ing coordinated water molecules will weaken and more easily be broken. Thus the rate of loss of water molecule, *i.e.*, the rate of complex formation, will be faster. The effect of electron donation of ligands on the reactivity of the metal is quantitatively accounted for by the linear free energy relationship shown in Figure 3.

In a study on the rates of reaction of diethylenetriamine and of nitrilotriacetate ion with mono(5-X-1,10-phenanthroline)nickel(II) complexes, Steinhaus and Margerum[33] have indicated that the rates of formation of the mixed complexes increase with increasing electron-donating properties of the substituents (X). Moorhead and Sutin[10] have shown that the monohydroxoiron(III) complex loses water molecule from the inner sphere about 20 times faster than observed for the hexaaquoiron(III) ion in the formation of the monooxalate complex of iron(III). The results of studies[34,35] on the formation of monoazidoiron(III) indicate that $Fe(H_2O)_5OH^{2+}$ undergoes reaction more rapidly than $Fe(H_2O)_6^{3+}$. Plumb and Harris[36] have shown by measurements of the exchange of water between oxygen-18-labeled solvent and aquorhodium(III) ion that the rate for the dissociation of a water molecule from the monohydroxopentaaquorhodium(III) ion is about 150 times faster than that from the hexaaquorhodium(III) ion. Recently, Hunt, *et al.*,[37] have provided evidence that water exchange is labilized by the coordinated ammine ligand. The increase of these rates can be mainly attributed to the effect of loosening the water–metal bond owing to the electron donation of ligands coordinated to metal. Such an effect of coordinated ligands on the ease of replacement of the leaving ligands is also of particular importance in the stepwise coordination and dissociation of ligands.

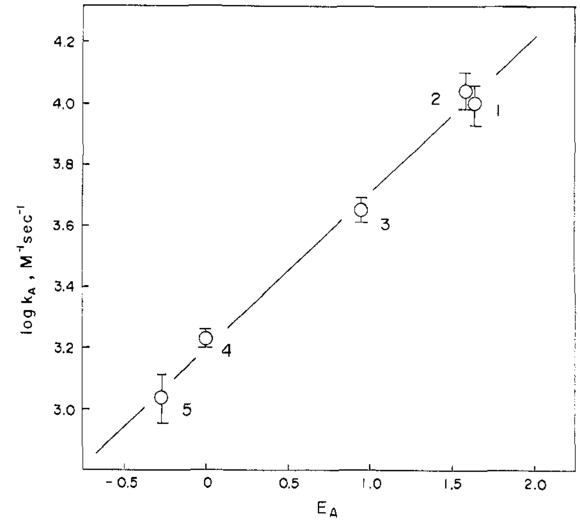

Figure 3.—Plot of log k_A *vs.* E_A: 1, k_{OH}; 2, k_{N_3}; 3, $k_{CH_3CO_2}$; 4, k_{H_2O}; 5, k_F.

Acknowledgment.—The financial support given by the Ministry of Education (Japan) is gratefully acknowledged.

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The Preparation and Properties of Some Triphenylarsine- and Triphenylstibine-Stabilized Organoplatinum(II) Compounds

BY C. R. KISTNER,[1] JON D. BLACKMAN, AND WILLIAM C. HARRIS

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The reaction of alkyl- and arylplatinum(II)–olefin complexes with triphenylarsine and triphenylstibine yields a series of compounds of the type L_2PtR_2, where L is$(C_6H_5)_3As$ or $(C_6H_5)_3Sb$ and R is a σ-bonded aryl or alkyl group. The properties of these compounds differ with the size of the stabilizing ligand and the position of substitution on the benzene ring. These properties are reported and discussed.

Introduction

Aryl and alkyl derivatives of platinum(II) have been prepared using various tertiary phosphines and triethylarsine as strong-field-splitting ligands.[2–5] It has been reported[3,6] that the stability of tertiary-phosphine-stabilized complexes of platinum(II), palladium(II), and nickel(II) containing alkyl–metal σ bonds decreases with an increase in the size of the alkyl chain. Also, the stability of complexes containing σ-bonded aryl groups varies with the position of substitution on the benzene ring; the *ortho*-substituted derivatives have greater thermal stability and are less reactive. This stability is attributed to the steric effects of the *ortho* groups which cause the aromatic rings to lie perpendicular to the square plane of the complex. In the platinum(II) compounds, this allows a maximum overlap

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Table I

Analytical Data

Compound	Color	Dec pt, °C	Yield, %	% carbon		% hydrogen	
				Calcd	Found	Calcd	Found
$C_8H_8Pt(m\text{-}C_6H_4CH_3)_2$	Cream	143–148	62	54.86	54.30	4.60	4.45
$(C_5H_5N)_2Pt(m\text{-}C_6H_4CH_3)_2$	White	127–132	59.5	53.81	54.73	4.51	4.71
$[(C_6H_5)_3As]_2PtI_2$	Orange	288–293	94	40.73	39.93	2.85	3.23
$[(C_6H_5)_3As]_2Pt(CH_3)_2$	Cream	203–205	60.5	54.49	52.54	4.33	3.92
$[(C_6H_5)_3As]_2Pt(C_6H_5)_2$	Cream	169–171	21	59.94	59.02	4.19	3.87
$[(C_6H_5)_3As]_2Pt(p\text{-}C_6H_4CH_3)_2$	Cream	168–172	11	60.66	60.42	4.48	4.14
$[(C_6H_5)_3As]_2Pt(m\text{-}C_6H_4CH_3)_2$	Cream	173–176	17.3	60.66	59.97	4.48	4.72
$[(C_6H_5)_3As]_2Pt(o\text{-}C_6H_4CH_3)_2$	White	218–220	89	60.66	60.16	4.48	4.04
$[(C_6H_5)_3Sb]_2PtI_2$	Red	225	94.3	37.42	37.53	2.62	2.26
$[(C_6H_5)_3Sb]_2Pt(CH_3)_2$	Cream	243–245	70	49.00	50.02	3.90	3.74
$[(C_6H_5)_3Sb]_2Pt(C_6H_5)_2$	White	272	64.7	54.62	53.43	3.63	3.81
$[(C_6H_5)_3Sb]_2Pt(p\text{-}C_6H_4CH_3)_2$	Cream	222	54	55.43	54.26	3.72	4.01
$[(C_6H_5)_3Sb]_2Pt(m\text{-}C_6H_4CH_3)_2$	White	235	51	55.43	54.66	3.72	3.47
$[(C_6H_5)_3Sb]_2Pt(o\text{-}C_6H_4CH_3)_2$	White	170–173	29	55.43	55.70	3.72	3.70

between the $5d_{xy}$ orbitals of the metal and the π electrons of the benzene rings resulting in lowering the energy of the $5d_{xy}$ orbital and causing a greater difference in energy between it and the lowest energy antibonding orbital. The *ortho*-substituted compounds are also less reactive due to the steric effects of the *ortho* substituent directed toward the apical positions.

In a previous paper,[5] we reported that the same stability trends were observed in alkyl- and arylplatinum(II) compounds stabilized with pyridine, triphenylphosphine, and cyclic polyolefins.

A series of substituted arylplatinum(II) compounds stabilized by triphenylarsine and triphenylstibine was prepared in order to extend the number of compounds containing substituted aryl groups σ bonded to platinum(II) and to investigate the extent of these steric effects on stability and reactivity.

Experimental Section

$C_8H_8PtI_2$.—Diiodo(cyclooctatetraene)platinum(II) was prepared by a previously described modification[5] of a procedure reported by Jensen.[7]

Grignard Reactions.—Compounds of the type $C_8H_8PtR_2$ or $C_8H_8Pt_2R_4'$, where R is aryl and R′ is methyl or phenyl, were prepared using a modification of previously described procedures.[5,8] An excess of Grignard was prepared in the usual manner, filtered, and added slowly to a suspension of diiodo(cyclooctatetraene)-platinum(II) in anhydrous benzene. The resulting solution was stirred 0.5–1.0 hr and was hydrolyzed in aqueous ammonium chloride. The benzene–ether layer was separated, decolorized with charcoal, and filtered; the product was recovered by evaporation of the solvent at room temperature. The oily product was washed with cyclohexane, dissolved in dichloromethane, and recrystallized from a dichloromethane–cyclohexane mixture. This solvent pair gave good yields of compounds prepared by this procedure.

All known compounds of the type $C_8H_8PtR_2$ or $C_8H_8Pt_2R_4'$ were identified by comparison of infrared spectra. The analytical data for all new compounds are reported in Table I.

$(C_5H_5N)_2Pt(m\text{-}C_6H_4CH_3)_2$.—A 0.1-g (0.208-mmol) sample of bis(*m*-tolyl)cyclooctatetraeneplatinum(II) was placed in a 25-ml flask with 3 ml of pyridine and 5 ml of benzene and maintained at 75° for 1.0 hr. The resulting solution was cooled and the solvent was evaporated at room temperature. The brown, oily product was dissolved in benzene, and the solution was decolorized with charcoal and filtered. The white, crystalline product, 0.066 g, was recrystallized from benzene. (See Table I.)

Reactions with $(C_6H_5)_3As$.—A sample of $C_8H_8PtR_2$ or $C_8H_8Pt_2R'_4$ and a twofold excess of triphenylarsine were placed in 100 ml of benzene in a 250-ml flask fitted with a reflux condenser. The mixture was heated and maintained at 80° for 0.5 hr. The resulting solution was cooled and evaporated at room temperature. The residue was dissolved in dichloromethane, the solution was decolorized with charcoal and filtered, and the product was recrystallized from a dichloromethane–cyclohexane mixture.

Reactions with $(C_6H_5)_3Sb$.—These reactions were conducted using the same procedure described for the triphenylarsine reactions.

Infrared Spectra.—The infrared absorption spectra of all compounds were determined in potassium bromide disks using a Perkin-Elmer Model 137 infracord spectrophotometer.

Discussion

The triphenylarsine and triphenylstibine derivatives are less reactive and decompose at higher temperatures than the analogous cyclic polyolefin, pyridine, and tertiary phosphine compounds previously reported.[5] This increase in stability with an increase in ligand size may be attributed to the interaction of the 4d orbitals of arsenic and the 5d orbitals of antimony with the filled $5d_{xz}$ and $5d_{yz}$ orbitals of platinum. Chatt[2] has proposed that a similar interaction involving the 3d orbitals of phosphorus with the filled 5d orbitals of platinum accounts for the stability of compounds stabilized by tertiary phosphines. The stability of these compounds indicates that this π-type bonding is more significant the larger the stabilizing ligand, complex stability being in the order: $(C_6H_5)_3Sb > (C_6H_5)_3As > (C_6H_5)_3P$. With one exception, this trend is observed in all series of compounds reported in which platinum(II) is σ bonded to an aryl or alkyl carbon. The exception, bis(*o*-tolyl)bis(triphenylstibine)platinum(II), decomposes at a lower temperature than the triphenylphosphine and triphenylarsine analogs. This may be due to the combined steric effects of the large ligand, triphenylstibine, and the methyl group in the *ortho* position on the benzene ring.

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The relative stability of complexes containing substituted aryl groups σ bonded to platinum(II) has been reported to be: 1-naphthyl > *o*-tolyl > *p*-tolyl.[5] The *m*-tolyl derivatives decompose at slightly higher temperatures than the analogous *p*-tolyl compounds indicating that *meta* substitution may result in added stabilization similar to that reported for *ortho*-substituted aryl groups. In the triphenylstibine series of compounds *ortho* substitution decreases thermal stability. This is apparently due to the previously mentioned combined steric effects of the large ligand and the *ortho*-substituted benzene rings.

The reactivity and solubility of the compounds follow the same trends observed from decomposition temperatures, decreasing with *ortho* substitution and increasing size of the stabilizing ligand. The solubility of these compounds in polar chlorinated hydrocarbons follows the order: $C_5H_5N > (C_6H_5)_3P > (C_6H_5)_3As > (C_6H_5)_3Sb$ and *p*-tolyl $\cong$ *m*-tolyl > *o*-tolyl.

Although addition and displacement reactions of compounds of the type L_2PtR_2, where L is pyridine or a tertiary phosphine, with alkyl iodides have been reported,[2,5,9] preliminary investigations indicate that triphenylarsine- and triphenylstibine-stabilized platinum(II) complexes do not react with alkyl iodides.

The infrared spectra of all compounds reported are similar to the spectra of previously described *cis*-triphenylphosphine complexes of platinum(II). The spectra of these compounds are also similar to those of triphenylarsine and triphenylstibine, the main difference being the reduced intensity of the absorption peak at 909 cm^{-1} in the triphenylstibine compounds and the 912-cm^{-1} peak in triphenylarsine compounds. The presence of absorption peaks associated with the substituted aryl groups was also noted.

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Preparations, Far-Infrared Spectra, and Raman Spectra of Pentahaloindium(III) and -thallium(III) Complexes

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The addition of excess tetraalkylammonium halide to indium(III) and thallium(III) halides in a variety of nonaqueous solvents leads to the formation of pentahaloindates and pentahalothallates—*e.g.*, $[(C_2H_5)_4N]_2[InCl_5]$, $[(C_2H_5)_4N]_2[TlCl_5]$, $[(CH_3)_4N]_2[TlCl_5]$, $[C_8H_{18}N_2][TlCl_5]$, and $[C_8H_{18}N_2][TlBr_5]$. Vibrational spectra of $[(C_2H_5)_4N]_2[InCl_5]$ are those expected for a square-pyramidal geometry for $InCl_5^{2-}$, which is known from previous single-crystal X-ray data to have rigorous C_{4v} symmetry in the tetraethylammonium salt. Spectra of the corresponding thallium compound also are indicative of a square-pyramidal geometry for the anion. Similarly, the X-ray powder patterns of the tetraethylammonium pentachlorothallate(III) indicates this salt is isomorphous (and presumably isostructural) with the corresponding indium complex. In the presence of the cation $C_8H_{18}N_2^{2+}$, vibrational spectra indicate irregular geometries for the pentahalo complexes. Therefore it appears probable that the square-pyramidal structure found for the tetraethylammonium salts results from peculiarities of the crystal packing. Raman spectra for nitromethane solutions of $InCl_5^{2-}$ and $TlCl_5^{2-}$ indicate significant dissociation to the tetrahalo complexes, and the intensities may be analyzed in terms of the equilibrium: $[(C_4H_9)_4N][TlCl_4] + [(C_4H_9)_4N]Cl = [(C_4H_9)_4N]_2[TlCl_5]$. In nitromethane or alcohol it is possible that the MX_5^{2-} species are coordinated by the solvent to produce pseudooctahedral complexes.

Introduction

Many five-coordinate halide complexes of group V and IV elements are known. The phosphorus(V) halides readily come to mind and anionic species of the type MX_5^- have been reported for group IV elements such as silicon, germanium, and tin. In fact, it appears that where both four- and six-coordinate complexes are known for an element, the preparation of intermediate five-coordinate species should only require discovery of the necessary experimental conditions.

There is an extensive literature[2,3] on four- and six-coordinate thallium and indium halide complexes, prepared principally by classical methods from aqueous solutions. Also, a series of complexes $MCl_5H_2O^{2-}$ (M = Tl, In) is known, and in the case of thallium the interesting binuclear species $Tl_2Cl_9^{3-}$ has been prepared. Of importance to the present work is a series of double salts[4] containing $InCl_3$ and $InBr_3$, with formulas like $[R_4N]_nX \cdot InX_3$ (n = 1–4). Recently, a different

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