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(4) The success of these reactions is critically dependent upon the purity of the starting materials and solvents. Matheson Freon-11 and Fisher carbon tetrachloride (99 mol %) could be used without further purification.

(5) All photoproducts were characterized spectroscopically and by elemental analysis of their acetate derivatives. The photoproducts and/or their acetates had the following data. **1a:** mp 101.9–102.5 °C; IR (KBr) 3340, 1730 cm^{-1}; NMR (Unisol) (δ, ppm) 3.98–4.16 (m, 2 H), 4.60–5.10 (m, 1 H). Acetate of **1b:** mp 109–110 °C; IR (KBr) 1735 (lactone) 1758 cm^{-1} (acetate); NMR ($CDCl_3$) (δ, ppm) 4.59 (dd, $J = 4$, 10 Hz, 1 H), 5.57 (d, $J = 4$ Hz, 1 H). Acetate of **3**: mp 63.5–64.0 °C; IR (KBr) 1760 cm^{-1}; NMR ($CDCl_3$) (δ, ppm) 3.60 (complex, 5 H). Acetate of **4**: mp 82.2–82.7 °C; IR (KBr) 1755 (acetate), 1735 cm^{-1} (sh) (lactone and α-acetoxy ketone); NMR ($CDCl_3$) (δ, ppm) 2.22–3.01 (m, 4 H).

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Synthesis of η^2-Coordinated Enamines by Amination of a Platinum(II) Coordinated Allene. A Chemical and X-ray Diffraction Study

Sir:

During our studies on the reaction of amines with Pt(II) coordinated allenes,[1] we observed a novel reaction of primary aromatic amines with 1,1-dimethylallene (DMA), leading to η^2-coordinated secondary enamines. To our knowledge this observation represents the first example of successful trapping of a fairly unstable enamine by a transition metal ion. Since the ligand produced can be easily displaced from the metal without decomposition, the method can be useful for synthetic purposes, even if at present it is hard to speculate about its applicability to other metal ions. We report here our preliminary results in this field, including the first structural characterization of a metal–enamine η^2 complex.

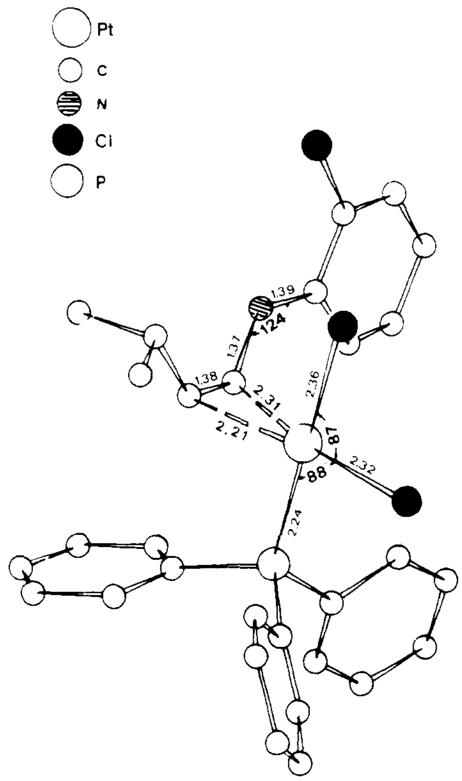
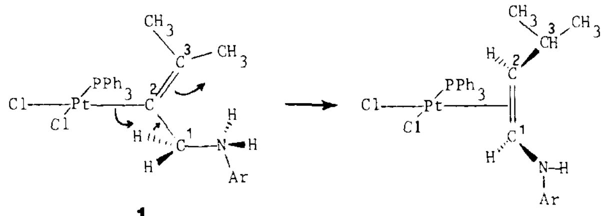


Figure 1. Molecular structure of *cis*-dichloro-η^2-[(*Z*)-2-chloro-*N*-(3-methylbut-1-enyl)benzenamine](triphenylphosphine)platinum(II).

The β-ammonioalkenyl complexes (**1**) obtained upon addition of primary aromatic amines to *cis*-$PtCl_2(DMA)(PPh_3)$[1] are nearly insoluble in the reaction solvent ($CHCl_3$ or CH_2Cl_2) and indefinitely stable after crystallization. However, they undergo a rather unexpected rearrangement if their precipitation is slowed down by the use of larger amounts of solvent, giving the corresponding enamine complexes (**2**). For instance, on addition of an equimolar amount of 2-chloroaniline to a solution of 1.0 mmol of $PtCl_2(DMA)(PPh_3)$ in 20 mL of $CHCl_3$ while the mixture is kept at room temperature for 8 h, a fairly soluble yellow compound (**2**, Ar = 2-ClC_6H_4), mp 151–153 °C, is obtained in ~80% yield. The molecular formula **2** was inferred by the elemental analysis and the IR[2] and ^1H, and ^{13}C NMR spectra of the compound[3] and the ^1H NMR spectrum of the displaced enamine ligand,[4] the ultimate evidence being furnished by the results of an X-ray diffraction analysis. The ^1H NMR spectrum (270 MHz), recorded at room temperature, shows very broad signals for the isopropyl, NH, and olefinic protons. At low temperature (−30 °C) the spectrum becomes fully resolved, displacing two equally intense sets of signals for each CH and NH proton and for each methyl group.[3] The observed spectra indicate the presence in solution of two slowly interconverting isomers in equal abundance, most likely rotamers about the Pt-‖ axis.[5]



1

2

Treatment of **2** with sodium cyanide in chloroform solution results in the displacement of the coordinated organic moiety $ArNHCH{=}CHCHMe_2$ without decomposition or enamine–imine isomerization,[6,7] as evidenced by the ^1H NMR spectrum of the resulting colorless solution.[4]

The structure of **2** (Ar = 2-ClC_6H_4) was elucidated by a three-dimensional X-ray structural analysis.[8] Figure 1 shows the molecular structure as viewed along the *c* axis; some internal geometrical parameters are also indicated. The complex displays the usual square-planar arrangement of the ligands

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around the platinum atom, the deviations from planarity being <0.01 Å. The enamine is bound to platinum through the olefinic C=C double bond, the midpoint of the C=C bond being ~0.20 Å displaced from the principal coordination plane. The double bond has a cis configuration and is nearly orthogonal to the coordination plane. The nonhydrogen atoms of the moiety CH—CH=CH—NH—C lie almost in a plane (deviations from planarity are <0.04 Å). The phenyl group forms an angle of ~10° with this plane, which is tilted of ~20° with respect to the normal from Pt to the double bond. Some relevant bond lengths follow: C(arom)—N = 1.39 (2), C(olef)—N = 1.37(2), C=C = 1.38 (2) Å; the bond angle C-N-C is 124.4 (5)°. The relatively short distance C(olef)—N [cf. N—Me = 1.48 (4) Å in 4-nitro-*N,N*-dimethylaniline[9]] is consistent with a substantial amount of conjugation of the nitrogen atom with the carbon-carbon double bond,[10] as well as with the aromatic ring. The Pt—C bond lengths are among the largest observed for monoolefin complexes[11,12] and are significantly different from each other (2.213 ± 0.014 and 2.314 ± 0.016 Å; see Figure 1). A comparable difference has been found in other Pt(II) complexes of olefinic compounds containing electron-releasing substituents, i.e., a *p*-(*N,N*-dimethylamino)styrene,[13] a vinyl alcohol,[12] and two vinyl ether complexes,[14] and is also consistent with the negative polarization of the C(2) atom arising from the quoted conjugation.[12,15]

We have observed the quoted isomerization β-ammonioalkenyl η^1 complex → η^2-enamine complex for a variety of primary aromatic amine derivatives; however, we have found a strong dependence of the isomerization rate on the basicity of the amine, a poorer basicity favoring the rearrangement reaction. As two limiting cases, the rearrangement was not observed for the *p*-anisidine (pK_a = 5.34[16]) derivative, whereas for the *p*-nitroaniline (pK_a = 1.0[16]) derivative only the η^2-enamine complex was isolable. Moreover, by using N-deuterated 2-chloroaniline the enamine complex specifically deuterated at the isopropyl secondary carbon atom was obtained. These findings suggest that the rearrangement very likely proceeds through the attack of an acidic N-H hydrogen of the zwitterionic complex (**1**) on the C(3) carbon atom with successive proton transfer from the C(1) atom to the C(2) atom and reconstitution of the double bond between the C(1) and C(2) atoms. It should be noted that the stereospecificity of this reaction leading to a coordinated cis olefin is also consistent with the proposed intramolecular mechanism.

Acknowledgment. This work was supported by the Consiglio Nazionale delle Ricerche. We thank the C.I.M.C.F. of the University of Naples for the access to the Bruker WH-270 spectrometer. We also wish to thank Dr. G. Zannotti for helpful suggestions in X-ray data collection.

Supplementary Material Available: Table of the atomic coordinates and thermal parameters for *cis*-dichloro-η^2-[(*Z*)-2-chloro-*N*-(3-methylbut-1-enyl)benzenamine](triphenylphosphine)platinum(II) (1 page). Ordering information is given on any current masthead page.

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(3) $PtCl_2(PPh_3)(ClC_6H_4NHCH^a{=}CH^bCH^cMe_2)$, isomers A and B. ^1H NMR (270 MHz, $CDCl_3$), δ (ppm): T = 298 K, 0.86 (d, 3 H), 1.47 (d, 3 H), 2.82 (br, 1 H), 3.23 (br, 1 H), 5.82 (br, 0.5 H), 6.04 (br, 0.5 H), 6.9–8.4 (20 H); T = 243 K, for isomer A (excluding aromatic protons), 0.82 (d, Me), 1.47 (d, Me), 3.2 (m, H^c), 2.77 (ddd, H^b, $J_{H^b-H^c}$ = 10.5, $J_{H^b-H^a}$ = 5.9, J_{H^b-P} = 3.5 Hz), 5.99 (dd, H^a, $J_{H^a-H^b}$ = 5.9, J_{H^a-NH} = 13 Hz); for isomer B (excluding aromatic protons), 0.86 (d, Me), 1.43 (d, Me), 2.86 (m, H^c), 3.21 (ddd, H^b, $J_{H^b-H^c}$ = 9.8, $J_{H^b-H^a}$ = 12, J_{H^b-P} = 7 Hz), 5.81 (d, NH, J_{NH-H^a} = 12.5 Hz), 7.65 (H^a, obscured by the aromatic proton signals, but revealed by double irradiation techniques). ^{13}C NMR (67.88 MHz, $CDCl_3$), δ (ppm) (excluding aromatic carbons): T = 243 K, 20.23 (Me), 22.72 (Me), 23.71 (Me), 25.23 (Me), 26.43 ($C^c{}_A$), 30.41 ($C^c{}_B$), 65.88 ($C^b{}_A$), 71.70 ($C^b{}_B$), 110.41 ($C^a{}_A$), 115.10 ($C^a{}_B$). In the ^1H NMR spectra the assignments were made with the aid of decoupling experiments and through selective deuteration of the NH and/or H^c protons. In the ^{13}C NMR spectra the assignments were made with the aid of selective ^1H-decoupling techniques. The ^{195}Pt satellite peaks of the olefinic protons were observable as broad bands ($J_{H^b{}_A-Pt} \simeq 70$, $J_{H^b{}_B-Pt} \simeq 55$, $J_{H^a{}_A-Pt} \simeq 55$ Hz). The satellite peaks of the olefinic carbons disappeared in the noise and were not detected.

(4) $ClC_6H_4NHCH^a{=}CH^bCH^cMe_2$. ^1H NMR (270 MHz, $CDCl_3$), δ (ppm): 1.07 (d, 2 Me), 2.60 (m, H^c), 4.49 (dd, H^b), 6.16 (d, br, NH), 6.27 (dd, H^a), 6.70 (dt, 1 H), 6.86 (dd, 1 H), 7.15 (dt, 1 H), 7.29 (dd, 1 H).

(5) This hypothesis appears to be the only consistent with the spectral and analytical data. In fact the compound was found to be monomeric and undissociated in solution by molecular weight determination [calcd 724, found (osmometry) 732], and the possibility of a π–σ rearrangement such as $[PtCl_2(PPh_3)\text{-}\eta^2\text{-}(ArNHCH{=}CHCHMe_2)] \rightleftharpoons [PtCl_2(PPh_3)\text{-}\eta^1(ArN^+H{=}CHC^-HCHMe_2)]$ (cf. Tsutsui, M.; Courtney, A. *Adv. Organomet. Chem.* **1977,** *16*, 241–252) can be ruled out on the basis of the ^{13}C chemical shifts of the two isomers (the conversion π-bonded sp^2 carbon → σ-bonded sp^3 carbon is expected to result in an upfield shift in the range 15–80 ppm; cf., e.g., Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1973,** *60*, 427). In addition the IR spectra of the compound in the solid state (single crystals in Nujol mull) and in solution ($CHCl_3$) are nearly identical, supporting the conclusion that only a conformational equilibrium is involved in solution.

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(8) Crystals are orthorhombic, space group *Pbca*; a = 21.199 (10), b = 17.550 (10), c = 15.567 (7) Å; V = 5791.6 Å^3; Z = 8; d(calcd) = 1.66, d(exptl) = 1.64 g/cm^3. Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer (Mo Kα radiation) using the ϑ–2ϑ scan method. The positional and anisotropic thermal parameters of all atoms were refined by full-matrix least-squares calculations. The resulting discrepancy index is R_F = 0.059 for the 5097 reflections having $I \geq 3\sigma(I)$.

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$^2B_2$ Benzoyloxy, a Delocalized σ Radical

Sir:

In connection with other work we have needed to know the spin distribution in the ground state of benzoyloxy radical.[1] Theory alone is of little help. The "doublet-instability" problem, which afflicts calculations on the allyl radical even at the Hartree-Fock limit,[2] is compounded in heteroatom-containing analogues by alternative Σ and Π ground states.[3] Calculations including limited configuration interaction seem to avoid the former problem, but do not permit a clear choice of ground state, since they predict Σ–Π gaps of <10 kcal/mol for many heteroallylic radicals.[4] Calculation of formyloxy by STO 4-31G CI with geometry optimization predicts that the $^2A_2$ (Π) ground state of C_{2v} symmetry lies only 1.4 kcal/mol below the $^2A'$ (Σ) state of C_s symmetry.[4]

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