Cationic Rhodium(I) Complexes. 4.[1] Oxidative Addition Reactions of Di(tertiary phosphine and arsine) Complexes

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The reactions of the rhodium(I) complexes [Rh(L$_2$)$_2$]X (L$_2$ = *cis*-(C$_6$H$_5$)$_2$AsCH=CHAs(C$_6$H$_5$)$_2$ (vdiars), *o*-C$_6$H$_4$(As(CH$_3$)$_2$)$_2$ (diars), CH$_3$(C$_6$H$_5$)PCH$_2$CH$_2$P(C$_6$H$_5$)CH$_3$ (MPPE); X$^-$ = Cl$^-$, PF$_6^-$) with halogens, acid chlorides, sulfonyl chlorides, sulfur dioxide, and molecular oxygen are described. While only [Rh(diars)$_2$]PF$_6$ reacts with acid chlorides to give *trans*-[Rh(COR)Cl(diars)$_2$]PF$_6$ (R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$, 3,5-(NO$_2$)$_2$C$_6$H$_3$), all three complexes give the sulfinato-*S* complexes *trans*-[Rh(S(O)$_2$R)Cl(L)$_2$]PF$_6$ (R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$, *p*-BrC$_6$H$_4$, *m*-NO$_2$C$_6$H$_4$, *p*-CH$_3$C$_6$H$_4$, 1-naphthyl) with sulfonyl halides. For L$_2$ = MPPE and R = *m*-NO$_2$C$_6$H$_4$, *p*-CH$_3$C$_6$H$_4$, or 1-naphthyl, *O*-sulfinate species are also produced. Reaction with dioxygen or sulfur dioxide produces five-coordinate 1:1 adducts containing "side-on" bonded dioxygen and S-bonded sulfur dioxide, respectively. The dioxygen adducts react further with sulfur dioxide to give sulfate derivatives, [Rh(SO$_4$)(L$_2$)$_2$]X, which can also be prepared from the sulfur dioxide adducts upon treatment with dioxygen. The [Rh(O$_2$)(L$_2$)$_2$]X complexes also react with nitrogen dioxide to yield a variety of nitrate derivatives including [Rh(OH)(NO$_3$)(MPPE)$_2$]PF$_6$, [Rh-(Cl)(NO$_3$)(diars)$_2$]PF$_6$, and [Rh(NO$_3$)(NO$_2$)(vdiars)$_2$]Cl.

Introduction

Although there has been considerable study of oxidative addition reactions of neutral Rh(I) and Ir(I) complexes,[2-8] that reported on similar reactions of cationic species has been less extensive.[9-12] Following the preparation of a series of complexes of formula [Rh(L$_2$)$_2$]X (L$_2$ = di(tertiary phosphine or arsine); X = Cl$^-$, PF$_6^-$, BF$_4^-$)[1,13] we undertook to study their oxidative addition reactions. Unlike the systems studied previously, the absence of labile, monodentate ligands and the coordinative saturation of the adducts formed suggested that problems of dissociation, isomerization, and further reaction of the adducts once formed would be minimized. This in turn should enable a more direct study of the course of the oxidative addition process to be made. We report here some results of this study.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under nitrogen. All reactions were routinely performed in an atmosphere of prepurified nitrogen as the starting complexes and many of the reactant molecules are sensitive to air and/or moisture. The ligands *cis*-1,2-bis(diphenylarsino)ethylene (vdiars),[14] *o*-phenylenebis(dimethylarsine) (diars),[15] and 1,2-bis(methylphenyl-phosphino)ethane (MPPE)[1] and the starting complexes [Rh(L$_2$)$_2$]Cl (L$_2$ = vdiars, diars, and MPPE)[1] were prepared by published procedures while 1,2-bis(diphenylarsino)ethane (EDA) was purchased from Strem Chemicals. Hydrated rhodium(III) chloride was obtained from A. D. Mackay, Inc. The acid chlorides and sulfonyl chlorides used were either vacuum distilled or recrystallized from diethyl ether under nitrogen and were stored under nitrogen. All other chemicals were reagent grade and were used as received. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Meade Microanalytical Laboratory, Amherst, Mass. Infrared spectra were obtained on Beckman IR-18A and IR-11 or Perkin-Elmer 521 spectrophotometers using Nujol mulls unless otherwise specified while NMR spectra were obtained on JEOL MH-100 and C6O-HL spectrometers.

Preparation of [Rh(L$_2$)$_2$]PF$_6$. To 0.295 g (0.60 mmol) of [Rh(C$_8$H$_{12}$)Cl]$_2$ in 40 ml of tetrahydrofuran was added 0.304 g (1.20 mmol) of AgPF$_6$ and the mixture stirred for 20 min. The precipitated AgCl was removed by filtration under nitrogen through a pad of diatomaceous earth and to the yellow filtrate was added 2.4 mmol of the appropriate ligand. Crystallization was induced by the addition of diethyl ether and the yellow to orange crystalline product was filtered under nitrogen, washed with more ether, and dried in vacuo. Of the four complexes prepared, only [Rh(diars)$_2$]PF$_6$ is oxygen sensitive in the solid state. The avidity of this species for oxygen, even in the solid state, is such that it is best prepared just prior to use.

Preparation of Sulfonyl Chloride Adducts. To 0.3 mmol of the appropriate di(tertiary phosphine or arsine) complex in 15 ml of dichloromethane was added 0.35 mmol of the sulfonyl chloride. The yellow-orange solution quickly turned bright yellow and after 5 min of stirring the product was precipitated with diethyl ether. The yellow, air-stable adduct was recrystallized from dichloromethane–diethyl ether and was dried in vacuo.

Preparation of Chloroacylbis(*o*-phenylenebis(dimethylarsine))-rhodium(III) Hexafluorophosphate, [Rh(COR)Cl(diars)$_2$]PF$_6$. To a solution of 0.33 g (0.4 mmol) of [Rh(diars)$_2$]PF$_6$ in acetone was added 0.4 mmol of the appropriate acyl chloride. After stirring for 10 min the solution had become light yellow and solid had precipitated. The reaction mixture was filtered through a pad of diatomaceous earth and hexane was slowly added to the filtrate to precipitate a pale yellow solid. The solid was taken up in acetone and chromatographed on a 1.5 × 25 cm column of deactivated Florisil (60/100 mesh, 1 g of H$_2$O/100 g of Florisil). Elution with acetone gave a yellow band from which the product could be obtained by precipitation with diethyl ether followed by filtration and drying in vacuo.

Dichlorobis(*o*-phenylenebis(dimethylarsine))rhodium(III) Hexa-fluorophosphate–Hemi(dichloromethane), [RhCl$_2$(diars)$_2$]PF$_6$·0.5CH$_2$Cl$_2$. A solution of 0.206 g (0.3 mmol) of [Rh(diars)$_2$]PF$_6$ in 15 ml of dichloromethane was stirred under 1 atm of Cl$_2$ for 15 min by which time the yellow-orange solution had turned to a cloudy yellow. Removal of the excess Cl$_2$ followed by addition of 30 ml of diethyl ether afforded the product as a yellow powder which was filtered off, washed with ether, and dried in vacuo.

Dibromobis(*o*-phenylenebis(dimethylarsine))rhodium(III) Hexa-fluorophosphate Acetone Solvate, [RhBr$_2$(diars)$_2$]PF$_6$·CH$_3$COCH$_3$. To a solution of 0.41 g (0.5 mmol) of [Rh(diars)$_2$]PF$_6$ in 20 ml of methylene chloride was added 0.08 g (0.5 mmol) of Br$_2$. After 10 min of stirring, the solution became yellow and a solid began to precipitate. Addition of diethyl ether and cooling to 0 °C completed the precipitation. The product was filtered off and was recrystallized from acetone–diethyl ether to yield bright yellow crystals which were washed with diethyl ether and dried in vacuo.

Diiodobis(*o*-phenylenebis(dimethylarsine))rhodium(III) Hexa-fluorophosphate Acetone Solvate, [RhI$_2$(diars)$_2$]PF$_6$·CH$_3$COCH$_3$. To a solution of 0.123 g (0.15 mmol) of [Rh(diars)$_2$]PF$_6$ in 25 ml of acetone was added 0.38 g (0.15 mmol) of I$_2$. The solution immediately became a dirty brown and upon being stirred for 10 min changed further to a cloudy orange-red color. The reaction mixture was filtered to yield a small amount of red and orange crystals which from the infrared spectrum was judged to be a mixture of [RhI$_2$(diars)$_2$]PF$_6$ and [RhI$_2$(diars)$_2$]I$_3$. Addition of diethyl ether to the yellow-orange filtrate afforded the product as orange crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

The following complexes were prepared analogously: **dichloro-bis(1,2-bis(methylphenylphosphino)ethane)rhodium(III) hexa-fluorophosphate dichloromethane solvate, [RhCl$_2$(MPPE)$_2$]PF$_6$·0.25CH$_2$Cl$_2$,** pale yellow crystals on addition of diethyl ether; **di-bromobis(1,2-bis(methylphenylphosphino)ethane)rhodium(III) hex-afluorophosphate acetone solvate, [RhBr$_2$(MPPE)$_2$]PF$_6$·CH$_3$COCH$_3$,** bright yellow crystals from acetone–diethyl ether; **diiodobis(1,2-

bis(methylphenylphosphino)ethane)rhodium(III) hexafluorophosphate, [RhI$_2$(MPPE)$_2$]PF$_6$, brown crystals from *N,N*-dimethylform-amide–methanol–diethyl ether; **dibromobis(*cis*-1,2-bis(diphenyl-arsino)ethylene)rhodium(III) hexafluorophosphate acetone solvate, [RhBr$_2$(vdiars)$_2$]PF$_6$·CH$_3$COCH$_3$,** yellow-orange crystals from methanol–acetone–diethyl ether; **diiodobis(*cis*-1,2-bis(diphenyl-arsino)ethylene)rhodium(III) hexafluorophosphate, [RhI$_2$(vdiars)$_2$]PF$_6$,** yellow-brown crystals from acetone–diethyl ether.

Dioxygenbis(1,2-bis(methylphenylphosphino)ethane)rhodium Hexafluorophosphate, [Rh(O$_2$)(MPPE)$_2$]PF$_6$. Dioxygen was bubbled through a solution of 0.2 g (0.25 mmol) of [Rh(MPPE)$_2$]PF$_6$ in 10 ml of 2-butanone for 5 min by which time the solution had become brown. Addition of diethyl ether precipitated the product as pale brown microcrystals which were filtered off, washed with diethyl ether, and air-dried.

Dioxygenbis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium Hexafluorophosphate, [Rh(O$_2$)(vdiars)$_2$]PF$_6$. This was prepared in an analogous manner to the previous complexes and obtained as tan crystals from 2-butanone–diethyl ether.

Disulfurbis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium Hexafluorophosphate, [Rh(S$_2$)(vdiars)$_2$]PF$_6$. A solution of 0.2 g (0.406 mmol) of [Rh(C$_8$H$_{12}$)Cl]$_2$ in 20 ml of tetrahydrofuran was treated with 0.204 g (0.812 mmol) of AgPF$_6$ and the precipitated AgCl removed by filtration through a pad of diatomaceous earth. To the filtrate was added 0.79 g (1.624 mmol) of *cis*-1,2-bis(diphenyl-arsino)ethylene followed by 0.052 g (0.203 mmol) of S$_8$. The solution immediately became dark brown and a yellow solid, presumed to be [Rh(vdiars)$_2$]PF$_6$, precipitated. The precipitate was dissolved by the addition of the minimum volume of acetone and a further 0.052 g of S$_8$ was added. After being stirred for 3 h the solution was concentrated to half its original volume under reduced pressure and filtered to remove unreacted S$_8$. Addition of diethyl ether and cooling to 0 °C precipitated the product as brown crystals. Upon filtration in air, part of the product turned green but on dissolution in a mixture of acetone and dichloromethane a dark brown solution was obtained. This solution was filtered, concentrated to ca. 5 ml under reduced pressure, and treated with diethyl ether to afford the product as dark brown crystals.

Disulfurbis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium Chloride, [Rh(S$_2$)(diars)$_2$]Cl. To an acetone solution of 0.25 g (0.23 mmol) of [Rh(vdiars)$_2$]Cl was added 0.0146 g (0.0575 mmol) of S$_8$. The solution immediately became a dark greenish color and a purplish solid precipitated. After 2 h of stirring diethyl ether was added and the solid filtered off. This solid was dissolved in dichloromethane and the solution filtered to remove unreacted sulfur. Addition of acetone followed by diethyl ether afforded the product as light purple needles.

(Sulfur dioxide)bis(*o*-phenylenebis(dimethylarsine))rhodium Hexafluorophosphate, [Rh(SO$_2$)(diars)$_2$]PF$_6$. A solution of freshly prepared [Rh(diars)$_2$]PF$_6$ (0.20 g, 0.25 mmol) in 10 ml of di-chloromethane was stirred in an atmosphere of sulfur dioxide. After a few minutes, yellow crystals began to form and the precipitation was completed by addition of diethyl ether. The product was filtered under nitrogen, washed with diethyl ether, and dried in vacuo.

Reaction of Sulfur Dioxide with [Rh(diars)$_2$]Cl. A solution of [Rh(diars)$_2$]Cl (0.2 g, 0.29 mmol) in 10 ml of dichloromethane was added dropwise to a saturated solution of sulfur dioxide in 10 ml of acetonitrile. An extremely insoluble, orange, crystalline precipitate formed immediately which was filtered off, washed with diethyl ether, and dried in a nitrogen stream.

(Sulfur dioxide)bis(1,2-bis(methylphenylphosphino)ethane)rhodium Hexafluorophosphate, [Rh(SO$_2$)(MPPE)$_2$]PF$_6$. Sulfur dioxide was passed through a solution of 0.2 g (0.25 mmol) of [Rh(MPPE)$_2$]PF$_6$ in 15 ml of dichloromethane for 2 min. Diethyl ether was added to the resulting orange solution to precipitate the product as yellow orange crystals. These were filtered off, washed with diethyl ether, and dried in a nitrogen stream.

(Sulfur dioxide)bis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium Hexafluorophosphate Dichloromethane Solvate, [Rh(SO$_2$)(diars)$_2$]-PF$_6$·CH$_2$Cl$_2$. A solution of 0.2 g (0.17 mmol) of [Rh(vdiars)$_2$]PF$_6$ in 10 ml of dichloromethane was stirred in an atmosphere of sulfur dioxide for 5 min to yield an orange solution. Addition of diethyl ether precipitated the product as yellow crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

Sulfatobis(1,2-bis(methylphenylphosphino)ethane)rhodium(III) Hexafluorophosphate, [Rh(SO$_4$)(MPPE)$_2$]PF$_6$. Dioxygen was bubbled through a solution of [Rh(MPPE)$_2$]PF$_6$ (0.2 g, 0.25 mmol) in 10 ml

of dichloromethane to give a dirty brown solution. After being swept with nitrogen to remove excess O$_2$, the solution was briefly treated with gaseous SO$_2$ whereupon the solution became a cloudy yellow. Addition of ethanol gave a clear yellow solution from which the product could be obtained following dilution with diethyl ether. Recrystallization from dichloromethane–ethanol–diethyl ether afforded yellow crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

Sulfatobis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium(III) Hexafluorophosphate, [Rh(SO$_4$)(vdiars)$_2$]PF$_6$. Dioxygen was passed through a solution of [Rh(vdiars)$_2$]PF$_6$ (0.24 g, 0.2 mmol) in 10 ml of 2-butanone until it became purplish brown. After sweeping of the solution with nitrogen, sulfur dioxide was passed through to give an immediate yellow precipitate. Removal of the solvent under reduced pressure followed by recrystallization of the residue from acetone–diethyl ether afforded the product as yellow crystals which were filtered off, washed with diethyl ether, and dried in vacuo at 100 °C.

Sulfatobis(*o*-phenylenebis(dimethylarsine))rhodium(III) Hexafluorophosphate, [Rh(SO$_4$)(diars)$_2$]PF$_6$. Dioxygen was bubbled through a solution of freshly prepared [Rh(diars)$_2$]PF$_6$ (0.2 g, 0.25 mmol) in 10 ml of acetone until the orange solution became greenish yellow. Sulfur dioxide was then admitted to the reaction vessel and the solution stirred under 1 atm of this gas. A pale yellow solid rapidly formed and after several minutes precipitation was completed by addition of diethyl ether. This was filtered off under nitrogen, washed with diethyl ether and dried in vacuo.

Hydroxonitratobis(1,2-bis(methylphenylphosphino)ethane)rhodium(III) Hexafluorophosphate Monohydrate, [Rh(OH)(NO$_3$)-(MPPE)$_2$]PF$_6$·H$_2$O. Dioxygen was passed through a solution of [Rh(MPPE)$_2$]PF$_6$ (0.2 g, 0.25 mmol) in 10 ml of methanol–acetone (1:1, v/v) until it became brown. Sweeping with nitrogen followed by passage of nitrogen dioxide gave a yellow solution from which a white solid soon precipitated. This was collected and recrystallized from acetone–diethyl ether to give the product as off-white crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

Chloronitratobis(*o*-phenylenebis(dimethylarsine))rhodium(III) Hexafluorophosphate, [RhCl(NO$_3$)(diars)$_2$]PF$_6$. Dioxygen was passed through a solution of [Rh(diars)$_2$]Cl (0.18 g, 0.25 mmol) in 10 ml of dichloromethane for 5 min. Excess dioxygen was removed with a nitrogen sweep and nitrogen dioxide was bubbled through the solution whereupon it became a pale green color. After sweeping out of excess NO$_2$ a solution of LiPF$_6$ (0.046 g, 0.30 mmol) in 5 ml of methanol was added, followed by diethyl ether, whereupon a sticky, pale green solid precipitated. This was filtered off and triturated with acetone to give a yellow solution and a small gray-green solid residue. The residue was removed by filtration and the two filtrates were combined and concentrated under reduced pressure until a pale yellow solid precipitated. This was collected and recrystallized from acetone–methanol–diethyl ether to give the product as light yellow crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

Chloronitratobis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium(III) Hexafluorophosphate, [RhCl(NO$_3$)(vdiars)$_2$]PF$_6$. In a similar manner, [Rh(vdiars)$_2$]Cl (0.2 g, 0.17 mmol) in 10 ml of dichloromethane was treated successively with dioxygen and nitrogen dioxide. Addition of 0.033 g (0.2 mmol) of NH$_4$PF$_6$ in ethanol (5 ml) followed by concentration of the solution under reduced pressure yielded a light yellow solid. Recrystallization from acetone–ethanol afforded the product as light yellow crystals which were filtered off, washed with diethyl ether, and dried in vacuo.

Nitronitratobis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium(III) Chloride, [Rh(NO$_2$)(NO$_3$)(vdiars)$_2$]Cl. Dioxygen was passed through a solution of [Rh(vdiars)$_2$]Cl (0.2 g, 0.18 mmol) in 2-butanone (10 ml) whereupon it became purplish brown and a solid precipitated. Removal of excess O$_2$ with a nitrogen sweep and passage of nitrogen dioxide resulted in dissolution of the solid and a production of a yellow solution. Addition of a large volume of diethyl ether precipitated a buff-orange solid. This was dissolved in dichloromethane and the solution concentrated under reduced pressure. Addition of tetra-hydrofuran and diethyl ether precipitated the product as light orange crystals which were filtered off, washed with diethyl ether, and dried in vacuo at 100 °C.

Results and Discussion

Analytical data for all complexes are presented in Table I while Tables II–IV contain pertinent infrared spectroscopic data. The complexes [Rh(diars)$_2$]PF$_6$, [Rh(vdiars)$_2$]PF$_6$, and

Table I. Analytical Data

No.	Complex	Fd.				Calc.				MP(°C)[a]	Yield(%)
		C	H	Cl	y[b]	C	H	Cl	y[b]		
1	[Rh(CH$_3$SO$_2$)Cl(diars)$_2$]PF$_6$	26.5	3.6	4.2		26.98	3.78	3.79		155d	70
2	[Rh(C$_2$H$_5$SO$_2$)Cl(diars)$_2$]PF$_6$	26.9	4.1	4.0		27.85	3.94	3.74		195d	66
3	[Rh(C$_6$H$_5$SO$_2$)Cl(diars)$_2$]PF$_6$	30.7	3.7	3.7		31.33	3.74	3.56		235d	71
4	[Rh(p-BrC$_6$H$_4$SO$_2$)Cl(diars)$_2$]PF$_6$·0.5CH$_2$Cl$_2$	29.0	3.5	6.5	2.8[c]	28.47	3.31	6.52	2.87[c]	181d	75
5	[Rh(m-O$_2$NC$_6$H$_4$SO$_2$)Cl(diars)$_2$]PF$_6$	30.6	3.6	3.9		29.98	3.49	3.40		230d	60
6	[Rh(p-CH$_3$C$_6$H$_4$SO$_2$)Cl(diars)$_2$]PF$_6$	31.8	3.8	3.6	3.0[c]	32.06	3.90	3.51	3.17[c]	255d	57
7	[Rh(2-C$_{10}$H$_7$SO$_2$)Cl(diars)$_2$]PF$_6$	34.6	4.2	3.6	2.7[c]	34.43	3.73	3.38	3.06[c]	177d	65
8	[Rh(CH$_3$SO$_2$)Cl(vdiars)$_2$]PF$_6$·CH$_2$Cl$_2$	45.8	3.8	7.7	2.3[c]	45.51	3.29	7.45	2.25[c]	201	89
9	[Rh(C$_2$H$_5$SO$_2$)Cl(vdiars)$_2$]PF$_6$	48.5	4.0	3.1		48.29	3.53	2.64		195d	92
10	[Rh(C$_6$H$_5$SO$_2$)Cl(vdiars)$_2$]PF$_6$·0.5CH$_2$Cl$_2$	49.0	3.5	4.6		48.94	3.52	4.94		217	94
11	[Rh(p-BrC$_6$H$_4$SO$_2$)Cl(vdiars)$_2$]PF$_6$	47.1	3.5			47.32	3.29			220d	86
12	[Rh(m-O$_2$NC$_6$H$_4$SO$_2$)Cl(vdiars)$_2$]PF$_6$	48.5	3.3	2.5	2.2[c]	47.31	3.29	2.97	2.25[c]	194d	78
13	[Rh(p-CH$_3$C$_6$H$_4$SO$_2$)Cl(vdiars)$_2$]PF$_6$	50.0	3.65	2.75		50.43	3.59	2.52		205d	84
14	[Rh(2-C$_{10}$H$_7$SO$_2$)Cl(vdiars)$_2$]PF$_6$·CH$_2$Cl$_2$	49.9	3.3	6.9	2.1[c]	49.51	3.44	6.93	2.28[c]	210	83
15	[Rh(p-BrC$_6$H$_4$SO$_2$)Cl(EDA)$_2$]PF$_6$	47.1	3.4			47.19	3.56			185	82
16	[Rh(p-CH$_3$C$_6$H$_4$SO$_2$)Cl(EDA)$_2$]PF$_6$	49.7	3.9	2.6		50.21	3.94	2.51		189d	78
17	[Rh(CH$_3$SO$_2$)Cl(MPPE)$_2$]Cl	48.5	5.5			49.45	5.42			298d	65
18	[Rh(m-O$_2$NC$_6$H$_4$SO$_2$)Cl(MPPE)$_2$]Cl	49.6	4.8	8.1		50.23	4.89	7.81		232d	82
19	[Rh(p-CH$_3$C$_6$H$_4$SO$_2$)Cl(MPPE)$_2$]Cl	49.8	5.4	8.5		53.37	5.41	8.08		274d	92
20	[Rh(2-C$_{10}$H$_7$SO$_2$)Cl(MPPE)$_2$]Cl	54.3	5.5	8.1	3.6[c]	55.21	5.20	7.76	3.51[c]	225d	89
21	[Rh(CH$_3$CO)Cl(diars)$_2$]PF$_6$	29.7	4.1	4.0		29.89	3.87	3.88		280d	26
22	[Rh(C$_2$H$_5$CO)Cl(diars)$_2$]PF$_6$	29.8	4.1	4.8		29.75	4.02	3.82		226d	29
23	[Rh(C$_6$H$_5$CO)Cl(diars)$_2$]PF$_6$	33.5	4.1	4.1		33.76	3.85	3.69		226d	38
24	[Rh(3,5-(O$_2$N)$_2$C$_6$H$_3$CO)Cl(diars)$_2$]PF$_6$	28.4	3.4	3.3		28.65	3.21	3.13		—	25
25	[(RhCl(diars)$_2$)$_2$(OC(CH$_2$)$_4$CO)]PF$_6$	29.9	4.0	3.5		30.31	3.95	3.89		—	21
26	[RhCl$_2$(diars)$_2$]PF$_6$·0.5CH$_2$Cl$_2$	24.0	3.4	11.9		24.24	3.43	11.41		>330	61
27	[RhBr$_2$(diars)$_2$]PF$_6$·CH$_3$COCH$_3$	27.5	3.8		16.5[d]	26.62	3.66		16.12[d]	>330	33
28	[RhI$_2$(diars)$_2$]PF$_6$·CH$_3$COCH$_3$	24.1	3.4		22.0[e]	24.40	3.36		22.22[e]	—	25
29	[RhCl$_2$(MPPE)$_2$]PF$_6$·0.25CH$_2$Cl$_2$	42.3	4.8	9.7	12.7[f]	43.58	4.56	9.97	12.83[f]	—	82
30	[RhBr$_2$(MPPE)$_2$]PF$_6$·CH$_3$COCH$_3$	40.8	4.65		13.9[d]	41.14	4.58		15.75[d]	301d	76
31	[RhI$_2$(MPPE)$_2$]PF$_6$	36.7	4.0		26.6[e]	36.59	3.85		24.16[e]	269d	68
32	[RhBr$_2$(vdiars)$_2$]PF$_6$·CH$_3$COCH$_3$	46.0	3.5		10.9[d]	46.05	3.52		11.14[d]	309d	74
33	[RhI$_2$(vdiars)$_2$]PF$_6$	42.2	3.0		16.9[e]	42.47	3.02		17.26[e]	299d	82
34	[Rh(O$_2$)(MPPE)$_2$]PF$_6$	46.3	4.9		13.0[f]	46.39	4.88		13.76[f]	150d	67
35	[Rh(O$_2$)(vdiars)$_2$]PF$_6$	50.5	3.5		9.2[f]	50.02	3.56		9.13[f]	130d	92
36	[Rh(S$_2$)(vdiars)$_2$]Cl	52.7	4.2	3.35	4.45[c]	53.33	3.79	3.03	5.48[c]	217d	85
37	[Rh(S$_2$)(vdiars)$_2$]PF$_6$·0.25CH$_3$COCH$_3$	48.4	3.7		5.5[c]	48.91	3.55		4.95[c]	250d	62
38	[Rh(SO$_2$)(diars)$_2$]PF$_6$	27.0	3.7		3.9[c]	27.17	3.66		3.63[c]	—	85
39	[Rh(SO$_2$)(MPPE)$_2$]PF$_6$	43.1	4.7		3.4[c]	44.66	4.69		3.73[c]	—	84
40	[Rh(SO$_2$)(vdiars)$_2$]PF$_6$·CH$_2$Cl$_2$	46.6	3.2		2.2[c]	46.61	3.40		2.35[c]	155d	83
41	[Rh(SO$_4$)(MPPE)$_2$]PF$_6$	42.6	4.85		3.8[c]	43.06	4.53		3.59[c]	172d	73
42	[Rh(SO$_4$)(vdiars)$_2$]PF$_6$	47.25	3.4			47.58	3.39			290d	68
43	[Rh(SO$_4$)(diars)$_2$]PF$_6$	26.2	4.1		3.8[c]	26.22	3.53		3.50[c]	>330	66
44	[Rh(OH)(NO$_3$)(MPPE)$_2$]PF$_6$·H$_2$O	42.6	4.3		1.5[g]	43.01	4.86		1.57[g]	203d	45
45	[RhCl(NO$_3$)(diars)$_2$]PF$_6$	26.2	3.3	4.05	1.6[g]	26.18	3.52	3.86	1.55[g]	310d	42
46	[RhCl(NO$_3$)(vdiars)$_2$]PF$_6$	47.3	3.4	2.7	1.3[g]	47.53	3.38	2.70	1.07[g]	—	63
47	[Rh(NO$_2$)(NO$_3$)(vdiars)$_2$]Cl	51.6	3.7	2.7	2.1[g]	51.40	3.66	2.92	2.31[g]	—	51

[a] d = decomposed. [b] Analysis for indicated element. [c] Sulfur analysis. [d] Bromine analysis. [e] Iodine analysis. [f] Fluorine analysis. [g] Nitrogen analysis.

[Rh(EDA)$_2$]PF$_6$ react rapidly with sulfonyl chlorides to give the adducts 1–7, 8–14, and 15 and 16, respectively. The infrared spectra of these complexes (Table II) show the presence of S-bonded sulfinate in all cases.[16,17] An analogous reaction occurred between [Rh(MPPE)$_2$]Cl and CH$_3$SO$_2$Cl to give the S-bonded sulfinate complex 17. All complexes are assigned a trans stereochemistry on the basis of ^{1}H NMR and far-infrared spectral data. Thus 3, 4, 6, and 7 each exhibit a pair of singlet resonances of equal intensity at τ ca. 8.00 and 8.20 indicating that only two types of arsenic methyl groups

Table II. Infrared Spectral Data for $[Rh(RSO_2)Cl(L_2)_2]^+$ Complexes[a,b]

Complex	ν_{S-O}(asym)	ν_{S-O}(sym)
1	1189 s	1053 s
2	1190 s	1045 s
3	1203 s, 1180 sh	1050 s
4	1201 s	1051 s, 1041 sh
5	1202 s	1054 s, 1037 sh
6	1199 s, 1180 sh	1049 s, 1040 sh
7	1186 s	1051 s
8	1212 s	1057 s
9	1207 s	1063 s
10	1210 s	1051 s
11	1211 s	1051 s
12	1229 s, 1221 sh	1059 s
13	1210 s	1040 s
14	1207 s, 1193 sh	1042 s
15	1218 sh, 1208 m	1044 s
16	1211 m	1043 s
17	1214 s, 1194 sh	1035 s
18	1232 s, 1206 s	1030 m
19	1225 m, 1192 m	1036 s
20	1226 m, 1200 m, 1195 sh	1027 s

[a] Band maxima in cm^{-1}. [b] Key: s, strong; m, medium; sh, shoulder.

Table III. Infrared Spectral Data for $[Rh(RCO)Cl(diars)_2]PF_6$ Complexes

Complex	$\nu_{C=O}$, cm^{-1}	Complex	$\nu_{C=O}$, cm^{-1}
21	1624 s[a]	24	1603 s
22	1640 s	25	1635 s
23	1608 s		

[a] s = strong.

Table IV. Infrared Spectral Data for SO_2 and SO_4 Adducts

Complex	ν_{S-O},[a] cm^{-1}
38	1167 s, 1020 s
39	1188 s, 1035 s
40	1192 m, 1038 s
41	1250 sh, 1238 s, 1165 sh, 1143 vs, 637 m
42	1284 m, 1162 sh, 1151 vs, 643 s
43	1232 m, 1151 s, 1106 s, 1094 sh, 1041 sh, 1027 s, 989 m, 638 sh, 618 s

[a] Key: vs, very strong; s, strong; m, medium; sh, shoulder.

are present as expected in a complex with two dissimilar trans ligands. Although the 300–350-cm^{-1} region of the infrared spectrum is obscured by strong ligand absorptions, making it impossible to identify Rh–Cl bands there, no bands attributable to Rh–Cl stretching vibrations appear in the 250–280-cm^{-1} region. The absence of absorptions in this region further supports the assignment of trans stereochemistry since if the adducts were cis, the chloride ligand would be trans to arsenic and ν_{Rh-Cl} would be expected to be in this lower range.[18] The remainder of the arsine complexes are also assigned trans stereochemistry by analogy with the complexes just discussed and because no bands attributable to ν_{Rh-Cl} are found in the 250–280-cm^{-1} region. Complex **17** exhibits a band at 328 cm^{-1} which can be assigned to ν_{Rh-Cl} thus indicating a trans stereochemistry for this complex.[18]

In contrast to that of methanesulfonyl chloride, the reactions of *m*-nitrobenzene-, *p*-toluene-, and α-naphthalenesulfonyl chloride with $[Rh(MPPE)_2]Cl$ are more complex. When first prepared, the products **18–20** appear to be mixtures of isomers containing both O- and S-bonded sulfinate. In addition to the S–O stretching vibrations which can be assigned to S-bonded sulfinate (Table II), each complex shows an additional pair of bands at lower energy which are in the regions associated with O-bonded sulfinate,[16] viz.: **18**, 1040 (s), 979 (s); **19**, 1052 (s), 978 (s); **20**, 1058 (s), 971 (s) cm^{-1}. All three complexes

show ν_{Rh-Cl} at ca. 325 cm^{-1} thus confirming them to be trans adducts.

While the isomeric composition of **18** appears unaffected by recrystallization and the O-bonded isomer is stable to prolonged exposure to the ambient atmosphere in the solid state, this is not the case with **19** or **20**. After these complexes stood in the air for about 2 years with no apparent change in color or crystalline habit, their infrared spectra in the S–O stretching region changed and now showed bands at 1224 (vs), 1200 (sh), 1192 (vs), 1033 (s), 1011 (s) and 1240 (sh), 1225 (vs), 1205 (vs), 1195 (sh), 1030 (s) cm^{-1}, respectively. The marked increase in the intensities of the bands at ca. 1200 cm^{-1} and the disappearance of the band at ca. 974 cm^{-1} suggest that conversion of the O-bonded sulfinate to an S-bonded species has occurred. A number of O- to S-bonded sulfinate conversions have been reported to occur in solution[19,20] but this appears to be the first instance of this rearrangement occurring in the solid state.

It has been reported that certain metal sulfinate complexes can be desulfonated to yield alkyl or aryl species.[17] This was not observed for the complexes reported here even when they were heated in vacuo at just below the melting point presumably because no vacant or easily vacated coordination site is available. Gas evolution was apparent upon melting of the complexes but the resulting material rapidly became dark and could not be characterized. Evidently extensive decomposition had occurred.

Of the various substrate complexes studied, only $[Rh(diars)_2]PF_6$ yielded oxidative adducts with acyl chlorides (**21–25**). The infrared data presented in Table III indicate the presence of a metal-bonded acyl group in each case.[5] For **25** the observation of a single $\nu_{C=O}$ band together with the analytical data suggests the presence of two $[RhCl(diars)_2]$ moieties bridged by a $-C(O)(CH_2)_2C(O)-$ group. $[Rh(diars)_2]PF_6$ also reacts with phthaloyl chloride, o-$C_6H_4(C(O)Cl)_2$, to produce a light yellow product. Because of the extremely low yield, no analytical data were obtained, but since the infrared spectrum showed only one acyl band at 1635 cm^{-1}, both acyl groups must be attached to the metal and the product is tentatively formulated as a cis adduct containing a chelating o-$C_6H_4(C(O)-)_2$ moiety.

The initial product obtained in the reaction of acid chlorides with $[Rh(diars)_2]PF_6$ was shown by infrared spectroscopy to be a mixture of the desired acyl complex and $[RhHCl(diars)_2]PF_6$[13] (ν_{Rh-H} at ca. 2000 cm^{-1}). The mixture was separated by chromatography on Forisil with the hydrido complex being eluted first. The most reasonable source of the HCl which generates the hydride complex is hydrolysis of the acid chloride either by traces of moisture or by hydroxylic impurities in the acetone solvent which could have resulted from its being stored over molecular sieves. It is noteworthy that the reaction of $[Rh(vdiars)_2]PF_6$, which does not give isolable acyl complexes, with RCOCl (R = CH$_3$, C$_2$H$_5$) in acetone produces only $[RhHCl(vdiars)_2]PF_6$. In one experiment **21** was prepared in dry benzene and again it was contaminated with the hydrido complex. The most probable source of HCl is hydrolysis of the acetyl chloride by adventitious moisture.

The failure of $[Rh(MPPE)_2]PF_6$ and $[Rh(vdiars)_2]PF_6$ to oxidatively add acyl chlorides was surprising in light of their ready formation of sulfinate adducts and particularly in light of the fact that the latter reacts readily with dihydrogen[12] which indicates it is quite basic. However it has been pointed out that steric factors[5] and the strength of the bond being altered in the added molecule[3] are also important in determining the reactivity of d^8 complexes toward oxidative addition. Although the available data do not permit a detailed discussion of the question, we suggest that $[Rh(MPPE)_2]PF_6$

is insufficiently basic to react with the stronger C–Cl bond[21-23] while with [Rh(vdiars)$_2$]PF$_6$ the failure to react is primarily due to steric factors.

Although the complexes [RhX$_2$(diars)$_2$]X (X = Cl, Br, I) have been known for 25 years,[24] they were prepared directly from the appropriate Rh(III) halides rather than by oxidative addition to [Rh(diars)$_2$]$^+$. We have obtained these cations as hexafluorophosphate salts (**26–28**) and other dihalo adducts (**29–33**) by reaction of molecular halogens with the appropriate Rh(I) complexes. In these reactions it is important to avoid the use of halide counterions and to use only stoichiometric quantities of the halogen reactant to prevent formation of trihalide salts of the [RhX$_2$(L$_2$)$_2$]$^+$ ions. The far-infrared spectra of these complexes are uninformative particularly for the diarsine species since strong ligand absorptions obscure much of the Rh–Cl stretching region and Rh–Br and Rh–I bands could not be unequivocally identified. Assignments of trans stereochemistry for the [RhX$_2$(L$_2$)$_2$]PF$_6$ species could nevertheless be made on the basis of their ^{1}H NMR spectra in (CD$_3$)$_2$SO solution. Thus **26** and **27** each show a singlet at τ 8.03 and 7.93, respectively, which can be assigned to the arsenic methyl groups while the aromatic protons appear as typical AA′BB′ patterns centered at τ 2.63 and 2.64, respectively. A static cis structure should show four methyl resonances and a more complex pattern for the aromatic protons. Although the observed spectrum could be produced by a cis isomer which is undergoing rapid intramolecular rearrangement, the related complex cis-[IrCl$_2$-((C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$)$_2$]Cl has been shown to be static at 35 °C[25] so it is unlikely that the present complexes are fluxional. Similarly **30** and **31** show broadened ($\sim$7 Hz) singlets at τ 8.45 and 8.09, respectively, indicating equivalence of all the methyl groups as expected in a trans structure. The broadness of these resonances is presumably due to the presence of unresolved P–H couplings although it is surprising that these are so small in light of the large P–H couplings usually observed in complexes containing monodentate phosphines bearing methyl groups. The acetone of solvation is also evident in the spectrum of **30** as a singlet at τ 7.93. Finally, the spectra of **32** and **33** show the vinyl protons of the ligands as sharp singlets at τ 2.27 and 2.25, respectively. This is indicative of *trans* structures of these complexes as static cis isomers should give AB patterns for these protons as is observed for **35–37** (vide infra). Again the presence of fluxional cis isomers is considered unlikely.

Dioxygen reacts with [Rh(L$_2$)$_2$]PF$_6$ (L$_2$ = diars, vdiars, MPPE) to give adducts which are formulated as containing "side-on" bonded O$_2$ by analogy with previous work.[26] Further confirmation comes from the observation of bands in the infrared spectra of the chloride analogues of **34** and **35** at 886 (m) and 861 (m) cm^{-1}, respectively, which are characteristic of the RhO$_2$ moiety.[27] Although the dioxygen adduct of [Rh(diars)$_2$]PF$_6$ could not be isolated pure, its existence in solution was inferred from the further reactions of this solution with sulfur dioxide and nitrogen dioxide (vide infra) which parallel those of **34** and **35**. The uptake of O$_2$ by the arsine complexes is irreversible while **34** slowly deoxygenates under reduced pressure. The avidity of [Rh(diars)$_2$]PF$_6$ for dioxygen is shown by its oxygenation even in the solid state. The ^{1}H NMR spectrum of **35** shows that significant interaction occurs between the ortho protons of two ligand phenyl groups and the coordinated dioxygen molecule as has been observed in [Ir(O$_2$)(diphos)$_2$]Cl (diphos = 1,2-bis(diphenylphosphino)ethane).[28] Thus a doublet of relative intensity 4 appears at τ 3.61 (CD$_2$Cl$_2$ solution, J_{H-H} = 8 Hz). The ligand vinyl protons appear as a AB pattern centered at τ 2.19.

The three Rh(I) complexes also react with *cyclo*-octasulfur; however, only for [Rh(vdiars)$_2$]X (X$^-$ = Cl$^-$, PF$_6^-$) could pure

products be obtained. The infrared spectra of **36** and **37** both show a weak band at 554 cm^{-1} which can be assigned to a vibration of an RhS$_2$ moiety[28] indicating that both contain "side-on" bonded disulfur. The presence of the acetone of solvation in **37** is confirmed by both infrared ($\nu_{C=O}$ = 1713 cm^{-1}) and NMR spectroscopy (τ 7.88 (s)). The color of the [Rh(S$_2$)(vdiars)$_2$]$^+$ moiety depends markedly on the mode of preparation but with no obvious correlation with the solvent or counterion used. Thus in either dichloromethane or acetone [Rh(vdiars)$_2$]PF$_6$ reacts over a period of hours with S$_8$ to yield a brown solution from which reddish brown [RhS$_2$-(vdiars)$_2$]PF$_6$ (**37**) can be obtained. By contrast reaction of S$_8$ with [Rh(vdiars)$_2$]Cl in dichloromethane occurs in minutes to yield a blue-green solution from which light blue-violet needles of **36** can be obtained. The same rapid reaction occurs in acetone but **36** precipitates immediately. Metathesis of **36** prepared in either solvent with NH$_4$PF$_6$ in acetone–dichloromethane yields bright blue-green crystals which analyze for [Rh(S$_2$)(vdiars)$_2$]PF$_6$ (**36a**). The infrared spectra of **36** and **36a** are identical with the exception that the latter also shows absorptions due to the hexafluorophosphate ion. In particular, the RhS$_2$ absorption also occurs at 554 cm^{-1} in the spectrum of **36a**. Although **36** and **36a** have different colors in the solid state, both give identical aqua solutions in a variety of solvents. In dichloromethane both exhibit a broad absorption at 16 600 cm^{-1} having a molar extinction coefficient of 98. The NMR spectra in CD$_3$NO$_2$ are also identical with the most notable feature being a doublet at τ 3.36 (4 H, J_{H-H} = 8 Hz) which can be assigned to the ortho protons of two of the ligand phenyl groups. A similar upfield shift of these protons has been observed for [Ir(S$_2$)(diphos)$_2$]Cl as a result of significant interaction with the S$_2$ moiety.[28] The vinyl protons of the ligand appear as an AB pattern with τ_A 1.87, τ_B 1.79, and J_{AB} = 8.4 Hz. Although **36a** and **37** have identical compositions, their colors are strikingly different. The electronic spectrum of **37** consists of two bands which appear at 19 150 (332) and 21 270 (351) cm^{-1} as shoulders on the intense charge-transfer bands. That the color difference is not due to the presence of acetone in **37** is shown by the preparation of an identical red-brown product in dichloromethane. While **37** also shows an RhS$_2$ absorption at 554 cm^{-1}, its infrared spectrum is noticeably different from that of **36a**. Thus **36a** shows bands at 1111 (m), 1078 (m), 748 (sh), 738 (vs), 721 (s), 706 (sh), 690 (s), 489 (s), 478 (s), 467 (m), and 450 (m) cm^{-1} while **37** shows bands at 1080 (m), 1070 (m), 755 (sh), 743 (vs), 735 (sh), 722 (s), 713 (s), 703 (sh), 691 (s), 488 (sh), 482 (sh), 479 (s), 470 (sh), 460 (sh), and 449 (m) cm^{-1}. These bands are clearly associated with the diarsine ligands, but as no assignments have been made, it is not possible to say more than that the dispositions of these ligands differ in the two complexes. Unlike diphos the backbone of vdiars is not particularly flexible so it should not be possible to significantly alter the ligand dispositions without changing the coordination geometry about the metal. Whatever this change, it must be such as to still permit interaction of ortho hydrogens from only two phenyl rings with the S$_2$ unit as a high-field doublet (τ 3.44 (4 H, J_{H-H} = 8 Hz)) is also evident in the NMR spectrum of **37**. It must also maintain the nonequivalence of the vinyl protons on the ligand which still appear as an AB pattern (τ_A 1.92, τ_B 1.84, J_{AB} = 8 Hz). Examination of molecular models indicates that these requirements can be met in both trigonal-bipyramidal and square-pyramidal geometries provided the S$_2$ moiety remains aligned approximately parallel to one As–Rh–As unit. In an approximately square-pyramidal arrangement there are closer contacts between certain phenyl groups and between the appropriate ortho hydrogens and the S$_2$ moiety. The increased complexity of the infrared spectrum of **37** in the 690–760-cm^{-1}

region and the slight upfield shift of the ortho proton resonance as compared with what is observed for **36a** suggest that the former may be closer to a square pyramid while the latter more closely resembles the trigonal-bipyramidal structure found for [Ir(S$_2$)(diphos)$_2$]Cl.[28] These suggestions must however remain tentative until crystal structure studies now in progress are completed.

The complexes [Rh(L$_2$)$_2$]PF$_6$ (L$_2$ = diars, MPPE, vdiars) react with gaseous SO$_2$ to yield the adducts **38–40**. The infrared spectra of these complexes (Table IV) show two strong bands which can be assigned to S–O stretching frequencies of coordinated SO$_2$. These are in the ranges previously found for similar adducts[29,30] and the complexes are formulated as square-pyramidal species with apical SO$_2$. By contrast, [Rh(diars)$_2$]Cl reacts with SO$_2$ to give an extremely insoluble product having ν_{SO} at 1099 (s) and 984 (s) cm^{-1}. Although such low values for ν_{SO} have previously been found only in the SO$_2$-bridged dimers K$_6$[(NC)$_5$Co(SO$_2$)Co(CN)$_5$][31] and [(π-C$_5$H$_5$Fe(CO)$_2$)$_2$SO$_2$],[32] the analytical data for the present complex clearly show it to be a 1:1 adduct.[33] The "normal" values for ν_{SO} found in **38** and the related species [Rh(SO$_2$)(fdma)$_2$]PF$_6$ (fdma = 1,1'-bis(dimethylarsino)ferrocene)[34] indicate that the explanation cannot be a high basicity of the metal because of the presence of the diars ligand. Although formulation as an SO$_2$-bridged polymer is consistent with the available data, this would require the presence of six-coordinate Rh(I) which would be quite unusual. Such a structure also appears inconsistent with the observation that the complex reacts with atmospheric oxygen over a period of months *in the solid state* to partially convert the SO$_2$ to sulfate (ν_{SO_4} 1217 (w), 1167 (sh), 1150 (s), 1128 (s), 622 (s) cm^{-1}). We suggest that in the solid state the [Rh(SO$_2$)(diars)$_2$]$^+$ units stack so that weak interactions occur between one metal and the SO$_2$ coordinated to the adjacent one. This could account for the unusually low S–O stretching frequencies but still provide a site for activating the incoming dioxygen molecule in the conversion of SO$_2$ to sulfate. Unfortunately the extreme insolubility of the complex has prevented our obtaining crystals suitable for a structural analysis to support this.

Complexes **38–40** are members of the small group of SO$_2$ adducts which will react with dioxygen to yield sulfato complexes (**41–43**). Alternatively these complexes can be obtained by the action of SO$_2$ on the corresponding dioxygen adducts. The infrared spectra (Table IV) show bands consistent with the presence of bidentate sulfate.[28,3] The spectrum of **43** is more complex than is observed for the others which may be due to contamination with the insoluble SO$_2$ species described above. It may also be that this product is a mixture of monomeric and polymeric species containing chelating and bridging sulfate, respectively.

The dioxygen complexes [Rh(O$_2$)(L$_2$)$_2$]Cl (L$_2$ = diars, vdiars) and [Rh(O$_2$)(MPPE)$_2$]PF$_6$, prepared in situ, react with nitrogen dioxide but the course of these reactions is very dependent on reaction conditions. Thus in acetone–methanol, **34** reacts to give the hydroxonitrato complex **44**. The infrared spectrum shows ν_{OH} for the hydroxyl group at 3648 cm^{-1}, bands due to the lattice water at 3510 (w), 3440 (w), and 1620 (w) cm^{-1}, and nitrate absorptions at 1494 (sh), 1488 (vs), 1273 (vs), 1255 (m), 1001 (m), and 980 (sh) cm^{-1}.[35] If on the other hand, this reaction is performed in acetone or 2-butanone, a mixture of complexes containing hydroxo, NO$_x$, and possibly other NO-containing ligands as well as lattice water is produced. This mixture has so far defied separation in part because at least a portion of it appears to be labile and undergoes further reaction during subsequent workup. It is tempting to postulate that the formation of **44** proceeds in a manner analogous to that suggested for the formation of [Ir(CO)(SO$_4$)ClL$_2$] from [Ir(O$_2$)Cl(CO)L$_2$].[36] Thus the

attack of NO$_2$ on **34** could produce an oxonitrato species which can then abstract a proton from methanol or traces of water in the solvent. If this is indeed the mechanism, then the major source of protons for the hydroxy group must be methanol since significant amounts of other species are formed in acetone or 2-butanone even when no attempt was made to dry these solvents.

When the complexes [Rh(O$_2$)(L$_2$)$_2$]Cl (L$_2$ = diars, vdiars) are reacted with NO$_2$ in dichloromethane followed by addition of LiPF$_6$ or NH$_4$PF$_6$ in methanol, the chloronitrato complexes **45** and **46**, respectively, are obtained. The infrared spectrum of **45** shows bands at 1504 (sh), 1500 (vs), 1280 (vs), 1264 (vs), 992 (s), and 979 (sh) cm^{-1} which are assigned to vibrations of coordinated nitrate.[35] Similar bands at 1510 (sh), 1468 (m), 1262 (s), and 983 (m) cm^{-1} are observed for **46**. The reaction of [Rh(O$_2$)(vdiars)$_2$]Cl with NO$_2$ in 2-butanone but without addition of PF$_6^-$ yields the nitronitrato complex **47**. The infrared spectrum of this complex shows bands at 1420 (m), 1345 (sh), 1334 (s), 1308 (s), and 816 (m) cm^{-1} due to coordinated nitrite and bands at 1508 (sh), 1493 (s), 1260 (vs), 995 (s), and 983 (sh) cm^{-1} due to coordinated nitrate.

The course of these reactions is unknown. In dichloromethane the initial solution is green while in 2-butanone it is yellow. It is unlikely therefore that a species similar to **47** is formed initially in the former solvent but attempts to characterize the green material failed. Possibly it is a mixture of species containing nitrate and a variety of NO$_x$ ligands. Clearly, however, these other ligands must be relatively labile since, upon addition of hexafluorophosphate, they are ultimately replaced by the original chloride counterion.

Conclusions

The complexes [Rh(L$_2$)$_2$]$^+$ (L$_2$ = di(tertiary phosphine or arsine)) have been shown to be versatile substrates for oxidative addition reactions despite their cationic nature. It is important, however, to use counterions which are poor ligands to avoid their possible incorporation into the coordination sphere.

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Complexes of the Platinum Metals. 7.[1] Homogeneous Ruthenium and Osmium Catalysts for the Dehydrogenation of Primary and Secondary Alcohols

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Ruthenium and osmium complexes [M(OCOR$_F$)₂(CO)(PPh₃)₂] (R$_F$ = CF₃, C₂F₅, or C₆F₅) are catalysts for the dehydrogenation of primary and secondary alcohols to aldehydes and ketones, respectively. The catalysis is promoted by the addition of small amounts of free acid (R$_F$COOH) and is inhibited by the accumulation of aldehyde or ketone and by the addition of large amounts of acid. In the presence of acid, R$_F$COOH, the hydride complexes [MH(OCOR$_F$)(CO)(PPh₃)₂] also function as catalysts. The mechanism proposed for the catalytic process involves solvolysis of the catalysts [M(OCOR$_F$)₂(CO)(PPh₃)₂] to form alkoxides [M(OAlk)(OCOR$_F$)(CO)(PPh₃)₂] which subsequently undergo a β elimination to generate aldehyde (or ketone) and form the hydrides [MH(OCOR$_F$)(CO)(PPh₃)₂]. Acid attack on the hydrides liberates dihydrogen and regenerates the catalysts. Dehydrogenation has been observed to occur with an extensive range of primary, secondary, and cyclic alcohols. Kinetic data have been recorded; the initial rate of dihydrogen elimination increases with increasing boiling point of the alcohol and for the primary alcohols ranges from 7.50×10^{-3} mol s^{-1} (mol of catalyst)$^{-1}$ (ethanol) to 2.27 mol s^{-1} (mol of catalyst)$^{-1}$ (benzyl alcohol) for the catalyst [Ru(OCOCF₃)₂(CO)(PPh₃)₂] under optimum conditions. Catalyst efficiency decreases in the sense Ru > Os and CF₃ ∼ C₂F₅ > C₆F₅ for a given alcohol under standard conditions.

The reactions of alcohols with platinum metal species in the presence of base have been extensively employed as a route for the formation of hydride complexes.[2] These syntheses are accompanied by liberation of aldehyde or ketone and have been shown to involve the elimination of hydride ions from the α-CH₂ group of a coordinated alkoxide anion (the β-elimination process).[3] We now describe a homogeneous catalytic reaction for the dehydrogenation of primary and secondary alcohols based on this process and employing the ruthenium and osmium perfluorocarboxylates [M(OCOR$_F$)₂(CO)(PPh₃)₂][4] as catalysts. Although the stoichiometric dehydrogenation of alcohols by group 8 metal species is a commonplace phenomenon, extensively employed in the synthesis of metal hydride complexes, homogeneous systems capable of catalyzing this reaction are rare. The only system directly comparable with that discussed in this paper is the one reported by Charman involving use of rhodium trichloride,[5] preferably in the presence of stannous chloride.[6] Charman's catalyst is less efficient than the present one and its nature and mode of operation are less clearly defined. However, other workers

have described numerous transition metal species capable of catalyzing hydrogen transfer from primary or secondary alcohols to a variety of substrates including aldehydes or ketones,[7-13] olefins,[14-17] acetylenes[18,19] and carbon tetrachloride.[20] Evidence supporting the α-hydrogen-transfer (β-elimination) mechanisms proposed for these reactions has been obtained from H–D exchange and from racemization reactions involving optically active alcohols.[21] More extensive surveys of transition metal catalyzed hydrogen-transfer reactions are given in recent reviews.[22,23] A preliminary report on this work has been published.[24]

Experimental Section

Alcohols were dried and distilled using standard techniques; catalysts were prepared as previously described.[4] Reactions were performed at the boiling point of the alcohol using a reflux apparatus attached to a gas buret. The refluxing alcohol was allowed to reach equilibrium; then a measured quantity of catalyst was introduced, the system was closed, and the volume of evolved gas was measured at atmospheric pressure. An efficient double-walled condenser was employed to remove volatile organic products from the vapor phase; therefore