Inorg. Chem. **1995,** *34,* 3173−3181

Spectroscopy and Photochemistry of Nickel(II), Palladium(II), and Platinum(II) *β*-Diketonates

Frederick D. Lewis,* Alan M. Miller, and Gwen D. Salvi

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received September 8, 1994[⊗]

The spectroscopy and photochemistry of several group 10(II) *β*-diketonates have been investigated. The spectral shifts observed upon replacing the methyl groups of the acetylacetonate ligand with phenyl groups have been correlated with the changes in frontier orbital energies and the allowed electronic transitions calculated using the semiempirical INDO/S−SCF−CI (ZINDO) algorithm. All of the group 10(II) *β*-diketonates undergo inefficient decomposition upon 254 nm irradiation in ethanol or dichloromethane solution to produce free metal and *β*-diketone. Photoisomerization of *cis*- and *trans*-platinum(II) benzoylacetonate is more efficient than photodecomposition. Irradiation of the platinum *β*-diketonates in the presence of hydrosilanes or olefins results in the formation of primary products which revert to starting material in the dark and can be converted to free metal and *β*-diketone by continued irradiation or heating. Reaction with added hydrosilane effectively inhibits photoisomerization. Both the efficiency of intermediate formation and its dark stability are dependent upon the structure of the hydrosilane or olefin and the *β*-diketonate ligand. A mechanism is proposed in which one-bond cleavage results in the formation of a short-lived three-coordinate intermediate which can recombine with retention or inversion of configuration, react with solvent to form unstable intermediates, or react with added hydrosilanes or olefins to form primary photoproducts of variable stability. Possible structures for the primary photoproducts are discussed.

Introduction

The photochemical decomposition of transition metal bis(*β*-diketonates) to yield the reduced metal and the *β*-diketones was initially reported by Gafney and Lintvedt[1] over two decades ago. A revival in interest in the thermal and photochemical decomposition of metal *β*-diketonates has been sparked by observations that these processes can be employed in the production of homogeneous and heterogeneous catalysts[2] and for thin-film metal−organic chemical vapor phase deposition.[3] Our interest in the photochemistry of the group 10(II) *β*-diketonates was stimulated by a report that irradiation of Pt(II) *β*-diketonates in the presence of hydrosilanes and olefins results in efficient hydrosilation.[2d] Investigation of the mechanism of hydrosilation suggested that a highly reactive homogeneous hydrosilation catalyst could be formed upon irradiation of Pt(II) *β*-diketonates in the presence of either hydrosilanes or olefins.[4] This homogeneous catalyst can be converted either thermally or photochemically to a less active colloidal platinum catalyst. In order to obtain an understanding of the mechanism of this hydrosilation process, we have undertaken an investigation of the electronic structure, spectroscopy, and primary photochemistry of platinum acetylacetonate (acac), hexafluoroacetylacetonate (hfac), benzoylacetonate (ba), and dibenzoylmethanate (dbm). For purposes of comparison, the properties of some Ni(II) and Pd(II) *β*-diketonates have also been investigated. The efficiency of photodecomposition is found to be dependent upon the excitation wavelength, the choice of metal, ligand, solvent, and the presence of oxygen. Irradiation of Pt(II) *β*-diketonates in the presence of hydrosilanes or olefins results in the formation of primary photoproducts which can be detected spectroscopically but have not been isolated. The efficiency of primary photoproduct formation and its stability in the absence of continued irradiation are dependent upon the choice of *β*-diketonate ligand and hydrosilane or olefin.

Results

Absorption Spectra and Electronic Structure. The *β*-diketones acetylacetone (Hacac), hexafluoroacetylacetone (Hhfac), benzoylacetone (Hba), and dibenzoylmethane (Hdbm) are known to exist predominantly in the intramolecularly hydrogen-bonded cis enol form in nonpolar solvents. Their electronic absorption spectra in dichloromethane solution consist of a single allowed band which shifts to longer wavelength with extended conjugation in the order Hacac (274 nm) = Hhfac (274 nm) < Hba (310 nm) < Hdbm (340 nm). This band is assigned to an essentially pure $\pi \rightarrow \pi^*$ (HOMO → LUMO) transition.[5] Deprotonation of the *β*-diketones results in red-shifted absorption spectra for the sodium *β*-diketonates of acac (294 nm) < hfac (302 nm) < ba (324 nm) < dbm (350 nm) in ethanol solution.[5d]

The electronic absorption spectra of Pt(acac)$_2$, Pt(ba)$_2$ (mixture of trans and cis isomers), and Pt(dbm)$_2$ in dichloromethane solution are shown in Figure 1. The longest wavelength band and higher energy bands appear to shift to longer wavelength and increase in intensity with extended conjugation in the ligand. Similar band shifts are observed for the Pd *β*-diketonates (Table

---

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

(1) (a) Gafney, H. D.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1970**, *92*, 6996−6997. (b) Gafney, H. D.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 1623−1628.

(2) (a) Cullen, W. R.; Wickenheiser, E. B. *J. Organomet. Chem.* **1989**, *370*, 141−154. (b) Belyakova, Z. V.; Knyazeva, L. K.; Chernyshev, E. A. *Zh. Obshch. Khim.* **1983**, 53, 1591−1596. (c) Rao, C. D.; Rase, H. F. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 95−101. (d) Oxman, J. D.; Boardman, L. D. Eur. Pat. Appl. EP 398,701, 1990.

(3) (a) Kodas, T. T.; Comita, P. B. *Acc. Chem. Res.* **1990**, *23*, 188−194. (b) Mikami, N.; Ohki, R.; Kido, H. *Chem. Phys.* **1990**, *141*, 431−440. (c) Willwohl, H.; Wolfrum, J.; Zumbach, V.; Albers, P.; Seibold, K. *J. Phys. Chem.* **1994**, *370*, 2242−2247.

(4) Lewis, F. D.; Salvi, G. D. *Inorg. Chem.* **1995**, *34*, 3182−3189.

(5) (a) Veierov, D.; Bercovici, T.; Fischer, E.; Mazur, Y.; Yogev, A. *J. Am. Chem. Soc.* **1977**, *99*, 2723−2729. (b) Nakanishi, H.; Morita, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2255−2261. (c) Nakanishi, H.; Morita, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1723−1729. (d) Morita, H.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 378−386.

0020-1669/95/1334-3173$09.00/0

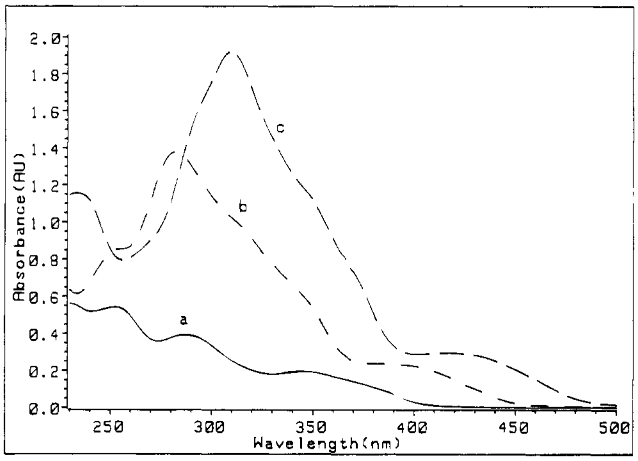


Figure 1. Electronic absorption spectra of 5 × 10^{-5} M CH_2Cl_2 solutions of (a) $Pt(acac)_2$, (b) $Pt(ba)_2$, and (c) $Pt(dbm)_2$.

Table 1. Observed and Calculated Electronic Transitions for the Pd(II) β-Diketonates

ligand	λ_{obsd}, nm	λ_{calcd}, nm	f	description
acac	326	309	0.445	74% $\pi_2 \rightarrow \pi_3^*$ 21% $\pi_1 \rightarrow \pi_4^*$
	250	222	0.178	20% $\pi_2 \rightarrow \pi_3^*$ 66% $\pi_1 \rightarrow \pi_4^*$
	228	210	0.673	94% d $\rightarrow \pi_3^*$
ba	352	313	1.05	72% $\pi_2 \rightarrow \pi_3^*$ 21% $\pi_1 \rightarrow \pi_4^*$
	280	255	0.797	*a*
	258	228	0.130	$\pi \rightarrow \pi^{*\,b}$
dbm	379	330	1.42	67% $\pi_2 \rightarrow \pi_3^*$ 28% $\pi_1 \rightarrow \pi_4^*$
	303	262	0.728	$\pi \rightarrow \pi^{*\,b}$
	263	251	0.725	*a*

[a] Extensive configuration interaction involving transitions between several filled and vacant orbitals. [b] Extensive configuration interaction involving phenyl π orbitals.

1). Fluorination also shifts the absorption maxima to longer wavelength. The spectrum of $Pt(hfac)_2$ (not shown) displays maxima at 260, 326, and 424 nm ($10^{-3}\epsilon$ = 10, 4.9, and 1.9, respectively). The absorption spectra of both Pd and Pt complexes are similar in coordinating (ethanol) and noncoordinating (dichloromethane) solvents, unlike the spectrum of $Ni(acac)_2$, which displays a single strong band at 298 nm in ethanol and two strong bands at 264 and 313 nm in dichloromethane solution. The solvent effect for $Ni(acac)_2$ is attributed to the existence of a monomeric solvated square planar complex in ethanol and a trimeric complex in dichloromethane.[6]

In order to obtain further information about the effects of extended ligand conjugation on the electronic structure and spectra of the Pd bis(β-diketonates), semiempirical ZINDO calculations[7] have been carried out for *trans*-$Pd(ba)_2$ and $Pd(dbm)_2$[8a] and the results compared to those previously published for $Pd(acac)_2$.[8b] A correlation diagram showing the ZINDO-derived virtual molecular orbital energies is shown in Figure 2. Replacement of ligand methyl groups with phenyl groups does not change the description of the three highest occupied and lowest unoccupied orbitals; however it does decrease the HOMO−LUMO gap and introduce additional phenyl-localized occupied and unoccupied π orbitals which are, respectively, lower in energy than the enol-π orbitals (π_1 and π_2) and higher in energy than the enol π* orbitals (π_3^* and π_4^*). The lowest energy allowed transitions for all three complexes are ligand-localized π → π* transitions resulting from extensive configuration interaction between the $\pi_2 \rightarrow \pi_3^*$ and $\pi_1 \rightarrow \pi_4^*$ transitions. The two next higher energy-allowed transitions display more extensive configuration interaction. The calculated energies, oscillator strengths, and character of these transitions are reported in Table 1. We have not undertaken calculations for fluorinated ligands, and ZINDO is not parametrized for platinum.

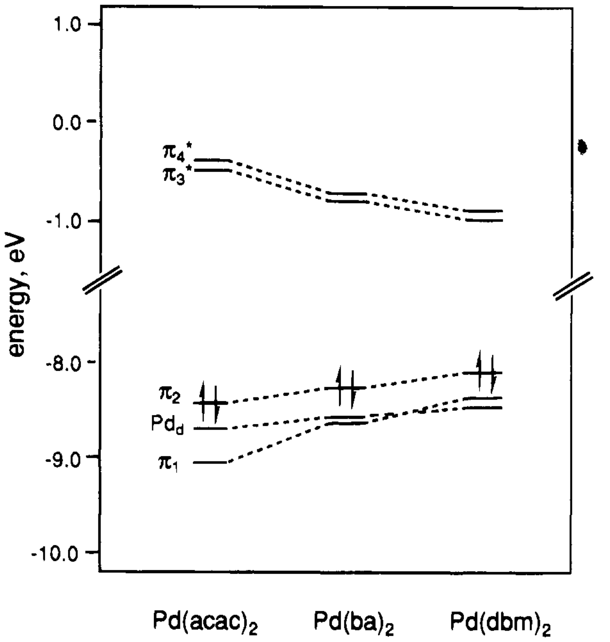


Figure 2. Correlation diagram between ZINDO-derived virtual molecular orbital energies of $Pd(acac)_2$, $Pd(ba)_2$, and $Pd(dbm)_2$.

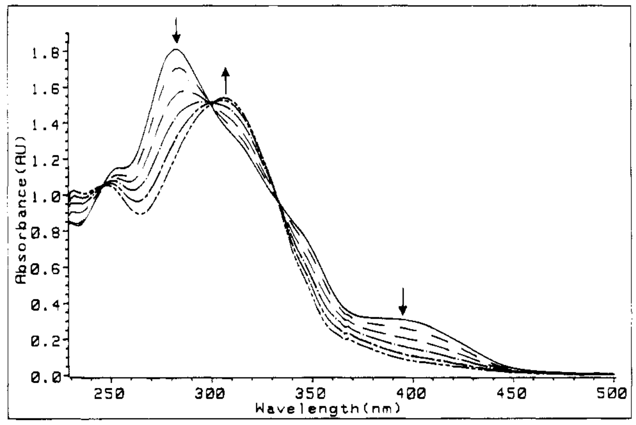


Figure 3. Spectral changes during photolysis of 5 × 10^{-5} M $Pt(ba)_2$ in deaerated CH_2Cl_2 solution with Pyrex-filtered light at 0, 0.5, 1.0, 1.5, 2.0, and 2.5 h of irradiation.

Photodecomposition and Photoisomerization. The changes which occur upon irradiation of the group 10(II) β-diketonates have been monitored by UV and ^1H NMR spectroscopy. As shown in Figure 3, irradiation of 5 × 10^{-5} M $Pt(ba)_2$ with Pyrex-filtered light (λ > 300 nm) in deaerated dichloromethane solution results in disappearance of starting material and appearance of absorption maxima at 308 and 248 nm characteristic of Hba with isosbestic points at 334, 300, and 246 nm as well as weak structureless absorption extending into the visible region attributed to colloidal platinum. Irradiation of

---

(6) Cotton, F. A.; Fackler, J. P. *J. Am. Chem. Soc.* **1961**, *83*, 2818−2825.

(7) (a) Ridley, J.; Zerner, M. *Theor. Chim. Acta* **1973**, *32*, 111−134. (b) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21−54. (c) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589−599. (d) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728−2732.

(8) (a) Details of the ZINDO calculations for $Pd(ba)_2$ and $Pd(dbm)_2$ are available as supplementary material. (b) Lewis, F. D.; Salvi, G. D.; Kanis, D. R.; Ratner, M. A. *Inorg. Chem.* **1993**, *32*, 1251−2158.

Table 2. Quantum Yields for the Reactions of Pt(II) β-Diketonates with Hydrosilanes and Olefins

	$10^3\Phi$		
additive[a]	$Pt(acac)_2$[b]	$Pt(ba)_2$[b]	$Pt(dbm)_2$[b]
none	<0.1	<0.1	<0.1
Et_3SiH	1.8	4.7	10
i-Pr_3SiH		0.1	
Cl_2CH_3SiH		24	20
Ph_3SiH		2.6	
$(EtO)_3SiH$		1.3	
1-hexene	2.6	5.9	5.7
Et_3Si(vinyl)		2.3	
2,3-dimethyl-2-butene	0.8	0.3	1.3

[a] Additive concentration 0.4 M. [b] Concentrations of complexes adjusted to provide an optical density of ca. 2.0 at 365 nm. $Pt(acac)_2$ 3.0×10^{-4}, $Pt(ba)_2$ 2.4×10^{-4}, and $Pt(dbm)_2$ 1.9×10^{-4} M.

more concentrated (10^{-3} M) solutions results in the appearance of Pt^0 as a dark precipitate or mirror. The absorption spectral changes observed upon Pyrex-filtered irradiation of $Pt(acac)_2$ and $Pt(dbm)_2$ in dichloromethane solution are similar to those for $Pt(ba)_2$ (Figure 3). Bleaching of the long-wavelength absorption band of these Pt β-diketonates was used to estimate the quantum yield for consumption of starting material (Φ_r). As reported in Table 2, values of Φ_r obtained using monochromatic 313 or 365 nm irradiation are $<10^{-4}$ and are the same in deoxygenated and oxygenated solutions. Irradiation of the Pt β-diketonates in ethanol solution results in more complex absorption spectral changes indicative of the formation of primary or secondary photoproducts other than the liberated β-diketone (HL). In the case of $Pt(hfac)_2$, bleaching of the long-wavelength absorption band is incomplete even after prolonged irradiation and thus accurate quantum yields could not be determined by the method employed for the other Pt β-diketonates.

Irradiation of $Pd(acac)_2$ and $Pd(ba)_2$ in their long-wavelength absorption bands (313 and 365 nm, respectively) in either dichloromethane or ethanol solution results in significantly less efficient decomposition ($\Phi_r \ll 10^{-4}$) than that observed for the Pt β-diketonates. We have also confirmed the report of Gafney and Lintvedt[1] that $Ni(acac)_2$ is unaffected by 313 nm irradiation in ethanol solution. Irradiation of $Ni(acac)_2$ at 313 nm in dichloromethane solution results in a change in the appearance of the absorption spectrum from that of the trimeric complex to that of the monomeric complex observed in coordinating solvents such as ethanol. The quantum yield for this process is 0.011 ± 0.001. Irradiation of $Ni(acac)_2$ in ethanol solution and $Pd(acac)_2$ and $Pd(ba)_2$ in either ethanol or dichloromethane solution with 254 nm irradiation results in their conversion to metal(0) and β-diketones.

The irradiation of $Pt(acac)_2$ in $CDCl_3$ solution (10^{-3} M) using Pyrex-filtered light was also monitored by ^1H NMR. Irradiation resulted in a continuous decrease in the reactant methyl and vinyl peaks (1.96 and 5.35 ppm) and the appearance of peaks attributed to the enol tautomer of Hacac methyl and vinyl (2.05 and 5.51 ppm) hydrogens. At higher conversions, peaks assigned to the keto tautomer (2.26 and 3.60 ppm) and to an unidentified secondary photoproduct (1.87 and 5.48 ppm) are detected and a brown metallic film forms on the surface of the NMR tube.

The cis and trans isomers of $Pt(ba)_2$ can be separated by column chromatography and are configurationally stable at room temperature in solution. While these isomers have similar UV spectra, they can be distinguished on the basis of their ^1H NMR chemical shifts. The effect of 254 nm irradiation upon a 1×10^{-3} M CD_2Cl_2 solution containing an 8.2:1 ratio of cis:trans isomers is shown in Figure 4. After 15 min of irradiation, the isomer ratio is 3.8:1 and little photodecomposition has occurred. After 30 min of irradiation, the isomer ratio is 1.2:1 and peaks attributed to unidentified photoproducts are also observed. Continued irradiation results in appearance of peaks assigned to the keto and enol tautomers of Hba. Irradiation of *trans*-$Pt(ba)_2$ also results in the formation of a 1.2:1 ratio of cis:trans isomers prior to significant photodecomposition. The quantum yield for photoisomerization determined at moderate conversions (<30%) using monochromatic 420 nm light is $\Phi_i = 3 \times 10^{-4}$. Similar values were obtained using 365 or 313 nm irradiation.

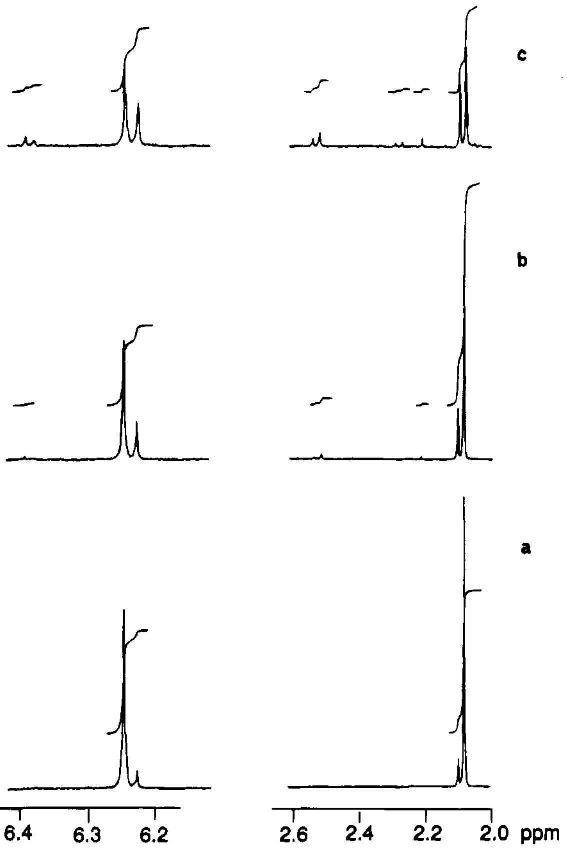


Figure 4. Photoisomerization of 10^{-3} M *cis*-$Pt(ba)_2$ in deaerated CD_2Cl_2 solution upon 254 nm irradiation. Shown are the spectral changes in the methyl and vinyl ^1H NMR regions upon (a) 0, (b) 30, and (c) 120 min of photolysis.

The cis and trans isomers of $Pd(ba)_2$ can be separated by fractional crystallization and are configurationally stable in the solid state. However, as reported by Okeya et al.,[9] they undergo thermal isomerization in solution at room temperature. We have investigated the isomerization of *cis*-$Pd(ba)_2$ in $CDCl_3$ solution by ^1H NMR spectroscopy and find that it undergoes rapid thermal isomerization at 20 °C, reaching a ca. 1:1 mixture of cis and trans isomers within 30 min. Irradiation (254 or 350 nm) results in neither accelerated isomerization nor photodecomposition on the time scale of thermal isomerization.

Effects of Additives. Irradiation of the group 10(II) β-diketonates in the presence of high concentrations (>0.1 M) of hydrosilanes or olefins results in accelerated photodecomposition with formation of HL and precipitated metal. For example, conversion of 5×10^{-5} M $Ni(acac)_2$ to Hacac upon 254 nm irradiation is complete within 15 min in the presence of 0.5 M Et_3SiH but requires several hours in its absence. Irradiation at 313 nm results in complete conversion within 2.5 h of irradiation

---

(9) Okeya, S.; Ooi, S.; Matsumoto, K.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1085–1095.

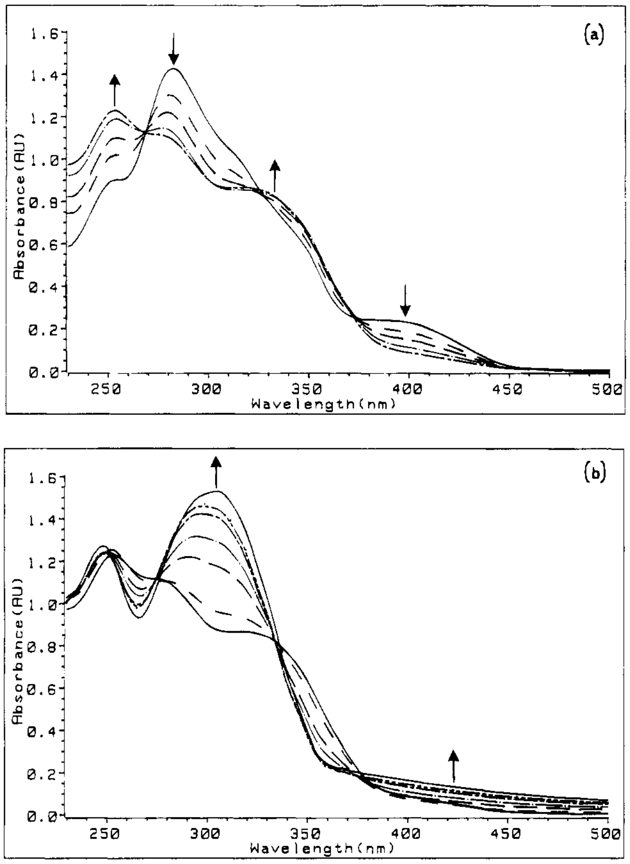


Figure 5. Spectral changes during 420 nm photolysis of 5 × 10^{-5} M $Pt(ba)_2$ and 0.5 M Et_3SiH in deaerated CH_2Cl_2 solution at (a) 0, 0.5, 1, 2, 3 min and (b) 3, 5, 10, 15, 30, 45, 120 min of irradiation.

in the presence of Et_3SiH, whereas no conversion is observed in the absence of Et_3SiH. A slow dark reaction is also observed but requires ca. 18 h for complete conversion of $Ni(acac)_2$ to Hacac. Similarly, 254 nm irradiation of a dichloromethane solution of $Pd(acac)_2$ in the presence of Et_3SiH requires 15 min for complete conversion of starting material to Hacac. Long-wavelength irradiation of $Pd(acac)_2$ (313 nm) or $Pd(ba)_2$ (365 nm) in the presence of Et_3SiH results in inefficient bleaching of their absorption bands ($\Phi_r < 10^{-4}$).

The changes in the absorption spectrum which occur upon irradiation of 5 × 10^{-5} M $Pt(ba)_2$ in its lowest energy absorption band (420 nm) in the presence of 0.5 M Et_3SiH are shown in Figure 5. The reaction appears to occur in two stages. The first stage, which occurs during the first 3 min of 420 nm irradiation, is characterized by the complete disappearance of the $Pt(ba)_2$ 386 nm band and the appearance of absorption maxima at 318, 276, and 254 nm (Figure 5a) attributed to a primary photoproduct P_1. The second stage occurs between 3 and 120 min of irradiation during which the bands attributed to P_1 disappear and bands attributed to Hba (306 nm, 248 nm) and colloidal Pt^0 (visible absorption tail) appear (Figure 5b). High concentrations (>0.1 M) of Et_3SiH are necessary in order to observe the formation of P_1. At lower concentrations of Et_3SiH, $Pt(ba)_2$ is converted slowly to Hba and colloidal Pt^0 without the appearance of the absorption bands attributed to P_1. When irradiation is terminated after 3 min, the absorption bands of P_1 decrease in intensity over a period of ca. 20 h with partial reversion to starting material as well as formation of Hba. Warming of the irradiated solution results in more rapid disappearance of P_1. Irradiation at shorter wavelengths also results in more rapid conversion of P_1 to Hba. Attempts to isolate P_1 by low-temperature crystallization or chromatography were unsuccessful. The presence of oxygen has little effect on the first stage of reaction (Figure 5a); however more complex changes in the absorption spectrum are observed during the second stage of irradiation in the presence of oxygen.

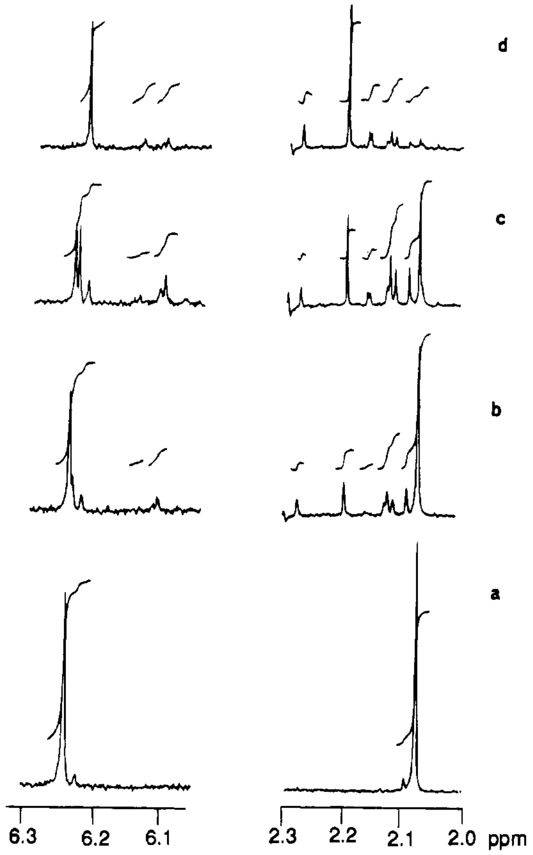


Figure 6. NMR spectral changes during 420 nm photolysis of 10^{-3} M *cis*-$Pt(ba)_2$ and 0.5 M Et_3SiH in deaerated CD_2Cl_2 solution at (a) 0, (b) 5 min, (c) 10 min, and (d) 30 min of photolysis. Only those changes occurring in the vinyl and methyl regions are displayed.

The reaction of $Pt(ba)_2$ with Et_3SiH was also followed by ^1H NMR spectroscopy. The results obtained for 420 nm irradiation of 10^{-3} M *cis*-$Pt(ba)_2$ (initially containing 5% trans isomer) are shown in Figure 6. After 5 min of irradiation, peaks attributed to the trans isomer (2.08 ppm), a product with peaks at 2.13 (m), 6.12 (m), and 7.39–7.89 ppm, and the keto and enol tautomers of Hba are detected. Continued irradiation results in the appearance of a second intermediate with NMR peaks at 2.17 (d), 6.15 (m), and 7.39–7.89 (m) ppm and the eventual conversion of starting material and both intermediates to Hba. Irradiation of *trans*-$Pt(ba)_2$ results in similar changes except that the order of appearance of the intermediates is reversed. Thus we assign the 2.13 ppm product as P_{cis} and the 2.17 ppm product as P_{trans}. On the basis of these assignments, integration of NMR peaks in the methyl region provides the plots of reactant and product concentration vs irradiation time shown in Figure 7.

The reactions of $Pt(acac)_2$ and $Pt(ba)_2$ with 1-hexene have been investigated using UV and ^1H NMR spectroscopy. Irradiation of 5 × 10^{-5} M $Pt(acac)_2$ and 0.5 M 1-hexene using 366 nm light results in the appearance of absorption bands at 310 and 264 nm attributed to a primary photoproduct followed by the appearance of bands characteristic of Hacac at longer irradiation times. The UV changes observed upon 420 nm irradiation of 5 × 10^{-5} M $Pt(ba)_2$ and 0.5 M 1-hexene in dichloromethane solution are similar to those observed during the initial stages of the reaction of $Pt(ba)_2$ with Et_3SiH (Figure 5). However, complete conversion of $Pt(ba)_2$ and 1-hexene to a primary photoproduct with maxima at 334 and 252 nm requires longer irradiation times (ca. 20–30 min) than reaction with Et$_3$-

SiH (ca. 3 min). The intermediate formed with 1-hexene is more stable in the dark or upon 420 nm irradiation than is the intermediate formed with Et_3SiH. Formation of the 1-hexene intermediate can also be observed at lower concentrations (0.05 M 1-hexene) than is possible for Et_3SiH. The 1-hexene intermediate is rapidly converted to Hba and colloidal Pt^0 upon irradiation with Pyrex-filtered light. The presence of oxygen has little effect upon the formation or stability of the 1-hexene intermediate. ^1H NMR spectroscopy was used to monitor the reactions of 0.05 M 1-hexene with 1×10^{-3} M $Pt(acac)_2$ or $Pt(ba)_2$. While peaks attributed to primary photoproducts could be detected, attempts at product isolation were unsuccessful.

Quantum yields for the disappearance of the Pt β-diketonates in the presence of several hydrosilanes or olefins are reported in Table 2. These values were determined using monochromatic 365 nm irradiation and monitoring the bleaching of the long-wavelength absorption band. Values determined at low to moderate conversion (10–50%) are independent of conversion and are the same in the absence or presence of oxygen. The dark stability of the primary photoproducts is dependent upon the choice of hydrosilane, decreasing in the order Et_3SiH > Bu_3SiH > $i\text{-}Pr_3SiH$ > Ph_3SiH > $(EtO)_3SiH$ > Cl_2CH_3SiH. The relative efficiency of the reaction of 5×10^{-5} M $Pt(ba)_2$ in the presence of ethylene is similar to that for 1-hexene; however, the quantum yield for reaction with ethylene was not determined. The dark stability of the primary photoproducts is greater for ethylene or 1-hexene than for $Et_3Si(vinyl)$ or 2,3-dimethyl-2-butene. The stability of the primary photoproducts formed in the presence of ethylene increases with increasing ligand size (acac < ba < dbm).

Discussion

Electronic Structure and Spectra. The structure and spectroscopy of the group 10(II) β-diketonates have been extensively investigated both in the solid state and in solution.[6,8b,10–15] These complexes adopt square planar geometries in the solid state with the central metal and two chelating β-diketonate ligands in the same plane, as established by X-ray crystal structures in the case of $Ni(acac)_2$,[10] $Pd(acac)_2$,[11] *trans*-$Pd(ba)_2$,[12] and $Pt(acac)_2$.[13] $Ni(acac)_2$ has been proposed to adopt a solvated monomeric square planar geometry in coordinating solvents such as ethanol and a trimeric structure in noncoordinating solvents such as dichloromethane, thus accounting for the solvent dependence of its electronic absorption spectra.[6] The β-diketonates of palladium and platinum are square planar monomers in both coordinating and noncoordinating solvents.

We recently reported[8b] the results of an investigation of the electronic structure and absorption spectra of $Ni(acac)_2$ and $Pd(acac)_2$ using the semiempirical INDO/S-SCF-CI (ZINDO) algorithm.[7] The electronic structure calculations indicate that increasing the atomic number of the group 10(II) metal results in an increase in metal–ligand covalency, an increase in the separation of the two highest occupied and lowest unoccupied ligand-localized π orbitals, and a decrease in the separation between occupied and unoccupied orbitals. The lowest energy allowed transitions for both $Ni(acac)_2$ and $Pd(acac)_2$ were attributed to ligand-localized $\pi \rightarrow \pi^*$ transitions with extensive configuration interaction involving the two highest occupied and two lowest unoccupied π orbitals. For both complexes, the presence of lower energy, symmetry-forbidden transitions is indicated by the ZINDO calculations. In the case of $Ni(acac)_2$, the lowest singlet states appear in the infrared and visible regions and are assigned to essentially pure d → d transitions.[6,8b] In the case of $Pd(acac)_2$, the lowest singlet states are calculated to be of mixed ligand and metal character and to lie in the ultraviolet region, below the allowed $\pi \rightarrow \pi^*$ transitions. Extrapolation of this trend suggests that no forbidden transitions lie below the lowest allowed $\pi \rightarrow \pi^*$ transition of $Pt(acac)_2$. None of the low-energy excited states of the group 10(II) β-diketonates can be characterized as metal–ligand antibonding.

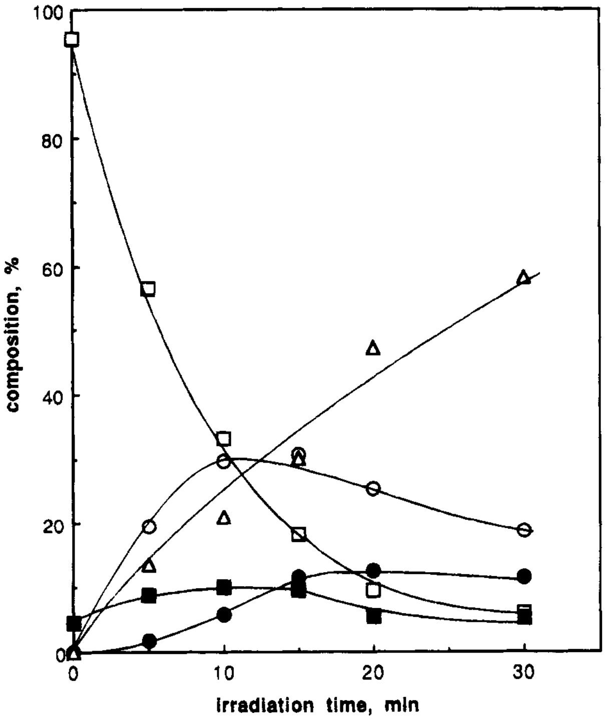


Figure 7. Relative percentages of *cis*-$Pt(ba)_2$ (□), *trans*-$Pt(ba)_2$ (■), P_{cis} (○), P_{trans} (●), and Hba (△) during the 420 nm photolysis of *cis*-$Pt(ba)_2$ and Et_3SiH in deaerated CD_2Cl_2 solution.

The absorption spectra of metal β-diketonates are known to be dependent upon the extent of conjugation in the ligand as well as the choice of the central metal atom. Replacement of the methyl groups in the acetylacetonate complexes of Fe(III), Al(III), Cu(II), Pd(II), and Pt(II) with phenyl groups results in a shift in absorption bands attributed to ligand-localized $\pi \rightarrow \pi^*$ transitions to lower energies.[14] Calculation of the electronic structure and optical spectra of $Pd(acac)_2$, $Pd(ba)_2$, and $Pd(dbm)_2$ using the semiempirical INDO/S–SCF–CI (ZINDO) algorithm indicates that phenyl substitution does not significantly alter the appearance of the two highest occupied and two lowest unoccupied ligand-localized enol-π orbitals, but it does result in a decrease in the energetic separation of occupied and unoccupied orbitals and introduce additional phenyl-localized π orbitals (Figure 2). We previously assigned the 326 and 250 nm absorption bands of $Pd(acac)_2$ to $\pi \rightarrow \pi^*$ transitions arising from extensive configuration between $\pi_2 \rightarrow \pi_3^*$ and $\pi_1 \rightarrow \pi_4^*$ excitations.[8b] ZINDO calculations for $Pd(ba)_2$ and $Pd(dbm)_2$ correctly predict both a shift to lower energies and an increase

---

(10) (a) Bullen, G. J.; Mason, R.; Pauling, P. *Nature* **1961**, *189*, 291–292. (b) Hursthouse, M. B.; Laffey, M. A.; Moore, P. T.; New, D. B.; Raithby, P. R.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1982**, 307–312.

(11) Burton, N. A.; Hillier, I. H.; Guest, M. F.; Kendrick, J. *Chem. Phys. Lett.* **1989**, *155*, 195–198.

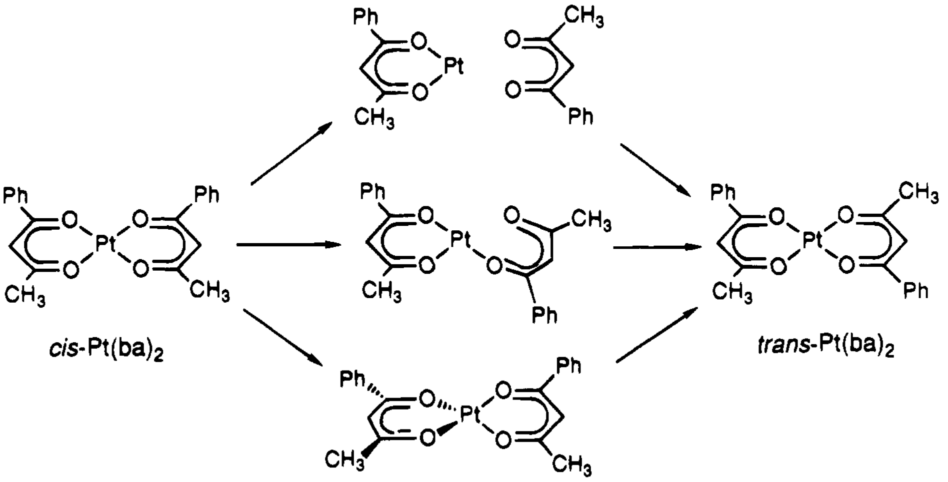
(12) Hon, P.-K.; Pfluger, C. E.; Belford, R. L. *Inorg. Chem.* **1967**, *6*, 730–735.

(13) Onuma, S.; Horioka, K.; Inoue, H.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2679–2680.

(14) (a) Singh, P. R.; Sahai, R. *J. Indian Chem. Soc.* **1969**, *46*, 945–950. (b) Lintvedt, R. L.; Kernitsky, L. K. *Inorg. Chem.* **1970**, *9*, 491–494. (c) Zharkova, G. I.; Igumenov, I. K.; Tkachev, S. V.; Zemscov, S. V. *Sov. J. Coord. Chem.* **1982**, *8*, 41–48. (d) Zharkova, G. I.; Igumenov, I. K.; Tyukalevskaya, N. M. *Sov. J. Coord. Chem.* **1988**, *14*, 42–49.

(15) Fackler, J. P., Jr.; Cotton, F. A.; Barnum, D. W. *Inorg. Chem.* **1963**, *2*, 97–101.

Scheme 1



in oscillator strength for these transitions with increasing ligand conjugation (Table 1). As previously observed,[8a] the calculated transition energies lie at somewhat higher energy than the observed band maxima.

Trifluoromethyl substitution also shifts the $\pi \rightarrow \pi^*$ transitions of the acetylacetonate complexes of Cu(II), Fe(II), Pd(II), and Pt(II) to lower energies.[14,15] These shifts are smaller than those observed for phenyl substitution, except in the case of Pt(II). The origin of the trifluoromethyl effect remains to be elucidated.

Photochemistry. The photochemical behavior of the group 10(II) β-diketonates in ethanol or dichloromethane solution is characterized by inefficient decomposition with the formation of colloidal metal and β-diketones, as initially reported by Gafney and Lintvedt[1] in the case of Ni(acac)$_2$. The formation of β-diketones is supported by comparison of UV and ^{1}H NMR spectra (see Figures 3 and 4) and GC coinjection with authentic samples. The formation of reduced metals is consistent with the changes observed in the UV–visible spectra during irradiation of the metal β-diketonates at low concentrations (5×10^{-5} M) and the observation of precipitate formation using higher concentrations (10^{-3} M) of the metal β-diketonates. The spectral changes are similar to those reported for photochemical formation of colloidal gold, silver, palladium, and platinum from other precursors.[16] While the quantum yields for these reactions are low, in the absence of additives, the use of low concentrations and continuous light sources of moderately high intensity makes it possible to conveniently monitor these reactions by UV spectroscopy. The higher concentrations ($>10^{-3}$ M) required for monitoring these reactions by ^{1}H NMR spectroscopy necessitated longer irradiation times and resulted in the formation of light-scattering metal mirrors or dense precipitates.

All of the group 10(II) β-diketonates investigated undergo photodecomposition upon irradiation at 254 nm. The nickel and palladium complexes are unreactive upon irradiation into their long-wavelength absorption bands (>300 nm), whereas the platinum complexes undergo photodecomposition with comparable low efficiency upon irradiation at 254 nm or longer wavelengths. This difference may reflect the presence of low-energy metal-localized d,d singlet states in the case of Ni(acac)$_2$ and Pd(acac)$_2$ but not Pt(acac)$_2$.[8b] The d,d state could provide a pathway for internal conversion from the initially populated π,π^* state to the ground state. Photodecomposition of Ni(acac)$_2$ and Pd(acac)$_2$ upon 254 nm irradiation may result from population of higher excited states from which decomposition can compete with internal conversion to the lower energy excited states populated with 313 nm or longer wavelength irradiation.

Photoisomerization of *trans*- and *cis*-Pt(ba)$_2$ in dichloromethane is much more efficient ($\Phi_i = 3 \times 10^{-3}$) than photodecomposition (Figure 4). The photoisomerization of Pt β-diketonates has not previously been investigated; however the thermal isomerization of several Pd and Pt β-diketonate complexes has been reported.[9,17] May and Powell[17] observed that the trifluoromethyl groups in nonsymmetric Pd(hfac)L$_2$ complexes undergo rapid exchange at room temperature. They proposed that either a square planar ↔ tetrahedral rearrangement or a partial dissociation of the hfac ligand to give a three-coordinate intermediate is involved. Okeya et al.[9] observed that the cis and trans isomers of Pd(ba)$_2$ and Pd(tfac)$_2$ (tfac = trifluoroacetylacetonate) undergo isomerization at room temperature, while Pt(tfac)$_2$, like Pt(ba)$_2$, is configurationally stable under the same conditions. They also observed that no ligand exchange occurs upon heating Pd or Pt β-diketonates and on this basis proposed an intramolecular mechanism for thermal isomerization. Separation of the cis and trans isomers of Ni(ba)$_2$ has not, to our knowledge, been reported, possibly reflecting a low activation energy for thermal isomerization. An increase in the activation energy for thermal cis,trans isomerization in the order Ni < Pd < Pt parallels the increase in metal–ligand covalency indicated by electronic structure calculations.[8b]

The observation of cis,trans photoisomerization for Pt(ba)$_2$ suggests that the very low efficiency of photodecomposition of the group 10(II) β-diketonates may result from energy-wasting photoisomerization, as well as nonradiative decay. At least three mechanisms for photoisomerization can be considered: two-bond cleavage resulting in ligand dissociation followed by recombination; one-bond cleavage to form a three-coordinate intermediate followed by recombination; and the formation of a tetrahedral intermediate (Scheme 1). In each case, the intermediate could re-form either the original isomer or its configurational isomer, thus reducing the apparent efficiency of photoisomerization. Two-bond cleavage has been observed by Chow et al.[18] in the triplet-sensitized reactions of Ni(acac)$_2$. The resulting acetylacetonyl radical and a Ni(I) species decay

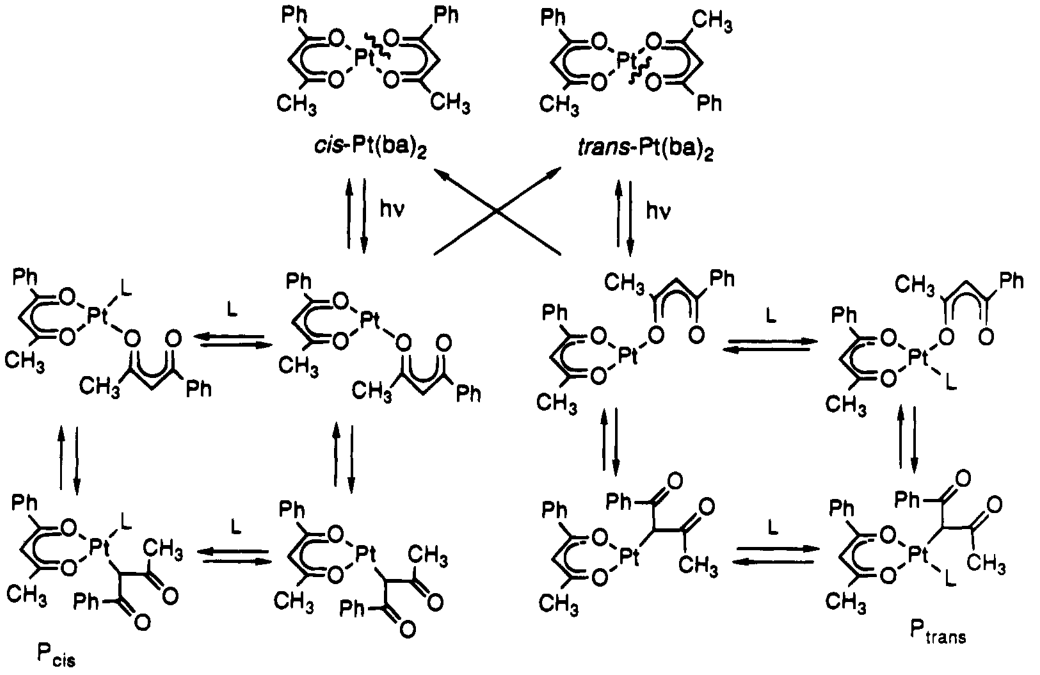
---

(16) (a) Klassen, R. B.; Baum, T. H. *Organometallics* **1989**, *8*, 2477–2482. (b) Vogler, A.; Quett, C.; Kunkely, H. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1486–1492. (c) Yonezawa, Y.; Sato, T.; Ohno, M.; Hada, H. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 1559–1567. (d) Sato, T.; Yonezawa, Y.; Hada, H. *Nippon Shash. Gakk.* **1988**, *51*, 122–134. (e) Kurihara, K.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6152–6153. (f) Boardman, L. D. *Organometallics* **1992**, *11*, 4194–4201.

(17) May, C. J.; Powell, J. *Inorg. Chim. Acta* **1978**, *26*, L21–L22.

(18) Chow, Y. L.; Li, H. *Can. J. Chem.* **1986**, *64*, 2229–2231.

Scheme 2



via homogeneous recombination. Balzani and co-workers[19] used isotopic labeling to rule out the possibility of either an intermolecular mechanism or an intramolecular bond-breaking mechanism involving a three-coordinate intermediate for the photoisomerization of *cis*-platinum(II) bis(glycinate) in aqueous solution. Photoisomerization of Pt(glycinate)$_2$ was proposed to occur via an intramolecular twisting mechanism involving a triplet-state tetrahedral intermediate, in accord with an earlier suggestion by Martin et al.[20] that the lowest energy excited state of d^8 metal complexes is a triplet state with a stable tetrahedral or pseudotetrahedral conformation.

The occurrence of two bond photodissociation (either concerted or stepwise) of the Pt β-diketonates can be excluded on the basis of the absence of either ligand exchange or the interception of the resulting intermediates by oxygen or added ligands. Gafney and Lintvedt[1] reported that the photodecomposition of Ni(II) and Cu(II) β-diketonates is inhibited by oxygen. Exposure of irradiated solutions of Cu(acac)$_2$ to air was observed to result in reconversion of Cu^0 and Hacac to Cu(acac)$_2$. Oxygen does not inhibit the photodecomposition of the Pt β-diketonates. This indicates that neither the reactive excited state nor intermediates in the photodecomposition process are intercepted by oxygen at concentrations present in saturated organic solvents (ca. 3×10^{-3} M) and that the primary products are not reactive with oxygen. Irradiation of Pt(acac)$_2$ (1×10^{-4} M in dichloromethane solution) in the presence of Hba (1×10^{-4} M) does not result in the appearance of the long-wavelength UV band characteristic of Pt(ba)$_2$.

The photodecomposition of the group 10(II) β-diketonates is accelerated in the presence of Et$_3$SiH and other hydrosilanes. Relatively high concentrations (>0.1 M) are necessary in order to observe this effect, suggesting that accelerated decomposition requires either occupation of an axial coordination site in a square pyramidal or octahedral complex prior to electronic excitation or that a short-lived excited state or reactive intermediate is intercepted by Et$_3$SiH. Irradiation of Ni(acac)$_2$, Pd(acac)$_2$, or Pt(acac)$_2$ in the presence of Et$_3$SiH results in conversion to colloidal metal and Hacac without the accumulation of intermediates detectable by UV. Since Ni(acac)$_2$ or Pd(acac)$_2$ undergoes slow thermal reactions with Et$_3$SiH, it is possible that primary products formed in the photochemical reaction are converted to colloidal metal and Hacac more rapidly than they are formed.

Evidence for the formation of Pt(ba)(ba′)L (ba′ = monodentate ba and L = Et$_3$SiH or 1-hexene) as the primary photoproduct in the reactions of Pt(ba)$_2$ is provided by the formation of different primary photoproducts in the photochemical reactions of *trans*- and *cis*-Pt(ba)$_2$ with Et$_3$SiH (Figures 6 and 7) and by the slow dark reversion of these products to Pt(ba)$_2$. Regioselective (O$_1$ vs O$_3$) one-bond cleavage followed by reaction of either an O- or a C-bonded nonsymmetric three-coordinate intermediate with Et$_3$SiH or 1-hexene would result in the formation of diastereomeric Pt(ba)(ba′)L square planar complexes (P$_{cis}$ and P$_{trans}$). These complexes could revert to starting Pt(ba)$_2$ with loss of the ligand or proceed to secondary products. The spectral changes observed upon irradiation of Pt(ba)$_2$ in the presence of hydrosilanes or olefins are similar to those reported for the thermal reaction (100 °C) of Pt(acac)$_2$ with pyridine, which results in the initial production of Pt(acac)(γ-acac)(pyridine) (γ-acac = 2,4-pentanedionato-C^3) followed by the production of Pt(γ-acac)$_2$(pyridine)$_2$.[21] For this reason, we favor a C- vs an O-bonded structure for the monodentate β-diketonate in the primary photoproduct.

An integrated mechanism for the photoisomerization, photosubstitution, and photodecomposition of *trans*- and *cis*-Pt(ba)$_2$ is outlined in Scheme 2. Irradiation results in one-bond cleavage to give an O-bonded three-coordinate intermediate which may rearrange to a C-bonded intermediate. Either the O- or C-bonded intermediate could revert to Pt(ba)$_2$ with partial inversion of stereochemistry or react with added hydrosilane or olefin to form the primary photoproduct. The higher quantum yields for reaction with additives (Table 2) vs isomerization and the quenching of isomerization by Et$_3$SiH (Figure 7)

---

(19) (a) *Photochemistry of Coordination Compounds*; Balzani, V., Carassiti, V., Eds.; Academic: New York, 1970; pp 250–256. (b) Balzani, V.; Carassiti, V. *J. Phys. Chem.* **1968**, *72*, 383–388. (c) Scandola, F.; Traverso, O.; Balzani, V.; Zucchini, G. L.; Carassiti, V. *Inorg. Chim. Acta* **1967**, *1*, 76–80. (d) Balzani, V.; Carassiti, V.; Moggi, L.; Scandola, F. *Inorg. Chem.* **1965**, *4*, 1243–1247.

(20) Martin, D. S.; Tucker, M. A.; Kassman, A. J. *Inorg. Chem.* **1965**, *4*, 1682–1689.

(21) Ito, T.; Kiriyama, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3257–3264.

indicates that the three-coordinate intermediate preferentially returns to the starting material with retention of configuration.

Quantum yields for consumption of the Pt β-diketonates in the presence of hydrosilanes or olefins (Table 2) are dependent upon both ligand and additive structure. Quantum yields for the reaction of Pt(acac)$_2$ with both Et$_3$SiH and 1-hexene are lower than those for Pt(ba)$_2$ or Pt(dbm)$_2$. Higher quantum yields for reactions of Pt(ba)$_2$ and Pt(dbm)$_2$ with Et$_3$SiH or Bu$_3$SiH vs *i*-Pr$_3$SiH or with 1-hexene vs 2,3-dimethyl-2-butene are consistent with the anticipated steric effect for the reaction of a coordinatively unsaturated Pt complex.[22] The decrease in reactivity for the series of hydrosilanes Cl$_2$CH$_3$SiH > Et$_3$SiH > Ph$_3$SiH > (EtO)$_3$SiH is surprising since electron-withdrawing chlorine and ethoxy substituents might have both been expected to decrease the rate of a hydride addition reaction. The use of a single additive concentration for the measurement of quantum yields (0.4 M, Table 2) may result in kinetic saturation for the most reactive additives and thus compress the difference between the most and least reactive additives (e.g. 1-hexene and 2,3-dimethyl-2-butene).

In the absence of isolation and characterization of the primary photoproducts, we can only speculate as to the mode of metal−ligand binding. Platinum(II)−olefin complexes typically involve η^2-bonding of olefin.[23] The stability of such complexes is known to decrease with an increase in substitution at the carbon−carbon double bond in accord with our observation of the formation of more stable primary products with ethylene or 1-hexene than with 2,3-dimethyl-2-butene. The reaction of the three-coordinate intermediate with a hydrosilane could result in either η^2 coordination or oxidative addition.[22,24] The mode of hydrosilane reaction is known to be dependent upon silicon substituents and the metal. Since the primary photoproduct in the reaction of Pt(ba)$_2$ with Et$_3$SiH apparently retains both a bidentate and monodentate ba ligand, oxidative addition would of necessity yield a pentacoordinate product. The dark stability of hydrosilane primary products decreases in the order Et$_3$SiH > Bu$_3$SiH > *i*-PrSi$_3$H > Ph$_3$SiH ~ (EtO)$_3$SiH > Cl$_2$CH$_3$SiH, indicating that both electron-withdrawing and bulky substituents destabilize the primary photoproduct. Since electron-withdrawing substituents on silicon are known to stabilize the products of transition metal R$_3$Si−H insertion,[22] the instability of the primary photoproducts formed in the reactions of Pt(ba)$_2$ with (EtO)$_3$SiH or Cl$_2$CH$_3$SiH suggests that they may be η^2-coordinated hydrosilane adducts. While increasing the size of the olefin or hydrosilane ligand decreases the stability of the primary photoproduct, increasing the size of the β-diketonate appears to increase the stability of the primary photoproduct formed with ethylene in the order Pt(acac)$_2$ < Pt(ba)$_2$ < Pt(dbm)$_2$.

The thermal and photochemical decomposition of the primary photoproducts presumably proceeds via sequential C−O cleavage, ultimately leading to the formation of colloidal metal and reduced ligand. While no evidence was obtained by UV or ^{1}H NMR spectroscopy for the accumulation of intermediates in the decomposition of the primary photoproduct, our investigation of the mechanism of photoinitiated hydrosilation using Pt β-diketonate catalyst precursors provides compelling evidence for the formation of a highly active homogeneous hydrosilation catalyst upon irradiation of the primary photoproducts obtained in the presence of hydrosilane or olefin additives. This investigation is the subject of the following paper.

Experimental Section

General Methods. Ultraviolet−visible absorption spectra were measured on a Hewlett-Packard 8452A diode-array spectrophotometer using a 1 cm path length quartz cuvette. ^{1}H NMR spectra were recorded on a Varian XLA-400 spectrometer. Chemical shifts were measured relative to internal TMS using CDCl$_3$ (Aldrich) or CD$_2$Cl$_2$ (Isotech) as solvent. Irradiations were conducted with a Rayonet reactor equipped with 254, 350, or 420 nm lamps or with a Hanovia 450 W medium-pressure mercury lamp in a water-cooled Pyrex lamp well ($\lambda \geq 300$ nm). A potassium chromate solution was used in conjunction with the Hanovia lamp to isolate the 313 nm line, and Corning glass filters 7−54 and 0−52 were used to isolate the 365 nm line. Quantum yields of photodecomposition were determined using monochromatic light provided by an optical bench by measuring the disappearance at low to moderate conversions (5−50%) of the long-wavelength absorption band in the ultraviolet−visible spectrum of the metal(II) β-diketonate. Light intensities were measured using *trans*-stilbene[25] (254, 313 nm) or Aberchrome[26] (366 nm) chemical actinometers run in triplicate. Reported errors are the standard deviations from multiple determinations.

Materials. Dichloromethane (Aldrich, spectrophotometric grade) was distilled over calcium hydride prior to use. Spectrophotometric grade carbon tetrachloride, chloroform, 1,2-dichloroethane, and ethanol were used as purchased from Aldrich. Ni(acac)$_2$ (Aldrich) was dried under vacuum at 80 °C overnight. Pt(acac)$_2$ (Aldrich) was sublimed prior to use. Pd(acac)$_2$ (Aldrich) was used as purchased. *cis-* and *trans*-palladium(II) bis(benzoylacetonates) [Pd(ba)$_2$] were synthesized and isolated using the method of Okeya et al.[9] Pt(hfac)$_2$ was prepared using the method of Okeya and Kawaguchi[27] and sublimed at 65 °C prior to use. Triethylsilane, triisopropylsilane, tributylsilane, triphenylsilane, dichloromethylsilane, triethoxysilane, and trimethoxysilane were used as purchased from Aldrich. 2,3-Dimethyl-2-butene and 1-hexene were purchased from Aldrich and distilled prior to use. Triethylvinylsilane (Pfaltz and Bauer) and triethoxyvinylsilane (Strem) were used as purchased.

Platinum(II) bis(benzoylacetonate) [Pt(ba)$_2$] (cis and trans) was prepared by the method of Zharkova et al.[14c] (dec 235 °C, lit.[14c] 240 °C), and the isomers were separated by column chromatography on silica gel using dichloromethane as eluent. The initial fractions were enriched in the trans isomer and later fractions in the cis isomer. Platinum(II) bis(dibenzoylmethanate) [Pt(dbm)$_2$] was synthesized using the method of Zharkova et al.[14c,d] (dec 245 °C).

Irradiation of Metal(II) Bis(β-diketonates). For ultraviolet−visible spectroscopic studies, 2.00 mL of a 5×10^{-5} M M(L)$_2$ solution plus excess solvent (to compensate for evaporation during the gas-bubbling process) was added to a 1 cm path length quartz cuvette. Deaerated solutions were prepared by bubbling the solutions with dry nitrogen for 10−15 min to reach a 2.0 mL volume. Oxygenated solutions were prepared by bubbling the solutions with oxygen for 30−60 s. For NMR studies, 2.0×10^{-6}−4.0×10^{-6} mol of M(L)$_2$ was dissolved in 1.0 mL of deuterated solvent in a 5 mm (o.d.) Pyrex NMR tube; the solution was bubbled slowly with dry nitrogen for 10−15 min to reach a 0.8 mL volume of 2.5×10^{-3}−5.0×10^{-3} M solution. The solutions were irradiated using the appropriate light source while being maintained at room temperature. Photodecomposition was followed by ultraviolet−visible or NMR spectroscopic analysis.

Irradiation of Metal(II) Bis(β-diketonates) in the Presence of Additives. To 2.00 mL of a 5.0×10^{-5} M M(L)$_2$ solution in a 1 cm path length quartz cuvette was added 1.2×10^{-3}−1.4×10^{-3} mol of additive plus excess solvent. Deaerated solutions were prepared by bubbling the solutions with dry nitrogen for 10−15 min, and oxygenated solutions were prepared by bubbling the mixture with oxygen for 30−60 s to reach a 2.0 mL volume of 5.0×10^{-5} M M(L)$_2$ and 0.5 M

---

[22] Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151−187.

[23] (a) Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 1732−1737. (b) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 1653−1658. (c) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1969**, 53−57.

[24] (a) Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8329−8333. (b) Zhang, S.; Dobson, G. R.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 6908−6916.

[25] Lewis, F. D.; Johnson, D. E. *J. Photochem.* **1977**, *7*, 421−423.

[26] Heller, H. G.; Langan, *J. Chem. Soc., Perkin Trans 2* **1981**, 341−343.

[27] Okeya, S.; Kawaguchi, S. *Inorg. Synth.* **1980**, *20*, 65−69.

additive. Solutions were irradiated using the appropriate light source, and reactions were followed by ultraviolet–visible or NMR spectroscopic analysis.

Acknowledgment. The authors thank 3M Corp. for partial funding of this project, J. D. Oxman and L. D. Boardman for attracting our attention to the photochemistry of platinum(II) β-diketonates, and D. R. Kanis for guidance in the interpretation of ZINDO calculations.

Supplementary Material Available: Tables of eigenvalues, eigenvectors, and symmetries for $Pd(ba)_2$ and $Pd(dbm)_2$ frontier orbitals, tables of calculated absorption maxima, oscillator strengths, and configuration interactions of their excited singlet states, figures of eigenvectors for the frontier orbitals, and a correlation diagram showing calculated and observed singlet state energies (9 pages). Ordering information is given on any current masthead page.

IC9410607