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NUCLEOPHILIC ATTACK OF THE ACETYLACETONATE CARBANION ON THE NITRILE CARBON IN trans-$[\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$: X-RAY STRUCTURE OF THE PRODUCT N-ACETYL-β-KETOAMINE CHELATE

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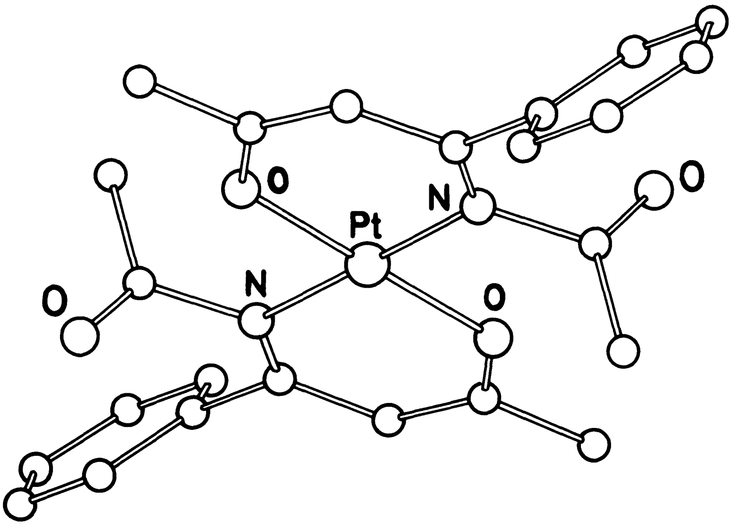
trans-Dichlorobis(benzonitrile)platinum(II) reacted with thallium(I) acetylacetonate in dichloromethane at room temperature to give three kinds of yellow products. One of them was obtained as fine crystals and revealed by an X-ray analysis to be N-acetyl-β-ketoamine chelate, trans-$[\overline{\text{Pt}(\text{N}(\text{COCH}_3)=\text{C}(\text{C}_6\text{H}_5)\text{CH}=\text{CO}}\text{CH}_3)_2]$.

The nitrile group coordinated to a metal ion readily reacts with nucleophiles such as water, alcohols, and amines to yield the corresponding carboxamide, iminoether, and amidine, respectively.1) A similar reaction with the acetylacetonate carbanion has not yet been examined, although the nucleophile is known to add to the coordinated olefins2) and imines.3)

trans-Dichlorobis(benzonitrile)palladium(II) has been widely used as a starting material for the preparation of organopalladium(II) complexes because of its ease of displacement of the coordinated nitrile molecule, but the corresponding platinum(II) complex is rather substitution-inert and reacts with an acetylacetonate anion without cleavage of the metal-nitrogen bond. When, under a nitrogen atmosphere, trans-dichlorobis(benzonitrile)platinum(II)4) was allowed to react with a twice molar amount of thallium(I) acetylacetonate in dichloromethane at room temperature, three kinds of yellow products were isolated from the reaction mixture after filtration of thallium(I) chloride produced. In this letter, we report on the X-ray structure of one of these products separated by means of thin-layer chromatography, together with its IR and NMR spectral characterization.

The elemental analysis of the compound: Found; C, 48.8; H, 4.04; N, 4.63%; mol wt, 580 in CH_2Cl_2. Calcd for $C_{24}H_{24}N_2O_4Pt$: C, 48.1; H, 4.04; N, 4.68%; mol wt, 600. Crystal data: monoclinic, $a = 8.426(2)$, $b = 9.347(3)$, $c = 15.293(9)$ Å, $\beta = 111.62(4)°$, $U = 1119.8(9)$ Å^3, $D_c = 1.77$ g·cm^{-3}, $Z = 2$, μ(MoKα) = 66.2 cm^{-1}, space group $P2_1/c$.

Intensity data were collected on a diffractometer using graphite-monochromated MoKα radiation. A total of 1433 reflections with $I > 3\sigma(I)$ were classified as ovserved. The structure was solved by the heavy-atom method and refined by a least-squares method to an R value of 3.89%, the anisotropic temperature factor being used for the Pt atom.



As is seen in the Figure showing a perspective view, the compound is bis(N-acetyl-β-ketoamine) chelate of platinum(II), $[\overline{\mathrm{Pt}(\mathrm{N}(\mathrm{COCH_3}){=}\mathrm{C}(\mathrm{C_6H_5})\mathrm{CH}{=}\mathrm{CO}}\mathrm{CH_3})_2]$. Since the Pt atom is located at the crystallographically imposed center of symmetry, the PtN_2O_2 moiety is exactly trans planar. The six-membered chelate ring is approximately planar. The interplanar angle between the chelate ring and the phenyl group is 89.7°, which is much larger than the values obtained for cis-bis(benzoylacetonato)palladium(II) (40.8° and 15.8°)[5)] and related complexes, indicating nonexistence of conjugation between phenyl and chelate rings in the present case. The N-acetyl group makes an angle of 59.2° with the chelate ring. The Pt-O bond length (1.98(1) Å) is in good agreement with the Pt-O bond length (1.968(14) Å) in $K[PtCl(acac)_2]$.[6)] The Pt-N bond length (2.01(1) Å) is slightly longer than the Pt-N distance in the oxime complexes (1.98(1) Å[7)] - 1.99(1) Å[8)]), but is not longer than the platinum to amine nitrogen distance (2.01 - 2.08 Å).[9-12)]

The IR and NMR spectra of the compound are compatible with this structure. The IR spectrum shows no absorption due to the nitrile group at about 2200 cm^{-1}, but instead shows a strong band at 1748 cm^{-1} and three medium to strong bands at 1580 - 1500 cm^{-1}. The former band can be assigned to the C=O stretching vibration in the N-acetyl group. The latter three bands may be ascribed to the C=C and C=N stretching vibrations in the β-ketoamine chelate ring and skeletal vibration of the phenyl ring, but cannot be identified separately.13) The ^1H NMR spectrum in CD_2Cl_2 (100 MHz) shows one methine signal at 5.10 ppm relative to internal TMS and two methyl signals at 2.00 and 1.81 ppm, together with phenyl resonances. Of these, the methine signal and one of the methyl signals at 1.81 ppm are accompanied by ^{195}Pt satellites, the coupling constants being $^4J_{PtH}$ = 4.0 and 4.7 Hz, respectively, and assigned to the ring proton and the methyl group attached to the β-ketoamine chelate ring, respectively. The other methyl signal at 2.00 ppm, which is not coupled to ^{195}Pt, is attributed to the N-acetyl methyl protons.

At the present stage, the detailed course of the reaction is not clear, but the initial step is thought to involve the nucleophilic attack by an acetylacetonate carbanion on the coordinated nitrile carbon atom, followed by facile acetyl migration to the coordinated nitrogen atom in order to stabilize the imino anion formed, and by coordination of the carbonyl group in the acetonylidene residue to form the N,O-chelate ring.

References and Note

1) B. N. Storhoff and H. C. Lewis, Jr., Coord. Chem. Rev., 23, 1 (1977).

2) B. F. G. Johnson, J. Lewis, and M. S. Subramanian, J. Chem. Soc. (A), 1968, 1993.

3) B. T. Golding, J. MacB. Harrowfield, G. B. Robertson, A, M. Sargeson, and P. O. Whimp, J. Am. Chem. Soc., 96, 3691 (1974).

4) We have isolated cis- and trans-$[PtCl_2(C_6H_5CN)_2]$ for the first time and the details will be reported elsewhere.

5) S. Okeya, H. Asai, S. Ooi, K. Matsumoto, S. Kawaguchi, and H. Kuroya, Inorg. Nucl. Chem. Lett., 12, 677 (1976).

6) R. Mason, G. B. Robertson, and P. J. Pauling, J. Chem. Soc. (A), 1969, 485.

7) E. O. Schlemper, Inorg. Chem., 8, 2740 (1969).

8) G. Ferraris and D. Viterbo, Acta Crystallogr., B25, 2066 (1969).

9) K. Yokoho, K. Matsumoto, S. Ooi, and H. Kuroya, Bull. Chem. Soc. Jpn., 49, 1864 (1976).

10) K. Matsumoto, S. Ooi, M. Sakuma, and H. Kuroya, Bull. Chem. Soc. Jpn., 49, 2129 (1976).

11) R. G. Ball, N. J. Bowman, and N. C. Payne, Inorg. Chem., 15, 1704 (1976).

12) Y. Nakayama, K. Matsumoto, S. Ooi, and H. Kuroya, Bull. Chem. Soc. Jpn., 50, 2304 (1977).

13) K. Ueno and A. E. Martell, J. Am. Chem. Soc., 59, 998 (1955).

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