Table IV. Measured Infrared Frequencies (cm^{-1}) for Nitrogen Coordinated Nickel Methylene in Solid Argon and Solid Nitrogen[a]

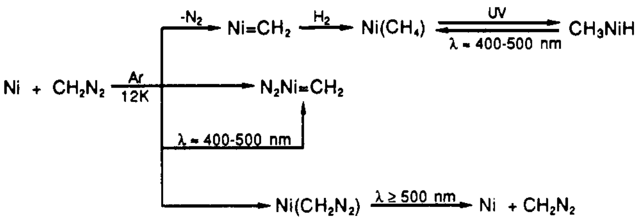
		frequency			
vibrn mode	x	$(N_2)_x$-$NiCH_2$	$(N_2)_x$-$Ni^{13}CH_2$	$(N_2)_x$-NiCHD	$(N_2)_x$-$NiCD_2$
CH_2 s-stretch	1	2907.2	2901.4		
	x	2889.1	2883.3		
		2890.8	2885.2		
CH_2 bend	1	1328.5	1319.7		
Ni=C stretch	1	688.9	671.5	677.0	633.0
	x	692.8			
CH_2 a-stretch	1	2960.2	2948.9	2932.7	
	x	2934.9	2927.2		
CH_2 rock	1	538.5	534.4		409.5
	x	528.6	523.0		
		525.5	519.7		
CH_2 wag	1	834.3	826.3	759.6	679.1
	x	860.1	850.7		
		862.0	852.6		
N≡N stretch	1	2180.1	2180.1	2180.1	2180.1

[a] $(N_2)NiCH_2$ was isolated in argon matrices. $(N_2)_xNiCH_2$ was isolated in nitrogen matrices.

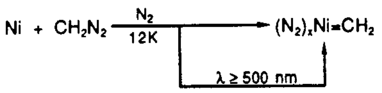
Prolonged photolysis with $\lambda \approx 400-500$ nm leads to reductive elimination (spectrum E), whereas ultraviolet photolysis regenerates CH_3NiH (spectrum F).

Discussion

These nickel atom/diazomethane reactions in argon matrices can be summarized as follows:

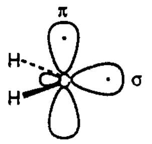


The reactions of Ni with CH_2N_2 in nitrogen matrices yields $(N_2)_xNi{=}CH_2$, $x \geq 1$, as the only product. The number of dinitrogen molecules adducted to the nickel cannot be determined because of the complex Ni/N_2 reactions.[13] A comparison of the Ni/CH_2N_2 reaction in argon and nitrogen matrices is presented in Figure 6.



The observed frequencies of $N_2Ni{=}CH_2$ and $(N_2)_xNi{=}CH_2$ are listed in Table IV.

The nature of the bonding in $Ni{=}CH_2$ is of interest. The rather high Ni–C stretching frequency would seem to indicate that the species can be represented in its ground state with significant double-bond character. As a basis for describing this bonding, the CH_2 ligand in its ground state ($^3B_1$) with a single electron in each of two nonbonding orbitals denoted as σ and π in **1** would bond to the Ni 4s orbital through the σ orbital, whereas the weak π interaction would result from overlap of the π lobe with nickel d orbitals. Theoretical calculations support this assumption.[12]



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Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation and the 3M Co. for support of this work.

Registry No. Ni, 7440-02-0; CH_2N_2, 334-88-3; $Ni{=}CH_2$, 60187-22-6; $N_2Ni{=}CH_2$, 129391-83-9; CH_3NiH, 86392-32-7; $Ni^{13}CH_2$, 129391-84-0; NiCHD, 129391-85-1; $NiCD_2$, 129391-86-2.

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Generation of Reactive Intermediates in the Photochemistry of Binuclear Trihydridodiplatinum Complexes

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The photochemistry of the complexes trans–trans monohydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) and trans–cis dihydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]$ (**2**) is reported. Photolysis of **1** and **2** using 334-nm light occurs with good quantum yields to give *trans*-$[PtH_2(PEt_3)_2]$ (**3a**) and *trans*-$[PtH(S)(PEt_3)_2]^+$ (**4**) (S = solvent, e.g. acetonitrile). Photoproducts **3a** and **4** are highly reactive and undergo a multiplicity of reactions depending upon experimental conditions. Evidence of H_2 elimination, photoinduced insertion of CO_2 into the Pt–H bond of **3a**, and abstraction of Cl from chlorocarbon solvents by **3a** and **4** is reported.

Introduction

The photoinduced elimination of H_2 from cis hydride ligands in transition-metal complexes has proven to be a very general photochemical reaction.[1] Photolysis of inorganic and organometallic complexes is a convenient method for generating coordinatively unsaturated compounds that undergo potentially important reactions such as activation of molecular H_2, CO_2 fixation, and saturated carbon–hydrogen bond cleavage.[2,3] This paper reports the photolysis of trans–trans monohydrido-bridged complex **1** and trans–cis dihydrido-bridged complex **2** and describes a useful route to highly reactive mononuclear platinum(II) intermediates.

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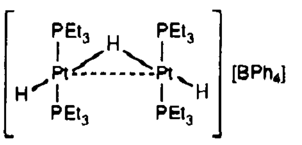
(1) Geoffroy, G. L. *Prog. Inorg. Chem.* **1980**, *27*, 123.
(2) Geoffroy, G. L.; Wrigton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.
(3) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

0020-1669/90/1329-4376$02.50/0



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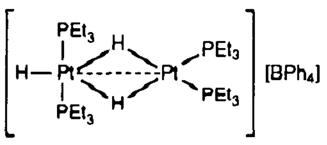

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Results

The binuclear trihydridodiplatinum complexes $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) and $[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]$ (**2**) are thermally stable and show no tendency to lose H_2. They are, however, photosensitive, and three distinct classes of photoreactions are observed depending on experimental conditions.

1. Photoreactions in Acetone. Irradiation (λ = 335 nm) of acetone solutions of trans–trans monohydrido-bridged complex **1** results in a gradual loss of its characteristic ^1H NMR resonances at −8.20 ppm (δ_{H_t}) and at −6.42 ppm (δ_{H_b}) and emergence of new peaks at −4.92 ppm (δ_{H_t}) and at −3.55 ppm (δ_{H_b}). These high-field shifts correspond to those of the trans–cis isomer of dihydrido-bridged complex **2**. ^1H NMR spectroscopic data for compounds relevant to this study are presented in Table I.

After 1 h of irradiation, a 1:1 molar ratio of complex **1** and complex **2** is observed.

The photolysis of trans–cis dihydrido-bridged complex **2**, under conditions identical with those used for complex **1**, causes a reduction in intensity of its ^1H NMR signals and growth of new peaks at −8.20 ppm (δ_{H_t}) and at −6.42 ppm (δ_{H_b}) due to the formation of trans–trans monohydrido-bridged isomer **1**. The intensity ratio of each set of ^1H NMR signals remains constant (1:1 molar ratio) upon steady-state irradiation for 1 h. The optical spectra of each of the binuclear compounds are characterized by two prominent bands (see Table II). The optical changes in the first stages of photoreaction of **1** or **2** show a gradual disappearance of the absorption at 339 nm due to the starting material with a concomitant presence of two isosbestic points at 282 and 378 nm. In the dark or upon steady-state irradiation for 1 h, the original absorption at 339 nm is reestablished, indicating the high reactivity of the primary photoproducts.

The ^1H NMR and electronic spectra, taken together, demonstrate that the overall photoprocess is an isomerization reaction (eqs 1 and 2). In order to identify possible reactive intermediates

$$\underset{\mathbf{1}}{[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]} \xrightleftharpoons[\Delta]{h\nu} \underset{\mathbf{2}}{[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]} \quad (1)$$

$$\underset{\mathbf{2}}{[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]} \xrightleftharpoons[\Delta]{h\nu} \underset{\mathbf{1}}{[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]} \quad (2)$$

in the photochemistry of complexes **1** and **2**, the early stages of the photoreactions were examined by FT-IR spectroscopy. The results are presented in Table III. Most notably, the FT-IR profile of the photoreactions indicated that ν_{Pt-H_t} (2140 cm^{-1}) and ν_{Pt-H_b} (1680 cm^{-1}) vibrations of **1** steadily decreased in intensity and new bands appeared at 1724 and 2218 cm^{-1}. The absorption at 1724 cm^{-1} is probably due to *trans*-$[PtH_2(PEt_3)_2]$ (**3a**), whereas the frequency at 2218 cm^{-1} is due to *trans*-$[PtH(S)(PEt_3)_2]^+$ (**4**). Thermal studies[8] as well as matrix isolation experiments have verified the above spectral assignments. Similarly, observation of the frequencies at 1724 and 2210 cm^{-1} from irradiation of **2** could be analogously ascribed to formation of complexes *trans*-$[PtH_2(PEt_3)_2]$ (**3a**) and *trans*-$[PtH(S)(PEt_3)_2]^+$ (**4**). The two new IR peaks decay at the same rate, by second-order kinetics, to re-form the peaks of binuclear isomers **1** and **2**. All of the evidence suggests that *trans*-$[PtH_2(PEt_3)_2]$ (**3a**) and *trans*-$[PtH(S)(PEt_3)_2][BPh_4]$ (**4a**) are the primary photoproducts.

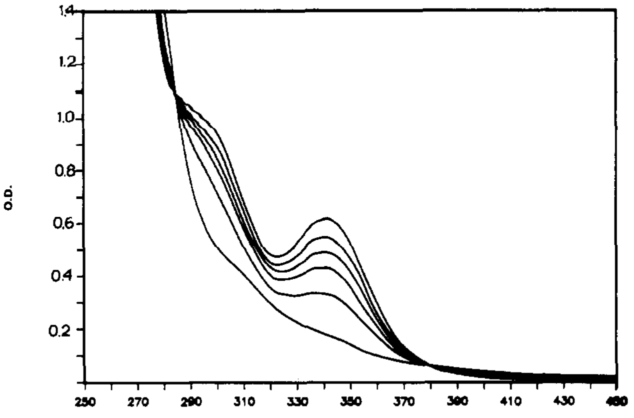

Figure 1. Electronic absorption spectral changes accompanying the photolysis (334 nm) of a 9×10^{-5} M solution of **1** in $CHCl_3$. Isosbestic points occur at 294 and 380 nm. Curves 0–5 correspond to 0, 1, 2, 4, 6, and 10 min of irradiation, respectively.

Additional evidence for the formation of **3a** and **4a** as initial photoproducts was obtained by addition of PEt_3 in the first stage of the photoreaction of **1** in acetone solution. The presence of PEt_3 led to the evolution of H_2 with formation of $[PtH(PEt_3)_3][BPh_4]$ (**5**), which precipitated, and of $[Pt(PEt_3)_3]$ (**6**) according to the stoichiometry shown in eqs 3 and 4. Moreover,

$$\underset{\mathbf{1}}{[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]} \xrightarrow{h\nu} \underset{\mathbf{3a}}{[PtH_2(PEt_3)_2]} + \underset{\mathbf{4a}}{[PtH(acetone)(PEt_3)_2][BPh_4]} \quad (3)$$

$$\mathbf{3a} + \mathbf{4a} \xrightarrow{2PEt_3} \underset{\mathbf{6}}{[Pt(PEt_3)_3]} + \underset{\mathbf{5}}{[PtH(PEt_3)_3][BPh_4]} + H_2 \quad (4)$$

analogous photochemical behavior of the dihydrido-bridged complex **2** occurred only when PEt_3 was present, i.e.

$$\underset{\mathbf{2}}{[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]} \xrightarrow{h\nu} \underset{\mathbf{3a}}{[PtH_2(PEt_3)_2]} + \underset{\mathbf{4a}}{[PtH(acetone)(PEt_3)_2][BPh_4]} \quad (5)$$

$$\mathbf{3a} + \mathbf{4a} \xrightarrow{2PEt_3} \underset{\mathbf{6}}{[Pt(PEt_3)_3]} + \underset{\mathbf{5}}{[PtH(PEt_3)_3][BPh_4]} + H_2 \quad (6)$$

The spectroscopic data for the products generated by the experiments outlined above are also included in Table III. Since these processes were specifically promoted by excitation of the hydrido binuclear complexes **1** and **2** we conclude that intermediates **3a** and **4a** react thermally with PEt_3 according to eqs 4 and 6, respectively.

At this juncture, it is important to emphasize that attempts to isolate intermediates **3a** and **4a** from the irradiated solution of **1** or **2** in acetone led to the formation of a mixture of isomers **1** and **2**.

2. Photoreactions in Acetonitrile. Acetonitrile solutions of trans–trans monohydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) or trans–cis dihydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]$ (**2**) under irradiation ($\lambda \geq$ 335 nm) irreversibly evolved 0.50 mol of H_2. This evolution was accompanied by decay of the hydride resonances of complex **1** or **2** and growth of only one new hydride resonance, at δ = −17.9 ppm, due to formation of the solvento complex *trans*-$[PtH(CH_3CN)(PEt_3)_2][BPh_4]$ (**4b**). The principal ^1H NMR data of the photoproducts, together with those of relevant compounds for comparison, are given in Table I.

When the photolysis of **1** in acetonitrile was repeated with FT-IR detection, both the depletion of the starting material (ν_{Pt-H_b} = 1710 cm^{-1}, ν_{Pt-H_t} = 2150 cm^{-1}) and formation of product bands at 2210 and 1720 cm^{-1} were observed. The IR band at 1720 cm^{-1},

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(4) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038.
(5) Chaloupka, S.; Venanzi, L. M. *Inorg. Synth.* **1990**, *27*, 30.
(6) Church, M. J.; Mays, M. J. *J. Chem. Soc. A* **1968**, 3074.
(7) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.
(8) Packet, D. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 5036.
(9) Laing, K. R.; Roper, U. R. *J. Chem. Soc. A* **1969**, 1889.

Table I. Hydride ^{1}H NMR Data for Relevant Compounds

compd	terminal hydride δ_{H_t}, ppm	bridging hydride δ_{H_b}, ppm	ref
$[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]^a$ (**1**)	-8.20 ($^1J_{Pt-H} = 1100$ Hz, $^2J_{PtH} = 122$ Hz, $^2J_{P_{cis}-H} = 12.2$ Hz)	-6.42 ($^1J_{Pt-H} = 5.30$ Hz, $^2J_{P_{cis}-H} = 8.55$ Hz)	4, 5
$[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]$ (**2**)	-4.92 ($^1J_{Pt-H} = 1316$ Hz, $^2J_{P-H} = 13.31$ Hz, $^2J_{Pt-H} = 192$ Hz)	-3.55 ($^1J_{Pt-H} = 361, 592$ Hz, $^2J_{P_{trans}-H} = 106$ Hz)	4, 5
$[PtH_2(PEt_3)_2]^a$ (**3a**)	-6.24 ($^1J_{Pt-H} = 790$ Hz, $^2J_{P_{trans}-H} = 157$ Hz)		6, this work
$[PtH(CH_3CN)(PEt_3)_2][BPh_4]^b$ (**4b**)	-17.9 ($^1J_{Pt-H} = 1290$ Hz, $^2J_{P_{cis}-H} = 14$ Hz)		this work
$[PtHCl(PEt_3)_2]^d$ (**7**)	-18.2 ($^1J_{Pt-H} = 1335$ Hz, $^2J_{P_{cis}-H} = 14.5$ Hz)		7, this work
$[PtH(HCO_2)(PEt_3)_2]^{a,c}$ (**8**)	-24.05 ($^1J_{Pt-H} = 1360$ Hz, $^2J_{P_{cis}-H} = 15.3$ Hz)		this work

[a] Acetone-d_6. [b] CD_3CN. [c] Signal of formato hydrogen at $\delta = 9.2$ ppm. [d] CD_2Cl_2.

Table II. Optical Absorption Data for Binuclear Trihydridodiplatinum Complexes in $CHCl_3$ at 20 °C

complex	λ_{max}, nm	ϵ, $M^{-1}\,cm^{-1}$
$[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**)	339	4010
	299 (sh)	6100
$[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]$ (**2**)	340	4310
	299 (sh)	6737

Table III. Spectroscopic FT-IR Data for Relevant Compounds

compd^a	ν_{Pt-H_t}, cm^{-1}	ν_{Pt-H_b}, cm^{-1}	ref
$[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**)	2140	1680–1710 (w, br)	5
$[(PEt_3)_3HPt(\mu\text{-}H)_2Pt(PEt_3)]_2[BPh_4]$ (**2**)	2150	1700 (m)	5
trans-$[PtH_2(PEt_3)_2]^b$ (**3a**)	1724		8, this work
cis-$[PtH_2(PEt_3)_2]$ (**3b**)	2090, 2060		8
trans-$[PtH(S)(PEt_3)_2][BPh_4]$ (**4a,b**)	2218,^{d} 2210^e		this work
$[PtH(PEt_3)_3][BPh_4]$ (**5**)	2090		6, this work
trans-$[PtHCl(PEt_3)_2]^c$ (**7**)	2210		6
trans-$[PtH(HCO_2)(PEt_3)_2]$ (**8**)	1600–1650 (w, br)		9, this work

[a] All data were recorded in acetonitrile solution at 295 K. [b] Packet and Trogler[8] give a value of ν_{Pt-H} of 1720 cm^{-1} for *n*-hexane on toluene solutions. [c] $\nu_{Pt-Cl} = 280$ cm^{-1}. Solvent: acetonitrile. [d] **4a**; S = acetone. [e] **4b**; S = acetonitrile.

Table IV. Quantum Yields for the Disappearance of Complexes **1** and **2**^{a}

complex	irrn λ, nm	$\Phi \pm 0.01$	complex	irrn λ, nm	$\Phi \pm 0.01$
1	334	0.48	**2**	334	0.45
1	299	0.24	**2**	299	0.26

[a] Degassed $CHCl_3$ or CH_2Cl_2 solutions irradiated at 20 °C.

assigned to ν_{Pt-H} of *trans*-$[PtH_2(PEt_3)_2]$ (**3a**) (Table III), on continuous photolysis or on standing, decayed, and higher frequency bands (2090 and 2060 cm^{-1}) gradually appeared. These are tentatively assigned to the ν_{Pt-H} of *cis*-$[PtH_2(PEt_3)_2]$ (**3b**).[8] Thus the IR data show that complex **3a** exists as an equilibrium mixture of cis and trans isomers in a ratio that is strongly affected by the irradiation time. The failure to observe **3a** and **3b** in the NMR experiment mentioned above is consistent with the observation by Packet and Trogler[8] that these two complexes are in equilibrium, and their observation is possible only at low temperatures. The entire photolysis sequence is reported in Scheme I.

Scheme I

$$\underset{\mathbf{1}}{[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]} \xrightarrow[\text{MeCN}]{h\nu} \underset{\mathbf{3a}}{\textit{trans}\text{-}[PtH_2(PEt_3)_2]} + \underset{\mathbf{4b}}{\textit{trans}\text{-}[PtH(MeCN)(PEt_3)_2][BPh_4]} \quad (7)$$

$$\underset{\mathbf{3a}}{\textit{trans}\text{-}[PtH_2(PEt_3)_2]} \xrightarrow{h\nu} \underset{\mathbf{3b}}{\textit{cis}\text{-}[PtH_2(PEt_3)_2]} \quad (8)$$

$$\underset{\mathbf{3b}}{\textit{cis}\text{-}[PtH_2(PEt_3)_2]} + \underset{\mathbf{4b}}{\textit{trans}\text{-}[PtH(MeCN)(PEt_3)_2][BPh_4]} \xrightarrow{h\nu} \underset{\mathbf{5}}{\textit{trans}\text{-}[PtH(PEt_3)_3][BPh_4]} + \underset{\mathbf{6}}{[Pt(PEt_3)_3]} + H_2 + \text{“Pt”} + \text{MeCN} \quad (9)$$

Formation of $[Pt(PEt_3)_3]$ and the evolution of H_2 (Experimental Section) indicated that a sequential photoinduced reductive elimination/thermal rearrangement occurs upon continuous photolysis according to Scheme I. Clearly, the stoichiometry of eq 9 requires some comment. The formation of **5** and **6**, both containing three PEt_3 molecules per platinum atom, starting from **3b**, which contains only two such ligands, implies the occurrence of a disproportionation reaction. The nature of the possible product, denoted as "Pt" in Scheme I, will be discussed later.

3. Photoreactions in Chlorocarbon Solvents. Photolysis ($\lambda \geq 334$ nm) of thoroughly degassed $CHCl_3$ (or CH_2Cl_2) solutions of trans–cis dihydrido-bridged complex **2** gave the UV–visible spectral changes shown in Figure 1. The extent of the reaction was determined by monitoring the decrease in optical density at 340 nm, and when correction was made for the inner-filter effects, a plot of the degree of conversion against the irradiation time proves to be linear. The results of quantum yield measurements are reported in Table IV. The photochemistry of monohydrido-bridged complex **1** in $CHCl_3$ gave UV–vis and IR spectral changes like those described for dihydrido-bridged complex **2** under the same conditions. Prolonged photolysis of **2** in $CHCl_3$ solution led to further changes in the absorption spectrum, indicating that the primary photoproducts *trans*-$[PtH_2(PEt_3)_2]$ (**3a**) and *trans*-$[PtH(S)(PEt_3)_2]^+$ (**4**) reacted with $CHCl_3$. The FT-IR spectral changes accompanying the photolysis of **2** showed the decline of the bands of photoproducts **3a** and **4**, and the growth of a band at 2210 cm^{-1} assigned to ν_{Pt-H} of *trans*-$[PtHCl(PEt_3)_2]$ (**7**) (Table III). Incidentally, $CHCl_3$ solutions of complex **2** did not evolve H_2 photochemically, even under an argon purge. However, the photolysis was accompanied by decay of the hydrido resonance due to **2** and growth of a new hydride resonance at $\delta = -18.2$ ppm due to *trans*-$[PtHCl(PEt_3)_2]$ (**7**) (Table I).

In order to obtain more information about the reaction mechanism and to assess the role of chlorocarbon solvents in this photoreaction, a careful ESR spin-trapping study was carried out.

Thus photolysis of **1** and **2** in $CHCl_3$ containing the radical scavenger $PhCH(NO)CMe_3$ (PBN) yielded ESR signals consisting of a triplet of doublets (Figure 2). The hyperfine splittings $a_N = 15.2$ G and $a_H = 2.12$ G are consistent with the data previously reported[10] for the spin adduct $PhCH(CHCl_2)N(\dot{O})CMe_3$. This points to the formation of $^{\bullet}CHCl_2$ radicals, presumably generated by abstraction of chlorine from $CHCl_3$ by the reactive intermediates produced in the overall photolysis. The feasibility of such a process is substantiated by a report concerning the Cl atom abstraction from $CHCl_3$ by the reactive $[Pt(PPh_3)_2]$ intermediate in the photolysis of $[(PPh_3)_2Pt{\cdot}C_2H_4]$ in $CHCl_3$.[11]

A possible reaction of the intermediates produced in $CHCl_3$ with respect to the platinum products is given in eq 10.

The acid $HBPh_4$ could not be detected directly, presumably because it is very unstable and rapidly decomposes into benzene (Experimental Section) and BPh_3.[12]

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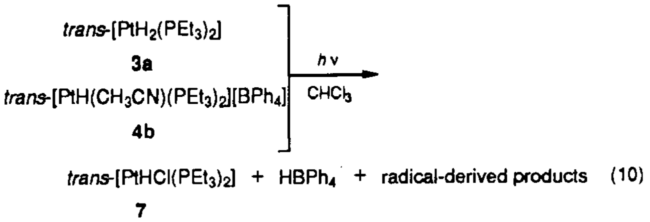
(10) Rehorek, D. *Z. Chem.* **1980**, *20*, 325.

(11) Bartocci, C.; Maldotti, A.; Sostero, S.; Traverso, O. *J. Organomet. Chem.* **1983**, *253*, 253.



$$\left.\begin{array}{c} trans\text{-}[PtH_2(PEt_3)_2] \\ \mathbf{3a} \\ trans\text{-}[PtH(CH_3CN)(PEt_3)_2][BPh_4] \\ \mathbf{4b} \end{array}\right] \xrightarrow[CHCl_3]{h\nu}$$

$$\underset{\mathbf{7}}{trans\text{-}[PtHCl(PEt_3)_2]} + HBPh_4 + \text{radical-derived products} \quad (10)$$

4. Photoinduced Insertion Reactions of CO_2 into the Pt–H Bond. Having demonstrated that the primary photoproducts **3a,b** and **4a,b** are highly reactive intermediates, we next investigated the effect of light for the insertion of CO_2 into metal–hydrogen bonds to produce metal–formato complexes. Examination of the ^1H NMR spectrum of the acetone solution of **1** photolyzed in the presence of CO_2 revealed a signal characteristic for formato-hydrogen ($\delta = 9.2$) and a signal typical for a hydride ligand $\delta = -24.05$ ppm ($^1J_{Pt-H} = 1360$ Hz, $^2J_{P-H} = 15.2$ Hz) (Table I). A broad infrared absorption at 1600–1650 cm^{-1} (Table III) observed during the photoreaction is consistent with a monodentate formato species $[PtH(HCO_2)(PEt_3)_2]$ (**8**). Product **8** is likely to be formed from the reaction of CO_2 with *trans*-$[PtH_2(PEt_3)_2]$ (**3a**), as indicated by the simultaneous presence of the cation of solvento complex **4a** in a 1:1 ratio. The insertion reaction of CO_2 into the Pt–H bond does not occur thermally, and **8** must be formed by the scavenging of **3a** with CO_2 according to the reactions reported in Scheme II.

Scheme II

$$\underset{\mathbf{1}}{[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]} \xrightarrow{h\nu}$$

$$\underset{\mathbf{3a}}{trans\text{-}[PtH_2(PEt_3)_2]} + \underset{\mathbf{4a}}{trans\text{-}[PtH(acetone)(PEt_3)_2][BPh_4]}$$

$$\mathbf{3a} \xrightarrow[CO_2]{h\nu} \underset{\mathbf{8}}{trans\text{-}[PtH(HCO_2)(PEt_3)_2]}$$

Discussion

This study illustrates how photolysis with UV–vis and FT-IR detection, in combination with NMR and ESR methods, can be used to provide detailed mechanistic information about the photochemistry of the binuclear trihydridodiplatinum complexes **1** and **2**. Photolysis of **1** and **2** yields the primary photoproducts *trans*-$[PtH_2(PEt_3)_2]$ (**3a**) and *trans*-$[PtH(S)(PEt_3)_2][BPh_4]$ (**4a,b**). Compounds **3a** and **4a,b** are very unstable intermediates and afford a rich chemistry depending on experimental conditions (irradiation time, solvent, and purge rate with argon or CO_2). Thus the only reaction observed in acetone is the photoisomerization process described in eqs 1 and 2. These photoreactions are effectively reversible, since, under the present experimental conditions, the photogenerated intermediates **3a** and **4** recombine according to the donor–acceptor formalism[13] illustrated in Scheme III.

Attempts to isolate intermediates **3a** and **4** from the irradiated acetone solutions gave a mixture of the isomers **1** and **2**.

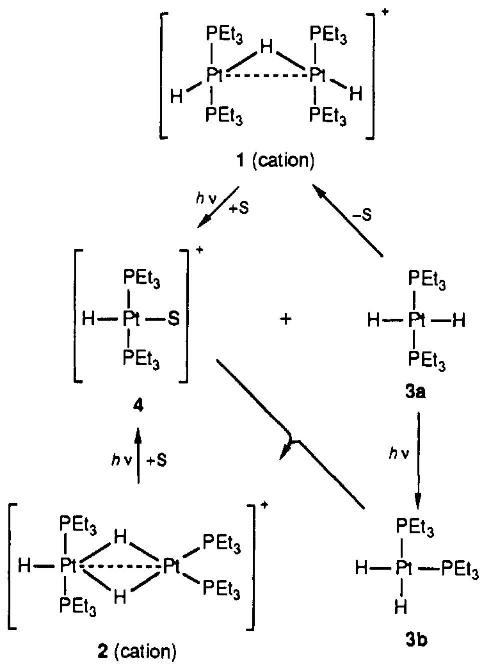
Significantly, by use of acetonitrile or chlorocarbon solvents, different reactions are observed (Schemes I and II), demonstrating the key role the solvent plays in the photoisomerization process.

In acetonitrile the photogenerated intermediate **3a** undergoes a secondary photochemical reaction forming the isomer *cis*-$[PtH_2(PEt_3)_2]$ (**3b**). Sequential photoinduced reductive elimination/thermal rearrangement steps evolve H_2 to ultimately yield $[Pt(PEt_3)_3]$ and *trans*-$[PtH(PEt_3)_3][BPh_4]$ (eq 9). On the basis of these results it is concluded that the cis isomer **3b** represents a significant component of the mixture, which shows photosensitivity with respect to H_2 loss.

In chlorocarbon solvents the primary photoproducts, **3a** and **4**, react with the solvent to give *trans*-$[PtHCl(PEt_3)_2]$. The abstraction of Cl from $CHCl_3$ by intermediates **3a** and **4** has been verified by the observation of the adduct $PhCH(CHCl_2)N(\dot{O})CMe_3$ in the spin-trapping experiments.

Figure 2. ESR spectrum of spin adduct $PhCH(CHCl_2)N(\dot{O})CMe_3$ formed during irradiation of a chloroform solution of the trans–trans monohydrido-bridged complex $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) in the presence of PBN.

Scheme III



As mentioned earlier, the Pt:P ratio in the starting materials and detectable products in eq 9 requires that some new platinum species be formed in which the Pt:P ratio is lower than 2. Experimentally it is found that, in general, no precipitation of metallic platinum occurs but that red-brown solutions are formed. These colors are generally indicative of the formation of Pt cluster compounds. One such cluster $[Pt_4H_7(PBu^t_3)_4][BPh_4]$ (A), with a Pt:P ratio of 1:1, was described by Spencer et al.[14] Furthermore, always using bulky phosphines, Goel and Goel[15] described the formation of $[(P\text{-}C)Pt(H)_2Pt(P\text{-}C)]$ (B) $[(P\text{-}C) = Bu^t_2PCMe_2CH_2]$, where the Pt:P ratio is 1:1. Thus, the "third phosphine" added to **4b** to give **5** and to **3b** to give **6** after loss of H_2 could become available through formation of compounds of either type A or type B. If these were to be fluxional at room temperature on the NMR time scale, they would go undetected

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(12) Steinberg, H.; Brotherton, R. J. *Organoboron Chemistry*; Interscience-Wiley: New York, 1967; Vols. 1, 2.

(13) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

(14) Goodfellow, R. J.; Hamon, E. M.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1604.

(15) Goel, A. B.; Goel, S. *Inorg. Chim. Acta* **1983**, *69*, 233.

in the experiments described above.

The ability to photogenerate the reactive intermediate *trans*-[$PtH_2(PEt_3)_2$] from the binuclear complexes **1** and **2** has prompted us to investigate the photoinduced insertion of CO_2 into the metal-hydrogen bond of **3a**. Photolysis of **1** and **2** under CO_2 in acetone or acetonitrile gave equimolar amounts of the formato complex *trans*-[$PtH(HCO_2)(PEt_3)_2$] (**8**) and the solvento complex **4**, *trans*-[$PtH(S)(PEt_3)_2$]$^+$, with no evolution of H_2. The insertion reaction of CO_2 into the Pt-H bond does not occur thermally, and the monodentate formato complex **8** must be formed by the scavenging of the intermediate **3a** and by CO_2.

The results presented demonstrate that the solvent or purge with CO_2 exerts great control over the binuclear-forming reactions illustrated in Scheme III. Irradiation in acetonitrile or in chlorocarbon solvents as well as under CO_2 thus supresses the recombination between [$PtH_2(PEt_3)_2$] and *trans*-[$PtH(S)(PEt_3)_2$]$^+$ and allows the reactions presented in sections 2-4 to be observed.

The electronic spectra of the trihydrido binuclear complexes **1** and **2** are listed in Table II. Calculations by Dedieu et al.[16] indicate that the LUMO energy level in complexes of this type has a metal-metal character, while the HOMO has antibonding metal d-orbital character. The irradiation using 335-nm light is expected to lead to the HOMO-LUMO transition (λ_{max} = 340 nm). Thus the primary excitation of **1** and **2** leads not only to a significant weakening of the Pt-Pt interaction but also to a cleavage of the $Pt_2(\mu\text{-}H)$ and $Pt_2(\mu\text{-}H)_2$ bridges. The wavelength dependence of the quantum yields (Table IV) substantiates the conclusion that HOMO-LUMO excitation is responsible for the photochemistry.

Experimental Section

FT-IR spectra were recorded with a Bruker IFS 88 spectrophotometer, UV-visible spectra with a Jasco-Uvidec 650 spectrophotometer, and NMR spectra with a Bruker 300 spectrometer. Chemical shifts are quoted with respect to Me_4Si. Analysis for H_2 by gas chromatography was carried out by using a Perkin-Elmer F17 gas chromatograph with a 5 Å molecular sieve column.

Both [$(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2$][$BPh_4$] and [$(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2$][$BPh_4$] were prepared and purified in accordance with the literature procedures.[5] All solvents used were purified and degassed. All described chemical manipulations were carried out under an inert atmosphere of argon.

Irradiation. Irradiations were carried out with an Applied Photophysics xenon lamp equipped with an *f*/3.4 monochromator. Light flux was measured by ferrioxalate actinometry.[14] The progress of the photoreactions was monitored by UV-visible spectral measurements. For the quantum yield determinations, the conversions to products were kept below 10%, and over this period, plots of conversion vs time were linear.

Photolysis of 1 or 2 in the Presence of PEt_3. A solution of complex **1** or **2** (0.15 mm) and PEt_3 (0.30 mm) in acetone was irradiated for 4 h at λ ≥ 335 nm. During the irradiation a yellow precipitate formed. The precipitate was collected and identified by its ^1H NMR and IR spectra (Table I and III) as *trans*-[$PtH(PEt_3)_3$][BPh_4].

Photolysis of Complexes 1 or 2 in Acetonitrile. Complex **1** or **2** (0.1 M) in acetonitrile was irradiated for 4 h. Analysis of the gases above the irradiated solutions showed the presence of H_2 (see GC Measurements). The solvent was removed in vacuo and the brown residue identified as a mixture of [$Pt(PEt_3)_3$] and [$PtH(PEt_3)_3$][BPh_4].

GC Measurements. A 10^{-3} M solution of **1** or **2** in CH_3CN was deoxygenated by bubbling with argon for 30 min. Photolyses of these solutions were carried out to completion (~4 h) by using 334-nm light. A sample of the gas phase above the irradiated solutions was extracted with a gas syringe and analyzed by GC (after a preliminary calibration had been made). The total H_2 evolved was $(0.5 \pm 0.1) \times 10^{-3}$ mol. GC analysis of the gases above a solution of 10^{-3} M **1** in $CHCl_3$ irradiated with ≥335-nm light for 4 h showed only C_6H_6; no H_2 was detected.

Radical-Trapping Experiments. Solutions of **1** or **2** (10^{-3} M) in carefully purified $CHCl_3$ were introduced into a 4-mm cylindrical ESR tube in the dark and degassed by bubbling with a slow stream of argon for 20 min. They were then introduced into the cavity of a Bruker ER 200 spectrometer. Irradiation was carried out with a Bruker lamp. The light (λ > 330 nm) was focused directly into the ESR cavity. The spin trap used was phenyl-*tert*-butylnitrone (PBN) in a 2×10^{-3} M concentration. The degassed solutions prepared in the dark did not show any signals. Upon irradiation (1 h) a signal consisting of a triplet of doublets is observed, which can be assigned to the $PhCH(CHCl_2)N(\dot{O})CMe_3$ adduct,[9] implying the formation of the radical $^{\bullet}CHCl_2$.

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Registry No. **1**, 84624-72-6; **2**, 81800-05-7; **3a**, 62945-61-3; **3b**, 80581-70-0; **4a**, 129364-91-6; **4b**, 129364-90-5; **5**, 22276-37-5; **6**, 39045-37-9; **7**, 16842-17-4; **8**, 81768-78-7; $CHCl_3$, 67-66-3; MeCN, 75-05-8; H_2, 1333-74-0; CO_2, 124-38-9.

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(16) Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

(17) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

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Thiophenophane-Metal Complexes. 4. Structural and NMR Study of a 1,4-Fluxional Pivot about a Pd-S(thiophene) Bond

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The preparation and X-ray structure of [$Pd(\eta^3\text{-allyl})(L)$][$CF_3SO_3$] (L = $C_{10}H_{14}S_4$, 2,5,8-trithia[9](2,5)thiophenophane) are described. Crystal data for the complex: orthorhombic, space group $P2_12_12_1$; a = 8.7067 (4), b = 9.1259 (3), c = 22.540 (10) Å; Z = 4; R_F = 0.048, R_w = 0.050. The cation is pseudo-square-pyramidal with an exceptionally short apical Pd(II)-S(thiophene) bond length of 2.786 (4) Å. Effects of temperature and solvent on the NMR spectra of the complex are discussed. Observed spectral characteristics are explained by assuming the operation in solution of two processes. One is a 1,4-fluxional shift of [Pd(allyl)]$^+$ proceeding by a pivot about the Pd-S(thiophene) bond, while the other is a solvent-assisted dissociative inversion of thioether sulfur.

Introduction

We have been interested in the influence of structural constraints in macrocyclic thioether ligands upon the properties of their metal complexes and have reported recently several consequences of ligand rigidity.[1-3] In particular, we have described several Pd(II) and Pt(II) complexes of 2,5,8-trithia[9](2,5)thiophenophane, L, the solution NMR spectra of which are invariant with temperature and reflect clearly the highly rigid nature of

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(1) Lucas, C. R.; Liu, S.; Thompson, L. K. *Inorg. Chem.* **1990**, *29*, 85.

(2) Lucas, C. R.; Liu, S.; Newlands, M. J.; Charland, J. P.; Gabe, E. J. *Can. J. Chem.* **1990**, *68*, 644.

(3) Lucas, C. R.; Liu, S.; Newlands, M. J.; Gabe, E. J. *Can. J. Chem.* **1990**, *68*, 1357.