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Substitution Reactions of Palladium(II) Complexes Involving a Bidentate Tertiary Arsine Ligand[1]

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The reaction of ethylene-α,β-bis-(diphenylarsine), $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$ (EDA), with $[Pd(en)X_2]$, where X = Cl and Br, has been shown to yield $[Pd(EDA)X_2]$ and $[Pd(en)_2]X_2$, while $[Pd(en)I_2]$ produces only $[Pd(EDA)I_2]$. Ethylenediamine is completely displaced from $[Pd(en)_2]X_2$ by EDA, giving $[Pd(EDA)X_2]$, but when X is ClO_4^-, $[Pd(EDA)_2](ClO_4)_2$ is formed. The ligand EDA can be displaced from $[Pd(EDA)_2](ClO_4)_2$ by halide ion to produce $[Pd(EDA)X_2]$; the relative ease of displacement is I > Br > Cl. The order: I > Br < Cl has been demonstrated for the ability to displace halide ion from $[Pd(EDA)X_2]$; evidence for an intermediate of the type $[Pd(en)(EDA)]^{2+}$ is given.

For use in these studies, compounds of the type $[Pd(EDA)X_2]$ were prepared from K_2PdX_4 and EDA in methanol, except for X = I, where PdI_2 was employed. X-Ray diffraction patterns were obtained and the resulting data, in conjunction

$$K_2PdX_4 + EDA \longrightarrow [Pd(EDA)X_2] + 2KX \quad (1)$$

with analyses, were used to identify the products of subsequent reactions.

When $[Pd(en)X_2]$ is refluxed with EDA in methanol, a mixture of $[Pd(en)_2]X_2$ and $[Pd(EDA)X_2]$ is obtained in a mole ratio of approximately 1 for the chloride and the bromide. However, when the iodide is used, complete displacement of ethylenediamine is observed and only $[Pd(EDA)I_2]$ can be isolated from the reaction mixture. Since $[Pd(en)_2]I_2$ was not detected,

$$2[Pd(en)X_2] + EDA \longrightarrow [Pd(en)_2]X_2 + [Pd(EDA)X_2] \quad (2)$$

it either did not form, and thus the reaction is not analogous to (2), or it was consumed by further reaction. The latter seems to be the case, for when $[Pd(en)_2]X_2$ (X = Cl, Br, and I) is refluxed with EDA in methanol, complete displacement of

$$[Pd(en)I_2] + EDA \longrightarrow [Pd(EDA)I_2] + en \quad (3)$$

ethylenediamine again is observed and $[Pd(EDA)X_2]$ is produced. However, when X is the weakly coördinating perchlorate ion, the bisdiarsine is obtained. Reaction 4 appears to be an

$$[Pd(en)_2]X_2 + EDA \longrightarrow [Pd(EDA)X_2] + 2en \quad (4)$$

equilibrium reaction, since starting material was recovered after several days of reflux in the cases of both chloride and bromide. It then would

$$[Pd(en)_2](ClO_4)_2 + 2EDA \rightleftharpoons [Pd(EDA)_2](ClO_4)_2 + 2en \quad (5)$$

seem that the mole ratio of product in (2) would depend upon both concentration and time. The iodide product is sufficiently insoluble to displace the equilibrium in favor of $[Pd(EDA)I_2]$.

While the iodide obtained from (4) can be identified unequivocally by X-ray diffraction patterns, the chloride and the bromide presented a problem, since the X-ray diffraction pattern of the product of (4) is different from that obtained for the compounds prepared by (1). However, for the bromide the elemental analysis corresponds to the correct formulation; hence it appears that $[Pd(EDA)Br_2]$ occurs in two crystal modifications.

To determine whether EDA could be displaced from the bisdiarsine, $[Pd(EDA)_2](ClO_4)_2$ was refluxed in methanol with an excess of potassium halide. Iodide and bromide efficiently displaced EDA (yield: I, 90%; Br, 83%) while only enough $[Pd(EDA)Cl_2]$ for an X-ray diffraction pattern was obtained from the reaction with

$$[Pd(EDA)_2](ClO_4)_2 + 2X^- \longrightarrow [Pd(EDA)X_2] + 2ClO_4^- + EDA \quad (6)$$

chloride ion. It is concluded that in (6) the relative ability of halide ion to displace EDA is I > Br > Cl. However, a different order has been observed for the direct displacement of one halide by another in $[Pd(EDA)X_2]$ (reactions 7). While iodide can displace both chloride and bromide, there is no detectable displacement of chloride by

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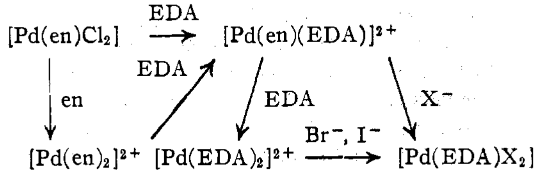
$$[Pd(EDA)Cl_2] + KBr \longrightarrow \text{No reaction}$$

$$[Pd(EDA)Cl_2] + 2KI \longrightarrow [Pd(EDA)I_2] + 2KCl$$

$$[Pd(EDA)Br_2] + 2KI \longrightarrow [Pd(EDA)I_2] + 2KBr \quad (7)$$

bromide; accordingly, the order is I > Br < Cl.

The redistribution of ligands in (2) is similar to the action of ethylenediamine on $[Pd(NH_3)_2Cl_2]$,[3] KI on $[Pd(NH_3)_2C_2O_4]$,[4] and diethyl sulfide and ethylenediethyldisulfide on $[Pd(en)Cl_2]$.[5] Drew and Wyatt[5] suggested that in the case of diethyl sulfide, the unstable mixed complex, $\{Pd[en][(C_2H_5)_2S]_2\}^{2+}$, was first formed and then rearranged to $[Pd(en)_2]^{2+}$ and $\{Pd[(C_2M_5)_2S]_4\}^{2+}$, with the latter losing two moles of $(C_2H_5)_2S$ to form $\{Pd[(C_2H_5)_2S]_2Cl_2\}$. The intermediate was postulated in view of the fact that the mixed platinum analog could be isolated. By assuming a similar intermediate for the displacement with EDA, the following scheme is a reasonable one.



In order to obtain evidence for the proposed intermediate the change in spectra was observed for (4) and (5) as a function of time. The largest change occurred at a wave length of 325 mμ (Fig. 1). The peak at 325 mμ increases during the reaction, reaches a maximum, and then decreases in a manner consistent with the postulation of the intermediate in two consecutive reactions. It should be noted that the change for (5) is the most pronounced, while that for the chloride and iodide show a less spectacular change. Although the identity of the intermediate is not established, the evidence strongly suggests the formation of an intermediate in these reactions, and the one postulated corresponds to that expected for a stepwise reaction.

Experimental

Unless otherwise indicated, X-ray diffraction patterns were obtained for all principal starting materials and reaction products (Table I); supporting analytical data were obtained where necessary.

All materials except those indicated below were reagent grade and used without further purification. Compounds of the type $[Pd(en)_2]X_2$, where X = Cl, Br, and I, were prepared according to previously reported procedures.[6-8] The diammines, $[Pd(en)X_2]$, where X = Cl, Br, and I, were prepared by acidifying aqueous solutions of the tetrammines.[3]

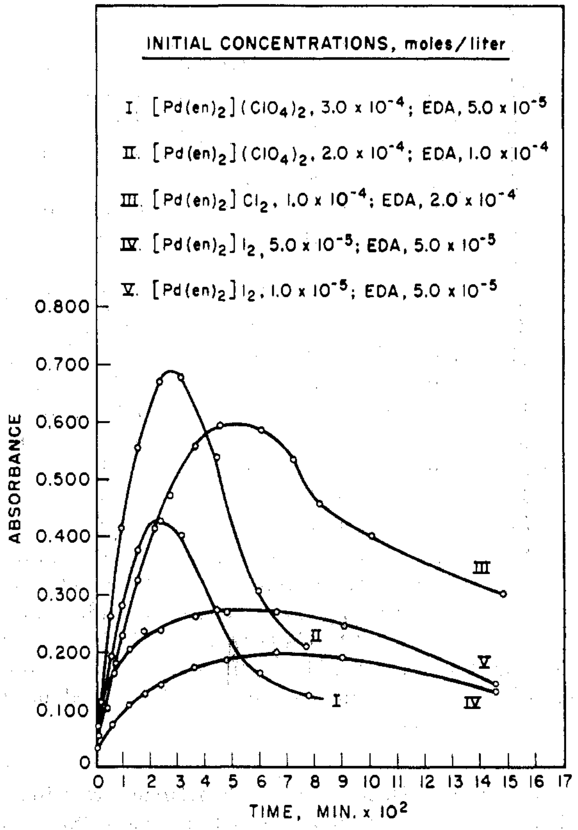


Fig. 1.—Change of absorbance with time at 325 mμ.

EDA was prepared by the method of Chatt and Mann.[9]

Bisethylenediaminepalladium(II) Perchlorate.—A solution of 2.0 g. of $[Pd(en)_2]Cl_2$ in 100 ml. of water was treated with 0.1 *M* $AgClO_4$ to complete precipitation of AgCl; this was filtered and the filtrate evaporated to dryness. The residue was redissolved in a minimum amount of water, filtered, and reprecipitated by adding 200 ml. of ethanol; the product was filtered and washed with ethanol.

Anal. Calcd. for $[Pd(en)_2](ClO_4)_2$: Pd, 25.2. Found: Pd, 26.0.

Dichloroethylene-α,β-bis-(diphenylarsine)-palladium-(II).—The method used was a modification of that of Chatt and Mann.[9] A mixture of 0.6335 g. of K_2PdCl_4 and 1.0728 g. of EDA was refluxed in 200 ml. of methanol. After 12 hr. the volume was reduced to 100 ml. and an equal volume of water was added. The resulting precipitate (1.0728 g.) was filtered and washed with water and ether.

Anal. Calcd. for $[Pd(EDA)Cl_2]$: Pd, 16.0; C, 47.1; H, 3.65. Found: Pd, 15.9; C, 46.9; H, 3.95.

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TABLE I

X-RAY DIFFRACTION DATA[a]

d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
$[Pd(en)_2](ClO_4)_2$		$[Pd(EDA)_2](ClO_4)_2$		$[Pd(EDA)Cl_2]$	
8.12	1.0	10.91	1.0	11.38	1.0
5.21	0.8	10.27	1.0	8.70	0.9
4.72	.7	9.20	0.5	6.86	1.0
4.46	.9	8.70	.4	6.30	0.6
4.26	1.0	8.34	.4[b]	5.80	.5
3.98	0.9	4.37	.9	4.38	.4[b]
3.82	.5[b]	3.99	.7	4.14	.7
$[Pd(EDA)Br_2]$[c]		$[Pd(EDA)Br_2]$[d]		$[Pd(EDA)I_2]$	
8.37	1.0	12.41	0.5	10.31	0.7
7.24	1.0	11.32	1.0	8.51	1.0
6.88	0.5[b]	10.39	0.7	7.31	0.9
5.37	.8	9.00	1.0	6.90	.5
4.37	.6	8.04	0.4	5.44	.5
4.15	.6	6.23	.3[b]	4.63	.3
3.57	.7	4.18	.5	4.39	.3[b]

[a] All powder patterns were obtained using CuKα radiation (Ni filter), 35 kv. tube voltage, 15 ma. filament current, and 3–4 hr. exposures. Relative intensities were estimated visually. [b] Less intense lines not included here. [c] Obtained from K_2PdBr_4. [d] Obtained from $[Pd(en)_2]Br_2$; identical data were found for $[Pd(EDA)Cl_2]$ formed under similar conditions.

Dibromoethylene-α,β-bis-(diphenylarsine)-palladium-(II).—A mixture of 0.4987 g. of K_2PdBr_4 and 0.487 g. of EDA was refluxed in 75 ml. of methanol for 24 hr. The product (0.6843 g.) was filtered and washed with water and methanol.

Anal. Calcd. for $[Pd(EDA)Br_2]$: Pd, 14.1; C, 41.5; H, 3.31. Found: Pd, 14.3; C, 41.3; H, 3.20.

Diiodoethylene-α,β-bis-(diphenylarsine)-palladium(II). A mixture of 0.3034 g. of PdI_2 and 0.4290 g. of EDA was refluxed in 75 ml. of benzene for 48 hr. The product was filtered and extracted with benzene for 3 days, leaving 0.0944 g. of PdI_2. The product (0.5089 g.) which crystallized from the solvent was filtered and washed with benzene.

Anal. Calcd. for $[Pd(EDA)_2]I_2$: Pd, 12.5; I, 30.0; C, 36.8; H, 2.86. Found: Pd, 11.9; I, 30.6; C, 36.6; H, 2.85.

Reactions of $[Pd(en)X_2]$ with EDA.—After refluxing separately 0.4869, 0.2530, and 0.2421 g. of EDA with 0.2374 g. of $[Pd(en)Cl_2]$, 0.1636 g. of $[Pd(en)Br_2]$, and 0.2100 g. of $[Pd(en)I_2]$, respectively, in 100 ml. of methanol for 2.5 hr., 24 hr., and 4 days, respectively, products were separated as follows. **Chloride:** Evaporation of 75 ml. of methanol and addition of 100 ml. of acetone provided 0.1208 g. of $[Pd(en)_2]Cl_2$. Evaporation of the filtrate and addition of 10 ml. of ether yielded 0.3535 g. of $[Pd(EDA)Cl_2]$; thus $[Pd(en)_2]Cl_2/[Pd(EDA)Cl_2]$ = 0.99. **Bromide.** The reaction product was filtered and washed with methanol and water to provide 0.1859 g. of $[Pd(EDA)Br_2]$. The filtrate was evaporated to dryness and the resulting residue was extracted with water from which 0.0897 g. of $[Pd(en)_2]Br_2$ was recovered by evaporation. Accordingly, $[Pd(en)_2]Br_2/[Pd(EDA)Br_2]$ = 0.91. **Iodide:** The solvent was evaporated and the residue extracted with $CHCl_3$, leaving 0.0654 g. of $[Pd(en)I_2]$. The $CHCl_3$ extract was evaporated and extracted with ether to remove unreacted ligand, leaving 0.3345 g. of $[Pd(EDA)I_2]$. Efforts to detect $[Pd(en)_2]I_2$ were unsuccessful.

Reactions of $[Pd(en)_2]X_2$ with EDA.—The bromide (0.1939 g.) and 0.2430 g. of EDA were refluxed for 15 hr. in 100 ml. of methanol, the solvent was evaporated, and the residue extracted with $CHCl_3$. The residual solid was filtered and washed with $CHCl_3$ to provide 0.0915 g. of unreacted $[Pd(en)_2]Br_2$. The $CHCl_3$ extract was evaporated, leaving an oil which crystallized when extracted with ether. This product (0.1878 g.) had the same composition as the $[Pd(EDA)Br_2]$ described above but gave a different X-ray diffraction pattern (Table I).

Similar treatment of $[Pd(en)_2]Cl_2$ with EDA under a variety of conditions yielded products that could not be positively identified.

After 0.5002 g. of $[Pd(en)_2]I_2$ and 0.4995 g. of EDA were refluxed in 125 ml. of methanol for 5 days, the solid was filtered and washed with water, acetone, and benzene to give 0.4888 g. of $[Pd(EDA)I_2]$.

Similar treatment of 0.4984 g. of $[Pd(en)_2](ClO_4)_2$ with 1.1342 g. of EDA in 200 ml. of methanol for 24 hr. yielded 1.1499 g. of $[Pd(EDA)_2](ClO_4)_2$.

Anal. Calcd. for $[Pd(EDA)_2](ClO_4)_2$: Pd, 8.32; C, 48.9; H, 3.79. Found: Pd, 8.05; C, 48.8; H, 3.76.

Reactions of $[Pd(EDA)_2](ClO_4)_2$ with KX.—Samples of the perchlorate (0.1483, 0.9869, and 0.1954 g.) and 1.0 g. of KCl, 2.5 g. of KBr, and 1.0 g. of KI, respectively, were refluxed separately for 5 days in 100 ml. of methanol. For the chloride and bromide, the methanol was evaporated and the residues were extracted with $CHCl_3$ to separate unchanged starting material (0.1053 and 0.6010 g., respectively) from *ca.* 2 mg. of $[Pd(EDA)Cl_2]$ and 0.1896 g. of $[Pd(EDA)Br_2]$, both of which were recovered from $CHCl_3$ extracts. The X-ray diffraction pattern for the bromide was identical with that for the product from $[Pd(en)_2]Br_2$. For the iodide, 0.1123 g. of $[Pd(EDA)I_2]$ was separated directly by filtration; unchanged perchlorate was not found.

Reaction of $[Pd(EDA)X_2]$ with Halide Ion.—The procedure employed was to reflux a mixture of $[Pd(EDA)X_2]$ and the potassium halide (excess) in methanol, and isolate the products according to the above procedures and identify them by X-ray diffraction patterns. Use of $[Pd(EDA)Cl_2]$ and KBr led to complete recovery of the starting material; with KI, $[Pd(EDA)I_2]$ was isolated in 82% yield; the reaction of $[Pd(EDA)Br_2]$ with KI gave $[Pd(EDA)I_2]$ in 90% yield.

Change in Spectra with Time.—Several of the above reactions were studied by observing the change of visible and ultraviolet spectra *vs.* time by mixing the components dissolved in absolute methanol and withdrawing samples periodically for analysis. The spectra were obtained with a Beckman Model DU spectrophotometer at the wave length indicated. The temperature was maintained at 41.5° ± 0.1 during all of the experiments; the results are given in Fig. 1.