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1,2,3-Benzotriazole Complexes of Palladium(II)

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1,2,3-Benzotriazoles are known to decompose thermally and photochemically to give biradicals, with an accompanying evolution of nitrogen.[1] We attempted to prepare 1,2,3-benzotriazole complexes of transition metals[2] and to compare the complexes with free compounds. This note will describe how the reaction of 1*H*-, 1-benzyl-, and 1-vinyl-1,2,3-benzotriazoles with dichlorobis(benzonitrile)palladium(II) and di-π-allyl-μ,μ'-dichlorodipalladium(II) gives benzotriazole complexes of palladium(II). The pyrolysis and the photolysis of these complexes will bediscussed later.

1*H*-1,2,3-Benzotriazole readily reacts with dichlorobis(benzonitrile)palladium(II) in benzene at room temperature to give a yellow complex of the PdCl$_2$(1*H*-1,2,3-benzotriazole)$_2$ type almost quantitatively. The infrared spectrum of this complex has a very strong band at 3200 cm^{-1}, indicating that the >N–H group remains in the complex and that some of the nitrogen atoms in the benzotriazole act as donors. 1-Benzyl- and 1-vinyl-1,2,3-benzotriazoles react similarly with dichlorobis(benzonitrile)palladium(II) to give complexes of the PdCl$_2$(benzotriazole)$_2$ type. These complexes are also formed from palladium(II) chloride and the benzotriazoles in ethanol, but those reactions proceed very slowly.

The benzotriazoles react with di-π-allyl-μ,μ'-dichlorodipalladium(II) in benzene at room temperature to give white or yellow complexes of the (π-allyl)PdCl(benzotriazole) type. The PMR spectra of these complexes indicate that the allyl group gives a signal of the A$_2$B$_2$X type in CDCl$_3$ and of the AX$_4$ type in dimethyl sulfoxide (DMSO-d_6), and that the chemical shifts and the coupling constants of protons of methylene and the vinyl group are similar to those of the free corresponding benzotriazoles. In DMSO-d_6, the PMR spectra of the allyl groups depend on the temperature (20—70°C). Over 40°C all four terminal protons are equivalent (AX$_4$, τ 6.2 ppm doublet, 4.2 ppm quintet); this is best described in terms of a rapid dynamic equilibrium between the two possible σ-bonded forms.[3] However, at 20°C, the signal at the higher field appears as a broad singlet, suggesting that the dynamic equilibrium may be affected by the temperature. The fact that the PMR signals of the 1-methylene and 1-vinyl group in the 1-benzyl- and 1-vinyl-benzotriazoles are not affected by the complex formation strongly suggests that the nitrogen atom at the 2 or 3-position of the benzotriazoles acts as the donor in the complexes.

Experimental[4]

All the reactions were carried out in an argon atmosphere. The products, benzotriazole complexes of Pd(II), were stable in air in the solid state.

Dichlorobis(1H-1,2,3-benzotriazole)palladium(II). Into 380 mg of dichloro bis(benzonitrile)palladium(II) in 10 m*l* of benzene, we stirred 240 mg of 1*H*-1,2,3-benzotriazole at room temperature. A yellow substance (340 mg) precipitated out in a few minutes; this was filtered off and washed several times with benzene; mp>290°C; insoluble in benzene, ethanol, water, chloroform, and acetone, but slightly soluble in DMSO and *N,N*-dimethylformamide(DMF).

Found: C, 35.10; H, 2.55; N, 19.95; Cl, 16.80; Pd, 24.80%. Calcd for C$_{12}$H$_{10}$N$_6$Cl$_2$Pd: C, 34.68; H, 2.43; N, 20.23; Cl, 17.06; Pd, 25.60%.

IR (KBr): 3200 (very strong, broad), 1620(m), 1605(m), 1505(m), 1455(m), 1425(w), 1405(m), 1305(m), 1235(s), 1125(m), 1050(s), 915(m), 780(s), 760(m), 740(s) cm^{-1}. (s= strong, m=medium, w=weak intensity)

Dichlorobis(1-benzyl-1,2,3-benzotriazole)palladium(II). 1-Benzyl-1,2,3-benzotriazole[5] (105 mg) in 5 m*l* of benzene was similarly treated with dichlorobis(benzonitrile)palladium(II) (96 mg) for 5 min to give a pale yellow precipitate (120 mg); mp 250°C decomp.; insoluble in benzene, ethanol, chloroform, and acetone, but slightly soluble in DMSO and DMF.

Found: C, 51.58; H, 4.00; N, 13.61%. Calcd for C$_{26}$H$_{22}$N$_6$Cl$_2$Pd: C, 52.41; H, 3.72; N, 14.11%.

IR (KBr): 3080(m), 3050(m), 3000(w), 2940(m), 1615(m), 1595(m), 1495(m), 1480(m), 1455(m), 1330(w), 1310(m), 1300(w), 1245(s), 1165(m), 1140(m), 770(m), 745(s) cm^{-1}.

PMR (60 MHz, in DMSO-d_6); τ 1.8—2.6(multiplet, 4H), 2.65(singlet, 5H), 3.95(singlet, 2H).

Dichlorobis(1-vinyl-1,2,3-benzotriazole)palladium(II). 1-Vinyl-1,2,3-benzotriazole[6] (150 mg) was similarly treated with dichlorobis(benzonitrile)palladium(II) (190 mg) in 5 m*l* of benzene to give a pale yellow precipitate (180 mg); mp 265°C decomp.; insoluble in benzene, ethanol, chloroform, and acetone, but slightly soluble in DMSO and DMF.

Found: C, 41.86; H, 3.11; Pd, 23.31%. Calcd for C$_{16}$H$_{14}$N$_6$Cl$_2$Pd: C, 41.09; H, 3.02; Pd, 22.75%.

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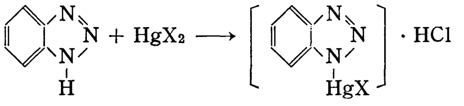
1) E. M. Burgess, R. Carithers, and L. MuCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968): A. J. Hubert, *J. Chem. Soc., C*, **1969**, 1334: M. Ohashi, K. Tsujimoto, and T. Yonezawa, *Chem. Commun.*, **1970**, 1089.

2) Benzotriazole complexes of mercury were prepared by the reaction of 1*H*-benzotriazole with mercury salts.



X=O$_2$CCH$_3$ and Cl

E. Müller and H. Meier, *Ann. Chem.*, **716**, 11 (1968).

3) J. C. Chien and H. C. Dehm, *Chem. Ind.* (London), **1961**, 745.

4) The PMR and IR spectra were obtained on a JEOL H-60 NMR Spectrometer and a 215 Hitachi Grating Infrared Spectrophotometer, respectively.

5) Prepared by the published method: M. S. Gibson, *J. Chem. Soc.*, **1956**, 1076.

6) Prepared by the published method: J. Hopff, U. Wyss, and H. Lussi, *Helv. Chim. Acta*, **43**, 135 (1960).

IR (KBr): 3100(m), 2940(w), 1645(s), 1600(m), 1500(m), 1460(s), 1360(m), 1320(m), 1310(m), 1210(s), 1170(m), 1140 (m), 1120(m), 960(m), 920(m), 780(m), 760(m), 750(s) cm^{-1}. PMR (in DMSO-d_6); τ 1.5—2.8(multiplet, 5H), 3.8(1H), 4.5(1H).

*Chloro(π-allyl)(1*H*-1,2,3-benzotriazole)palladium(II).* Into 183 mg of di-π-allyl-μ,μ'-dichloropalladium(II) in 15 m*l* of benzene, we stirred 300 mg of 1*H*-1,2,3-benzotriazole at room temperature. After 10 min, a pale yellow precipitate (250 mg) was filtered off. Recrystallization from chloroform gave yellow prisms; mp 160°C decomp.; soluble in chloroform and DMSO.

Found: C, 36.50; H, 3.30; N, 14.04; Cl, 11.94; Pd, 36.42%. Calcd for $C_9H_{10}N_3ClPd$: C, 35.79; H, 3.34; N, 13.91; Cl, 11.74; Pd, 35.23%.

IR (KBr): 3080(s), 1620(m), 1600(m), 1455(m), 1390(s), 1280(m), 1220(s), 1150(m), 1105(m), 980(w), 960(m), 935(m), 910(m), 815(m), 780(m), 765(m), 740(s) cm^{-1}. PMR (in DMSO-d_6); at 20°C, τ 2.0—2.5(multiplet, 4H), 4.15(quintet, 1H, J=10.0 Hz), 6.2(singlet, broad, 4H); at 70°C; τ 2.0—2.5(multiplet, J=10.0 Hz), 4.15(quintet, J=10.0 Hz), 6.2 (doublet, J=10.0 Hz).

Chloro(π-allyl)(1-benzyl-1,2,3-benzotriazole)palladium(II). 1-Benzyl-1,2,3-benzotriazole (210 mg) and di-π-allyl-μ,μ'-dichlorodipalladium (270 mg) in 3 m*l* of benzene at room temperature gave a pale yellow precipitate (360 mg). Recrystallization from chloroform gave yellow prisms; mp 125°C (dec.); soluble in chloroform and DMSO.

Found: C, 48.75; H, 3.90; N, 10.71%. Calcd for $C_{16}H_{16}N_3ClPd$: C, 49.00; H, 4.11; N, 10.72%.

IR (KBr): 3100(m), 3050(m), 2960(m), 1595(m), 1500(m), 1455(m), 1385(m), 1310(m), 1240(m), 1230(m), 1160(m), 1140(m), 1120(m), 1005(m), 960(m), 950(m), 770(m), 745(s), 725(s), 700(m) cm^{-1}. PMR (in $CDCl_3$); τ 1.55(multiplet, 1H), 2.6 and 2.7(multiplet and singlet, 8H), 4.15(singlet, 2H), 4.2(multiplet, 1H), 5.85(doublet, 2H, J=7.0 Hz), and 6.85 (doublet, 2H, J=12.0 Hz), (π-allyl: A_2B_2X). PMR (in DMSO-d_6) at 65°C; τ 1.7—2.6(multiplet), 2.65(singlet), 4.0 (singlet), 4.15(quintet, J=10.0 Hz), 6.23(doublet, J=10.0 Hz), (π-allyl: AX_4). At 20°C, the singal at τ 6.23 was a broad singlet.

Chloro(π-allyl)(1-vinyl-1,2,3-benzotriazole)palladium(II). 1-Vinyl-1,2,3-benzotriazole (100 mg) and di-π-allyl-μ,μ'-dichlorodipalladium(II) (126 mg) in 5 m*l* of benzene at room temperature gave a white precipitate (190 mg). Recrystallization from chloroform gave pale yellow prisms; mp 140°C (dec.); soluble in chloroform and DMSO.

Found: C, 40.94; H, 4.04; Pd, 32.43%. Calcd for $C_{11}H_{12}N_3ClPd$: C, 40.27; H, 3.69; Pd, 32.43%.

IR (KBr): 3105(m), 3060(w), 3040(m), 1650(s), 1600(w), 1500(m), 1465(m), 1365(m), 1330(m), 1310(m), 1300(m), 1270(m), 1205(s), 1195(s), 1165(m), 1135(m), 1110(m), 970(m), 910(m), 795(m), 770(m), 760(m) cm^{-1}. PMR (in $CDCl_3$): τ 1.6(multiplet, 1H), 2.2—2.8(multiplet, 4H), 3.97-(doublet of doublets, 1H, J_{ac}[7]=15.0 Hz, J_{ab}=2.0 Hz), 4.2-(multiplet, 1H), 4.63(doublet of doublets, 1H, J_{bc}=12.0 Hz, J_{ab}=2.0 Hz), 5.85(doublet, 2H, J=7.0 Hz), and 6.85(doublet, 2H, J=12.0 Hz), (π-allyl: A_2B_2X). PMR (in DMSO-d_6): at 65°C; τ 4.15(quintet, J=10.0 Hz) and 6.2(singlet, broad).

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7) 1-Vinyl group: