The Addition of Arylpalladium Chloride to 1,5-Cyclooctadiene and *endo*-Dicyclopentadiene

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(Received February 8, 1974)

1,5-Cyclooctdiene reacted with phenylpalladium chloride to give di-μ-chloro-bis-(1-phenylcyclooct-4-ene-8σ,4π)-dipalladium(II). Similarly, the reaction of *endo*-dicyclo-pentadiene with phenylpalladium chloride led to di-μ-chloro-bis-[*endo*-6-phenyl-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene-*endo*-5σ,(2—3)π]-dipalladium (II). The σ-bonded structures of these complexes have been confirmed by studies of the IR and NMR spectra.

Heck[1] has previously reported that the reaction of 1,3-diolefins with arylpalladium chloride gave 1-arylmethyl-π-allylpalladium chloride dimers in moderate yields. In this paper, we wish to report that 1,5-cyclooctadiene (**1**) and *endo*-dicyclopentadiene (**2**) react with arylpalladium chloride to form complexes containing a carbon–palladium σ bond.

Experimental

Materials. All the melting points are uncorrected. The arylmercuric chlorides were prepared by the methods described in the literature: *p*-tolylmercuric chloride,[2] mp 232—233 °C; *p*-anisylmercuric chloride,[3] mp 173—174 °C. The phenylmercuric chloride, 1,5-cyclooctadiene (**1**), and *endo*-dicyclopentadiene (**2**) were of a commercial grade and were used after purification.

*The General Procedure for The Preparation of Di-μ-chloro-bis-(1-arylcyclooct-4-ene-8σ,4π)-dipalladium(II) (**3a—c**) and Di-μ-chloro-bis-*[endo-*6-aryl-3a,4,5,6,7,7a-hexahydro-*endo-*4,7-methano-indene-*endo-*5σ,(2—3)π]-dipalladium(II) (**3d—f**).* 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 added with stirring at room temperature for ten min, after which 12 mmol of **1** or **2** was added in one portion. After the mixture had been stirred at room temperature for 6 hr, the solution was filtered and evaporated to dryness. 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 (**4a—c**). Further elution with chloroform and recrystallization from chloroform–cyclohexane afforded yellow products (**3a—f**). The results are summarized in Table 1.

*The Preparation of Chloro-(1-arylcyclooct-4-ene-8σ,4π)-pyridine-palladium Complexes (**5a—c**)* and *Chloro-*[endo-*6-aryl*]-*3a,4,5,6,7,7a-hexahydro-*endo-*4,7-methano-indene-*endo-*5σ,(2—3)π]-pyridine-palladium Complexes (**5d—f**).* A solution of the palladium complex (**3a—f**) (0.10 g) in methylene chloride was treated with a solution of pyridine (5% excess) in ether. After 30 min, the solvent was removed under reduced pressure; the residue was then recrystallized from benzene-cyclohexane to give yellow crystals. The results are summarized in Table 2.

*Sodium Borohydride or Deuteride Reductions of Arylated σ-Complexes (**3a—f**).* Into a suspension of sodium borohydride or deuteride in 50—70 ml of dry monoglyme **3a—f** was added with stirring over a period of 30 min (molar ratio of 2 : 1, hydride to complex). After the solution has been stirred at room temperature for 1 hr, an exual volume of water was added and the solution was heated on a steam bath for 1 hr. The reaction was heated on a steam bath for 1 hr. The reaction mixture was then cooled, and the palladium precipitate which had formed was collected on a filter. The filtrate was extracted with three 75-ml portions of *n*-hexane. The combined extracts were dried over anhydrous magnesium sulfate and then fractionally distilled to afford to product, **6a—f** or **7a—c** (see Table 3). The products were identified by comparison with authentic samples and by the observation of the NMR spectra.

Results and Discussion

At room temperature, **1** reacted with phenylpalladium chloride to give yellow di-μ-chloro-bis-(1-phenylcyclooct-4-ene-8σ,4π)-dipalladium(II) (**3a**) in a 28% yield, accompanied by a small amount of biphenyl (**4a**). *p*-Tolyl- and *p*-anisylpalladium chloride also reacted to afford yellow σ-complexes (**3b—c**).

The reduction of **3a** with sodium borohydride in monoglyme to afford phenylcyclooctane (**6a**) showed that the addition of the phenyl group occurred at an olefinic bond by means of the formation of a new carbon-carbon bond and that the reaction occurred without any rearrangement of the carbon skeleton. The σ-bonded structure of the complex (**3a**) was supported by the molecular-weight measurements and by the bridged splitting reaction with pyridine to give a readily soluble monomeric derivative (**5a**). Moreover, the far-infrared spectrum of **3a** showed a bridged Pd–Cl stretching absorption at about 278 and 227 cm^{-1}. The NMR spectrum of **3a** was consistent with the four resonances at 1.18—2.75 (the protons of methylene and methine groups), 6.09 (the olefinic proton), 6.46 (the olefinic proton), and 7.25 ppm (the phenyl protons), and was in agreement with the proposed structure. Similarly, in the NMR spectra of **3b—c**, all the resonances can be satisfactorily accounted for by the presence of the σ-bond.

In the presence of lithium chloropalladite, the reaction of **2** with arylmercuric chloride in acetonitrile also gave the yellow chloro-bridged complex, di-μ-chloro-bis[*endo*-6-aryl-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene-*endo*-5σ,(2—3)π]-dipalladium(II) (**3d—f**), accompanied by a small amount of **4a—c**. The molecular-weight measurements, the observation of far-infrared spectra, and the bridge-splitting reaction with pyridine supported the chloro-bridged binuclear structures for **3d—f**. Furthermore, the NMR spectra of **3d—f** were in agreement with the proposed structures.

TABLE 1. THE REACTION OF ARYLPALLADIUM CHLORIDE WITH 1,5-CYCLOOCTADIENE (**1**) AND *endo*-DICYCLOPENTADIENE (**2**)

Arylating Agent ArHgCl	Product	Yield (%)[a]	Mp °C (lit.)	Found % (Calcd) and mol wt[b]	IR (cm^{-1}) and NMR (δ, ppm) spectra.
a) Reaction with 1,5-cyclooctadiene (**1**).					
Ar=Ph	Biphenyl (**4a**)	8	68—69 (69—70[c])		
	3a (Ar=Ph)	28	176—178 (dec.)	C, 51.28 (51.40) H, 5.17 (5.23) Mol wt 645 (654)	IR 745, 690, 278 and 227. NMR 1.18—2.75 (m, 10H), 6.09 (m, 1H), 6.46 (m, 1H), and 7.25 (m, 5H).
Ar=*p*-Tolyl	Bi-*p*-tolyl (**4b**)	10	119—120 (120[c])		
	3b (Ar=*p*-Tolyl)	32	154—155 (dec.)	C, 52.77 (52.80) H, 5.57 (5.61) Mol wt 675 (682)	IR 800, 280, and 228. NMR 1.15—2.84 (m, 10H, methylene and methine protons), 2.28 (s, 3H, methyl protons), 6.11 (m, 1H, olefinic proton), 6.45 (m, 1H, olefinic proton), and 7.08—7.34 (m, 4H, *p*-tolyl protons).
Ar=*p*-Anisyl	Bi-*p*-anisyl **4c**)	11	170—171 (170—172[c])		
	3c (Ar=*p*-anisyl)	33	182—184 (dec.)	C, 50.35 (50.44) H, 5.30 (5.36) Mol wt 708 (714)	IR 805, 280, and 230. NMR 1.16—2.78 (m, 10H, methylene and methine protons), 3.65 (s, 3H, methoxy protons), 6.06 (m, 1H, olefinic proton), 6.43 (m, 1H, olefinic proton), and 7.01—7.43 (m, 4H, *p*-anisyl protons).
b) Reaction with *endo*-dicyclopentadiene (**2**).					
Ar=Ph	**4a**	10	68—69 (19—70[c])		
	3a (Ar=Ph)	40	108—110 (dec.)	C, 54.61 (54.72) H, 4.76 (4.87) Mol wt 693 (702)	IR 750, 690, 294, and 216. NMR 1.08—2.43 (m, 8H, methylene and methine protons), 2.80 (q, 1H, H_A, $J_{A,X}$= 9.5 and $J_{A,4}$=3.5 Hz), 6.86 (m, 2H, olefinic protons), and 7.23 (m, 5H, phenyl protons).
Ar=*p*-Tolyl	**4b**	12	119—120 (120[c])		
	3e (Ar=*p*-tolyl)	48	147—149 (dec.)	C, 55.83 (55.91) H, 5.17 (5.24) Mol wt 719 (730)	IR 800, 294, and 215. NMR 1.01—2.05 (m, 8H), 2.28 (s, 3H), 2.85 (q, 1H), 3.23 (q, 1H), 6.50 (m, 2H), and 7.23 (m, 4H).
Ar=*p*-Anisyl	**4c**	8	170—171 (170—172[c])		
	3f (Ar=*p*-anisyl)	42	118—120 (dec.)	C, 53.38 (53.52) H, 4.87 (5.01) Mol wt 758 (762)	IR 800, 297, and 215. NMR 1.10—2.55 (m, 8H, methylene and methine protons), 2.78 (q, 1H, H_X), 3.19 (q, 1H, H_A, $J_{A,X}$=9.5 and $J_{A,4}$=3.5 Hz), 3.65 (s, 3H, methoxy protons), 6.58 (m, 2H, olefinic protons), and 7.34 (m, 4H, anisyl protons).

a) Yields are based upon the arylmercuric chloride. b) IR spectra were measured on KBr disks (4000—650 cm^{-1}) or in Nujol mulls mounted on thin polythene windows (700—200 cm^{-1}). NMR spectra were observed in $CDCl_3$ 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 pattern (s, singlet; q, quartet; m, multiplet) and the relative strengths. Molecular weight was determined in $CHCl_3$, using a Hitachi 115 vapor-pressure osmometer. c) E. Müller and T. Topel, *Ber.*, **72**, 273 (1939).

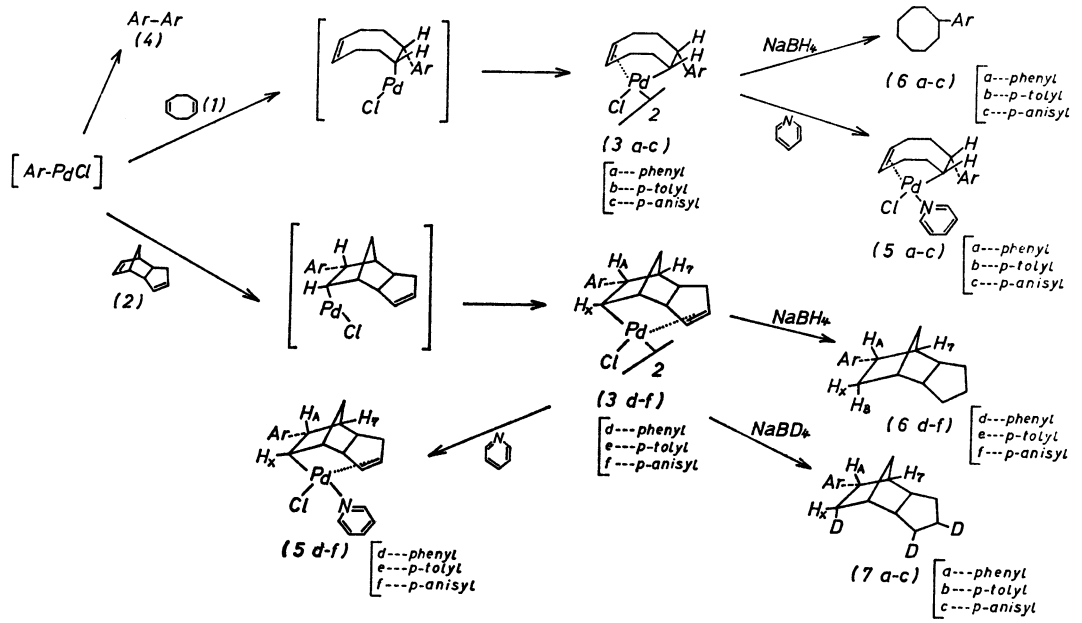

Fig. 1.

Table 2. The properties of pyridine derivatives (**5a—f**) of complexes (**3a—f**)

Complex	Mp °C (dec)	Found (Calcd) % and mol wt	IR (cm^{-1}) and NMR (δ, ppm) spectra
5a (Ar=Ph)	138—140	C, 55.95(56.10) H, 5.27 (5.45) N, 3.32 (3.44) Mol wt 394 (406)	IR 750, 740, 690, 284 (terminal Pd-Cl) and 235 (Pd-Py). NMR 1.14—2.78 (m, 10H, $-CH_2-+-CH-$), 6.12 (m, 1H, -CH=CH-), 6.51 (m, 1H, -CH=CH-), and 7.02—8.58 (m, 10H, phenyl+pyridine protons).
5b (Ar=*p*-tolyl)	157—160	C, 57.01(57.15) H, 5.58 (5.75) N, 3.25 (3.44) Mol wt 413 (420)	IR 800, 750, 287 (terminal Pd-Cl) and 238 (Pd-Py). NMR 1.10—2.83 (m, 10H, $-CH_2-+-CH-$), 2.29 (s, 3H, CH_3-), 6.14 (m, 1H, -CH=CH-), 6.48 (m, 1H, -CH=CH-), and 7.00—8.68 (m, 9H, tolyl+pyridine protons).
5c (Ar=*p*-anisyl)	156—157	C, 54.87(55.05) H, 5.39 (5.54) N, 3.14 (3.21) Mol wt 430 (436)	IR 800, 750, 283 (terminal Pd-Cl) and 235 (Pd-Py). NMR 1.15—2.74 (m, 10H, $-CH_2-+-CH-$), 3.68 (s, 3H, CH_3O-), 6.11 (m, 1H, -CH=CH-), 6.48 (m, 1H, -CH=CH-), and 6.98—8.64 (m, 9H, anisyl+pyridine protons).
5d (Ar=Ph)	129—131	C, 59.88(60.02) H, 5.14 (5.27) N, 3.26 (3.33) Mol wt 408 (420)	IR 740, 690, 293 (terminal Pd-Cl) and 233 (Pd-Py). NMR 1.10—2.51 (m, 8H, $-CH_3-+-CH-$), 2.84 (q, 1H, H_X), 3.22 (q, 1H, H_A, $J_{A,X}=9.0$ and $J_{A,4}=3.0$ Hz), 6.82 (m, 2H, olefinic protons), and 7.04—8.55 (m, 10H, phenyl+pyridine protons).
5e (Ar=*p*-tolyl)	155—157	C, 58.87(59.04) H, 5.41 (5.44) N, 3.06 (3.15) Mol wt 439 (444)	IR 800, 750, 291 (terminal Pd-Cl), and 235 (Pd-Py). NMR 1.06—2.14 (m, 8H, $-CH_2-+-CH-$), 2.27 (s, 3H, CH_3-), 2.91 (q, 1H, H_X), 3.28 (q, 1H, $J_{A,X}=9.5$ and $J_{A,4}=4$ Hz), 6.68 (m, 2H, olefinic protons), and 7.01—8.80 (m, 9H, tolyl+pyridine protons).
5f (Ar=*p*-anisyl)	144—146	C, 57.35(57.40) H, 5.07 (5.25) N, 2.96 (3.04) Mol wt 451 (460)	IR 804, 750, 294 (terminal Pd-Cl), and 235 (Pd-Py). NMR 1.08—2.58 (m, 8H, $-CH_2-+-CH-$), 2.81 (q, 1H, H_X), 3.25 (q, 1H, H_A, $J_{A,X}=9.5$ and $J_{A,4}=3.0$ Hz), 3.62 (s, 3H, CH_3O-), 6.65 (m, 2H, olefinic protons), and 7.01—8.84 (m, 9H, anisyl+pyridine protons).

TABLE 3. REDUCTION OF ARYLATED σ-COMPLEXES (**3a—f**) WITH $NaBH_4$ OR $NaBD_4$

Product[a]	Yield %	Bp °C/mmHg (lit.)	NMR spectra (δ, ppm).
6a (Ar=Ph)	68	110—115/1 (100—102/0.55—0.6[b])	
6b (Ar=*p*-tolyl)	70	123—125/1	1.38—1.81 (m, 14H, -C**H**$_2$-), 2.28 (s, 3H, C**H**$_3$), 2.80 (m, 1H, -C**H**-), and 7.22 (q, 4H, tolyl protons).
6c (Ar=*p*-anisyl)	71	118—121/1	1.40—1.79 (m, 14H, -C**H**$_2$-), 2.83 (m, 1H, -C**H**-Ar), 3.71 (s, 3H, C**H**$_3$O-), and 7.18 (q, 4H, anisyl protons).
6d (Ar=Ph)	75	134—136/2	1.36—1.90 (m, 14H, -C**H**$_2$-+-C**H**-), 3.03 (d-q, 1H, H_A, $J_{A,X}$=8.5 Hz, $J_{A,B}$=2.0 Hz, $J_{A,7}$=3.5 Hz), and 7.23 (m, 5H, phenyl protons).
7a (Ar=Ph)	70	132—135/2	1.35—1.90 (m, 11H, -C**H**$_2$-+-C**H**- -C**H**D-), 3.04 (q, 1H, H_A, $J_{A,X}$ =8.5 Hz, $J_{A,7}$=3.6 Hz), and 7.23 (m, 5H, phenyl protons).
6e (Ar=*p*-tolyl)	68	144—147/2	1.30—1.96 (m, 14H, -C**H**$_2$-+-C**H**-), 2.30 (s, 3H, C**H**$_3$-), 2.97 (d-q, 1H, H_A, $J_{A,X}$=8.4 Hz, $J_{A,B}$=2.1 Hz, $J_{A,7}$=3.6 Hz), and 7.11 (m, 4H, tolyl protons).
7b (Ar=*p*-tolyl)	65	144—148/2	1.34—1.93 (m, 11H, -C**H**$_2$-+-C**H**-+-C**H**D-), 2.29 (q, 1H, H_A, $J_{A,X}$ =8.6 Hz, $J_{A,7}$=3.6 Hz), and 7.13 (m, 4H, tolyl protons).
6f (Ar=*p*-anisyl)	65	150—151/3	1.30—1.98 (m, 14H, -C**H**$_2$-+-C**H**-), 2.96 (d-q, 1H, H_A, $J_{A,X}$=8.0 Hz, $J_{A,B}$=2.0 Hz, $J_{A,7}$=3.5 Hz), 3.74 (s, 3H, C**H**$_3$O-), and 7.25 (m, 4H, anisyl protons).
7c (Ar=*p*-anisyl)	68	148—150/3	1.28—1.98 (m, 11H, -C**H**$_2$-+-C**H**-+-C**H**D-), 2.94 (q, 1H, H_A, $J_{A,X}$ =8.2 Hz, $J_{A,7}$=3.5 Hz), 3.74 (s, 3H, C**H**$_3$O-), and 7.28 (q, 4H, anisyl protons).

a) The elemental analyses were consistent with the assigned structures and the deuterium-content of the products was calculated from the mass-spectral results. b) A. C. Cope and E. C. Hermann, *J. Amer. Chem. Soc.*, **72**, 3405 (1950).

For example, the NMR spectrum of **3e** consists of six groups of bands centered at δ 1.01—2.05 (the methylene and methine protons), 2.28 (the methyl protons), 2.85 (H_X proton), 3.23 (H_A proton), 6.50 (the olefinic protons), and 7.32 ppm (the tolyl protons), with relative intensities of 8 : 3 : 1 : 1 : 2 : 4. The quartet peak (J=10 and 4 Hz) at δ 3.23 ppm is assigned to the proton (H_A) on the aryl-bearing carbon, and the coupling of 10 Hz between the (CH-*p*-tolyl) and (CH-Pd) protons is a result of a coupling to a vicinal proton with a 0° dihedral angle ($J\simeq$7—9 Hz).[4] The palladium–carbon bond must be *endo* so that palladium can remain coordinated to the double bond; the *p*-tolyl moiety is, therefore, *endo*. In addition, the reduction of **3e** with sodium borohydride or deuteride gave a saturated hydrocarbon, $C_{17}H_{22}$ (**6e**) or $C_{17}H_{19}D_3$ (**7b**). The NMR spectrum of **6e** shows a very characteristic pair of quartets ($J_{A,X}$=8.4 Hz, $J_{A,B}$=2.1 Hz, $J_{A,7}$= 3.6 Hz) for the H_A proton at 2.97 ppm. The coupling constant of $J_{A,X}$ correlates with the calculated value ($J\simeq$7—9 Hz) between H_A and a proton at a 0° angle, and the coupling constant of $J_{A,B}$ is that expected for a 120° dihedral angle ($J\simeq$2 Hz). Furthermore, the NMR spectrum of deuterated hydrocarbon (**7b**) was very similar to that of **6e**, and the *endo*-configuration of the deuterium was established by the H_A quartet ($J_{A,X}$=8.6 Hz, $J_{A,7}$=3.6 Hz). These results support the proposed structure for **3e**. Similarly, in the NMR spectra for **3d** and **3f** and monomeric pyridine derivatives (**5d—f**), all the resonances can be satisfactorily accounted for by the proposed structures.

Recently, Maitlis[5] has reported that the reaction of diphenylmercury with dichloronorbornadiene palladium gave di-μ-chloro-bis-(*endo*-3-phenylnorbornen-2-yl-*endo*-palladium) and that the reaction proceeds *via* an *endo*-attack on co-ordinated norbornadiene. In the reaction of **1** or **2** with arylpalladium chloride, the reaction undoubtedly proceeds by means of *cis* arylpalladation at the double bond.

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