Cationic Complexes of Ruthenium-(II) and -(III) with Uni- and Poly-dentate Ligands

Mirza M. Taqui Khan,* Hari C. Bajaj, and Md. Rafiq H. Siddiqui
Central Salt and Marine Chemicals Research Institute, Bhavnagar-364002, India
Badar Taqui Khan, M. Satyanarayan Reddy, and K. Veera Reddy
Department of Chemistry, Osmania University, Hyderabad-500007, India

The reaction of ruthenium(III) perchlorate with some polytertiary phosphines or arsines has been investigated. With bidentate ligands in ethanol cationic complexes of the type $[Ru(L\text{-}L)_3(ClO_4)]ClO_4$ (L–L = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, or $Ph_2AsCH_2CH_2PPh_2$) are obtained. With terdentate ligands the complexes obtained are of the type $[RuL_2(ClO_4)][ClO_4]_2$ [L = $NH(CH_2CH_2PPh_2)_2$ or $NH(CH_2CH_2AsPh_2)_2$]. The reaction of the complex $[RuCl_3(AsPh_3)_2(MeOH)]$ with $AsPh_3$ and PPh_3 in the presence of an excess of $NaClO_4$ in methanol gave $[Ru(AsPh_3)_4(ClO_4)_2]ClO_4$ and $[Ru(AsPh_3)(PPh_3)_3(ClO_4)_2]ClO_4$ respectively. With terdentate ligands $[RuCl_3(AsPh_3)_2(MeOH)]$ afforded mixed-ligand cationic complexes of the type $[Ru(AsPh_3)_2L(ClO_4)][ClO_4]_2$ [L = $NH(CH_2CH_2PPh_2)_2$ or $NH(CH_2CH_2AsPh_2)_2$]. Perchlorate co-ordination is discussed in terms of the i.r. spectra of complexes, and structures are proposed based on the ^1H, ^{31}P, and ^{14}N n.m.r. spectra.

An extensive series of stable cationic ruthenium complexes containing a wide variety of ligands which co-ordinate *via* carbon,[1,2] oxygen,[3,4] nitrogen,[5,6] or phosphorus[7] atoms have been reported during the past few years. The cationic complexes of ruthenium(II) containing phosphines or arsines are of interest in view of their importance as catalytic species in a variety of homogeneous reactions.[8–11]

In the present paper the preparation of cationic complexes of ruthenium-(II) and -(III) obtained by the interaction of ruthenium(III) perchlorate with some uni- and poly-dentate phosphine and arsine ligands is reported. The displacement reactions of $AsPh_3$ and MeOH from $[RuCl_3(AsPh_3)_2(MeOH)]$ in the presence of excess of sodium perchlorate and some uni- and poly-dentate ligands were also investigated.

Results and Discussion

Complexes (**1**) and (**2**) were obtained by the reaction of $[RuCl_3(AsPh_3)_2(MeOH)]$ with an excess of sodium perchlorate followed by the addition of $AsPh_3$ or PPh_3 respectively. Complex (**1**) was obtained in an attempt to prepare simple spherically symmetric octahedral cationic species of the type $[RuL_6]^{n+}$. Although the reaction was conducted with a 6-mol excess of $AsPh_3$ in methanol, it resulted in the formation of a

Table 1. Analytical and other physical data for ruthenium-(II) and -(III) complexes

Complex	Colour	Melting or decomp. point (°C)	$\mu_{eff.}$[a]	Conductivity, Λ[b]/ S cm^2 mol^{-1}	Analysis[c] (%)			
					C	H	Cl	N
(**1**) $[Ru(AsPh_3)_4(ClO_4)_2]ClO_4 \cdot MeOH$	Brown	172	1.99	61.4	53.3 (52.9)	3.8 (3.8)	6.1 (6.4)	—
(**2**) $[Ru(AsPh_3)(PPh_3)_3(ClO_4)_2]ClO_4 \cdot MeOH$	Dark grey	181	1.98	69.7	56.6 (57.5)	4.2 (4.2)	6.9 (7.0)	—
(**3**) $[Ru(dppm)_3(ClO_4)]ClO_4$	Orange	200—204	Diamagnetic	71.6	61.2 (62.0)	4.4 (4.5)	5.0 (4.9)	—
(**4**) $[Ru(dppe)_3(ClO_4)]ClO_4$	Yellow	215—217	Diamagnetic	78.3	61.3 (62.6)	4.8 (4.8)	4.9 (4.7)	—
(**5**) $[Ru(dpae)_3(ClO_4)]ClO_4$	Orange	315—320	Diamagnetic	72.1	52.9 (53.2)	3.9 (4.1)	4.2 (4.0)	—
(**6**) $[Ru(dadpe)_3(ClO_4)]ClO_4$	Yellow	238—241	Diamagnetic	68.7	58.0 (57.5)	4.5 (4.4)	4.3 (4.4)	—
(**7**) $[Ru(dpa)_2(ClO_4)][ClO_4]_2 \cdot MeOH$	Brownish grey	210—214	1.83	138.0	51.6 (52.1)	4.8 (4.7)	8.3 (8.1)	2.0 (2.1)
(**8**) $[Ru(daa)_2(ClO_4)][ClO_4]_2 \cdot MeOH$	Red	176—178	1.87	127.7	49.4 (48.8)	4.2 (4.4)	7.3 (7.6)	1.9 (2.0)
(**9**) $[Ru(AsPh_3)_2(dpa)(ClO_4)][ClO_4]_2 \cdot MeOH$	Grey	125	2.01	149.2	50.8 (52.5)	4.2 (4.2)	7.0 (7.2)	0.8 (0.9)
(**10**) $[Ru(AsPh_3)_2(daa)(ClO_4)][ClO_4]_2 \cdot MeOH$	Pink	137—140	1.89	154.0	51.1 (51.0)	4.0 (4.1)	6.9 (7.0)	0.8 (0.9)

[a] Magnetic susceptibility measured on a Faraday balance at room temperature. [b] Conductivity measured in dimethylacetamide. [c] Calculated values in parentheses.

Table 2. Proton n.m.r. spectra of ruthenium complexes[a]

	Chemical shift (τ)[b]		
Complex	Phenyl protons	Methylene protons	Methyl protons[c]
(1)	2.72(br,m)	—	6.24
(2)	2.44(br,m), 2.80(br,m)	—	6.36
(3)	2.65—2.88(br,m)	5.00(t), 8.56(s)	—
(4)	2.76—3.03(br,m)	7.28(br), 8.44(s)	—
(5)	2.76—3.00(br,m)	7.36(br,s), 8.48(s)	—
(6)	2.76—3.00(br,m)	7.20(t), 7.46(t), 8.48(s)	—
(7)	2.88(br,m)	7.96(br,s), 8.76(s)	6.44
(8)	2.64(br,m)	8.32(s), 8.62(s)	6.18
(9)	2.12(m), 2.64(m)	7.72(s), 8.24(s)	6.20
(10)	2.24(m), 2.64(m)	7.80(br,m)	6.20

[a] Recorded in $CDCl_3$. [b] s = Singlet, d = doublet, t = triplet, m = multiplet, and br = broad. [c] Of methanol which occurs as solvent of crystallisation.

Table 3. Phosphorus-31 and ^{14}N n.m.r. spectra of the ligands and some of their ruthenium complexes[a]

	^{31}P Chemical shifts[b] (p.p.m.)		^{14}N Chemical shifts,[c] δ/p.p.m.
Ligand/Complex	δ	Δ	
PPh_3	−6.0[d]	—	—
(2)	29.97(s), 32.7(s)	35.97, 38.7	—
dppm	−23.6[e]	—	—
(3)	6.13 (br), −7.66(s) −21.2(br)	29.73, 15.94	—
dppe	−12.5[e]	—	—
(4)	58.4(d), 45.12(s) −10.5(s)	70.9, 57.62	—
dadpe	−12.6[f]	—	—
(6)	57.18(br), 54.36(br)	69.78, 66.96	—
dpa	−21.1[g]	—	−66.5
(7)	31.546(s)	52.646	−64.5
daa	—	—	−64.6
(8)	—	—	−65.7
(9)	29.68(s)	51.78	−60.4
(10)	—	—	−59.4

[a] Measured in $CDCl_3$ solution relative to 85% H_3PO_4 with positive shifts taken as downfield of H_3PO_4. [b] Δ Co-ordination chemical shift = δ (complex) − δ (ligand). [c] Ammonium nitrate as reference. [d] 'Topics in Phosphorus Chemistry,' eds. M. Grayson and E. J. Griffith, Interscience, New York, 1967, vol. 5. [e] Ref. 18. [f] Ref. 19. [g] Measured in $CDCl_3$.

species containing two perchlorate groups in the co-ordination sphere of the metal ion. The preparation of complex **(2)** was an attempt to obtain a mixed-ligand phosphine–arsine complex. Slow addition of PPh_3 to a refluxing methanol solution containing $[RuCl_3(AsPh_3)_2(MeOH)]$ and an excess of sodium perchlorate resulted in the formation of the mixed-ligand complex **(2)**. Complexes **(1)** and **(2)** are 1 : 1 electrolytes and their paramagnetism corresponds to one unpaired electron (Table 1).

Based on the i.r. absorption peaks at 1 070 and 1 150 cm^{-1} and at 1 080 and 1 180 cm^{-1} respectively, a unidentate co-ordination of the perchlorate groups is proposed in complexes **(1)** and **(2)**. These peaks may be considered as the split peaks due to ν_3.[12] The far-i.r. spectrum of complex **(1)** has a strong absorption at 470 cm^{-1} due to Ru–As stretching, and that of complex **(2)** displays strong bands due to both Ru–P and Ru–As vibrations at 540 and 470 cm^{-1} respectively.

The ^1H n.m.r. spectrum of complex **(1)** gave a multiplet at τ 2.72 due to the phenyl protons, as expected on the basis of a *trans* configuration with the arsines in the equatorial positions and the two perchlorates in axial positions. Complex **(2)** exhibits two sets of multiplets (intensity ratio 1 : 3) due to the two groups of phenyl protons, at τ 2.44 ($AsPh_3$) and 2.80 (PPh_3) (Table 2). A *trans* configuration for the perchlorates and equatorial arsine and phosphines may be tentatively proposed. The ^{31}P n.m.r. spectrum of this complex is in conformity with the assigned structure, displaying two signals (intensity 2 : 1) at 29.97 and 32.70 p.p.m. (Table 3) and confirming the meridional disposition of the phosphines.[13,14] The presence of solvent methanol in complexes **(1)** and **(2)** is indicated by their ^1H n.m.r. spectra; the methyl proton peaks appear at τ 6.24 and 6.36 respectively.[15] Wilkinson and co-workers[16] had observed a resonance absorption at τ 6.40 due to the methyl protons of methanol in the complex $[RuH(\eta^6\text{-}PhO)(PPh_3)_2]\cdot MeOH$.

Complexes **(3)**—**(6)** were prepared by the general method of treating ruthenium(III) perchlorate with an excess of the ligand (L–L) in absolute alcohol at reflux. Complexes **(4)** and **(5)** were also obtained by an alternative route through the interaction of $[RuCl_3(AsPh_3)_2(MeOH)]$ with a 10-mol excess of sodium perchlorate followed by the addition of the ligands 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylarsino)ethane (dpae), respectively. In both methods ruthenium(III) was reduced to ruthenium(II) by the excess of the ligand used. Conductivity and analytical data suggest that complexes **(4)** and **(5)** are 1 : 1 electrolytes with one of the perchlorates inside the co-ordination sphere (Table 1).

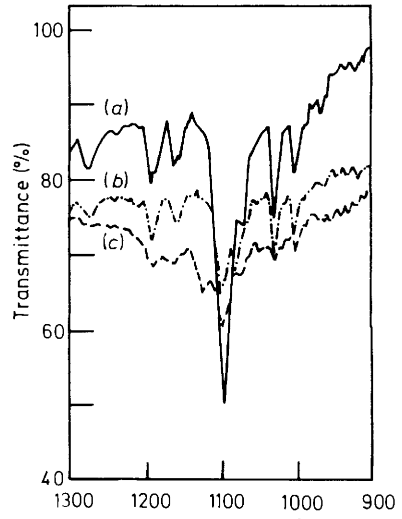

Figure. I.r. spectra of (*a*) $[Ru(dppe)_3(ClO_4)]ClO_4$, (*b*) $[Ru(dadpe)_3(ClO_4)]ClO_4$, and (*c*) $[Ru(dpa)_2(ClO_4)][ClO_4]_2\cdot MeOH$

The i.r. spectra of complexes **(3)**—**(6)** reveal bands due to co-ordinated and ionic perchlorates (Figure). Thus the strong bands at 1 070 and 1 100 cm^{-1} and two weak bands at 1 160 and 1 180 cm^{-1} are due to splitting of the ν_3 fundamental in complex **(3)**. The bands at 1 090 cm^{-1} with a shoulder at 1 070 cm^{-1} and 1 150 and 1 190 cm^{-1} of complex **(4)** [Figure (*a*)], 1 070, 1 100, and 1 180 cm^{-1} of complex **(5)**, and 1 080, 1 100, 1 160, and 1 190 cm^{-1} of complex **(6)** [Figure (*b*)] respectively are assigned to the co-ordinated perchlorate.

Complexes **(3)**—**(6)** are six-co-ordinate cationic species where the ligands L–L may act either in a bi- or uni-dentate mode. Their ^1H n.m.r. spectra are very well resolved and provide information to support the configurations assigned (Table 2). The spectrum of complex **(3)** shows two types of peaks due to methylene protons, at τ 5.00 and 8.56. The first peak is a lowintensity triplet and the multiplicity may be due to the interaction of methylene protons with ^{31}P of phosphine. Its position is in accordance with bidentate co-ordination of the bis(diphenylphosphino)methane (dppm) ligand. The strong singlet may be due to a unidentate diphosphine ligand. The phenyl protons of complex (**3**) absorb between τ 2.65 and 2.88 as a broad multiplet.

These assignments are in accord with those from the ^{31}P n.m.r. spectrum (Table 3). The peak at lowest field, 6.13 p.p.m., is assigned to the co-ordinated phosphorus atom of the unidentate dppm and the high-field peak, which has a chemical shift similar to that of free dppm at −21.20 p.p.m., is assigned to the unco-ordinated phosphorus atom. The large peak at −7.66 p.p.m. corresponds to the phosphorus atoms of two of the dppm ligands forming the four-membered rings, which are more shielded.[17] The two types of co-ordination observed with this ligand in complex (**3**) are in accord with the earlier observation by Mague and Mitchiner.[18]

The ^{1}H n.m.r. spectrum of complex (**4**) exhibits peaks (intensity 2:1) for the methylene protons at τ 7.28 and 8.44 respectively, corresponding to chelated and unidentate dppe ligands. The phenyl protons appear as a broad multiplet between τ 2.76 and 3.03. The peak at τ 7.28 for the bidentate dppe appears as a broad but unresolved singlet. The methylene protons appear to be equivalent despite the formation of a non-planar five-membered chelate ring in the complex. This may be due to some fluxionality involving the flip-flop type of dynamic equilibrium. Unidentate co-ordination is also proposed for dppe despite the separation of donor sites by a longer chain. The peak at comparatively higher field (τ 8.44) corresponds to the unidentate dppe. Grim *et al.*[19] have noted an anomalously large downfield shift upon co-ordination of di(tertiary phosphines) to form five-membered chelate rings. A similar effect is found for complex (**4**) in its ^{31}P n.m.r. spectrum which contains a lower-field doublet at 58.4 p.p.m. due to the phosphorus atoms of the chelated dppe ligands. Another low-field resonance at 45.12 p.p.m. is assigned to the phosphorus atom of the unidentate dppe group. The spectrum also contains a higher-field resonance at −10.5 p.p.m. which is close to that of free dppe[20] and is assigned to the uncomplexed phosphorus atom.[15]

The ^{1}H n.m.r. spectrum of complex (**5**) displays similar features to that of (**4**) (Table 2). The methylene protons of chelated dpae absorb at τ 7.36 and of unidentate dpae at τ 8.48. These two peaks are structureless and appear as strong singlets with a proton integration ratio of 2:1. The absorption due to the phenyl protons appears as a complicated multiplet between τ 2.76 and 3.00.

The ^{1}H n.m.r. spectrum of complex (**6**) shows the phenyl protons as a multiplet at τ 2.76—3.00 as they are from mixed donor (P and As) centres. There are two sets of methylene peaks at τ 7.30 and 8.48 with an integration ratio of 2:1. The peak around τ 7.30 is broad and appears as two sets of triplets centred at τ 7.46 and 7.20. The former may be due to the methylene protons attached to phosphorus and the latter due to the methylene protons attached to arsenic. This is expected because of the difference in the electronegativity between P and As. The appearance of the triplet in each peak can be explained in terms of the interaction of one set of methylene protons with the other. The peak at τ 8.48 corresponds to the unidentate 1-diphenylarsino-2-diphenylphosphinoethane (dadpe) ligand. The overall analysis of these peaks does not clearly indicate which end of the non-chelated ligand, P or As, is bonded to the metal ion. However, ^{31}P n.m.r. spectroscopy can be used to distinguish between these two forms of complexation (Table 3).[21] The peak at 54.36 p.p.m. which is shifted downfield by 66.96 p.p.m. on going from the free ligand to the complex is assigned to the co-ordinated phosphorus atom of unidentate dadpe. This may be due to the superior nucleophilicity of the phosphorus donor site than that of arsenic in a competitive situation. The observation of a peak at 57.18 p.p.m. with a slightly larger downfield shift is in conformity with the higher deshielding effect of the phosphorus atoms of the chelated dadpe ligands.[17,19]

Complexes (**7**) and (**8**) were obtained by the prolonged interaction of ruthenium(III) perchlorate with a 2-mol excess of the ligands dpa and daa, respectively. They are 1:2 electrolytes with one of the perchlorates co-ordinated to the metal ion, based on the appearance of strong i.r. bands at 1 095 and 1 125 cm^{-1} for complex (**7**) [Figure (*c*)] and 1 085 and 1 110 cm^{-1} for complex (**8**).

The ^{1}H n.m.r. spectrum of complex (**7**) reveals a phenyl-proton resonance at τ 2.88 and the methylene proton resonance as singlets at τ 7.96 and 8.76 (Table 2). There is also a methyl proton resonance of methanol at τ 6.44. The ^{1}H n.m.r. spectrum of complex (**8**) shows the same pattern of peaks, those at τ 2.64 and 6.18 corresponding to phenyl and methyl (of methanol) protons respectively. The singlets at τ 8.32 and 8.62 may be assigned to the methylene protons of the ethyl chains. Though the ligands dpa and daa are basically terdentate, they seem to act as bidentate in complexes (**7**) and (**8**) co-ordinating through phosphorus and arsenic atoms, respectively. The ^{31}P n.m.r. spectrum of complex (**7**) gives a broad singlet at 31.546 p.p.m. assigned to co-ordinated phosphorus in a *trans* configuration. The ^{14}N n.m.r. spectra of (**7**) and (**8**) confirm the conclusion that dpa and daa are bidentate, with no co-ordination of nitrogen. The ^{14}N n.m.r. spectra of the ligands dpa and daa show a singlet at −66.5 and −64.6 p.p.m. with respect to NH_4NO_3 (Table 3). The corresponding spectra of complexes (**7**) and (**8**) show singlets at −64.5 and −65.7 p.p.m. respectively. Thus (**7**) and (**8**) appear to be distorted square pyramidal with four phosphorus or arsenic atoms of dpa or daa in the plane of the square pyramid and one co-ordinated perchlorate at the apex.

Complexes (**9**) and (**10**) were prepared by displacement of the co-ordinated methanol and chloro-groups from $[RuCl_3(AsPh_3)_2(MeOH)]$. Reaction of the complex with an excess of sodium perchlorate followed by the addition of ligand L yielded $[Ru(AsPh_3)_2L(ClO_4)][ClO_4]_2{\cdot}MeOH$ [L = dpa (**9**) or daa (**10**)]. The conductivity of the complexes measured in dimethylacetamide confirms that they are 1:2 electrolytes. Magnetic susceptibility measurements show that they are spin-paired ruthenium(III) complexes. The i.r. spectra contain strong absorption bands due to co-ordinated perchlorate at 1 085 and 1 110 cm^{-1} for complex (**9**) and 1 080 and 1 110 cm^{-1} for complex (**10**). Methanol appears as a weak broad band recorded at 3 440 cm^{-1}. The far-i.r. spectrum of complex (**9**) shows strong bands at 470 and 510 cm^{-1} which may be assigned to ν(Ru–As) and ν(Ru–P) modes respectively. Complex (**10**) displays a single intense band at 470 cm^{-1} due to ν(Ru–As).

The ^{1}H n.m.r. spectrum of complex (**9**) shows two types of phenyl-proton absorptions at τ 2.12 and 2.64 due to the presence of dpa and $AsPh_3$ respectively. The methylene protons show two peaks at τ 7.72 and 8.24. There is also a signal at τ 6.20 due to the methyl protons of solvent methanol. A structure with *trans*-arsines and a *trans* disposition of the phosphorus atoms of the dpa ligand is suggested for this complex. A single peak at 29.68 p.p.m. in the ^{31}P n.m.r. confirms this structure (Table 3). The ^{1}H n.m.r. spectrum of complex (**10**) shows phenyl-proton absorptions at τ 2.24 and 2.64. The methylene absorption at τ 7.80 is a broad but not a well resolved multiplet. The structure of this complex may be similar to that of (**9**). The ^{14}N n.m.r. spectra of complexes (**9**) and (**10**) show downfield shifts of about 7 and 5 p.p.m. with respect to dpa and daa respectively (Table 3). Corresponding shifts for d^6 amine complexes of Co^{III} and Rh^{III} were reported[22,23] to be 40—80 p.p.m. upfield with respect to aqueous NH_3. The small downfield shifts of complexes (**9**) and (**10**) thus preclude the co-ordination of the nitrogen of dpa or daa. The complexes may be square pyramidal with phos-

Table 4. U.v.–visible spectral data for ruthenium complexes in dichloromethane

Complex	$\lambda_{max.}$*/nm
(1)	860(820), 490(712), 445(742), 380(651), 260(64 637), 230(89 768)
(2)	595(580), 450(1 325), 345(1 988), 270(12 422), 258(13 043), 230(81 988)
(3)	484(138), 426(358), 340(3 500), 266(28 000), 230(30 000)
(4)	444(266), 310(6 875), 260(88 750), 250(90 000), 230(92 500)
(5)	475(265), 310(4 780), 260(88 446), 250(83 665), 230(70 518)
(6)	455(201), 310(3 181), 262(53 181), 248(53 636), 232(48 863)
(7)	645(533), 515(1 107), 445(1 805), 330(32 786), 265(194 262)
(8)	440(630), 300(12 978), 265(17 759), 230(22 199)
(9)	850(359), 530(637), 265(113 411), 232(221 422)
(10)	480(580), 300(8 370), 270(23 788), 265(25 550), 258(24 229), 230(42 290)

* Molar absorption coefficients, ε/dm^3 mol^{-1} cm^{-1}, are given in parentheses.

phorus or arsenic of dpa and daa spanning the *trans* equatorial position with *trans* arsines. The ClO_4^- is co-ordinated in the axial position.

The u.v.–visible spectral data for complexes **(1)**—**(10)** are presented in Table 4. The molar absorption coefficients of all the complexes are much higher than the conventional values for *d–d* transitions. Complexes **(1)** and **(2)** are octahedral, **(7)**—**(10)** are square-pyramidal ruthenium(III) species with a spin-paired t_{2g}^5 ground-state configuration. The bands around 500 nm for complexes **(1)** and **(2)** may be assigned to the $^2T_2 \longrightarrow {}^2E$ transition, while the bands in the lower-energy region 600—860 nm may be assigned to the spin-forbidden transitions $^2T_2 \longrightarrow {}^4T_1$ or $^4T_2$. For complexes **(3)**—**(6)**, which are diamagnetic octahedral ruthenium(II) species with a spin-paired t_{2g}^6 configuration, two spin-allowed *d-d* transitions are expected in their electronic spectra, $^1A_1 \longrightarrow {}^1T_1$ and $^1A_1 \longrightarrow {}^1T_2$ in increasing order of energy. The bands in the regions 440—485 and 300—340 nm are tentatively assigned to $^1A_1 \longrightarrow {}^1T_1$ and $^1A_1 \longrightarrow {}^1T_2$ respectively. The intensities of the $^1A_1 \longrightarrow {}^1T_2$ transition are high since it is located near intense charge-transfer bands. The strong band at 230 nm of all complexes has been assigned to the $\pi \longrightarrow \pi^*$ transition of the phenyl rings, whereas the other higher-energy bands may be due to ligand-to-metal charge transfer or charge transfer involving the P or As lone pairs and the phenyl rings.

Experimental

Ruthenium trichloride was purchased from Johnson Matthey. The ligands triphenylarsine, bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylarsino)ethane, and 1-diphenylarsino-2-diphenylphosphinoethane were obtained from Strem Chemicals Inc. Bis(2-diphenylphosphinoethyl)amine[24] and bis(2-diphenylarsinoethyl)amine[25] were prepared by published procedures. The complex $[RuCl_3(AsPh_3)_2(MeOH)]$ was synthesised according to Stephenson and Wilkinson.[26]

Microanalyses of the elements carbon, hydrogen, nitrogen, and chlorine were done by Amdel, Australia. The magnetic susceptibilities of the solid samples were measured at room temperature (302 K) on a Faraday balance. Proton n.m.r. spectra were recorded on FX100 MHz spectrometer in $CDCl_3$. The proton-decoupled ^{31}P n.m.r. spectra were recorded on a 500-MHz spectrometer with external 85% H_3PO_4 as reference and the complexes were dissolved in $CDCl_3$. The ^{14}N n.m.r. spectra were recorded on a JEOL FX100 spectrometer with NH_4NO_3 as the external standard. Melting points were determined on a hot-plate melting point apparatus. Conductivity measurements were done on a Digisun direct reading conductivity bridge (DL-90) with a cell which had been calibrated previously. Infrared spectra were recorded on a Beckman IR-12 spectrometer, electronic spectra for dichloromethane solutions on a Shimadzu UV 240 instrument.

Preparations.—Ruthenium(III) *perchlorate*. This was prepared by two different methods.

(*i*) Ruthenium trichloride (0.261 g, 1 mmol) was stirred with a stoicheiometric amount of silver perchlorate (0.622 g, 3 mmol) in absolute alcohol for 2—3 h and the precipitated silver chloride removed by centrifugation for 3—4 h. The remaining light red-brown ruthenium(III) perchlorate solution was immediately utilised for preparations.

(*ii*) Alternatively, metathesis between ruthenium(III) chloride and an excess of sodium perchlorate in methanol or ethanol was adopted. Ruthenium trichloride trihydrate (0.261 g, 1 mmol) in methanol or ethanol was either stirred with a 10-fold excess of sodium perchlorate (1.405 g, 10 mmol) for 24 h or refluxed in a nitrogen atmosphere for about 2 h when a red-brown solution of ruthenium perchlorate was obtained. A fresh sample was prepared for each preparation and used immediately.

Bis(*perchlorato*)*tetrakis*(*triphenylarsine*)*ruthenium*(III) *perchlorate–methanol* (1/1), **(1)**. To the methanolic solution of sodium perchlorate (0.70 g, 5 mmol), $[RuCl_3(AsPh_3)_2(MeOH)]$ (0.425 g, 0.5 mmol) was added and the entire suspension was refluxed for about 1—2 h when it became a clear light brown solution. Triphenylarsine (0.612 g, *ca.* 2 mmol) in methanol was then added and the solution refluxed for 5 h. The solution was reduced to a small volume under vacuum on a roto-evaporator when a brown solid separated. The compound was purified as a brown solid by precipitating it with light petroleum (b.p. 60—80 °C) from a dichloromethane solution. The product was washed several times with water and light petroleum to free it from salts and the excess of $AsPh_3$ and recrystallised from dichloromethane. Yield: 0.63 g (76%).

Bis(*perchlorato*)*triphenylarsinetris*(*triphenylphosphine*)-*ruthenium*(III) *perchlorate–methanol* (1/1), **(2)**. A methanolic suspension containing $[RuCl_3(AsPh_3)_2(MeOH)]$ (0.425 g, 0.5 mmol) and sodium perchlorate (0.70 g, 5 mmol) was refluxed under a nitrogen atmosphere for 1—2 h, when the solid dissolved to give a light brown homogeneous solution. At this stage triphenylphosphine (0.524 g, 2 mmol) dissolved in methanol was added dropwise to the refluxing solution over a period of an hour. After the addition of PPh_3 was complete the solution turned dark brown. It was refluxed for another 6 h. The solution was concentrated to one fourth of its volume and water (*ca.* 100 cm^3) was added when a floating solid was obtained. The solid was dissolved in dichloromethane and precipitated with light petroleum b.p. (60—80 °C) as a dark grey product. After several washings with diethyl ether, the complex was dried over P_2O_5 under vacuum. Yield: 0.62 g (81%).

Tris[*bis*(*diphenylphosphino*)*methane*]*perchloratoruthenium*-(II) *perchlorate*, **(3)**. The alcoholic solution of ruthenium perchlorate (0.40 g, 1 mmol) and the ligand bis(diphenylphosphino)methane (dppm) (1.15 g, 3 mmol) were refluxed in a nitrogen atmosphere for about 4 h. At the end of the reaction the orange crystalline compound was filtered off and washed with alcohol and diethyl ether. Yield: 1.05 g (72%).

Tris[1,2-*bis*(*diphenylphosphino*)*ethane*]*perchlorato*-*ruthenium*(II) *perchlorate*, **(4)**. To the refluxing ethanolic solution of ruthenium perchlorate (0.40 g, 1 mmol), 1,2-bis(diphenylphosphino)ethane (dppe) (1.20 g, 3 mmol) was added in a nitrogen atmosphere and refluxed for 6 h. After the addition of the ligand the initial brown colour changed to light orange and the same colour persisted throughout the reaction. On cooling the solution to room temperature a light yellow crystalline complex was obtained which was filtered off and washed repeatedly with cold ethanol–diethyl ether (1:5). The complex was recrystallised from dichloromethane and light petroleum (b.p. 60—80 °C) and then dried *in vacuo*. Yield: 1.16 g (78%).

Tris[1,2-*bis*(*diphenylarsino*)*ethane*]*perchloratoruthenium*(II) *perchlorate*, (**5**). To the hot alcoholic solution of ruthenium perchlorate (0.40 g, 1 mmol) was added 1,2-bis(diphenylarsino)ethane (dpae) (1.46 g, 3 mmol) and the mixture refluxed for 5 h. The orange crystalline compound formed was filtered off and recrystallised from chloroform–light petroleum (b.p. 60—80 °C). Yield: 1.27 g (72%).

Tris(1-*diphenylarsino*-2-*diphenylphosphinoethane*)*perchloratoruthenium*(II) *perchlorate*, (**6**). The ligand (*ca.* 1.33 g, 3 mmol) was dissolved in boiling ethanol and added to a refluxing alcoholic solution of ruthenium perchlorate (0.40 g, 1 mmol). About 30 min after the addition of the ligand yellow crystals started to appear. The contents were refluxed for another 2 h when the bulk of the complex had separated as yellow needles. The complex was filtered off and washed with hot alcohol and ether. Yield: 1.38 g (85%).

Bis[*bis*(2-*diphenylphosphinoethyl*)*amine*]*perchloratoruthenium*(III) *perchlorate–methanol* (1/1), (**7**). Ruthenium trichloride trihydrate (0.261 g, 1 mmol) was refluxed with a 10-fold excess of sodium perchlorate (1.40 g) in methanol (15 cm^3) for 2 h. The ligand dpa (1.43 g, 3 mmol) in methanol (10 cm^3) was added and the heating continued for 5 h. At the end of the reaction a dark grey product was filtered off and washed several times with water–methanol (1:1) to remove the excess of sodium salts. The compound was finally dried over P_2O_5 in vacuum. Yield: 0.80 g (58%).

Bis[*bis*(2-*diphenylarsinoethyl*)*amine*]*perchloratoruthenium*(III) *perchlorate–methanol* (1/1), (**8**). To a methanolic solution of ruthenium trichloride (0.261 g, 1 mmol) was added solid sodium perchlorate (1.40 g, 10 mmol) and the solution refluxed for 2 h. The ligand daa (1.70 g, 3 mmol) was added to the refluxing solution when the whole solution turned orange-red. An hour after refluxing the red solid was filtered off, washed with methanol and water, and dried over P_2O_5 in vacuum. Yield: 0.97 g (62%).

[*Bis*(2-*diphenylphosphinoethyl*)*amine*]*perchloratobis*(*triphenylarsine*)*ruthenium*(III) *perchlorate–methanol* (1/1), (**9**) *and* [*bis*(2-*diphenylarsinoethyl*)*amine*]*perchloratobis*(*triphenylarsine*)*ruthenium*(III) *perchlorate–methanol* (1/1), (**10**). A suspension of the green complex $[RuCl_3(AsPh_3)_2(MeOH)]$ (0.425 g, 0.5 mmol) in methanol was refluxed with a 5-mmol excess of sodium perchlorate (0.70 g) for about 2 h to give a clear light brown solution. Complexes (**9**) and (**10**) were obtained by the addition of dpa and daa (1 mmol) respectively to the above refluxing solutions. The colour of the solution changed from light to dark brown in the case of dpa and to light orange in the case of daa. The reaction mixtures were heated for 4 h, evaporated to dryness under vacuum, and the compounds extracted with dichloromethane. The brown (dpa) and orange (daa) solutions thus obtained were reduced to small volumes and the respective complexes precipitated as grey (**9**) and pink (**10**) products. Yields: 0.50 (72) (**9**); 0.50 g (67%) (**10**).

References

1 M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc. A*, 1971, 794.

2 D. J. Doonam and A. L. Balch, *Inorg. Chem.*, 1974, **13**, 921.

3 D. F. Christian and W. R. Roper, *J. Organomet. Chem.*, 1974, **80**, C35.

4 R. J. Young and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 719.

5 R. R. Schrock, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1974, 951.

6 P. C. Ford, *Coord. Chem. Rev.*, 1970, **5**, 75.

7 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

8 G. M. Bancroft, M. J. Mays, B. F. Prater, and F. F. Stefanini, *J. Chem. Soc. A*, 1970, 2146.

9 J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 1973, 743.

10 M. M. Taqui Khan and A. E. Martell, 'Homogeneous Catalysis by Metal Complexes,' Academic Press, New York, 1974, vol. 1.

11 B. E. Cavit, K. R. Grandy, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1972, 60; T. V. Ashworth and E. Singleton, *J. Organomet. Chem.*, 1974, **77**, C31.

12 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091 and refs. therein; B. J. Hathaway, D. J. Holah, and M. Hudson, *ibid.*, 1963, 4586.

13 R. Mason and D. W. Meek, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 183.

14 J. B. Letts, T. J. Mazanoc, and D. W. Meek, *Organometallics*, 1983, **2**, 695.

15 J. A. Elvidge, in 'Nuclear Resonance for Organic Chemists,' ed. D. W. Mathieson, Academic Press, New York, 1967, p. 180.

16 D. J. C. Hamilton, R. J. Young, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 1995.

17 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229 and refs. therein.

18 J. T. Mague and J. P. Mitchiner, *Inorg. Chem.*, 1972, **11**, 2714.

19 S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.

20 H. G. Horn and K. Sommer, *Spectrochim. Acta, Part A*, 1971, **27**, 1049.

21 J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 1973, 347.

22 R. Bromley, B. N. Figgis, and R. S. Nyholm, *J. Chem. Soc. A*, 1967, 861.

23 J. Mason, *Chem. Rev.*, 1981, **81**, 205.

24 L. Sacconi and R. Morasi, *J. Chem. Soc. A*, 1968, 2997.

25 L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1968, **7**, 1417.

26 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.

Received 25*th March* 1985; *Paper* 5/598