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The Heck Reaction of 2-Vinylpyridine

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In the presence of lithium chloropalladite, 2-vinylpyridine reacted with phenylmercuric chloride to give di-μ-chloro-bis[2-phenyl-2-(α-pyridyl)ethyl]dipalladium(II). Similar complexes were obtained from *p*-tolyl-, *p*-anisyl-, or *m*-nitrophenylmercuric chloride. The σ-bonded structures of these complexes have been confirmed by a study of their absorption and of the NMR spectra.

We wish to report that 2-vinylpyridine (**1**) reacted with arylmercuric chloride in the presence of lithium chloropalladite(II) to give complexes (**2**) containing both a carbon-palladium σ-bond and an aryl group.

Experimental

Materials. All the melting points are uncorrected. The arylmercuric chlorides were prepared by the methods described in the literature: *p*-tolylmercuric chloride,[1] mp 232—233 °C; *p*-anisylmercuric chloride,[2] mp 173—174 °C; *m*-nitrophenylmercuric chloride,[3] mp 218—221 °C. Phenylmercuric chloride (mp 250—251 °C) was obtained from the commercially available phenylmercuric acetate by treating with alcoholic lithium chloride.

The General Procedure for the Preparation of Di-μ-chloro-bis-[2-aryl-2-(α-pyridyl) ethyl] dipalladium (II) (2a—d). A lithium chloropalladite solution was prepared by stirring 0.42 g (10 mmol) of anhydrous lithium chloride and 1.77 g (10 mmol) of anhydrous palladium chloride overnight at room temperature in 100 ml of acetonitrile. Into the lithium chloropalladite solution, arylmercuric chloride (10 mmol) was then stirred at room temperature for five minutes, after which 1.26 g (12 mmol) of **1** was added in one portion. After the mixture had then been stirred at room temperature for 6 hr, the product was isolated by filtration to remove a precipitated palladium and by distillation under reduced pressure to remove the solvent. The residue was dissolved in chloroform and chromatographed on neutral alumina. The first elution with chloroform and recrystallization from methanol afforded colorless crystals, which were identified as biphenyls (**3a**—**d**) by a comparison of the IR spectra and by a mixed-melting-point determination with an authentic sample. Further elution with chloroform and recrystallization from chloroform–cyclohexane afforded yellow products (**2a**—**d**). The results are summarized in Table 1.

The Preparation of Chloro-[2-aryl-2-(α-pyridyl)ethyl]-pyridine-palladium Complexes (4a—d). A solution of the chloro-bridged palladium complex (**4**) (0.10 g) in methylene chloride was treated with a solution of pyridine (5% excess) in ether. After 10 min, the solvent was removed under reduced pressure; the residue was then recrystallized from benzene–cyclohexane to give pale yellow crystals. The results are summarized in Table 1.

Results and Discussion

In the presence of lithium chloropalladite, **1** reacted with phenylmercuric chloride in acetonitrile to give a yellow crystal, di-μ-chloro-bis[2-phenyl-2-(α-pyridyl)-ethyl]dipalladium(II) (**2a**), accompanied by a small amount of biphenyl (**3a**). Similarly, *p*-tolylmercuric chloride, *p*-anisylmercuric chloride, and *m*-nitrophenylmercuric chloride all reacted with **1** to afford yellow complexes (**2b**—**d**).

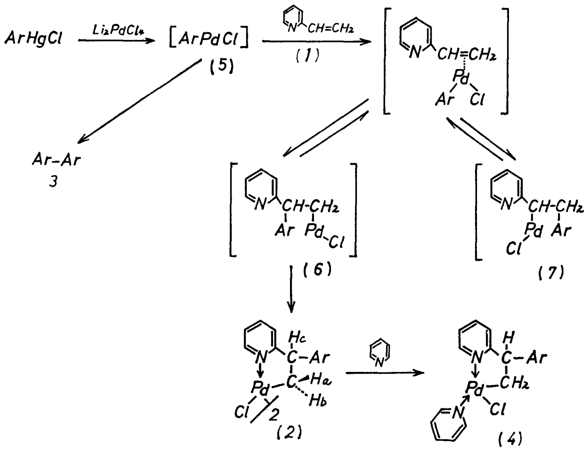

Fig 1.

The mechanism of the formation of **3a**—**d** as a by-product may involve a coupling reaction of aryl-palladium chloride (**5**), prepared *in situ* from aryl-mercuric chloride and lithium chloropalladite in acetonitrile. The σ-bonded structure for the yellow complexes (**2a**—**d**) was supported by the molecular-weight determinations and by the reaction with pyridine to give readily soluble monomeric derivatives (**4a**—**d**). Moreover, the far-infrared spectra of **2a**—**d** showed a bridged Pd–Cl stretching absorption at about 290 and 255 cm^{-1}. The NMR spectra of **2a**—**d** were in agreement with the proposed structures. For example, the NMR spectrum of **2a** consists of four resonances, at σ 3.48, 3.73 (the protons of the *N*-methylene group (H_a and H_b)), 4.55 (the methine proton H_c), and 7.05—8.52 ppm (the protons of the phenyl and pyridyl groups). The nonequivalence of the methylene protons (H_a and H_b) can most easily be explained in terms of a cyclic system in which nitrogen is coordinated to the metal. Similarly, in the NMR spectra of **2a**—**d**, all the resonances can be satisfactorily accounted for by the presence of the σ-bond and a cyclic system.

Recently, Heck[4] has reported that the arylation of olefin with **5** was stereospecific with internal olefin, giving products consistent with a *cis* addition of the organopalladium reagent to the olefin, followed by a *cis* elimination of a hydridopalladium(II) species. In

TABLE 1. THE HECK REACTION OF 2-VINYLPYRIDINE (**1**)

Arylating agent RC_6H_4HgCl	Product	Yield (%)[a]	Mp °C (lit.)	Found % (Calcd) C	H	N	IR (cm^{-1}) and NMR (δ, ppm) spectra,[b] mol wt (in $CHCl_3$) and pyridine derivative (**4**)
R=H	Biphenyl (**3a**)	15	68—69 (69—70[c])				
	2a (Ar=Phenyl)	28	162—163 (dec.)	48.26 (48.17)	3.78 (3.70)	4.12 (4.31)	IR 750 and 690 (phenyl), 294 and 257 (bridged Pd–Cl stretching). NMR 3.48 (*q*, 1H, H_a or H_b, A or B part of an ABX spin system, J_{AB} = 16 Hz, J_{AX}=8 Hz, J_{BX}= 1.5 Hz), 3.73 (*q*, 1H, H_b or H_a, B or A part of an ABX spin system), 4.55 (*d-d*, 1H, H_c, X part of an ABX spin system) and 7.05—8.52 (*m*, 9H, phenyl and pyridyl protons). Mol. wt, 637 (648). Pyridine derivative (**4a**), mp 126—128 °C (dec.).
R=*p*-Me	Bi-*p*-tolyl (**3b**)	18	119—120 (120[c])				
	2b (Ar=*p*-Tolyl)	24	148—150 (dec.)	49.66 (49.71)	4.01 (4.14)	4.12 (4.12)	IR 805 (tolyl), 292 and 253 (bridged Pd–Cl stretching). NMR 2.07 (*s*, 3H, CH_3), 3.51 (*q*, 1H, H_a or H_b, A or B part of an ABX spin system, J_{AB}= 15 Hz, J_{AX} =7.5 Hz, J_{BX}=1.5 Hz), 3.72 (*q*, 1H, H_b or H_a, B or A part of an ABX spin system), 4.64 (*q*, 1H, H_c, X part of an ABX spin system), and 6.90—8.56 (*m*, 8H, tolyl and pyridyl protons). Mol wt 670 (675). Pyridine derivative (**4b**), mp 128—130 °C (dec.).
R=*p*-MeO	Bi-*p*-anisyl (**3c**)	16	170—171 (170—172[c])				
	2c (Ar=*p*-Anisyl)	30	128—131 (dec.)	47.62 (47.78)	3.85 (3.97)	3.88 (3.96)	IR 808 (anisyl), 292 and 255 (bridged Pd–Cl stretching). NMR 3.50 (*q*, 1H, H_a or H_b, A or B part of an ABX spin system, J_{AB} = 15Hz, J_{AX}=8 Hz, J_{BX}= 1.5 Hz), 3.67 (*s*, 3H, CH_3O–), 3.73 (*q*, 1H, H_b or H_a, B or A part of an ABX spin system), 4.65 (*q*, 1H, H_c, X part of an ABX spin system), and 6.99—8.55 (*m*, 8H, anisyl and pyridyl protons). Mol wt 698 (707). Pyridine derivative (**4c**), mp 125—127 °C (dec.).
R=*m*-NO_2	3,3′-Dinitrobiphenyl (**3d**)	20	201—203 (198.5—199.5[d])				
	2d (Ar=*m*-Nitrophenyl)	25	145—148 (dec.)	42.22 (42.30)	2.89 (3.00)	7.51 (7.55)	IR 1530 and 1350 (–NO_2), 860 and 805 (*m*-disubstituted aromatic ring), 293 and 255 (bridged Pd–Cl stretching). NMR 3.16—3.45 (*m*, 2H, H_a+H_b), 4.15 (*q*, 1H, H_c), and 6.88—8.87 (*m*, 8H, aromatic and pyridyl protons). Mol wt 722 (738). Pyridine derivative (**4d**), mp 134—136 °C (dec.).

[a] Yields are based upon the arylating agent.

[b] IR spectra were measured on KBr disks (4000—650 cm^{-1}) or in Nujol mulls mounted on thin polythene windows. NMR spectra were observed by means of a Hitachi R-22 NMR spectrometer at 90 MHz, using TMS as an internal standard. The chemical shifts were followed by the splitting patterns (*s*, singlet; *q*, quartet; *d-d*, double-doublet; *m*, multiplet) and the relative strengths.

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the reactions of **1** with **5**, the formation of σ-complexes (**2a**—**d**) suggests that the reaction involves the intermediate formation of an arylpalladium chloride–olefin adduct and favors the formation of the adduct (**6**), where palladium is attached to the terminal methylene carbon, over with the formation of the *anti*-Markovnikov adduct (**7**).

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