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ACETONITRILE COMPLEXES OF PLATINUM(II)

Thomas Weil^a; Len Spaulding^a; Milton Orchin^a

^a Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, U.S.A.

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ACETONITRILE COMPLEXES OF PLATINUM(II)

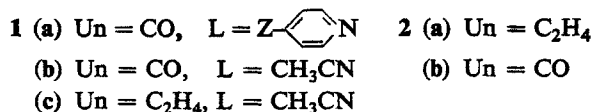
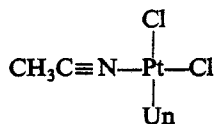
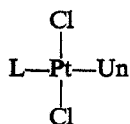
THOMAS WEIL, LEN SPAULDING and MILTON ORCHIN†

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

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Monoacetonitrile complexes of the formula $\text{CH}_3\text{CNPtCl}_2\text{Un}$ have been prepared where Un is ethylene or carbon monoxide. The infrared spectra of these complexes showed them to have the *cis*-configuration with the nitrile bonded through the lone pair electrons on nitrogen. The coordinated nitrile fails to exchange with solvent nitrile even on long standing but the ethylene can be readily exchanged.

We have reported previously¹ that chloroform solutions of complexes **1a** show one carbonyl stretching frequency in the infrared and the position of this band varies in the expected manner as a function of the electronic properties of Z.



In acetone and acetonitrile, however, a second carbonyl band appears at lower frequency. The frequency of this second band is invariant with respect to Z; in acetonitrile it appears at 2095 cm⁻¹.

We earlier suggested¹ the possibility that this band could be ascribed to the presence of a second carbonyl species in which L was displaced by acetonitrile to give **1b**. We now wish to report the synthesis of a compound whose method of preparation lead us to anticipate the formation of authentic **1b**. However, the infrared spectrum in acetonitrile of this new complex shows one strong carbonyl band at 2130 cm⁻¹ rather than at the expected frequency of 2095 cm⁻¹. Further examination showed that the new and remarkably stable complex is not the *trans* isomer **1b**, but the corresponding *cis* isomer **2b**. The acetonitrile ligand in **2b** as well as in its precursor **2a** (which also has the *cis* configuration) is extremely tightly bound to the platinum atom and we wish to report the preparation and properties of these new complexes.

† To whom correspondence should be addressed.

EXPERIMENTAL SECTION

The infrared spectra reported herein were obtained with either KBr pellets or nujol mulls (polyethylene plates) using a Perkin Elmer 237 instrument, and for the far infrared, the Beckman IR-12. Nmr spectra were obtained using the Varian A-60 or occasionally the T-60 instrument. Melting points were determined in air on a Fisher-Johns apparatus.

Preparation of PtCl₂(CH₃CN)(C₂H₄). To 3.0 g of K₂PtCl₄ in 25 ml of H₂O was added 0.45 ml of CH₃CN with stirring. The reddish solution was allowed to stir overnight, whereupon a small amount of the *bis* complex, PtCl₂(CH₃CN)₂,² precipitated. This was filtered, leaving an orange solution containing K[PtCl₃(CH₃CN)] and KCl.³ This solution was then treated with ethylene at 42 psi for 30 minutes. The solution gradually became colorless due to the conversion to white insoluble product, PtCl₂(CH₃CN)(C₂H₄). Longer reaction time under ethylene caused darkening of the product. The precipitated product was filtered, washed with H₂O and dried. During the melting point determination the sample gradually turned black, with no sharp melting. *Anal.* Calcd for C₄H₇PtCl₂N: C, 14.33; H, 2.11. Found: C, 14.41; H, 2.25.

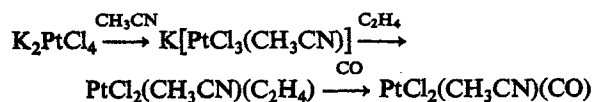
Preparation of PtCl₂(CH₃CN)(CO). A suspension of PtCl₂(C₂H₄)(CH₃CN) in CHCl₃ was treated with carbon monoxide at atmospheric pressure until a clear solution was obtained. The CO stream was then stopped and within a few minutes precipitation of a tan material resulted. Addition of pentane to the solution caused further solid product to precipitate. The product was filtered and dried;

m.p. 92–96°. *Anal.* Calcd for $C_3H_3PtCl_2NO$: C, 10.75; H, 0.89; Pt, 58.23. Found: C, 10.80; H, 0.86; Pt, 57.96.

RESULTS AND DISCUSSION

Infrared Spectra

The infrared spectrum of the platinum-acetonitrile-carbonyl complex prepared by the reactions:



shows a single sharp carbonyl band at 2134, and at 2130 cm^{-1} in chloroform and acetonitrile, respectively. The spectrum in the far infrared (nujol) shows two Pt–Cl bands, at 344 and 353 cm^{-1} . The spectrum of the precursor **2a** also showed two Pt–Cl bands, at 331 and 357 cm^{-1} . These bands unquestionably can be assigned to the *cis* configuration of the chlorides. In *trans* compounds there is always a single Pt–Cl stretching⁴ frequency usually in the 340–355 cm^{-1} region.

Free acetonitrile has $\nu_{C\equiv N}$ at 2254 cm^{-1} (and a

combination band at 2290 cm^{-1}). In the few examples where the $C\equiv N$ has been shown to be π -complexed, this frequency shifts by 185–230 cm^{-1} to lower frequencies.⁵ In our *cis* compounds with acetonitrile, **2a** has $\nu_{C\equiv N}$ at 2332 and 2303 cm^{-1} , while **2b** has these bands at 2350 cm^{-1} and 2324 cm^{-1} . These spectra confirm coordination through the lone pair on nitrogen; coordination through the lone pair always increases the $C\equiv N$ frequency because of kinematic coupling and the ionic character of the C–N bond.⁶

The infrared spectra clearly shows that our original observation of the appearance of a second carbonyl band in the infrared when *trans* complexes such as **1a** are dissolved in acetonitrile cannot be ascribed to the formation of some *cis* isomer and may be associated with the *trans* isomer **1b** as originally suggested. Efforts are presently being made to prepare authentic **1b**.

NMR Spectra

The nmr spectrum of the ethylene complex, **2a**, in D_3 -acetonitrile, is shown in Figure 1. Coupling of the ethylene protons and the methyl protons of

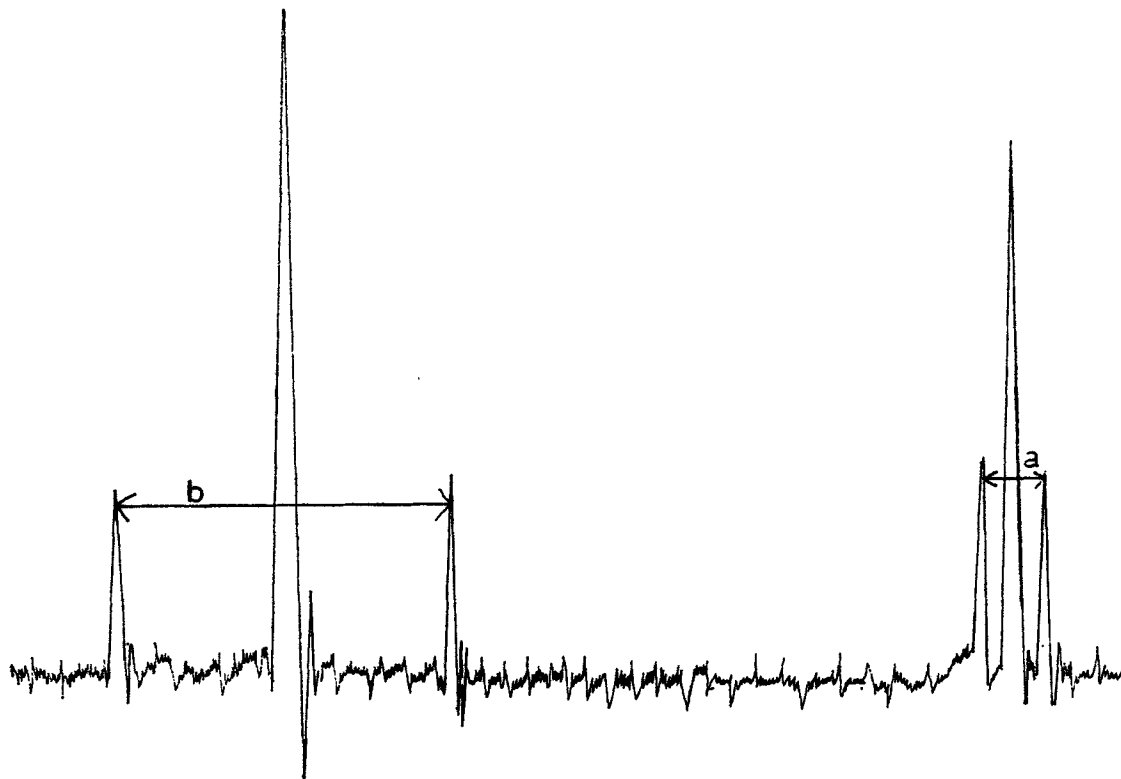


FIGURE 1 The nmr spectra of $(C_2H_4)PtCl_2(CH_3CN)$ in CD_3CN . (a) $J_{Pt-N=CCH_3} = 13$ Hz. (b) $J_{Pt-C_2H_4} = 61$ Hz.

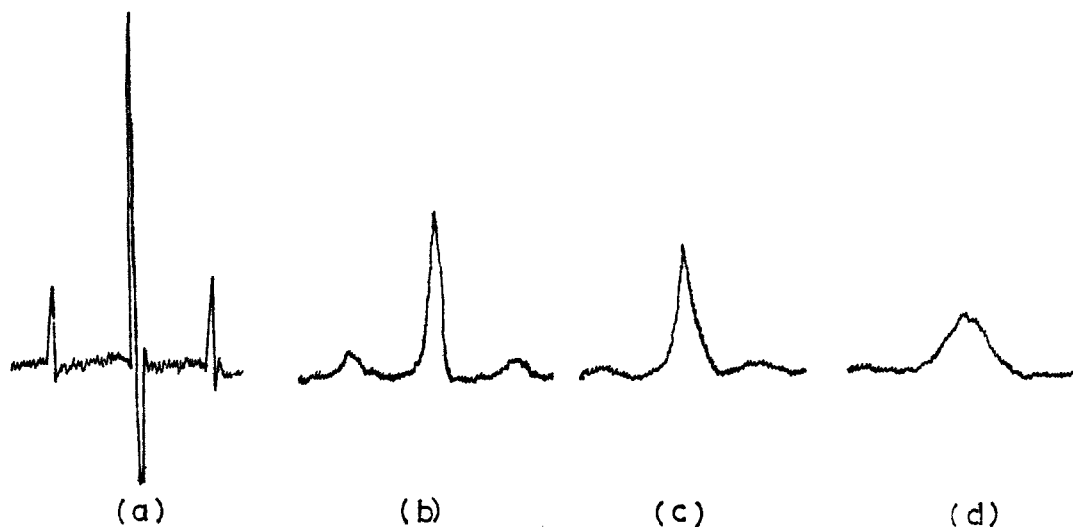


FIGURE 2 The nmr spectra of $(C_2H_4)PtCl_2CH_3CN$ in CD_3CN with (a) no KBr; (b) with KBr : complex 1 : 4; (c) with KBr : complex 1 : 2; (d) with KBr : complex 1 : 1.

acetonitrile, with platinum, is observed at room temperature. The $^{195}Pt-H$ coupling constants, $J_{Pt-C_2H_4}$ and $J_{Pt-N\equiv C-CH_3}$ are 61 Hz and 13 Hz respectively, values which agree well with reported constants for similar couplings.⁷⁻¹¹ Even after seven days in acetonitrile the nmr spectrum remains unchanged. The chemical shift of the methyl protons of coordinated acetonitrile occurs at 2.45 ppm (δ); free acetonitrile protons have a chemical shift of 2.00 ppm. Exchange of coordinated CH_3CN with CD_3CN would be accompanied by a decrease in intensity of the peak at 2.45 ppm and appearance of a peak at 2.00 ppm. That no such behavior is observed shows that coordinated CH_3CN does not undergo exchange with the solvent CD_3CN in this complex.

In another experiment, D_2O alone and D_2O containing varying amounts of KBr were added to

D_3 -acetonitrile (and D_6 -acetone) solutions of $(CH_3CN)PtCl_2(C_2H_4)$. Addition of varying amounts of D_2O alone to the solutions had no apparent effect on the nmr spectrum of $(CH_3CN)PtCl_2(C_2H_4)$. However aqueous KBr had a significant effect; the results are recorded in Table I and Figure 2. With a 1 : 1 mol ratio of complex to KBr, loss of coupling between platinum and ethylene occurs. Surprisingly, platinum coupling to acetonitrile remains, and even addition of excess KBr causes no change.¹²

The collapse of the ethylene signal to a broad singlet suggests a rapid exchange of the olefin with solvent. Rapid exchange of ethylene with solvent, has been reported in acetone solutions of *trans*- $PtCl_2(C_2H_4)(Pyridine)$ at temperatures above 30.¹³ Ethylene exchange also occurs in solutions of Ziese's salt at temperatures as low as -70° .¹⁴ The chemical shift of the broadened peak due to the

TABLE I
NMR spectra of *cis*- $C_2H_4PtCl_2CH_3CN$ in CD_3CN -aqueous (D_2O) KBr

Ml of .75M KBr in D_2O	Mole ratio KBr : complex	$J_{PtC_2H_4}$ (Hz)	Chem. shift C_2H_4 ppm(δ)	Chem. shift ^a CH_3CN ppm(δ)
0	—	61	4.67	2.45
0.05	1 : 4	62	4.70	2.47
0.10	1 : 3	62 (slightly broadened)	4.73	2.48
0.15	1 : 2	broadened	4.80	2.50
0.20	2 : 3	uncoupled	4.81	2.50
0.25	1 : 1	uncoupled and broad	4.81	2.50

^a The coupling constant $J_{CH_3C\equiv N-Pt}$ is 13 Hz for all the tested complexes.

ethylene protons in **2a** is at 4.81 ppm, while the chemical shift of the signal for coupled ethylene protons is at 4.67 ppm. Free C₂H₄ in HCCl₃ has a chemical shift of 5.41 ppm. If rapid exchange of ethylene occurs, the chemical shift value for the broadened ethylene protons is a time-averaged value. Further, the chemical shift data for the olefin protons indicates that, despite the rapid exchange of the ethylene, the equilibrium must lie on the side of the undissociated complex. The KBr experiments suggested that **2a** undergoes ready nucleophilic displacement. That ethylene can be readily replaced by other olefins in the *cis* complex **2a** was shown by treating it briefly with 1-dodecene and with isobutylene and observing the rapid formation of the analogous olefin complexes, identified by their infrared and nmr spectra.

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