

Preliminary communication

**ISOLATION OF THE YLIDIC FORM OF AN ENAMINE. REACTION OF
N-(1-BUTENYL)PYRROLIDINE WITH ZEISE'S DIMER**

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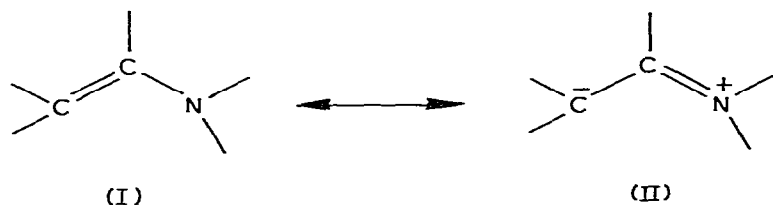
Summary

Enamines containing tertiary nitrogens react with Zeise's dimer to give air-stable platinum complexes containing the ylidic resonance form of the enamine coordinated to platinum through the formally anionic carbon. For the complex derived from *N*-(1-butenyl)pyrrolidine this structure has been established by infrared and NMR (¹H, ¹³C) data. The complex also contains coordinated pyrrolidine, formed by cleavage of the butenylpyrrolidine precursor.

In the presence of certain platinum complexes, α,β -unsaturated ketones such as mesityl oxide undergo a double-bond migration to form the β,γ -unsaturated isomers, which are isolated as complexes containing the ketone coordinated to platinum through both the olefin and the carbonyl oxygen [1]. The apparent driving force for this reaction is steric, the 5½-membered ring which results being considerably less strained than the 4½-membered ring which would result from direct coordination of the α,β -unsaturated ketone. Similar steric constraints are apparently operative with unsaturated amines. Thus, 2-allylpyridines readily form chelate complexes with platinum which contain the 5½-membered ring [2], but allylamines form non-chelated dimeric platinum complexes [3]. Apparently, formation of the allylamine-bridged dimer is favored over the sterically demanding 4½-membered ring monomeric chelate complex.

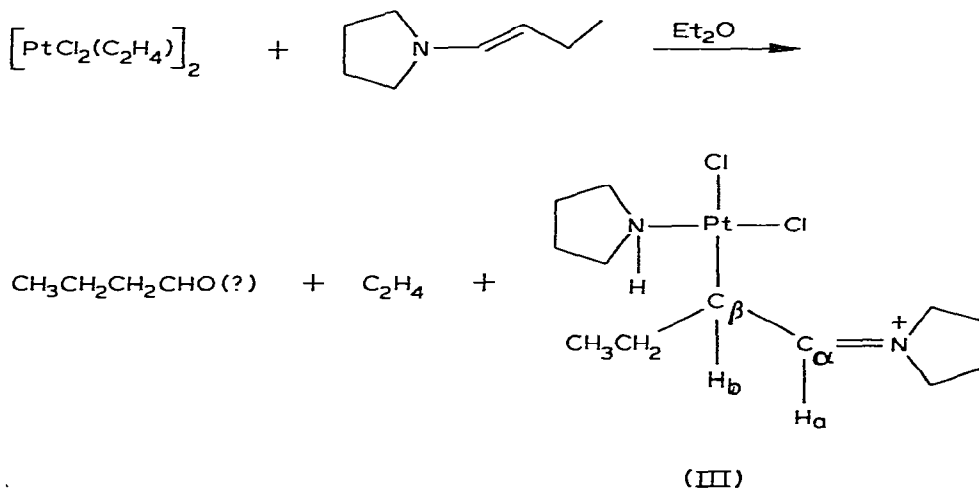
α,β -Unsaturated amines (enamines) are even more sterically constrained, and chelation would appear impossible unless significant isomerization occurs. Furthermore, because of the electronic structure of enamines it is not easy to predict how they would coordinate to transition metals. We have consequently initiated a study of the interaction of simple enamines with platinum complexes. Enamines are both structurally and synthetically versatile [4], and could in principle bind to transition metals in several ways.

Enamine I could coordinate as a monodentate nitrogen donor, as an η^2 -olefin donor, or, possibly, as an η^3 -heteroallylic system. To the extent that the resonance form II is available, an η^1 -ylidic complex might be possible.



Surprisingly, there have been few reports of the interaction of enamines with transition metal complexes.

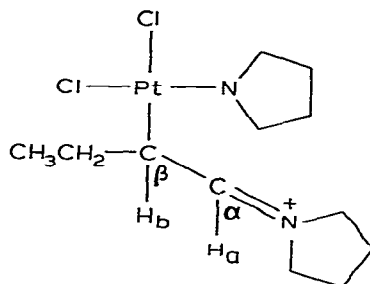
Reaction of Zeise's dimer [5], $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, with *N*-(1-butenyl)pyrrolidine*, in dry ether produces bright yellow air-stable crystals which have elemental analyses** consistent with the formulation $\text{PtCl}_2(\text{pyrrolidine})(N\text{-(1-butenyl)pyrrolidine})$. On the basis of spectroscopic evidence, we formulate this complex, III, as containing the ylidic form of the enamine, coordinated through the formally anionic carbon.



The ^1H NMR spectrum (250 MHz, CDCl_3 solution) exhibits resonances attributable to both coordinated pyrrolidine and the pyrrolidine fragment of the ylidic enamine. In addition, there are resonances due to the ethyl protons (t, 3H, δ 1.10 ppm, $J(\text{HH})$ 7.7 Hz; m, 2H, δ 2.0 ppm) and protons H_a (d, 1H, δ 7.55 ppm, $J(\text{H}_a\text{H}_b)$ 11.5 Hz, $J(\text{PtH}_a)$ 38 Hz) and H_b (dt, 1H, δ 3.92 ppm, $J(\text{H}_b\text{CH}_2)$ 6.5 Hz, $J(\text{H}_b\text{H}_a)$ 11.5 Hz, $J(\text{PtH}_b)$ 91 Hz). The very large chemical shift for H_a is consistent with an environment having significant positive charge, as in the proposed structure. The large value of $J(\text{PtH}_b)$ suggests the presence of a platinum-carbon σ bond. For comparison, η^1 -allylplatinum complexes, $\text{PtC}(\text{H}_\alpha)\text{C}=\text{C}$, have $J(\text{PtH}_\alpha) \approx 107$ Hz [7]. Similar system with pyridinium substituents have $J(\text{PtH})$ in the same range. Thus, α -*N*-ylides $\text{PtC}(\text{H}_\alpha)\text{N}^+$ have $J(\text{PtH}_\alpha) \approx 112$ Hz [8] and β -*N*-ylides $\text{PtC}(\text{H}_\alpha)\text{CN}^+$ have

*All enamines used were prepared by the methods of Stork [6].

**Anal. Found: C, 31.04; H, 5.27; N, 5.92; Pt, 41.99; Cl, 15.78. $\text{PtCl}_2\text{C}_{10}\text{H}_{23}\text{N}_2$. calcd.: C, 31.10; H, 5.00; N, 6.08; Pt, 42.29; Cl, 15.43%.



$J(\text{PtH}_\alpha) \approx 80 \text{ Hz}$ [9]. III, which has similarities to all of these compounds, has $J(\text{PtH})$ in the same range.

Alternative structures can be ruled out on the basis of NMR and IR data. An olefinic complex would be expected to exhibit an infrared C=C stretch below 1600 cm^{-1} , but III has a strong absorption at 1615 cm^{-1} , comparable to that observed [7] for η^1 -allyl complexes. Similarly, ^1H chemical shifts and Pt-H coupling constants are well outside the range generally observed for olefin complexes of platinum. An η^3 -allylic structure is also inconsistent with both the infrared ($\nu(\text{CCN})$ expected at ca. 1500 cm^{-1}) and NMR ($J(\text{PtH})$ expected to be $< 50 \text{ Hz}$) data. Because two absorptions attributable to platinum-chloride stretching are observed, we have assigned the *cis*-stereochemistry to platinum.

^{13}C NMR data also support the proposed structure. In particular, the large value of $J(\text{PtC}_\beta)$ 359 Hz and the C_β chemical shift of 37.05 ppm are consistent with a Pt-C σ bond. Chemical shifts and platinum-carbon coupling constants for the methylene carbon (δ 16.76 ppm, $J(\text{PtCH}_2)$ 51 Hz) and C_α (δ 154.52 ppm, $J(\text{PtC}_\alpha)$ 46 Hz) are as expected for the proposed structure and charge distribution.

There are only two other reports of enamine complexes of platinum. Vitagliano et al. [10] have recently reported that β -ammonioalkenyl complexes of platinum, derived from the addition of primary aromatic amines to a platinum-dimethylallene complex, rearrange to form η^2 -enamine complexes in which the enamine coordinates through the olefinic π -system. Ponti et al. [11] have examined the reactions of 1,1-bis(dimethylamino)ethylene and of 1,3-dimethyl-2-methylimidazoline with Zeise's dimer. In each case, mixtures resulted which contained both the enamine coordinated through the olefinic π -system (η^2) and also the ylidic resonance form coordinated through the formally anionic carbon (η^1), as in III. Although the factors which favor ylidic, rather than olefinic, bonding are not obvious, it is clear that a range of behavior may be observed.

The pyrrolidine ligand clearly is formed by cleavage of the enamine starting material. Although the reaction was carried out under nominally dry conditions (N_2 atmosphere, ether dried over sodium), it is possible that enough moisture was present for hydrolysis of the enamine to occur. If carried out in the presence of pyridine, the reaction produces the same ylidic compound, but with pyridine coordinated in place of pyrrolidine. Spectroscopic data suggests that complexes analogous to III are also formed in the reactions of

N,N,2-trimethylpropenylamine and 1-piperidino-1-isobutene with Zeise's salt, although these complexes have not yet been thoroughly characterized.

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