the presence of H_2; quantitative measurements gave an average value of 0.90 mol of H_2 evolved per mole of complex irradiated. The red solid obtained from such solid-state photolysis shows a broad IR band at 2145 cm^{-1} (Nujol), indicative of a terminal hydride. Exposure of this material to CO rapidly gave the formation of $[Pt_2H(CO)(dppm)_2]PF_6$; reaction with H_2 slowly regenerated $[Pt_2H_3(dppm)_2]PF_6$. These various results indicate the solid-state reaction shown in eq 2. The exact nature

$$[Pt_2H_3(dppm)_2]PF_6 \xrightarrow[\text{solid state}]{h\nu} H_2 + [Pt_2H(dppm)_2]PF_6 \quad (2)$$

of the $[Pt_2H(dppm)_2]PF_6$ photoproduct is presently unclear although the 2145-cm^{-1} IR band implies a terminal, rather than bridging, hydride.

Similar results obtain for photolysis of solutions of **2** although the reactions occur much more slowly. Photolysis of **2** in THF gives a color change from colorless to yellow and evolution of H_2. A yellow precipitate can be isolated from the photolyzed solution, and this material rapidly reacts with CO in CH_2Cl_2 solution to give the known $[Pt_2Cl(CO)(dppm)_2]PF_6$ complex.[13] A reaction analogous to that in eq 1 is thus indicated but with $[Pt_2Cl(THF)(dppm)_2]PF_6$ as the photoproduct. Photolysis of solid samples of **2** also leads to H_2 evolution and an orange solid, although the photoreaction is not nearly as efficient as for $[Pt_2H_3(dppm)_2]PF_6$.

The 366-nm quantum yields of H_2 loss from CH_3CN solutions of **1** and **2** are 0.62 and 0.06, respectively, consistent with the qualitative observations noted above. Elimination of H_2 from the trihydride complex is presumably more efficient because each Pt center is ligated by two hydrides, and concerted H_2 elimination can readily occur from one metal. Elimination of H_2 from $[Pt_2H_2Cl(dppm)_2]^+$, which has the two hydrides in terminal positions on different Pt atoms in the ground state, could occur via intramolecular hydride migration to give an activated intermediate with both hydrides bound to the same Pt atom, such as **4** or **5**, followed then by concerted elimination of H_2. Alternatively, loss of H_2 from **2** could occur via an intermolecular pathway involving two molecules of **2**, although bimolecular reactions have not been observed for the various monomeric hydride complexes which undergo photoinduced loss of H_2,[1,2] or via coupling of the two hydrides across the two metal centers of **2**.



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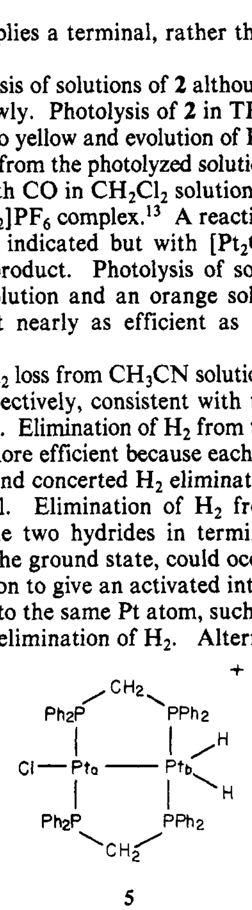

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This study has shown that H_2 elimination can be photoinduced from dinuclear complexes in which at least one of the hydrides is bound in a terminal fashion. It still remains to be determined whether H_2 elimination can occur from di- and polynuclear complexes when both hydrides occupy bridging positions or from

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[19] IR (Nujol): ν_{CO} = 2038 cm^{-1}, lit.[16] ν_{CO} = 2040 cm^{-1}.

[20] IR (Nujol): ν_{Pt-H} = 2092 cm^{-1}. ^1H NMR (acetone-d_6): δ -12.8 (m) with ^{195}Pt coupling (J_{Pt-H} = 1054 Hz; $^2J_{Pt-H}$ = 245 Hz).

dinuclear complexes where the hydrides are terminal but no reasonable mechanism exists for simultaneously placing both hydrides on the same metal. Our search for that and related photoactivity is continuing.

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A Novel Series of Macrocyclic Lactones

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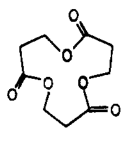
A variety of macrocyclic polyethers have been synthesized and shown to bind metal and ammonium ions efficiently[1,2] and to effect transport or catalytic modification.[3-14] Naturally occurring cyclic ionophores, on the other hand, contain not only ether groups but often amides and lactones arranged in a "head-to-tail" fashion around the ring.[15] Investigations on synthetic macrocyclic compounds with amide or lactone groups have largely been confined to cyclic peptides[16] or lactones with mirror plane symmetry,[17] whereas lactones with rotational symmetry have received only limited attention. The few examples reported in the literature include the penta- and hexalactones derived from glycolic acid[18] and the di-, tetra- and hexalactones synthesized from a bicyclic monomer.[19] We wish in this communication to describe a series of novel macrocyclic lactones with rotational symmetry axes derived from 3-hydroxypropionic acid. An efficient and convenient method for preparing them will also be described as will the X-ray structure of the lowest homolgue, the trilactone **2** with a cyclic backbone analogous to that of the natural iron carrier enterobactin.[20-22] The method of synthesis is based on the use of cyclic tin-oxygen compounds as templates[23] in order to catalyze the condensation of propiolactone to form macrocyclic products in up to 80% yields.



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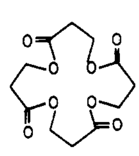

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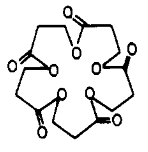

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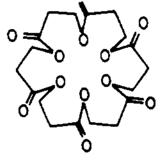

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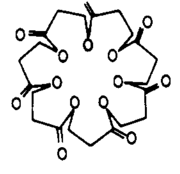

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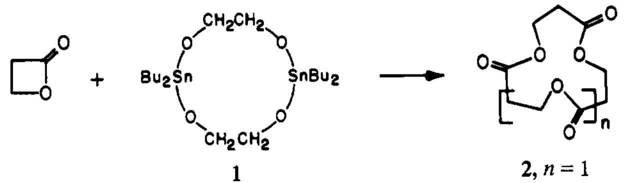
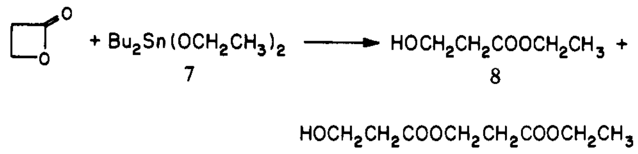


1

2, $n = 1$
3, $n = 2$
4, $n = 3$
5, $n = 4$
6, $n = 5$

Distannoxane **1** (24) (1.18 g, 2.0 mmol) and propiolactone (9.84 mL, 133 mmol) are heated in 800 mL of chloroform overnight. On concentrating the reaction mixture and chromatographing it on silica gel (elution with benzene-ethyl acetate), the following cyclic oligomers can be isolated as major products: 2.126 g (9.84 mmol, 22.2%) of the trimer **2**, 1.16 g (4.03 mmol, 12%) of the tetramer **3**, 1.067 g (3.04 mmol, 11.4%) of the pentamer **4**, 0.65 g (1.58 mmol, 6.7%) of the hexamer **5**, and 0.231 g (0.45 mmol, 2.4%) of the heptamer **6**, in addition to mixtures of the five macrocycles (2.5 g, 26%).[25]

The unique properties of a stannoxane as a template and the importance of its cyclic structure were demonstrated by experiments with linear stannoxanes. Refluxing propiolactone (0.54 mL, 8.6 mmol) with dibutyltin diethoxide (**7**) (1.4 g, 4.31 mmol) in 100 mL of chloroform did not yield any macrocyclic compounds but rather the hydroxy esters **8** and **9** (131 mg, 1.12 mmol, 12%; 91 mg, 0.313 mmol, 3.6%). However, on replacing the distannoxane **1** by the cyclic stannoxane 1,1-dibutyltin 4,4-dimethyl-1,2-dioxacyclohexane all macrocyclic oligomers are formed in



$+ Bu_2Sn(OCH_2CH_3)_2 \longrightarrow HOCH_2CH_2COOCH_2CH_3 +$

7 **8**

$HOCH_2CH_2COOCH_2CH_2COOCH_2CH_3$

9

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(25) The melting points of the macrocyclic polylactones are 56-58 °C for the trilactone **2**, 116-120 °C for the tetralactone **3**, 80-85 °C for the pentalactone **4**, 133-135 °C for the hexalactone **5**, and 84-86 °C for the heptalactone **6**. Their IR, NMR, and mass spectra and elemental analyses are consistent with the assigned structures; see supplemental material.

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