

REACTION OF DIAZONIUM SALTS WITH TRANSITION METALS

V *. CATIONIC ARYLDIAZENIDO COMPLEXES OF PALLADIUM

ROKUYA YAMASHITA, KIYOSHI KIKUKAWA, FUMIO WADA and TSUTOMU MATSUDA *

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812 (Japan)

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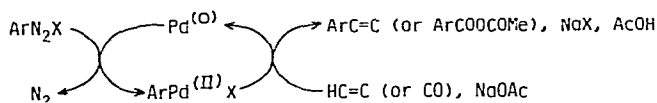
Summary

The title complex, $[\text{ArN}_2\text{Pd}(\text{PPh}_3)_3]\text{PF}_6$ (Ar = 4-methoxyphenyl), was prepared by the reaction of ArN_2PF_6 with $(\text{PPh}_3)_4\text{Pd}^0$. Other ArN_2X (Ar = phenyl, 4-tolyl, 4-fluorophenyl, 2,4,6-trichlorophenyl; X = BF_4 , PF_6) gave a mixture of aryldiazenido and arylpalladium complexes. The aryldiazenido complexes decompose to arylpalladium compounds at room temperature, UV irradiation facilitates this decomposition.

Introduction

Arenediazonium salts react with various transition metal complexes to give aryldiazenido or arylmetal complexes [2]. Recently Rattray and Sutton [3] reported that binuclear aryldiazenido palladium complexes were obtained by the reaction of arenediazonium salts with a Pd^{I} complex, $[\text{Pd}_2(\text{dppm})_2\text{Cl}_2]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), but the reaction with zerovalent palladium complexes resulted in spontaneous elimination of nitrogen to give arylpalladium complexes [3,4]. Arylpalladium complexes play a role as intermediates in the palladium(0) catalyzed alkenylation [5] or carboxylation [1] of arenediazonium salts (Scheme 1). By analogy to the behavior of the corresponding platinum

SCHEME 1



* For Part IV see ref. 1.

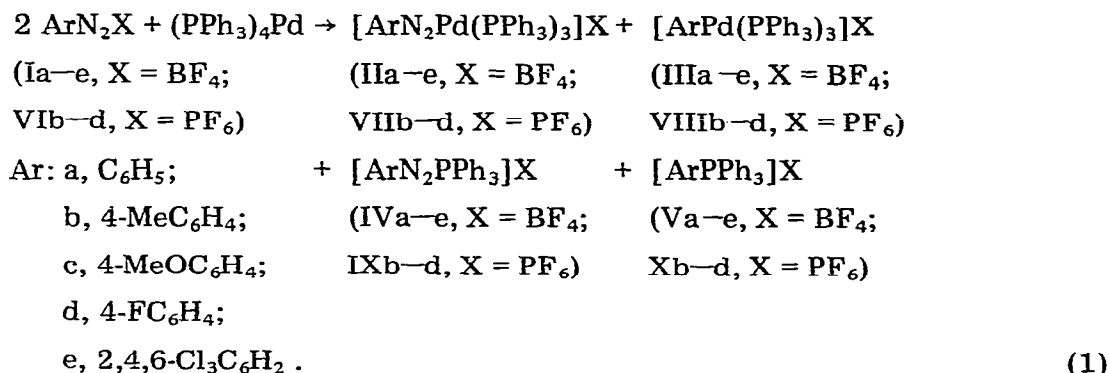
complexes [6], it seemed reasonable to expect that the arylpalladium intermediates are produced by extrusion of nitrogen from initially formed aryldiazenido palladium complexes.

After many attempts to isolate the aryldiazenido complexes using various zerovalent palladium complexes, the reaction of $(\text{PPh}_3)_4\text{Pd}^0$ with diazonium hexafluorophosphates proved to be promising and gave the crystalline 4-methoxyphenyldiazenido palladium complex.

Results and discussion

Reaction with arenediazonium tetrafluoroborates (ArN_2BF_4)

Two equivalents of ArN_2BF_4 (I) was added to a suspension of $(\text{PPh}_3)_4\text{Pd}^0$ in dichloromethane at -78°C , and the mixture was stirred at room temperature to give a reddish-brown solution, which afforded a yellow powder on addition of ether. When an equimolar amount of I was used, some of the palladium complex remained unreacted (eqn. 1). The phosphonium salts, IV and V, in the



reaction mixture could be removed by dissolution of the solid in dichloromethane followed by reprecipitation by the addition of benzene. Elemental analyses of the resulting yellow solids showed variable nitrogen contents which depended on reaction conditions and on the substituent(s) in I (Table 1). An NMR spectrum of the product from Ic showed two signals at 3.78 and 3.94 (δ , ppm, TMS), both assignable to methoxy protons. Irradiation of a yellow dichloromethane solution of the product from Ic with UV light caused nitrogen evolution and decolorization, and the NMR signal at 3.78 ppm disappeared with concomitant increase of that at 3.94 ppm (Fig. 1). Thus, the signals at 3.78 and 3.94 ppm are reasonably assigned to IIc and IIIc, respectively. The yellow solid obtained from Ib, whose NMR spectrum showed two signals at 2.20 and 2.50 ppm, behaved similarly and gave a white solid IIIb (one signal at 2.50 ppm) on UV irradiation. The nitrogen extrusion of II also proceeded spontaneously both in the solid and in solution. The instability of II may account for the difficulty of isolation of II in pure form and for the poor reproducibility of analytical data in this system.

Reaction with arenediazonium hexafluorophosphates (ArN_2PF_6)

A reaction of VIc with $(\text{PPh}_3)_4\text{Pd}$ in dichloromethane at -20°C for 20 min gave reddish oily products after removal of the solvent. Recrystallization from

TABLE 1
REACTION OF ArN_2BF_4 OR ArN_2PF_6 WITH $\text{Pd}(\text{PPh}_3)_4$

Run I or VI No.	Solvent	Reaction temp. ($^{\circ}\text{C}$)	Products ^a Yield (%)	Analytical data ^b (%)		
				C	H	N
1 Ia	CH_2Cl_2	$-78 \sim \text{r.t.}$	42	65.15 (66.47)	4.67 (4.64)	0.44 (2.58)
2 Ib	CH_2Cl_2	$-78 \sim \text{r.t.}$	77	67.97 (66.65)	5.10 (4.77)	1.62 (2.55)
3 Ic	CH_2Cl_2	$-78 \sim \text{r.t.}$	84	65.79 (65.70)	4.88 (4.70)	2.28 (2.51)
4 Id	CH_2Cl_2	$-78 \sim \text{r.t.}$	59	65.20 (65.32)	4.49 (4.48)	0.20 (2.54)
5 Id	acetone	r.t.	84 ^c	63.96 (65.07) ^c	5.04 (4.94) ^c	1.85 (2.34) ^c
6 Ie	CH_2Cl_2	$-78 \sim \text{r.t.}$	78	59.59 (60.63)	3.97 (3.99)	1.38 (2.36)
7 VIb	CH_2Cl_2	$-78 \sim -20$	28	61.92 (63.30)	4.36 (4.54)	0.79 (2.42)
8 VIc	CH_2Cl_2	-20	90	61.64 (62.44)	4.40 (4.47)	2.12 (2.39)
9 VIc	$\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$	0	51	62.35 (62.44)	4.33 (4.47)	2.45 (2.39)
10 VIId	CH_2Cl_2	$-78 \sim -20$	48	61.22 (62.05)	4.23 (4.25)	0.95 (2.41)

^a The products are considered to be a mixture of II and III (or VII and VIII) except for Run 9 (pure VIIC). The yields are calculated as the products are pure II or VII. ^b Found values with calculated values for II or VII in parentheses. ^c Calculated values for IIId(acetone)_{1.6}. The presence of acetone was assumed by NMR and IR.

methanol at -78°C gave orange crystals (90%), which showed a strong NMR signal at δ 3.82 ppm and a weak one at 3.98 ppm as well as a slightly low nitrogen content (Table 1, run 8). The reaction in methanol-benzene (1 : 2.5) solvent at 0°C gave a clear reddish solution within 2 min. Addition of benzene caused slow precipitation of VIIC as orange crystals in 51% yield; m.p. (dec.) $161-162.5^{\circ}\text{C}$. The product gave a satisfactory analysis and showed only one NMR signal at δ 3.80 ppm in the aliphatic region. The complex VIIC is no more stable than IIC. If a solution of VIIC was allowed to stand at room temperature for one week, a marked increase of the signal at 3.98 ppm, attributable to VIIC was observed (Fig. 1). The other arenediazonium salts, however, still gave mixtures of VII and VIII under various reaction conditions (Table 1).

All efforts to obtain neutral aryldiazenido palladium complexes from IIC and VIIC (or IIb) have failed due to the extremely facile denitrogenation on addition of an anionic ligand to give an arylpalladium complex (eqn. 2).



This facile transformation should provide a new route to arylpalladium complexes bearing various anionic ligands.

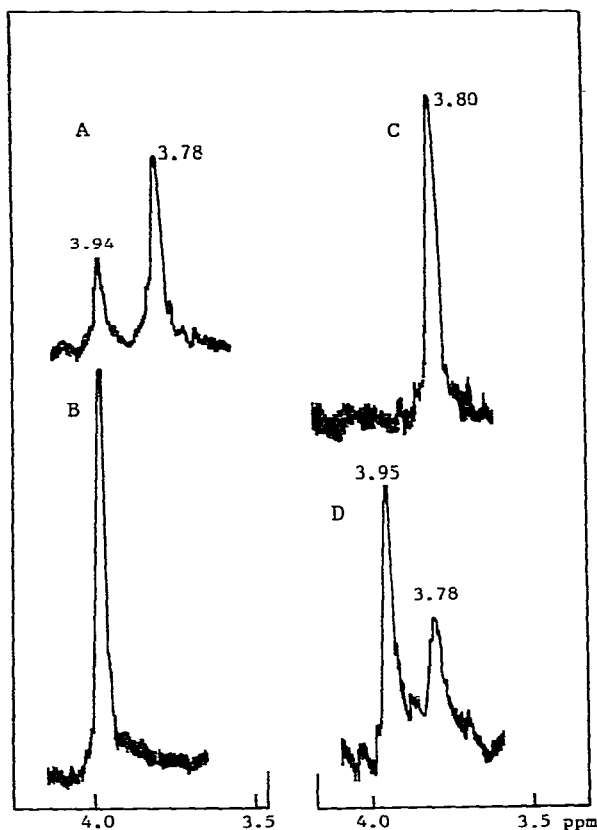


Fig. 1. NMR spectra of IIC, IIIC and VIIC (in CDCl_3 at 60 MHz). A, Products of Run 3 (IIC + IIIC); B, IIIC (prepared by UV irradiation); C, VIIC (Run 9); D, After 1 week standing of C at r.t.

Infrared spectra. The instability of complexes VIIC and IIC prevented detailed examination of their structures. IR spectra, however, provided information concerning the structure of their diazo moiety. No characteristic absorption was observed in the region between 2600 and 1600 cm^{-1} . The absorption in the region near 1590 and 1250 cm^{-1} is noticeable (Fig. 2) and those of a similar diazenido complex of platinum, $[4\text{-MeO-C}_6\text{H}_4\text{N}_2\text{Pt}(\text{PPh}_3)_3]\text{-BF}_4$ (XI) [6], also are shown in Fig. 2 for comparison. In Fig. 2, two absorptions at 1250 and 1267 cm^{-1} can reasonably be attributed to $\nu(\text{C-O})$ of the 4-methoxyphenyldiazenido and the 4-methoxyphenyl groups, respectively. The relative intensities of the absorptions of 1575 and 1569 cm^{-1} in the products of Run 3 (mixture of IIC and IIIC) and IIIC seem to support the postulate that the former is $\nu(\text{N=N})$ of IIC and that the latter arises from the 4-methoxyphenyl ring. The assignment is supported by the presence of the former absorption in VIIC in greater intensity. The product of Run 2 also showed a new absorption at 1573 cm^{-1} , together with those at 1600 and 1586 cm^{-1} , while IIIb showed only the higher two. The absorption of 1585 cm^{-1} in XI has been assigned to $\nu(\text{N=N})$ and constitutes the basis of supporting its diazenido structure as an anionic one-electron donor terminal ligand [2,6]. Thus, in VIIC, IIC

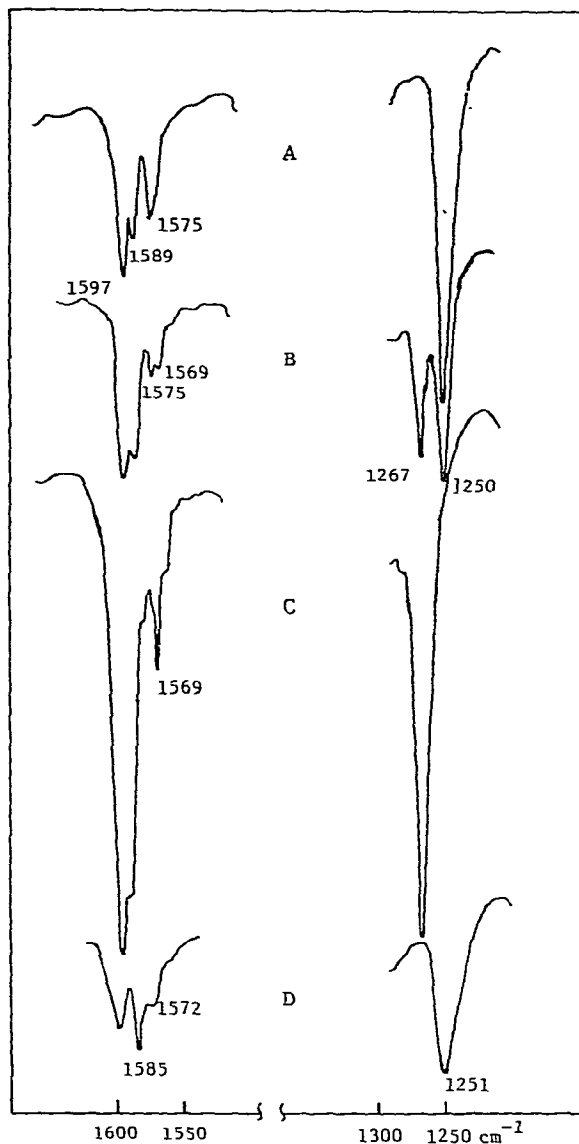


Fig. 2. IR spectra of IIc, IIIc, VIIc and XI (Nujol mull). A, VIIc (Run 9); B, Products of Run 3 (IIc + IIIc); C, IIIc; D, XI.

and also IIb, the aryldiazenido groups are considered to be donating to divalent palladium in the same way.

Experimental

NMR and IR spectra were recorded using Varian A-60 and JASCO IRE instruments, respectively.

Diazonium salts [7], $(PPh_3)_4Pd$ [8], $[4-MeO-C_6H_4N_2Pt(PPh_3)_3]BF_4$ [6], and

Pt(PPh₃)₃ [9] were prepared by conventional methods. Solvents were distilled and stored under nitrogen.

General procedure of preparation of II or VII

All procedures used were carried out under nitrogen.

To a mixture of 0.4–0.5 mmol of (PPh₃)₄Pd (weighed accurately) and two molar equivalents of ArN₂BF₄ or ArN₂PF₆ was added 15 ml of dichloromethane at –78°C and the mixture was allowed to warm to room temperature. The resulting reddish-brown solution was filtered and the solvent was removed under reduced pressure. Addition of 20 ml of methanol to the oily (or solid) residue gave a homogeneous solution from which fine orange crystals slowly deposited. After cooling the mixture to –78°C the crystals were filtered at –78°C and washed with cold methanol (–78°C) and ether (0°C), and dried under reduced pressure.

Essentially the same procedure was employed for Runs 1–4, 7, 8 and 10. For Runs 5 or 9, acetone or methanol-benzene (1 : 2.5) was used as solvent, respectively. The products were isolated by precipitation from the homogeneous reaction mixture with benzene.

Preparation of IIIb or IIIc

A solution of II (ca. 0.4 g from Run 2 or 3) and 20 ml of dichloromethane at 0°C in a Pyrex reaction vessel was irradiated (high pressure mercury lamp, Riko UVL-100HA) for 1 to 3 h. The yellow color faded during the irradiation with evolution of ca. 6 ml of nitrogen. A white solid was isolated by precipitation with benzene. [4-MeC₆H₄Pd(PPh₃)₃]BF₄ (IIIb); yield, 68%, Anal. Found: C, 67.95; H, 5.13; N, 0.00, C₆₁H₅₂P₃BF₄Pd, calcd.: C, 68.45; H, 4.89; N, 0%. [4-MeO-C₆H₄-Pd(PPh₃)₃]BF₄ (IIIc); yield, 42%, m.p. 223–226°C, Anal. Found: C, 67.45; H, 4.70; N, 0.00, C₆₁H₅₂OP₃BF₄Pd, calcd.: C, 67.39; H, 4.82; N, 0%.

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