

Chemistry of Ruthenium. 5.¹ Reaction of *trans*-Dihalobis[2-(aryloxy)pyridine]ruthenium(II) with Tertiary Phosphines: Chemical, Spectroelectrochemical, and Mechanistic Characterization of Geometrically Isomerized Substitution Products

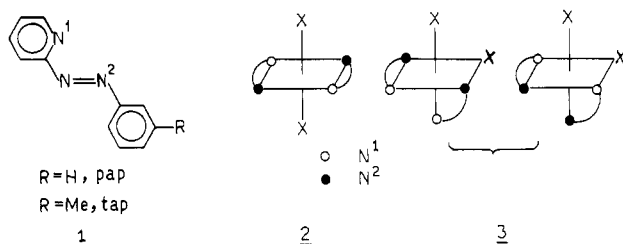
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The green *trans* isomer (**2**) of RuX_2L_2 , though unreactive to pyridine bases and Ag^+ , reacts relatively slowly but smoothly with tertiary phosphines giving rise to species of types $[\text{RuXPL}_2]^+$, $[\text{RuP}_2\text{L}_2]^{2+}$, and $[\text{Ru(P-P)L}_2]^{2+}$ in which XP , P_2 , and P-P respectively occupy *cis* positions [$\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{P} = \text{P}(p\text{-tol})_3$, PPh_3 , PPh_2Me , PPhMe_2 ; $\text{P-P} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$; $\text{L} = 2\text{-(aryloxy)pyridine}$]. The cations have been isolated as perchlorates. The complexes display allowed $t_2(\text{Ru}) \rightarrow \pi^*(\text{L})$ transitions in the visible region. A systematic shift of this MLCT band to higher energy occurs in the order $\text{X}_2 < \text{XP} < \text{P}_2 \sim \text{P-P}$. The ruthenium(III)–ruthenium(II) couple occurs at high potentials (>1.3 V vs. SCE). The MLCT band energies of *cis*- RuX_2L_2 , $[\text{RuXPL}_2]^+$, $[\text{RuP}_2\text{L}_2]^{2+}$, and $[\text{Ru(P-P)L}_2]^{2+}$ correlate linearly with ruthenium(III)–ruthenium(II) formal potentials (E°_{298}). The data point of **2** falls widely outside the line. This and other facts taken together prove that during phosphine substitution geometrical isomerization of the RuL_2 fragment occurs. The reaction of **2** ($\text{X} = \text{Cl}$, $\text{L} = 2\text{-(phenyloxy)pyridine}$) with PPhMe_2 is shown to be kinetically second order with $k_2 = 9.64 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ($40 \pm 0.2^\circ \text{C}$). The rate decreases very considerably on increasing phosphine bulk: $\text{PPhMe}_2 > \text{PPh}_2\text{Me} \gg \text{PPh}_3$. An associative pathway involving nucleophilic *trans* attack or edge displacement is proposed, and the possible role of specific Ru-N(azo) bond labilization is indicated. The observed isomerization is a logical consequence of such a mechanism. Brief mention is made of certain observations and current activities. These include geometrical isomerization in nucleophilic displacement with OH^- , greater lability of the *cis* isomers, and the *cis* diaquo species $[\text{Ru}(\text{H}_2\text{O})_2\text{L}_2]^{2+}$ and its role as an intermediate for preparation of many interesting complexes of RuL_2 .

Introduction

The high affinity of the azopyridine ligand system (**L**), **1**,



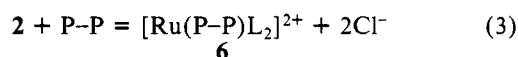
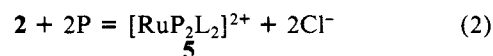
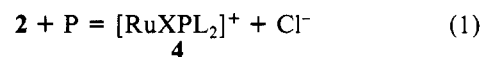
for ruthenium(II) is manifest in the dihalo species (RuX_2L_2) reported by us² (in part 2 of this series) as well as by others.³ These dihalo species have thus far been obtained in three isomeric forms,⁴ one of which is green and the other two are blue. With consideration of the coordinated atoms in three pairs, viz., X, X ; N^1, N^1 ; and N^2, N^2 , the green isomer has^{2,3} *trans-trans-trans* (ttt) configuration (**2**) and one of the blue isomers has^{3,4} *cis-cis-cis* (ccc) structure. It is not known^{4,5} whether the second blue isomer which has a C_2 axis is *cis-trans-cis* (ctc) or *cis-cis-trans* (cct); we shall call it simply the C_2 isomer (**3**). The redox stability of all RuX_2L_2 isomers

is evidenced by the relatively high formal potential^{2,3} of the ruthenium(III)–ruthenium(II) couple. Substitutional stability is particularly characteristic of **2**, which is unreactive toward both silver ion and pyridine bases even under relatively forcing conditions.² However, **2** reacts with tertiary phosphines and displacement of X^- occurs. The primary concern of this paper is this reaction. Several new complexes formed by the reaction have been isolated and structurally characterized with spectroscopic and electrochemical data. In one case, the reaction kinetics is studied and the results are used to rationalize the interesting stereochemical rearrangement that accompanies the substitution reaction. We note that ruthenium(II) complexes in which both nitrogen and phosphorus atoms occupy coordination positions are relatively uncommon.^{6,7}

Results and Discussion

The complexes of type **2** and **3** were synthesized and characterized with reported methods.^{2,3} The C_2 variety of $\text{RuCl}_2(\text{tap})_2$ is reported here for the first time.⁸ It displays a single sharp methyl ^1H NMR signal in CDCl_3 ; δ_{Me} 2.14. Other data: E°_{298} for ruthenium(III)–ruthenium(II) couple in CH_3CN , 1.10 V; band maximum for metal-to-ligand charge-transfer transition, 578 nm.

Reactions of 2 with Phosphines. The following phosphines were used: $\text{P}(p\text{-tol})_3$, PPh_3 , PPh_2Me , PPhMe_2 , $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$. The mono- and diphosphines are abbreviated as P and P-P , respectively. The reactions of these with **2** proceed somewhat slowly but quite



- (1) Part 4: Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 615.
- (2) Part 2: Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, 20, 2246.
- (3) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, 19, 2600.
- (4) Five geometrical isomers are possible in principle: ttt, tcc, ctc, cct, and ccc (see text for meaning of symbols). The tcc isomer has the serious steric disadvantage of pendant aryl groups on adjacent (*cis*) N^2 atoms located on two nearly coplanar chelate rings. This isomer may not exist at all. On heating, both ttt and ccc are converted³ to the C_2 isomer (ctc or cct). A three-dimensional X-ray study of the crystal structure of *ccc*- $\text{RuCl}_2(\text{pap})_2$ has recently been completed (Seal, A.; Ray, S., private communication). The triclinic ($\text{P}\bar{1}$) structure is made up of asymmetric units consisting of two independent complexes differing in orientation only. Crystal structure determination of the C_2 variety is in progress.
- (5) The cct structure may appear to have some advantage over ctc since the aryl groups (at N^2) are further away in the former than in the latter. However, the two chelate rings are in different planes and the steric interaction of the aryl groups are likely to be relatively small. This is also evident in the existence and stability^{2,4} of the ccc isomer.

(6) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J., *Inorg. Chem.* **1978**, 17, 3334.

(7) Seddon, K. R. *Coord. Chem. Rev.* **1981**, 35, 41.

(8) The isomer of C_1 symmetry also isolated has two equally intense methyl signals: δ 2.21 and 2.40 (CH_3).

Table I. Selected Infrared and Visible-Ultraviolet Spectral and Molar Conductivity Data

compd	IR ^{a,b} $\nu_{\max}$, cm ⁻¹			vis-UV ^c $\lambda_{\max}$, nm (ϵ , M ⁻¹ cm ⁻¹)	Λ_M , ^c Ω^{-1} cm ² M ⁻¹
	RuX	N=N	C=N		
[RuCl(PPh ₃)(pap) ₂](ClO ₄)·H ₂ O	322	1325	1600	536 (7100), 468 (4100), ^d 360 (16 000), ^e 332 (16 500), ^e 300 (15 900) ^e	150
[RuCl(PPh ₃)(tap) ₂](ClO ₄)·H ₂ O	320	1325	1605	536 (6400), 468 (3800), ^d 360 (14 400), ^e 332 (14 700), ^e 300 (14 100) ^e	142
[RuCl(P(<i>p</i> -tol) ₃)(pap) ₂](ClO ₄)·H ₂ O	315	1330	1605	536 (7200), 464 (3600), ^d 360 (14 800), ^e 332 (15 600), ^e 300 (15 500) ^e	158
[RuCl(PPh ₂ Me)(pap) ₂](ClO ₄)·H ₂ O	320	1320	1600	534 (5600), 472 (3400), ^d 354 (12 000), ^e 328 (11 400), ^e 300 (11 000) ^e	145
[RuBr(PPh ₂ Me)(pap) ₂](ClO ₄)·H ₂ O	268	1325	1600	530 (6600), 470 (4100), ^d 360 (14 400), ^e 320 (14 500) ^e	140
[RuI(PPh ₂ Me)(pap) ₂](ClO ₄)·H ₂ O	245	1325	1600	540 (5400), 488 (4400), ^d 360 (14 700), ^e 332 (15 600) ^e	130
[RuCl(PPh ₂ Me)(tap) ₂](ClO ₄)·H ₂ O	320	1320	1600	534 (7300), 464 (4100), ^d 362 (14 900), ^e 328 (14 500), ^e 300 (14 200) ^e	164
[RuCl(PPhMe ₂)(pap) ₂](ClO ₄)·H ₂ O	320	1320	1595	536 (7000), 460 (3500), ^d 360 (13 000), ^e 328 (15 000), ^e 300 (15 300) ^e	160
[Ru(PPhMe ₂) ₂ (tap) ₂](ClO ₄) ₂ ·H ₂ O		1350	1600	490 (10 000), 385 (10 600), 310 (12 550)	340
[Ru(Ph ₂ P(CH ₂) ₃ PPh ₂)(pap) ₂](ClO ₄) ₂ ·H ₂ O		1375	1605	488 (8700), 370 (29 700), 286 (24 200)	305
[Ru(Ph ₂ P(CH ₂) ₂ PPh ₂)(tap) ₂](ClO ₄) ₂ ·H ₂ O		1380	1595	476 (8400), 374 (25 900), 286 (20 300)	300

^a All bands are sharp and strong. ^b In polyethylene disk (400–100 cm⁻¹) and in KBr disk (4000–400 cm⁻¹). ^c In acetonitrile. ^d Shoulder. ^e Broad.

smoothly in boiling aqueous methanol. Triphenylarsine fails to react. The cation **4** is violet while **5** and **6** are orange. These are isolated as crystalline perchlorates and are purified chromatographically. Among monophosphines, PPhMe₂ yields both **4** and **5**, while PPh₂Me and PPh₃ could be made to react only⁹ to the level of monosubstitution (**4**). On the other hand, **6** is readily formed with the two diposphines both of which have the PPh₂CH₂ group and are therefore as hindered as PPh₂Me. Thus steric and chelate effects are controlling factors in the synthetic reactions.

The complexes are all diamagnetic as expected (*t*_{2g}⁶) and the perchlorates of **4–6** behave respectively as 1:1, 1:2, and 1:2 electrolytes in acetonitrile (Table I).

Infrared Spectra. Only a few characteristic frequencies are considered here (Table I). All complexes show bands near 1100 and 620 cm⁻¹ assignable to ClO₄⁻ and at ~3400 cm⁻¹ due to H₂O; $\nu_{N=N}$ and $\nu_{C=N}$ are seen near 1330 and 1600 cm⁻¹, respectively.^{10,11} All [RuXPL₂](ClO₄)·H₂O species display a sharp ν_{RuX} in the range 300–250 cm⁻¹ in the frequency order I < Br < Cl. Well-characterized haloruthenium complexes in which the halogen atom is systematically varied from Cl to Br to I are relatively uncommon.^{2,12}

Charge-Transfer Spectra. The phosphine complexes have several absorption maxima in the region 300–700 nm (Table I). We consider here the band that occurs near 540 and 500 nm in **4** and **5** (or **6**), respectively. The corresponding band in **2** is near 630 nm and that in **3** is at ~580 nm. The gross energy order is thus **2** < **3** < **4** < **5** ~ **6** (Figure 1). The above band is assigned to metal to ligand charge-transfer (MLCT) transition: *t*₂(Ru) → $\pi^*(L)$, where $\pi^*(L)$ is primarily an azimine orbital.² The systematic shift to higher frequencies on increasing P coordination is understandable since P is expected to stabilize the *t*₂ level better than X⁻ due to Ru → P π back-bonding.⁶ The order **2** < **3** can arise from the better M → L π bonding in **3**. Last, we note that the MLCT band

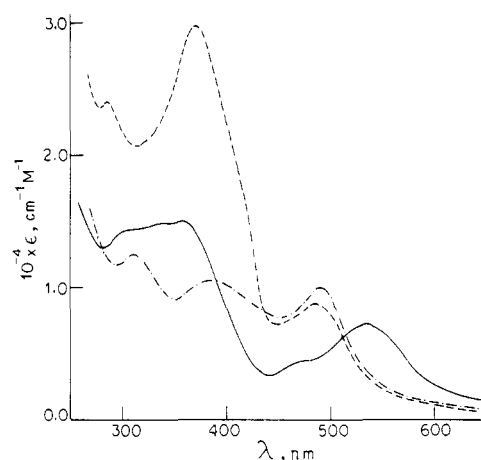


Figure 1. Electronic spectra in acetonitrile: —, [RuCl(PPh₂Me)(tap)₂](ClO₄)₂·H₂O; ---, [Ru(PPhMe₂)₂(tap)₂](ClO₄)₂·H₂O; - · -, [Ru(Ph₂P(CH₂)₃PPh₂)(pap)₂](ClO₄)₂·H₂O.

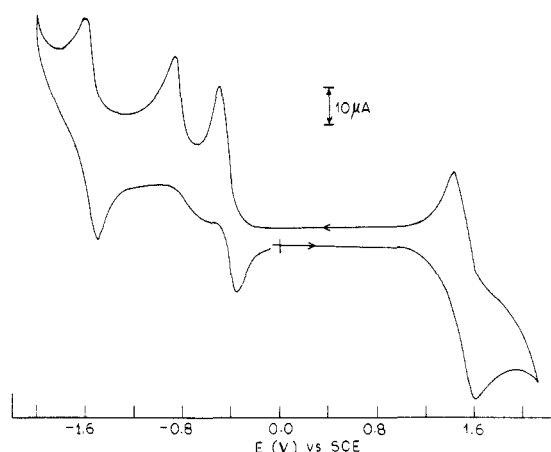


Figure 2. Cyclic voltammogram of [RuCl(PPh₃)(pap)₂](ClO₄)₂·H₂O in acetonitrile (0.1 M TEAP) at platinum electrode vs. SCE; scan rate = 50 mV s⁻¹.

of **4** is associated with a shoulder at higher energy and the same is true of **3** (Figure 1); such a shoulder is absent² in **2**.

Electrochemistry. The electron-transfer behavior of the complexes in acetonitrile solution was examined cyclic voltammetrically¹³ at a platinum electrode (Figure 2; Table II).

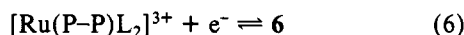
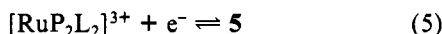
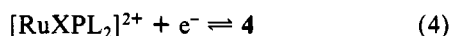
- (9) During chromatographic purification of [RuX(PPh₂Me)L₂]⁺, a small orange band remains near the top of the column. It may be due to [RuP₂L₂]²⁺, but we have not been able to isolate it.
- (10) In our earlier report,² a band near 1455 cm⁻¹ was assigned to $\nu_{N=N}$. Since MLCT contribution to the ground state is expected¹¹ to shift $\nu_{N=N}$ to lower frequencies, it is more appropriate to assign the ~1350-cm⁻¹ band (which is also present^{2,3} in RuX₂L₂) to $\nu_{N=N}$.
- (11) Raghavendra, B. S.; Chakravorty, A. *Indian J. Chem., Sect. A*. **1976**, *14A*, 166.
- (12) Raichart, D. W.; Taube, H. *Inorg. Chem.* **1972**, *11*, 999. Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1981**, 495.

Table II. Cyclic Voltammetric Data^{a-c} at a Platinum Electrode (298 K)

compd	E°_{298} , V (ΔE_p , mV)	
	Ru(III)-Ru(II)	ligand redn
[RuCl(PPh ₃)(pap) ₂](ClO ₄) ₂ ·H ₂ O	1.500 (80)	-0.425 (90), -0.860, ^d -1.540 (80)
[RuCl(PPh ₃)(tap) ₂](ClO ₄) ₂ ·H ₂ O	1.455 (80)	-0.412 (75), -0.780, ^d -1.490 (80)
[RuCl(P(<i>p</i> -tol) ₃)(pap) ₂](ClO ₄) ₂ ·H ₂ O	1.505 (170)	-0.430 (100), -0.820, ^d -1.495 (90)
[RuCl(PPh ₂ Me)(pap) ₂](ClO ₄) ₂ ·H ₂ O	1.550 (180)	-0.460 (100), -0.960, ^d -1.540 (120)
[RuBr(PPh ₂ Me)(pap) ₂](ClO ₄) ₂ ·H ₂ O	1.425 (160)	-0.465 (70), -0.850, ^d -1.555 (90)
[RuI(PPh ₂ Me)(pap) ₂](ClO ₄) ₂ ·H ₂ O		-0.440 (60), -0.760, ^d -1.535 (80)
[RuCl(PPh ₂ Me)(tap) ₂](ClO ₄) ₂ ·H ₂ O	1.550 (170)	-0.510 (100), -0.940, ^d -1.520 (80)
[RuCl(PPhMe ₂)(pap) ₂](ClO ₄) ₂ ·H ₂ O	1.538 (175)	-0.505 (90), -0.920, ^d -1.535 (70)
[Ru(PPhMe ₂) ₂ (tap) ₂](ClO ₄) ₂ ·H ₂ O	2.040 ^e	-0.320 (80), -0.680 (160), -1.550 (60)
[Ru(Ph ₂ P(CH ₂) ₃ PPh ₂)(pap) ₂](ClO ₄) ₂ ·H ₂ O	2.080 (240)	-0.170 (80), -0.700 (80), -1.435 (170)
[Ru(Ph ₂ P(CH ₂) ₃ PPh ₂)(tap) ₂](ClO ₄) ₂ ·H ₂ O	2.240 ^f	-0.165 (70), -0.575 (85), -1.360 (120)

^a Meaning and units of symbols are the same as in text. ^b Solvent is acetonitrile. ^c Supporting electrolyte TEAP (0.1 M), solute concentration $\sim 10^{-3}$ M, scan rate 50 mV s⁻¹. ^d Cathodic peak potentials (see text). ^e Value obtained from differential-pulse polarography (see text). ^f Extrapolated value, obtained from linear relationship of λ (MLCT) vs. E°_{298} .

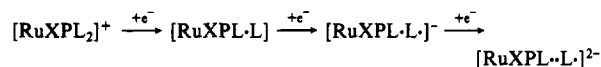
Three 1e steps are observed in the range -0.1 to -1.6 V due to ligand reduction localized at the azo groups.^{2,14-16} These are not considered any further. Our concern here is the quasireversible 1e metal redox response^{17,18} occurring at >1.3 V (couples (4)-(6)). The corresponding couples^{2,3,19} in 2 and 3 occur near 1 V. Formal potentials (E°_{298}) are in Table II.



In [Ru(Ph₂P(CH₂)₃PPh₂)(pap)₂]²⁺, the couple (6) lies beyond the experimentally accessible potential. The value given in Table II is extrapolated from $E^{\circ}_{298} - \nu_{\text{CT}}$ correlation (see below). The E°_{298} values of the Ru(III)-Ru(II) couples of 4, 5, and 6 are among the highest in ruthenium(II) chemistry.⁶ (Arylazo)pyridine and phosphine together endow superior redox stability to ruthenium(II).

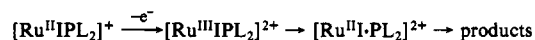
Spectroelectrochemical Correlation and Structure. We return to reconsider the MLCT band energy (ν_{CT}) discussed

- (13) Solvent cutoff occurs above +2.0 V vs. saturated calomel electrode. Observation of responses near this limit is better achieved by using differential-pulse polarography. This technique was used in the case of 6 to locate the ruthenium(III)-ruthenium(II) couple.
- (14) Bard, A. J.; Sadler, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 1979. Boto, K. G.; Thomas, F. G. *Aust. J. Chem.* **1973**, *26*, 1251; **1971**, *24*, 975. Aylward, G. H.; Garnett, J. L.; Sharp, J. H. *Anal. Chem.* **1967**, *39*, 457. Loferty, R. O.; Sharp, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 4049.
- (15) Bandyopadhyay, P.; Mascharak, P. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 675. Mukherjee, R. N.; Chakravorty, A., unpublished results.
- (16) We have reason¹⁵ to believe the three observed reductions probably arise from successive addition of 1e alternately to the two azo functions location on the two ligands:



where L· and L·- represent L reduced by 1e and 2e, respectively. The [RuXPL·L·]²⁻ stage is not observable since due to unknown reactions the current increases rapidly after the [RuXPL·L·]²⁻ stage is reached.

- (17) In the iodo complex, [RuI(PPh₂Me)(pap)₂](ClO₄)₂·H₂O, only a broad anodic peak is observed with no response on the cathodic side. Rapid secondary oxidation of iodide by intramolecular electron transfer may be the reason.



where I· is the iodine atom.

- (18) Coulometric confirmation of 1e stoichiometry is vitiated by the continuous electrolysis that occurs at potentials higher than the anodic peak potential. However, the 1e nature of each couple is established beyond doubt from comparison of current heights with those of the RuX₂L₂⁺/RuX₂L₂ couples.²
- (19) Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 3138.

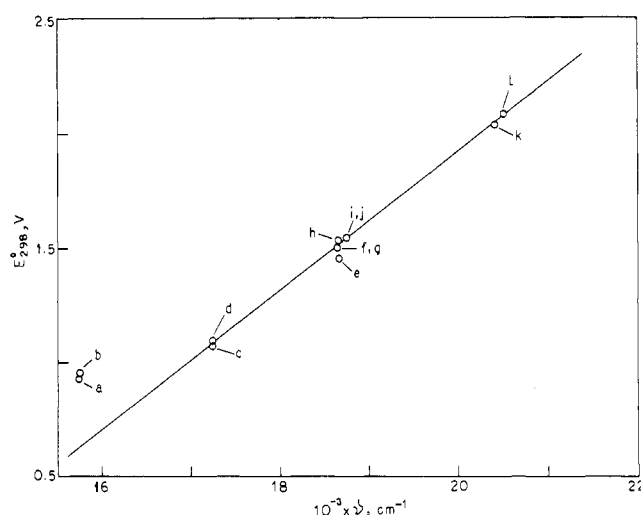


Figure 3. Linear correlation between MLCT band energies and E°_{298} : a, ttt-RuCl₂(pap)₂; b, ttt-RuBr₂(pap)₂; c, C₂-RuCl₂(pap)₂; d, C₂-RuCl₂(tap)₂; e, [RuCl(PPh₃)(tap)₂](ClO₄)₂·H₂O; f, [RuCl(PPh₃)(pap)₂](ClO₄)₂·H₂O; g, [RuCl(P(*p*-tol)₃)(pap)₂](ClO₄)₂·H₂O; h, [RuCl(PPhMe₂)(pap)₂](ClO₄)₂·H₂O; i, [RuCl(PPh₂Me)(tap)₂](ClO₄)₂·H₂O; j, [RuCl(PPh₂Me)(pap)₂](ClO₄)₂·H₂O; k, [Ru(PPhMe₂)₂(tap)₂](ClO₄)₂·H₂O; l, [Ru(Ph₂P(CH₂)₃PPh₂)(pap)₂](ClO₄)₂·H₂O.

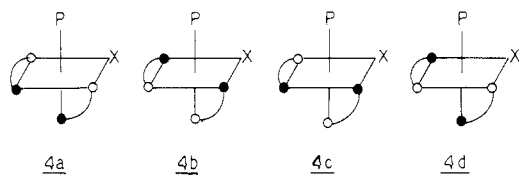
earlier. If ligand π^* levels are left more or less unaffected, ν_{CT} would increase as the stability of the t_2 level increases. A parallel shift of E°_{298} to more positive potentials is anticipated^{6,20} since electron transfer (couples (4)-(6)) involves the t_2 level. There is indeed an excellent linear correlation between ν_{CT} and E°_{298} among the entire group of complexes of types 3-6 (Figure 3). Most significantly, 2 falls conspicuously outside this correlation.²¹ This is an excellent proof that in 4 and 5 the RuL₂ moiety is cis-cis and not trans-trans. This is buttressed by the well-behaved nature of [Ru(Ph₂P(CH₂)₃PPh₂)(pap)₂]²⁺ with regard to $E^{\circ}_{298} - \nu_{\text{CT}}$ correlation. This complex can only have cis-cis RuL₂ configuration because of the chelating nature of the diphosphine.

Within the framework of cis-cis RuL₂, [RuXPL₂]⁺ can have four possible geometrically isomeric forms²² (4a-4d; each of these can have *d* and *l* forms). Of these 4a is related to the ctc isomer of RuX₂L₂ by the replacement of one X by one P.

- (20) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107.

(21) We have noted earlier in the text that the order of ν_{CT} is 2 < 3 and that this order arises from stronger π bonding in 3. This makes the t_{2g} level more stable in 3 but this also makes the π^* level less stable. Hence in going from 2 to 3, ν_{CT} undergoes large blue shift while the increase in E°_{298} is relatively small. In the series 3-6, the changing interactions primarily involve t_2 and phosphorus orbitals; the π^* (L) level is affected only slightly. The electrochemical results indicate that this is so.

- (22) Similarly [RuP₂L₂]²⁺ and [Ru(P-P)L₂]²⁺ have three possible isomers.



Similarly **4b** can be considered to be derived from the *cct* isomer while both **4c** and **4d** are related to the *ccc* isomer. The ^1H NMR spectrum of $[\text{RuCl}(\text{PPh}_3)(\text{tap})_2]^+$ has two equally intense methyl signals (δ_{Me} 1.96 and 2.02) as required for **4a–4d**. Since only one pair of signals is observed, it is very likely that we are dealing with only one *cis* isomer.²³ The reaction kinetics and probable mechanism of reaction 1 proposed in the next section suggest that the isomer is probably **4a** or **4b**.

Kinetics and Probable Mechanism. We have undertaken a systematic study on the kinetics of reactions 1–3 as well as of similar reactions of **3** in order to rationalize the mechanisms of substitution and structure of products. Here we briefly report on reaction 1 between *ttt*- $\text{RuCl}_2(\text{pap})_2$ and PPhMe_2 in methanol containing 20% chloroform at $40.0 \pm 0.2^\circ\text{C}$ (the parent complex taken alone is indefinitely stable in this solvent). In the course of the reaction, the intensity of the MLCT band of *ttt*- $\text{RuCl}_2(\text{pap})_2$ at 625 nm progressively decreases while the band of $[\text{RuCl}(\text{PPhMe}_2)(\text{pap})_2]^+$ develops at 530 nm; a sharp isosbestic point occurs at 560 nm. The reaction rate was monitored from the decrease of intensity at 625 nm. The observed rate constant²⁴ (k_{obsd}), determined in the presence of excess phosphine, was found to vary linearly with the phosphine concentration with zero intercept (Figure 4). The second-order rate constant (k_2), is $9.64 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Under similar conditions the rate of the reaction with PPh_3 is at least 1 order of magnitude slower and that with PPh_3 is very very slow. Thus phosphine cone angle²⁵ is an important controlling factor in determining the reaction rate.

The above results indicate that the phosphine gets bound in the transition state and that we have a basically $\text{S}_{\text{N}}2$ pathway. The observed stereochemical rearrangement is readily rationalized in terms of a trans attack or an edge displacement mechanism.²⁶ The resultant isomer can be either **4a** or **4b** (Scheme I). We wish to point out an additional feature here. In grossly planar arylazo oximates of palladium(II), it has been shown²⁷ that phosphine attack brings about a selective displacement of the $\text{Pd}-\text{N}(\text{azo})$ bond. A qualitatively similar labilization of the $\text{Ru}-\text{N}^2$ bond in the $\text{RuX}_2\text{L}_2 + \text{P}$ reaction system^{28,29} may facilitate the chelate ring motion necessary in the edge displacement pathway. The motion will then occur primarily at the $\text{Ru}-\text{N}^2$ and while $\text{Ru}-\text{N}^1$ can act more or less as the pivot. Such a pathway is expected to produce the **4a** isomer. It is stressed that we are *not* proposing that bond labilization is a necessary condition for rationalization of the observed reaction. Thus *ttt*- $\text{RuX}_2(\text{pap})_2$ itself

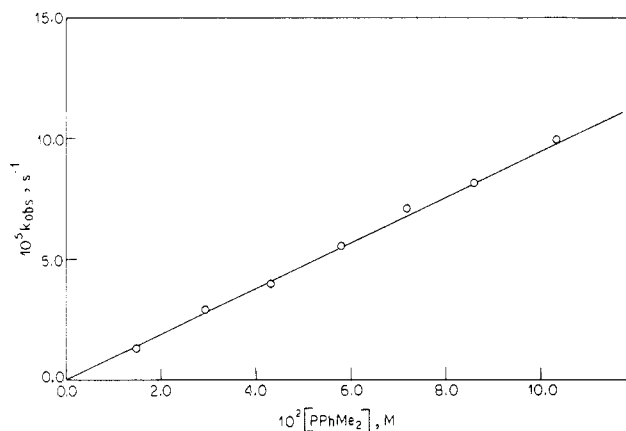
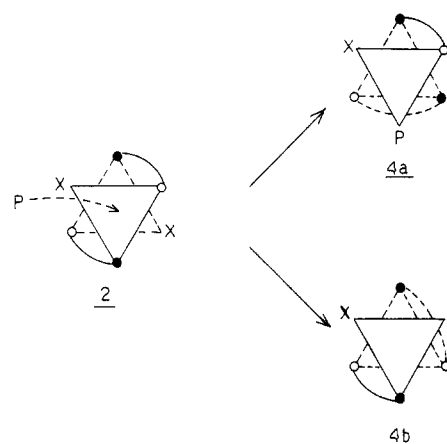


Figure 4. Dependence of k_{obsd} on concentration of PPhMe_2 for the reaction of *ttt*- $\text{RuCl}_2(\text{pap})_2$ with PPhMe_2 (40°C ; 4:1 methanol-chloroform).

Scheme I



isomerizes slowly to the C_2 form on boiling in xylene: an intramolecular process which probably proceeds by edge displacement.³

The substitutional stereodynamism^{30,31} reported here is novel in ruthenium(II) chemistry—at least among dihaloruthenium complexes.^{33–39} The aquation of a group of *trans*- $\text{Ru}(\text{Am})_2\text{X}_2$ (Am = one or more ammine ligands occupying four coordination positions) is reported to be dissociative and stereore-

- (23) No isomer separation could be achieved by chromatography on silica. This of course is no proof that isomers do not exist, since polarity differences among the isomers are likely to be small.
- (24) After the reaction has proceeded to a considerable extent, a faster reaction pathway becomes available probably due to catalysis by $[\text{RuCl}(\text{PPhMe}_2)_2]^+$. Similar acceleration is *not* observed in the case of PPh_3 reaction. The results reported here refer to the initial pathway only.
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- (28) Significantly, the $\text{Pd}-\text{N}(\text{azo})$ bond is very much less labile^{27,29} to nitrogen bases than to tertiary phosphines. Also *ttt*- RuCl_2L_2 is unreactive toward pyridine.
- (29) Mascharak, P. K.; Chakravorty, A. *Indian J. Chem., Sect. A* **1979**, *18A*, 471.

- (30) The thermal isomerization^{3,4} of RuX_2L_2 is equally interesting. Photochemical *cis* $\rightarrow$ *trans* conversion is described³¹ for *cis*- $[\text{Ru}(\text{H}_2\text{O})_2(\text{bpy})_2]^{2+}$ (bpy = 2,2'-bipyridine). The aquation of the later complex is associative.³²
- (31) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.
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- (33) Outside simple amines³⁴ few halo ruthenium species are known where both *cis* and *trans* species occur. The occurrence of the *trans* analogue of the common³⁵ *cis*- $\text{RuX}_2(\text{bpy})_2$ was recently claimed,³⁶ but no substitution reaction of this isomer is reported. The displacement of X^- from *cis*- $\text{RuX}_2(\text{bpy})_2$ by pyridine bases³⁷ and tertiary phosphines⁶ proceed with retention of $\text{Ru}(\text{bpy})_2$ stereochemistry. In the case of pyridine bases, the mechanism is dissociative;³⁷ rate studies for phosphines are missing.
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- (37) Maspero, F.; Ortaggi, G. *Ann. Chim. (Rome)* **1974**, *64*, 115.
- (38) The substitution of dimethyl sulfoxide (Me_2SO) by PPh_3 in $\text{RuX}_2(\eta\text{-C}_6\text{H}_5)(\text{Me}_2\text{SO})$ proceeds³⁹ by a dissociative mechanism. This reaction is unrelated to our work since halide displacement does not occur.
- (39) Carr, C. M.; Davies, D. M.; Gower, M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1981**, 923.

tentive.⁴⁰ The substitution of coordinated water by pyridines and nitriles in $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ is also dissociative.⁴¹

Concluding Remarks

The substitution of a halogen by phosphines in **2** is invariably attended with stereochemical rearrangement of the trans-trans RuL_2 fragment, and this is neatly reflected in the MLCT band energy and E°_{298} values. Examples of such rearrangement are rare in ruthenium chemistry. We reported earlier that OH^- converts $\text{trans-RuX}_2\text{L}_2$ to a blue substance in methanol-water mixture, and it was suggested that this phenomenon could arise from nucleophilic attack in the pyridine ring.² We have now found that the green to blue transformation is actually a substitution reaction attended with stereochemical rearrangement. The blue product $\text{cis-}[\text{Ru}(\text{OH})(\text{H}_2\text{O})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ has been obtained from the reaction. It reacts with protons in aqueous media giving $\text{cis-}[\text{Ru}(\text{H}_2\text{O})_2\text{L}_2]^{2+}$, which is a useful starting material for the synthesis of interesting mononuclear and binuclear complexes, e.g., $[\text{RuL}'\text{L}_2]^{2+}$ ($\text{L}' = \text{L}$, bipyridine, etc.) and $[\text{L}_2\text{Ru}(\mu\text{-Cl})_2]^{2+}$. The same dihydrate is obtainable by Ag^+ -assisted displacement of halide ion from the C_2 isomer of RuX_2L_2 (**3**); we reiterate that **2** does not react with the Ag^+ . The higher reactivity of **3** is also reflected in its reactions with phosphines. Thus it reacts with PPhMe_2 much faster than does **2**. The reaction is of second order, and in the product **X** and **P** are in cis positions.⁴² Further studies on these topics are in progress and will be reported in due course.

Experimental Section

Materials: The ligand **L** was prepared as before.² The various phosphines were obtained from Strem Chemical Inc. or Eastman Organic Chemicals. The purification/preparation of solvent and supporting electrolyte for electrochemical work was done as before.² Methanol and chloroform, used in kinetic studies, were of analytical reagent grade. All other solvents used for preparations were of reagent grade and were used without further purification.

Measurements. Electronic spectra were recorded with a Cary 17D spectrophotometer; IR spectra (KBr disk, $4000\text{--}400\text{ cm}^{-1}$; polyethylene disk, $400\text{--}100\text{ cm}^{-1}$) were obtained with a Beckman IR-20A and a IR-720M spectrophotometers. ^1H NMR data were collected in CDCl_3 solvent with a varian T-60 or Bruker WP-270 spectrometer. Solution electrical conductivity was measured with a Philips PR 9500 bridge with a solute concentration of $\sim 10^{-3}\text{ M}$. Cyclic voltammetric measurements were carried out with the help of PAR models: 174A, polarographic analyser; 175, universal programmer; RE 0074, XY recorder; 377A, cell system. The three-electrode measurements were carried out by using planar Beckman Model 39273 platinum-inlay working electrode, platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The results collected at $298 \pm 1\text{ K}$ are uncorrected for junction potentials.

Rate Measurements. The rate of isomerization in the substitution reaction was studied spectrophotometrically with the help of a Pye-Unicam Model SP8-150 recording spectrophotometer. The initial concentration of $\text{trans-RuCl}_2(\text{pap})_2$ was $\sim 10^{-4}\text{ M}$ in 80:20 (v/v) methanol-chloroform mixture. The solution was thermostated at $40.0 \pm 0.2^\circ\text{C}$. Kinetics were run under pseudo-first-order conditions keeping a large excess of PPhMe_2 . The absorbance (A) was measured at 625 nm as a function of time. The plot of $-\ln(A_t - A_\infty)$ vs. time was a straight line, the slope of which is k_{obsd} . The k_{obsd} values were determined at several PPhMe_2 concentrations (C). The $k_{\text{obsd}}\text{--}C$ plot was a straight line with zero intercept. The second-order rate constant, k_2 , was taken as the slope of this line.

Preparation of Complexes. $\text{trans-RuX}_2\text{L}_2$ was prepared as before.² It was converted to the C_2 isomer by boiling in xylene.³ The C_2 isomer of $\text{RuCl}_2(\text{tap})_2$ is new. Anal. Calcd for $\text{RuC}_{22}\text{H}_{18}\text{N}_6\text{Cl}_2$: C, 49.06;

H, 3.34; N, 15.61; Cl, 13.19. Found: C, 49.14; H, 3.40; N, 15.68; Cl, 13.60.

Chloro(triphenylphosphine)bis[2-(phenylazo)pyridine]ruthenium(II) Perchlorate Hydrate, $[\text{RuCl}(\text{PPh}_3)(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$. To a suspension of 0.1 g (0.18 mmol) of $\text{trans-RuCl}_2(\text{pap})_2$ in a 1:1 methanol-water mixture (15 mL) was added 0.1 g (0.38 mmol) of PPh_3 . The mixture was heated to reflux for 4 h. The initial green solution gradually turned violet. After cooling to room temperature, the reaction mixture was filtered and the filtrate was poured into 15 mL of water containing excess sodium perchlorate. Crystals started depositing immediately. After the mixture was kept in the refrigerator for 2–3 h, the violet crystals were filtered and washed thoroughly with water and finally with diethyl ether. These were then dried in vacuo over P_2O_{10} . The dried product was dissolved in a small volume of 3:2 benzene-acetonitrile mixture and was subjected to chromatography on a silica gel (60–120 mesh) column ($20 \times 1\text{ cm}$). On elution with 9:1 benzene-acetonitrile, green and blue bands moved out and were rejected. The eluant was then changed to a 3:2 benzene-acetonitrile mixture. A red-violet band was eluted out with the solvent. An orange band remained near the top of the column. Crystals were obtained with complete evaporation of the violet eluate at room temperature. The yield was 70%. Anal. Calcd for $\text{RuC}_{40}\text{H}_{35}\text{N}_6\text{O}_5\text{Cl}_2\text{P}_3$: C, 54.41; H, 4.00; N, 9.52; P, 3.52. Found: C, 54.18; H, 4.06; N, 9.69; P, 3.90. $[\text{RuCl}(\text{PPh}_3)(\text{tap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$, $[\text{RuCl}(\text{P}(p\text{-tol})_3)(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$, $[\text{RuCl}(\text{PPh}_2\text{Me})(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$, and $[\text{RuCl}(\text{PPh}_2\text{Me})(\text{tap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ were prepared similarly by using the appropriate $\text{trans-RuCl}_2\text{L}_2$ and phosphine. The analytical data and yields are as follows. Anal. Calcd for $[\text{RuCl}(\text{PPh}_3)(\text{tap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{C}_{42}\text{H}_{39}\text{N}_6\text{O}_5\text{Cl}_2\text{P}_3$): C, 55.38; H, 4.32; N, 9.23; Cl, 7.79. Found: C, 55.26; H, 4.14; N, 9.29; Cl, 7.90. The yield was 70%. Calcd for $\text{RuCl}(\text{P}(p\text{-tol})_3)(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{RuC}_{43}\text{H}_{41}\text{N}_6\text{O}_5\text{Cl}_2\text{P}_3$): C, 55.83; H, 4.47; N, 9.09. Found: C, 55.68; H, 4.63; N, 9.06. The yield was 80%. Calcd for $[\text{RuCl}(\text{PPh}_3\text{Me})(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{RuC}_{35}\text{H}_{33}\text{N}_6\text{O}_5\text{Cl}_2\text{P}_3$): C, 51.22; H, 4.06; N, 10.24. Found: C, 51.28; H, 4.40; N, 9.97. The yield was 70%. Calcd for $[\text{RuCl}(\text{PPh}_2\text{Me})(\text{tap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{RuC}_{37}\text{H}_{34}\text{N}_6\text{O}_5\text{Cl}_2\text{P}_3$): C, 52.35; H, 4.04; N, 10.02; Cl, 8.47. Found: C, 52.20; H, 4.25; N, 9.58; Cl, 9.00. The yield was 65%.

The bromo and iodo complexes were prepared similarly by using the same reactant stoichiometry and conditions starting with $\text{trans-RuX}_2\text{L}_2$ ($\text{X} = \text{Br}, \text{I}$). The yield and analytical data are as follows. Anal. Calcd for $[\text{RuBr}(\text{PPh}_2\text{Me})(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{RuC}_{35}\text{H}_{33}\text{N}_6\text{O}_5\text{BrClP}_3$): C, 48.58; H, 3.85; N, 9.71. Found: C, 49.23; H, 4.09; N, 9.25. The yield was 65%. Calcd for $[\text{RuI}(\text{PPh}_2\text{Me})(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{RuC}_{35}\text{H}_{33}\text{N}_6\text{O}_5\text{ClIP}_3$): C, 46.07; H, 3.65; N, 9.21. Found: C, 46.05; H, 3.93; N, 9.43. The yield was 60%.

Chloro(dimethylphenylphosphine)bis[2-(phenylazo)pyridine]ruthenium(II) Perchlorate Hydrate, $[\text{RuCl}(\text{PPhMe}_2)(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$. A 0.1-g (0.18-mmol) sample of $\text{trans-RuCl}_2(\text{pap})_2$ was reacted with 0.025 g (0.18 mmol) of PPhMe_2 in 15 mL of a 1:1 methanol-water mixture. The mixture was boiled for 4 h. After cooling to room temperature, the reaction mixture was added to a saturated aqueous solution of sodium perchlorate. The precipitated complex was washed with water and finally with diethyl ether and then dried in vacuo over P_2O_{10} . The dried product was chromatographed by using a procedure similar to that given above. The violet band was eluted out with a 1:1 benzene-acetonitrile mixture. Slow evaporation gave crystals of the desired product. The yield was 50%. The concentration of PPhMe_2 must be controlled otherwise the disubstituted product will be formed. Anal. Calcd for $\text{RuC}_{30}\text{H}_{31}\text{N}_6\text{O}_5\text{Cl}_2\text{P}_2$: C, 47.47; H, 4.12; N, 11.08. Found: C, 47.87; H, 4.25; N, 10.83.

Bis(dimethylphenylphosphine)bis[2-(tolylazo)pyridine]ruthenium(II) Perchlorate Hydrate, $[\text{Ru}(\text{PPhMe}_2)_2(\text{tap})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. A 0.1-g (0.18-mmol) sample of $\text{trans-RuCl}_2(\text{tap})_2$ was mixed with 0.05 g (0.36 mmol) of PPhMe_2 in 15 mL of a 1:1 methanol-water mixture. The mixture was heated to reflux for 8 h. The solution color changed from green to violet to orange. After cooling to room temperature, the compound was precipitated, washed, and dried by using the same procedure as given above. The crude product was then chromatographed on silica gel column as before. An orange band was eluted and collected by using 1:4 benzene-acetonitrile as eluant. Crystals were obtained by complete evaporation of the solvent. The yield was 50%. Anal. Calcd for $\text{RuC}_{40}\text{H}_{46}\text{N}_6\text{O}_9\text{Cl}_2\text{P}_2$: C, 48.58; H, 4.69; N, 8.50. Found: C, 48.28; H, 4.62; N, 8.20.

(1,2-Bis(diphenylphosphino)ethane)bis[2-(tolylazo)pyridine]ruthenium(II) Perchlorate Hydrate, $[\text{Ru}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\text{tap})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. The water-methanol mixture (15 mL, 1:1 v/v) con-

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(42) This does not mean that the substitution is not attended with isomerization of the RuL_2 fragment. For example, the transformation of RuL_2 from *tc* (or *ct*) to *cc* leaves *cis* positions available for **X,P**.

taining 0.1 g (0.18 mmol) of *ttt*-RuCl₂(tap)₂ and 0.07 g (0.18 mmol) of Ph₂P(CH₂)₂PPh₂ was boiled for 12 h. The solution color changed from green to orange. The compound was isolated as the perchlorate salt with a procedure similar to that given above. The purification was done by chromatography. An orange band was eluted out by using a 1:4 benzene-acetonitrile mixture. Crystals were obtained by complete evaporation of the solvent. The yield was 40%. Anal. Calcd for RuC₅₀H₄₈N₆O₉Cl₂P₂: C, 54.74; H, 4.41; N, 7.66; Cl, 6.48. Found: C, 54.68; H, 4.72; N, 7.23; Cl, 6.20.

(1,3-Bis(diphenylphosphino)propane)bis[2-(phenylazo)pyridine]ruthenium(II) Perchlorate Hydrate, [Ru(Ph₂P(CH₂)₃PPh₂)(pap)₂](ClO₄)₂·H₂O. This was prepared by following the method given in the cases of [Ru(Ph₂P(CH₂)₂PPh₂)(tap)₂](ClO₄)₂·H₂O but with *ttt*-RuCl₂(pap)₂ and Ph₂P(CH₂)₃PPh₂ used instead of *ttt*-RuCl₂(tap)₂ and Ph₂P(CH₂)₂PPh₂, respectively. The yield was 40%. Anal. Calcd for RuC₄₉H₄₆N₆O₉Cl₂P₂: C, 53.64; H, 4.23; N, 7.66; Cl, 6.49. Found:

C, 53.95; H, 4.19; N, 7.58; Cl, 6.60.

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Registry No. [RuCl(PPh₃)(pap)₂]ClO₄, 81554-91-8; [RuCl(PPh₃)(tap)₂]ClO₄, 81554-93-0; [RuCl(P(*p*-tol)₃)(pap)₂]ClO₄, 81554-95-2; [RuCl(PPh₂Me)(pap)₂]ClO₄, 81554-64-5; [RuCl(PPh₂Me)(tap)₂]ClO₄, 81554-66-7; [RuBr(PPh₂Me)(pap)₂]ClO₄, 81554-68-9; [RuI(PPh₂Me)(pap)₂]ClO₄, 81554-70-3; [RuCl(PPhMe₂)(pap)₂]ClO₄, 81554-72-5; [Ru(PPhMe₂)₂(tap)₂](ClO₄)₂, 81554-74-7; [Ru(Ph₂P(CH₂)₂PPh₂)(tap)₂](ClO₄)₂, 81554-76-9; [Ru(Ph₂P(CH₂)₃PPh₂)(pap)₂](ClO₄)₂, 81554-78-1; C₂-RuCl₂(tap)₂, 81600-80-8; *ttt*-RuCl₂(pap)₂, 77321-07-4; *ttt*-RuBr₂(pap)₂, 77321-08-5; *ttt*-RuI₂(pap)₂, 77341-75-4; *ttt*-RuCl₂(tap)₂, 77321-09-6.

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Preparation and Characterization of Heteropolytungstates Containing Group 3A Elements

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The polytungstate ions α -XM^{III}(OH₂)W₁₁O₃₉ⁿ⁻ (X = B, Si, Ge, P, As; M^{III} = Al, Ga, In, Tl) and X₂M^{III}(OH₂)W₁₇O₆₁⁷⁻ (X = P, As; M^{III} = as above) are reported. Their stability in acidic to slightly basic aqueous solution, both with and without supporting electrolyte, is classified in terms of X and M(III). The sensitivity to changes in M(III) of the P-O asymmetric stretch vibration splitting in the tungstophosphates is described. All anions are reducible to W(V)-containing species; their redox behavior resembles that of the parent lacunary anions. A series of two-electron reduced gallatotungstates has been isolated. The crystal symmetries found for the alkali metal and ammonium salts can be classified according to the number of cations and, to a lesser degree, the number of molecules of hydration water. Differences in behavior of the group 3A element substituted polyanions are generally small for a given central atom.

Introduction

Among the extensive class of heteropolyoxoanions of the group 5 and 6 transition metals, the best studied series of compounds are those having, or derived from, the so-called Keggin structure² and the related Dawson structure³ of general formula XM₁₂O₄₀ⁿ⁻ (X = B, Si, Ge, P, As, various transition metals; M = W, Mo) and X₂M₁₈O₆₂ⁿ⁻ (X = P, As; M = W, Mo).

The basic unit in both structural types is a M₃O₁₃ group consisting of three edge-sharing octahedra that are slightly (in the case of W) or more severely (in the case of Mo) distorted, the metal atoms being displaced outwardly. Several isomers of both structures are known,⁴⁻¹¹ e.g., through rotation

of one M₃O₁₃ unit, the most symmetric ones, generally labeled α ,⁹ are usually thermodynamically the most stable.

Increasing the basicity of a solution of such a polyanion may result in the formation of so-called lacunary polyanions, which have lost one or more M-O groups while maintaining the same basic structure.⁴ The more easily prepared series have the general formula XM₁₁O₃₉ⁿ⁻ (X and M as above) and X₂M₁₇O₆₁ⁿ⁻ (X and M as above) (see Figure 1).

It is possible to refill the lacuna with one of numerous transition- and main-group-metal ions^{12-14,18} or to complex two lacunary units around a sufficiently large central metal ion capable of high coordination numbers (e.g., some lanthanides and actinides).^{15,16} The lacunary compound may be considered as a pentadentate or tetradentate ligand, respectively. Most 1:1 complexes that have so far been prepared contain bivalent transition-metal ions,¹²⁻¹⁴ probably because they are comparatively easy to synthesize and isolate as solids. Several compounds have been studied however that contain tri-, tetra-, or pentavalent transition-metal ions: Co(III),^{12,17,18} Mn(III),¹⁹

- (1) (a) Abstracted in part from the Thèse d'Etat of Frans Zonnevillje, U.S.T.L., 34060 Montpellier Cedex, France; CNRS No. AO 13.026. (b) Institut de Chimie Minérale et Analytique, Université de Lausanne, CH-1005 Lausanne, Switzerland.
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