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A NEW PREPARATION OF IMIDAZOLIDINYLIDENE PALLADIUM(II) COMPLEXES

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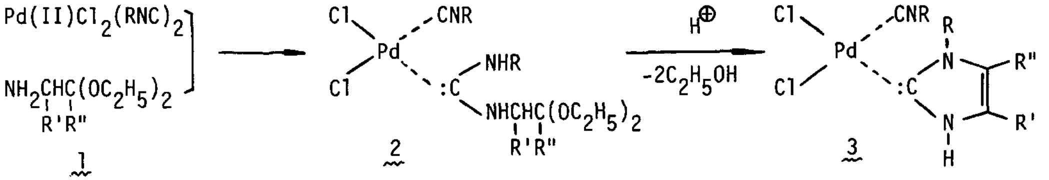
In the preceding papers[1)] we reported new synthetic methods of some nitrogen-containing heterocyclic compounds, in which diaminocarbene palladium(II) complexes generated from amines and $PdCl_2(RNC)_2$ may be involved as key intermediates. Here we wish to report the preparation of an imidazolidinylidene palladium(II) complex (3) by the intramolecular cyclization of a diaminocarbene palladium(II) complex (2) which is prepared by the reaction of α-aminoacetal (or α-aminoketal) (1) with $PdCl_2(RNC)_2$.

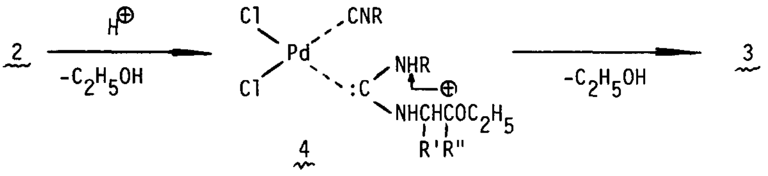


(1)

As shown in Table I, some diaminocarbene palladium(II) complexes (2) were prepared by the reactions of α-aminoacetals or ketal with $PdCl_2(RNC)_2$ according to the reported procedure.[2)] The structure of 2 has been established by elemental analysis, IR,[3)] NMR and molecular weight determination.[3)] Cyclization of the diaminocarbene palladium(II) complexes (2) leading to the formation of imidazolidinylidene palladium(II) complexes (3) was carried out as follows. A solution of 0.529 g (1 mmol) of complex (2b) and 0.344 g (2 mmol) of p-toluenesulfonic acid (or concd sulfuric acid (1 mmol)) in 9 ml of chloroform was stirred at room temperature under nitrogen for 24 hr. The chloroform solution was treated with Norit after aqueous work up and concentrated. The residue was triturated with ether-hexane (5:1) to precipitate imidazolidinylidene palladium(II) complex (3b) in 82% yield. 3b : IR (KBr) 3430, 3200, 3100, 2218, 1573, 1450, and (nujol mull) 320, 292 cm^{-1}; NMR ($CDCl_3$ with TMS) δ 0.9$\sim$2.5 (m, 20H), 3.6$\sim$4.3 (m, 2H)

6.96 (m, 1H), 7.15 (m, 1H), 12.0 (broad s, 1H); Molecular weight (Vapor pressure osmometer in CH_3OH) Calcd 437 Found 416. The cis-configuration of imidazolidinylidene palladium(II) complex (3) is supported by two bands at ca. 300 cm^{-1}, which are assigned to ν_{Pd-Cl}. Syntheses of some imidazolidinylidene palladium(II) complexes (3)[4,5] are summarized in Table II.

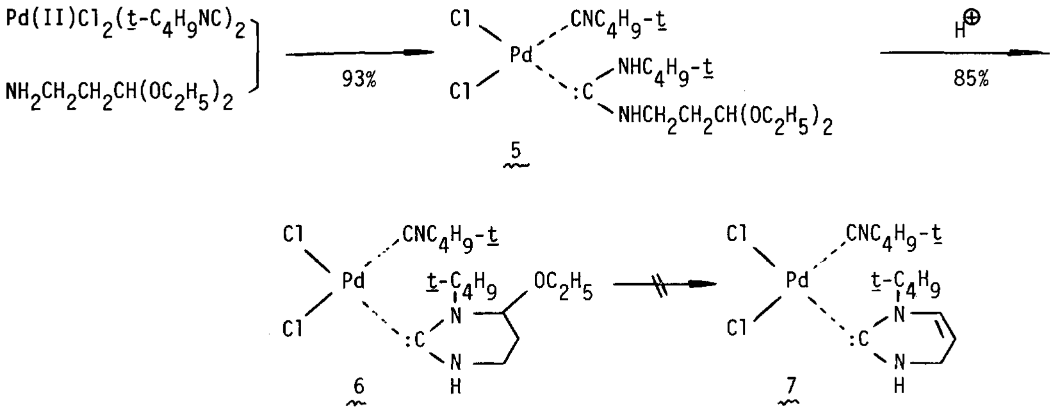
The intramolecular cyclization of diaminocarbene palladium(II) complex (2) may be explained by a scheme in which carbonium ion (4) attacks the amino nitrogen atom of the diaminocarbene ligand and then alcohol is eliminated.



(2)

The intramolecular cyclization of 2 may be taken as an interesting contrast to the fact that N,N'-dialkyl-diaminocarbene palladium(II) complex is inert toward methyl iodide and acyl halides.

Diaminocarbene palladium(II) complex (5),[5] which was prepared by the reaction of β-aminopropionaldehyde diethyl acetal with $PdCl_2(t\text{-}C_4H_9NC)_2$ also underwent the acid-catalyzed intramolecular cyclization to form a cyclic diaminocarbene palladium(II) complex (6).[5] Complex (6) was not susceptible to the elimination of ethyl alcohol to give complex (7) under the reaction conditions.

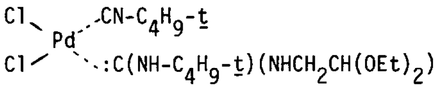
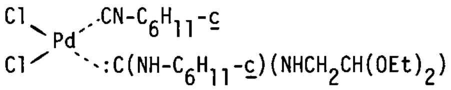
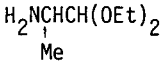
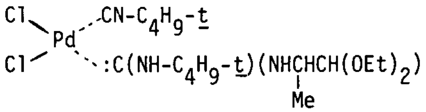
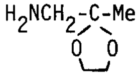
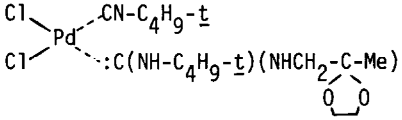


(3)

Finally, imidazolidinylidene palladium(II) complexes (3) thus obtained were treated with Ag_2O in benzene at room temperature to afford imidazole derivatives (8),[5] which were derived

TABLE I

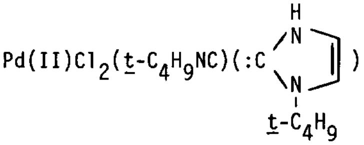
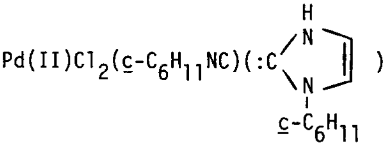
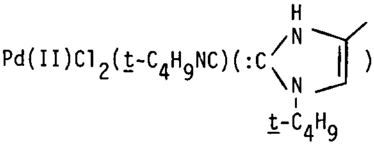
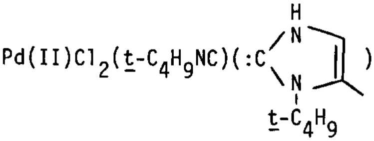
Preparation of Diaminocarbene Palladium(II) Complex (2)[a)]

Aminoacetal or Ketal	Isonitrile	Carbene Complex (2)		(Isolated Yield %)
$H_2NCH_2CH(OEt)_2$	$t\text{-}C_4H_9NC$		2a	(79)
$H_2NCH_2CH(OEt)_2$	$c\text{-}C_6H_{11}NC$		2b	(80)
 $H_2NCH(Me)CH(OEt)_2$	$t\text{-}C_4H_9NC$		2c	(78)
	$t\text{-}C_4H_9NC$		2d	(84)

a) Reaction condition: room temperature, 24 h.

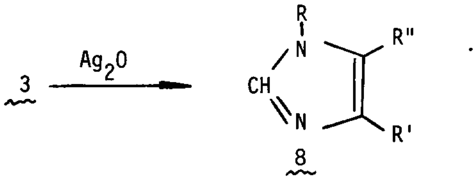
TABLE II

Preparation of Imidazolidinylidene Palladium(II) Complex (3)[a)]

Complex (2)	Acid[b)]	Time (h)	Imidazolidinylidene Pd(II) Complex (3)		(Isolated Yield %)
2a	s	24		3a	(76)
	t	50			(78)
2b	s	24		3b	(83)
	t	24			(82)
2c	t	24		3c	(91)
2d	t	24		3d	(92)

a) Reaction temperature : room temperature. b) Acid: s=sulfric acid, t=p-toluenesulfonic acid.

via the release of the imidazolidinylidene ligands from palladium with the concomitant 1,2-hydrogen migration. For instance, a mixture of 76.9 mg (0.2 mmol) of imidazolidinylidene palladium(II) complex (**3a**) and 46.3 mg (0.2 mmol) of Ag_2O in 1 ml of benzene was stirred at room temperature under nitrogen for 24 hr. Product of N-*tert*-butylimidazole was isolated by glpc in 72% yield : IR (neat) 1485, 1460 cm^{-1}; NMR ($CDCl_3$ with TMS) δ 1.51 (s, 9H) 6.98 (s, 2H), 7.55 (s, 1H).



(4)

a: 72% **b**: 61% **c**: 60% **d**: 52%

References and Notes

1) (a) Y. Ito, T. Hirao and T. Saegusa, J. Organometal. Chem., **82**, C47 (1974).
   (b) Y. Ito, T. Hirao and T. Saegusa, ibid, **131**, 121 (1977).

2) B. Crociani, T. Boschi and U. Belluco, Inorg. Chem., **9**, 2021 (1970).

3) **2a** : IR (KBr disk) 3400, 3225, 3070, 2217, 1578, and (nujol mull) 318, 282 cm^{-1};
   Molecular weight (Vapor pressure osmometer in $CHCl_3$) Calcd 477 Found 493.
   2b : IR (KBr disk) 3400, 3270, 3045, 2218, 1595, and (nujol mull) 312, 285 cm^{-1}.
   2c : IR (KBr disk) 3430, 3230, 3060, 2217, 1578, and (nujol mull) 315, 276 cm^{-1}.
   2d : IR (KBr disk) 3400, 3240, 3070, 2220, 1580, and (nujol mull) 316, 284 cm^{-1}.

4) **3a** : IR (KBr disk) 3430, 3150, 2216, 1575, 1454, and (nujol mull) 321, 289 cm^{-1};
   NMR ($CDCl_3$ with TMS) δ 1.40 (s, 9H), 1.95 (s, 9H), 7.23 (m, 2H), 12.1 (broad s, 1H).
   3c : IR (KBr disk) 3430, 3230, 3075, 2216, 1636, 1450, and (nujol mull) 320, 290 cm^{-1};
   NMR ($CDCl_3$ with TMS) δ 1.43 (s, 9H), 1.91 (s, 9H), 2.30 (s, 3H), 6.83 (m, 1H), 11.9 (broad s, 1H).
   3d : IR (KBr disk) 3400, 3230, 3070, 2219, 1574, 1475, and (nujol mull) 314, 292 cm^{-1};
   NMR ($CDCl_3$ with TMS) δ 1.40 (s, 9H), 2.00 (s, 9H), 2.38 (s, 3H), 6.97 (m, 1H), 11.8 (broad s, 1H).

5) All products **3**, **5**, **6** and **8** showed satisfactory analytical data.