Contribution from the Inorganic Chemistry Laboratory,
University of Oxford, South Parks Road, Oxford, United Kingdom

Some Ruthenium Complexes with Multidentate Ligands Containing Phosphorus, Arsenic and Antimony Donor Atoms

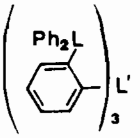
M. T. Halfpenny[1] and L. M. Venanzi[1]

Received September 14, 1970

We report the preparation and properties of (1) six-coordinate complexes $[RuX_2(ligand)]$ *containing the quadridentate ligands* $(o-Ph_2L . C_6H_4)_3L'$ $(L=L'=P$, *QP;* $L=L'=As$, *QAS;* $L=P$, $L'=As$, *ASTP;* $L=As$, $L'=P$, *PTAS;* $L=As$, $L'=Sb$, *SBTAS) and* $(o-Me_2As . C_6H_4)_3As$ *(Qas), where* $X=Cl$, *Br, I, NCS, CN for ligand = QP,* $X=Cl$, *CN for ligand = QAS, and* $X=Cl$ *for ligand = ASTP, PTAS, SBTAS and Qas, and (2) five-coordinate complexes* $[Ru(CO)(ligand)]$ *where ligand = QP and QAS, and (3) five-coordinate complexes* $[Ru(CO)_2(ligand)]$ *containing the tridentate ligands* $(o-Ph_2P . C_6H_4)_2PPh$ *(TP) and* $(o-Ph_2As . C_6H_4)_2AsPh$ *(TAS). Reductive carbonylation of the complexes* $[RuCl_2(ligand)]$ *(ligand = QP and QAS) yields the complexes* $[Ru(CO)(ligand)]$*, and* $[Ru(CO)(QP)]$ *reverts to the ruthenium(II) complexes* $[RuX_2(QP)]$ $(X=Cl$ *and I) on halogen oxidation.*

Introduction

In previous publications[2,3] we reported that the potentially quadridentate ligands tris-(*o*-diphenylphosphinophenyl)phosphine, QP, (I), and the corresponding tetra-arsine, QAS, (II), give octahedral complexes of the type $[RuX_2(QL)]$ ($QL=QP$, $X=Cl$; $QL=QAS$, $X=Cl$, Br, I, NCS, and NO_3).



R=Ph; L=P; L'=P; QP; (I)
R=Ph; L=As; L'=As; QAS; (II)
R=Ph; L=P; L'=As; ASTP; (III)
R=Ph; L=P; L'=Sb; SBTP; (IV)
R=Ph; L=As; L'=P; PTAS; (V)
R=Ph; L=As; L'=Sb; SBTAS; (VI)
R=Me; L=As; L'=As; Qas; (VII)

We report here (1) a more complete investigation of the preparation, properties and reactions of complexes $[RuX_2(QL)]$ (QL = ligands (I) to (VII) above); (2) the preparation, properties and some reactions of complexes $[Ru(CO)(QL)]$ (QL = QP and QAS); (3) the preparation and properties of complexes $[Ru(CO)_2(TL)]$ $[TL=(o-Ph_2P . C_6H_4)_2PPh$, TP, and $(o-Ph_2As . C_6H_4)_2AsPh$, TAS].

Experimental Section

The ligands PTAS, QAS, and TAS were obtained from *o*-bromophenyldiphenylarsine, prepared as described by Cannon *et. al.*,[4] using the method of Howell *et. al.*[5] The ligand SBTAS (m.p. 218-219°) was obtained similarly by substituting antimony trichloride in the last stage. Ligands QP, ASTP, and SBTP were prepared as described elsewhere,[6] as were Qas[7] and TP.[8]

Comercial « ruthenium trichloride trihydrate » was used without further purification. Complexes $[RuCl_2(PPh_3)_3]$[9] and $[Ru_3(CO)_{12}]$[10] were prepared by literature methods. Several methods of preparation of $[Ru(CO)_3(PPh_3)_2]$ have been reported;[11-14] in this work the best yields (50%) of this complex were obtained by the carbonylation and reduction[11] of *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ which was prepared essentially as described by Chatt *et al.*[15] and Stephenson *et. al.*[9]

Cyclohexanone was redistilled before use. 'AnalaR' or A.C.S. reagent grade benzene was used. Chlorobenzene was dried with silica gel. Xylene (B.D.H. Sulphur-free) was purified and dried by distillation from sodium wire and stored in contact with sodium wire. Hexane was dried with sodium wire. Before use in preparations involving ruthenium(O) compounds these solvents were de-oxygenated by passing a vigorous stream of dry nitrogen through the refluxing solvent.

The complexes prepared, their yields and analytical data are given in Table I.

Ruthenium(II) Complexes. Unless otherwise stated, the complexes were purified by repeated recrystallization from dichloromethaneethanol mixture, and dried *in vacuo* at 135° for 6-15 hrs.

---

[1] Present address: Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203.
[2] J. G. Hartley and L. M. Venanzi, *J. Chem. Soc.*, 1962, 182.
[3] J. G Hartley, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc.*, 1963, 3930.
[4] R. D. Cannon, B. Chiswell, and L. M. Venanzi, *J. Chem. Soc.*, (A), 1967, 1277.
[5] T. E. W. Howell, S. A. J. Pratt, and L. M Venanzi, *J. Chem. Soc.*, 1961, 3167.
[6] J. W. Dawson and L. M. Venanzi, *J. Amer. Chem. Soc.*, 1968, *90*, 7229.
[7] O. St C. Headley, Sir Ronald Nyholm, M. L. Tobe, C. A. McAuliffe, L. Sindellari, and L. M. Venanzi, *Inorg. Chim. Acta*, submitted for publication.
[8] B. Chiswell and L. M. Venanzi, *J. Chem. Soc.* (A), 1966, 417.
[9] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, *28*, 945 (1966).
[10] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (A), 1238, (1967).
[11] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, *87*, 4008 (1965).
[12] F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nuclear Chem.*, *27*, 1389 (1967).
[13] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 7, 1290 (1968).
[14] F Piacenti, M. Bianchi, E. Benedetti, and G. Braca, *Inorg. Chem.*, 7, 1815 (1968).
[15] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).

Table I. Yields and Analytical Data for the Complexes.

Complex	Yield (%) A	Yield (%) B	Found (%) C	H	Ru	As	P	Hal/N	Reqd. (%) C	H	Ru	As	P	Hal/N
[RuCl$_2$(QP)]	34	65	65.8	4.4	10.2		12.4	7.2	65.7	4.3	10.2		12.6	7.2
[RuCl$_2$(ASTP)]	35	60	62.9	4.2	9.7		8.9		62.9	4.1	9.8		9.0	
[RuCl$_2$(PTAS)]	55	56	57.7	3.9	9.0	20.0			58.0	3.8	9.0	20.1		
[RuCl$_2$(QAS)]	74	11	55.7	3.6	8.8	25.6		5.9	55.8	3.6	8.7	25.8		6.1
[RuCl$_2$(SBTAS)]	56		53.4	3.4		18.4		6.0	53.6	3.5		18.6		5.9
[RuCl$_2$(Qas)]	12		36.8	4.0		37.9			36.5	3.8		38.0		
[RuBr$_2$(QP)]	46		60.3	4.0	9.4		11.4	14.8	60.3	3.9	9.4		11.5	14.9
[RuI$_2$)QP)]	50		54.9	3.6	8.7		10.5	21.5	55.4	3.6	8.6		10.6	21.7
[Ru(NCS)$_2$(Qp)]	70		65.4	3.9	9.7		12.0	2.8	65.2	4.1	9.8		12.0	2.7[a]
[Ru(CN)$_2$(QP)]	43				10.3		12.8				10.4		12.8	
[Ru(CN)$_2$(QAS)]	23				8.8	26.0						8.8	26.2	
[Ru(CO)(QP)]	72	58	69.4	4.4	10.7		13.0		60.0	4.5	10.7		13.1	
[Ru(CO)(QAS)]	9	58			8.9	26.4					9.0	26.8		
[Ru(CO)$_2$(TP)]	46	43			12.9		11.7				12.8		11.8	
[Ru(CO)$_2$(TAS)]		48			10.9	24.0					11.0	24.4		

[a] S, Found, 6.1; Reqd., 6.2%

[RuCl$_2$(QP)]. *Procedure A.* Hydrated ruthenium trichloride (0.49 g) in ethanol (100 ml) was stirred under reflux for 24 hrs. The initial dark brown solution changed through dark green to deep blue. QP (1.19 g) in dichloromethane (60 ml), followed by *n*–butanol (70 ml), were added to the cooled blue solution. The mixture was stirred while the dichloromethane and some of the ethanol were boiled off, then refluxed for 18 hrs, and the product separated out.

Procedure B. [RuCl$_2$(PPh$_3$)$_3$] (0.20 g) and QP (0.16 g) in benzene (40 ml) were refluxed under nitrogen for 1 hr., and the product separated from the hot orange solution.

Complexes [RuCl$_2$(ASTP)], [RuCl$_2$PTAS)] and [RuCl$_2$(QAS)] were prepared by Procedures A and B; [RuCl$_2$(SBTAS)] was obtained by Procedure A.

[RuCl$_2$(Qas)]. To 60 ml of an ethanolic blue solution [from hydrated ruthenium trichloride (0.31 g)] were added Qas (0.70 g) and *n*-butanol (50 ml) and the mixture was refluxed for 3 hr. The cooled, filtered, solution was reduced on a rotary evaporator to 20 ml and the product separated on standing. It was recrystallized from a dichloromethane-*n*-butanol mixture.

[RuBr$_2$(QP)]. The chloro-complex (0.31 g) and sodium bromide (0.10 g) in cyclohexanone (50 ml) were refluxed for 14 hrs. The filtered, orange-brown solution was reduced on a rotary evaporator to dryness, ethanol (10 ml) was added, and the product was filtered off.

[RuI$_2$(QP)]. [RuCl$_2$(QP)] (0.27 g) and sodium iodide (0.16 g) in cyclohexanone (50 ml) were refluxed for 7 hrs, then the mixture was stirred at *ca.* 75° for a further 12 hrs. The filtered, orange-brown solution was reduced on a rotary evaporator to dryness. Methanol was added and the product was filtered off and recrystallized from a dichloro-methane-ethanol mixture (in which it gave an orange-red solution), yielding yellow crystals.

[Ru(NCS)$_2$(QP)]. [RuCl$_2$(QP)] (0.39 g) and sodium thiocyanate (0.10 g) in cyclohexanone (60 ml) were refluxed for 14 hrs. The filtered, clear yellow solution was rotary evaporated to dryness, ethanol (3 ml) was added, and the product was filtered off.

[Ru(CN)$_2$(QP)]. [RuCl$_2$(QP)] (0.28 g) in cyclohexanone (40 ml) and sodium cyanide (0.06 g) in a mixture of cyclohexanone (20 ml) and ethanol (40 ml) were mixed and refluxed for 12 hrs. The filtered, almost colorless, solution was rotary evaporated to dryness. Petroleum ether (60-80°) was added and the product was filtered off and purified by adding ethyl acetate to a filtered dichloromethane solution, removing the dichloromethane by rotary evaporation in the cold, and allowing to stand.

[Ru(CN)$_2$(QAS)]. Sodium cyanide (0.03 g) in tetrahydrofurfuryl alcohol (20 ml) was added to a stirred solution of [RuCl$_2$(QAS)] (0.22 g) in tetrahydrofurfuryl alcohol (50 ml) and the mixture was stirred at *ca.* 120° for 12 hrs. The cooled, filtered, pale yellow solution was rotary evaporated to dryness, then *n*-butanol (3 ml) was added and the product was filtered off. It was purified using an ethanol-*n*-butanol mixture.

Reduction of [RuCl$_2$(QP)]. The complex (0.25 g) in dimethylformamide (30 ml) and zinc dust (4 g) were placed in a glass liner in an autoclave. The autoclave was flushed twice with carbon monoxide then charged with carbon monoxide to 20 atm and rocked and heated to 70° for 18 hrs. After cooling and venting, the liner was removed and the dark orange solution was decanted from the zinc dust and evaporated at the pump using a nitrogen-fed leak. The product separated out and was filtered off as an orange solid (0.1 g), which had a single carbonyl absorption at 1900 cm^{-1}, indicating that it was [Ru(CO)(QP)]. Attempts to remove the adhering dimethylformamide by heating *in vacuo* resulted in some decomposition.

Reduction of [RuCl$_2$(QAS)]. This was carried out as above, yielding an orange-yellow solid which had a single carbonyl absorption at 1890 cm^{-1}, indicating that [Ru(CO)(QAS)] was produced. Again the dimethylformamide could not be completely removed from the product without the occurrence of some decomposition.

Ruthenium(0) Complexes. All complexes were dried *in vacuo* at 80-135° for several hours.

« [$Ru(CO)_2(QP)$] ». Dodecacarbonyltriruthenium (0.15 g) and QP (0.57 g) were refluxed in hexane under nitrogen for 40 hrs, and the yellow product (0.52 g, 55%) was filtered from the hot solution. No satisfactory method of purification for this compound was found, but its formulation, which implies that one phosphorus atom of QP is uncoordinated, was based on the close analogy of its infrared spectrum in the carbonyl region with that of [$Ru(CO)_2$(TP)] (see later). When a chlorobenzene solution of the product was heated under nitrogen to 100° for 24 hrs, carbon monoxide was evolved and the orange product recovered had an infrared spectrum and melting point identical with those of an authentic sample of [Ru(CO)(QP)].

[Ru(CO)(QP)]. *Procedure A.* Dodecacarbonyltriruthenium (0.15 g) and QP (0.57 g) in chlorobenzene (20 ml) were stirred at 100° under nitrogen for 48 hrs giving a dark orange-red solution. On cooling, the product separated as orange crystals, which were purified by recrystallization from hot chlorobenzene under nitrogen. Xylene was used as an alternative solvent for this reaction, and infrared studies indicated that it proceeded through [$Ru(CO)_2(QP)$].

Procedure B. [$Ru(CO)_3(PPh_3)_2$] (0.78 g) and QP (0.89 g) in chlorobenzene (15 ml) were stirred under nitrogen at 100° for 20 hrs and the product separated on cooling. It was purified as described above. Infrared studies indicated that this reaction also proceeded through [$Ru(CO)_2(QP)$].

[Ru(CO)(QAS)]. This was best prepared by *Procedure B* above, although a 50 hr reaction time was required. It could also be prepared in lower yield (9%) by *Procedure A* using [$Ru_3(CO)_{12}$] (0.20 g) and QAS (0.95 g) in chlorobenzene (15 ml) at a reaction temperature of 120°. Evaporation of the filtrate followed by the addition of hexane gave a brown solid (0.17 g) which had strong infrared bands at 1998, 1973 and 1935 cm^{-1}, and may have been a trinuclear species of the type [$Ru_3(CO)_9L_3$] (L = PPh_3 and P^nBu_3).[12]

[$Ru(CO)_2(TP)$]. *Procedure A.* Dodecacarbonyltriruthenium (0.10 g) and TP (0.30 g) in clorobenzene (10 ml) were stirred under nitrogen at 110° for 18 hrs. The cooled, dark orange solution was evaporated *in vacuo,* using a nitrogen-fed leak, to *ca.* 3 ml and the product separated out. It was purified by recrystallization, under nitrogen, from a chlorobenzene hexane mixture.

Procedure B. [$Ru(CO)_3(PPh_3)_2$] (0.41 g) and TP (0.36 g) in chlorobenzene (10 ml) were stirred under nitrogen at 110° for 20 hrs. The cooled, orange solution was filtered at the pump and the filtrate evaporated *in vacuo* (nitrogen leak) until yellow crystals appeared. Hexane was added and the product was filtered off and purified as above.

[$Ru(CO)_2(TAS)$]. This was prepared by *Procedure B* from [$Ru(CO)_3(PPh_3)_2$] (0.20 g) and TAS (0.19 g) in chlorobenzene (7 ml).

Oxidation of [Ru(CO)(QP)] *with Chlorine.* [Ru(CO)(QP)] (0.10 g) was dissolved in cold chlorobenzene under nitrogen, then chlorine was passed through the solution until it became very pale yellow. The solution was rotary evaporated to dryness and the residue was recrystallized from dichloromethane-methanol. The product analyzed for [$RuCl_2(QP)$] (Found: P, 12.4%) and its visible and ultraviolet spectrum was identical with that of an authentic sample of this complex.

Oxidation of [Ru(CO)(QP)] *with Iodine.* A solution of [Ru(CO)(QP)] (0.10 g) in chlorobenzene (10 ml) was stirred vigorously under nitrogen while a chlorobenzene solution of iodine (0.027 g) was added over 5 min. There was a noticeable gas evolution and the dark orange-red solution became pale yellow during the addition. Stirring was continued for a further 10 min., then the filtered solution was rotary evaporated to dryness. The product, after purification, was shown by analysis (Found: P, 10.5%) and its visible and ultraviolet spectrum to be [$RuI_2(QP)$].

There was no evidence of further oxidation when excess oxidizing agent was used in the above reactions. All attempts to oxidize the complexes [$Ru(CO)_2(TL)$] (TL=TP and TAS) with halogens led to decomposition.

Analyses. Arsenic and phosphorus were generally determined as described elsewhere.[16] However, phosphorus in compounds which contained also arsenic was determined spectrophotometrically as molybdovanadophosphoric acid, using the procedure described by Higginson *et al.*[17] Arsenic in phosphorus-containing compounds was determined by atomic absorption spectrophotometry: absorbances of cyclohexanone solutions containing 70-140 mg As/ℓ were measured at 193.7 mμ and compared with those of cyclohexanone solutions of triphenylarsine. An atomic absorption spectrophotometric method was used for the determination of ruthenium, using the line at 349.9 mμ in the atomic spectrum of ruthenium; measurements were made on cyclohexanone solutions containing 30-70 mg Ru/ℓ, and the calibration curve was constructed using *cis*-dicarbonyldichlorobis(triphenylphosphine)ruthenium(II). Carbon, hydrogen, nitrogen, halogen, and sulphur analyses were variously performed by Dr. A. Berhardt at the Mikroanalytisches Laboratorium in Max Planck Institut für Kohlenforschung, Mulheim, West Germany, Mr. D. Chapple in the Inorganic Chemistry Laboratory, Oxford, and Galbraith Laboratories, Inc., Knoxville, Tennessee.

Physical Measurements. Conductivities were measured for approximately 10^{-3} *M* nitrobenzene solutions using a 'Cambridge Instruments' or Wayne-Kerr B641 Bridge and cells with platinum black electrodes. Air-sensitive solutions were kept in an atmosphere of nitrogen during the determinations. Infrared spectra were recorded on Perkin-Elmer Model 337 and 225 Spectrophotometers using sodium chloride or caesium bromide cells or plates. Visible and ultraviolet spectra of 10^{-3}-10^{-5} *M* solutions were

---

(16) G. Dyer, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965)

(17) B. R. Higginson, C. A. McAuliffe, and L. M. Venanzi, *Inorg. Chim. Acta*, 5, 37 (1971)

Table II. Physical Properties of the Complexes.

Complex	Colour	Decomp. pt.	Λ_N[a]	Carbonyl stretching frequencies (cm^{-1})[b] Nujol	Dichloromethane
$[RuCl_2(QP)]$[c]	Pale yellow	378-384°	0		
$[RuCl_2(ASTP)]$	Yellow	ca. 400	0		
$[RuCl_2(PTAS)]$	Yellow	>400	0		
$[RuCl_2(QAS)]$[d]	Yellow	>400	0		
$[RuCl_2(SBTAS)]$	Yellow	323-326	0		
$[RuCl_2(Qas)]$	Yellow	385-400	0		
$[RuBr_2(QP)]$[e]	Pale yellow	366-369	0		
$[RuI_2(QP)]$	Yellow	357-363	0		
$[Ru(NCS)_2(QP)]$[f]	Cream	371-375	0		
$[Ru(CN)_2(QP)]$	White	387-393	0		
$[Ru(CN)_2(QAS)]$	V. pale yellow	>400	0		
«$[Ru(CO)_2(QP)]$»	Yellow	130-170	2	1945, 1890	1950, 1888
$[Ru(CO)(QP)]$[g]	Orange	160-167	5	1901	1891
$[Ru(CO)(QAS)]$	Yellow-orange	212-220	4	1893	1885
$[Ru(CO)_2(TP)]$	Yellow	176-184	2	1957, 1880	1951, 1886
$[Ru(CO_2(TAS)]$	Yellow	178-185	2	1938, 1891	1940, 1890

[a] In mho cm^2 mole^{-1}, for *ca.* 10^{-3} *M* nitrobenzene solutions; only «$[Ru(CO)_2(QP)]$ reacts with iodomethane in this solvent. [b] All carbonyl bands are very strong. [c] $10^6\chi_{M(corr.)} = +13$ e.m.u. mole^{-1}. [d] $10^6\chi_{M(corr.)} = +60$ e.m.u. mole^{-1}. [e] $10^6\chi_{M(corr.)} = +87$ e.m.u. mole^{-1}, independent of temperature in the range 160-300°K. [f] $10^6\chi_{M(corr)} = +55$ e.m.u. mole^{-1}. [g] $10^6\chi_{M(corr.)} = +180$ e.m.u. mole^{-1}.

Table III. Visible and Ultraviolet Spectra of the Ruthenium(II) Complexes[a]

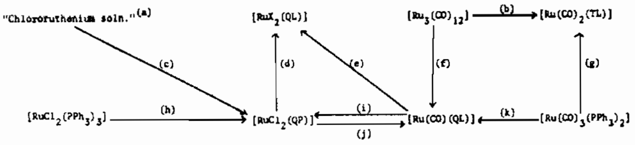
Complex	Dichloromethane Solution E_{max} (cm^{-1})	ε_{max}	Solid E_{max} (cm^{-1})	«A»[b]
$[RuCl_2(QP)]$	41,000	sh[c]	40,700	sh
	28,700	7600	28,150	0.60
$[RuCl_2(ASTP)]$	40,000	sh	38,500	sh
	26,900	7360	26,400	0.64
$[RuCl_2(PTAS)]$	38,500	sh	39,200	sh
	27,800	6890	27,400	0.67
$[RuCl_2(QAS)]$[d]	39,200	sh	38,500	sh
	32,000	sh	31,750	sh
	26,500	6430	25,800	0.41
$[RuCl_2(SBTAS)]$	38,700	sh	38,200	0.87
	33,000	sh	31,250	sh
	25,600	6080	25,200	0.62
$[RuCl_2(Qas)]$[d]	38,100	sh	37,850	0.38
	37,000	2100	36,900	sh
	28,600	3280	27,600	0.45
$[RuBr_2(QP)]$	39,000	sh	39,600	0.71
	28,500	7420	27,600	0.53
$[RuI_2(QP)]$	38,700	sh	38,200	0.75
	33,000	sh	32,500	sh
	26,400	6300	25,900	0.56
$[Ru(NCS)_2(QP)]$	39,000	sh	39,000	1.04
	29,800	9710	30,200	0.79
$[Ru(CN)_2(QP)]$	40,400	sh	40,000	sh
	31,950	9270	31,100	0.56
$[Ru(CN)_2(QAS)]$	40,400	sh	39,500	sh
	29,900	6870	29,700	0.51

[a] The spectra also have a very intense band ($\varepsilon < 60{,}000$) at 43,000-45,000 cm^{-1}; these are not recorded as there is extensive absorption by dichloromethane in this region. [b] «A»= arbitrary absorbance scale. [c] Sh=shoulder. [d] At liquid nitrogen temperature, in 1:2 dichloromethane/2-methyltetrahydrofuran mixtures, the spectrum of $[RuCl_2(QAS)]$ exhibits bands at 31,750 (3160), 27,250 (8980), and 25,640 (sh) cm^{-1}, and the spectrum of $[RuCl_2(Qas)]$ shows bands at 39,030 (4290), 38,100 (4050), 37,040 (3620), 36,540 (3200), 29,590 (4360) and 27,030 (sh) cm^{-1} (ε values in parentheses).

recorded on a Unicam SP700 or Cary 14 spectrophotometer using 1 cm fused silica cells; low temperature spectra were obtained using a Unicam SP700 spectrophotometer fitted with a Unicam SP735 diffuse reflectance attachment, and a Cary 14 spectrophotometer with a Model 1411 diffuse reflectance accessory; the complexes were examined as finely ground powders in potassium chloride. Magnetic susceptibility measurements were carried out on a balance of the Faraday type. Molecular weight determinations were attempted on a Mechrolab Vapour Pressure Osmometer Model 301A; the ruthenium(0) complexes decomposed during attempted determinations and deposited ruthenium on the probe.

Results and Discussion

The preparative methods used are shown in the Scheme.



[a] The composition of this deep blue solution, obtained by refluxing « hydrated ruthenium trichloride » in ethanol, is uncertain. (P. L. Loader, B. Sc. Thesis, Oxford University, 1965). [b] TP. [c] QP, QAS, ASTP, PTAS, SBTAS, and Qas; ligands SBTP, TP and TAS give dark green products which are still under investigation. [d] For QL=QP, by reaction with NaX (X=Br, I, NCS, CN); for QL=QAS, by reaction with NaCN. [e] For QL=QP, by reaction with I_2. [f] QP and QAS. [g] TP and TAS. [h] QP, QAS, ASTP, and PTAS; QAS also gives a red triphenylphosphine-containing product, as do the ligands SBTP, SBTAS, TP and TAS. These are still under investigation. [i] For QL=QP, by reaction with Cl_2. [j] For QL=QP and QAS, by reaction with Zn/DMF under carbon monoxide. [k] QP and QAS.

The complexes prepared and some of their physical properties are listed in Table II. The electronic spectra of the ruthenium(II) complexes in the solid state and in solution are given in Figure 1 and Table III. All the above evidence indicates (1) that all the ruthenium(II) complexes have the distorted octahedral structure found for [$RuBr_2$(QAS)],[18] and (2) that the ruthenium(0) complexes have trigonal bipyramidal structure similar to that found for complexes [Co(CO)(QP)]$^+$X$^-$.[19]

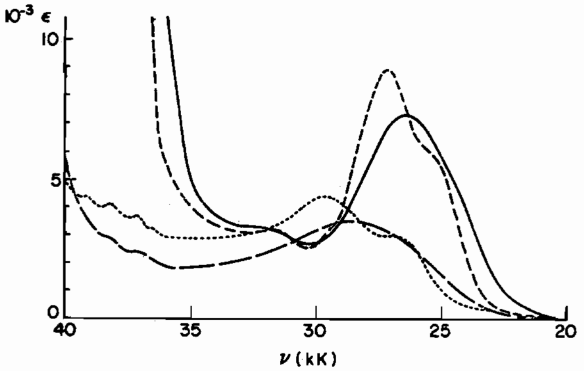


Figure 1. The visible and ultraviolet spectra of ——— [$RuCl_2$(QAS)] (300° K), ---- (100° K); — — — [$RuCl_2$(Qas)] (300° K), ---- (100° K).

The ^{31}P nmr spectra of some of the ruthenium(II) phosphine complexes have been reported elsewhere and are consistent with an octahedral configuration.[6]

The main feature of the visible and ultraviolet spectra of the species [RuX_2(QL)] is an unresolved high-intensity band in the region 26-32 kK, the precise frequency being dependent on the nature of the anionic ligands (CN > NCS > Cl > Br > I) and on the chelate ligand (QP > PTAS > ASTP > QAS > SBTAS). When the spectra of [$RuCl_2$(QAS)] and [$RuCl_2$(Qas)] were recorded at liquid nitrogen temperature, their main bands were partially resolved into two components, separated by approximately 1.6 and 2.5 kK, respectively. Despite the high intensity (ε ~ 7000) of the main bands in the spectra of the complexes [RuX_2(QL)] (QL = ligands I-VI), we suggest that they can be assigned to d-d transitions on the following grounds: (1) Bands assignable to ligand field transitions in the electronic spectra of complexes with QP type ligands invariably have molar extinction coefficients of the order of 10^3.[20] (2) The band maxima occur in the same energy region as the low intensity (ε ~ 100) ligand-field bands in the electronic spectra of the complexes *trans*–[RuX_2(DL)$_2$] (DL = $Me_2P.CH_2.CH_2.PMe_2$, $Ph_2P.CH_2.CH_2.PPh_2$ and *o*–$Me_2As.C_6H_4.AsMe_2$), which may be considered as the *trans* analogues of our (*cis*–)[RuX_2(QL)] complexes.[21] (3) Comparison of the electronic spectra of [$RuCl_2$(QAS)] and [$RuCl_2$(Qas)] shows that in the latter the main band exhibits a shift to higher energy of about 2.0 kK but an approximately twofold reduction in intensity, compared with the former; these are almost exactly the differences between bands in the spectra of [NiX(QAS)]$^+$ and [NiX(Qas)]$^+$ which can certainly be assigned to « d-d transitions ».[7]

The spectra of low-spin complexes of d^6-ions have been extensively studied. Complexes with O_h symmetry show two spin-allowed transitions: $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$. Lowering of symmetry to D_{4h}, C_{2v} and C_s splits the T-terms as shown in Figure 2.[22] Furthermore, the overall splitting of the T_{1g} levels in D_{4h} complexes is expected to be much larger than that in C_{2v} complexes, as observed experimentally.[23]

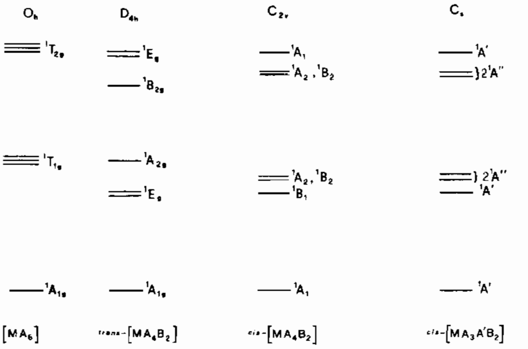


Figure 2. The effect of a descent in symmetry on the terms arising from a low-spin d^6-metal ion in an octahedral environment, assuming that $\delta\sigma(\sigma_A - \sigma_B)$ is negative, that $\delta\pi(\pi_B - \pi_A)$ is positive and that $|\delta\sigma| > |\delta\pi|$, ($\delta\sigma$ being the difference between the σ-antibonding power of the A and B ligands and $\delta\pi$ being similarly defined).

In our complexes, which for this purpose can be regarded as having C_{2v} symmetry, the absorption region 26-32 kK is assigned to $({}^1A_2 + {}^1B_1 + {}^1B_2) \leftarrow {}^1A_1$ transitions by comparison with the spectra of related compounds. Transitions $({}^1A_1 + {}^1A_2 + {}^1B_2) \leftarrow {}^1A_1$ would then be masked by charge-transfer bands and, therefore, will not be discussed further.

The observation that the splitting seen in the spectra of the *trans*–[RuX_2(DL)] complexes is about 9 kK, *i.e.* relatively large, make it not unexpected that the main band in the spectra of our complexes is in fact a composite of more than one band although this is clearly evident only at low temperatures. This provides additional evidence that the main band can be assigned to a ligand field transition.

The infrared spectrum of [Ru(NCS)$_2$(QP)] (nujol mull) shows strong bands at 2102 and 2096 cm^{-1} (ν_{CN}), a broad medium band at 807 cm^{-1} (ν_{CS}), and a weak band at 462 cm^{-1} (δ_{SCN}), all of which are absent in the spectra of the chloro-complex and the free ligand, indicating that the thiocyanate ligands are N-bonded in this complex.[24]

The formation of complexes [Ru(CO)(QL)] (QL = QP or QAS) from [$Ru_3(CO)_{12}$] and the organic ligand appears to go through two distinct stages, the first of which is the formation of a substituted polynuclear carbonyl which is probably followed by the production of a mononuclear complex with a « trailing » phosphorus or arsenic donor atom (see Experimental Section). Our preparative work indicates that the

---

[18] R. H. B. Mais and H. M. Powell, *J. Chem. Soc.*, 7471 (1965).
[19] J. G Hartley, D. G. E. Kerfoot, and L. M. Venanzi, *Inorg. Chim. Acta*, *1*, 145 (1967).
[20] M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.* (A), 540 (1967).
[21] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 722 (1961), D. M. Klassen, and G. A. Crosby, *J. Mol Spectroscopy*, 25, 398 (1968).
[22] H. Watanabe, « Operator Methods in Ligand Field Theory » Prentice-Hall, Englewood Cliffs, N. J., 1966.
[23] H. Yamatera, *Bull. Chem. Soc. Japan*, *31*, 95 (1958).
[24] M. M Chaimberlain and J. C. Bailar, *J. Amer. Chem. Soc.*, *81*, 6412 (1959), A. Sabatini and I. Bertini, *Inorg. Chem.*, *4*, 1665 (1965).

depolymerization of the arsenic substituted species appears to require more drastic experimental conditions.

Although molecular weight determinations were unsuccessful (see Experimental Section), the complexes [Ru(CO)(QL)] (QL = QP and QAS) have been assumed to be mononuclear as they could be obtained from the mononuclear complexes $[Ru(CO)_3(PPh_3)_2]$ and $[RuCl_2(QL)]$. The single carbonyl band in their infrared spectra is assigned to an A_1 mode in C_{3v} symmetry. The small positive conductivities of these complexes are probably due to some decomposition: the complexes rapidly decompose in, or in contact with, all but dry and de-oxygenated solvents. They are somewhat more stable in the solid state, although even in this state decomposition in air is complete after about a month. The complexes $[Ru(CO)_2(TL)]$ (TL=TP or TAS) are more air stable than their QL analogues, and have been assigned the structure below as molecular models show it to be that most easily adopted by the organic ligand. The complexes have C_s symmetry and the two carbonyl bands observed in their infrared spectra can be assigned to the $2A'$ modes.

Acknowledgments. We thank Professor F. G. A. Stone for a gift of dodecacarbonyltriruthenium and Dr. J. W. Dawson for much useful discussion M. T. H. was supported by a N.A.T.O. Research Grant.