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Trichlorobis(Tri-p-tolylarsine)(methanol)ruthenium(III) and Some of Its Reactions with Nitrogen Donor Ligands

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The interaction of tri-p-tolylarsine with ruthenium trichloride trihydrate in acidified methanol under reflux gave a complex, $RuCl_3(AsTol_3^P)_2$(MeOH) (1). Complex 1 has been employed as a useful starting material for the preparation of other ruthenium(II) and (III) complexes. On treating complex 1 with excess of nitriles, complexes of the type $RuCl_3(AsTol_3^P)_2(RCN)$ (R = CH_3, C_6H_5, $C_6H_5CH_2$) were obtained. Complex 1 gave $RuCl_3(AsTol_3^P)(Py)_2$ and $RuCl_2(Py)_4$ respectively, on reaction with excess of pyridine in n-hexane and dichloromethane. The reactions of 2,2'-bipyridine and 1,10-phenanthroline (N–N) with complex 1 in dichloromethane resulted in the formation of $RuCl_3(AsTol_3^P)(N–N)$. A five coordinate complex $RuCl_3(AsTol_3^P)_2$ was isolated from dichloromethane, chloroform or benzene solutions of complex 1. The dissolution of complex 1 in acetone gave a stable adduct $RuCl_3(AsTol_3^P)_2(Me_2CO)$.

Introduction

The growing interest in the synthesis and reactivity of ruthenium(II) and (III) complexes containing tertiary phosphines and arsines during the past few years has provided a fairly extensive series of stable complexes [1–8]. Several successful methods for the preparation of these complexes have been developed and reported [3–8]. The syntheses of a wide range of ruthenium complexes containing phosphines or arsines were achieved by using such starting materials as $[Ru_2Cl_3(PR_3)_6]Cl$ [2], $RuX_2(PPh_3)_n$ (X = Cl or Br, n = 3 or 4) [3–5], $RuX_3(EPh_3)_2$(MeOH) (X = Cl or Br, E = P or As) [3a, 5, 6], $RuCl_2(DMSO)_4$ [7] and the blue methanolic solutions of $Ru_5Cl_{12}^{2-}$ [8]. These complexes are highly labile in solution making them ideal precursors for a range of new ruthenium complexes, as well as for many known ruthenium complexes. We report here the synthesis and characterization of yet another complex, $RuCl_3(AsTol_3^P)_2$(MeOH). Some of its representative reactions to demonstrate its usefulness as the starting material for the preparation of both known and unknown ruthenium(II) and (III) complexes are reported in this paper.

Experimental

The ligand tri-p-tolylarsine ($AsTol_3^P$) was obtained from Strem Chemicals, Inc. (U.S.A.). The nitriles, pyridine and other organic solvents used in this investigation were of *Analar* grade and used without further purification. The ligands 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen) were purchased from BDH Chemicals (London). Ruthenium trichloride trihydrate used was from Johnson Matthey (England). Microanalyses of the complexes were done by Amdel, Australia. Magnetic susceptibilities of the solid samples were measured on a Faraday balance at room temperature. Melting point determinations and infrared spectral measurements were performed as reported earlier [5]. Molecular weight was determined on a Knauer vapour pressure Osmometer Model No. 11.00 at 37 °C in chloroform (in the concentration range 0.01–0.1 *M*).

Microanalyses and other physical data are presented in Table I. The far-infrared spectral data (in the range 100–650 cm^{-1}) are presented in Table II.

Preparation of Ruthenium Complexes

Trichlorobis(tri-p-tolylarsine)(methanol)ruthenium(III)

Ruthenium trichloride trihydrate (0.20 g, 0.76 m*M*) was dissolved in methanol (60 ml), few drops of conc. HCl added and the resulting solution refluxed

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TABLE I. Analytical and Other Physical Data of Ruthenium Complexes.

No.	Complex[a]	Colour	M.Pt. (°C)[b]	μ_{eff} (B.M.)[c]	Elemental analysis[d] C%	H%	N%
1.	$RuCl_3(AsTol^P_3)_2(MeOH)$	Brownish green	130–135	1.93	55.0 (55.1)	5.0 (4.9)	11.8[e] (11.4)
2.	$RuCl_3(AsTol^P_3)_2$	Brown	140–145	–	55.2 (55.7)	4.7 (4.6)	–
3.	$RuCl_3(AsTol^P_3)_2(Me_2CO)$	Brown	160–163	–	57.0 (56.2)	5.0 (5.0)	–
4.	$RuCl_3(AsTol^P_3)_2(CH_3CN)$	Green	205–210	–	55.0 (55.9)	4.7 (4.8)	1.5 (1.5)
5.	$RuCl_3(AsTol^P_3)_2(C_6H_5CH_2CN)$	Green	185–190	–	59.1 (58.8)	4.7 (4.8)	1.4 (1.4)
6.	$RuCl_3(AsTol^P_3)_2(C_6H_5CN)$	Bright green	197–200	–	56.6 (58.4)	4.4 (4.6)	1.5 (1.4)
7.	$RuCl_3(AsTol^P_3)(Py)_2$	Orange	170–180	2.10	51.1 (52.1)	4.3 (4.3)	3.8 (3.9)
8.	$RuCl_2(Py)_4$	Orange-red	270–274	Diamag.	50.2 (49.2)	4.2 (4.1)	12.1 (11.5)
9.	$RuCl_3(AsTol^P_3)(Bipy)$	Orange-yellow	230	1.88	51.7 (52.2)	3.9 (4.0)	3.9 (3.9)
10.	$RuCl_3(AsTol^P_3)(Phen)$	Red-brown	160–165	2.05	53.2 (53.8)	4.0 (3.9)	3.6 (3.8)

[a] Me, Methyl; Py, Pyridine; Bipy, 2,2'-bipyridine; Phen, 1,10-phenanthroline; Tol^P, p-tolyl. [b] Decomposition temperatures. [c] Magnetic susceptibility measurements were done on a Faraday Balance at 302 °K. [d] Calculated values are in parentheses. [e] Chlorine analysis.

TABLE II. Far Infrared Spectral Data for Ruthenium Complexes (100–650 cm^{-1}).[a]

No.	Complex	ν(Ru–As) (cm^{-1})	ν(Ru–Cl) (cm^{-1})	Other bands (cm^{-1})
1.	$RuCl_3(AsTol^P_3)_2(MeOH)$	495(vs)	340(vs), 325(sh) 300(s), 290(s)	640(w), 590(s), 380(s), 180(m), 170(w)
2.	$RuCl_3(AsTol^P_3)_2$	490(vs)	335(vs), 320(s) 290(w)	590(s), 375(s), 190(m), 170(w)
3.	$RuCl_3(AsTol^P_3)_2(Me_2CO)$	500(sh) 490(vs)	335(vs), 325(vs) 305(w), 290(s)	640(m), 590(s), 550(m), 445(m), 378(s), 245(m), 200(w), 180(w)
4.	$RuCl_3(AsTol^P_3)_2(CH_3CN)$	495(vs)	340(vs), 322(s) 300(w), 285(m)	640(m), 595(s), 378(s), 185(m), 150(m)
5.	$RuCl_3(AsTol^P_3)_2(C_6H_5CH_2CN)$	500(vs) 490(sh)	335(s), 328(s) 305(w)	560(w), 395(s), 245(w), 180(m)
6.	$RuCl_3(AsTol^P_3)_2(C_6H_5CN)$	495(vs) 485(sh)	335(vs), 320(vs) 300(s), 280(w)	635(w), 595(s), 545(s), 380(s), 242(w), 215(w), 190(s), 175(w), 155(m)
7.	$RuCl_3(AsTol^P_3)(Py)_2$	500(vs) 485(sh)	340(vs), 325(s) 305(w), 295(w)	640(w), 590(m), 550(w), 450(w), 388(s), 260(m), 240(m), 220(m), 210(w), 180(w)
8.	$RuCl_2(Py)_4$	–	340(vs)	590(m), 530(w), 410(w), 380(m), 180(w), 150(m)
9.	$RuCl_3(AsTol^P_3)(Bipy)$	500(vs)	341(s), 325(m), 300(w)	600(w), 450(w), 390(s), 245(m), 185(w)
10.	$RuCl_3(AsTol^P_3)(Phen)$	500(vs) 490(sh)	335(s), 320(s) 300(w)	590(m), 410(m), 370(m), 250(w), 225(w), 200(w)

[a] Key: s = strong; m = medium; w = weak; sh = shoulder; vs = very strong.

for 5–10 minutes under a nitrogen atmosphere. A three-fold excess of the ligand tri-p-tolylarsine (0.80 g, 2.29 m*M*) was added and the mixture refluxed for 3–4 hours. On cooling the reaction mixture to room temperature, a brownish-green crystalline complex was deposited, which was washed with ether and dried. Yield: 0.60 g (84%).

Trichlorobis(tri-p-tolylarsine)ruthenium(III)

Dissolution of the complex $RuCl_3(AsTol_3^P)_2$-(MeOH) (0.10 g) in benzene, dichloromethane or chloroform gave a dark brown solution. Addition of n-hexane or petroleum ether (60–80 °C) gave the brown product which analyses as $RuCl_3(AsTol_3^P)_2$. Yield: 0.09 g (93%).

Trichlorobis(tri-p-tolylarsine)(acetone)ruthenium-(III)

$RuCl_3(AsTol_3^P)_2(MeOH)$ (0.10 g) was suspended in acetone (10 ml) and heated for 5–10 minutes. Addition of n-hexane to the resulting brown solution gave a brown product. Yield: 0.09 g (89%).

Trichlorobis(tri-p-tolylarsine)(methylcyanide)-ruthenium(III)

The complex $RuCl_3(AsTol_3^P)_2(MeOH)$ (0.10 g) was suspended in acetonitrile (5 ml) and stirred for 3–4 hours at room temperature. The resulting green complex was filtered and washed with n-hexane. The complex was recrystallised from CH_2Cl_2–n-hexane to give green crystals. Yield: 0.085 g (84%). Alternatively, the complex was obtained by dissolving $RuCl_3(AsTol_3^P)_2(MeOH)$ in dichloromethane and refluxing for an hour with a two-fold excess of methylcyanide. The solvent was reduced in volume and the complex precipitated with n-hexane.

Trichlorobis(tri-p-tolylarsine)(benzylcyanide)ruthenium(III)

The complex $RuCl_3(AsTol_3^P)_2(MeOH)$ (0.10 g) was dissolved in dichloromethane (10 ml) and about 0.5 ml of benzylcyanide was added. The solution slowly turned from brown to green in about 10–15 minutes after the addition of the ligand, and remained bright green throughout the 2-hour period of stirring. The solvent was completely removed under reduced pressure and the complex was scratched in n-hexane and filtered. The complex was recrystallized from CH_2Cl_2–n-hexane mixture to give dark green crystals. Yield: 0.07 g (64%).

Trichlorobis(tri-p-tolylarsine)(phenylcyanide)ruthenium(III)

A dichloromethane solution of $RuCl_3(AsTol_3^P)_2$-(MeOH) (0.10 g) was refluxed for an hour with phenylcyanide (0.5 ml). Ten minutes after the addition of phenylcyanide the entire solution turned from dark brown to light green. The resulting green solution was reduced in volume under reduced pressure, and the bright green crystals were filtered off. The same product was obtained by stirring the reaction contents for 24 hours. The complex was recrystallised from CH_2Cl_2–n-hexane. Yield: 0.08 g (74%).

Trichlorotri-p-tolylarsinebis(pyridine)ruthenium-(III)

Pyridine (0.2 ml) was added to a suspension of $RuCl_3(AsTol_3^P)_2(MeOH)$ (0.10 g) in n-hexane (50 ml) which was then heated under reflux for an hour. During the period of heating the hexane layer slowly turned orange; at the end of the reaction an orange crystalline complex settled on the walls of the reaction flask. The reaction mixture was filtered hot and the product was recrystallised by treating with CH_2Cl_2 and then with n-hexane. Yield: 0.06 g (66%).

trans-*Dichlorotetrakis(pyridine)ruthenium(II)*

The complex $RuCl_3(AsTol_3^P)_2(MeOH)$ (0.10 g) dissolved in dichloromethane was refluxed for an hour with excess of pyridine (0.4 ml). An orange-red crystalline product was obtained on evaporating the solvent to a small volume. The compound was filtered and washed repeatedly with hot n-hexane. Yield: 0.045 g (86%).

Trichlorotri-p-tolylarsine(2,2′-bipyridyl)ruthenium-(III)

The complex $RuCl_3(AsTol_3^P)_2(MeOH)$ (0.10 g) dissolved in CH_2Cl_2 (20 ml) was stirred with a mol excess of 2,2′-bipyridyl (0.017 g) for 1–2 hours under nitrogen atmosphere. The resulting dark red solution was concentrated to a small volume and the complex precipitated with petroleum ether (60–80 °C), as an orange-yellow product. The complex was recrystallized from CH_2Cl_2–petroleum ether (60–80 °C). Yield: 0.065 g (85%).

Trichlorotri-p-tolylarsine(1,10-phenanthroline)ruthenium(III)

The complex was prepared by the same method as the corresponding bipyridyl complex. Colour: red-brown. Yield: 0.05 g (69%).

Results and Discussion

The reaction of excess of the ligand, tri-p-tolylarsine with ruthenium trichloride trihydrate in acidified methanol at reflux resulted in the formation of a complex, $RuCl_3(AsTol_3^P)_2(MeOH)$ (*I*) which is an analogue of Wilkinson's complex, $RuCl_3(EPh_3)_2$-(MeOH) (where E = P or As) [3a]. The presence of a coordinated methanol is indicated by the appearance of a weak hydroxy peak at 3495 cm^{-1} in its infrared spectrum. The methanol bands in the 1000 cm^{-1} region were obscured by the appearance of several ligational bands due to $AsTol_3^p$. Complex *1* is a monomeric paramagnetic ruthenium(III) species with magnetic moment (1.93 B.M.) corresponding to spin-paired t_{2g}^5 configuration. Complex *1* is soluble in most of the common organic solvents. On dissolving in benzene, chloroform and dichloromethane the complex readily loses the coordinated methanol giving a red-brown solution from which a brown complex $RuCl_3(AsTol_3^p)_2$ (*2*) was isolated. The infrared spectrum (4000–650 cm^{-1}) of complex *2* is identical with that of complex *1*, except for the absence of a band at 3495 cm^{-1} due to coordinated methanol. The far-infrared spectrum of complex *1* with intense bands at 340, 300 and 290 cm^{-1} due to ν(Ru–Cl), is consistent with a meridional arrangement of chlorides in the complex [9] (Table II). The configuration of complex *1* may be either *cis* or *trans*-disposed arsine ligands along with a mer-$RuCl_3$ unit. A distinction between these two possibilities cannot be made based on far-infrared studies alone, but a tentative *trans*-arsine structure is more likely since a similar structure has been suggested for the complexes $RuX_3(EPh_3)_2(MeOH)$ (X = Cl or Br; E = P or As) [3a, 6a] and the anions, $[MX_4(PPh_3)_2]^-$ (M = Ru or Rh) [10].

Complex *2* displays intense ν(Ru–Cl) absorptions at 335, 320 and 290 cm^{-1} with no evidence for bridging chloro-groups [11] (Table II). A molecular weight measurement on this complex confirms that it is a monomer (found: 873; calcd.: 904). The infrared data tentatively support the formulation of this complex as axially symmetric with three chlorides in the trigonal base and two arsine groups in the axial positions. This is in accord with the observations made earlier on a similar complex $RuCl_3(AsPh_3)_2$ [12a]. Several such five coordinate complexes are known and have been reported by various workers [6a, 12].

The complex $RuCl_3(AsTol_3^p)_2(Me_2CO)$ (*3*) is air-stable and this can be recrystallized without loss of acetone from the coordination sphere. A sharp infrared band at 1655 cm^{-1} due to carbonyl stretching in the acetone complex confirms the coordination of acetone. This is in accordance with the observations made earlier on similar adducts, $RuX_3(EPh_3)_2(Me_2CO)$ (E = P or As; X = Cl or Br) [3a] and $F_3B\cdot OCMe_2$ [13]. The bands at 335, 325, 290 cm^{-1} could be due to the meridionally disposed Ru–Cl stretching vibrations (Table II).

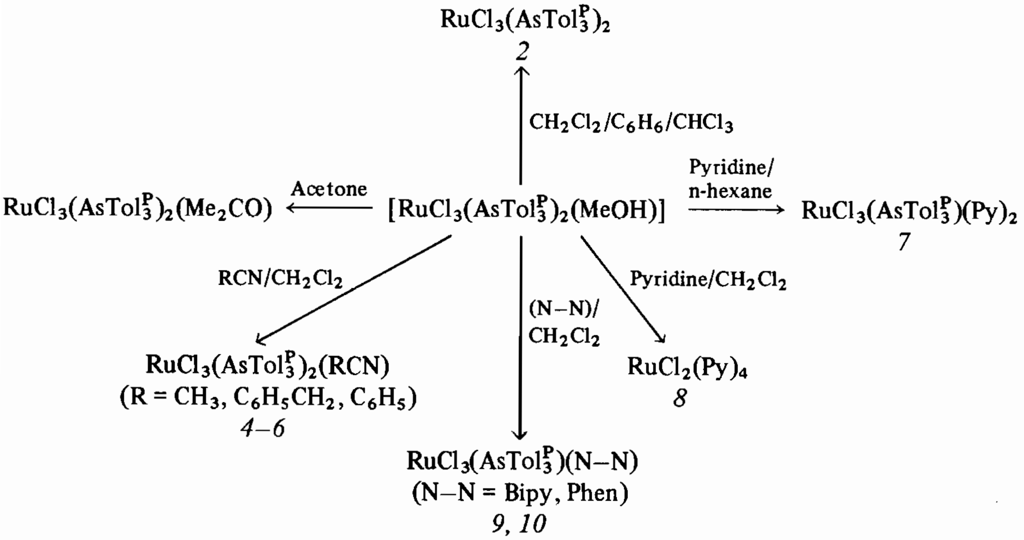
Complexes of the type $RuCl_3(AsTol_3^p)_2(RCN)$ (R = CH_3, $C_6H_5CH_2$, C_6H_5) (*4–6*) were prepared from complex *1* by displacement of methanol with excess of the appropriate nitrile in boiling dichloromethane solution. Similar complexes were obtained when the reaction mixtures were shaken for longer periods in dichloromethane. There was no evidence for the formation of reduced species during these reactions. The complexes are bright-green crystalline materials and are soluble in common organic solvents. All these complexes contain a very weak band at 2300 cm^{-1}, due to ν(CN) of the coordinated RCN group [14]. Complexes *4* and *5* exhibit weak bands at 2300 cm^{-1} and complex *6* at 2280 cm^{-1} in their infrared spectra due to ν(CN) modes. The far-infrared data (Table II) strongly suggest that the nitrile complexes (*4–6*) are similar in structure to the methanol complex (*1*).

The reaction between complex *1* and pyridine depends very much on the reaction conditions. When a dichloromethane solution of complex *1* was refluxed with an excess of pyridine for an hour an orange-red crystalline product, $RuCl_2(Py)_4$ (*8*) was obtained, whereas a suspension of complex *1* in n-hexane refluxed with excess of pyridine gave $RuCl_3(AsTol_3^p)(Py)_2$ (*7*). Complex *7* is a ruthenium(III) species with one arsine still in the coordination sphere; the presence of pyridine and $AsTol_3^p$ was confirmed by infrared spectroscopy and elemental analysis. The presence of a strong ν(Ru–Cl) band at 340 cm^{-1} is indicative of a *trans*-$RuCl_2$ group in the complex (Table II). Two different isomers are possible for a complex like this, with *cis*- and *trans*-pyridine groups, keeping the *mer*-$RuCl_3$ unit intact. Since far infrared spectral data cannot be of much help in distinguishing between these two geometries, on the basis of other evidence such as the higher *trans* effect of arsine ligand compared to pyridine [15], a configuration with *cis*-pyridines may be favoured. The configuration with *cis*-pyridines and meridionally arranged chloro groups was proposed earlier for complexes like $RuX_3(EPh_3)(Py)_2$ (X = Cl or Br; E = P or As) by Stephenson and coworkers [6a].

Complex $RuCl_2(Py)_4$ (*8*) is a well known compound which has been prepared by several methods in the *trans*-form. A *cis*-form also has been reported by Raichart and Taube [16]. Complex *8* is a reduced species which was found to be diamagnetic. A single intense band at 340 cm^{-1} in its far-infrared spectrum due to ν(Ru–Cl) confirms the *trans* configuration for the complex (Table II). Also there are no bands observed corresponding to the coordinated arsine.

Complexes *9* and *10* were characterised by elemental analyses and far-infrared spectra (Tables I and II). A configuration with a *trans*-$RuCl_2$ unit and the other chloride and arsine groups being each *trans* to the nitrogens of the chelated group (N–N) can be tentatively assigned to these complexes.

The reactions of complex *1* with nitrogen donor ligands are illustrated in Scheme I. From Scheme I it is obvious that complex *1* behaves in a manner similar to that of Wilkinson's green complex, $RuCl_3(AsPh_3)_2(MeOH)$ [3a, 6]. However, the time taken for the completion of a particular reaction is shorter than those observed for Wilkinson's complex [6]. From this it appears that the tri-p-tolylarsine com-



Scheme I

plex, $\mathrm{RuCl_3(AsTol_3^p)_2(MeOH)}$ is more reactive than the triphenylarsine complex. This is to be expected on the basis of the enhanced basicity of tri-p-tolylarsine as compared to triphenylarsine.

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