

STABLE COMPLEX-FORMATION AND ISOMERIZATION OF DEWAR PYRIDINE
DERIVATIVE WITH TRANSITION-METAL SALTS

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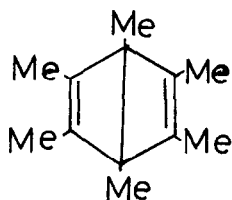
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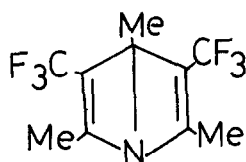
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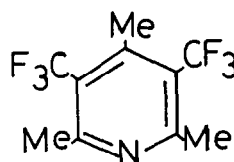
Isomerization of the ring system of hexamethyl Dewar benzene (I) by Rh^{III} 1) and Hg^{II} 2) and formation of stable complexes of I with Cr^0 , 3) Rh^I , 4) Pd^{II} , 5) and Pt^{II} , 6) have been reported, but the reaction of Dewar pyridines with transition-metal complexes is unknown. We report in this paper isomerization of 2,4,6-trimethyl-3,5-bis(trifluoromethyl)-1-azabicyclo[2,2,0]hexa-2,5-diene (II), which is a stable Dewar pyridine, by transition-metal catalysis and formation of stable complexes in which II are present as ligands. II was obtained by photolysis of 2,4,6-trimethyl-3,5-bis(trifluoromethyl)pyridine⁷⁾ (III), and the reaction of II with transition-metal salts was studied.



I



II



III

When $Pd(PhCN)_2Cl_2$ (IV) or $PdCl_2$ (V) was added to a solution of II in $CD_3OD-CDCl_3$, 1H - and ^{19}F -NMR signals corresponding to II disappeared immediately with the appearance of new signals at the same time. When this solution was allowed to stand at room temperature gradual reduction of these new signals and growth of additional new signals resulted, the latter signals being identical with those

observed when IV or V was added to a solution of III. No free II or III was detected by gas-liquid chromatography, either from a mixture immediately after addition of palladium salts to the solution of II or from a mixture allowed to stand for several hours at room temperature. These facts indicate the formation of stable complexes between the bases and Pd^{II}.

After addition of excess IV or V to a solution of II in CHCl₃-MeOH, crystals somewhat unstable (VI) and stable (VII) were isolated. Conversion of VI to VII was effected by recrystallization from CHCl₃-benzene, and heating of VII in CHCl₃-benzene for several hours at 60° gave a powder (VIII), which was identified with the product synthesized from III and IV, and which consisted of 2 moles of III and 1 mole of V. NMR data of VI, VII, VIII, and other isolated complexes mentioned later are given in Table I.

Table I. NMR Data of Complexes in CDCl₃

Complex	¹ H-NMR (δ)				¹⁹ F-NMR (δ)*	
	II		III		II	III
	α-CH ₃	γ-CH ₃	α-CH ₃	γ-CH ₃	β-CF ₃	β-CF ₃
VI	2.35 or 2.38	--	--	--	1.3	--
VII	2.36 or 2.40	3.90	2.60	1.3	-10.0	
VIII	--	--	3.95	2.60	--	-10.0
VI'	2.35	2.17	--	--	1.25	--
VII'	2.40	2.33	3.88	2.68	1.25	-10.3
VIII'	--	--	3.90	2.68	--	-10.3

* Benzotrifluoride = 0 ppm as internal standard

Complexes VI, VII, and VIII did not show any melting point but underwent decomposition when heated at temperatures above 120°, leaving V. The molecular weights observed by osmometry in CCl₄ (669 for VI and 699 for VII) and elemental analyses are consistent with those for (C₁₀H₉NF₆)₂PdCl₂ both for VI and VII. Chlorine atoms in VI and VII were not exchanged by treatment with resin (Amberlite IRA-400, I⁻-type) in CHCl₃-MeOH. ¹H- and ¹⁹F-NMR showed that only II was liberated from VI and that equimolar II and III were released from VII by the

addition of excess pyridine. Hence, molecular formulas of VI and VII would be shown as $(II)_2 \cdot PdCl_2$ and $(II)(III) \cdot PdCl_2$, respectively.

It is known that hexamethyl Dewar benzene forms π -complexes⁵⁾ and pyridines form $(N)\sigma$ -complexes with Pd^{II} . IR spectrum of VII shows absorptions at 1580 (pyridine ring), 1730 cm^{-1} ($\nu(C=C)$), and that of VI only at 1730 cm^{-1} . Absorption pattern of VI is very similar to that of II, and the pattern of VII to that of II and III in the region of $1730\text{--}1200\text{ cm}^{-1}$. These facts suggest that, in VI and VII, II and III are not coordinating with the metal through their π -system. The structure of VII was established as a trans-form by X-ray diffraction analysis. The orange crystals of VII from CCl_4 are monoclinic, space group being $P2_1/c$ with $a = 11.30$, $b = 12.92$, $c = 18.92\text{ \AA}$, $\beta = 108.4^\circ$, $Z = 4$. The intensities of independent 2615 reflections were measured using Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method and refined by the method of least squares with anisotropic temperature factors. Refinement converged at $R = 10.7\%$. Projection of the molecule is shown in Fig. 1.

Coordination of Pd is square and planar. The atoms (N-1, C-1, C-2, C-3) and (N-1, C-5, C-4, C-3) are, respectively, coplanar and the dihedral angle between these planes is $113^\circ 50'$. The dihedral angles between the (C1-1, Pd, C1-2, N-1) plane and (Pd, N-1, C-3, C-8) plane and between the (C1-1, Pd, C1-2, N-2) plane and pyridine ring plane are $101^\circ 6'$ and $84^\circ 30'$, respectively.

In a similar manner, the reaction between II and $PtCl_2$ gave three kinds of crystals (VI', VII', and VIII') corresponding respectively to VI, VII, and VIII in the case of Pd^{II} . However, $(III)_2PtCl_2$ -(VIII') was not obtained from III and $PtCl_2$. Further, the following facts were observed by 1H - and ^{19}F -NMR spectra and gas-liquid chromatography; addition of $RhCl_3 \cdot 3H_2O$, $Fe(CO)_5$, or $Fe_2(CO)_9$ to a solution of II in CD_3OD - $CDCl_3$ resulted in the increased formation of free III and decrease of free II without formation of stable complexes with these metal ions. And II did not undergo any reaction with $AgClO_4$, K_2PtCl_4 or $Rh(PPh_3)_3Cl$.

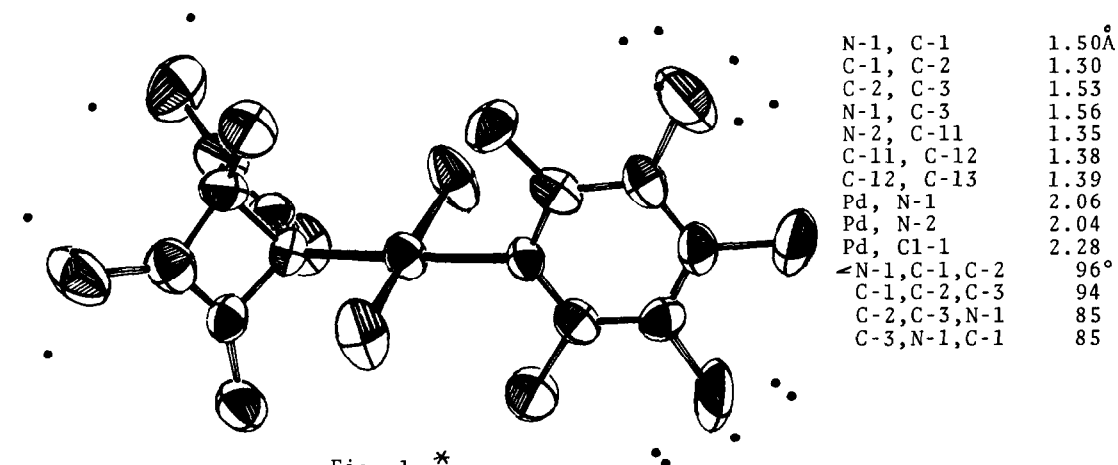
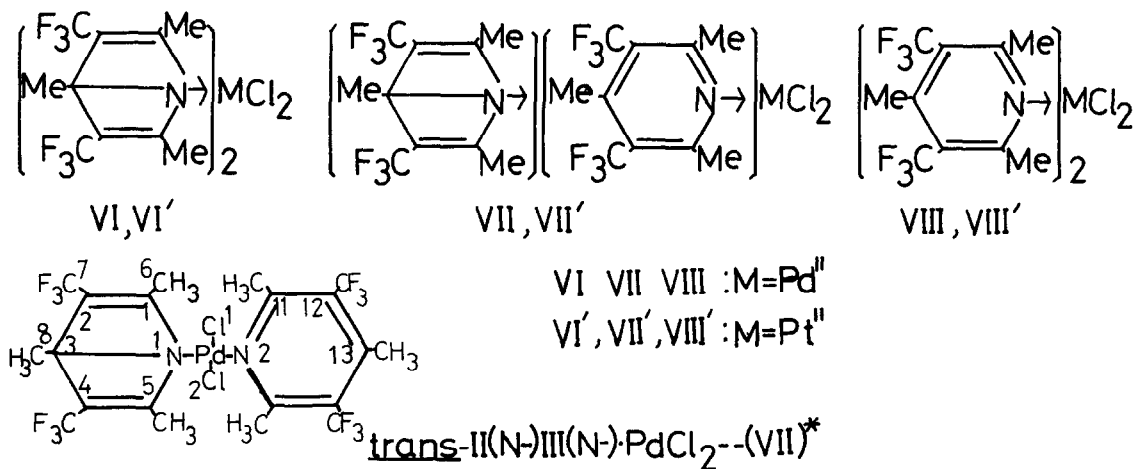


Fig. 1. *

* Thermal vibration of F-atoms is extraordinarily large and they are presented with dots in the figure. CF₃ groups of the pyridine ring are rotating around C-C bond. This figure shows the two alternative positions found on the Fourier map.

References

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