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Cationic Rhodium(I) Complexes. 5.[1,2] Preparation and Reactions of Complexes Containing Tris(*o*-dimethylarsinophenyl)arsine and 1,1′-Bis(dimethylarsino)ferrocene

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Attempts to prepare $[Rh(Qas)]PF_6$ (Qas = tris(*o*-dimethylarsinophenyl)arsine) were unsuccessful although Rh(I) species containing Qas and other neutral ligands could be obtained. Certain of these products undergo oxidative addition reactions with p-$CH_3C_6H_4SO_2Cl$, CH_3I, and $CHCl_3$. The complex $[Rh(fdma)_2]PF_6$ (fdma = 1,1′-bis(dimethylarsino)ferrocene) adds small molecules, L (L = CO, SO_2, $(CH_3)_3CNC$), to give five-coordinate complexes $[Rh(L)(fdma)_2]PF_6$ and undergoes oxidative addition reactions with a wide variety of molecules, XY (XY = H_2, O_2, Br_2, I_2, HCl, HBr, HI, CH_3SO_2Cl, CH_3I, $CF_3C{\equiv}CCF_3$, CH_3SSCH_3) to give $[RhXY(fdma)_2]PF_6$. Reaction with S_8 produces $[Rh(S_2)(fdma)_2]PF_6$. Reaction of $[Rh(O_2)(fdma)_2]PF_6$ with sulfur dioxide yields $[Rh(SO_4)(fdma)_2]PF_6$. Proton NMR studies indicate that several of the adducts are stereochemically nonrigid in solution.

Introduction

As a continuation of our studies on oxidative addition to cationic complexes of Rh(I) we have investigated the reactions of complexes containing tris(*o*-dimethylarsinophenyl)arsine (Qas) and 1,1′-bis(dimethylarsino)ferrocene (fdma). Although considerable work has been reported on oxidative addition of neutral complexes of d^8 metals,[3-9] fewer studies have been made of related cationic species.[10-13] Additionally it was of interest to study the course of oxidative addition when ligand constraints require that the addend occupy cis positions regardless of the nature of the bond being added.

Experimental Section

All solvents were dried and distilled prior to use and were stored under nitrogen. All reactions and manipulations were routinely performed in an atmosphere of prepurified nitrogen using standard Schlenk techniques. Infrared spectra were obtained on Beckman IR-18A and Perkin-Elmer 521 spectrophotometers in Nujol mulls unless otherwise specified. ^1H NMR spectra were obtained on Jeol C60-HL and MH-100 spectrometers using tetramethylsilane as an internal standard. Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Hydrated rhodium(III) chloride was purchased from A. D. Mackay, Inc. The complexes $[Rh(C_8H_{12})Cl]_2$,[14] $[Rh(C_2H_4)_2Cl]_2$,[15] and $[Rh(CO)_2Cl]_2$,[16] were prepared according to published procedures. Tris(*o*-dimethylarsinophenyl)arsine was prepared as described by Venanzi[17] except that the final purification was effected by chromatography on silica gel. Oily impurities could be removed by elution with hexane and further elution with benzene removed the arsine which was obtained as white crystals from methanol–ethanol, mp 111–114 °C (lit. mp 115 °C). 1,1′-Bis(dimethylarsino)ferrocene was prepared by the method of Davison[18] and obtained as a dark red liquid (bp 128–131 °C (0.3 mm)). Bis(ethylene)rhodium 2,4-pentanedionate, $Rh(C_2H_4)_2acac$, was prepared from $[Rh(C_2H_4)_2Cl]_2$ and Tl(acac) in diethyl ether. All other chemicals were reagent grade and were used as received.

Attempted Preparation of $[Rh(Qas)]PF_6$. (a) From $[Rh(C_8H_{12})Cl]_2$. A mixture of 0.097 g (0.196 mmol) of $[Rh(C_8H_{12})Cl]_2$ and 0.098 g (0.392 mmol) of $AgPF_6$ was stirred in 5 mL of acetone for 15 min followed by filtration through a pad of diatomaceous earth to remove the precipitated AgCl. To the filtrate was added 0.242 g (0.392 mmol) of Qas and the solution was refluxed for 30 min by which time it had become dark orange. Addition of diethyl ether precipitated an orange oil which eventually solidified to a yellow powder. This was filtered off, washed with diethyl ether, and dried in vacuo. The NMR spectrum in $(CD_3)_2SO$ was of poor quality but indicated the presence of both Qas and C_8H_{12} while the infrared spectrum showed the presence of acetone. Anal. Calcd for $C_{32}H_{42}As_4F_6PRh{\cdot}0.3(CH_3)_2CO$: C, 39.84; H, 4.46; F, 11.52. Found: C, 39.5; H, 4.3; F, 11.5.

(b) From $[Rh(C_2H_4)_2Cl]_2$. To 0.061 g (0.155 mmol) of $[Rh(C_2H_4)_2Cl]_2$ dissolved in 5 mL of 2-methoxyethanol was added 0.079 g (0.351 mmol) of $AgPF_6$. After stirring of the mixture for 10 min the AgCl was removed by filtration through a pad of diatomaceous earth and 0.192 g (0.351 mmol) of Qas was added whereupon the solution became green. After 2 h of refluxing a yellow-brown solid had precipitated which was filtered off, washed with diethyl ether, and dried in vacuo. Although the NMR spectrum indicated the presence of Qas and ethylene, the relative intensities of the resonances were not consistent with any simple formulation. Attempts at purification by fractional crystallization or chromatography led only to decomposition.

(c) From $Rh(C_2H_4)_2acac$. To a solution of 0.10 g (0.387 mmol) of $Rh(C_2H_4)_2acac$ in 10 mL of tetrahydrofuran was added 0.239 g (0.387 mmol) of Qas. After refluxing for 1 h the solution had become red. The solution was concentrated to ca. 5 mL under reduced pressure and 51.5 μL (0.387 mmol) of 48% aqueous HBF_4 was added whereupon the solution became orange and a solid precipitated. The NMR spectrum of the product was of extremely poor quality and yielded no useful information. Attempts to purify the product led only to decomposition.

Chloro-*p*-toluenesulfinato(tris(*o*-dimethylarsinophenyl)arsine)-rhodium(III) Hexafluorophosphate, $[RhCl(p\text{-}CH_3C_6H_4SO_2)(Qas)]PF_6$. Approximately equimolar quantities of the material prepared in section (a) and formulated as $[Rh(C_8H_{12})(Qas)]PF_6$ and *p*-toluenesulfonyl chloride were stirred for 24 h in acetone. Addition of diethyl ether precipitated the product as a yellow powder which was filtered off, washed with diethyl ether, and dried in vacuo.

Iodomethyl(tris(*o*-dimethylarsinophenyl)arsine)rhodium(III) Hexafluorophosphate, $[RhI(CH_3)(Qas)]PF_6$. To 5 mL of methyl iodide was added 0.2 g of $[Rh(C_8H_{12})(Qas)]PF_6$. After ca. 5 min, yellow crystals began to form. These were filtered off, washed with diethyl ether, and recrystallized from dichloromethane–petroleum ether.

Dichloro(tris(*o*-dimethylarsinophenyl)arsine)rhodium(III) Chloride Chloroform Solvate, $[RhCl_2(Qas)]Cl{\cdot}2CHCl_3$. $[Rh(C_8H_{12})Cl]_2$ (0.1 g, 0.203 mmol) and Qas (0.25 g, 0.406 mmol) were dissolved in 15 mL of acetone and stirred overnight to give a maroon solid. Dissolution of this solid in 15 mL of chloroform gave a red solution which on

standing for 24 h became yellow and yielded a yellow, crystalline precipitate. This was filtered, washed with diethyl ether, and dried in vacuo.

Bis(1,1′-bis(dimethylarsino)ferrocene)rhodium(I) Hexafluorophosphate, $[Rh(fdma)_2]PF_6$. To 0.122 g (0.248 mmol) of $[Rh(C_8H_{12})Cl]_2$ in 5 mL of THF was added 0.125 g (0.495 mmol) of $AgPF_6$ and the mixture was stirred for 30 min. After removal of AgCl by filtration through a pad of diatomaceous earth, 0.30 mL (0.400 g, 1.00 mmol) of fdma was added. The solution was refluxed for 1 h during which time golden-brown crystals precipitated. Cooling to 0 °C completed the precipitation and the product was filtered off, washed with diethyl ether, and dried in vacuo.

Carbonylbis(1,1′-bis(dimethylarsino)ferrocene)rhodium(I) Hexafluorophosphate Tetrahydrofuran Solvate, $[Rh(CO)(fdma)_2]PF_6 \cdot 0.25C_4H_8O$. Carbon monoxide was bubbled through a slurry of *freshly prepared* $[Rh(fdma)_2]PF_6$ (0.513 g, 0.495 mmol) in 5 mL of tetrahydrofuran to give a yellow solution from which yellow crystals of the product were obtained upon dilution with diethyl ether. The crystals were filtered, washed with diethyl ether, and dried in vacuo at 100 °C.

(Sulfur dioxide)bis(1,1′-bis(dimethylarsino)ferrocene)rhodium(I) Hexafluorophosphate, $[Rh(SO_2)(fdma)_2]PF_6$. Sulfur dioxide was bubbled through a solution of freshly prepared [Rh(fdma)$_2$]PF (0.65 g, 0.63 mmol) in 10 mL of acetone for 2 min whereupon the solution became dark red. The solution was concentrated to ca. 5 mL under reduced pressure and diluted with diethyl ether to precipitate the product as dark red-brown crystals. These were collected, washed with diethyl ether, and dried in vacuo at 100 °C.

(*tert*-Butyl isocyanide)bis(1,1′-bis(dimethylarsino)ferrocene)rhodium(I) Hexafluorophosphate Acetone Solvate, $[Rh(CNC(CH_3)_3)(fdma)_2]PF_6 \cdot (CH_3)_2CO$. To a solution of 0.330 g (0.318 mmol) of freshly prepared [Rh(fdma)$_2$]PF in 5 mL of acetone was added dropwise 0.025 g (0.31 mmol) of *tert*-butyl isocyanide in 50 μL of petroleum ether whereupon the dark red solution became orange. Dilution with petroleum ether precipitated the product as red-orange prisms. The complex was recrystallized from acetone–petroleum ether and was dried in vacuo.

Bis(*tert*-butyl isocyanide)bis(1,1′-bis(dimethylarsino)ferrocene)rhodium(I) Hexafluorophosphate, $[Rh(CNC(CH_3)_3)_2(fdma)_2]PF_6$. To an acetone solution of 0.33 g (0.318 mmol) of freshly prepared $[Rh(fdma)_2]PF_6$ was added 0.052 g (0.636 mmol) of *tert*-butyl isocyanide whereupon the solution became light orange. Addition of petroleum ether precipitated the product which was recrystallized from acetone–petroleum ether as yellow needles and dried in vacuo.

Dioxygenbis(1,1′-bis(dimethylarsino)ferrocene)rhodium Hexafluorophosphate Tetrahydrofuran Solvate, $[Rh(O_2)(fdma)_2]PF_6 \cdot C_4H_8O$. Dioxygen was bubbled through a slurry of freshly prepared [Rh(fdma)$_2$]PF$_6$ (0.44 g, 0.42 mmol) in 10 mL of tetrahydrofuran for several minutes to produce orange crystals which were filtered off, washed with diethyl ether, and dried in vacuo at 100 °C.

Disulfurbis(1,1′-bis(dimethylarsino)ferrocene)rhodium Hexafluorophosphate Acetone Solvate, $[Rh(S_2)(fdma)_2]PF_6 \cdot 0.2(CH_3)_2CO$. To a solution of 0.634 g (0.612 mmol) of freshly prepared [Rh(fdma)$_2$]PF$_6$ in 10 mL of acetone was added 0.039 g (0.153 mmol) of S_8. The mixture was stirred at 40 °C for 0.5 h to give a reddish brown solution and a small quantity of brown solid. Filtration through a pad of diatomaceous earth followed by concentration of the solution under reduced pressure and dilution with diethyl ether precipitated the product as a reddish brown powder which was recrystallized from acetone–diethyl ether and dried in vacuo at 100 °C.

Hexafluorobut-2-ynebis(1,1′-bis(dimethylarsino)ferrocene)rhodium Hexafluorophosphate, $[Rh(C_4F_6)(fdma)_2]PF_6$. A thick-walled Pyrex tube was charged with 0.3 g (0.29 mmol) of freshly prepared $[Rh(fdma)_2]PF_6$ and the tube was evacuated and cooled in liquid nitrogen. Benzene (ca. 3 mL) and hexafluorobut-2-yne (ca. 1 mL) were condensed in and the tube was sealed and shaken at room temperature for 4 days to yield yellow crystals of the product. Following recovery of the excess acetylene these were collected, recrystallized from acetone–diethyl ether, and dried in vacuo at 100 °C.

Sulfatobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate Acetone Solvate, $[Rh(SO_4)(fdma)_2]PF_6 \cdot (CH_3)_2CO$. Sulfur dioxide was passed through a solution of $[Rh(O_2)(fdma)_2]PF_6$ (0.40 g, 0.37 mmol) in 10 mL of acetone whereupon the orange solution immediately became dark red. Addition of diethyl ether precipitated the product as a dark red powder which was collected, washed with tetrahydrofuran, and dried in vacuo at 100 °C.

***cis*-Dihydridobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate, *cis*-$[RhH_2(fdma)_2]PF_6$.** Dihydrogen was bubbled through a solution of freshly prepared $[Rh(fdma)_2]PF_6$ (0.252 g, 0.244 mmol) in 5 mL of acetone whereupon the solution became orange. Dilution with diethyl ether precipitated the product as yellow microcrystals which were collected, washed with diethyl ether, and dried in vacuo.

***trans*-Methyliodobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate, $[Rh(CH_3)I(fdma)_2]PF_6$.** To a solution of 0.252 g (0.244 mmol) of freshly prepared $[Rh(fdma)_2]PF_6$ in 5 mL of acetone was added 17 μL (0.039 g, 0270 mmol) of methyl iodide. The solution rapidly became orange and upon addition of diethyl ether gold crystals precipitated which were collected, washed with tetrahydrofuran, and dried in vacuo at 100 °C.

***trans*-Chloromethylsulfinatobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate, $[Rh(CH_3SO_2)Cl(fdma)_2]PF_6$.** To a solution of freshly prepared $[Rh(fdma)_2]PF_6$ (0.396 mmol) in 8 mL of acetone was added 30 μL (0.045 g, 0.396 mmol) of CH_3SO_2Cl. The solution rapidly became dark red and a dark red solid precipitated. The precipitation was completed by the addition of diethyl ether and the product was collected, washed with diethyl ether, and dried in vacuo.

***trans*-Dibromobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate, $[RhBr_2(fdma)_2]PF_6$.** Bromine (26 μL, 0.080 g, 0.50 mmol) was added to a slurry of freshly prepared [Rh(fdma)$_2$]PF$_6$ (0.576 g, 0.556 mmol) in 10 mL of tetrahydrofuran to produce a red solution from which the product precipitated as copper-colored crystals. These were collected and dissolved in 30 mL of acetone, and the solution was filtered through a pad of diatomaceous earth. Reduction of the solution volume to ca. 20 mL followed by addition of diethyl ether (ca. 20 mL) in 2-mL aliquots over 0.5 h yielded the product as yellow-orange crystals which were collected, washed with diethyl ether, and dried in vacuo at 100 °C.

***trans*-Diiodobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate, $[RhI_2(fdma)_2]PF_6$.** Iodine (0.055 g, 0.206 mmol) was added to a solution of freshly prepared $[Rh(fdma)_2]PF_6$ (0.214 g, 0.206 mmol) in 5 mL of acetone. The product precipitated immediately as brown crystals which were collected, washed with tetrahydrofuran, and dried in vacuo at 100 °C.

***trans*-Hydridochlorobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate Tetrahydrofuran Solvate, $[RhHCl(fdma)_2]PF_6 \cdot 0.5C_4H_8O$.** A solution of 0.12 g (0.24 mmol) of $[Rh(C_8H_{12})Cl]_2$ and 0.28 mL (0.40 g, 0.96 mmol) of fdma in 10 mL of tetrahydrofuran was refluxed for 1 h. The addition of 0.08 g (0.48 mmol) of NH_4PF_6 caused the brown solution to become light orange and a yellow crystalline solid to precipitate. The product was filtered, washed with ethanol and diethyl ether, and dried in vacuo at 100 °C.

***trans*-Hydridobromobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate Tetrahydrofuran Solvate, $[RhHBr(fdma)_2]PF_6 \cdot 0.7C_4H_8O$.** This was prepared in an analogous manner to the previous complex from 0.2 g (0.344 mmol) of $[Rh(C_8H_{12})Br]_2$, 0.38 mL (0.54 g, 1.38 mmol) of fdma, and 0.112 g (0.688 mmol) of NH_4PF_6. The yellow crystalline product which precipitated was washed with ethanol and diethyl ether and dried in vacuo at 100 °C.

***trans*-Hydridoiodobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate Tetrahydrofuran Solvate, $[RhHI(fdma)_2]PF_6 \cdot 0.5C_4H_8O$.** To a solution of $[Rh(C_8H_{12})Cl]_2$ (0.132 g, 0.267 mmol) in 10 mL of tetrahydrofuran was added 0.135 g (0.533 mmol) of $AgPF_6$. The AgCl was removed by filtration through a pad of diatomaceous earth, 0.30 mL (0.42 g, 1.06 mmol) of fdma was added, and the mixture was refluxed for 1 h. Passage of anhydrous HI through the solution caused the brown solid to dissolve and a yellow-green solid to precipitate. This was collected, washed with diethyl ether, and dried in vacuo at 100 °C.

***cis*-Hydridochlorobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate Acetone Solvate, $[RhHCl(fdma)_2]PF_6 \cdot 0.25(CH_3)_2CO$.** An acetone solution (10 mL) containing 0.120 g (0.240 mmol) of $[Rh(C_8H_{12})Cl]_2$ and 0.27 mL (0.40 g, 0.97 mmol) of fdma was refluxed for 1 h by which time it had become dark brown. The addition of 0.080 g (0.480 mmol) of NH_4PF_6 caused the solution to become orange and after 30 min of stirring a yellow-orange solid precipitated. This was filtered off, washed with ethanol and diethyl ether, and dried in vacuo at 100 °C.

***cis*-Hydridobromobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate, $[RhHBr(fdma)_2]PF_6$.** This was prepared in an

Table I. Analytical Data

No.	Complex	Found(%) C	H	F	Y[b]	Calc.(%) C	H	F	Y[b]	M.P.(°C.)[a]	Yield(%)
1	$[Rh(p\text{-}CH_3C_6H_4SO_2)Cl(Qas)]PF_6$[c]	35.8	3.4		3.9[d]	35.24	3.53		3.36[d]	238d	56
2	$[Rh(CH_3)I(Qas)]PF_6$	30.2	3.5	11.9	12.3[e]	29.79	3.30	11.30	12.69[e]		87
3	$[RhCl_2(Qas)]Cl\cdot 2CHCl_3$	29.1	3.2		28.3[d]	29.28	3.02		29.93[d]	300d	86
4	$[Rh(fdma)_2]PF_6$	32.65	3.8	11.2		32.46	3.89	11.00			78
5	$[Rh(CO)(fdma)_2]PF_6\cdot 0.25C_4H_8O$	32.7	3.8	9.7		33.00	3.88	10.44		218d	90
6	$[Rh(SO_2)(fdma)_2]PF_6$	30.5	3.6	10.1	2.9[g]	30.57	3.67	10.36	2.91[g]	239d	90
7	$[Rh(CNC(CH_3)_3)(fdma)_2]PF_6\cdot (CH_3)_2CO$	36.5	4.6		1.0[f]	36.73	4.63		1.19[f]	186d	82
8	$[Rh(CNC(CH_3)_3)_2(fdma)_2]PF_6$	37.0	4.9		2.4[f]	37.96	4.87		2.33[f]		76
9	$[Rh(O_2)(fdma)_2]PF_6\cdot C_4H_8O$	33.7	4.2	9.3		33.71	4.24	9.98		163d	80
10	$[Rh(S_2)(fdma)_2]PF_6\cdot 0.2(CH_3)_2CO$	30.3	3.7	10.0	4.8[g]	30.90	3.74	10.25	5.77[g]	220d	63
11	$[Rh(C_4F_6)(fdma)_2]PF_6$	32.35	3.3	18.05		32.08	3.37	19.02		234d	65
12	$[Rh(SO_4)(fdma)_2]PF_6\cdot (CH_3)_2CO$	31.6	4.0	9.45	2.6[g]	31.29	3.90	9.57	2.69[g]	238d	57
13	cis-$[RhH_2(fdma)_2]PF_6$	32.2	4.1	10.6		32.40	4.08	10.98		160d	82
14	trans-$[Rh(CH_3)I(fdma)_2]PF_6$	29.5	3.6	9.8	10.8[e]	29.51	3.68	9.68	10.77[e]	248d	77
15	trans-$[Rh(CH_3SO_2)Cl(fdma)_2]PF_6$[h]	30.4	3.8	9.7	3.2[d]	30.28	3.77	9.91	3.08[d]	245d	75
16	trans-$[RhBr_2(fdma)_2]PF_6$	28.25	3.5	9.3	13.2[i]	28.12	3.37	9.53	13.37[i]	273d	65
17	trans-$[RhI_2(fdma)_2]PF_6$	25.4	3.0	8.3	19.1[e]	25.10	3.01	8.51	18.95[e]	288d	86
18	trans-$[RhHCl(fdma)_2]PF_6\cdot 0.5C_4H_8O$	32.3	4.15	10.15	3.2[d]	32.61	4.01	10.31	3.21[d]	183d	70
19	trans-$[RhHBr(fdma)_2]PF_6\cdot 0.7C_4H_8O$	31.9	4.0	9.6	6.8[i]	31.62	4.01	9.78	6.86[i]	182d	76
20	trans-$[RhHI(fdma)_2]PF_6\cdot 0.5C_4H_8O$	30.1	3.95	9.7	11.0[e]	30.03	3.70	9.50	10.58[e]	202d	66
21	cis-$[RhHCl(fdma)_2]PF_6\cdot 0.25(CH_3)_2CO$	31.7	3.8	10.4	3.5[d]	31.77	3.94	10.48	3.26[d]	230d	83
22	cis-$[RhHBr(fdma)_2]PF_6$	30.0	3.7	10.1	7.1[i]	30.11	3.70	10.20	7.16[i]	239d	48
23	cis-$[RhHI(fdma)_2]PF_6$	28.9	3.4	9.8	11.0[e]	28.90	3.55	9.79	10.90[e]	235d	65
24	cis-$[Rh(SCH_3)_2(fdma)_2]PF_6$	30.8	3.7		5.65[g]	31.88	4.11		5.67[g]		63

[a] d, decomposed. [b] Analysis for indicated element. [c] Sulfur analysis: Found, 3.1; Calc., 3.57%. [d] Chlorine analysis. [e] Iodine analysis. [f] Nitrogen analysis. [g] Sulfur analysis. [h] Sulfur analysis: Found, 2.8; Calc., 2.79%. [i] Bromine analysis.

analogous manner to the previous complex from 0.15 g (0.26 mmol) of $[Rh(C_8H_{12})Br]_2$, 0.29 mL (0.41 g, 1.03 mmol) of fdma, and 0.076 g (0.465 mmol) of NH_4PF_6 in 10 mL of acetone. Following addition of the NH_4PF_6, the orange solution was refluxed for 5 h during which time the product precipitated as orange crystals which were collected, washed with ethanol and diethyl ether, and dried in vacuo at 100 °C.

cis-**Hydridoiodobis(1,1′-bis(dimethylarsino)ferrocene)rhodium(III) Hexafluorophosphate, [RhHI(fdma)$_2$]PF$_6$.** To a solution of 0.411 g (0.396 mmol) of freshly prepared $[Rh(fdma)_2]PF_6$ in 6 mL of acetone was added 45 μL (0.086 g, 0.550 mmol) of ethyl iodide and the solution was stirred for 1 h at 40 °C. The orange solid which precipitated was collected, washed with diethyl ether, and dried in vacuo at 100 °C.

cis-**Bis(methanethiolato)bis(1,1′-bis(dimethylarsino)ferrocene)-rhodium(III) Hexafluorophosphate, [Rh(SCH$_3$)$_2$(fdma)$_2$]PF$_6$.** To 0.23 g (0.22 mmol) of freshly prepared $[Rh(fdma)_2]PF_6$ in 5 mL of acetone was added 20 μL (0.021 g, 0.22 mmol) of CH_3SSCH_3. After refluxing for 1 h the solution was cooled and diluted with 5 mL of diethyl ether whereupon the product precipitated as red-orange microcrystals. These were filtered off, washed with diethyl ether, and dried in vacuo.

Results and Discussion

Analytical data are presented in Table I while Table II gives pertinent spectroscopic data.

Complexes of Qas. Although dihydrogen appears to react with square-planar d^8 complexes such as $Ir(CO)Cl(P(C_6H_5)_3)_2$ in a concerted fashion to give *cis*-dihydrido species,[19] in the majority of cases where oxidative addition of a single bond to such species occurs, trans adducts are formed. The latter reaction is thought to proceed via a two-step displacement[19] or a radical[20] process when performed in a homogeneous system. It was of interest, therefore, to determine whether a concerted cis addition of molecules such as methyl iodide, halogens, or hydrogen halides, which normally give trans adducts, would occur when ligand constraints on the substrate d^8 complex would permit only a cis adduct to be formed. A possible substrate of this type would be $Rh(Qas)^+$ (Qas = tris(*o*-dimethylarsinophenyl)arsine). Initial attempts to prepare this species via cationic rhodium(I)–olefin complexes were generally unsuccessful. Reaction of Qas with "$[Rh(C_8H_{12})]PF_6$"[21] gave a product analyzing for $[Rh(C_8H_{12})(Qas)]PF_6\cdot 0.3(CH_3)_2CO$. Although it appeared to react with $(CD_3)_2SO$, the NMR spectrum of a fresh solution suggested the presence of bidentate cyclooctadiene (resonances at τ 6.17 s, 7.73 m, 8.48 d[14]) and tridentate Qas (τ 7.93 s, 8.30 s, 8.90 s, 9.27 s). The acetone of solvation showed a singlet at τ 7.90.

Table II. Spectroscopic Data for fdma Complexes

Complex	Infrared Band Maxima[a] (cm^{-1})	Assignment	^1H NMR(τ)[b]	Solvent	Assignment[c]
4			8.27(s)		As-CH_3
			5.39(m), 5.54(m)	CD_3NO_2	cp
5	1914(s)	C≡O	8.18(s)		As-CH_3
			5.35(m), 5.52(m)	$(CD_3)_2CO$	cp
6	1173(s), 1020(s)	S-O	8.12(s)		As-CH_3
			5.37(m), 5.52(m)	CH_2Cl_2	cp
7	2052(sh), 2026(s)	N≡C	8.26(s)		As-CH_3
			8.32(s)		-$C(CH_3)_3$
			5.48(m), 5.55(m)	$(CD_3)_2CO$	cp
8	2116(s), 2065(sh)	C≡N	8.42(s)	$(CD_3)_2CO$	C-CH_3
			8.29(s)		As-CH_3
			5.51(m)		cp
9			8.12(s), 8.29(s), 8.31(s), 8.61(s)		As-CH_3
			5.18(m), 5.30(m), 5.57(m)	$(CD_3)_2SO$	cp
10	542(m)	RhS_2	7.85(s), 8.17(s), 8.35(s), 8.54(s)		As-CH_3
			5.42(m)	$(CD_3)_2SO$	cp
11	1815(m), 1780(sh)	C≡C	7.94(s), 8.04(s), 8.44(s), 8.60(s)		As-CH_3
			5.46(m)	$(CD_3)_2SO$	cp
12	1242(s), 1145(s), 890(s), 632(s)	SO_4	7.94(s), 7.99(s), 8.03(s), 8.09(s)		As-CH_3
			4.58(m), 5.22(m), 5.37(m), 5.54(m)	$(CD_3)_2SO$	cp
13	1982(m), 1961(m)	Rh-H	22.6(d), $^1J_{Rh-H}$ =14.5Hz		Rh-H
			8.26(s), 8.28(s), 8.29(s), 8.38(s)		As-CH_3
			5.49(m)	$(CD_3)_2CO$	cp
14			8.75(d), $^2J_{Rh-H}$ = 2Hz		Rh-CH_3
			7.84(s), 8.17(s)		As-CH_3
			4.98(m), 5.55(m)	CD_3NO_2	cp
15	1200(s), 1050(s)	S-O	7.96(s), 8.14(s)		As-CH_3
			6.68(s)		S-CH_3
			5.11(m), 5.24(m), 5.54(m)	$(CD_3)_2SO$	cp
16			7.93(s)		As-CH_3
			5.13(m), 5.40(m)	CD_3NO_2	cp
17			7.71(s)		As-CH_3
			5.08(m), 5.38(m)		cp
18	2032(m)	Rh-H	28.17(d), $^1J_{Rh-H}$ = 12Hz	CH_2Cl_2	Rh-H
			8.09(s), 8.17(s)		As-CH_3
			5.25(m), 5.45(m)		cp
19	2024(m)	Rh-H	27.07(d), $^1J_{Rh-H}$ = 13Hz	CH_2Cl_2	Rh-H
			8.01(s), 8.14(s)		As-CH_3
			5.29(m), 5.41(m)		cp
20	2018(m)	Rh-H	25.07(d), $^1J_{Rh-H}$ = 14Hz	CH_2Cl_2	Rh-H
			7.88(s), 8.11(s)		As-CH_3
			5.33(m), 5.43(m)		cp
24			8.30(s)	$(CD_3)_2SO$	S-CH_3
			7.98(s), 8.00(s), 8.08(s), 8.17(s)		As-CH_3
			5.07(m), 5.21(m), 5.47(m)		cp

[a] s = strong; m = medium; sh = shoulder.

[b] s = singlet; d = doublet; m = multiplet

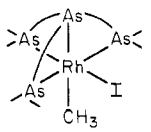
[c] cp = cyclopentadienyl

On standing, a new signal appears at τ 4.56 at the expense of the τ 6.17 resonance while the τ 8.30 singlet shows a marked increase in intensity at the expense of the other resonances assigned to Qas. This suggests a partial conversion to a species containing monodentate cyclooctadiene and tetradentate Qas. A similar route starting from "$[Rh(C_2H_4)_2]PF_6$" yielded a product whose NMR spectrum ($(CD_3)_2SO$) showed the anticipated singlet for Qas at τ 8.32 but also showed an additional resonance at ca. τ 8.0 attributable to coordinated ethylene. In both cases attempts to remove the coordinated olefins led to decomposition.

Further attempts to produce $[Rh(Qas)]PF_6$ from neutral precursors were equally unsuccessful. Thus the dark red, air-sensitive solid produced from $[Rh(C_8H_{12})Cl]_2$ and Qas in dichloromethane (presumed to be [Rh(Qas)Cl] by analogy with [Rh(QAS)Cl] (QAS = tris(*o*-diphenylarsinophenyl)-arsine)[22]) underwent oxidation upon treatment with $AgPF_6$ in ethanol with the precipitation of metallic silver. Reaction of Qas with $[Rh(CO)_2Cl]_2$ gave a yellow-green solid having $\nu_{C\equiv O}$ at 1984 cm^{-1} and showing a singlet in its NMR spectrum at τ 8.23 ($CDCl_3$). This is presumed to be [Rh(Qas)(CO)]Cl by analogy with [Rh(QAS)(CO)]Cl.[22] Metathesis with $LiPF_6$ in ethanol gave $[Rh(Qas)(CO)]PF_6$ which was subjected to prolonged reflux in decalin and in 2-methoxyethanol and to

photolysis in acetonitrile under a nitrogen purge but decarbonylation did not occur.

The failure to obtain $[Rh(Qas)]PF_6$ made it impossible to carry out the planned mechanistic studies but the chemistry of the species formulated as $[Rh(C_8H_{12})(Qas)]PF_6$ was briefly studied. Reaction with *p*-toluenesulfonyl chloride produced a yellow species formulated as $[Rh(p\text{-}CH_3C_6H_4SO_2)Cl(Qas)]PF_6$ (**1**) whose infrared spectrum showed strong absorptions at 1187 and 1040 cm^{-1} which can be assigned to ν_{SO} of a sulfinate-*S* ligand. The NMR spectrum ($(CD_3)_2SO$) showed seven resonances in the τ 7.6–8.4 region which is consistent with a cis adduct in which all three dimethylarsino groups are coordinated. With methyl iodide $[Rh(CH_3)I(Qas)]PF_6$ (**2**) is produced which has an NMR spectrum consisting of three resonances of equal intensity at τ 7.94, 8.11, and 8.36 due to the arsenic methyl groups and a rather broad absorption at τ 7.73 due to the methyl group bound to rhodium. Although no Rh–H coupling was resolved, the breadth of this last resonance and the appearance of three arsenic methyl resonances suggest that the methyl iodide has in fact undergone oxidative addition to give a six-coordinate cis adduct. Although these data do not permit a definite assignment of stereochemistry, models indicate that the axial site may be somewhat more favorable for the methyl group, viz.



Solutions of [Rh(Qas)Cl] in chloroform gradually turn yellow, and crystals of $[RhCl_2(Qas)]Cl\cdot 2CHCl_3$ (**3**) precipitate. The presence of chloroform of solvation is shown by the appearance of a singlet in the NMR spectrum at τ 1.54 which is absent in the product obtained from $CDCl_3$. The infrared spectrum of the latter shows bands due to C–D stretching vibrations at 2190 and 2230 cm^{-1}. The NMR spectrum of **3** ($(CD_3)_2SO$) also shows three singlet resonances of equal area at τ 7.86, 7.90, and 8.30.

It appears that Rh(I) when bound to Qas has a considerably greater tendency to bind an additional ligand than when coordinated to other methyl-substituted arsines such as *o*-phenylenebis(dimethylarsine)[1] (diars) or 1,1′-bis(dimethylarsino)ferrocene (fdma). While this might be due to the desired $Rh(Qas)^+$ species having somewhat less than the 16-electron configuration attained by these other complexes as a result of a weak interaction with the axial arsenic, this does not seem to be the case as the available evidence (including models) indicates that ligands of this type should give "axially compressed" complexes.[23] The only other explanation seems to be that the expected trigonal-pyramidal coordination for $Rh(Qas)^+$ is very unfavorable and that Rh(I) prefers trigonal-bipyramidal coordination if a square-planar, four-coordinate arrangement is not possible.

Complexes of fdma. We have previously reported on oxidative addition reactions of $[Rh(diars)_2]PF_6$,[1] a complex which possesses considerable Lewis basicity. These studies were hampered by difficulties in obtaining pure products. For this reason we decided to study $[Rh(fdma)_2]PF_6$ since it should have a comparable basicity and because its increased bulk was expected to lead to more tractable products. The desired complex $[Rh(fdma)_2]PF_6$ (**4**) was readily prepared by the established procedure[1] and like $[Rh(diars)_2]PF_6$ is extremely sensitive to oxygen with which it forms an adduct even in the solid state. The fdma ligand is quite flexible and several conformations for **4** are possible. The most probable are either one in which the iron atoms are coplanar with the $RhAs_4$ moiety which necessitates staggered cyclopentadienyl rings or a stepped structure in which the iron atoms are above and below this plane with the cyclopentadienyl rings eclipsed.[24] Each of these conformations if static should place the methyl groups in both quasi-axial and -equatorial positions. Interconversion of the quasi-axial and -equatorial methyl groups in both possible structures can occur readily.[24] The observation of a single methyl resonance and an AA′BB′ pattern for the cyclopentadienyl protons (Table II) is thus consistent with either structure and indicates that rapid interconversion is taking place.

Neutral molecules such as carbon monoxide, sulfur dioxide, and *tert*-butyl isocyanide add to **4** to produce $[Rh(CO)(fdma)_2]PF_6\cdot 0.25C_4H_8O$ (**5**), $[Rh(SO_2)(fdma)_2]PF_6$ (**6**), $[Rh(CNC(CH_3)_3)(fdma)_2]PF_6\cdot(CH_3)_2CO$ (**7**), and $[Rh(CNC(CH_3)_3)_2(fdma)_2]PF_6$ (**8**). The monoadduct **7** can only be obtained if a slight deficiency of the isocyanide is used. Otherwise the bis(isocyanide) complex **8** is formed. The CO and SO_2 ligands are substitution labile and **5** and **6** can be interconverted by treatment with the appropriate ligand. Conversion of **5** into $[Rh(O_2)(fdma)_2]PF_6$ (**9**) also occurs readily upon treatment with dioxygen. By contrast, the *tert*-butyl isocyanide ligand cannot be replaced. Thus although treatment of **5** with the isocyanide produced **8**, the action of CO on **7** yields what appears to be $[Rh(CO)(t\text{-}BuNC)(fdma)_2]PF_6$ from infrared spectral data ($\nu_{C\equiv N}$ 2120 cm^{-1}, $\nu_{C\equiv O}$ 1930 cm^{-1}) although it could not be obtained pure. A similar mixed carbonyl–isocyanide complex of iridium has been previously reported.[12]

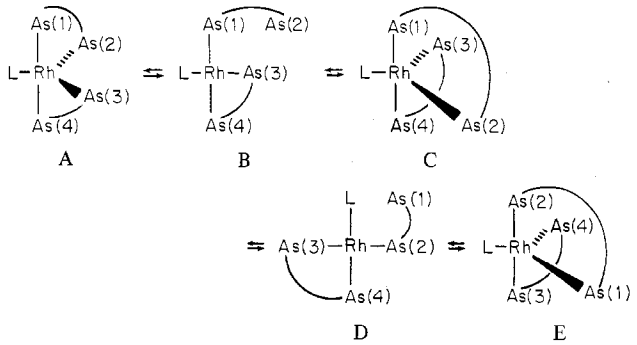
The energies of $\nu_{C\equiv O}$, ν_{S-O}, and $\nu_{C\equiv N}$ in **5**–**7** (Table II) occur at rather low energies for this type of complex indicating the considerable basicity of the fdma ligand. For comparison, $\nu_{C\equiv O}$ appears at 1953 cm^{-1} in $[Rh(CO)(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]PF_6$[25] and at 1956 cm^{-1} in $[Rh(CO)(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2]B(C_6H_5)_4$.[13] Similarly ν_{SO} is 1192 and 1038 cm^{-1} in $[Rh(SO_2)(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2]PF_6$[1] and ν_{SO} is 1208 and 1053 cm^{-1} in $[Rh(SO_2)(CO)Cl(P(C_6H_5)_3)_2]$.[26] These data suggest a "bent" SO_2 moiety (i.e., Rh–S–O $\approx$ 120°) since the "planar" SO_2 group in $[(\eta^5\text{-}C_5H_5)Rh(SO_2)(C_2H_4)]$[27] shows ν_{SO} at 1258 and 1105–1093 cm^{-1}. No information is provided however concerning the coordination geometry about rhodium. The position of $\nu_{C\equiv N}$ in **7** is 113 cm^{-1} below that for the free isocyanide indicating that it behaves as a π acceptor. Again for comparison, $\nu_{C\equiv N}$ occurs at 2125 cm^{-1} in $[Rh(CNC(CH_3)_3)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]BF_4$.[28] The energies of $\nu_{C\equiv N}$ in **8** are also rather low since in $[Rh(CNC(CH_3)_3)_2(P(CH_3)(C_6H_5)_2)_3]PF_6$[12] this absorption occurs at 2148 cm^{-1}.

The simplicity of the ^1H NMR spectra of **5** and **7** (Table II) clearly indicates that at room temperature dynamic processes are occurring in solution. Cooling to −80 °C causes some broadening of all resonances but no limiting spectra could be obtained. That the simple spectra are not the result of dissociation of the monodentate ligand is demonstrated by the observation that neither CO nor *t*-BuNC can be removed at 100 °C in vacuo and that **5** can be recovered after refluxing for 8 h in tetrahydrofuran in a stream of nitrogen. In order to discuss other possible averaging processes some assumptions must be made about the structures of **5** and **7**. The most reasonable choice is one based on a trigonal bipyramid (TBP) with CO or *t*-BuNC in an equatorial site. This is the structure adopted by the similar complexes $[Ir(CO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$,[29] $[Ir(CO)Cl(P(CH_3)_2C_6H_5)_3]$,[30] and $[Ir(CNCH_3)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]ClO_4$.[31] It is also the structure predicted by Kepert's work[32] based on the large "normalized bite" of fdma as well as that which best minimizes intramolecular interactions between the bulky fdma ligands. Furthermore, in $[Ni(CO)I_2(fdma)]$[33] the diarsine ligand

readily spans axial–equatorial positions in a TBP while minimizing distortions of the ferrocene moiety. It also adopts the "step" conformation which models show to be preferred in the present case.

With the assumption of a TBP structure (C_{2v}) a static molecule will have four pairs of As–CH_3 groups and two pairs of cyclopentadienyl rings (attached to axial and equatorial arsenic atoms, respectively) which are symmetry inequivalent. The static molecule should therefore exhibit four methyl resonances and two ABCD patterns for the cyclopentadienyl protons. To account for the observed single methyl resonance and the narrow AA′BB′ cyclopentadienyl pattern one can postulate several schemes which average all four pairs of methyl groups and both sides of the cyclopentadienyl rings together with interchanges of the latter between "axial" and "equatorial" environments. As such schemes are rather elaborate, it could be argued that accidental chemical shift degeneracies occur between "axial" and "equatorial" cyclopentadienyl rings and between methyl groups bound to the same arsenic atom or between axial and equatorial methyl groups so that less extensive rearrangement processes would suffice to give the observed spectra. While no evidence was found for two distinct ABCD patterns in the spectra of the effectively five-coordinate TBP complexes $[RhY(fdma)_2]PF_6$ (Y = O_2, S_2, $CF_3C{\equiv}CCF_3$ (**9**–**11**)) which are assumed to be nonfluxional since four relatively well-separated methyl resonances are observed (vide infra) thereby implying closely similar chemical shifts for corresponding protons on "axial" and "equatorial" cyclopentadienyl rings, it does not seem likely that accidental chemical shift degeneracies also occur among the various sets of methyl groups. First, the single methyl resonance remains sharp and symmetrical down to −50 °C, and even though broadened at lower temperatures it is still symmetrical. This is more consistent with exchange equivalence of all methyl groups than with an accidental degeneracy of chemical shifts. Also, the spectra of **9**–**11** show that the four sets of methyl groups have distinctly different chemical shifts. While one might expect that the separations between the various methyl resonances would be greater in **9**–**11** as compared with those in **5** and **7**, it is difficult to see why they should be so decreased in the latter that degeneracies would occur. Thus while it cannot be proved that accidental degeneracies of chemical shift for some of the methyl groups do not occur, this seems to be more likely.

Assuming, therefore, that **5** and **7** should show four distinct methyl resonances, we are left to consider a variety of aeae and ae permutations within a five-coordinate complex or a series of ring-openings and rearrangements via four-coordinate intermediates in order to explain the observed spectra. The various aeae and/or ae permutations involve rather extensive series of molecular motions besides necessitating that the π-acceptor ligand traverse the less favorable[34,35] axial position. These, together with the considerable steric congestion evident from models, suggest that such processes are also unlikely. The more plausible given the available data is the latter, viz.



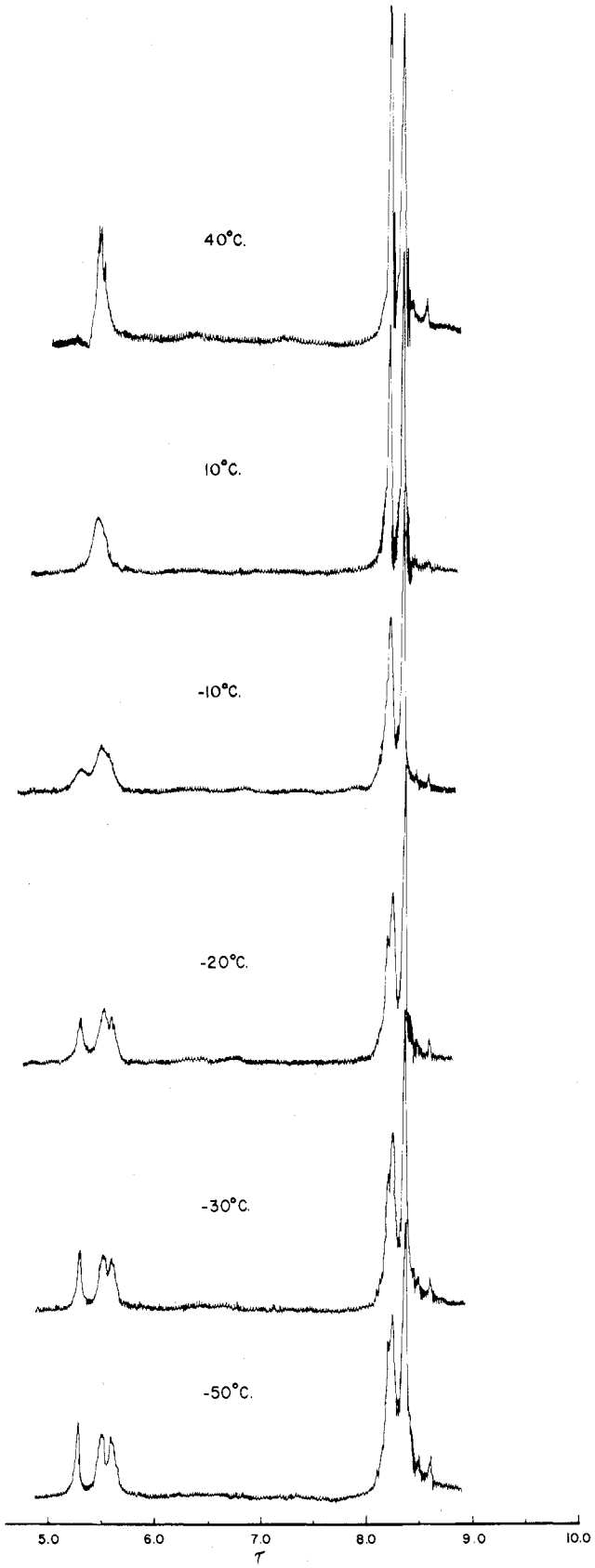


Figure 1. ^1H NMR spectrum of $[Rh(CNC(CH_3)_3)_2(fdma)_2]PF_6$ (**8**) in $(CD_3)_2CO$ as a function of temperature.

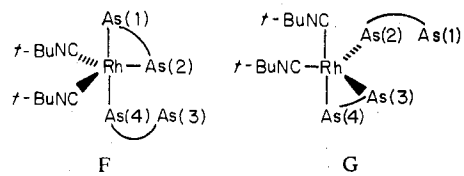
Neither the transformation A → B → C nor C → D → E by itself is sufficient to perform all of the equilibrations necessary to yield the observed spectra. Thus the first with simultaneous flexing of the fdma ligands (either from one "step" confor-

mation to the other or by rotation of the cyclopentadienyl rings relative to one another) equilibrates both sides of the cyclopentadienyl rings and interchanges methyl groups on each arsenic. With the presumed C_{2v} symmetry this can at best give two sets of equivalent methyl groups as there is no interchange of axial and equatorial $As(CH_3)_2$ groups. The latter sequence performs the axial–equatorial averaging as well as that of both sides of the cyclopentadienyl rings but does not average the methyl groups within a given $As(CH_3)_2$ moiety. Although it would seem that these two processes should have different activation energies, it is not clear how much this should be. Evidently both must be rather low.

Several lines of evidence support this scheme. The complex $[Ir(CO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$ shows interchange of axial and equatorial phosphorus environments,[36] and while it is suggested that no bond breaking occurs, this statement apparently refers only to Ir–CO and not Ir–P cleavage. Moreover, the complexes $[Ir(CNCH_3)(L_2)_2]ClO_4$ (L_2 = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$) have been shown to be fluxional down to −60 °C[37] and an "arm-off" process has been suggested.[31] Further support is provided by the ready conversions of **5** into **6**, **8**, and **9**, by the facile addition of CO and *tert*-butyl isocyanide to **7** and by the observation that **5** undergoes CO exchange readily at room temperature. Thus when a dichloromethane solution of **5** is treated with ^{13}CO (1 atm) for 30 s, the infrared spectrum shows, in addition to the 1940-cm^{-1} band of the original ^{12}CO complex, a new band at 1898 cm^{-1} attributable to $\nu_{C\equiv O}$ of $[Rh(^{13}CO)(fdma)_2]PF_6$. Reintroduction of ^{12}CO causes a diminution of the intensity of the latter absorption but further sweeping with nitrogen has no effect. Also, the infrared spectrum of a dichloromethane solution of **5** under a slight positive pressure of CO shows, in addition to the strong band at 1940 cm^{-1}, two further weak bands at 1968 and 2013 cm^{-1} which disappear when the solution is flushed with nitrogen. Similar bands have been observed for $[Rh(CO)_2(PCH_3(C_6H_5)_2)_3]ClO_4$ ($\nu_{C\equiv O}$ 1980, 2027 cm^{-1}; CH_2Cl_2 solution[38]) and $[Ir(CO)_2(P(CH_3)_2C_6H_5)_3]B(C_6H_5)_4$ ($\nu_{C\equiv O}$ 1947, 1998 cm^{-1}; $CHCl_3$ solution[39]) which suggests the presence of a dicarbonyl complex. It is unlikely that these facile substitutions proceed via an associative attack on pentacoordinate **5** or **7** since these would be coordinatively saturated, 18-electron species. Dissociation of one end of a diarsine ligand, would, however, yield a 16-electron species which could readily coordinate an additional ligand. Four-coordinate Rh(I) complexes have been shown to undergo facile ligand exchange and redistribution via five-coordinate intermediates[40] and cationic carbonyl–phosphine and –arsine complexes of Rh(I) and Ir(I) are labile in solution.[38,39]

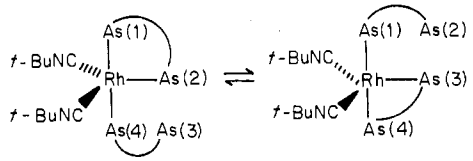
The close similarity of the ^1H NMR spectra of **5** and **6** suggests that **6** may also have a TBP structure. Although the SO_2 adducts studied previously are based on a tetragonal-pyramid (TP) structure with axial SO_2,[26] recent work has pointed to the similarities between SO_2 and NO as ligands and the isoelectronic complex $[Ru(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]B(C_6H_5)_4$ has been shown to be a TBP with equatorial NO.[42] The TBP structure would likely be preferred for **6** on steric grounds and is more consistent with the observed chemical and spectral behavior.

Two possible structures for **8** are



F G

Although a D_{3h} (trans) structure has been suggested for the related complexes $[Rh(CNR)_2(PCH_3(C_6H_5)_2)_3]PF_6$ (R = CH_3, $CH(CH_3)_2$, $C(CH_3)_3$),[12] this seems unlikely here because of the unfavorable requirement that fdma span two equatorial sites. Both structures are consistent with the infrared data (Table II) although F is to be preferred as it places the π-acceptor ligands in equatorial sites.[34,35] The room-temperature ^1H NMR spectrum again indicates that **8** is fluxional but unlike those for **5**–**7**, the spectrum of **8** is noticeably temperature dependent (Figure 1). Following our previous argument we consider that the room-temperature spectrum indicates that equilibration of all eight arsenic methyl groups and both sides of both cyclopentadienyl rings is occurring. This is particularly true here as it is not likely that a free $As(CH_3)_2$ group in a monodentate fdma would appear at the low chemical shift observed since in free fdma the methyl resonance occurs at τ 8.93 (CCl_4 solution). The low-temperature spectra indicate that two different arsenic methyl group environments now exist and that the two sides of the cyclopentadienyl rings are no longer equivalent. However, the absence of a signal attributable to a free $As(CH_3)_2$ group suggests that equilibrium of a free and a bound $As(CH_3)_2$ group must still be occurring, viz.



By assuming this to be the case, the low-temperature spectrum is explicable if As(3) in the above illustration always enters the coordination sphere from the "front" of the molecule while As(2) when free always enters from the "back". This is plausible since models show there to be considerable steric congestion in the molecule which would tend to prevent the free end of the monodentate fdma from swinging to the opposite side of the equatorial $As(CH_3)_2$ group before reentering the coordination sphere. The two methyl resonances observed in the low-temperature spectrum would then be assigned to the axial and equatorial sets.

It is not clear what additional process occurs at the higher temperatures but it must somehow also interchange axial and equatorial $As(CH_3)_2$ groups. The simplest would be an intramolecular ae process although again the steric congestion present would seem to make this difficult. Alternatively it may involve opening of the second chelate ring and rearrangement via a four-coordinate species. It apparently does not involve dissociation of the isocyanide since spectra of **8** in the presence of added *tert*-butyl isocyanide indicated that exchange does not occur but rather that a third isocyanide readily enters the coordination sphere. This provides tentative support for the second process.

An adduct of **4** with carbon disulfide tentatively formulated as $[Rh(\pi\text{-}CS_2)(fdma)_2]PF_6$ could also be prepared but was not obtained pure since it decomposed on attempts at recrystallization. The product showed a strong band at 1150 cm^{-1} which is similar to the spectra observed previously for π CS_2 complexes.[43] The ^1H NMR spectrum shows a complex signal for the cyclopentadienyl protons and seven overlapping singlets in the methyl region. The spectrum is thus consistent with a static species as formulated.

Reaction of **4** with dioxygen occurs rapidly in both the solid state and solution to give **9** which is presumed to have the approximate TBP structure found previously for $[Rh(O_2)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$.[44] The observed ^1H NMR spectrum (Table II) is in accord with a static structure of this type. Absorptions due to the RhO_2 moiety could not be identified in the infrared spectrum due to the presence of ligand bands in the 800–900-cm^{-1} region. The S_2

adduct $[Rh(S_2)(fdma)_2]PF_6$ (**10**) can also be formed and is presumed to have the same structure on the basis of its ^1H NMR spectrum and observation of a band of medium intensity (Table II) assignable to vibrations of the RhS_2 moiety.[45] Several attempts were made to cause reaction of the coordinated disulfur including treatment with CH_3SO_3F, O_2, SO_2, and $NaBH_4$ but only with the last was any reaction observed. No characterizable species could be recovered in that case, but the presence of H_2S was noted indicating that complete decomposition had occurred.

Hexafluorobut-2-yne forms the adduct $[Rh(C_4F_6)(fdma)_2]PF_6$ (**11**) with **4** which is assigned a structure based on a TBP with equatorial $CF_3C{\equiv}CCF_3$ on the basis of the spectral data presented in Table II and the observation of a singlet in the ^{19}F NMR spectrum 12.4 ppm downfield from internal α,α,α-trifluorotoluene. The low value of $\nu_{C\equiv C}$ is comparable to that found in $[RhCl(Sb(C_6H_5)_3)_3(C_4F_6)]$[46] and in $[Rh(C_4F_6)(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2]BF_4$[13] and indicates a significant amount of π back-bonding to the acetylene.

In common with a variety of other dioxygen complexes[48] **9** reacts readily with sulfur dioxide to produce the sulfato complex $[Rh(SO_4)(fdma)_2]PF_6{\cdot}(CH_3)_2CO$ (**12**). That sulfate functions as a bidentate ligand is supported by the spectral data presented in Table II. The mechanism of formation of sulfato complexes from SO_2 and dioxygen complexes has been studied previously[49] and it is presumed that the present reaction proceeds in a similar manner. Complex **12** can also be prepared by the action of dioxygen on **6**, a reaction which is observed to occur in only a limited number of cases. While a similar mechanism could be envisaged for this reaction, the ready replacement of SO_2 by CO in **6** and of CO by O_2 in **5** suggests that the reaction may proceed by initial displacement of SO_2 by O_2 followed by reaction of the liberated SO_2 with the coordinated dioxygen.

Dihydrogen is readily activated by **4** in solution to yield the dihydrido complex $[RhH_2(fdma)_2]PF_6$ (**13**) which from its infrared and ^1H NMR spectra (Table II) is formulated as the cis isomer. The appearance of four methyl resonances indicates a static structure at the temperature of measurement (25 °C). The activation of hydrogen occurs irreversibly as sweeping with nitrogen had no effect. Under ambient conditions **13** does not hydrogenate olefins as treatment of an acetone solution of the dihydride with hept-1-ene did not cause any diminution of the hydride resonance.

Other six-coordinate adducts $[Rh(CH_3)I(fdma)_2]PF_6$ (**14**), $[Rh(CH_3SO_2)Cl(fdma)_2]PF_6$ (**15**), $[RhBr_2(fdma)_2]PF_6$ (**16**), and $[RhI_2(fdma)_2]PF_6$ (**17**) are formed from **4** and CH_3I, CH_3SO_2Cl, Br_2, and I_2, respectively. The ^1H NMR spectrum of **14** clearly shows that the added methyl group is bound to rhodium. The complex is assigned trans stereochemistry on the basis of previous work[19] and the observation of two singlets for the arsenic methyl groups is consistent with this assignment. Such a spectrum could only be produced by a cis isomer if it were fluxional and it is difficult to see how this could occur because of the steric congestion which would be present. The NMR spectrum of the cyclopentadienyl protons is considerably different from that observed for **15** in that the two signals are in the ratio of 1:3 instead of the 1:1:2 ABCD pattern of the latter (vide infra). In fact the spectrum in CD_3NO_2 closely resembles an A_3X pattern. However, the appearance of both resonances (though not the relative intensities) is solvent dependent appearing as two broad singlets in $(CD_3)_2SO$ and two multiplets in CD_3CN. In the last solvent, irradiation of each multiplet in turn collapsed the other to a signal consisting of a large sharp line with a number of small, poorly resolved lines on the high-field side. The spectrum is therefore not A_3X despite its simple appearance but it is best described as approximately ABCX. This is consistent with a ligand conformation in which both ferrocene moieties are on the same side of the $RhAs_4$ plane as the iodide. Inspection of models indicates this to be the most favorable on steric grounds and the downfield shift of one set of cyclopentadienyl protons may then be the result of interaction with the iodide ligand. The infrared spectrum of **15** indicates it to be a sulfinato-*S* complex and the NMR spectrum is consistent with trans stereochemistry. The portion due to the cyclopentadienyl protons resembles that reported for the chelating ligand in μ-fdma-$[Mo(CO)_3(fdma)]_2$[50] although the fine structure of the expected ABCD pattern is poorly resolved. As with **13** models indicate that the probable ligand conformation is one with both ferrocene moieties on the same side of the $RhAs_4$ plane as the chloride.

The dihalo adducts **16** and **17** both exhibit ^1H NMR spectra consistent with trans stereochemistry. The single methyl resonance and the AA'BB' pattern for the cyclopentadienyl protons indicates a ligand conformation analogous to that in **4** with the same type of interconversion occurring.

The reaction of **4** with gaseous HX (X = Cl, Br) gives products which show Rh–H bands in the infrared region but frequently the bands due to PF_6^- are either weak or absent. Also halogen analyses were high and variable. We attribute this to the formation of mixtures of $RhHX(fdma)_2^+$ and $RhX_2(fdma)_2^+$ in which there has also been at least partial replacement of hexafluorophosphate by the corresponding bihalide ion, HX_2^-. The isolation of bihalide salts has been observed previously in the reaction of $[Ir((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$ with hydrogen halides[51,52] and the reaction of hydridohalo complexes with hydrogen halides to give dihalo complexes has also been noted.[53] It is thus evident that strict observance of a 1:1 molar ratio of HX to **4** is necessary to produce the desired hydrido complexes. Because of the ability of **4** to abstract a proton from the ammonium ion, the most convenient means of controlling the stoichiometry of the reaction is to react $[Rh(fdma)_2]X$ with NH_4PF_6. The nature of the products thus obtained depends on the conditions used in the preparation. When preparation is done in tetrahydrofuran at 25 °C, the yellow complexes $[RhHCl(fdma)_2]PF_6{\cdot}0.5C_4H_8O$ (**18**) and $[RhHBr(fdma)_2]PF_6{\cdot}0.7C_4H_8O$ (**19**) are obtained which are soluble in a variety of organic solvents and show ν_{Rh-H} in the region expected for hydride trans to halogen (Table II).[25,54] However, if the reaction is carried out in refluxing acetone, the yellow-orange to orange complexes **21** and **22** are obtained. These also analyze as $[RhHX(fdma)_2]PF_6$ but have distinctly higher melting points and are considerably less soluble than **18** and **19**. Also the rhodium–hydrogen stretching vibrations occur at lower energies (2002 and 1994 cm^{-1}, respectively) which is consistent with hydride trans to arsenic. It is generally observed that ν_{M-H} is at a lower energy when the hydride is trans to a phosphine or arsine than when it is trans to halogen.[53,55] We therefore formulate **18** and **19** as trans isomers in the solid state while **21** and **22** are assigned cis structures. Solutions of **18** and **19** in dichloromethane or acetone slowly deposit orange crystals over several hours at room temperature which from their infrared spectra and melting points are identical with **21** and **22**, respectively.

Because HI shows little tendency to form the HI_2^- anion,[56] it was possible to form an HI adduct $[RhHI(fdma)_2]PF_6$ (**20**) directly from **4** and anhydrous HI in tetrahydrofuran. Reaction of **4** with ethyl iodide in refluxing acetone yielded **23** which also analyzes as $[RhHI(fdma)_2]PF_6$. The same species can also be prepared from **4** and HI in refluxing acetone but in poorer yield.

As with the previous HX adducts, **20** and **23** differ in color, melting point, solubility, and the position of ν_{Rh-H} (2018 and

1998 cm^{-1}, respectively) and are formulated as trans and cis isomers, respectively. We note in passing that only in the reaction of **4** with methyl iodide is an isolable alkylrhodium complex formed. Higher alkyl halides yield either the *cis*-hydridohalo- or *trans*-dihalorhodium species. Details of these interesting reactions are under study and will be reported subsequently.

The results of the preparative work indicate that trans → cis isomerization is possible. The retention of Rh–H coupling in the NMR spectra of all solutions studied (vide infra) indicates that HX dissociation does not occur but whether isomerization involves Rh–As bond fission is not clear. It appears that in solution the preferred isomer is the trans which would be that predicted by steric arguments but that conversion to the cis is accomplished because of its much lower solubility. However, in a solvent where the cis isomers are appreciably soluble, reversion to the trans isomers occurs. This is indicated by the ^1H NMR spectra of the six complexes. The data in Table II for dichloromethane solutions of **18–20** are consistent with the postulated trans formulations particularly as the variation in τ_{Rh-H} with the nature of the halogen ligand is in the order expected for hydride trans to halide.[57,58] These values are also higher than might be expected for hydride trans to arsenic (cf. **13**) which further supports the stereochemical assignments. Although the cis isomers precipitate slowly from these solutions, treatment of the solution of **19** with ether after 10 min led to the recovery of unchanged **19** with no evidence (infrared spectrum) of **22**. Rather unexpectedly, analogous treatment of the solution of **18** yielded **21** as the solid product. While it could be argued that **18** had isomerized to **21** on dissolution with the simple NMR spectrum resulting from stereochemical nonrigidity as has been observed for the related complexes *cis*-$[IrHCl(L_2)_2]PF_6$ ($L_2 = (C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, $n = 2, 3$),[36] we feel that this is not the case but rather that the isomerization occurs on precipitation. From the study of the iridium complex it was found that two independent permutational processes were operative. One involved pairwise permutations of axial and equatorial phosphorus nuclei while the other permuted equatorial sites trans to H and Cl. The latter was rapid over the temperature range studied while the rate of the other depended on the size of the chelate ring and was capable of being stopped for the larger chelate but not for the smaller. In the present case a combination of these processes is capable of averaging the methyl groups so as to give two sets of four if it be assumed that the experiment does not distinguish optical isomers. It is difficult to predict the magnitude of the barrier to rearrangement for the aeae process in the present complex although the bulk of the ligand and the considerable steric congestion of the methyl groups evident in models would suggest it should be high enough to be at least slowed at accessible temperatures. In fact no change in the appearance of the methyl resonances occurred down to −60 °C. Further evidence against the presence of appreciable concentrations of a dynamic cis isomer is the appearance of the cyclopentadienyl proton resonances. If the aeae and ee processes required to produce the observed pair of methyl resonances are operative, then equilibration of both sets of cyclopentadienyl rings must also occur leading to a simple AA′BB′ spectrum as observed for **4**. This is not the case and in fact the spectrum in this region more closely resembles that of **14** than it does the cis complexes **12**, **13**, and **24**. Moreover it is virtually identical with those of **19** and **20** which, because of our ability to recover the complexes without isomerization, are considered to be the spectra expected of authentic trans isomers. Finally we point again to the high value of τ_{Rh-H} which is more consistent with H trans to Cl in this type of complex than trans to arsenic.

The cis isomers **21–23** are insufficiently soluble in dichloromethane to obtain satisfactory NMR spectra. However in $(CD_3)_2SO$ the spectrum of **22** consists of broad multiplets at τ 5.22 and 5.46 due to the cyclopentadienyl protons, two sharp singlets at τ 8.05 and 8.19 attributable to the arsenic methyl groups, and a hydride resonance at τ 27.17 (doublet, $^1J_{Rh-H} = 13$ Hz). The spectrum of **19** in this solvent was identical. Neither spectrum changed with time. The solid recovered from each of these solutions by precipitation with ether after ca. 0.45 h showed ν_{Rh-H} at 2024 and 1992 cm^{-1} indicating a mixture of cis and trans isomers. In both cases the higher energy absorption (trans isomer) was significantly more intense indicating a predominance of the trans isomer in solution. Similar results were obtained with the HI adducts **20** and **23** in $(CD_3)_2SO$ solution with both showing multiplets at τ 5.19 and 5.27 due to the cyclopentadienyl protons, methyl singlets at τ 7.92 and 8.14, and a hydride doublet at τ 25.31 ($^1J_{Rh-H} = 14$ Hz). Attempted recovery of the HI adducts from solution was accompanied by some decomposition; however, infrared spectral data indicated that what hydride remained was predominantly the trans isomer. Solutions of **18** and **21** in $(CD_3)_2SO$ tended to decompose rapidly which made it difficult to obtain satisfactory spectra. On one occasion a spectrum was obtained for **21** in which this was minimal and it closely resembled those of **22** and **23** in the same solvent with cyclopentadienyl multiplets at τ 5.21 and 5.45, two methyl singlets at τ 8.10 and 8.17, and a hydride doublet at τ 28.38 ($^1J_{Rh-H} = 12$ Hz). The limited low-temperature range of the solvent made it impossible to determine if these solutions contained fluxional cis isomers but this is unlikely since again the values of τ_{Rh-H} showed a marked dependence on the nature of the halogen ligand and in fact are essentially those observed for the trans isomers in dichloromethane.

Reaction of **4** with CH_3SSCH_3 yielded the orange complex $[Rh(SCH_3)_2(fdma)_2]PF_6$ (**24**). The appearance of five singlets in the methyl region of the ^1H NMR spectrum is consistent with its formulation as a cis complex which is in contrast to the observation that trans adducts result from the reaction of $[Ir(CO)Cl(PCH_3(C_6H_5)_2)_2]$ and $(C_6H_5)SS(C_6H_5)$.[59] We tentatively assign the singlet at τ 8.30 to the S–CH_3 group. This is based on the observation that in the other cis complexes **12** and **13** the arsenic methyl groups appear in a very narrow range of chemical shifts (0.12–0.15 ppm). Also in *cis*-$[Rh(CO)(SCH_3)(P(C_6H_5)_3)_2]$[60] the *S*-methyl group appears at τ 8.62 while in $(\eta^5\text{-}C_5H_5)Fe(CO)_2SCH_3$[61] it appears at τ 8.39.

Conclusions

Although it was not possible to prepare $[Rh(Qas)]PF_6$ because of its apparent avidity for an additional ligand, a few complexes which could be considered oxidative adducts of it were obtained and are evidently cis complexes. By contrast, $[Rh(fdma)_2]PF_6$ is a versatile substrate for oxidative addition reactions and both cis and trans derivatives could be prepared. Several five-coordinate adducts are fluxional over a considerable temperature range, the rearrangements evidently occurring via opening of a chelate ring.

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Registry No. **1**, 62067-00-9; **2**, 62066-84-6; **3**, 62078-88-0; **4**, 62066-65-3; **5**, 62066-67-5; **6**, 62067-02-1; **7**, 62066-73-3; **8**, 62066-71-1; **9**, 62066-69-7; **10**, 62066-81-3; **11**, 62066-79-9; **12**, 62066-77-7; **13**, 62066-75-5; **14**, 62078-87-9; **15**, 62067-04-3; **16**, 62059-13-6; **17**, 62059-11-4; **18**, 62059-09-0; **19**, 62059-07-8; **20**, 62059-05-6; **21**, 62076-16-8; **22**, 62076-14-6; **23**, 62076-12-4; **24**, 62059-15-8; $[Rh(C_8H_{12})(Qas)]PF_6$, 62059-17-0; $[Rh(C_8H_{12})Cl]_2$,

12092-47-6; $[Rh(C_8H_{12})Br]_2$, 12092-45-4; CH_3SSCH_3, 624-92-0.

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Thermodynamics and Kinetics of Some Tetra-μ-carboxylato-dirhodium(II) Adduct Formation Reactions

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The thermodynamic and kinetic parameters have been determined for adduct formation reactions of tetra-μ-acetato, tetra-μ-propionato, and tetrakis(μ-methoxyacetato)-dirhodium(II) complexes with 5′-AMP, histidine, imidazole, and pyridine. Tetra-μ-propionato-dirhodium(II) forms more stable adducts than tetra-μ-acetato-dirhodium(II) with all of the ligands studied. With 5′-AMP and imidazole tetrakis(μ-methoxyacetato)-dirhodium(II) forms adducts which are the least stable whereas with histidine the reverse order of stability is observed. The rates of adduct formation among the three rhodium(II) carboxylates are in the order methoxyacetate < acetate < propionate. The presence of more than one donor atom on the adduct-forming ligand increases the foward rate constant by approximately an order of magnitude.

Introduction

For the past few years we have been investigating the biologic activity of several tetra-μ-carboxylato-dirhodium(II) complexes.[1-3] The antitumor activity of these complexes was found to increase with increasing number of carbon atoms in the carboxylate ion.[3] Since the tetra-μ-carboxylato-dirhodium(II) species readily forms adducts with various donor ligands by the replacement of the two axial water molecules, we have been investigating this reaction as a possible source of the anticancer activity. Very little is known about the thermodynamic and kinetic stability of these adducts in aqueous solution particularly with regard to how variations in structural properties and basicity of the carboxylate ions bridging the two rhodium ions affect the bonding characteristics at the two axial positions.

Recently we reported the formation constants for the reactions involving rhodium(II) methoxyacetate, acetate, and propionate and the ligands 5′-AMP, 5′-ADP, and 5′-ATP[4] as well as the detailed thermodynamics for the reaction of these carboxylates with imidazole.[5] In these studies the order of stability of the adducts was the same as the biologic activity, i.e., propionate > acetate > methoxyacetate. However the variation in the stability of the adducts was not nearly as large as that observed for their toxicity and antitumor activity.

The previous studies[4,5] indicate that the lipophilic nature of the bridging carboxylate ion is a dominant factor in determining the order of stability of the adducts. Since the methoxyacetate ion is less basic than the propionate ion, tetrakis(μ-methoxyacetato)-dirhodium(II) adducts should be more stable if an inductive effect was the stability-controlling factor. The thermodynamic studies with imidazole as the

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