Photoreaction of Platinum(II) *β*-Diketonate Complexes with Olefins[†]

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$Pt(hfac)_2$ [hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato] reacts with ethylene when irradiated at 350 nm to yield a single photoproduct which we have isolated for the first time. X-ray diffraction reveals this to be $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$, a five coordinated complex, with two bidentate hfac ligands remaining intact. When $Pt(hfac)_2$ and ethylene were irradiated at 300 nm, a second product that could not be isolated was detected by ^1H NMR and ^{19}F NMR. $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ was also shown not to be stable at shorter wavelengths. The corresponding photoproducts of $Pt(hfac)_2$ with propene and of $Pt(tfac)_2$ [tfac = 1,1,1-trifluoro-2,4-pentanedionato] with ethylene were detected by ^1H NMR spectroscopy.

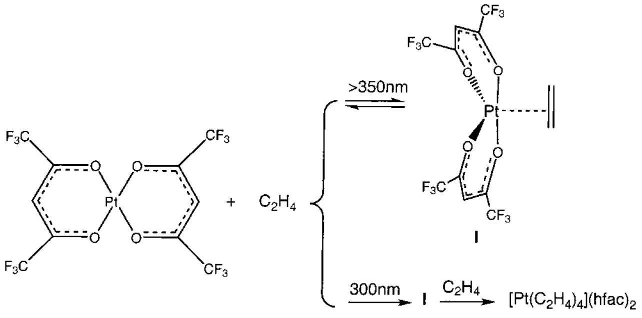
Introduction

Platinum complexes are reported to be among the most active thermal and photochemical catalysts for hydrosilylation reactions.[1−6] The original mechanism for such reactions attributed to Chalk and Harrod suggested formation of a square-planar platinum(II)-olefin complex during the activation step, followed by oxidative addition of hydrosilane to the metal, olefin insertion into the platinum-hydride bond, and reductive elimination forming the Si−C bond.[7] A heterogeneous mechanism in which colloidal platinum metal is the active species has also been proposed.[5] There are also numerous reports of Pt(0)-catalyzed hydrosilylation reactions in which Pt(0) complexes were used.[8,9]

Lewis and co-workers recently reported on the photochemistry of group 10(II) *β*-diketonates.[10] Though they isolated no products, they postulated formation of a soluble active species following photolysis. This highly active homogeneous catalyst can be converted to a less active heterogeneous catalyst by subsequent photochemical or thermal routes.

We now report that, when irradiated at 350 nm, $Pt(hfac)_2$ reacts with ethylene resulting in formation of an isolable five-coordinated complex, $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$. Though this adduct is unstable in solution in the absence of free ethylene, it can be obtained from an ethylene rich solution as a well-defined yellow crystalline material. Photoproducts of $Pt(hfac)_2$ with propene, $Pt(acac)_2$ with ethylene, and $Pt(tfac)_2$ with ethylene were also observed by ^1H NMR and ^{19}F NMR. Though attempts to isolate these complexes were not successful, similar structures are proposed.

Scheme 1



Results

Photoreaction of $Pt(hfac)_2$ with Ethylene. The absorption spectrum of $Pt(hfac)_2$ displays maxima at 326 and 424 nm (10^{-3} ϵ = 4.5 and 1.8, respectively). The lowest energy allowed absorption results from a ligand-centered $\pi-\pi^*$ transition. A slightly higher energy transition is that of the ligand-to-metal charge transfer (LMCT) excited state.[11,12] Irradiation of $Pt(hfac)_2$ with excess ethylene at both 350 and 420 nm in $CDCl_3$ gives the same final product. This is the complex involving η^2 bonding of ethylene to platinum(II), $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ (Scheme 1; 50−60%) [$\Phi = 0.012$] in which the two hfac ligands retain bidentate coordination with Pt(II) through each of the two oxygen atoms. The UV spectrum of the isolated product, $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$, in CH_2Cl_2 solution is shown in Figure 1. Two new peaks appear at 6.12 and 4.07 ppm in the ^1H NMR spectra, with the latter having two satellite peaks $|J(^{195}Pt-H)| = 84$ Hz. The changes in the ^1H NMR spectra occurring during the reaction are presented in the Supporting Information. Figure 2 shows the UV−vis spectra evolving during this same time period. Though

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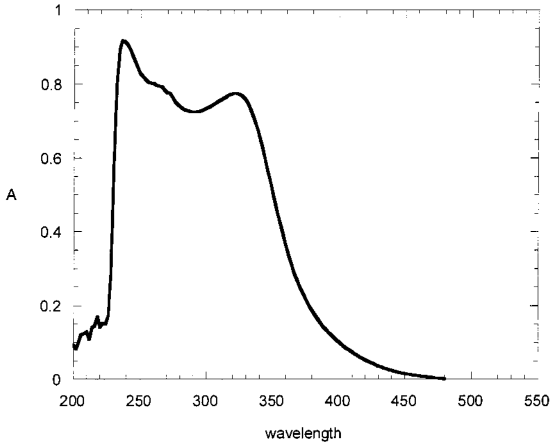


Figure 1. UV−vis absorption spectra of Pt(hfac)$_2$(η^2-C_2H_4) in CH_2Cl_2. ([Pt(hfac)$_2$(η^2-C_2H_4)] = 1.042 × 10^{-4} M)

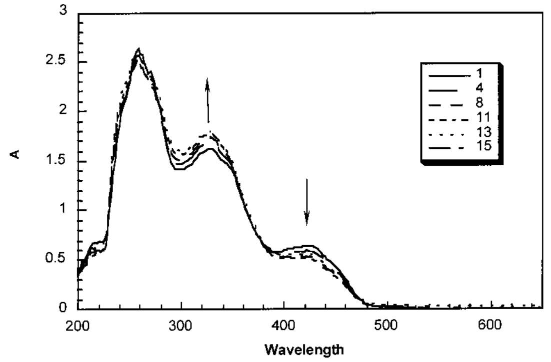


Figure 2. Steady-state UV−vis absorption spectra of Pt(hfac)$_2$ with C_2H_4 in CH_2Cl_2 at 350 nm (Inset: irradiation time, units/min).

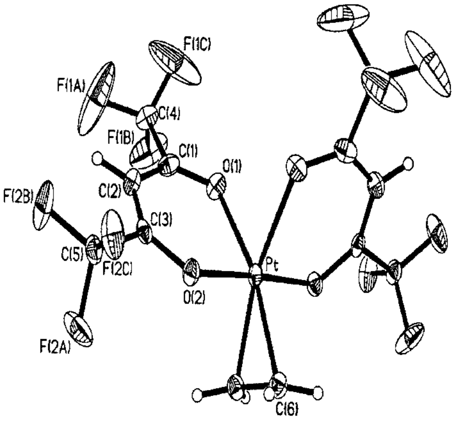


Figure 3. Single-crystal X-ray structure of product Pt(hfac)$_2$(η^2-C_2H_4).

the changes are not large, there is a slight increase in the absorption at 344 nm and decrease at 424 nm. The reaction proceeds directly. There are no obvious intermediates.

Single-Crystal X-ray Diffraction Analysis of Pt(hfac)$_2$(η^2-C_2H_4). A summary of the crystallographic data is presented in the Supporting Information. An ORTEP plot of the molecule is shown in Figure 3.

We note that the molecule has crystallographic 2-fold symmetry. Despite the low temperature used for data collection, the librational amplitude for the CF_3 groups is still high as clearly shown in Figure 3. The expected side on coordination of the ethylene molecule is clearly demonstrated.

Photoreaction of Pt(hfac)$_2$ with Ethylene (300 nm). A different photochemical process is observed when Pt(hfac)$_2$ is irradiated at 300 nm in the presence of excess ethylene in $CDCl_3$. The NMR data for the final products are compiled in Table 1. The changes in the ^{1}H NMR spectra occurring during the reaction are presented in the Supporting Information. The photoreaction initially results in the formation of Pt(hfac)$_2$(η^2-C_2H_4), the same product formed with 350 nm irradiation. However, with continuous irradiation at the shorter wavelength, Pt(hfac)$_2$(η^2-C_2H_4) decomposes. A new ^{1}H NMR peak at 6.36 ppm known to be that of the free ligand 1,1,1,5,5,5-hexafluoro-2,4-pentanedione appears. The formation of this product is further confirmed from the ^{19}F NMR spectrum (see Table 1). A new peak at 4.70 ppm with two satellites and coupling constant $|J(^{195}\text{Pt}-\text{H})|$ = 56 Hz belonging to the protons of ethylene also results. During this secondary reaction the peaks at 424 and 326 nm in the UV−vis absorption spectra disappear. This is accompanied by the appearance of a new band at 280 nm (Figure 4). Though the products could not be isolated, we conclude that, with the higher energy irradiation of the 300 nm light source, dissociation of the two bidentate hfac ligands is the result.

Table 1. NMR Data of the Photoreaction between Pt(hfac)$_2$ and C_2H_4 in $CDCl_3$

	^{1}H NMR			^{19}F NMR
	δH (C−H)	δH (C_2H_4)	$\lvert J(^{195}\text{Pt}-\text{H})\rvert$	δF (CF_3)
free ligand (hfac)	6.35			−76.99
reaction mixture before hν	6.5	5.4		−73.83
final product of 300 nm hν	6.35	4.71	56 Hz	−76.99
Final product of 350 nm hν	6.15	4.06	84 Hz	−74.0, −76.50

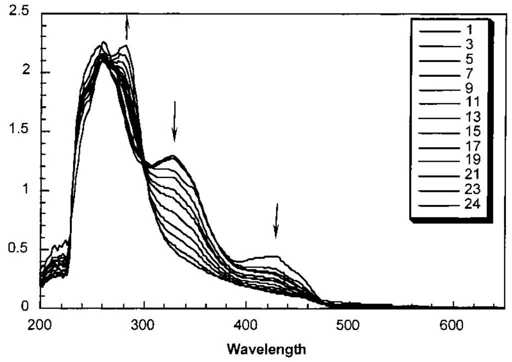


Figure 4. Steady-state UV−vis absorption spectra study of Pt(hfac)$_2$ with C_2H_4 in CH_2Cl_2 at 300 nm (Inset time of irradiation in minutes).

Decomposition of the isolated complex Pt(hfac)$_2$(η^2-C_2H_4) also occurs at 300 nm. This was confirmed from the irradiation of the isolated product in $CDCl_3$. The molar absorbances of Pt(hfac)$_2$(η^2-C_2H_4) are 7.0 × 10^3 and 4.8 × 10^3 lmol^{-1}cm^{-1} at 300 and 350 nm, respectively. In contrast, the corresponding molar absorbances of Pt(hfac)$_2$, the initial light absorbing starting material, are 4.8 × 10^3 and 4.7 × 10^3 lmol^{-1}cm^{-1}. When irradiated at 350 nm, excited Pt(hfac)$_2$ reacts with ethylene forming Pt(hfac)$_2$(η^2-C_2H_4). After 50−60% conversion, the Pt(hfac)$_2$(η^2-C_2H_4) competitively absorbs light but that is of insufficient energy to cause photodecomposition, and no further reaction occurs. When irradiated at 300 nm, Pt(hfac)$_2$(η^2-C_2H_4) becomes the main light absorbing species after some initial period of reaction. Because Pt(hfac)$_2$(η^2-C_2H_4) is unstable under the conditions of the experiment (300 nm irradiation), it undergoes further reaction leading, we suggest, to C_2H_4 ligand displacement (Scheme 1).[13]

The ^{1}H NMR spectrum of Pt(C_2H_4)$_3$ [14] [δ = 6.94 ppm; J(Pt−H) = 57 Hz in C_6D_6] is inconsistent with the spectrum observed when Pt(hfac)$_2$ is irradiated in the presence of ethylene

Table 2. NMR Data of the Reaction between Pt(tfac)$_2$ and C_2H_4 in $CDCl_3$

	δH (C−H)	δH (CH_3)	δH (C_2H_4)	$\|J(^{195}Pt-H)\|$
free ligand (tfac)	5.908	2.207		
reaction mixture before hν	5.998	2.076	5.4	
final product after 300 nm *hν*	5.914	2.205	4.701	56 Hz

in $CDCl_3$ at 300 nm. In view of the fact that the spectrum of $Pt(C_2H_4)_3$ had been reported in C_6D_6 solution, we irradiated Pt(hfac)$_2$ in the presence of ethylene in benzene at 300 nm but found no product. We conclude, therefore, that $Pt(C_2H_4)_3$ is not the product.

Photoreactions of Pt(hfac)$_2$ with Propene and 1-Hexene at 300 nm. Photoreactions of Pt(hfac)$_2$ in the presence of propene and 1-hexene were also observed (^{1}H NMR) upon irradiation at 300 nm. In both cases, a new peak belonging to the proton (C−H) of hfac at 6.12 ppm is observed. In the photoreaction with propene, new peaks of the propene protons were observed at 4.9 (multiple peaks) and 4.0 ppm (quartet peaks) with satellites indicating a Pt(propylene) adduct is formed.

The reactivity difference resulting from the position of the double bond of the olefin is striking. No reaction was observed (^{1}H NMR) between an internal olefin, 2,3-dimethyl-2-butene, with either Pt(hfac)$_2$ and Pt(acac)$_2$. However, terminal olefins such as ethylene, propene, and 1-hexene react with platinum(II) β-diketonate, giving rise to separable products that can sometimes be isolated and always be detected spectroscopically.

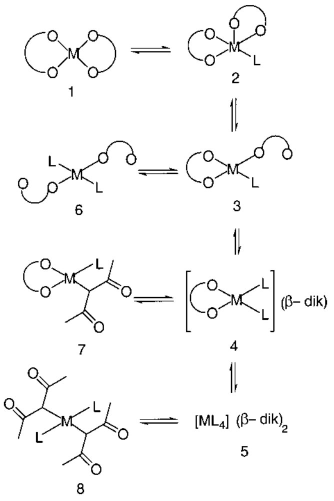
Photoreaction of Pt(tfac)$_2$ with Ethylene. The electronic absorption spectrum of Pt(tfac)$_2$ displays maxima at 254, 308, and 386 nm (10^{-3} ϵ =10, 6.5, and 2.3). No photoreaction was observed from Pt(tfac)$_2$ in the presence of ethylene (^{1}H NMR) upon 350 nm irradiation. When Pt(tfac)$_2$ was irradiated at shorter wavelength (300 nm) in the presence of ethylene, the ^{1}H NMR showed new peaks that were easily assigned to the protons of the free ligand tfac (5.91 and 2.21 ppm). An additional new peak at 4.70 ppm with two satellites and coupling constant $|J(^{195}Pt-H)| = 56$ Hz arises from the protons of ethylene, indicating a Pt(olefin) adduct is formed. The chemical shift and coupling constant between Pt and the ethylene protons are the same as are those of the product formed from Pt(hfac)$_2$ and ethylene when irradiated at 300 nm. The NMR data are shown in Table 2.

Photoreaction of Pt(acac)$_2$ with Ethylene. No photoreaction was observed to occur between Pt(acac)$_2$ and ethylene when a mixture was irradiated at 350 nm (^{1}H NMR). However, photoproduct did form after 7 h of irradiation of Pt(acac)$_2$ with C_2H_4 at 300 nm in $CDCl_3$ solution. After evaporating the unreacted C_2H_4, the ^{1}H NMR spectrum showed a new peak at 4.48 ppm with two satellites, the coupling constant for which was 64 Hz. Another new peak that is observed (5.51 ppm) is very close to the corresponding signal for acac.

Discussion

Stable five-coordinated platinum complexes have been previously reported. Okeya and co-workers synthesized and isolated the five-coordinated platinum complexes Pt(hfac)$_2$[P(cyclohexyl)$_3$] and five-coordinated anionic complexes $[Pt(hfac)_2X]^-$ (X = Cl, Br, and I).[15,16] A distorted square pyramidal structure with the phosphine ligand and halide ligand in the basal plane was observed by X-ray analysis.[15,16] Pt(hfac)$_2$(η^2-C_2H_4) is trigonal bipyramidal, and the two hfac ligands are symmetric. This was also confirmed by X-ray structure analysis.

Scheme 2



Thermal reactions of platinum complexes with nitrogen containing Lewis bases were also previously studied by Okeya[17,18] Scheme 2. Products 7 and 8 (Scheme 2) result from cleavage of the Pt−O bond and subsequent ligand rearrangement. The related photochemical process yields similar products.[19] However, Pt(hfac)$_2$(η^2-C_2H_4), the product we have isolated in this study, retains both the hfac ligands coordinating O,O′ with platinum (structure 2 in Scheme 2). The differences in these two reactions may lie in the fact that nitrogen bases are much stronger nucleophiles. With irradiation, the platinum−oxygen bond breaks following nucleophilic displacement and the ligand acac rearranges to the more stable γ-acac.[15] In the case of ethylene, the weakly coordinated η^2 ethylene platinum interaction is not strong enough to produce any further reaction (Scheme 1). When ethylene is in excess, Pt(hfac)$_2$(η^2-C_2H_4) forms. However, when the ethylene concentration is low, the initially formed product reverts to the starting materials. This is observed using overnight ^{13}C NMR detection in that the solution produces a mixture of the product and Pt(hfac)$_2$. Upon 300 nm irradiation and in the presence of excess ethylene, Pt(hfac)$_2$(η^2-C_2H_4) will undergo further reaction perhaps forming cationic complex $[Pt(C_2H_4)_4]$(hfac)$_2$, with both hfac ligands displaced by ethylene.

The olefin adduct reported herein is quite unstable in solution, and others have had difficulty isolating it.[20] In our hands, the product of Pt(hfac)$_2$ with ethylene is only isolable if an excess of ethylene is maintained during the preparation. The stability of several other adducts prepared from different platinum(II)

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[13] We proposed that the structure of this product is $[Pt(C_2H_4)_4]^{2+}(hfac)_2^{2-}$ from ^{1}H NMR and ^{19}F NMR evidence. Our conclusion from the spectra is that both hfac ligands are dissociated while ethylene remains coordinated to Pt. A referee has suggested that this product could be the known $Pt(C_2H_4)_3$. Because the ^{1}H NMR spectrum has been reported,[14] we are certain that this product is not present.

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complexes decreases in the order $Pt(hfac)_2 > Pt(tfac)_2 > Pt(acac)_2$ consistent with the catalytic activity of these complexes in hydrosilylation,[3] where $Pt(hfac)_2$ has the lowest catalytic activity. The ability to form stable products decreases the catalytic activity of $Pt(hfac)_2$ in the hydrosilylation process.

Based on these studies, we have demonstrated that a five-coordinated complex is formed in the photoreactions of $Pt(hfac)_2$ with terminal olefins. Steric effects likely cause the failure of the photoreaction of internal olefins with platinum(II) β-diketonate. This is also observed in the photoactivated hydrosilylation reactions.

Isolation of the five-coordinated complex $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ makes it possible to study the activity of $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ as the precatalyst for hydrosilylation. Using $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ as the catalyst, the hydrosilylation of triethylsilane with vinylsilane was observed after 2 h at room temperature without irradiation. Study of the activity of $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ as a catalyst for hydrosilylation reaction is continuing.

Experimental Section

Materials and Instruments. $Pt(hfac)_2$ and $Pt(tfac)_2$ were synthesized.[21] $Pt(acac)_2$ was purchased from Alfa Chemical Co. All other reagents were purchased from Aldrich Chemical Co. and used as received. ^1H and ^{19}F NMR spectra were recorded in $CDCl_3$ solution with a Varian Gemini 200 MHz and a Unity Plus 400 MHz, respectively. Chemical shift values are expressed in ppm relative to tetramethylsilane for ^1H and CF_3Cl for ^{19}F. UV−vis absorption spectra were recorded using a Hewlett-Packard 8452A diode array UV−vis spectrophotometer. GC/MS spectra were obtained on a Shimadzu GC/MS-QP5050 mass spectrometer coupled to a GC-17A (Restek ST1−5 column 30 m × 0.25 mm × 0.25 μm). Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analysis was obtained from Atlantic Microlab Inc. Irradiations were carried out on solutions in borosilicate glass containers in a Rayonet PRP-100 photochemical reactor equipped with a jacketed beaker (Pyrex). 8W × 16 RPR-3500 and 3000 Å lamps from Southern NE Ultraviolet Co. were used.

The quantum yield of disappearance of $Pt(hfac)_2$ in the presence of excess C_2H_4 was determined by measuring the amount of $Pt(hfac)_2$ that had reacted at a constant light intensity in a given period of time. The latter was measured by monitoring the decrease of the 350 nm absorption in the absorption spectrum of the reaction mixture. The light flux was measured using a benzophenone benzhydrol actinometer.[22]

Single-Crystal X-ray Diffraction Analysis. Preliminary examination and data collection were carried out with Mo Kα using a Bruker AXS SMART platform diffractometer.[23] Intensity data were collected using three different ϕ settings and 0.3° increment ω scans, $2\theta < 56°$, which corresponds to more than a hemisphere of data. Data integration was carried out with SAINT,[23] and corrections for absorption and decay were applied using SADABS.[24]Solution was by direct methods[25] and refinement by full matrix least squares [25] on F^2 using all 1855 unique data. The final refinement included anisotropic thermal parameters for non-hydrogen atoms and all hydrogen atoms with isotropic thermal parameters. The refinement converged to $wR2 = 0.064$ (for F^2, all data) and $R_1 = 0.025$ (F, 1772 reflections with $I > 2\sigma(I)$).

General Procedure for Irradiation and Product Detection. A 4 mL vial containing 70 mg of platinum complex in 3 mL of CH_2Cl_2 solution was degassed with dry argon for about 10 min. Ethylene or propylene was bubbled in for 10 min while the vial was cooled in a dry-ice−acetone bath. After warming to room temperature, the sealed vial was irradiated at ambient temperature in a Rayonet reactor. The same procedure was used for the NMR experiment and UV−vis absorptions experiments in which either a $CDCl_3$ solution in an NMR tube or a cuvette was used.

$Pt(hfac)_2(\eta^2\text{-}C_2H_4)$: The reaction mixture was irradiated at 350 nm for 2 h. After evaporation of the solvent, a yellow solid mixture of $Pt(hfac)_2$ and $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ was obtained. $Pt(hfac)_2(\eta^2\text{-}C_2H_4)$ was isolated by recrystallization from hexane and CH_2Cl_2 solution. X-ray quality crystals were prepared by slowly evaporating a CH_2Cl_2 solution in the presence of hexane vapor at low temperature. Melting point is 128−129 °C. ^1H NMR($CDCl_3$, 200 MHz): δ 6.15(s, 1 H) δ 4.06 (singlet with satellites, 4 H, $J = 84$ Hz). ^{19}F NMR ($CDCl_3$, 400 MHz): δ −74.0 (s, 3 F), δ −76.5 (s, 3 F). Anal. Calcd: C, 22.6; H, 0.95. Found: C, 22.43; H, 1.02.

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Supporting Information Available: Changes in the ^1H NMR spectra occurring during the reaction and a summary of the crystallographic data are reported, as well as the changes in the ^1H NMR spectra occurring during the reaction when $Pt(hfac)_2$ is irradiated at 300 nm in the presence of excess ethylene in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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