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Photochemical reactions of platinum(II) bis(acetylacetonato) with nitrogen containing Lewis bases

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Abstract

Upon 300 nm irradiation, the reactions of platinum(II) bis(acetylacetonato) with pyridine, piperidine, 2-picoline, 3-picoline and 4-picoline result in two types of stable complexes: Pt(acac)(γ-acac)base and Pt(γ-acac)$_2$base$_2$. These complexes have been characterized by ^{1}H NMR, ^{13}C NMR, IR, GC–MS (DIP), UV–vis absorption spectroscopy and crystal X-ray diffraction studies. The quantum yields of disappearance of Pt(acac)$_2$ and the first-order rate constants have also been measured.

Keywords: platinum(II) bis(acetylacetonato); nitrogen containing Lewis bases; photochemical reactions.

In addition to coordinating to the central metal in a bidentate fashion through two oxygen atoms, the acetylacetonato (abbreviated as acac) ligand also forms complexes in a unidentate way via the central (γ-)carbon (abbreviated as γ-acac). Thermal reactions of platinum(II) bis(acetylacetonato) and Pt(acac)$_2$ with Lewis bases, such as triphenylphosphine and pyridine, have been studied by Yamamoto et al.[1,2] As one of these Lewis bases coordinates with Pt, one enol type bidentate acac ligand rearranges to a diketo type unidentate γ-acac.

In this paper, we report on the photochemical reactions of Pt(acac)$_2$ in pyridine, piperidine, 2-picoline, 3-picoline and 4-picoline solutions (abbreviated as base), Scheme 1. We obtained similar products from the photochemical reactions as found in Yamamoto's studies.

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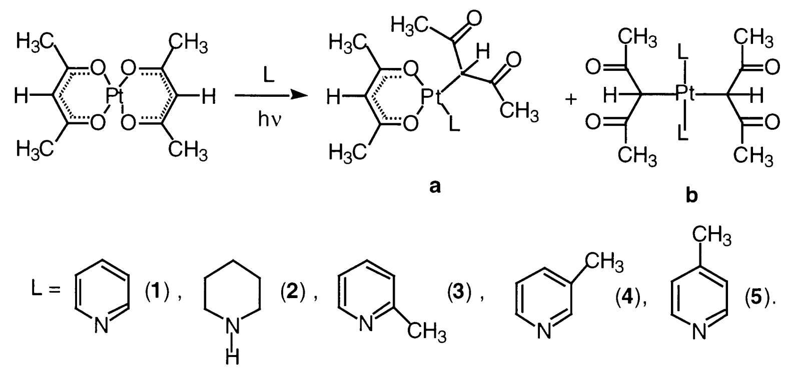
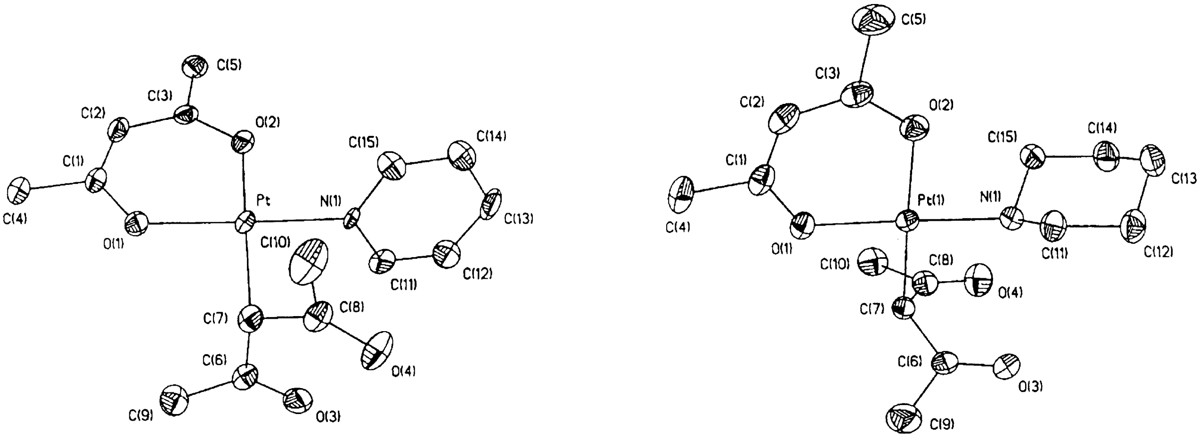


Scheme 1.

Typically, a solution of Pt(acac)$_2$ (0.0275 g, 0.07 mmol) in pyridine (3 mL) was irradiated at 300 nm in a Rayonet photochemical reactor (*T*% 40°) for 2 h after being purged with argon for 5 min. The light yellow solution turned to brown. Hexane (20 mL) was added to the solution to yield a brown oil, which was separated, washed with hexane and dried under vacuum. Separation by flash chromatography gave two products: (2,4-pentanedionato-C^3)(2,4-pentanedionato-O,O') pyridineplatinum(II), Pt(acac)(γ-acac)pyridine (**1a**) and bis(2,4-pentanedionato- C^3) bispyridineplatinum(II), Pt(γ-acac)$_2$pyridine$_2$ (**1b**). Two corresponding complexes were also obtained in the piperidine case, while only type **a** complexes were separated when 2-, 3-, and 4-picoline were used. Without irradiation, the same reaction mixtures afford none of these products under similar reaction conditions.

Pt(acac)(γ-acac)pyridine (**1a**) and Pt(γ-acac)$_2$pyridine$_2$ (**1b**) were characterized by ^{1}H and ^{13}C NMR. Structural assignments were made by comparing the spectra with the reported data for identical complexes formed by other pathways.[2] The two methyl groups in the acac ligand are non-equivalent in complex **a**, but are equivalent in complex **b**. The methine proton of the γ-acac ligand has the characteristic singlet with satellite peaks due to the coupling with ^{195}Pt. The coupling constant $|^2J(^{195}\text{Pt–H})|$ is 130 Hz and the chemical shift of this methine proton is 5.04 ppm for **1a** and 102 Hz and 4.26 ppm, respectively, for **1b**. In the IR, γ-acac has two characteristic carbonyl bands at 1676 and 1650 cm^{-1}, while the acac ligand shows absorptions at 1563 and 1523 cm^{-1}. These results are consistent with the literature.[2]

X-ray quality crystals of **1a** and **2a** were prepared by slowly evaporating a CH$_2$Cl$_2$ solution in the presence of hexane vapor at low temperature. These two complexes crystallized in the triclinic space group $\bar{P}$ and the geometry about the Pt atom is best described as distorted square planar. In the case of **1a**, there are two crystallographic independent molecules in the asymmetric unit, designated as molecule A and molecule B. The two coordination modes of the acetylacetonato ligands are also confirmed. In **2a**, the piperidine ring has a chair conformation with the nitrogen atom bound to the Pt atom in an equatorial manner such that the ring lies perpendicular to the square plane of the Pt coordination polyhedra. ORTEP drawings for **1a** and **2a** are shown in Fig. 1. Detailed results of the X-ray study will be published elsewhere.



1a **2a**

Figure 1. ORTEP drawings for **1a** (molecule A) and **2a** (30% probability ellipsoids)

Because these bases absorb strongly around 250–300 nm, we were unable to observe detailed UV–vis absorption changes in this region. In the case of pyridine, we observed the disappearance of the 344 nm band of the Pt(acac)$_2$ and the appearance of a new absorption at 380 nm. The latter disappeared with continuous irradiation. In the case of 3-picoline, a new absorption at 490 nm was observed and this also disappeared upon further irradiation. These new absorptions are clearly those of reaction intermediates. In other cases, the disappearance of the 344 nm band of Pt(acac)$_2$ is accompanied by the formation of permanent products.

The UV–vis absorption spectra of the products, recorded in CH_2Cl_2 solution, are reported in Table 1. Characteristically, the complexes have an absorption maximum at 234–238 nm with a molar extinction coefficient (ε) of approximately 10^4 M^{-1} cm^{-1}, and another absorption maximum at 272–300 nm with a smaller absorption coefficient. In the case of Pt(γ-acac)$_2$pyridine$_2$, **1b**, an additional shoulder at 260 nm was detected.

Table 1
Yields, UV–vis absorption data of the products, Pt(acac)$_2$ disappearance quantum yields and first-order rate constants of the reactions

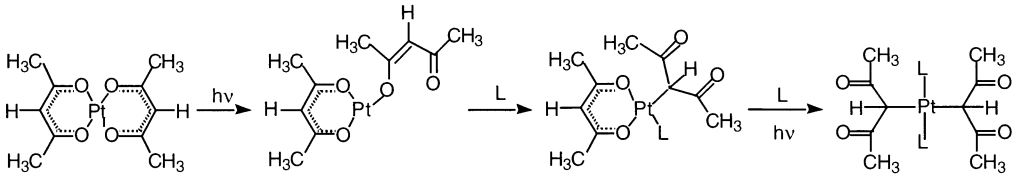
	Pt(acac)(γ-acac)L		Pt(γ-acac)$_2$L$_2$		ϕ	$10^3 \times k$ (s^{-1})
	Yield (%)	λ_{max} ($\varepsilon \times 10^{-4}$) (nm, M^{-1} cm^{-1})	Yield (%)	λ_{max} ($\varepsilon \times 10^{-4}$) (nm, M^{-1} cm^{-1})		
Pyridine	60	238 (1.0), 290 (0.55)	15	236 (1.4), 260 (1.1), 282 (0.80)	0.050	2.2
Piperidine	36	236 (0.82), 300 (0.31)	32	234 (1.1), 294 (0.24)	0.041	1.4
2-Picoline	49	238 (1.7), 272 (1.2)	–	–	0.026	0.95
3-Picoline	60	238 (1.5), 274 (0.96)	–	–	0.021	0.85
4-Picoline	50	236 (1.5), 278 (0.93)	–	–	0.016	0.37

The quantum yields of disappearance of $Pt(acac)_2$ in solution were determined by measuring the amount of $Pt(acac)_2$ that had reacted at a constant light intensity in a given period of time. The latter was measured by monitoring the decrease of the 344 nm band in the absorption spectrum of the reaction mixture. 2-Hexanone was used as an actinometer. The pseudo first-order rate constants were also measured according to Eq. (1). A is the optical density at 344 nm. These data are collected in Table 1.

$$\ln[A_0/A] = \ln\{[\mathrm{Pt(acac)_2}]_0/[\mathrm{Pt(acac)_2}]_t\} = kt \tag{1}$$

Excitation of group 10(II) β-diketonates gives rise to the weakening of the metal–oxygen bond, leading to bond dissociation in many cases. This has been evidenced by such observations as decomposition with the formation of colloidal metal and β-diketonates,[3,4] as well as photoisomerization[4] of the ligand. These reactions allow the application of these complexes in photoactivated catalysis.[5–8] Therefore, in this study, the quantum yields of disappearance of $Pt(acac)_2$ reflect the relative efficiency of the amines to trap the coordinately unsaturated intermediate formed by Pt–O bond cleavage. From Table 1, pyridine is more efficient than piperidine in this process, although the latter is a stronger base. This is understandable since the reactivity of an entering group in substitution reactions is not determined by its basicity but by its polarizability.[9] Since the amines are also used as solvents in these reactions, it is difficult to predict reactivity by comparing any one set of their parameters. The pseudo first-order rate constants bear the same trend as is found in the quantum yields, thus revealing the kinetic characteristics of the processes.

The mechanism proposed for these reactions is shown in Scheme 2. Excitation by UV irradiation causes Pt–O bond dissociation to form a 3-coordinate intermediate with a 'dangling' acac ligand. This was also proposed by Lewis et al. in their study of photochemistry of group 10(II) β-diketonates.[4] In fact, in that study, similar complexes such as **a** have been assigned as the primary photoproducts in the presence of hydrosilanes or olefins. In Scheme 2, the timing of the conversion of acac to γ-acac and the entering of the displacing group into the coordination sphere of Pt is not clear.



Scheme 2.

Studies of photochemical reactions of Pt(II) β-diketonates with other labile additives are under way.

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