Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PERHALOARYL–METAL CHEMISTRY
VI*. THE FORMATION AND PROPERTIES OF SOME σ-PERHALOARYL DERIVATIVES OF PALLADIUM**

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(Received October 17th, 1969)

SUMMARY

A series of new σ-aryl–palladium compounds have been prepared from the reaction of perhaloaryl Grignard or -lithium reagents and $[CH_3(C_6H_5)_2P]_2PdCl_2$. The proton NMR spectra of these products are consistent with a *trans*-planar configuration in each case. Similar reactions involving $BipyPdCl_2$ (Bipy = 2,2′-bipyridine) have afforded the diamagnetic *cis*-complexes $BipyPd(\sigma\text{-}C_6X_5)_2$ (X = F, Cl). Attempted extensions of these reactions to (norbornadiene)$PdCl_2$ have thus far failed to yield σ-perhaloaryl derivatives, but the platinum analog (norbornadiene)$Pt(\sigma\text{-}C_6F_5)_2$ has been realized.

INTRODUCTION

During the course of our studies on σ-perhaloaryl derivatives of nickel, it became desirable to investigate briefly the formation and properties of certain analogous compounds of palladium. Surprisingly, few σ-aryl–palladium derivatives have been described in the literature. Following an important, definitive paper on this topic by Calvin and Coates[2] in 1960, several other studies dealing briefly and in part with σ-aryl–palladium compounds have been reported[3-5]. Moreover, all the presently known σ-aryl–palladium compounds have been derived from the complexes $[(C_2H_5)_3P]_2PdCl_2$. In our studies, we decided to investigate the possible stabilization of σ-aryl–palladium compounds derived from $[CH_3(C_6H_5)_2P]_2PdCl_2$ (I), since the proton NMR spectra of the resulting products should facilitate the determination of their stereochemistries via "virtual coupling" techniques[6]. We also decided to investigate the formation and properties of *cisoid*-σ-aryl–palladium derivatives derived from $BipyPdCl_2$ (Bipy = 2,2′-bipyridine) and (norbornadiene)$PdCl_2$.

RESULTS AND DISCUSSION

A reaction between (I) and pentafluorophenylmagnesium bromide proceeded

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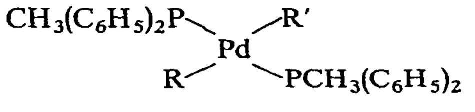
* For Part V see ref. 1.

** Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, California, March 31-April 5, 1968.

readily to produce the mono-aryl complex (II) in 72% yield. Treatment of (I) with the



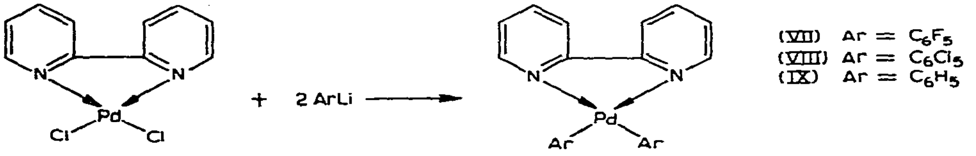
(I) R,R′=Cl
(II) R=C_6F_5, R′=Cl
(III) R,R′=C_6F_5
(IV) R=C_6Cl_5, R′=Cl
(V) R,R′=C_6Cl_5

more reactive reagent pentafluorophenyllithium produced, after separation of the products by chromatography, a 56% yield of the bis-aryl derivative (III) as well as a 15% yield of (II). The mono-aryl complex (IV) was isolated in low yield as a dihydrate from a reaction between (I) and pentachlorophenylmagnesium chloride. Complex (IV) and several other σ-aryl–palladium derivatives prepared in this study tended to form hydrates readily, and it was necessary to dry each analytical sample at *ca.* 77° *in vacuo* in order to obtain suitable elemental analyses for the un-hydrated compound. As in the analogous nickel system[1], attempted arylation of (IV) by means of pentachlorophenyllithium failed to produce the bis-aryl derivative (V); (IV) was largely recovered together with a small amount of organic decomposition products.

The proton NMR spectra of all the above palladium complexes (I)–(IV) are consistent with diamagnetic, *trans*-planar structures in solution in each case. A symmetrical 1/2/1 triplet in the vicinity of τ 8.0 is observed in the spectrum of each complex, and is assigned to the phosphine-methyl protons. The strong spin-coupling of two phosphorus nuclei in *trans*-positions in such derivatives is well-known, and since the phosphine-methyl proton resonance thus depends on the spin states of both phosphorus nuclei, it appears as a triplet (virtual coupling)[6].

The generally high thermal and oxidative stabilities of these σ-pentahaloaryl derivatives of palladium are in marked contrast to analogous σ-phenyl analogs, which are reported to decompose slowly at room temperature and which usually had to be purified by recrystallization at low temperatures[2]. Our results are therefore in agreement with earlier findings by Calvin and Coates[2], who observed that σ-aryl–palladium complexes in which the aryl ligand contains an electron-withdrawing substituent in the *para*-position are appreciably more stable than those in which either hydrogen or an electron-donating substituent is present in this position. Presumably, the σ-pentachlorophenyl derivative also receives some kinetic stabilization from attack by external reagents by means of an "*ortho*-effect" imposed by the two bulky *ortho*-chlorine atoms, although the magnitude of this effect is believed to be relatively less marked in palladium than in the nickel series[2,7]. This "*ortho*-effect" probably accounts for our failure to prepare the bis-pentachlorophenyl complex (V) from (IV).

We next turned our attention to the possible formation of σ-aryl derivatives derived from BipyPdCl_2 (VI). The 2,2′-bipyridine ligand in coordination chemistry



(VI)

(VII) Ar = C_6F_5
(VIII) Ar = C_6Cl_5
(IX) Ar = C_6H_5

is frequently considered to function as a strong σ-donor supplemented by back-bonding through overlap of ligand π*-orbitals with filled *d*-orbitals of the metal atom[8]. A 2,2'-bipyridine ligand is also postulated to cause a splitting of the *d*-orbital energy levels in nickel or palladium compounds in which it is coordinated[9]. Thus, many of the factors which are believed to stabilize σ-organotransition metal compounds containing tert-phosphine ligands should also be applicable to similar 2,2'-bipyridine compounds, at least to some extent. The formation and surprising stability of $BipyPd(CH_3)_2$ has already been noted by Calvin and Coates[2], and since that time, Maitlis and Stone[10] have described several n-heptafluoropropyl analogs. On the other hand, all attempts by the former workers to prepare *cis*-diaryl derivatives of palladium during the course of their studies failed, and even a reaction between (VI) and mesityllithium did not result in the formation of a σ-aryl–palladium compound[2].

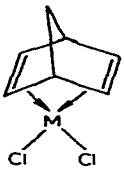
In contrast, we have found that (VI) undergoes reaction readily with either pentafluorophenyl- or pentachlorophenyllithium to produce the corresponding bis-aryl complexes (VII) and (VIII) in yields of 79% and 30%, respectively. A reaction also occurred readily with phenyllithium, but instead of the desired organopalladium derivative (IX), a 55% yield of the coupling product, biphenyl, was isolated. Although the 2,2'-bipyridine–palladium derivatives (VI)–(VIII) proved to be too insoluble to permit NMR studies, a magnetic susceptibility test was conducted with a simplified Faraday magnetic apparatus on each complex. All were found to be diamagnetic, suggesting a *cis*-planar structure in each case.

Both 2,2'-bipyridine complexes (VII) and (VIII), like the tert-phosphine derivatives (II)–(IV) described above, were found to be stable in air at room temperature. Complex (VIII) also proved to be very stable thermally, since it has a melting point of 335–337° and showed signs of decomposition only above *ca.* 370°. To our knowledge, (VIII) represents the first example of an organotransition metal compound containing two bulky, electronegative pentachlorophenyl substituents σ-bonded to the same transition metal in a *cisoid* manner. Molecular models indicate that such a structure is reasonable on steric grounds, providing that the two C_6Cl_5 groups are oriented essentially perpendicular to the *xy*-plane of the complex.

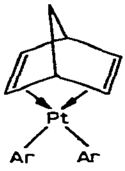
During the course of some related work, we were able to repeat the synthesis of $BipyNi(\sigma\text{-}C_6F_5)_2$ from a reaction between $BipyNiCl_2$ and pentafluorophenyllithium reported earlier by Stone *et al.*[11]. On the other hand, attempts to substitute phenyl- for pentafluorophenyllithium resulted in high conversion to biphenyl and 2,2'-bipyridine instead of the desired bis-aryl derivative[12]. A similar reaction between $BipyNiCl_2$ and pentachlorophenyllithium also failed to produce the desired bis-aryl derivative, and only a product believed to be decachlorobiphenyl was isolated.

It thus appears that a 2,2'-bipyridine ligand can stabilize a compound in which two pentafluorophenyl ligands, but not two phenyl ligands, are σ-bonded to the same nickel or palladium atom. The nickel analog of (VIII) is either not stable enough to permit its isolation, or more likely, steric factors imposed by two pentachlorophenyl substituents do not allow its formation. Since the covalent radius of palladium is significantly larger than the covalent radius of nickel, steric factors would be expected to be substantially lowered in the formation of (VIII).

Doyle and coworkers[13] have recently shown that a number of σ-bonded organic derivatives of platinum are accessible from reactions of $(norbornadiene)PtI_2$ and Grignard reagents. We have been able to prepare the bis-phenyl complex (XI) from a reaction between $(norbornadiene)PtCl_2$ (X) and phenylmagnesium chloride, and have extended the series to include the bis-pentafluorophenyl derivative (XII).



(X) M = Pt
(XIII) M = Pd



(XI) Ar = C_6H_5
(XII) Ar = C_6F_5

Both (XI) and (XII) were found to be generally stable to oxygen and water at room temperature. On the other hand, our attempts to prepare corresponding palladium derivatives starting with (XIII) have thus far been unsuccessful. A reaction of (XIII) with phenylmagnesium chloride produced a 98% yield of the coupling product, biphenyl, and none of the desired bis-phenyl derivative. A reaction also occurred between (XIII) and pentafluorophenylmagnesium bromide, but again, no pure organometallic compound could be isolated from the reaction mixture. The norbornadiene ligand therefore apparently does not contribute sufficient stabilization of the type provided by tert-phosphine or even 2,2'-bipyridine ligands to permit the isolation of σ-aryl derivatives in the palladium series under normal conditions.

EXPERIMENTAL

Proton NMR spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Melting points were determined under nitrogen on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, and by Mr. Charles Meade of the Microanalysis Laboratory, Office of Research Services, University of Massachusetts. Ethyl ether was purified by distillation from lithium aluminum hydride immediately before use. Benzene and n-hexane were purified by procedures described by Vogel[14]. The final fractional distillations were conducted under a nitrogen atmosphere into nitrogen-filled storage containers where the purified solvents were stored under nitrogen until use. All reactions involving the formation of organopalladium compounds were run under an atmosphere of nitrogen.

Bis(diphenylmethylphosphine)dichloropalladium (I)

To a stirred, filtered solution of ammonium tetrachloropalladite [prepared from anhydrous palladium chloride (1.77 g, 10 mmole), ammonium chloride (1.07 g, 20 mmole), and 15 ml of distilled water] at room temperature was rapidly added with stirring 4.0 g (20 mmole) of diphenylmethylphosphine[15]. The mixture was stirred for 24 h, and the yellow precipitate was collected by filtration and dried in air. The residue was extracted with 50 ml of boiling toluene, and the extracts were filtered and cooled to produce 4.50 g (78%) of yellow crystals, m.p. 198–200°. An analytical sample, prepared by subsequent recrystallizations from ethanol and from toluene, had a m.p. of 201–203°. (Found: C, 54.26; H, 4.52; Cl, 12.51. $C_{26}H_{26}Cl_2P_2Pd$ calcd.: C, 54.05; H, 4.54; Cl, 12.28%.)

The NMR spectrum ($CDCl_3$ soln.) of (I) exhibited an aromatic multiplet centered at τ 2.40, and a triplet [J(H–P) 3.8 Hz] at τ 7.93.

trans-Bis(diphenylmethylphosphine)(σ-pentafluorophenyl)chloropalladium (II)

To a stirred mixture of (I) (0.577 g, 1.0 mole) and 25 ml of ethyl ether at 0° was added dropwise a solution of pentafluorophenylmagnesium bromide (prepared from bromopentafluorobenzene (0.494 g, 2.0 mmole), magnesium turnings (0.061 g, 2.5 mg-atom) and 5 ml of ethyl ether)[16]. The mixture was stirred at 0° for 30 min, allowed to warm to room temperature, and was stirred for an additional 6 h, after which time the solvent was removed *in vacuo* to produce a light-brown residue. The latter was extracted with 40 ml of n-hexane-benzene (6/1) and the extract was filtered and cooled to yield 0.515 g (72%) of white crystals, m.p. 196–198°. An analytical sample was prepared by a subsequent recrystallization of the product from n-hexane/benzene (4/1); m.p. 195–197°. (Found*: C, 52.57; H, 3.68; Cl, 4.64; F, 13.50; P, 8.73. $C_{32}H_{26}ClF_5P_2Pd$ calcd.: C, 54.18; H, 3.70; Cl, 5.00; F, 13.39; P, 8.73%.)

The NMR spectrum ($CDCl_3$) of (II) exhibited an aromatic multiplet centered at τ 2.60 and a triplet [J(H–P) 3.5 Hz] at τ 7.77. The IR spectrum (KBr pellet) exhibited absorptions at 949, 1050, and 1495 cm^{-1} which are characteristic of the pentafluorophenyl group[18].

trans-Bis(diphenylmethylphosphine)-bis(σ-pentafluorophenyl)palladium (III)

To a stirred solution of pentafluorophenyllithium at −78° [prepared from bromopentafluorobenzene (0.617 g, 2.5 mmole), n-butyllithium in hexane (2.5 mmole) and 30 ml of ethyl ether at −78°][19] was added (I) (0.577 g, 1.0 mmole) in small amounts over a 10 min period. The mixture was stirred at −78° for 30 min, allowed to warm to room temperature over a 30 min period, and then was heated to reflux for 3 h. The solvent was evaporated, leaving a residue which was dissolved in 20 ml of benzene and chromatographed on a column (constructed with Florisil which had been treated with a UV indicator). Two bands were visible in UV light. The first band was rapidly eluted with benzene to produce a solid which on recrystallization from n-hexane-benzene (3/1) gave 0.47 g (56%) of (III) as white crystals, m.p. 199–202°. Before a sample of (III) was submitted for elemental analysis, it was dried in an Abderhalden apparatus at 77°/0.3 mm (phosphorus pentoxide as the drying agent) until a sample of constant weight was obtained, m.p. 198.5–201°. (Found: C, 54.49; H, 3.38; F, 22.32; P, 7.19. $C_{38}H_{26}F_{10}P_2Pd$ calcd.: C, 54.27; H, 3.12; F, 22.59; P, 7.37%.) A molecular weight determination (vapor pressure osmometer, benzene, 50°) gave values of 812 and 824 (theory 841).

The NMR spectrum ($CDCl_3$ soln.) of (III) exhibited an aromatic multiplet centered at τ 2.72 and a triplet [J(H–P) 3.5 Hz] at τ 8.23. The IR spectrum (KBr pellet) exhibited absorptions at 940, 1050, and 1495 cm^{-1} which are characteristic of the pentafluorophenyl group[18].

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* For several compounds prepared in this and related studies[1], suitable elemental analyses were obtained for all elements determined with the exception of carbon, which was consistently several percent lower than theory. In various organophosphorus compounds, low analytical values for carbon content are sometimes obtained, due to incomplete combustion resulting from difficulty in breaking the carbon–phosphorus bond[17]. For the same reason, low analytical values for carbon are sometimes obtained in organofluorine compounds[17]. Low values for carbon in various tert-phosphine-stabilized, σ-aryl–palladium compounds have been previously discussed[2]. Evidence for incomplete combustion in some of our products has been observed, despite the utilization of various oxidation catalysts in the analyses (C. Meade, personal communication).

A second, much slower moving band was eluted with ethyl ether, producing 0.125 g of white crystals, m.p. 189–193°. This material was identified as (II) by comparison with an authentic sample. The yield of (II) was 15%, based on (I).

trans-Bis(diphenylmethylphosphine)(σ-pentachlorophenyl)chloropalladium (IV)

Complex (I) (1.58 g, 2.7 mmole) was added in small portions over a 10 min period to a stirred solution of pentachlorophenylmagnesium chloride[20,21] [prepared from hexachlorobenzene (1.40 g, 4.9 mmole), magnesium turnings (0.120 g, 4.9 mg-atom) and 35 ml of tetrahydrofuran]. The reaction mixture was maintained at −10° throughout the addition period and for 30 min thereafter. The mixture was subsequently warmed to 50° for 30 min, heated to reflux for 5 min, cooled, and the solvent evaporated *in vacuo*. The residue was extracted with 100 ml of benzene, the extract treated with satd. aqueous ammonium chloride, and the organic portion was dried. The solvent was evaporated and the resulting material was heated to 100°/0.3 mm for 24 h, during which time volatile organic material was removed by sublimation. The residue was further purified by preparative TLC on UV-indicating silica gel (chloroform as eluent). The product band readily separated from a band containing (I), and produced material which on recrystallization from n-hexane/benzene (4/1) afforded 0.265 g (12%) of (IV) in the form of white crystals, m.p. 251–253°. (Found: C, 46.19; H, 3.19; Cl, 25.82; Pd, 12.84. $C_{32}H_{30}Cl_6O_2P_2Pd$ calcd.: C, 46.44; H, 3.65; Cl, 25.70; Pd, 12.86%.)

Since a dried sample of the above product was found to gain weight on standing in air, the above material was redried in an Abderhalden apparatus at 77°/0.3 mm (phosphorus pentoxide as the drying agent) until a sample of constant weight was obtained. This sample was then re-analyzed. (Found: C, 48.35; H, 3.34; Cl, 27.11. $C_{32}H_{26}Cl_6P_2Pd$ calcd.: C, 48.55; H, 3.31; Cl, 26.87%.)

The NMR spectrum ($CDCl_3$ soln.) of (IV) exhibited an aromatic multiplet centered at τ 2.58 and a triplet [J(H–P) 3.8 Hz] at τ 7.69. The IR spectrum (KBr pellet) exhibited absorptions at 678 (doublet) and 1098 cm^{-1} which are characteristic of the pentachlorophenyl group[22].

(2,2′-Bipyridine)dichloropalladium (VI)

A modification of the literature procedure[23] was employed. A solution of 2,2′-bipyridine (2.34 g, 15 mmole) in 50 ml of ethanol was added to a stirred solution of ammonium tetrachloropalladite [prepared from ammonium chloride (1.07 g, 20 mmole) and palladium dichloride (1.77 g, 10 mmole) in 15 ml of distilled water]. After stirring for 24 h, the precipitate was collected by filtration, washed with water and with ethanol, and dried at 25°/0.3 mm to give 2.93 g (88%) of (VI) as yellow microcrystals, m.p. 377–380° dec. The product was used without further purification.

(2,2′-Bipyridine)bis(σ-pentafluorophenyl)palladium (VII)

To a stirred solution of pentafluorophenyllithium[19] (5.0 mmole) in 20 ml of ethyl ether at −78° was added (VI) (0.68 g, 2.0 mmole) in small portions. The mixture was stirred at −78° for 1 h, then allowed to warm to room temperature. At −10°, a rapid change in color from yellow to white occurred. After the mixture had been stirred at room temperature for 2 h, the solvent was evaporated *in vacuo*. The residue was extracted with 50 ml of boiling acetone, and the extracts were filtered and cooled. There resulted 0.94 g (79%) of (VII) in the form of white needles. An analytical sample was prepared by recrystallization of the product from acetone and subsequently from methanol; m.p. 334–335°. (Found: C, 44.48; H, 1.79; F, 31.50; Pd, 17.97. $C_{22}H_8F_{10}N_2Pd$ calcd.: C, 44.28; H, 1.35; F, 31.84; Pd, 17.83%.)

IR spectrum (KBr pellet): Absorptions characteristic of the pentafluorophenyl group[18] occurred at 951, 1050, and 1500 cm^{-1}.

(2,2′-Bipyridine)bis(σ-pentachlorophenyl)palladium (VIII)

Small portions of (VI) (0.68 g, 2.0 mmole) were added over a 10 min period to a stirred solution of pentachlorophenyllithium[22] (5.0 mmole) in 45 ml of ethyl ether at −78°. The reaction mixture was stirred at −78° for 1 h, then allowed to warm to room temperature over a 4 h period. The solvent was evaporated under reduced pressure and the resulting solid, on recrystallization from nitrobenzene, produced white crystals of (VIII) (0.465 g, 30%). After washing with acetone and drying, the product had a m.p. of 335–337° (dec. at *ca.* 370°). (Found: C, 34.81; H, 1.49; Cl, 46.80; Pd, 14.19. $C_{22}H_8Cl_{10}N_2Pd$ calcd.: C, 34.71; H, 1.06; Cl, 46.57; Pd, 13.98%.)

An IR spectrum (KBr pellet) of (VIII) exhibited absorptions characteristic of the pentachlorophenyl[22] group at 665, 835, and 1105 cm^{-1}.

Reaction of phenyllithium and (VI)

To a stirred mixture of (VI) (0.68 g, 2.0 mmole) in 25 ml of ethyl ether at −78° was rapidly added an ethyl ether/benzene solution of phenyllithium (4.0 mmole). The mixture was stirred at −78° for 1 h and then allowed to warm to room temperature, during which time the color had changed from light-yellow to dark-brown. The reaction mixture was filtered from a black residue, and the filtrate was evaporated *in vacuo* to yield a yellow-brown solid. Recrystallization of the latter from n-hexane produced 0.17 g (55%) of white crystals, m.p. 67.5–69°, which were shown to be biphenyl by means of a mixture m.p. and TLC comparison with an authentic sample.

(Norbornadiene)bis(σ-pentafluorophenyl)platinum (XII)

To a stirred suspension of (norbornadiene)dichloroplatinum (X)[24] (0.358 g, 1.0 mmole) in 40 ml of benzene at room temperature was added dropwise a solution of pentafluorophenylmagnesium bromide [prepared from bromopentafluorobenzene (0.976 g, 4.0 mmole) and magnesium turnings (0.175 g, 7.2 mg-atom) in 10 ml of ethyl ether[16]]. The mixture was heated to reflux for 1 h, allowed to cool, and was hydrolyzed with 10 ml of satd. aqueous ammonium chloride. The organic portion was separated, dried, and the solvent was evaporated *in vacuo*. The residue on recrystallization from n-hexane/benzene (2/1) gave white crystals (0.190 g, 31%) of m.p. 244–245° dec. (Found: C, 36.61; H, 1.23; Pt, 31.03. $C_{19}H_8F_{10}Pt$ calcd.: C, 36.73; H, 1.30; Pt, 31.30%.).

Absorptions at 960, 1060, and 1504 cm^{-1} which are characteristic of the pentafluorophenyl group[18] were noted in the IR spectrum (KBr pellet) of (XII).

(Norbornadiene)bis(σ-phenyl)platinum (XI)

By a procedure identical to that just described, a solution of phenylmagnesium chloride in tetrahydrofuran (3.2 mmole, Fisher Scientific Co.) was allowed to react with a suspension of (X) (0.358 g, 1.0 mmole) in 40 ml of benzene to produce, after one recrystallization from n-hexane, 0.049 g (11%) of white crystals of (XI), m.p. 145–150° dec. (reported[13] m.p. 146–152° dec.).

Reaction of phenyllithium and (norbornadiene)dichloropalladium (XIII)

In a manner similar to that described above, a solution of phenylmagnesium chloride (3.2 mmole) was added to a suspension of (XIII)[24] (0.352 g, 1.0 mmole) in benzene. Following hydrolysis and workup, 0.15 g of biphenyl (98% based on (XIII)), m.p. 66–68.5°, was obtained. The product was shown to be identifical to an authentic sample.

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Foundation for a grant in support of this research program, and to Prof. R. Archer for assistance in obtaining the magnetic measurements.

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