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Partial Nucleophilic Displacement of Chloride in *mer*-Trichlorotris(triphenylstibine)rhodium(III)

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Chatt, *et al.*, have prepared the orange complexes *mer*-$[RhL_3Cl_3]$ by addition of LR_3 to hot alcoholic $RhCl_3$ ($R_3 = Et_3$, n-Pr_3, n-Bu_3, Me_2Ph, Et_2Ph, L = P) (R = Et_3, n-Pr_3, n-Bu_3, L = As).[1] The trans chlorines are more labile than the chlorine trans to the phosphine and, on treatment with MX in hot acetone or ethanol, complexes of the type *mer*-$[RhL_3ClX_2]$ are formed. Under reflux for extended periods the third chlorine is replaced to give *mer*-$[RhL_3X_3]$ (L = PMe_2Ph, $AsMe_2Ph$; X = NCO, Br, I, N_3, NCS).[2] It is also well-established that, as well as producing complexes of type $[RhL_3Cl_3]$, mono(tertiary arsines) react with $RhCl_3 \cdot 3H_2O$ to yield the chloro-bridged $[Rh_2L_4Cl_6]$ or $[Rh_2L_3Cl_6]$, according to the amount of arsine employed.[1]

We wish to report here the reaction of $RhCl_3 \cdot 3H_2O$ with triphenylstibine in ethanol yields only the product *mer*-$[Rh(SbPh_3)_3Cl_3]$. This product is formed regardless of the ratio of reactants and differs significantly from similar complexes of phosphines and arsines, in that substitution by nucleophiles does not proceed to completion but stops at *mer*-$[Rh(SbPh_3)_3Cl_2X]$ (X = Br, I, NCS, $SnCl_3$).

Table I

Compd	Color	Analyses, % C Calcd	C Found	H Calcd	H Found	Cl Calcd	Cl Found	Other Calcd	Other Found
$[Rh(SbPh_3)_3Cl_3]$	Orange	51.0	50.0	3.5	3.6	8.3	8.3		
$[Rh(SbPh_3)_3Cl_2Br]$	Orange-brown	49.4	49.6	3.4	3.7	5.4	5.7	6.1[a]	6.1
$[Rh(SbPh_3)_3Cl_2I]$	Brown	47.6	47.7	3.3	3.4	5.2	5.4	9.3[b]	9.5
$[Rh(SbPh_3)_3Cl_2(NCS)]$	Orange	51.2	51.0	3.5	3.5	5.5	5.5	1.1[c]	1.1
$[Rh(SbPh_3)_3Cl_2(SnCl_3)]$	Orange	44.4	45.0	3.1	3.3	12.2	12.4		

[a] Bromine. [b] Iodine. [c] Nitrogen.

Table II. Electronic Spectra of the Complexes in Dichloromethane (cm^{-1})[a]

$Rh(SbPh_3)_3Cl_3$	$Rh(SbPh_3)_3Cl_2Br$	$Rh(SbPh_3)_3Cl_2I$	$Rh(SbPh_3)_3Cl_2(NCS)$	$Rh(SbPh_3)_3Cl_2(SnCl_3)$
39,200 (20,900)	39,190 (29,500)	38,580 (24,200)		39,100 (34,100)
31,950 (19,650)	31,250 (15,100)	32,400 (15,800)	33,300 (13,400)	32,900 (11,700)
		27,700 (15,650)		
25,640 (22,500)	25,300 (9530)	25,000 (13,100)	27,800 (23,200)	26,040 (31,000)
				20,900 (1960)

[a] Molar extinction coefficients in parentheses.

Experimental Section

mer-**$[Rh(SbPh_3)_3Cl_3]$.** Rhodium trichloride trihydrate (2.6 g, 0.01 mol) and triphenylstibine (10.6 g, 0.03 mol) in ethanol (150 ml) were stirred under reflux for 3 hr, during which time an orange solid formed. This was filtered while hot and washed with hot ethanol (150 ml). The complex was recrystallized from dichloromethane–ethanol and dried *in vacuo*; yield 11.8 g (89%).

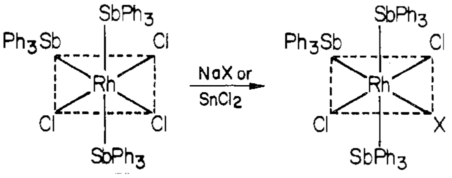
mer-**$[Rh(SbPh_3)_3Cl_2X]$.** To a suspension of *mer*-$[Rh(SbPh_3)_3Cl_3]$ (2.0 g) in ethanol (50 ml) was added a 5 molar equiv of NaX (X = Br, I, SCN) or $SnCl_2$. The mixture was stirred under reflux for 24 hr and filtered while hot. The resulting solids were extracted into dichloromethane, filtered to remove any insoluble material, allowed to crystallize, and dried *in vacuo*; yields ~70–80%.

Physical Measurements. Dipole moments of *mer*-$[Rh(SbPh_3)_3Cl_3]$ (7.4 D) and *mer*-$[Rh(SbPh_3)_3Cl_2Br]$ (7.6 D) were determined in benzene at 25° and calculated as described.[3] Other physical measurements were carried out as previously reported.[4]

Results and Discussion

The reaction of $SbPh_3$ with $RhCl_3 \cdot 3H_2O$ in ethanol was found to yield only one product, the orange *mer*-$[Rh(SbPh_3)_3Cl_3]$. Varying the metal:ligand ratio did not effect the production of any complexes of the type $[Rh_2(SbPh_3)_4Cl_6]$ or $[Rh_2(SbPh_3)_3Cl_6]$ analogous to the arsine complexes.[1] The mer configuration was assigned by a dipole moment measurement in benzene. A value of *ca.* 7 D is expected for a mer complex; fac complexes are associated with moments of *ca.* 11 D.[1]

On refluxing *mer*-$[Rh(SbPh_3)_3Cl_3]$ with NaX (X = Br, I, NCS) or $SnCl_2$ in ethanol we were surprised to find that reaction was complete after only one chlorine, presumably the one trans to antimony, is substituted by the nucleophile to produce complexes of type *mer*-$[Rh(SbPh_3)_3Cl_2X]$ (Table I), *i.e.*



Extended reflux with excess nucleophile did not lead to further substitution. Thus triphenylstibine reverses the substitution trend of analogous phosphine and arsine complexes which at first yield $[RhL_3ClX_2]$ and subsequently $[RhL_3X_3]$. The first and only product of the reactions we carried out yields $[Rh(SbPh_3)_3Cl_2X]$ derivatives.

Table II lists the electronic spectral maxima of the complexes which are characterized by three bands. The highest energy band, *ca.* 39 kK, is probably due to rhodium-antimony charge transfer, and the band *ca.* 32 kK is due to rhodium-halogen charge transfer. The lowest energy absorption is obviously dependent on the nature of X and moves to

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lower energy in the order NCS $>$ $SnCl_3$ $>$ Cl $>$ Br $>$ I. All of the visible absorptions are extremely intense, indicative of a large amount of "borrowing" of charge-transfer intensity.[5] While the expected Cl $>$ Br $>$ I order suggests that these visible bands are d-d transitions and hence are indicative of a spectrochemical series in which the ligand field strength of $SnCl_3^-$ is only slightly greater than that of chloride, in view of the high intensities of these bands it is unwise to speculate too freely on their origin.

We observed a broad band at 2090 cm^{-1} in the Nujol mull infrared spectrum of $[Rh(SbPh_3)_3Cl_2(NCS)]$, which is evidence of the Rh-NCS linkage. This complex did not isomerize on heating, as does $[Rh(PMe_2Ph)_3(NCS)_3]$.[2]

Registry No. $[Rh(SbPh_3)_3Cl_3]$, 51261-83-7; $[Rh(SbPh_3)_3Cl_2Br]$, 51157-43-8; $[Rh(SbPh_3)_3Cl_2I]$, 51157-44-9; $[Rh(SbPh_3)_3Cl_2(NCS)]$, 51157-45-0; $[Rh(SbPh_3)_3Cl_2(SnCl_3)]$, 51157-46-1.

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Metal Ion Induced Pyrrole Ionization in 2-(2'-Pyridyl)imidazole[1]

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Pyrrole hydrogen ionizations in imidazole and derivatives coordinated to the metal ions of metmyoglobin, methemoglobin, and vitamin B_{12} derivatives have been invoked to account for features of potentiometric titrations and changes in absorption spectra in these systems. Transition metal ion induced pyrrole ionization takes place across the imidazole ring from the site of metal ion coordination at the pyridine nitrogen. Substitution of the pyrrole hydrogen by the metal ion is not thought to be occurring in these systems.[2] Due to their complexity, comparative studies are not practical on the macromolecules, and there is a need for greater knowledge of the extent of transition metal ion induced pyrrole ionizations in small well-defined complexes of imidazole and derivatives. Pyrrole ionization occurs from the 2:1 L-histidine complexes of Cu(II) and Co(II) with pK_a values of 11.7 and 12.5, respectively,[3] compared to 14.4 for the free ligand.[4] However, due to the high-pH region, it is uncertain how many bound ligand molecules undergo metal ion induced pyrrole ionization in these and similar complexes.[3]

The ligand 2-(2'-pyridyl)imidazole, PH, promised to be capable of metal ion induced pyrrole ionization across the imidazole ring after chelation at two pyridine nitrogens, one on the pyridine and the other on the imidazole ring, to form a chelate ring system similar to that of 2,2'-bipyridine. Also similar to bipyridine, the ligand PH is known to form tris complexes with Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) and the stability constants have been determined.[5] Neutral complexes of several transition metal ions and ligands that have undergone pyrrole ionization have been prepared in the solid state.[6] However, no solution studies characterizing the pH region in which pyrrole ionization occurs in metal complexes have been reported. This paper describes the promotion of pyrrole hydrogen ionization in solutions induced by transition metal ions coordinated across the imidazole ring.

Experimental Section

The ligand 2-(2'-pyridyl)imidazole was synthesized according to a published procedure,[5,6] mp 137–138° (uncor). $Pd(en)PH^{2+}$ was prepared by a method previously described.[7] Potentiometric titrations confirmed the purity of the preparations. Titrations were performed under nitrogen with a Radiometer TTT1-SBR2 titrimeter–titrigraph equipped with a Sargent combination electrode that was standardized with National Bureau of Standards aqueous buffer solutions at pH 4.00 and 7.00. In order to obtain a measure of the hydrogen ion activity referred to the standard state in the mixed 50% by volume ethanol solutions, 0.15 log unit was subtracted from each pH meter reading before reporting values in this paper.[8] Overlapping acidity constants involving two deprotonations were evaluated objectively,[9] and those with three deprotonations were estimated from the titration curves. Solution magnetic susceptibilities were determined by an nmr method.[10] Circular dichroism spectra were recorded on a Jasco J-10B instrument and visible spectra on a Cary 14R spectrophotometer. All solutions were 0.20 M in KCl and all measurements were made at room temperature, near 23°.

Results

Titrations with standard base conducted in water solutions containing 2:1 or greater molar ratios of 2-(2'-pyridyl) imidazole and added acid (PH_2^+) to transition metal ion indicated formation of complexes, but after complex formation is complete, precipitation occurs in the pH region of pyrrole hydrogen ionization. To avoid precipitation in the pH region of interest, a solvent system of 50% by volume ethanol in water was employed, and unless stated otherwise all experiments refer to this mixed-solvent medium.

For the deprotonation reaction $PH_2^+ \rightleftarrows PH + H^+$, potentiometric titration gave pK_a = 5.09 in 50% ethanol and 5.54 in water. Spectrophotometric titrations monitored at 325 nm were used to evaluate the acidity constant for ionization of the pyrrole hydrogen in the free ligand ($PH \rightleftarrows P^- + H^+$). In 50% ethanol p$K_a$ = 14.2 ± 0.2 and in water a lesser value of 13.4 ± 0.1 was obtained consistent with relative stabilization of oppositely charged ions in the higher dielectric constant medium.

In the presence of Fe(II), Co(II), Ni(II), Cu(II), or Zn(II) the deprotonation occurring with pK_a = 5.09 is depressed on the pH axis. In a solution containing a 3:1 ligand to transition metal ion ratio, complex formation is complete by pH 7 and in no case does any ligand titrate as if unbound. Thus all of the above transition metal ions form relatively stable 3:1 complexes with PH as with bipyridyl. These results are consistent with the stability constants that have already been reported for 3:1 complexes of PH with transition metal ions.[5] Addition of excess ligand so that the ratio is

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