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COMPLEXES OF HEXATERTIARY PHOSPHINES AND ARSINES AND THEIR REACTION WITH SMALL MOLECULES†

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The synthesis of a new sexadentate ligand, P,P,P',P'-tetrakis(2-diphenylarsinoethyl) α,α' -diphospha-p-xylene (TDADX) and the preparation of its iridium(I), rhodium(I) and ruthenium (II) complexes are described. When M = Ir and Rh, MCl(CO)(PPh₃)₂ reacts in benzene solution with the ligand TDADX to yield the complexes, [Ir(TDADX)]Cl and Rh₂Cl₂(TDADX). RuCl(CO)(PPh₃)₃Cl reacts with this ligand to yield [RuCl(TDADX)]Cl. Complexes of P,P,P',P'-tetrakis(2-diphenylphosphinoethyl) α,α' -diphospha-p-xylene (TDDX) were also studied for comparison. Molecular hydrogen reacts with the complexes Ir₂Cl₂(TDDX), [Ir(TDADX)]Cl and [RuCl(TDADX)]Cl to form the corresponding hydrido complexes. Reaction of molecular oxygen with Rh₂Cl₂(TDADX) resulted in the formation of the dioxygen complex. Ir(I), Rh(I) and Ru(II) complexes of TDDX and TDADX react with carbon-monoxide to give mixed ligand carbonyl complexes. The complexes Ir₂Cl₂(TDDX), [Ir(TDADX)]Cl, and [RuCl(TDADX)]Cl react with nitric oxide to yield nitrosyl complexes. Infrared spectral data are provided for adducts formed with hydrogen, oxygen, carbon monoxide and nitric oxide.

INTRODUCTION

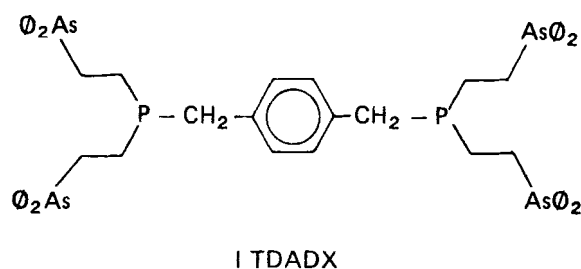
Much interest has been shown in recent years in the synthesis of poly-dentate phosphine and arsine ligands and their metal complexes. Several complexes of C₆H₅P[CH₂CH₂P(C₆H₅)₂]₂-triphos, (C₆H₅)₂PCH₂CH₂P(C₆H₅)CH₂CH₂P(C₆H₅)CH₂CH₂P(C₆H₅)₂-tetraphos-1 and P[CH₂CH₂P(C₆H₅)₂]₃-tetraphos-2 were reported by King *et al.*¹ and by Taqui Khan and Martell². The complexes of the hexatertiary phosphine 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphospha-butane have been reported by King *et al.*³ In addition to hexaphos, an analogous sexadentate ligand, the polytertiary arsine C₆H₄{As[CH₂CH₂As(CH₃)₂]₂}₂ is also known⁴. Recently King and Cloyd have synthesized the hexatertiary phosphine [(CH₃)₂PCH₂CH₂]₂PCH₂CH₂P[CH₂CH₂P(CH₃)₂]₂⁵. Metal complexes of the hexatertiary phosphine P,P,P',P'-tetrakis(2-diphenylphosphinoethyl) α,α' -diphospha-p-xylene (TDDX) were investigated by

Taqui Khan and Martell⁶. The present paper describes the synthesis of the new ligand P,P,P',P'-tetrakis(2-diphenyl-arsinoethyl) α,α' -diphospha-p-xylene (TDADX, I) and the preparation of its complexes with Ir(I), Rh(I) and Ru(II). The reactions of these complexes and those obtained from TDDX, M₂Cl₂(TDDX), (M = Ir(I) and Rh(I)) with the small molecules H₂, O₂, CO and NO are described.

EXPERIMENTAL SECTION

Elemental analysis of the complexes was performed by the Australian Microanalytical Service, CSIRO Australia. The conductivity measurements were made with an Elico conductivity bridge in dimethyl acetamide solutions at 30°. Infrared spectra of the ligand and its complexes were recorded in Nujol Mulls on a Beckman IR-12 spectrophotometer. All the preparations were carried out under an oxygen free nitrogen atmosphere using the Schlenk tube technique. Oxygen gas was obtained from Indian Oxygen Limited. The gases carbon monoxide, nitric oxide and hydrogen were prepared and purified by standard procedures.

† The initial phase of this work was carried out at Texas A & M University with financial support from a research grant, No. GP 33266X, from the National Science Foundation.



The complexes $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$,⁷ $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$,⁸ and $\text{RuCl}_2(\text{PPh}_3)_3$ ⁹ were obtained by standard procedures. Ruthenium trichloride, rhodium trichloride, iridium trichloride and diphenyl chloroarsine were purchased from Ventron-Alpha Inorganics. Triethyl phosphite was obtained from BDH Chemicals. Vinylbromide and α, α' -dibromo-*p*-xylene were obtained from Aldrich Chemical Company and used without further purification. Diphenylvinylarsine was synthesized by an adaptation of the procedure of Berlin and Butler¹⁰.

Synthesis of *P, P', P', P'*-tetrakis(2-diphenylarsinoethyl)- α, α' -diphospha-*p*-xylene (TDADX)

The ligand was prepared by a modification of the procedure described for the preparation of hexaphos by King *et al.*³ The tetraester tetraethyl- α, α' -*p*-xylene diphosphonate was obtained by the method of Issleib and Weichmann¹¹ and its synthesis has been reported in an earlier paper⁶.

For the preparation of TDADX, 26 g (0.07 mole) of the tetraester was dissolved in 100 ml of dry ether and treated dropwise with a suspension of 10 g (0.225 mole) of lithium aluminium hydride in 250 ml of anhydrous ether at 0° over a period of three hours. The mixture was stirred at room temperature for another 35 hours. The reaction mixture was then cooled at 0° and treated dropwise with 200 ml of 6N-hydrochloric acid. The ether layer was separated, dried over anhydrous sodium sulphate and treated with 48.6 g (0.196 mole) of diphenylvinylarsine, 1.0 g of potassium-*t*-butoxide and 200 ml of tetrahydrofuran. The reaction mixture was subsequently treated by the method of King *et al.*³ to give approximately 12.32 g of TDADX (45% yield).

Anal.: Calculated for $\text{C}_{64}\text{H}_{64}\text{P}_2\text{As}_4$: C 64.32; H 5.36; P 5.19

Found: C 63.6; H 5.28; P 4.86.

The compound is very hygroscopic, dissolves readily in methanol, ethanol and chloroform, and is appreciably soluble in benzene. The nmr spectrum of the

ligand has a group of complex asymmetric phenyl proton resonances from τ 2.3–3.0. The *p*-xylene methylene protons give a peak at τ 4.6 and the C_2H_4 methylene protons are observed τ 6.2. The infrared spectrum of the ligand shows peaks at 570 (s), 600 (s), 725 (s) and 735 (s) cm^{-1} .

Preparation of the Complexes $[\text{Ir}(\text{TDADX})]\text{Cl}$ and $\text{Rh}_2\text{Cl}_2(\text{TDADX})$

A mixture of 1.0 mmole of $\text{M}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ (0.7 g for M = Rh(I) and 0.78 g for M = Ir(I)) and 0.50 mmole of TDADX (0.597 g) and 100 ml of benzene was refluxed for about sixteen to seventeen hours. The bright yellow color of the initial complexes $\text{M}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ became dark brown (Rh(I) complex) and light yellow (Ir(I) complex) respectively. After the reaction period was over, the complexes were precipitated by petroleum ether, and recrystallized from dichloromethane-hexane (Rh(I) complex) and chloroform (Ir(I) complex).

Preparation of $[\text{RuCl}(\text{TDADX})]\text{Cl}$

A mixture of 1.0 mmole of $\text{RuCl}_2(\text{PPh}_3)_3$ (1.0 g), 1.0 mmole (0.194 g) of TDADX, and 100 ml of benzene was refluxed for about 24 hours. The brownish black color of the solution changed to chocolate brown at the end of the reaction period. The solution was evaporated to a small volume under reduced pressure. The chocolate brown complex was precipitated by adding petroleum ether, and was recrystallized from chloroform.

Hydrogenation of the Complexes

About 0.020 mmole of each of the five complexes $\text{M}_2\text{Cl}_2(\text{TDDX})$ (M = Ir(I) and Rh(I)), $[\text{Ir}(\text{TDADX})]\text{Cl}$, $\text{Rh}_2\text{Cl}_2(\text{TDADX})$ and $[\text{RuCl}(\text{TDADX})]\text{Cl}$ were dissolved in chloroform and a stream of hydrogen gas was passed through the solutions for about 30 hours. Hydrides of the type $\text{Ir}_2\text{Cl}_2(\text{TDDX})(\text{H})_4$, $\text{Ir}(\text{TDADX})(\text{H})_2\text{Cl}$ and $\text{RuCl}(\text{TDADX})(\text{H})$ were precipitated by petroleum ether.

Oxygenation of the Complexes

Molecular oxygen was bubbled through a 0.020 mmolar solution of the complexes for 24 hours. In the case of the complexes $\text{M}_2\text{Cl}_2(\text{TDDX})$ (M = Ir(I) and Rh(I)) and $\text{Rh}_2\text{Cl}_2(\text{TDADX})$ the dioxygen

complexes were precipitated as dark brown solids. For $[\text{RuCl}(\text{TDADX})]\text{Cl}$ and $[\text{Ir}(\text{TDADX})]\text{Cl}$ there was no indication of any reaction with molecular oxygen.

Carbonylation of the Complexes

About 0.020 mmole of the complexes was dissolved in chloroform and a stream of carbon monoxide was passed through the solutions until there was no further color change. The solutions were concentrated to a small volume and the complexes precipitated by the addition of petroleum ether. The complexes

M_2Cl_2 (TDDX) gave yellow dicarbonyls. In the case of $[\text{Ir}(\text{TDADX})]\text{Cl}$ and $[\text{RuCl}(\text{TDADX})]\text{Cl}$ mono-carbonyls of the type $[\text{Ir}(\text{CO})(\text{TDADX})]\text{Cl}$ and $[\text{RuCl}(\text{CO})(\text{TDADX})]\text{Cl}$, respectively, were obtained. A tetracarbonyl of the type $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ TDADX was obtained with the Rh(I) complex Rh_2Cl_2 (TDADX).

Reaction of the Complexes with Nitric Oxide

Nitric oxide was passed through 0.020 mmole solutions of the complexes until there was no further color change. The complexes Ir_2Cl_2 (TDDX), $[\text{RuCl}(\text{TDADX})]\text{Cl}$ and $[\text{Ir}(\text{TDADX})]\text{Cl}$ yielded the nitrosyl complexes which were precipitated by petroleum ether as light brown solids.

RESULTS AND DISCUSSION

Table Ia presents the analytical data and the molar conductivities of the three TDADX complexes and Table Ib gives analytical data for the reactions of the Ir(I) and Rh(I) TDDX and TDADX complexes with CO , O_2 and NO . Conductivities of the complexes of Ir(I) and Ru(II), indicating uncoordinated chloride, were in the range expected for a 1 : 1 electrolyte in dimethylacetamide^{1,2}.

TABLE Ia
Analytical data for TDADX-metal complexes

Compound	Color	Analysis %*			Molar conductance† (ohm ⁻¹ cm ² mole ⁻¹)	Yield %
		C	H	Cl		
$[\text{Ir}(\text{TDADX})]\text{Cl}$	light	53.72	4.8	2.6	75.8	75
	yellow	(54.05)	(4.4)	(2.49)		
Rh_2Cl_2 (TDADX)	dark	51.82	4.19	5.2	19.8	80
	brown	(52.2)	(4.3)	(4.8)		
$[\text{RuCl}(\text{TDADX})]\text{Cl}$	chocolate	57.02	4.74	5.06	51.4	65
	brown	(56.23)	(4.68)	(5.20)		

*Calculated values in parentheses. †Conductance in dimethylacetamide at 30°C.

TABLE Ib
Analytical data for the products of reactions of Iridium(I)
and Rhodium(I) complexes of TDDX and TDADX with small
molecules

Entry	Compound	Analysis %*	
		C	H
1	Ir_2Cl_2 (TDDX)(O_2) ₂	48.55 (48.0)	4.05 (3.98)
2	Rh_2Cl_2 (TDDX)(O_2) ₂	56.05 (56.51)	4.72 (4.71)
3	Rh_2Cl_2 (TDADX)(O_2) ₂	49.98 (50.97)	4.25 (4.25)
4	Ir_2Cl_2 (TDDX)(CO) ₄	50.64 (51.41)	4.07 (4.19)
5	Rh_2Cl_2 (TDDX)(CO) ₄	57.46 (57.99)	4.46 (4.55)
6	Rh_2Cl_2 (TDADX)(CO) ₄	50.98 (51.54)	4.01 (4.04)
7	$[\text{IrCl}(\text{TDADX})(\text{CO})]$	52.62 (53.79)	4.47 (4.41)
8	$[\text{Ir}_2(\text{TDDX})(\text{NO})_2]\text{Cl}_4$	48.70 (47.8)	4.12 (3.98)
9	$[\text{Ir}(\text{TDADX})(\text{NO})]\text{Cl}_2$	50.78 (51.6)	4.25 (4.29)

*Calculated values in parentheses.

TABLE II
Infrared spectra of TDADX-metal complexes and the reaction products of TDADX and TDDX-metal complexes with
molecular hydrogen, molecular oxygen, carbon monoxide and nitric oxide

Entry	Compound	(M-Cl)	(M-H)	(M-O ₂)	(M-CO)	(M-NO)	Other bands
1	[Ir(TDADX)]Cl	325(s)	-	-	-	-	500(sh), 535(s), 575(w), 680(s) 730-740(s)
2	Rh ₂ Cl ₂ (TDADX)	315(s)	-	-	-	-	510(w), 540(vs), 690(s), 715(s), 745(w)
3	[RuCl(TDADX)]Cl	325(s)	-	-	-	-	540(s), 690(s), 715(s), 745(w)
4	Ir ₂ Cl ₂ (TDDX)(H) ₄	-	1950(w)	-	-	-	690(s), 720(s), 740(s)
5	Ir(H) ₂ (TDADX)Cl	-	2000(s)	-	-	-	680(s), 720(s), 800(s & br)
6	RuHCl(TDADX)	-	2050(m)	-	-	-	690(s), 715(s), 800(s), 1110(br)
7	Ir ₂ Cl ₂ (TDDX)(O ₂)	-	1960(s)	800-810 (s & br)	-	-	
8	Rh ₂ Cl ₂ (TDDX)(O ₂)	-	-	800(s & br)	-	-	695(s), 710(s), 1010(w)
9	Rh ₂ Cl ₂ (TDADX)(O ₂)	-	-	880(br)	-	-	510(sh), 530(s), 685(s), 735(s), 790-800(br)
10	Ir ₂ Cl ₂ (TDDX)(CO) ₄	-	-	-	1990(s)	-	680(s), 715(s), 730(s), 800(br)
11	Rh ₂ Cl ₂ (TDDX)(CO) ₄	-	-	-	1960(s)	-	530(s), 690(s), 720(s), 735(s)
12	Rh ₂ Cl ₂ (TDADX)(CO) ₄	-	-	-	2050(s)	-	610(s), 710(s), 740(w), 790(s), 1110(br)
13	[RuCl(TDADX)(CO)]Cl	-	-	-	1980(s & br)	-	
14	Ir(TDADX)(CO)Cl	-	-	-	2020(s & br)	-	680(s), 710(s), 735(s), 790(s), 1100(br)
15	[Ir ₂ TDDX(NO)] ²⁺	-	-	-	2010(s)	-	680(s), 735(s), 790(s)
16	[Ir(TDADX)(NO)] ²⁺	-	-	-	2015(s)	1750(s)	540(s & br), 720(sh), 740(s)
17	[RuCl(TDADX)(NO)] ²⁺	-	-	-	-	1740(s)	520(s), 700(w), 745(s), 865(w), 980(w)
		-	-	-	-	1865-1885 (s & br)	685(s), 710(s), 735(w), 790(s)

Table II presents the infrared spectra of the TDADX complexes and also the spectra of the reaction products with molecular hydrogen, molecular oxygen, carbon monoxide and nitric oxide, of the three TDADX complexes and the two TDDX complexes $M_2Cl_2(TDDX)$ ($M = Ir(I)$ and $Rh(I)$). The infrared spectrum of $[RuCl(TDADX)]Cl$ shows a single band of medium intensity at 325 cm^{-1} . In this case TDADX acts as a tetradentate ligand, which may be coordinated to a single ruthenium(II) atom either through one phosphorus and three arsenic or through all four arsenic donors. Since phosphorus has better donor properties than arsenic the former possibility seems more reasonable than the latter.

In the complex $Rh_2Cl_2(TDADX)$ the ligand acts as a hexaligand binuclear donor probably coordinating to each square planar rhodium(I) ion through one phosphorus and two arsenic donors. In the case of $[Ir(TDADX)]Cl$ only the mononuclear complex is obtained. The ligand in this case seems to bind the metal ion in a tetradentate fashion. It is interesting to compare the $M-Cl$ stretching frequency in $Rh_2Cl_2(TDADX)$ at 315 cm^{-1} to that obtained at 270 cm^{-1} for the corresponding $Rh_2Cl_2(TDDX)$ ⁶ complex. This difference is probably due to the fact that chlorine may be *trans* to arsine in the former complex whereas it is *trans* to phosphorus in the latter complex. As the arsine donor group has a low *trans* effect compared to that of the corresponding phosphine group, the TDADX complex forms the stronger *trans* chlorine bond.

Hydrogenation of the complexes in chloroform solution resulted in the formation of hydrido complexes which were very unstable. A *cis* dihydride was formed in the case of $Ir_2Cl_2(TDDX)$, confirmed by the appearance of IR peaks at 1950 and 2000 cm^{-1} . $[Ir(TDADX)]Cl$ and $[RuCl(TDADX)]Cl$ also reacted with molecular hydrogen to form $Ir(H_2)(TDADX)Cl$ and $RuH(TDADX)Cl$ but in the case of $Rh_2Cl_2(TDADX)$ and $Rh_2Cl_2(TDADX)$ stable hydrides could not be isolated from solution. The bis dioxygen complexes $Ir_2Cl_2(TDDX)(O_2)_2$, $Rh_2Cl_2(TDDX)(O_2)_2$ and $Rh_2Cl_2(TDADX)(O_2)_2$ are indicated by the appearance of strong broad bands at $800-810$, 800 , and 880 cm^{-1} , respectively. It is thus seen that for the compounds studied only binuclear complexes form stable dioxygen complexes.

Reaction with carbon monoxide resulted in the formation of monocarbonyls in the case of $[Ir(TDADX)]Cl$ and $[RuCl(TDADX)]Cl$ confirmed by the appearance of IR peaks at 2015 cm^{-1} and 2010 cm^{-1} , respectively. *Cis* dicarbonyls were obtained for the complexes $Rh_2Cl_2(TDDX)$ and $Rh_2Cl_2(TDADX)$, confirmed by IR peaks at 1960 , 2050 cm^{-1} and 1980 , 2020 cm^{-1} , respectively,

which are characteristic of *cis* dicarbonyls^{1,3}. For the complex $Ir_2Cl_2(TDDX)$ a *trans* dicarbonyl of the type $Ir_2Cl_2(CO)_4(TDDX)$ was obtained. The coordinated phosphine and arsine groups of the ligands TDDX and TDADX possibly undergo rearrangement of the coordination sites on the metal to provide coordination positions for the carbonyl groups. Nitric oxide combines with Ir(I) complexes to yield $[Ir_2(TDDX)(NO)_2]^{4+}$ and $[IrNO(TDADX)]^{2+}$. In these complexes the nitrosyl ligand has been assigned formally as NO^- on the basis of IR and elementary analysis data. The observed nitric oxide frequencies are similar to those of other Ir(III) nitrosyl complexes^{1,4} where NO is coordinated as a bent NO^- group. The ruthenium complex $[RuCl(TDADX)]Cl$ also gave a nitrosyl complex $[RuCl(NO)(TDADX)]^+$ in which NO is probably coordinated as NO^+ ^{5,16}. The value of ν_{NO} reported for this complex is in close agreement with the values reported previously for similar nitrosyl complexes of ruthenium(II)¹⁷

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