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A New σ-Bonded Complex Formation between 2-Vinylpyridine and Palladium(II) or Platinum(II) Chloride

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Sodium tetrachloropalladate(II) reacts with 2-vinylpyridine in methanol, ethanol, or isopropyl alcohol, to give, respectively, di-μ-chloro-bis[2-methoxy-2-(α-pyridyl)ethyl]dipalladium(II), di-μ-chloro-bis[2-ethoxy-2-(α-pyridyl)-ethyl]dipalladium(II), and di-μ-chloro-bis[2-isopropoxy-2-(α-pyridyl)ethyl]-dipalladium(II). The reaction of potassium tetrachloroplatinate(II) with 2-vinylpyridine in methanol or ethanol affords, respectively, di-μ-chloro-bis[2-methoxy-2-(α-pyridyl)ethyl]diplatinum(II) and di-μ-chloro-bis[2-ethoxy-2-(α-pyridyl)ethyl]diplatinum(II). The structures of these complexes containing the covalent metal - carbon bonding have been confirmed by a study of their absorptions and of the NMR spectra.

Recently, Cope and his co-workers reported that azobenzenes and *N*,*N*-dimethylbenzylamines react with palladium(II) halides or platinum(II) halides in an alcoholic solution to give complexes, **1**[3] and **2**[4], with carbon - methal σ-bonds.

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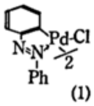
[3] A. C. Cope and R. W. Sieman, *J. Am. Chem. Soc.*, **87**, 3272 (1965).

[4] A. C. Cope and E. C. Friedrich, *ibid.*, **90**, 909 (1968).

Furthermore, they found palladium(II) halides to react with allylic amines in an alcoholic solution to give complexes **3** containing an alkoxy group.[5] Yukawa and Tsutsumi[6] have also reported propagylamines which react with palladium(II) chloride in the presence of lithium chloride to give chlorovinylated products 4. Here we wish to report that, in alcoholic media, 2-vinylpyridine undergoes a similar electrophilic substitution by palladium(II) or platinum(II) chloride, producing a new σ-bonded complex.



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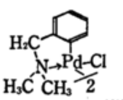

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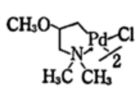

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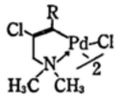

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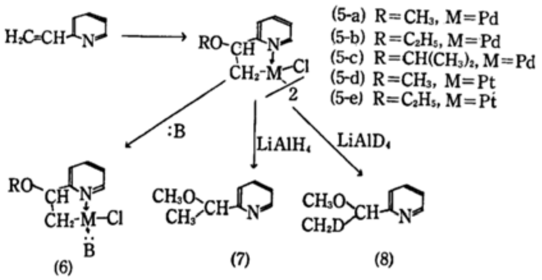

(5-a) R=CH_3, M=Pd
(5-b) R=C_2H_5, M=Pd
(5-c) R=$CH(CH_3)_2$, M=Pd
(5-d) R=CH_3, M=Pt
(5-e) R=C_2H_5, M=Pt

Experimental

All melting points and boiling points are uncorrected. Molecular weights were determined with an osmometer (benzene: at 45°C). The NMR spectra were recorded on a Hitachi H-60 spectrometer in deuteriochloroform, using tetramethylsilane as the internal reference.

Di-μ-chloro-bis[2-methoxy-2-(α-pyridyl)ethyl]-dipalladium(II) (5-a). To a solution containing 6.96 g (0.02 mol) of sodium tetrachloropalladate(II) in 70 m*l* of methanol, a solution of 2-vinylpyridine (2.10 g, 0.02 mol) in 20 m*l* of methanol was added. After standing at room temperature for 10 hr, the reaction mixture was evaporated *in vacuo* to dryness and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on alumina using dichloromethane. Recrystallization from benzene afforded yellow crystals (**5-a**); mp 157—159°C, (1.2 g, 11%). IR spectrum (KBr): 3018, 2950, 2830, 1608, 1580, 1495,1450, 1115, 842, and 765 cm^{-1}. NMR spectrum: 6.58 (singlet, $-OCH_3$), 5.82 (multiplet, $-CH_2-$), 4.55 (multiplet, $-CH-$), and 2.90—0.96 τ (multiplet, pyridyl protons).

Found: C, 34.68; H, 3.75; N, 5.11%; mol wt, 548. Calcd for $C_{16}H_{20}N_2O_2Pd_2Cl_2$: C, 34.56; H, 3.62; N, 5.03%; mol wt, 556.

Di-μ-chloro-bis[2-ethoxy-2-(α-pyridyl)ethyl]-dipalladium(II) (5-b). The ethoxy complex (**5-b**) was obtained similarly from sodium tetrachloropalladate(II) and 2-vinylpyridine in ethanol (100 m*l*). The yellow crystals were recrystallized from benzene-cyclohexane; mp 153—155°C. IR spectrum (KBr): 3020, 2970, 1602, 1580, 1490, 1450, 830, and 772 cm^{-1}. NMR spectrum: 8.77 and 6.38 (ethoxy protons), 5.80 (multiplet, $-CH_2-$), 4.50 (multiplet, $-CH-$), and 2.92—0.92 τ (multiplet, pyridyl protons).

Found: C, 37.22; H, 4.08; N, 4.89%; mol wt, 568. Calcd for $C_{18}H_{24}N_2O_2Pd_2Cl_2$: C, 37.04; H, 4.14; N, 4.79%; mol wt, 584.1.

Di-μ-chloro-bis[2-isopropoxy-2-(α-pyridyl)-ethyl]dipalladium(II) (5-c). The reaction between sodium tetrachloropalladate(II) and 2-vinylpyridine in isopropyl alcohol afforded the isopropoxy complex (**5-c**) (23% yield). The yellow crystals were recrystallized from benzene; mp 165—167°C. IR spectrum (KBr): 3020, 2980, 1608, 1580, 1490, 1450, 1385, 1377, 830, and 772 cm^{-1}. NMR spectrum: 8.87, 8.78, and 6.21 (isopropoxy protons), 5.86 (multiplet, $-CH_2-$), 4.38 (multiplet, $-CH-$), and 2.95—0.98 τ (multiplet, pyridyl (protons).

Found: C, 39.67; H, 4.63; N, 4.45%; mol wt, 601. Calcd for $C_{20}H_{28}N_2O_2Pd_2Cl_2$: C, 39.24; H, 4.61; N, 4.57%; mol wt, 612.1.

Di-μ-chloro-bis[2-methoxy-2-(α-pyridyl)ethyl]-diplatinum(II) (5-d). To a solution of 1.0 g (0.0024 mol) of potassium tetrachloroplatinate(II) in 20 m*l* of water and 5 m*l* of methanol, 0.25 g (0.0024 mol) of 2-vinylpyridine in 30 m*l* of methanol was added at room temperature. After the mixture had then stood for 2 days, a yellow-orange precipitate was filtered out and washed well with methanol (0.55 g, 62%); mp 240—243°C (dec). This yellow-orange solid was insoluble in all common solvents. IR spectrum (KBr): 3020, 2940, 2820, 1608, 1590, 1488, 1450, 1120, 790, and 758 cm^{-1}.

Found: C, 25.95; H, 2.62; N, 3.36%. Calcd for $C_{16}H_{20}N_2O_2Pt_2Cl_2$: C, 26.18; H, 2.74; N, 3.54%.

Di-μ-chloro-bis[2-ethoxy-2-(α-pyridyl)ethyl] diplatinum(II) (5-e). A yellow-orange product (**5-e**) was obtained similarly from potassium tetrachloroplatinate(II) and 2-vinylpyridine in ethanol-water (55% yield); mp 237—240°C (dec). IR spectrum (KBr): 3020, 2940, 1606, 1581, 1480, 1445, 1390, 830, 798, and 770 cm^{-1}.

Found: C, 28.04; H, 2.96; N, 3.43%. Calcd for $C_{18}H_{28}N_2O_2Pt_2Cl_2$: C, 28.27; H, 3.14; N, 3.67%.

The Preparation of 2-Alkoxy-2-(α-pyridyl)ethylpalladium(or platinum) Chloride *p*-Toluidine (6). A mixture of 0.10 g of Complex **5** and *p*-toluidine (5% excess) in benzene (30 m*l*) was heated to reflux for 30 min. After the solvent had then been removed under reduced pressure, the residue was recrystallized from a benzene-cyclohexane mixture to give the following complexes.

2-Methoxy-2-(α-pyridyl)-ethylpalladium(II) Chloride *p*-Toluidine (6, B:=*p*-Toluidine, R=CH_3, M=Pd). Yellow crystals, mp 215—218°C (dec).

Found: C, 48.45; H, 4.79; N, 7.16%. Calcd for $C_{16}H_{19}N_2OPdCl$: C, 48.38; H, 4.82; N, 7.02%.

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5) A. C. Cope, J. M. Kliegman and E. C. Friedrich, *ibid.*, **89**, 287 (1967).

6) T. Yukawa and S. Tsutsumi, *Inorg. Chem.*, **7**, 1458 (1968).

2-Ethoxy-2-(α-pyridyl)ethylpalladium(II) Chloride *p*-Toluidine (6, B:=*p*-Toluidine, R=CH_2CH_3, M=Pd). Yellow crystals, mp 231—233°C (dec).

Found: C, 49.77; H, 5.26; N, 6.84%. Calcd for $C_{17}H_{21}N_2OPdCl$: C, 49.65; H, 5.14; N, 6.81%.

2-Isopropyoxy-2-(α-pyridyl)ethylpalladium(II) Chloride *p*-Toluidine (6, B:=*p*-Toluidine, R=CH-$(CH_3)_2$, M=Pd). Yellow crystals, mp 175—178°C (dec).

Found: C, 51.04; H, 5.01; N, 6.63%. Calcd for $C_{18}H_{23}N_2OPdCl$: C, 50.86; H, 4.97; N, 6.58%.

2-Methoxy-2-(α-pyridyl)-ethylplatinum(II) Chloride *p*-Toludine (6, B:=*p*-Toluidine, R=CH_3, M=Pt). Yellow crystals, mp 198—200°C (dec).

Found: C, 39.71; H, 4.07; N, 5.66%. Calcd for $C_{16}H_{19}N_2OPtCl$: C, 39.54; H, 3.94; N, 5.74%.

2-Ethoxy-2-(α-pyridyl)ethylplatinum(II) Chloride *p*-Toluidine (6, B:=*p*-Toluidine, R=CH_2CH_3, M=Pt). Yellow crystals, mp 195—198°C (dec).

Found: C, 41.26; H, 4.25: N, 5.55%. Calcd for $C_{17}H_{21}N_2OPtCl$: C, 41.01; H, 4.23; N, 5.63%.

Reduction of Complex. General Procedure. To the complex (3.3 g) in absolute ether (200 m*l*), there was slowly added a mixture containing 1.0 g of lithium aluminum hydride or deuteride in 100 m*l* of absolute ether. The resulting black mixture was stirred at room temperature for 3 hr, then water or deuterium oxide (5 m*l*) was added with cooling. The ether layer was washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent, the product was isolated by distillation.

Reduction of Complex 5-a with Lithium Aluminum Hydride. This reduction gave a product, bp 205—208°C, which can be identified as 1-(α-pyridyl)-1-methoxyethane (**7**) on the basis of the following evidence. IR spectrum: 2820 cm^{-1} ($-OCH_3$). NMR spectrum: 8.71 (doublet, J=6.0 cps, $-CH_3$); 6.67 (singlet, $-OCH_3$); 6.37 (quartet, J=6.0 cps, –CH–), and 3.03—1.35 τ (multiplet, pyridyl protons).

Found: C, 69.85; H, 8.01; N, 10.09%, mol wt, 135. Calcd for $C_8H_{11}NO$: C, 70.03; H, 8.08; N, 10.21%, mol wt, 137.

Reduction of Complex 5-a with Lithium Aluminum Deuteride. This reduction gave 1-(α-pyridyl)-1-methoxyethane-2-d_1, bp 205—208°C. IR spectrum: 2820 cm^{-1} ($-OCH_3$). NMR spectrum: 8.70 (doublet, J=6.0 cps, $-CH_2D$), 6.67 (singlet, $-OCH_3$), 6.36 (triplet, J=6.0 cps, –CH–), and 3.02—1.32 τ (multiplet, pyridyl protons).

Found: C, 69.77; H, 8.69; N, 10.32%; mol wt, 136. Calcd for $C_8H_{10}DNO$: C, 69.54; H, 8.74; N, 10.13%, mol wt, 138.

Reduction of Complex 5-d with Lithium Aluminum Hydride. This reduction gave 1-(α-pyridyl)-1-methoxyethane (**7**), bp 205—208°C, which can be identified by means of its IR and NMR spectra.

Reduction of Complex 5-d with Lithium Aluminum Deuteride. This reduction gave 1-(α-pyridyl)-1-methoxyethane-2-d_1 (10), bp 205—208°C, which can be identified by means of its IR and NMR spectra.

Results and Discussion

The reaction of 2-vinylpyridine with sodium tetrachloropalladate(II) in alcohol produced di-μ-chloro-bis[2-alkoxy-2-(α-pyridyl) ethyl]dipalladium(II) (**5-a—c**). The dimeric structures for these complexes were supported by the molecular-weight determinations and by their reactions with *p*-toluidine, which give readily-soluble, monomeric derivatives. The structure of complex **5-a** was established by the following data.

The infrared spectrum of complex **5-a** shows new bands at 2830 and 1115 cm^{-1} which can be assigned to the CH_3O- stretching mode. In agreement with the proposed structure, the NMR spectrum of complex **5-a** shows four bands, at 6.58 (singlet), 5.82 (multiplet), 4.55 (multiplet), and 2.90—0.96 τ (multiplet), in the ratio 3 : 2 : 1 : 4. They are assigned to *O*-methyl protons, methylene protons, methine protons, and pyridyl protons respectively. The lithium-aluminum-hydride reduction of complex **5-a** gives 1-(α-pyridyl)-1-methoxy-ethane (**9**), whose structure can be established by means of its IR and NMR spectra. The lithium-aluminum-deuteride reduction of complex **5-a** gives deuterated amine (**10**), which was identified as 1-(α-pyridyl)-1-methoxyethane-2-d_1. The position of the deuterium and, therefore, the site of the carbon-to-palladium σ-bond, was established by a comparison of the NMR spectrum of **10** with that of the undeuterated **9**. The spectrum of **9** consists of a doublet at 8.71 τ (methyl protons, wt 3), a singlet at 6.67 τ (methoxy protons, wt 3), a quartet at 6.37τ (methine proton, wt 1), and a multiplet at 3.03—1.35 τ (pyridyl protons, wt 4), whereas **10** shows the corresponding signals at 8.70 (doublet), 6.67 (singlet), 6.36 (triplet), and 3.02—1.32 τ (multiplet) in the ratio 2 : 3 : 1 : 4. The above evidence establishes that a σ-bond has been formed between the metal and the terminal methylene group of the vinyl moiety. The structures of complexes **5-b** and **5-c** are also proved by their NMR spectra.

The reactions of 2-vinylpyridine with potassium tetrachloroplatinate(II) in aqueous methanol or in aqueous ethanol give di-μ-chloro-bis[2-alkoxy-2-(α-pyridyl)ethyl]diplatinum(II) (**5-d,e**). The insolubility of these complexes in common solvents made impossible any NMR-spectra or molecular-weight measurements. However, the reactions with *p*-toluidine and with lithium aluminum hydride or deuteride indicate that they have a dimeric structure of the same type as that obtained from 2-vinylpyridine and sodium tetrachloropalladate(II). The reduction of complex **5-d** with lithium aluminum hydride gives 1-(α-pyridyl)-1-methoxyethane (**7**), while that with lithium aluminum deuteride gives 1-(α-pyridyl)-1-methoxyethane-2-d_1 (**10**).

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