

The Reaction between the Tetrachloropalladate(II) Ion and 1,10-Phenanthroline

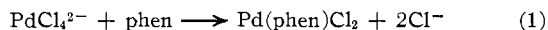
By JOHN V. RUND

Received October 31, 1969

The reaction of K_2PdCl_4 and 1,10-phenanthroline in aqueous solution gives a quantitative yield of $\text{Pd}(\text{phen})\text{Cl}_2$. The rate is first order in palladium complex and first order in phenanthroline. There are at least three routes to the product; phenanthroline attacks PdCl_4^{2-} ($k_2 = 2.23 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°) and $\text{Pd}(\text{H}_2\text{O})\text{Cl}_3^-$ ($k_2 = 71 \text{ M}^{-1} \text{ sec}^{-1}$) as well as one or more hydroxo complexes ($k_2 > 100 \text{ M}^{-1} \text{ sec}^{-1}$). The reaction is unusually slow and insensitive to the basicity of phenanthroline and to whether or not it is protonated. Both associative (A) and dissociative interchange (I_d) mechanisms are considered in analyzing the data.

Ligand-substitution mechanisms for square-planar coordination compounds have been studied principally for platinum(II).¹ The first systematic examination of palladium(II) reactions was carried out by Basolo and coworkers²⁻⁶ on cationic $\text{Pd}(\text{dien})\text{X}^+$ compounds, where dien is diethylenetriamine or a derivative and X is the leaving ligand. Substitution rates of a number of uncharged complexes have been measured,⁷⁻⁹ and some work has been done on reactions of cationic complexes containing ammonia.¹⁰ The reactions appear to have the same mechanistic characteristics as those of isoelectric platinum compounds. They are about 10^5 times as fast, however, presumably because the bond between palladium and the leaving group¹¹ is weaker.

This paper reports an investigation of reaction 1, which is unusually slow owing to steric hindrance to



bond formation between palladium(II) and phenanthroline.

Experimental Section

Chemicals. Potassium Tetrachloropalladate(II).—Palladium sponge (10.00 g) was added to 75 ml of 4 M HCl, and chlorine was bubbled through the solution for about 2 hr. As the palladium dissolved, the solution heated to 55° . The solution was filtered through a fritted-glass funnel of medium porosity, and a little water was used to wash all the solution through the frit. Potassium chloride (14.01 g) and concentrated HCl (100 ml) were added to the filtrate, precipitating K_2PdCl_6 . Maintained at constant volume by occasional additions of water, the suspension was stirred mechanically and boiled for 0.5 hr beyond the time that all the solid had disappeared. *Caution!* Cl_2 is evolved. The solution was then evaporated to a volume of 100 ml, and HCl (50 ml) was added. Upon evaporation nearly to dryness on the steam bath, the solution deposited brown crystals of K_2PdCl_4 ,

which were filtered out and dried for 24 hr at 100° under vacuum *Anal.* Calcd for K_2PdCl_4 : Cl, 43.47. Found: Cl, 43.14.

Dichloro(phenanthroline)palladium(II).—The reaction product was prepared under conditions used for kinetic runs. Phenanthroline monohydrate (49.5 mg 0.25 mmol) was dissolved in 1 l. of water containing 3 ml of 0.12 M HCl and 3 g of NaCl. After the solution had been cooled to 5° , K_2PdCl_4 (80.8 mg, 0.25 mmol) was added. The reaction was allowed to proceed at 5° for 15 hr. The light yellow product was collected, washed once with water, and dried under vacuum. It was identified as $\text{Pd}(\text{phen})\text{Cl}_2$ by comparison of its infrared spectrum with that of an authentic sample and by elemental analysis. *Anal.* Calcd for $\text{Pd}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Cl}_2$: N, 7.82; Cl, 19.82. Found: N, 8.04; Cl, 19.64. The reaction yield was determined under similar conditions with 260 mg (1.31 mmol) of phenanthroline monohydrate and 408.0 mg of K_2PdCl_4 (1.25 mmol). The collected product weighed 449 mg (theoretical weight 447 mg), which was quantitative within the accuracy of the determination. Ionic strength was regulated with NH_4BF_4 , which was prepared by the method of Booth and Rehmar¹² and recrystallized from water. Phenanthroline and bipyridyl were purchased from the J. T. Baker Chemical Co. All other chemicals were reagent grade materials.

Kinetics.—The progress of the reaction was monitored by pipetting portions of the reaction mixture into measured volumes of Fe^{2+} solution. Fe^{2+} reacted rapidly with free phenanthroline to give red $\text{Fe}(\text{phen})_3^{2+}$, which was assayed spectrophotometrically. Details of the procedure have been published for the analogous platinum reaction.¹³ The only modification for palladium was in the treatment of the Fe^{2+} solution. It was cooled in ice during the run and contained 16 g/l. of NaCl and enough acid, if necessary, to bring the $\text{Fe}(\text{phen})_3^{2+}$ solutions to neutrality. Kinetics data were treated as previously described.¹³

Results

Phenanthroline disappeared from solutions that also contained K_2PdCl_4 by a second-order process. Figure 1 shows some sample kinetic runs. Two features are unusual for palladium(II) reactions: (1) the absence of the first-order reaction route that ordinarily accompanies the second-order route and (2) abnormally low rates. The three reactions in Figure 1, having the concentration of complex equal to the concentration of entering ligand, fit second-order plots without significant curvature. These conditions ($[\text{PdCl}_4^{2-}] = [\text{phen}]$) are particularly favorable for detecting a first-order reaction route. For square-planar complexes, most substitution reactions having two-term

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, New York, N. Y., 1967, Chapter 5.

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(5) W. H. Baddley and F. Basolo, *ibid.*, **88**, 2944 (1966).

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(7) L. Cattalini, G. Marangoni, and M. Martelli, *ibid.*, **7**, 1495 (1968).

(8) R. G. Pearson and D. A. Johnson, *J. Am. Chem. Soc.*, **86**, 3983 (1964).

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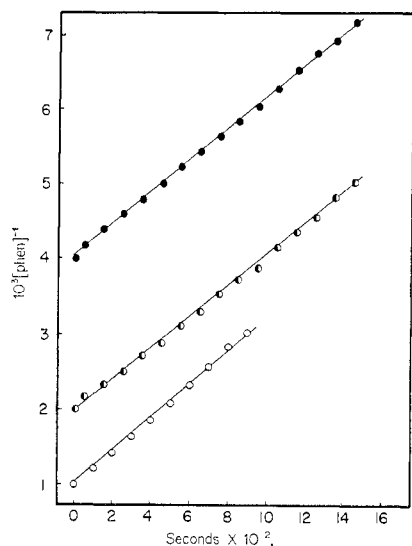


Figure 1.—Sample kinetics runs with equal concentrations of K_2PdCl_4 and phenanthroline. Conditions: ●, same as first entry in Table I; ○, same as fifth entry; ○, same as ninth entry.

rate laws would give almost entirely first-order kinetics when run with equal concentrations of reactants. The data in Table I show that the rate expression is first order in complex and first order in entering ligand. Although rates of reactions between $PdCl_4^{2-}$ and monodentate ligands have not been measured, published data on palladium(II) indicate that the reaction would be complete in the order of milliseconds. The reaction with phenanthroline, however, could be followed for 0.5 hr.

TABLE I
THE SECOND-ORDER RATE CONSTANTS AS A FUNCTION OF DIFFERENT INITIAL CONCENTRATIONS OF K_2PdCl_4 AND PHENANTHROLINE^a

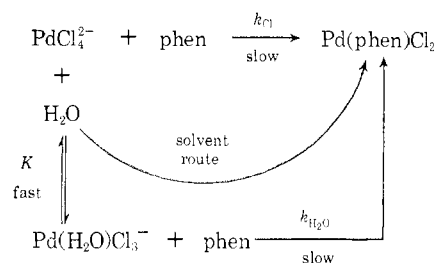
$10^4[PdCl_4^{2-}]$, M	$10^4[phen]$, M	k_2^b , $M^{-1} sec^{-1}$
2.50	2.50	2.1 ± 0.1
2.50	5.00	2.1 ± 0.1
2.50	10.00	2.1 ± 0.1
5.00	2.50	1.9 ± 0.04
5.00	5.00	2.0 ± 0.1
5.00	10.00	2.1 ± 0.04
10.00	2.50	1.8 ± 0.1
10.00	5.00	2.0 ± 0.03
10.00	10.00	2.2 ± 0.1

^a $[Cl^-] = 3.257 \times 10^{-2} M$, $[H^+] = 1.4 \times 10^{-3} M$, $\mu = 0.112$, temperature 5° . ^b Calculated assuming rate = $k_2[PdCl_4^{2-}][phen]$.

Substitution reactions of square-planar complexes ordinarily have a rate law with a first-order term and a second-order term (eq 2). The first-order term arises

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{ligand}] \quad (2)$$

from a two-step route to the product through an intermediate containing a solvent molecule. Attack by the solvent to give the intermediate is the rate-determining step. This solvent route occurred with phenanthroline (see the scheme below), but because its second step was rate determining, the route gave sec-



ond-order kinetics. Parallel second-order routes give second-order kinetics for the overall reaction and an observed rate constant that is a function of chloride concentration (eq 3).¹³ Table II shows the real variation of observed rate constant with $[Cl^-]$ and cal-

$$k_{\text{obsd}} = \frac{k_{H_2O}K + k_{Cl}[Cl^-]}{K + [Cl^-]} \quad (3)$$

culated values for the rate constants. The calculated values are the best fit of eq 3 using k_{Cl} , k_{H_2O} , and K as variable parameters. The best fit was obtained with $k_{Cl} = 2.23 M^{-1} sec^{-1}$, $k_{H_2O} = 71 M^{-1} sec^{-1}$, and $K = 0.0037 M$. The solution is unique, and an equally good fit cannot be obtained by increasing one param-

TABLE II
THE SECOND-ORDER RATE CONSTANT AS A FUNCTION OF $[Cl^-]$ ^a

$[Cl^-]$, M	k_{obsd} , $M^{-1} sec^{-1}$	k_{calcd} , $M^{-1} sec^{-1}$
0.275	3.1 ± 0.1	3.2
0.207	3.5 ± 0.1	3.5
0.137	4.2 ± 0.1	4.1
0.0691	5.9 ± 0.1	5.7
0.0348	8.7 ± 0.1	8.8
0.0176	13.5 ± 0.2	14.1
0.00908	22.3 ± 1.0	22.1
0.00479	32.7 ± 0.7	32.2

^a $[PdCl_4^{2-}] = [phen] = 5 \times 10^{-4} M$, pH 3.3, $\mu = 0.279$, temperature 25° .

eter while decreasing another. The equilibrium constant has been determined potentiometrically by other workers¹⁴ and, corrected to an ionic strength of 0.279, its value is $0.0037 \pm 0.0009 M$. This agreement, although fortuitous in degree, substantiates the identification of the tetrachloro-trichloroquo equilibrium as the one affecting the observed reaction rate. In particular, the author believes that it argues that the change in rate with $[Cl^-]$ is not the result of an ion-pair mechanism (involving a weak interaction between palladium(II) and a Cl^- in the axial position).

The ionic strength affects the rate, as shown in Table III. The decrease in rate constant with increasing ionic strength is indicative of a reaction between ions of opposite charge. Trying to determine what the charges are, however, is not very fruitful, because the ionic strength was high and also because the activated complex for this reaction is not like the conceptual model used to derive the Brønsted-Bjerrum-Christiansen equation.¹⁵

(14) H. A. Droll, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, **61**, 1000 (1957).

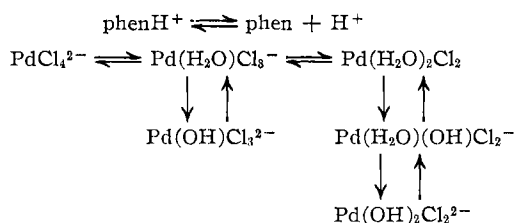
(15) J. A. Christiansen, *Z. Physik. Chem.*, **113**, 35 (1924).

TABLE III
THE SECOND-ORDER RATE CONSTANT AS A
FUNCTION OF IONIC STRENGTH^a

μ	$k_2, M^{-1} \text{ sec}^{-1}$	μ	$k_2, M^{-1} \text{ sec}^{-1}$
0.0426	2.88 ± 0.06	0.143	2.17 ± 0.10
0.0999	2.45 ± 0.12	0.283	1.71 ± 0.08

^a [PdCl₄²⁻] = [phen] = 5 × 10⁻⁴ M, [Cl⁻] = 3.57 × 10⁻² M, [H⁺] = 1.4 × 10⁻³ M, temperature 5°.

Several pH-dependent equilibria were established in the reaction mixture. These are shown in the scheme below. The pK_a of the phenanthroline ion is about



4.9.¹⁶ Measurement of the pH of PdCl₄²⁻ solutions as a function of [Cl⁻] gave 7 for the pK_a of Pd(H₂O)Cl₃⁻ and 4.3 for the pK_a of Pd(H₂O)₂Cl₂. Probably on account of interference from stronger acids in solution, ionization of the second proton of the diaquo complex was not detected. Production of Pd(phen)Cl₂ was studied as a function of pH to determine the effect of shifts in the various equilibria. Rate constants are given in Table IV, and Figure 2 presents a graph of

TABLE IV

THE SECOND-ORDER RATE CONSTANT AS A FUNCTION OF PH^a

5°		25°	
pH	$k_2, M^{-1} \text{ sec}^{-1}$	pH	$k_2, M^{-1} \text{ sec}^{-1}$
1.8	0.71 ± 0.03	2.0	3.80 ± 0.2
2.3	0.71 ± 0.01	3.9	3.89 ± 0.2
2.9	0.69 ± 0.03	5.2	6.20 ± 0.2
3.9	0.70 ± 0.03	5.7	8.60 ± 0.6
5.3	0.94 ± 0.02	6.5	13.50 ± 0.4
6.6	2.72 ± 0.16	6.7	15.00 ± 0.4
7.0	3.81 ± 0.11	6.8	17.20 ± 0.7
7.7	7.40 ± 0.60	7.2	30.50 ± 0.8
8.1	10.30 ± 0.10	7.5	47.30 ± 1.2
8.4	12.70 ± 0.40	8.3	36.40 ± 1.2
8.5	13.40 ± 0.50	9.6	~0
8.6	14.50 ± 0.70	10.1	~0
8.9	9.10 ± 0.50		
9.5	1.10 ± 0.60		
10.9	~0		

^a [PdCl₄²⁻] = [phen] = 5 × 10⁻⁴ M, [Cl⁻] = 0.207 M, μ = 0.211.

data taken at 5°. With increasing pH, the rate was at first invariant, then increased, and finally fell off sharply. The decrease at the highest pH was due to precipitation of palladium(II) oxide, which was visible in these reaction mixtures. The phenanthroline-phenanthroline ion equilibrium is most sensitive to pH at about pH 4.9, but at this point the rate was all but unchanged. The palladium complexes appear, then, to be about equally reactive toward phenanthroline and the phenanthroline ion. The increase in rate with increasing pH seems to be caused by con-

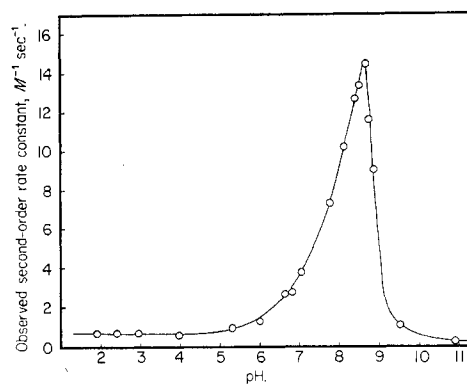
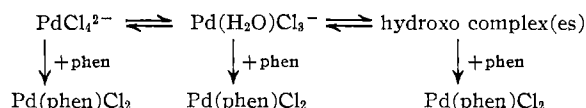


Figure 2.—Second-order rate constant for reaction 1 as a function of pH at 5°. Conditions are given in Table IV.

version of aquo ligands into hydroxo ligands and the more rapid reaction of hydroxo complexes with phenanthroline. This rate pattern, insensitivity to deprotonation of phenanthroline ion and an increase with formation of hydroxo complexes, was also found for the analogous reaction of platinum(II).^{18,17} The more complicated set of equilibria occurring for palladium precludes a unique solution for the rate constants involved. The qualitative conclusion, however, is the same as for platinum: a hydroxo complex is more reactive than the tetrachloro complex or the trichloroaquo complex toward phenanthroline. A more detailed argument for this point of view has been published elsewhere.¹⁷

The general scheme of the reaction is



When the leaving group is H₂O, the reaction is 20 times as fast as when it is Cl⁻. The relative rate cannot be calculated for hydroxide as a leaving group, but a lower limit of 50 may be set, because in base the overall reaction becomes 50 times as fast as the reaction of PdCl₄²⁻. This is a conservative lower limit, for the rate is still rising rapidly with pH when the oxide begins to precipitate. The trend is even more pronounced than in the analogous platinum reaction,¹⁷ where rates of reaction of phenanthroline with PtCl₄²⁻, Pt(H₂O)Cl₃⁻, and Pt(OH)Cl₃²⁻ are in the ratio of 1:4:10.

Rates for different reactants are shown in Table V. Results for related platinum compounds are also included. Changing from the dinegative tetrachloro complex of platinum to the neutral dichlorodiammines nearly stopped the reaction with phenanthroline. More energy was probably needed to dissociate leaving groups from the neutral complexes. The dichlorodiammines of palladium did not at first react with phenanthroline, but after an induction period, a moderately rapid reaction ensued. The kinetics was of the same form as was previously encountered in a phenanthroline reaction that occurred after a series of solvolysis reactions of the complex.¹⁸ The dichlorodiammines seem

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(18) J. V. Rund and F. A. Palocsay, *Inorg. Chem.*, **8**, 2242 (1969).

TABLE V
 SECOND-ORDER RATE CONSTANTS FOR VARIOUS REACTANTS

Complex	Ligand	$k_2, M^{-1} \text{ sec}^{-1}$	
		M = Pd, ^a 25°	M = Pt, ^b 45°
MCl ₄ ²⁻	1,10-Phenanthroline	3.3	0.0045
<i>trans</i> -M(NH ₃) ₂ Cl ₂	1,10-Phenanthroline	{ Moderately fast—not second order }	0.00001 (65°)
<i>cis</i> -M(NH ₃) ₂ Cl ₂	1,10-Phenanthroline		0.00012 (65°)
M(CN) ₄ ²⁻	1,10-Phenanthroline	NR (100°)	NR (100°)
M(C ₂ H ₄)Cl ₃ ⁻	1,10-Phenanthroline	Fast ^c	>40
MCl ₄ ²⁻	Bipyridyl	28	0.012
MCl ₄ ²⁻	Ethylenediamine	Fast	0.094 (25°)
MCl ₄ ²⁻	5,6-Dimethyl-1,10-phenanthroline	2.5	0.0020
MCl ₄ ²⁻	4,7-Dimethyl-1,10-phenanthroline	3.5	0.0059

^a [complex] = [ligand] = $5 \times 10^{-4} M$, pH 3.3, [Cl⁻] = 0.275 M, μ = 0.279. ^b See ref 14. ^c Same conditions as first entry, except solution is saturated with ethylene. Reaction is complete in less than 10 sec.

to react with phenanthroline only after some ligands are replaced by water. Cyanide is probably not easily dissociated without considerable assistance by an entering group, and phenanthroline could not react with either the platinum or the palladium complex. When the complex contained ligands that were very easily displaced, as with Zeise's salt or when the palladium reaction was run in a solution saturated with ethylene, introduction of phenanthroline was very fast.

Entries in the lower part of Table V involve changes in attacking ligand. Bipyridyl and ethylenediamine, unlike phenanthroline, can form nonchelating complexes with metals and in part owe their greater rates to their greater flexibilities.¹³ Insensitivity of the rate to basicity of the attacking ligand is demonstrated by the two dimethyl derivatives of phenanthroline. The methyl groups are in positions where they exert no steric influence on the reaction. They make significant changes in the basicity of the nitrogens, however. The 4,7-dimethyl compound is ten times as basic as phenanthroline, and the 5,6-dimethyl compound is one-fifth as basic.¹⁹ A 50-fold decrease in basicity was accompanied by less than a 30% decrease in rate.

Activation parameters were calculated from rate constants at 5 and 25°. They are $\Delta H^\ddagger = 14.8$ kcal/mol and $\Delta S^\ddagger = -7.9$ eu for the reaction between tetrachloropalladate(II) and phenanthroline and $\Delta H^\ddagger = 18.6$ kcal/mol and $\Delta S^\ddagger = 11.4$ eu for the reaction between trichloroquopalladate(II) and phenanthroline. Reactions of some similar complexes with monodentate ligands have activation enthalpies of about 5 kcal/mol.¹⁰ PdCl₄²⁻ reacts 10⁴ times as fast as PtCl₄²⁻ with phenanthroline, and Pd(H₂O)Cl₃⁻ reacts 2×10^5 as fast as Pt(H₂O)Cl₃⁻, if all reactions are brought to a common temperature (55°).

Discussion

The reaction between tetrachloropalladate(II) and phenanthroline has some unusual aspects, primarily arising from the bulkiness and rigidity of phenanthroline. Examination of the reaction is appropriate to see if it fits the generally accepted mechanism of sub-

stitution in square-planar complexes, designated by Langford and Gray²⁰ as *associative* (A). The A mechanism involves assistance by the entering ligand and formation of an intermediate of increased coordination number. The mechanism is consistent with many properties of the reaction, such as the second-order kinetics. The unusual slowness may be assigned to steric hindrance to bond formation between phenanthroline and palladium. A feature that is less expected is the insensitivity of rate to phenanthroline basicity, for the A mechanism requires strong participation by the entering ligand in the reaction energetics. A similar result, however, has been obtained in the reaction of Pt(bipy)Cl₂ with pyridine derivatives of different basicities. Cattalini, *et al.*, explained that reactivity of the pyridine toward platinum is probably governed by its polarizability rather than its basicity. Nitrogen atom polarizability is not a measurable quantity, but it might not vary much with pyridine basicity.²¹ The equal rates of reaction of phenanthroline and the phenanthrolium ion are probably not explicable within the framework of the A mechanism, nor are they likely to result from some fortuitous cancelling effect, since the same thing happens with PtCl₄²⁻.¹³

Another mechanism, called *dissociative interchange* (I_d), deserves examination because it can provide at least as good an explanation of the data. The mechanism requires the entering group to be present in the activated complex but not to participate in the energetics of its formation ("accidental bimolecularity"²⁰). Phenanthroline is appropriate for this mechanism because, as argued elsewhere,¹³ it cannot get close enough to the metal ion to form a bond until considerable rearrangement of the leaving group has occurred. Second-order kinetics is caused by the statistical probability that phenanthroline will be at the right position when the activation energy is available. The reaction is slow because there is no entering-group assistance of the kind found in other square-planar substitution reactions. Changes in phenanthroline do not affect the rate because the activation energy serves only to dissociate or reposition the leaving group. The same argument applies to the reactivity of the phenanthrolium ion. The ion must only be in the proper position in the encounter complex, because deprotonation can occur after the transition state has been reached. Another feature can be explained by the I_d mechanism. Although the results are fragmentary, the reaction seems to be unusually slowed down by decreases in negative charge on the complex. Pd(H₂O)Cl₃⁻ does react faster than PdCl₄²⁻, but not nearly as fast as expected for reactions going by the A mechanism. Neutral dichlorodiammine complexes do not seem to react at all. For a dissociative interchange process, a negative charge on the complex may give extra stability to a transition state in which the bond to the leaving

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(19) J. V. Rund and K. G. Claus, *Inorg. Chem.*, **7**, 860 (1968).

group is being weakened without assistance from the entering group.

Caution should be exercised in accepting an I_d mechanism for a substitution reaction of a square-planar complex, when all other such reactions go by the A mechanism. The I_d mechanism can be expected to occur, if

at all, only in cases of the most extreme steric hindrance to the approach of the entering group.

Acknowledgment.—This research was carried out under Grant GM 11989 from the National Institutes of Health.

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Arsenic-Sulfur Polydentate Ligands. I. Palladium(II) Complexes of Bis[phenyl(*o*-thiomethylphenyl)arsino]propane and Bis[phenyl(*o*-thiomethylphenyl)arsino]ethane

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Received November 18, 1969

Syntheses of two potentially quadridentate arsenic-sulfur ligands, 1,3-bis[phenyl(*o*-thiomethylphenyl)arsino]propane (C_3) and 1,2-bis[phenyl(*o*-thiomethylphenyl)arsino]ethane (C_2) are described. A variety of palladium(II) complexes of these two ligands have been prepared and structural assignments have been made on the basis of synthetic reactions, conductance, electronic spectra, molecular weight, and pmr data. The isolated complexes are of the following types: (1) $Pd(C_n)X_2$ ($n = 3$; $X = Cl, Br, I, SCN$; $n = 2$; $X = Cl, Br, I$) exist in nonpolar solvents with two anions and two arsenic atoms coordinated to palladium(II); (2) $Pd_2(C_n)X_4$ ($n = 2, 3$; $X = Cl, I$) have two halides, one thiomethyl group, and one arsenic atom (attached to the same benzene ring) coordinated to each palladium(II); (3) $Pd_2(C_n)_2X_2^{2+}$ are dimeric bi-univalent electrolytes in polar solvents and have two arsenic and one exchanging $-SCH_3$ group coordinated to palladium(II) along with a halide ion; (4) $Pd_2(C_n)_2^{4+}$ ($n = 2, 3$) are obtained as perchlorate salts and are square planar with the ligands functioning as bridging quadridentates. The complexes $Pd(C_3)Cl_2$ and $Pd(C_2)Cl_2$ undergo S-demethylation in hot dimethylformamide or hot dimethylformamide-butanol media, giving dimeric $[Pd(\text{demethylated } C_3 \text{ or } C_2)]_2$. The demethylated complexes can be alkylated with methyl iodide to provide $Pd(C_3)I_2$ and $Pd(C_2)I_2$. Several new palladium(II) complexes with the ligands 1,2-bis(diphenylarsino)ethane (dias), (*o*-methylthiophenyl)diphenylphosphine (SP), and bis(*o*-methylthiophenyl)phenylphosphine (DSP) have been prepared and studied in order to provide standards for comparison. These complexes are $Pd(\text{dias})I_2$, $Pd(\text{SP})I_2$, and $Pd(\text{DSP})I_2$.

Introduction

Polydentate ligands containing phosphorus-sulfur,²⁻⁶ arsenic-sulfur,^{5,7-9} nitrogen-sulfur,^{2,7} nitrogen-phosphorus,^{2,10-12} arsenic-phosphorus,¹³ and nitrogen-arsenic^{2,9,14} mixed donors, along with polydentate phosphorus^{15,16} and arsenic¹⁷⁻¹⁹ ligands, are of considerable

current interest. Several such ligands have been reported to give rise to less familiar coordination environments around the central transition metals, which include five-coordinate nickel(II), palladium(II), and platinum(II) with trigonal-bipyramidal or square-pyramidal geometries. The supposedly good π -acceptor properties of sulfur, arsenic, or phosphorus donors are thought to promote pentacoordination. It appears that the flexidentate character of such multidentate ligands has not been effectively exposed in earlier studies.

We describe herein the syntheses of two quadridentate ligands (structure I) containing soft arsenic and sulfur donors, namely, 1,3-bis[phenyl(*o*-thiomethylphenyl)arsino]propane (C_3) and 1,2-bis[phenyl(*o*-thiomethylphenyl)arsino]ethane (C_2), and a study of their palladium(II) complexes. Earlier studies related to palladium(II) complexes of dimethyl(*o*-methylthiophenyl)arsine (chel, structure II),⁸ 1,2-bis(*o*-diphenylarsinophenylthio)ethane (SAS, structure III),⁷ and tris(*o*-methylthiophenyl)arsine (TSA)⁵ have been made. Whereas chel, a close analog to the present series of ligands, can function in a bidentate fashion, our ligands are potentially quadrifunctional. Our experiences with these ligands reveal that the nature of the bridging

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