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## Metal Complexes of the Hexa(tertiary phosphine) *P,P,P',P'*-Tetrakis(2-diphenylphosphinoethyl)- $\alpha,\alpha'$ -diphospha-*p*-xylene

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Received February 1, 1974

AIC40072D

The synthesis of a new sexadentate ligand, *P,P,P',P'*-tetrakis(2-diphenylphosphinoethyl)- $\alpha,\alpha'$ -diphospha-*p*-xylene (TDDX) and the preparation of its Ir(I), Rh(I), and Ru(II) complexes is described. The reaction of  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  or  $\text{RhCl}(\text{PPh}_3)_3$  with TDDX in boiling benzene gave the binuclear complex  $\text{Rh}_2\text{Cl}_2(\text{TDDX})$ . The reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with TDDX gave the complex  $\text{Ir}_2\text{Cl}_2(\text{TDDX})$ . The treatment of  $\text{RuCl}_2(\text{PPh}_3)_3$  with TDDX formed the complexes  $\text{Ru}_2\text{Cl}_4(\text{TDDX})$  and  $\text{Ru}(\text{TDDX})(\text{PF}_6)_2$ . The reaction of hydrated ruthenium trichloride with TDDX in the presence of hexafluorophosphate gave  $\text{Ru}_2\text{Cl}_4(\text{TDDX})(\text{PF}_6)_2$ . A similar treatment of hydrated rhodium trichloride with TDDX gave the complex  $\text{Rh}_2\text{Cl}_6(\text{TDDX})$  and  $\text{Rh}_2\text{Cl}_4(\text{TDDX})(\text{PF}_6)_2$ . The reaction of iridium trichloride with TDDX gave the complexes  $\text{Ir}_3\text{Cl}_9(\text{TDDX})$  and  $\text{Ir}_2\text{Cl}_4(\text{TDDX})(\text{PF}_6)_2$ . Reaction of the metal hexacarbonyls,  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}$ ), and diiron nonacarbonyl,  $\text{Fe}_2(\text{CO})_9$ , with TDDX gave the binuclear complexes  $[\text{M}(\text{CO})_3]_2(\text{TDDX})$ . The complexes have been characterized by elemental analysis and their infrared and nmr spectra.

### Introduction

Hexa(tertiary phosphines) are of special interest because of the possibilities of the preparation of sexadentate mononuclear or binuclear complexes. Binuclear complexes of  $d^8$ ,  $d^6$ , and  $d^5$  transition metal ions are of special significance because of the possibility that such complexes may act as bifunctional catalytic species. As a part of a general research program in this laboratory to synthesize and study polyfunctional catalysts it was considered of interest to design chelating agents that would form binuclear complexes with the metal-metal spacing needed to produce cooperative catalytic effects.

King, *et al.*,<sup>1</sup> have reported the preparation of complexes of the hexa(tertiary phosphine) 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphospha-butane (hexaphos) which is analogous to EDTA in the relative disposition of the phosphorus donor atoms. In addition to hexaphos, an analogous sexadentate ligand, the poly(tertiary arsine)  $\text{C}_6\text{H}_4\{\text{As}[\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2]_2\}_2$ , is also known.<sup>2</sup> Because of the proximity of the phosphorus atoms of the 1,4-diphospha-butane moiety, hexaphos forms only a few binuclear derivatives. Molecular models indicate that a ligand such as *P,P,P',P'*-tetrakis(2-phenylphosphinoethyl)- $\alpha,\alpha'$ -diphospha-*p*-xylene (TDDX) would have a rigid aromatic ring separating the two potentially terdentate triphos moieties and thus would tend to act as a binucleating sexadentate ligand. Such a ligand would be well suited for the formation of binuclear complexes of  $d^5$ ,  $d^6$ , and  $d^8$  metal ions. The objective of this research was therefore to synthesize this new ligand and to study the properties of its metal complexes.

### Experimental Section

**Reagents.** All the complexes were prepared and the reactions conducted in a nitrogen atmosphere using Schlenk-tube techniques.

All solvents were AR grade reagents and were purged with purified nitrogen prior to their use. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz. The molecular weight determination of some of the complexes was done by the Australian Microanalytical Service, CSIRO, Australia. Infrared spectra of the ligand and its complexes were recorded in Nujol mull on a Beckman IR-12 spectrophotometer. The nmr spectra of the solution of some of the complexes in deuterated chloroform were recorded with a Varian T-60 spectrometer. The conductivity measurements were done in dimethylformamide solution at 30° with an Elico conductivity bridge.

The complexes  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ ,<sup>3</sup>  $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ ,<sup>4</sup>  $\text{RhCl}(\text{PPh}_3)_3$ ,<sup>5</sup> and  $\text{RuCl}_2(\text{PPh}_3)_3$ <sup>6</sup> were obtained by the appropriate published procedures. Ruthenium trichloride, rhodium trichloride, and iridium trichloride were purchased from Ventron-Alfa Inorganics. The metal carbonyls  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{Fe}_2(\text{CO})_9$  were obtained from Pressure Chemical Co. Triethyl phosphite was obtained from Mobil Chemicals. Diphenylchlorophosphine was purchased from Eastern Chemical Co. Vinyl bromide and  $\alpha,\alpha'$ -dibromo-*p*-xylene were obtained from Aldrich Chemical Co. and used without further purification. Diphenylvinylphosphine was synthesized by the published procedure.<sup>7</sup> Yields, analytical data, molecular weights, and conductivity data are presented in Table I.

**Synthesis of TDDX.** The ligand was prepared by a modification of the procedure described for the preparation of hexaphos by King, *et al.*<sup>1</sup> The ester tetraethyl  $\alpha,\alpha'$ -*p*-xylenediphosphonate was obtained by the method of Issleib and Weichmann.<sup>8</sup> Twenty-six grams (100 mmol) of  $\alpha,\alpha'$ -dibromo-*p*-xylene was refluxed with 34.9 g (0.200 mol) of triethyl phosphite for about 4–6 hr. Ethyl bromide was distilled off and the product on cooling formed a colorless crystalline solid. The product was recrystallized from ether-petroleum ether to give 34-g (90%) yield of the diester ( $\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  (mp 26°). *Anal.* Calcd for  $\text{C}_{16}\text{H}_{28}\text{P}_2\text{O}_6$ : C, 50.8; H, 7.4. Found: C, 50.01; H, 7.5. The diester is very soluble in water, ethanol, and ether and is very hygroscopic. The nmr spectrum of the diester (Figure 1) gave a peak corresponding to the aromatic protons at  $\tau$  2.8. The methylene proton of the ethyl groups gave a quartet centered at  $\tau$  6. The methylene protons of the *p*-xylene group gave

Table I. Analytical Data for TDDX Metal Complexes<sup>a</sup>

Entry	Compd	Color	% compn <sup>b</sup>				Mol wt <sup>b,c</sup>
			C	H	Cl	P	
1	Rh <sub>2</sub> Cl <sub>2</sub> (TDDX)	Yellow	60.6 (59.3)	5.5 (5.2)		14.1 (14.3)	1290 (1295)
2	Ir <sub>2</sub> Cl <sub>2</sub> (TDDX)	Yellow	57.3 (56.1)	4.9 (4.7)	3.6 (4.8)	13.5 (12.6)	1470 (1473)
3	Ru <sub>2</sub> Cl <sub>4</sub> (TDDX)(PPh <sub>3</sub> ) <sub>2</sub>	Yellow	61.2 (59.1)	5.4 (5.6)		14.5 (14.1)	1894 (1886)
4	Ru(TDDX)(PF <sub>6</sub> ) <sub>2</sub>	Yellow	54.0 (54.5)	4.3 (4.5)		17.0 (17.6)	
5	Ru <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	Yellow	48.4 (46.5)	4.4 (4.2)	8.4 (8.6)	16.2 (15.0)	1650 (1652)
6	Rh <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	Pale yellow	45.7 (46.4)	3.9 (3.9)		14.0 (14.9)	1652 (1950)
7	Rh <sub>2</sub> Cl <sub>6</sub> (TDDX)	Yellow	50.0 (51.5)	4.5 (4.5)		10.9 (11.9)	1442 (1437)
8	Ir <sub>3</sub> Cl <sub>9</sub> (TDDX)	Grayish yellow	38.2 (39.9)	3.5 (3.4)	14.0 (14.0)		
9	Ir <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	Yellow	40.6 (41.8)	4.1 (3.9)		15.1 (14.5)	
10	Cr <sub>2</sub> (CO) <sub>6</sub> (TDDX)	Yellow-green	64.9 (65.1)	4.8 (4.9)		14.1 (14.4)	1295 (1290)
11	Mo <sub>2</sub> (CO) <sub>6</sub> (TDDX)	Yellow-brown	60.3 (60.9)	5.9 (5.6)		13.2 (13.5)	1384 (1378)
12	Fe <sub>2</sub> (CO) <sub>6</sub> (TDDX)	Brown	64.3 (64.7)	4.7 (4.9)		13.9 (14.3)	1306 (1298)

<sup>a</sup> Conductivities of complexes ( $M^{-1} \text{ cm}^2 \text{ ohm}^{-1}$ ) are (1) 23, (2) 19, (3) 21, (4, 5) 150, (6) 152, (7) 148, (8, 9, 10) 25, (11) 23, (12) 21.  
<sup>b</sup> Calculated values in parentheses. <sup>c</sup> Measured in nitromethane.

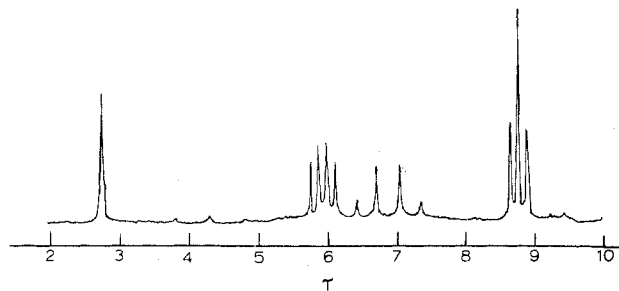


Figure 1. Nuclear magnetic resonance spectrum of the diester  $(\text{C}_2\text{H}_5\text{O})_2\text{POCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PO}(\text{C}_2\text{H}_5\text{O})_2$  in  $\text{CDCl}_3$ ; internal reference TMS.

a doublet of doublets in the range  $\tau$  6.7. The methyl protons were observed as a triplet centered at  $\tau$  8.5. The protons for the various peaks were integrated to give the expected numbers of protons, in agreement with the proposed composition of the product.

For the preparation of TDDX, 26 g (0.070 mol) of the diester was dissolved in 100 ml of dry ether and treated dropwise with a suspension of 10 g (0.225 mol) of lithium aluminum hydride<sup>9</sup> in 250 ml of anhydrous ether at 0° over a period of 3 hr. The mixture was stirred at room temperature for another 36 hr. The reaction mixture was then cooled to 0° and treated dropwise with 200 ml of 6 N hydrochloric acid. The ethereal layer was separated, dried over anhydrous sodium sulfate, and treated with 40 g (0.190 mol) of diphenylvinylphosphine, 1.0 g of potassium *tert*-butoxide, and 200 ml of tetrahydrofuran. The reaction mixture was subsequently treated by the method of King, *et al.*,<sup>1</sup> to give about 17 g of TDDX (25% yield), mp 96°. Anal. Calcd for  $\text{C}_{64}\text{H}_{64}\text{P}_6$ : C, 72.1; H, 6.1; P, 18.3. Found: C, 70.1; H, 6.0; P, 17.8. The compound is very hygroscopic and dissolves readily in benzene, toluene, chloroform, and ethanol. The nmr spectrum of the ligand presented in Figure 2 shows a complex asymmetric phenyl proton resonance at  $\tau$  2.5. A doublet due to the *p*-xylene methylene protons was observed at  $\tau$  5.3 and a complex pattern due to the  $\text{C}_2\text{H}_4$  methylene protons was found at  $\tau$  6.8–8.6. The infrared spectrum of the ligand shows peaks at 520 (s), 540 (s), 700 (s), 725 (s), and 740  $\text{cm}^{-1}$  (sh). The analytical data for the metal complexes are given in Table I.

**Preparation of the Complexes  $\text{M}_2\text{Cl}_2(\text{TDDX})$  ( $\text{M} = \text{Rh}(\text{I}), \text{Ir}(\text{I})$ ).** A mixture of 1.0 mmol of  $\text{M}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  ( $\text{M} = 0.70 \text{ g}$  of Rh(I), 0.78 g of Ir(I)) and 0.50 g (0.50 mmol) of TDDX and 100 ml of benzene was refluxed for about 16–17 hr. The bright yellow complexes,  $\text{M}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ , became yellowish brown (Rh(I) complex)

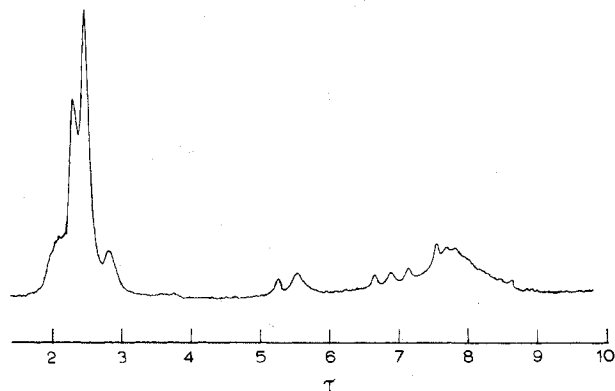


Figure 2. Nuclear magnetic resonance spectrum of TDDX in  $\text{CDCl}_3$ ; internal reference TMS.

or light yellow (Ir(I) complex), and after the reaction period was over, complexes of the corresponding color were precipitated. The complexes were recrystallized from a mixture of dichloromethane-hexane (Rh(I) complex) and chloroform (Ir(I) complex) to give 0.64 g (70% yield) of the yellowish brown complex  $\text{Rh}_2\text{Cl}_2(\text{TDDX})$  and 1.0 g (66% yield) of the yellow  $\text{Ir}_2\text{Cl}_2(\text{TDDX})$ , respectively. The complex  $\text{Rh}_2\text{Cl}_2(\text{TDDX})$  was also obtained in 75% yield by refluxing 0.90 g (1.0 mmol) of  $\text{RhCl}(\text{PPh}_3)_3$  and 0.50 g (0.50 mmol) of TDDX in 100 ml of benzene for about 12 hr.

**Preparation of the Ruthenium(II) Complexes  $\text{Ru}_2\text{Cl}_4(\text{TDDX})(\text{PPh}_3)_2$  and  $\text{Ru}(\text{TDDX})(\text{PF}_6)_2$ .** A mixture of 1.0 g (1.0 mmol) of  $\text{RuCl}_2(\text{PPh}_3)_3$ , 1.0 g (1 mmol) of TDDX, and 100 ml of benzene was refluxed for 24 hr. The dark brownish red color of the original complex became gradually lighter and turned brownish yellow at the end of the reaction period. After the reaction mixture was cooled to room temperature the brownish yellow precipitate obtained was recrystallized from chloroform to give 1.0 g (80% yield) of  $\text{Ru}_2\text{Cl}_4(\text{TDDX})(\text{PPh}_3)_2$ . The solvent was removed from the filtrate at 40°; the residue was dissolved in acetone and treated with an excess of ethanolic ammonium hexafluorophosphate. The yellow precipitate was filtered and recrystallized from a mixture of ethanol and acetone to give yellow crystals of  $\text{Ru}(\text{TDDX})(\text{PF}_6)_2$ , 0.35 g (20% yield).

**Preparation of the Ruthenium(III) Complex  $\text{Ru}_2\text{Cl}_4(\text{TDDX})(\text{PF}_6)_2$ .** A mixture of 0.3 g (1 mmol) of commercial ruthenium(III) chloride hydrate, 0.5 g (0.5 mmol) of TDDX, and 100 ml of ethanol was refluxed for 24 hr. The original dark brown color of the solution gradually turned yellow. Addition of excess of ethanolic ammonium

Table II. Proton Nmr Spectra<sup>a</sup> of the Complexes of TDDX

Entry	Compd	Chemical shifts ( $\tau$ ) <sup>b</sup>	
		Phenyl protons	Methylene protons
1	Rh <sub>2</sub> Cl <sub>2</sub> (TDDX)	2.6 d	8.0 d
2	Ir <sub>2</sub> Cl <sub>2</sub> (TDDX)	2.8 d	8.2 d
3	Ru <sub>2</sub> Cl <sub>4</sub> (TDDX)(PPh <sub>3</sub> ) <sub>2</sub>	2.5 m	7.6 m
4	Ru <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	2.3 m	7.0 m
5	Rh <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	2.3 m	7.0 m
6	Rh <sub>2</sub> Cl <sub>6</sub> (TDDX)	2.3 m	7.0 m
7	Cr <sub>2</sub> (CO) <sub>6</sub> (TDDX)	2.7 m	8.4 m
8	Mo <sub>2</sub> (CO) <sub>6</sub> (TDDX)	2.6 m	8.2 m
9	Fe <sub>2</sub> (CO) <sub>6</sub> (TDDX)	2.5 m	8.3 m

<sup>a</sup> Solvent CDCl<sub>3</sub>; internal reference TMS. <sup>b</sup> Key: d, doublet; m, multiplet.

hexafluorophosphate gave a precipitate which was crystallized from a mixture of ethanol and acetone to give yellow Ru<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub> (0.6 g, 50% yield).

**Preparation of the Rhodium(III) Complexes Rh<sub>2</sub>Cl<sub>6</sub>(TDDX) and Rh<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub>.** A mixture of 0.3 g (1 mmol) of commercial rhodium trichloride hydrate 0.5 g (0.5 mmol) of TDDX and 100 ml of ethanol was refluxed for 20 hr. The original red color of the complex soon became yellow through an intermediate orange-red color. After the reaction period was over, the reaction mixture was cooled to room temperature when the complex Rh<sub>2</sub>Cl<sub>6</sub>(TDDX) precipitated. The precipitate was removed by filtration and dried to give 0.6 g (40% yield) of yellow Rh<sub>2</sub>Cl<sub>6</sub>(TDDX). The yellow filtrate, after removal of this precipitate, was treated with an excess of ethanolic ammonium hexafluorophosphate. The resulting precipitate was collected by filtration and recrystallized from acetone-ethanol (1:1) to give 0.3 g (20% yield) of Rh<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub>.

**Preparation of the Iridium(III) Derivatives Ir<sub>3</sub>Cl<sub>9</sub>(TDDX) and Ir<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub>.** A mixture of 0.35 g (1 mmol) of commercial hydrated iridium trichloride, 0.50 g (0.50 mmol) of TDDX, and 100 ml of ethanol was refluxed for 24 hr. The original burgundy red color of the solution became yellowish brown during the heating period, and a grayish yellow precipitate separated out. After it was cooled to room temperature, the resulting precipitate was filtered, washed with petroleum ether, and dried to give 1.4 g (70% yield) of grayish yellow Ir<sub>3</sub>Cl<sub>9</sub>(TDDX). The yellow filtrate obtained after the removal of the precipitate was treated with excess ethanolic ammonium hexafluorophosphate. The yellow precipitate was recrystallized from

acetone-ethanol to give 0.20 g (15% yield) of yellow Ir<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub>.

**Reaction of the Metal Carbonyls Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, and Fe<sub>2</sub>(CO)<sub>9</sub> with TDDX.** A mixture of 1.0 mmol of the metal carbonyl (M = Cr, 0.22 g; M = Mo, 0.26 g; M = Fe, 0.36 g) and 0.50 g (0.50 mmol) of TDDX was refluxed with a 1:1 mixture of benzene and toluene for 40 hr. The crystals obtained upon cooling the reaction mixture to room temperature were washed with toluene and dried to give about 0.60 g (50% yield) of the yellow-green Cr<sub>2</sub>(CO)<sub>6</sub>(TDDX), yellow-brown Mo<sub>2</sub>(CO)<sub>6</sub>(TDDX), and brown Fe<sub>2</sub>(CO)<sub>6</sub>(TDDX).

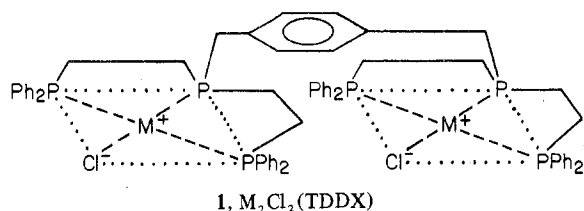
## Results and Discussion

**Rhodium(I) and Iridium(I) Complexes.** Reaction of the complexes M(CO)Cl(PPh<sub>3</sub>)<sub>2</sub> (M = Rh(I), Ir(I)) with TDDX in a 1:2 molar ratio in benzene gave the diamagnetic binuclear complexes M<sub>2</sub>Cl<sub>2</sub>(TDDX) by complete displacement of carbon monoxide and triphenylphosphine from M(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>. The complex Rh<sub>2</sub>Cl<sub>2</sub>(TDDX) was also obtained by the displacement of triphenylphosphine in RhCl(PPh<sub>3</sub>)<sub>3</sub> by TDDX. A simple 1:1 mononuclear derivative of Rh(I) or Ir(I) with TDDX could not be obtained even when the reaction was conducted with a 1:1 molar ratio of metal complex to TDDX. This result indicates a preference of TDDX to form polynuclear rather than mononuclear species. The presence of coordinated chloride in the complexes M<sub>2</sub>Cl<sub>2</sub>(TDDX) is indicated by the observation of a weak band at 276 cm<sup>-1</sup> for the rhodium(I) complex<sup>10,11</sup> and 220 cm<sup>-1</sup> for the iridium(I) complex.<sup>12</sup> The coordinated chloride could not be displaced by the hexafluorophosphate anion. Conductivity data on M<sub>2</sub>Cl<sub>2</sub>(TDDX) complexes (Table I) indicated that they are nonionic species.<sup>13</sup> The nuclear magnetic resonance spectra of the complexes M<sub>2</sub>Cl<sub>2</sub>(TDDX) (entries 1 and 2 Table II) exhibited a doublet at  $\tau$  2.8 corresponding to phenyl protons and a doublet at about  $\tau$  8.0 corresponding to the methylene protons. The spectra thus resemble the spectra<sup>14</sup> of [Ir(triphos)(CO)]Cl and [Rh(triphos)(CO)]Cl where triphos coordinates three coordination positions in the square plane of the metal ions. The complexes M<sub>2</sub>Cl<sub>2</sub>(TDDX) are therefore probably square planar with the ligand TDDX acting as a sixadentate donor binding three coordination sites on each metal ion of the binuclear species as shown in formula 1.

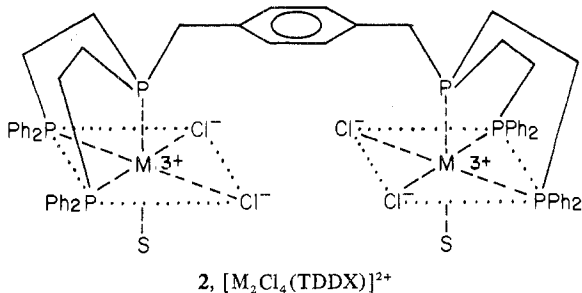
Table III. Infrared Spectra<sup>a</sup> of the Complexes of TDDX

Complex	$\nu(\text{M-Cl})$ , cm <sup>-1</sup>	$\nu(\text{CO})$ , cm <sup>-1</sup>	Other bands, cm <sup>-1</sup>
Rh <sub>2</sub> Cl <sub>2</sub> (TDDX)	276 w		530 s, 540 s, 700 s, 720 s, 740 m
Ir <sub>2</sub> Cl <sub>2</sub> (TDDX)	220 w		520 s, 540 s, 700 s, 720 s, 740 m
Ru <sub>2</sub> Cl <sub>4</sub> (TDDX)(PPh <sub>3</sub> ) <sub>2</sub>	350 w, 370 w		420 m, br, 520 s, 530 s, 565 m, 580 sh, 700 s, 720 s, 740 s
Ru(TDDX)(PF <sub>6</sub> ) <sub>2</sub>			520 s, 530 m, br, 580 sh, 700 s, 720 s
Ru <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	310 w, 335 w, 360 vw		570 s, 710 s, 740 s, 750 sh
Rh <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	320 w, 360 vw		520 m, br, 540 m, br, 570 s, 700 s, 725 s, 740 s
Rh <sub>2</sub> Cl <sub>6</sub> (TDDX)	320 vw, 340 w		530 s, br, 700 s, 730 s, br
Ir <sub>3</sub> Cl <sub>9</sub> (TDDX)	290 w, 310 m, 325 w, 325 w		540 m, br, 570 m, br, 700 m, 720 s, 740 s
Ir <sub>2</sub> Cl <sub>4</sub> (TDDX)(PF <sub>6</sub> ) <sub>2</sub>	310 m, 330 w		520 m, br, 540 m, br, 560 s, 700 s, 720 s
Cr <sub>2</sub> (CO) <sub>6</sub> (TDDX)		1830 m, br, 1890 s, 1920 s, 2010 m	520 s, 540 s, 690 s, 720 s, 740 s
Mo <sub>2</sub> (CO) <sub>6</sub> (TDDX)		1830 m, br, 1910 s, br, 1930 sh, 2010 m	520 s, 540 s, 700 s, 730 s, br
Fe <sub>2</sub> (CO) <sub>6</sub> (TDDX)		1880 m, br, 1940 s, 1980 m, 2020 m	520 s, 540 s, 695 s, 720 s, 740 s

<sup>a</sup> Key: m, medium; s, strong; w, weak; br, broad; vw, very weak.



**Ruthenium(III) and Ruthenium(II) Complexes.** The reaction between hydrated ruthenium trichloride and TDDX in boiling alcohol gave the  $Ru_2Cl_4(TDDX)^{2+}$  cation, isolated as its hexafluorophosphate salt. The conductivity of the compound (Table I) corresponds to a 2:1 electrolyte. The reported<sup>13</sup> conductivities ( $M^{-1} cm^2 ohm^{-1}$ ) for 1:1 and 2:1 electrolytes in DMF are 72–90 and 130–170, respectively. The presence of a coordinated chloride is indicated by infrared absorption bands at 310, 335, and 350  $cm^{-1}$  (Table III). The nmr spectrum of the compound (entry 4, Table II) shows multiplets at  $\tau$  2.3 and 7.0, corresponding to phenyl and methylene protons, respectively. The cation  $Ru_2Cl_4(TDDX)^{2+}$  is probably an octahedral ruthenium(III) derivative with TDDX acting as a sexadentate binucleating ligand. The sixth coordination site on ruthenium(III) may be occupied by a solvent molecule as illustrated by formula 2. The possibility of a five-coordinate

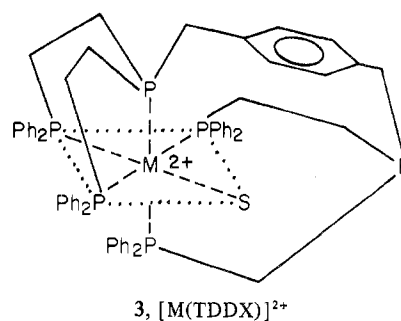


ruthenium(III) species with three coordination positions on each metal ion occupied by TDDX cannot, however, be ruled out. The nmr spectrum is in accord with both possibilities.

The reaction of  $RuCl_2(PPh_3)_2$  with TDDX in boiling benzene precipitated the binuclear complex  $Ru_2Cl_4(TDDX)(PPh_3)_2$ . The complex is diamagnetic and is probably an octahedral ruthenium(II) species with TDDX acting as a sexadentate binucleating donor. The nmr spectrum of the compound shows a multiplet of phenyl protons centered at  $\tau$  2.5 and a multiplet of methylene protons at  $\tau$  7.6. The spectrum of the compound is thus similar to those of tetraphos-2 complexes.<sup>14</sup> One coordination position on each ruthenium atom may thus be considered to be occupied by coordinated chloride. The presence of coordinated chloride in the complex is indicated by the observation of weak bands<sup>15</sup> at 350 and 370  $cm^{-1}$  (Table III). The presence of the coordinated triphenylphosphine is indicated by a medium broad band at 420  $cm^{-1}$ .

The addition of hexafluorophosphate to the solution remaining after the precipitation of  $Ru_2Cl_4(TDDX)(PPh_3)_2$  resulted in the precipitation of the complex  $Ru(TDDX)(PF_6)_2$ . The complex has no coordinated chloride and is the only example in the present work of a mononuclear complex containing penta- or sexadentate TDDX. The compound is insoluble in most of the common solvents, so that nmr and conductivity data could not be obtained. The most probable structure of the complex is shown by formula 3. In this case the use of molecular models indicates that the ligand cannot be sexadentate and cannot coordinate the sixth coordination position of the metal ion. The complex may be polymeric in the solid state.

**Rhodium(III) and Iridium(III) Complexes.** Reaction of hydrated rhodium trichloride with TDDX in boiling ethanol



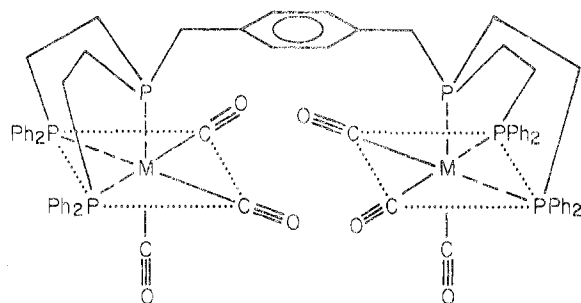
resulted in the precipitation of the binuclear complex  $Rh_2Cl_6(TDDX)$ . This compound exhibited an Rh–Cl stretching frequency at 320  $cm^{-1}$  and a very weak band at 360  $cm^{-1}$ . The Rh–Cl stretching frequency at 320  $cm^{-1}$  may be compared with that of the complex  $RhCl_2(\text{hexaphos})$ , for which a weak Rh–Cl band was observed<sup>1</sup> at 349  $cm^{-1}$ . Addition of ammonium hexafluorophosphate to the solution remaining after the precipitation of  $Rh_2Cl_6(TDDX)$  resulted in the precipitation of the complex  $Rh_2Cl_4(TDDX)(PF_6)_2$ . The compound  $Rh_2Cl_6(TDDX)$  may thus be formulated as  $[Rh_2Cl_4(TDDX)]Cl_2$ . This suggestion is supported by the conductivity data of the two complexes (Table I) which indicate<sup>13</sup> that they are 2:1 electrolytes. The nmr spectra of the complexes  $Rh_2Cl_6(TDDX)$  and  $Rh_2Cl_4(TDDX)(PF_6)_2$  (entries 6 and 5, Table II) were identical and exhibited a multiplet of phenyl protons at  $\tau$  2.3 and a multiplet of methylene protons at  $\tau$  7.3.

The reaction between hydrated iridium trichloride and the hexa(tertiary phosphine) TDDX in boiling ethanol gave a product of the composition  $Ir_3Cl_9(TDDX)$ . The compound exhibited Ir–Cl stretching frequencies at 290, 310, and 325  $cm^{-1}$  and may contain bridging as well as end-coordinated chloro groups. King, *et al.*,<sup>1</sup> have reported a complex of the composition  $(\text{hexaphos})_2Ir_3Cl_9$  by the reaction of hydrated iridium trichloride and hexaphos in ethanol. The complex  $Ir_3Cl_9(TDDX)$  thus differs from the complex prepared by King, *et al.*,<sup>1</sup> in having only one molecule of the hexa(tertiary phosphine) coordinated to two of the three iridium atoms. The insolubility of the compound in common organic solvents precluded the determination of molecular weight, nmr spectra, and conductivity.

Addition of an excess of ammonium hexafluorophosphate to the solution left over after the precipitation of  $Ir_3Cl_9(TDDX)$  precipitated the yellow complex  $Ir_2Cl_4(TDDX)(PF_6)_2$  which is analogous to  $Rh_2Cl_4(PF_6)_2$ . The complex shows Ir–Cl stretching frequencies at 310 (m) and 330 (w)  $cm^{-1}$  (Table III). Because of the insolubility of the compound, molecular weight, nmr spectra, and conductivity measurements could not be done. On the basis of analogy to  $Rh_2Cl_4(PF_6)_2$  the compound may have the structure shown in 2.

**Metal Carbonyls.** The three metal carbonyls  $Cr(CO)_6$ ,  $Mo(CO)_6$ , and  $Fe_2(CO)_9$ , reacted with the hexa(tertiary phosphine) TDDX in boiling 1:1 benzene–toluene solution to give the complexes  $Cr_2(CO)_6(TDDX)$ ,  $Mo_2(CO)_6(TDDX)$ , and  $Fe_2(CO)_9(TDDX)$ , respectively. The infrared frequencies tabulated in Table III all indicate the presence of TDDX as a sexadentate ligand coordinated to two metal ions. In this respect TDDX is analogous to hexaphos, for which complexes of the type  $(\text{hexaphos})M_2(CO)_6$  were obtained<sup>1</sup> by the reaction of hexaphos with  $M_2(CO)_6$  ( $M = Cr, Mo$ ). The conductivity data of the complexes (Table I) show that they are non-electrolytes.<sup>13</sup> The nmr spectra of the complexes  $M_2(CO)_6(TDDX)$  show multiplets around  $\tau$  2.6 and 8.4 corresponding to phenyl and methylene protons, respectively. The spectra thus resemble the spectra of tetraphos-2 complexes<sup>14</sup> where the three coordinating phosphorus atoms occupy facial positions on the octahedron. The probable structure of

$M_2(CO)_6(TDDX)$  is shown in formula 4.



4,  $M_2(CO)_6(TDDX)$

In conclusion it may be mentioned that TDDX differs from hexaphos in forming binuclear complexes in most cases. This behavior may be expected on the basis of the stereochemistry of the ligand, which has two triphos moieties separated by six carbon atoms of the rigid *p*-xylene aromatic system.

Further studies on the reactions of the complexes of TDDX with small molecules such as dioxygen, dinitrogen, hydrogen, carbon monoxide, and nitric oxide are in progress.

**Acknowledgment.** This work was supported by a research grant, No. GP-33266X, from the National Science Foundation.

**Registry No.**  $Rh_2Cl_2(TDDX)$ , 53862-63-8;  $Ir_2Cl_2(TDDX)$ , 53862-64-9;  $Ru_2Cl_4(TDDX)(PPh_3)_2$ , 53862-70-7;  $Ru(TDDX)(PF_6)_2$ , 53862-66-1;  $Ru_2Cl_4(TDDX)(PF_6)_2$ , 53862-72-9;  $Rh_2Cl_4(TDDX)$ ,

$(PF_6)_2$ , 53862-74-1;  $Rh_2Cl_6(TDDX)$ , 53862-75-2;  $Ir_3Cl_9(TDDX)$ , 53906-80-2;  $Ir_2Cl_4(TDDX)(PF_6)_2$ , 53862-68-3;  $Cr_2(CO)_6(TDDX)$ , 53906-82-4;  $Mo_2(CO)_6(TDDX)$ , 53862-69-4;  $Fe_2(CO)_6(TDDX)$ , 53906-81-3;  $\alpha, \alpha'$ -dibromo-*p*-xylene, 623-24-5; triethyl phosphite, 122-52-1;  $(C_2H_5O)_2P(O)CH_2C_6H_4CH_2P(O)(OC_2H_5)_2$ , 4546-04-7; diphenylvinylphosphine, 2155-96-6; TDDX, 53850-32-1;  $Rh(CO)Cl(PPh_3)_2$ , 13938-94-8;  $Ir(CO)Cl(PPh_3)_2$ , 14871-41-1;  $RhCl(PPh_3)_3$ , 14694-95-2;  $RuCl_2(PPh_3)_3$ , 15529-49-4.

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## Induced and Spontaneous Aquation of (Dimethyl sulfoxide)pentaamminecobalt(III) Perchlorate

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Received August 5, 1974

AIC405368

The reaction between permanganate ion and (dimethyl sulfoxide)pentaamminecobalt(III) in aqueous solutions containing hydrochloric and perchloric acids gave approximately the same ratios of chloro- to aquopentaamminecobalt(III) products as reactions between nitrous acid and the azido- or carbamatopentaamminecobalt(III) complexes and hence supplied further evidence for the formation and existence of the five-coordinate pentaamminecobalt(III) complex. Effects of variation of the composition of the reaction medium on the competition reactions of this five-coordinate complex were studied and an effect by so-called "inert" cations was found. Since the aquation of (dimethyl sulfoxide)pentaamminecobalt(III) may possibly proceed through the five-coordinate intermediate, the rate of aquation of the dimethyl sulfoxide complex was studied in  $HClO_4$  and in  $NaClO_4$  solutions to determine whether this effect also occurred in the aquation reaction; it did not.

### Introduction

It has been postulated<sup>1,2</sup> that the five-coordinate intermediate  $Co(NH_3)_5^{3+}$  (here symbolized by  $M^{3+}$ ) was formed in the induced aquations of  $MN_3^{2+}$  and of  $M(CO_2NH_2)_2^{2+}$  upon reaction with  $NO^+$ . Because these two complexes are of the same charge type and involve a common reactant, it is desirable to obtain, if possible, further evidence for the occurrence of  $M^{3+}$  by generating it from other reactions. Such evidence has been obtained by oxidizing (dimethyl sulfoxide)pentaamminecobalt(III), represented by  $M(DMSO)^{3+}$ , with permanganate ion in the presence of competing ligands and is reported here. The oxidation of dimethyl sulfoxide (DMSO) to dimethyl sulfone by  $KMnO_4$  is rapid and quantitative.<sup>3</sup> The dimethyl sulfone is a poor ligand and apparently leaves the first coordination shell of  $Co(III)$  generating  $M^{3+}$ . Also reported here are studies supporting an earlier conclusion<sup>4</sup> that

spontaneous aquation of  $M(DMSO)^{3+}$  in various aqueous media and mixed solvents proceeded by an  $I_d$  mechanism. Pearson and Moore<sup>5</sup> have already shown that the aquation of  $Co(NH_3)_5NO_3^{2+}$  involved a different intermediate than the one formed in the induced aquations.

### Experimental Section

**Chemicals.** (Dimethyl sulfoxide)pentaamminecobalt(III) perchlorate was prepared by the method of Mac-Coll and Beyer.<sup>6</sup> (Acetonitrile)pentaamminecobalt(III) perchlorate was prepared by heating the corresponding aquo complex with liquid acetonitrile containing just enough water to dissolve the aquo complex at 70° until a golden yellow precipitate began to form and the supernatant liquid was a clear yellow. Liquid acetonitrile was added from time to time to replace that lost by evaporation. The mixture was cooled to 0° and filtered, and the precipitate dissolved in a minimum amount of water with slight warming. The solution was cooled to 0° and 1:3 by volume of  $HClO_4-H_2O$  was added dropwise with continuous