

THE FORMATION OF COVALENT BONDS FROM TRANSITION METALS TO CARBON BY DIRECT SUBSTITUTION II. PLATINUM(II) HALIDES AND *N,N*-DIMETHYL-2-METHYLALLYLAMINE

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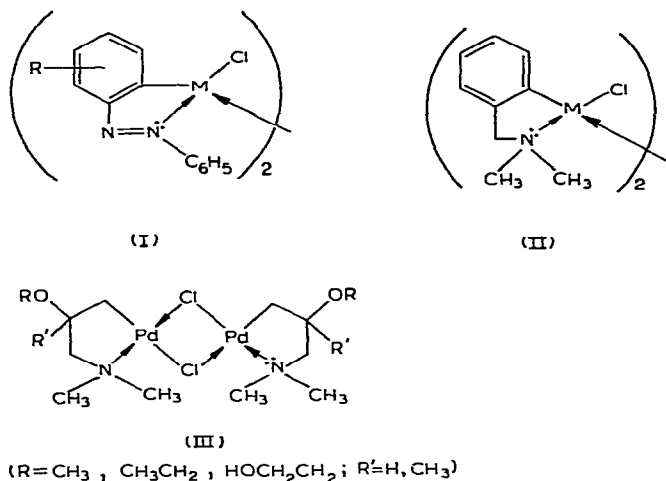
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SUMMARY

Platinum(II) chloride or lithium chloroplatinate(II) react with *N,N*-dimethyl-2-methylallylamine to give 2-methyl-3-(dimethylamino)propenylplatinum(II) chloride dimethylamine in 46% yield. Treatment of this compound with either triphenylphosphine or aniline causes elimination of dimethylamine and gives the corresponding triphenylphosphino or anilino complex.

INTRODUCTION

The observation¹ that azobenzenes and *N,N*-dimethylbenzylamines react with palladium(II) halides and platinum(II) halides in alcoholic solution to give complexes (I) and (II) having carbon-to-metal bonds prompted our attention to the reaction of

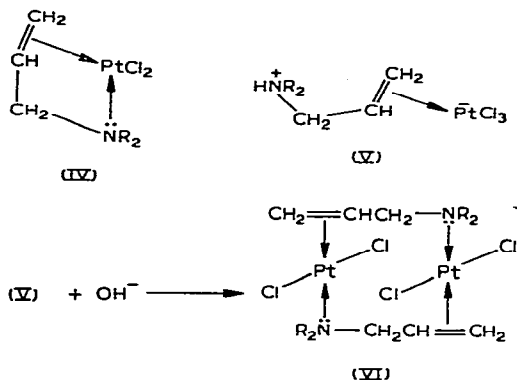


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tertiary allylic amines with both of these metal halides. We therefore recently reported² that palladium(II) chloride or lithium chloropalladate(II) react with *N,N*-dimethylallyl amines in alcoholic media to give complex (III) and not the expected product resulting from either allylic or vinyl substitution.

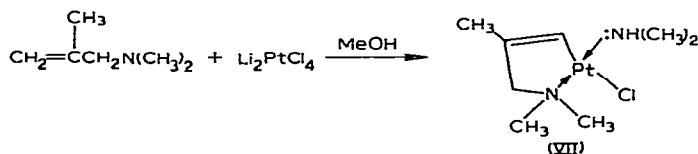
Venanzi *et al.*³, have reported that, contrary to earlier conclusions, the products of reaction between PtCl_4^{2-} and allylic amines in acid solution are not complexes such as (IV) but are in reality ammonium salts such as (V).



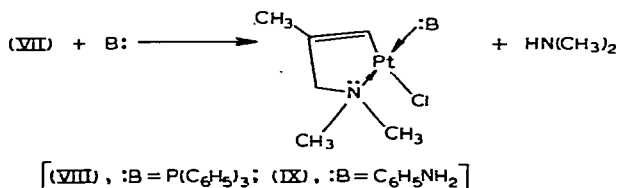
Furthermore, treatment of complex (V) with base leads to a dimeric complex (VI): More recently, Venanzi and coworkers have reported the determination of stability constants and thermodynamic data for these complexes by spectrophotometric methods⁴.

RESULTS

We have found that in neutral alcoholic media, *N,N*-dimethyl-2-methylallylamine (in excess) reacts with either platinum(II) chloride or lithium chloroplatinate(II) to give 2-methyl-3-(dimethylamino)propenylplatinum(II) chloride dimethylamine, (VII), in 46% yield.



Complex (VII) reacts with organic bases to give new complexes in which dimethylamine has been replaced. Thus, treatment of (VII) with triphenylphosphine or aniline results in the formation of 2-methyl-3-(dimethylamino)propenylplatinum(II) chloride triphenylphosphine, (VIII), in 72% yield, and 2-methyl-3-(dimethylamino)propenylplatinum(II) chloride aniline, (IX), in 43% yield:



The structure of (VII) was determined from the following information. The NMR spectrum contains an unresolved olefinic proton multiplet at 5.67 ppm, a three proton singlet at 1.53 ppm which corresponds to a methyl on a double bond, and a 14 proton series of complicated resonances in the region of 2.0–4.0 ppm. The mass spectrum of (VII) has a parent ion at m/e 372* (calcd. for $C_8H_{19}N_2^{194}Pt^{35}Cl$ 372.08) and the largest peak in the spectrum is at m/e 98 [100%; $(CH_3)_2NCH_2C(CH_3)=CH^+$]. The possibility that the m/e 372 peak arose from cleavage of a symmetrical molecule was alleviated by a cryoscopic molecular weight determination in benzene (379). Finally, complex (VII) was brought into reaction with triphenylphosphine to give dimethylamine (isolated as the picrate) and a new complex, (VIII).

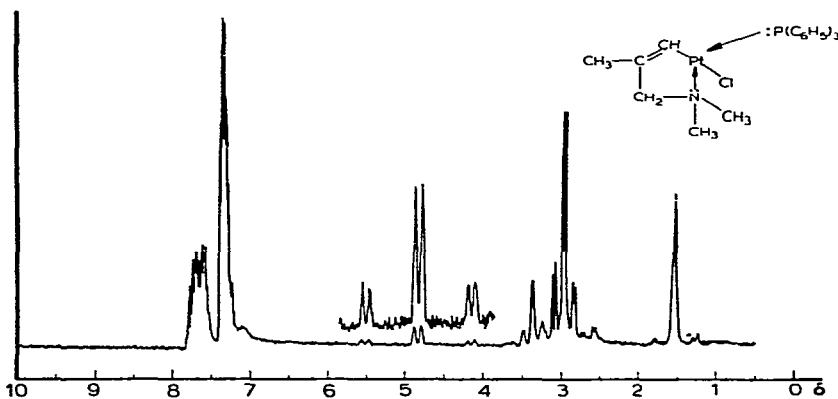


Fig. 1. PMR Spectrum (100 MHz) of 2-methyl-3-(dimethylamino)propenylplatinum(II) chloride triphenylphosphine, (VIII).

The structure of (VIII) was deduced from the following data. The nuclear magnetic resonance spectrum (Fig. 1) is in agreement with the proposed structure. The singlet at 1.54 ppm corresponds to the methyl group on the double bond. The multiplet at 2.96 ppm is due to the *N*-methyl groups coupled to both platinum (25.0 Hz) and phosphorus (3.0 Hz). Our conclusion from these couplings with platinum and phosphorus is that the nitrogen unshared pair is truly coordinated with the metal giving the five-membered ring. The olefinic proton appears at 4.86 ppm and is also coupled to platinum (139.0 Hz) and phosphorus (9.0 Hz). The high value of this platinum coupling places the olefinic proton closest to the metal. No change in the above coupling constants was observed between spectra obtained at 60 MHz and those at 100 MHz, thereby precluding a mixture of isomers.

Measurement of the ^{31}P spectrum indirectly by 1H - ^{31}P double resonance gives a value of the ^{31}P chemical shift ($\delta = -15.3$ ppm from 85% H_3PO_4 external reference); and the ^{31}P - ^{195}Pt coupling constant (4260 Hz) is indicative of the phosphorus being *cis* to a ligand capable of π -bonding⁵ and this gives the assigned configuration.

In the mass spectrum of VIII at 70 eV the parent ion appears at m/e 590.1098

* High resolution accuracy was not afforded on this sample.

(calcd. for $C_{24}H_{27}NP^{195}Pt^{35}Cl$ 590.1218). Further fragmentation gives major ions at m/e 262 [6%; $(C_6H_5)_3P^+$], 98 [100%; $(CH_3)_2NCH_2C(CH_3)=CH^+$], and 58 [33%, $(CH_3)_2N^+=CH_2$]. The appearance of a large m/e 58 peak establishes that the only isomer present is the one with the methylene adjacent to nitrogen*.

Further studies are currently in progress to elucidate the mechanism of this and other related reactions.

EXPERIMENTAL

Melting points are uncorrected. Ultraviolet spectra were recorded on a Carey Model 21 Spectrophotometer, infrared spectra on Perkin-Elmer Model 21 and Baird Model 455 spectrophotometers. Chemical shifts are reported with respect to internal tetramethylsilane in deuteriochloroform and were measured using Varian A-60 and HA-100 spectrophotometers. Mass spectra were obtained on an A.E.I. MS-9 High Resolution Mass Spectrophotometer. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Helsingør, Denmark, and Galbraith Laboratories, Knoxville, Tennessee.

Lithium chloroplatinate(II) was prepared by the method of Nilson⁶. *N,N*-Dimethyl-2-methylallylamine was prepared according to the method of Cope *et al.*⁷

2-Methyl-3-(dimethylamino)propenylplatinum(II) chloride dimethylamine, (VII)

A. A mixture of 1.50 g *N,N*-dimethyl-2-methylallylamine (0.015 mole) and 1.33 g platinum(II) chloride (0.005 mole) in 10 ml methyl alcohol was shaken for two days. Filtration of the resultant red solution afforded 0.148 g unreacted platinum(II) chloride. The red filtrate was dried *in vacuo* and the residue extracted with benzene. These operations all were attended by the appearance of platinum metal. Rapid column chromatography on silicic acid ($CHCl_3$, ethyl acetate, methyl alcohol) afforded a yellow, stable solid which upon recrystallization from benzene heptane gave 0.460 g yellow needles, m.p. 136–138° dec., mol. wt. 379 (cryosc. in benzene); 372 (mass spec.).

The IR spectrum (KBr) had absorption maxima at 2.90, 3.36, 3.45, 6.17, 6.87, 7.15, 7.30, and 11.80 μ . The ultraviolet spectrum ($CHCl_3$) had maxima at 350 $m\mu$ (ϵ 5,050), 295 $m\mu$ (sh, ϵ 6,657), 245 $m\mu$ (ϵ 13,850).

B. A solution of 1.76 g lithium chloroplatinate(II) (0.005 mole) and 1.50 g *N,N*-dimethyl-2-methylallylamine (0.015 mole) in 25 ml methyl alcohol was heated at reflux for 12 h. The methyl alcohol was removed *in vacuo* and the resulting intractable mass taken up in chloroform and quickly chromatographed on silicic acid. Elution with chloroform gave 0.863 g orange solid. Recrystallization from benzene heptane and filtration gave 0.516 g light colored needles, m.p. 139–140° dec., 46% yield. (Found: Cl, 9.33; N, 7.01; Pt, 51.46. $C_8H_{19}ClN_2Pt$ calcd: Cl, 9.50; N, 7.50; Pt, 52.21%.)

The PMR spectrum (60 MHz, $CDCl_3$) showed peaks in ppm from TMS at 1.53 (s, \approx 3 H) an extremely complicated series of peaks at 2.0–4.0 (\approx 14 H), and a multiple peak at 5.67 (\approx 1 H).

* Primary fragmentation of amines takes place with β -bond cleavage. Thus if the organic moiety were $(CH_3)_2NCH=C(CH_3)CH_2^+$ no m/e 58 peak would be forthcoming. See also ref. 8.

2-Methyl-3-(dimethylamino)propenylplatinum(II) chloride triphenylphosphine, (VIII)

A mixture of 0.100 g compound (VII) (0.000268 mole) and 0.136 g triphenylphosphine (0.00052 mole) was heated to reflux in 10 ml heptane and benzene added until solution occurred. The distillate from this operation was joined with 25 ml ethyl ether saturated with picric acid. The resultant yellow precipitate was collected on a filter and dried, 0.047 g, 64% yield m.p. 160–162°, mixed melting point with authentic dimethylamine picrate 161–163°.

The clear benzene/heptane solution was allowed to stand overnight and 0.115 g pale yellow needles were collected on a filter, m.p. 189–191°, 72% yield. (Found: C, 48.92; H, 4.66; Cl, 5.99; N, 2.37; P, 5.34; Pt, 32.62. $C_{24}H_{27}ClNPPt$ calcd: C, 48.75; H, 4.57; Cl, 6.01; N, 2.37; P, 5.25; Pt, 33.05%.)

Absorption in the IR (KBr) included maxima at 3.26, 3.34, 3.42, 3.49, 6.06, 6.32, 6.74, 6.89, 6.97, 7.20, 9.12, 11.70, 13.35, and 14.5 μ . The PMR spectrum (100 MHz, $CDCl_3$) showed peaks, in ppm from TMS, at 1.54 (s, 2.87 H); 2.96 [m, $J(^{195}Pt)$ 25.0 Hz, $J(^{31}P)$ 3.0 Hz, 6.1 H]; 3.38 [m, $J(^{195}Pt)$ 12.0 Hz, $J(^{31}P)$ >1 Hz, 2.1 H]; 4.86 [m, $J(^{195}Pt)$ 139.0 Hz, $J(^{31}P)$ 9.0 Hz, 1.0 H]; 7.34 and 7.66 (m, 15.0 H).

2-Methyl-3-(dimethylamino)propenylplatinum(II) chloride aniline, (IX)

A solution containing 0.050 g compound (VII) (0.000134 mole) and 5 drops aniline were heated at reflux in 10 ml ethyl acetate for one h. The ethyl acetate was removed in vacuo and the resulting residue taken up in hot benzene, filtered with Super-Cel, and heptane added to the filtrate to the cloud point. Cooling to room temperature and filtration afforded 0.024 g white crystals, m.p. 164–167°, 43% yield. (Found: C, 34.74; H, 4.63; Cl, 8.44; N, 6.67; Pt, 45.66. $C_{12}H_{19}ClN_2Pt$ calcd: C, 34.15; H, 4.51; Cl, 8.41; N, 6.64; Pt, 46.29%.)

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