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Organometallic Chemistry of the Transition Metals. XXXI. Stereoisomerism in Cyclopentadienylrhenium(III) Derivatives[1,2]

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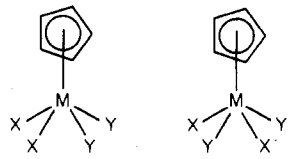
Reaction of $C_5H_5Re(CO)_3$ with bromine in trifluoroacetic acid gives $C_5H_5Re(CO)_2Br_2$ which can be separated into pure diagonal and lateral isomers by column chromatography. The lateral isomer $C_5H_5Re(CO)_2Br_2$ is readily converted to the corresponding diagonal isomer upon mild heating. Reactions of *diag*-$C_5H_5Re(CO)_2Br_2$ with the phosphites $(RO)_3P$ (R = CH_3, C_2H_5, and C_6H_5) in boiling benzene give *diag*-$C_5H_5Re(CO)[P(OR)_3]Br_2$ which isomerizes to *lat*-$C_5H_5Re(CO)[P(OR)_3]Br_2$ in boiling toluene. The reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with trimethyl phosphite in boiling toluene also results in methyl bromide elimination to give two isomers of the phosphonate $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$. Reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with *tert*-butyl isocyanide in boiling benzene gives an isomer of $C_5H_5Re(CO)[(CH_3)_3CNC]Br_2$ which is stable to isomerization in boiling toluene. Simple steric effects are sufficient to explain the stereochemistry of these reactions of cyclopentadienylrhenium(III) derivatives.

Introduction

Cyclopentadienylmetal derivatives of the type $C_5H_5MX_4$ are formed by many d^4 transition metals[4] of the 4d and 5d transition series including Nb(I), Ta(I), Mo(II), W(II), and Re(III). If the X ligands are not all equivalent but form at least two nonequivalent pairs in derivatives of the types $C_5H_5MX_2Y_2$ and $C_5H_5MX_2YZ$, then two stereoisomers are possible (Ia and Ib). Although these two stereoisomers are frequently called the cis (Ia) and trans (Ib) isomers, the more precise terms lateral (Ia: abbreviated in formulas as *lat*-) and diagonal (Ib: abbreviated in formulas as *diag*-) appear preferable since neither stereoisomer has the 180° ligand–metal–ligand bond angles present in a true trans isomer.



Ia Ib

The stereochemistry and interconversions of lateral and diagonal isomers of the types Ia and Ib have been studied in greatest detail for cyclopentadienylmolybdenum derivatives.[5,6] However, at the time the work described in this paper was initiated pure lateral and diagonal isomers of the same compound had not been separated by well-defined procedures suitable for preparation of pure isomers in multigram quantities, although a brief report[7] as well as more recent work[8] suggested the possibility of separating pure lateral and diagonal isomers of halide complexes of the type $C_5H_5Mo(CO)_2LX$ (L = $(CH_3)_3CNC$, C_6H_5NC, and $(C_6H_5)_3P$; X = Cl, Br, and I) by rather tedious and poorly described fractional crystallization procedures.[9]

The inability to isolate readily both the lateral and diagonal isomers of extensive series of related compounds because of rapid interconversions in solution limits the use of cyclopentadienylmolybdenum derivatives for establishing the stereochemistry of reactions of $C_5H_5MX_4$ derivatives. For this reason the chemistry of $C_5H_5MX_2Y_2$ derivatives of metals other than molybdenum and tungsten was of interest since the necessary changes in formal oxidation state of the metal might alter the chemistry in ways that would increase the number of systems for which pure lateral and diagonal isomers of the same compound could be obtained. This led to an investigation of the chemistry of cyclopentadienylrhenium(III) derivatives of the type $C_5H_5ReX_2Y_2$, the results of which are described in this paper.

At the time this work was started the only known cyclopentadienylrhenium(III) derivatives of the type $C_5H_5ReX_4$ were $[C_5H_5Re(CO)_3Cl][SbCl_6]$,[10] $C_5H_5Re(CO)_2Br_2$,[11] and $C_5H_5Re(CO)_2(CH_3)Br$.[12] Our original plan was to prepare some $C_5H_5Re(CO)_2Br_2$ by the reported method[11] and study its reactivity toward various Lewis base ligands such as tertiary phosphines, phosphites, and isocyanides as well as toward organometallic reagents potentially capable of substituting the bromine atoms. However, during the process of repeating the reported[11] preparation of $C_5H_5Re(CO)_2Br_2$ we found that both the lateral and diagonal isomers were obtained.[1] Furthermore, the two pure stereoisomers could each be readily separated in gram quantities by column chromatography thereby suggesting that the rhenium system was far better than the molybdenum and tungsten systems for studying the stereochemistry of reactions of $C_5H_5MX_4$ derivatives. Our subsequent studies on the reactions of $C_5H_5Re(CO)_2Br_2$ led to the development of well-defined procedures for the preparation of both stereoisomers of the phosphite complexes $C_5H_5Re(CO)[P(OR)_3]Br_2$ (R = CH_3, C_2H_5, and C_6H_5) as well as to the isolation of two of the three possible stereoisomers of the C_5H_5MXYZT derivative $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$. Apparently the only reported C_5H_5MXYZT derivative is the molybdenum complex $C_5H_5Mo(CO)[P(C_6H_5)_3][PF_2N(CH_3)_2]Cl$.[13]

Experimental Section

Microanalyses (Table I) were performed by Atlantic Microlab, Inc., Atlanta, Ga. Melting and decomposition points (Table I) were taken in capillaries and are uncorrected. Infrared spectra (Table II) in the 2200–1800-cm^{-1} ν(CO) region were taken in dichloromethane solution and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton NMR spectra (Table II) were taken in $CDCl_3$ or $(CD_3)_2CO$ solutions and recorded at 100 MHz on a Varian HA-100 spectrometer.

All of the reactions were conducted under nitrogen. However, the cyclopentadienylrhenium(III) derivatives were sufficiently air stable that they could be handled in air without decomposition, even in solution.

Commercial $Re_2(CO)_{10}$ (Pressure Chemical Co., Pittsburgh, Pa.) was converted to $Re(CO)_5Br$ in 98% yield by reaction with 1.1 equiv of bromine in dichloromethane solution at 0°.[14] The $Re(CO)_5Br$ was then converted to $C_5H_5Re(CO)_3$ in 87% yield by treatment with 1.1 equiv of thallium cyclopentadienide[15] in boiling redistilled tetrahydrofuran for 16 hr.[16] The $C_5H_5Re(CO)_3$ was recrystallized once from a mixture of dichloromethane and hexane before use.

Preparation of $C_5H_5Re(CO)_2Br_2$[11] and Separation of Its Stereoisomers. A solution of 8.0 g (50 mmol as Br_2) of bromine in 50 ml of trifluoroacetic acid was added dropwise at 25° to a solution of 17.0 g (51 mmol) of $C_5H_5Re(CO)_3$ in 150 ml of trifluoroacetic acid. After stirring the reaction mixture for an additional 10 min at room temperature, the reaction was quenched by pouring it into 1200 ml of water at 25°. The resulting brown precipitate containing any unreacted $C_5H_5Re(CO)_3$ and both isomers of $C_5H_5Re(CO)_2Br_2$ was filtered and dried at 25° (0.1 mm). This solid was chromatographed in 5 g lots on a 2 × 75 cm Florisil column prepared in dichloromethane. Successive elution with dichloromethane gave first

Table I. Preparation and Properties of the Cyclopentadienylrhenium(III) Derivatives

Compd[a]	Preparation[b]	Solvent	Temp, °C	Time, hr	Yield, %	Color and form	Mp, °C		Analyses, % C	H	Br
diag-$CpRe(CO)_2Br_2$	$CpRe(CO)_3 + Br_2$	CF_3COOH	25	0.17	61	Maroon plates	221–223 dec	Calcd	18.0	1.1	34.2
								Found	17.8	1.1	34.3
lat-$CpRe(CO)_2Br_2$	$CpRe(CO)_3 + Br_2$	CF_3COOH	25	0.17	21	Dark brown	217–220	Calcd	18.0	1.1	34.2
								Found	17.7	1.0	34.1
diag-$CpRe(CO)[P(OEt)_3]Br_2$	$CpRe(CO)_2Br_2 + P(OEt)_3$	Benzene	80	2	80	Dark red plates	161–163 dec	Calcd	23.8	3.3	26.4
								Found	24.0	3.3	26.2
lat-$CpRe(CO)[P(OEt)_3]Br_2$	$CpRe(CO)_2Br_2 + P(OEt)_3$	Toluene	110	26	35	Red-brown prisms	185–189 dec	Calcd	23.8	3.3	26.4
								Found	23.9	3.3	26.2
diag-$CpRe(CO)[P(OPh)_3]Br_2$	$CpRe(CO)_2Br_2 + P(OPh)_3$	Benzene	80	2	90	Red-brown needles	136–138	Calcd	38.5	2.7	21.3
								Found	38.3	2.7	21.3
lat-$CpRe(CO)[P(OPh)_3]Br_2$	$CpRe(CO)_2Br_2 + P(OPh)_3$	Toluene	110	24	45	Brown plates	188–190	Calcd	38.5	2.7	21.3
								Found	38.5	2.7	21.3
diag-$CpRe(CO)[P(OMe)_3]Br_2$	$CpRe(CO)_2Br_2 + P(OMe)_3$	Benzene	80	2	80	Maroon plates	204–206 dec	Calcd	19.2	2.5	28.4
								Found	19.1	2.5	28.2
lat-$CpRe(CO)[P(OMe)_3]Br_2$	$CpRe(CO)_2Br_2 + P(OMe)_3$	Toluene	110	3	40	Dark brown needles	205–207 dec	Calcd	19.2	2.5	28.4
								Found	19.2	2.4	28.3
$CpRe(CO)[P(OMe)_3][P(O)(OMe)_2]Br$ (isomer A)	$CpRe(CO)_2Br_2 + P(OMe)_3$	Toluene	110	30	35	Orange prisms	111–113 dec	Calcd	22.3	3.4	13.5
								Found	22.2	3.5	13.3
$CpRe(CO)[P(OMe)_3][P(O)(OMe)_2]Br$ (isomer B)	$CpRe(CO)_2Br_2 + P(OMe)_3$	Toluene	110	20	8	Lemon yellow needles	158–160 dec	Calcd	22.3	3.4	
								Found	22.1	3.5	
$CpRe(CO)(t\text{-BuNC})Br_2$	$CpRe(CO)_2Br_2 + t\text{-BuNC}$	Benzene	80	3.5	80	Maroon prisms	180 dec	Calcd	25.3	2.7	2.7 (N)
								Found	25.5	2.8	2.8 (N)

[a] Cp = cyclopentadienyl, Me = methyl, Et = ethyl, Ph = phenyl, *t*-Bu = *tert*-butyl. [b] Further details are given in the Experimental Section.

Table II. Spectroscopic Properties of the Cyclopentadienylrhenium(III) Derivatives

Compd[a]	Infrared spectrum ν(CO) in CH_2Cl_2, cm^{-1}	Proton NMR spectrum,[b] τ Solvent	C_5H_5	$(RO)_3P$	Other
diag-$CpRe(CO)_2Br_2$	2074, 1998	$(CD_3)_2CO$	4.00 s		
lat-$CpRe(CO)_2Br_2$	2056, 1975	$(CD_3)_2CO$	3.60 s		
diag-$CpRe(CO)[P(OMe)_3]Br_2$	1972	$CDCl_3$	4.50 s	6.26 d (11)	
lat-$CpRe(CO)[P(OMe)_3]Br_2$	1940	$CDCl_3$	4.20 s	6.15 d (11)	
diag-$CpRe(CO)[P(OEt)_3]Br_2$	1974	$CDCl_3$	4.53 s	CH_2: 5.91 quin (7); CH_3: 8.68 t (7)	
lat-$CpRe(CO)[P(OEt)_3]Br_2$	1939	$CDCl_3$	4.22 s	CH_2: 5.80 quin (7); CH_3: 8.66 t (7)	
diag-$CpRe(CO)[P(OPh)_3]Br_2$	1981	$CDCl_3$	4.84 s	~2.7 m	
lat-$CpRe(CO)[P(OPh)_3]Br_2$	1961	$CDCl_3$	4.32 s	2.71 s	
$CpRe(CO)[P(OMe)_3][P(O)(OMe)_2]Br$ (A)	1970	$CDCl_3$	4.46 s	6.22 d (11)	$(CH_3O)_2PO$: 6.34 d (11), 6.41 d (11)
$CpRe(CO)[P(OMe)_3][P(O)(OMe)_2]Br$ (B)	1931	$CDCl_3$	4.36 s	6.15 d (11)	$(CH_3O)_2PO$: 6.23 d (11)
$CpRe(CO)(t\text{-BuNC})Br_2$	1971	$CDCl_3$	4.42		$(CH_3)_3CNC$: 8.42 s

[a] Cp = cyclopentadienyl, Me = methyl, Et = ethyl, Ph = phenyl, *t*-Bu = *tert*-butyl. [b] s = singlet, d = doublet, t = triplet, quin = quintet, m = multiplet; coupling constants in Hz are given in parentheses.

unreacted $C_5H_5Re(CO)_3$ (5.96 g, 35% recovery), then *diag*-$C_5H_5Re(CO)_2Br_2$ (8.95 g, 38% conversion, 61% yield) from a red band, and finally *lat*-$C_5H_5Re(CO)_2Br_2$ (3.05 g, 13% conversion, 21% yield) from a brown band. The recovered $C_5H_5Re(CO)_3$ was recrystallized from a mixture of dichloromethane and hexane. Each $C_5H_5Re(CO)_2Br_2$ isomer was recrystallized from mixtures of dichloromethane and carbon tetrachloride; any unreacted $C_5H_5Re(CO)_3$ impurity in the $C_5H_5Re(CO)_2Br_2$ isomer remained in the carbon tetrachloride when the $C_5H_5Re(CO)_2Br_2$ crystallized out upon enrichment of the solvent mixture in carbon tetrachloride by slow evaporation.

The chromatographic separation of the $C_5H_5Re(CO)_2Br_2$ isomers from the crude reaction product could be facilitated if the unreacted $C_5H_5Re(CO)_3$ was removed by sublimation at 70° (0.1 mm) before the chromatography. This change in the procedure had little effect on the yield of $C_5H_5Re(CO)_2Br_2$ or on the relative quantities of the two isomers produced.

Preparation of *diag*-$C_5H_5Re(CO)[P(OR)_3]Br_2$. A mixture of *diag*-$C_5H_5Re(CO)_2Br_2$ (0.5 to 0.7 g) and 1.1 equiv of the phosphite $(RO)_3P$ (R = CH_3, C_2H_5, or C_6H_5) in 50 ml of benzene was boiled under reflux for 2 hr. Removal of solvent at 25° (25 mm) followed by crystallization from a mixture of diethyl ether and pentane gave the highly crystalline *diag*-$C_5H_5Re(CO)[P(OR)_3]Br_2$ products in 80–90% yields.

A similar reaction with triisopropyl phosphite resulted in no reaction. The only rhenium compound isolated was unchanged *diag*-$C_5H_5Re(CO)_2Br_2$, identified by its infrared ν(CO) frequencies.

The compound *diag*-$C_5H_5Re(CO)[P(OCH_3)_3]Br_2$ was also similarly prepared in tetrahydrofuran solution.

Preparation of *lat*-$C_5H_5Re(CO)[P(OR)_3]Br_2$. A mixture of *diag*-$C_5H_5Re(CO)_2Br_2$ (0.7 to 1.5 g) and 3.0 equiv of the phosphite $(RO)_3P$ (R = C_2H_5 or C_6H_5) in 50 ml of toluene was boiled under reflux for 24 hr. Removal of solvent at 25° (1 mm) followed by crystallization from a mixture of dichloromethane and pentane gave the corresponding *lat*-$C_5H_5Re(CO)[P(OR)_3]Br_2$ derivative in 35–45% yields.

Triisopropyl phosphite failed to react with *diag*-$C_5H_5Re(CO)_2Br_2$ under these conditions.

Thermal Isomerization of *diag*-$C_5H_5Re(CO)[P(OR)_3]Br_2$. A solution of 0.1 to 0.2 g of the *diag*-$C_5H_5Re(CO)[P(OR)_3]Br_2$ derivative (R = CH_3 or C_6H_5) in 15 ml of toluene was boiled under reflux for 7 to 14 hr. Removal of solvent at 25° (0.1 mm) gave a brown solid shown to be the corresponding lateral isomer by its ν(CO) frequency in dichloromethane solution.

Reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with *tert*-Butyl Isocyanide. (a) In Benzene. A mixture of 0.76 g (1.63 mmol) of *diag*-$C_5H_5Re(CO)_2Br_2$ and 0.136 g (1.64 mmol) of *tert*-butyl isocyanide was boiled under reflux for 3.5 hr in 50 ml of benzene. Solvent was removed at ~25° (25 mm). Chromatography of a concentrated solution of the residue in 4:1 dichloromethane–hexane on a Florisil column prepared in hexane followed by elution with a mixture of dichloromethane and hexane and crystallization from a mixture of

dichloromethane and methanol gave a 60% yield of $C_5H_5Re(CO)[(CH_3)_3CNC]Br_2$.

(b) In Toluene. A mixture of 0.60 g (1.28 mmol) of *diag*-$C_5H_5Re(CO)_2Br_2$ and 0.53 g (6.39 mmol) of *tert*-butyl isocyanide in 50 ml of toluene was boiled under reflux. Removal of solvent at 25° (0.1 mm) followed by crystallization from a mixture of dichloromethane and methanol gave 0.18 g (27% yield) of $C_5H_5Re(CO)[(CH_3)_3CNC]Br_2$, shown by its infrared and proton NMR spectra to be the identical isomer to the product prepared in boiling benzene as described above.

Reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with Trimethyl Phosphite. A mixture of 1.07 g (2.28 mmol) of *diag*-$C_5H_5Re(CO)_2Br_2$ and 0.85 g (6.85 mmol) of trimethyl phosphite in 50 ml of toluene was boiled under reflux for 24 hr. Solvent was removed at 25° (1 mm). The residue was dissolved in 5 ml of dichloromethane and 10 ml of diethyl ether. Pentane was added until the solution became cloudy. Storage at −10° caused the slow crystallization of the following three products, which were separated mechanically: (a) dark brown needles of *lat*-$C_5H_5Re(CO)[P(OCH_3)_3]Br_2$; (b) deep orange prisms of isomer A of $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$; (c) lemon yellow needles of isomer B of $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$. In each of the three cases, pure products were obtained by recrystallizing the mechanically separated crystals from mixtures of dichloromethane and diethyl ether with addition of pentane. Our maximum yields of *lat*-$C_5H_5Re(CO)[P(OCH_3)_3]Br_2$ and isomers A and B of $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$ of 40, 35, and 8%, respectively, were obtained after reaction times of 3, 30, and 20 hr, respectively, in boiling toluene.

An attempt to bypass the tedious mechanical separation of the above three products by using chromatography on a Florisil column prepared in hexane was unsatisfactory since ~80% of the total rhenium compounds decomposed during one passage through the chromatography column.

Reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with Methyldiphenylphosphine. A mixture of 0.77 g (1.65 mmol) of *diag*-$C_5H_5Re(CO)_2Br_2$ and 1.2 g (6.0 mmol) of methyldiphenylphosphine in benzene was boiled under reflux for 6 hr. The resulting mixture was chromatographed on a Florisil column in dichloromethane solution to give ~0.7 g (46% yield) of colorless *mer-cis*-$[CH_3P(C_6H_5)_2]_3Re(CO)_2Br$, mp 172–175° (lit.[17] mp 164–168°), ν(CO) in CH_2Cl_2 1948 and 1846 cm^{-1} (lit.[17] ν(CO) in $CHCl_3$: 1948 and 1850 cm^{-1}), after recrystallization from a mixture of diethyl ether and ethanol.

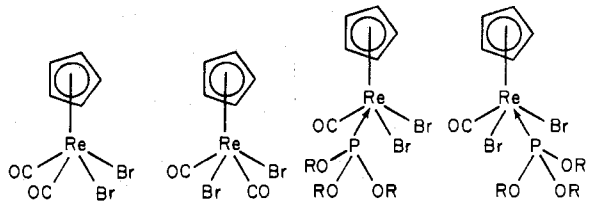
Anal. Calcd for $C_{41}H_{39}BrO_2P_3Re$: C, 53.4; H, 4.3. Found: C, 52.9; H, 4.2.

Reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with Dimethylphenylphosphine. A mixture of 1.08 g (2.32 mmol) of *diag*-$C_5H_5Re(CO)_2Br_2$ and 0.64 g (4.64 mmol) of dimethylphenylphosphine in benzene was boiled for 2 hr under reflux. Chromatography of the reaction mixture on a Florisil column in hexane solution gave an orange fraction which on slow crystallization from a mixture of diethyl ether and pentane at −10° gave an incompletely separated mixture of pale orange prisms of $C_5H_5Re(CO)_2P(CH_3)_2C_6H_5$ and cream needle clusters of *mer-trans*-$[(CH_3)_2PC_6H_5]_2Re(CO)_3Br$, identified by their infrared ν(CO) frequencies.[17]

A similar reaction between *diag*-$C_5H_5Re(CO)_2Br_2$ and dimethylphenylphosphine in tetrahydrofuran at room temperature resulted in an immediate color change from deep red to light orange, followed by formation of a dark brown solution after 10 sec, and then a light orange solution after 1 min. The infrared spectrum of this reaction mixture after 24 hr in $CHCl_3$ solution in the ν(CO) region indicated a mixture of unchanged *diag*-$C_5H_5Re(CO)_2Br_2$ and $C_5H_5Re(CO)_2P(CH_3)_2C_6H_5$.

Results

The reaction between bromine and $C_5H_5Re(CO)_3$ in trifluoroacetic acid was reported[11] to give only a single product of stoichiometry $C_5H_5Re(CO)_2Br_2$. However, we found this reaction to give two products of stoichiometry $C_5H_5Re(CO)_2Br_2$ which could be separated readily by chromatography. These two isomers exhibited C_5H_5 NMR resonances differing by about 0.4 ppm as well as detectably different ν(CO) frequencies. The less strongly adsorbed more soluble $C_5H_5Re(CO)_2Br_2$ isomer with a C_5H_5 NMR resonance at τ 4.00 was identified as the diagonal isomer IIb and the more strongly adsorbed less soluble $C_5H_5Re(CO)_2Br_2$ isomer with a C_5H_5 NMR resonance at τ 3.60 was identified as the lateral isomer IIa by measurements of the relative intensities of the two infrared ν(CO) bands performed by Darensbourg.[1] In these measurements, the angles between the two C–O bonds in the $C_5H_5Re(CO)_2Br_2$ isomers were determined by the relationship[18] $\tan^2\theta = I_a/I_s$ where 2θ is the angle between the two C–O bonds, I_a is the area under the asymmetric ν(CO) band (the band at lower frequency), and I_s is the area under the symmetric ν(CO) band (the band at higher frequency) with the ratio I_a/I_s being extrapolated to infinite dilution. Thus for the diagonal and lateral isomers of $C_5H_5Re(CO)_2Br_2$ the ratios I_a/I_s are 2.98 and 0.655, respectively, indicating angles 2θ of 120 and 78°, respectively, in accord with the postulated structures. The diagonal isomer of $C_5H_5Re(CO)_2Br_2$ possessed higher infrared ν(CO) frequencies and a higher field cyclopentadienyl proton NMR chemical shift than the corresponding lateral isomer. The lateral isomer of $C_5H_5Re(CO)_2Br_2$ appeared to be considerably less soluble in organic solvents than the corresponding diagonal isomer.



Both the diagonal (IIb) and lateral (IIa) isomers of $C_5H_5Re(CO)_2Br_2$ are stable in the solid state at room temperature with respect to isomerization. The diagonal isomer of $C_5H_5Re(CO)_2Br_2$ (IIb) is also stable to isomerization in solutions in inert solvents even at temperatures as high as 110°. The lateral isomer of $C_5H_5Re(CO)_2Br_2$ (IIa) is fairly stable in solution at room temperature over a period of days but readily isomerizes to the corresponding diagonal isomer IIb in solution at elevated temperatures below those at which all of the $C_5H_5Re(CO)_2Br_2$ reactions in this paper were carried out. Thus, the isomerization of *lat*-$C_5H_5Re(CO)_2Br_2$ to the corresponding diagonal isomer occurred over a period of hours in boiling dichloromethane (40°) and over a period of minutes in boiling chloroform (62°) as indicated by infrared spectra in the ν(CO) region. In view of the thermal instability of *lat*-$C_5H_5Re(CO)_2Br_2$ (IIa) in solution all of the reactions of $C_5H_5Re(CO)_2Br_2$ described in this paper were performed with the thermally stable diagonal isomer IIb.

Reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with the phosphites $(RO)_3P$ (R = CH_3, C_2H_5, and C_6H_5) in boiling benzene rapidly led to replacement of one carbonyl group by the phosphite to give one of the two possible stereoisomers of $C_5H_5Re(CO)[P(OR)_3]Br_2$. Attempts to effect replacement of the remaining carbonyl group in this $C_5H_5Re(CO)[P(OR)_3]Br_2$ isomer by reaction with excess phosphite in boiling toluene led instead to isomerization to the second $C_5H_5Re(CO)[P(OR)_3]Br_2$ isomer with retention of the single carbonyl group. These two $C_5H_5Re(CO)[P(OR)_3]Br_2$ isomers had distinctly different ν(CO) frequencies and cyclopentadienyl proton NMR chemical shifts.

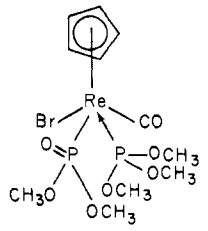
Assignment of lateral (IIIa) and diagonal (IIIb) isomer structures to the two $C_5H_5Re(CO)[P(OR)_3]Br_2$ isomers is less certain than for the two $C_5H_5Re(CO)_2Br_2$ isomers discussed above in view of the inapplicability of infrared ν(CO) relative intensity measurements to the monocarbonyls. However, in all three cases the low-temperature (boiling benzene) $C_5H_5Re(CO)[P(OR)_3]Br_2$ isomer had a higher infrared ν(CO) frequency, a higher field cyclopentadienyl proton NMR chemical shift, and a higher solubility in organic solvents such as chloroform than the corresponding high-temperature

(boiling toluene) isomer. Analogy to the trends in the ν(CO) frequencies, cyclopentadienyl proton NMR chemical shifts, and solubilities of the $C_5H_5Re(CO)_2Br_2$ isomers suggests that the low-temperature isomer of $C_5H_5Re(CO)[P(OR)_3]Br_2$ is the diagonal isomer IIIb and the high-temperature isomer of $C_5H_5Re(CO)[P(OR)_3]Br_2$ is the lateral isomer IIIa. This leads to the interesting contrast that in $C_5H_5Re(CO)_2Br_2$ the lateral isomer IIa converts to the diagonal isomer IIb upon heating whereas in $C_5H_5Re(CO)[P(OR)_3]Br_2$ (R = CH_3, C_2H_5, and C_6H_5) the diagonal isomer IIIb converts to the lateral isomer IIIa upon heating.

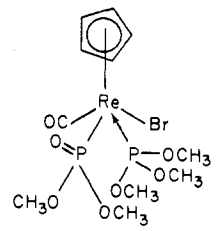
The remaining carbonyl group in $C_5H_5Re(CO)[P(OR)_3]Br_2$ could not be replaced by a second phosphite ligand upon reaction with excess ligand under more vigorous conditions. However, reaction of $C_5H_5Re(CO)_2Br_2$ with trimethyl phosphite in boiling toluene led not only to the high-temperature isomer *lat*-$C_5H_5Re(CO)[P(OCH_3)_3]Br_2$ but also to a Michaelis–Arbusov reaction with elimination of methyl bromide to give two of the possible three stereoisomers of the phosphonate $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$. Similar products were not obtained from corresponding reactions of triethyl and triphenyl phosphite. Related reactions have been reported for cyclopentadienylmolybdenum derivatives.[19]

The infrared spectra of the two phosphonate isomers $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$ exhibited the expected ν(CO) frequency and an extra infrared band at $\sim$1135 cm^{-1} in Nujol which can be assigned to the ν(P–O) of the phosphonate ligand.[19] In dichloromethane solution, this band was obscured by a relatively strong band at $\sim$1170 cm^{-1} observed in all trimethyl phosphite derivatives described here. The proton NMR spectra of each $C_5H_5Re(CO)[P(OCH_3)][P(O)(OCH_3)_2]Br$ isomer exhibited the expected resonances from the five cyclopentadienyl protons and the nine protons of the trimethyl phosphite ligand. In the orange isomer (isomer A) the two methoxy groups in the $P(O)(OCH_3)_2$ ligand exhibited a pair of proton NMR doublets indicating nonequivalence of these two methoxy groups but the absence of virtual coupling[20] arising from a strong interaction between the phosphite and phosphonate phosphorus atoms. In the yellow isomer (isomer B) the two methoxy groups in the $P(O)(OCH_3)_2$ ligand exhibited a single proton NMR doublet indicating equivalence of these two methoxy groups but again the absence of virtual coupling between the two phosphorus atoms.

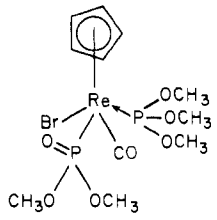
Three isomers IVa, IVb, and IVc are possible for $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$ as for any C_5H_5MXYZT derivative. All three isomers lack a plane of symmetry and thus should have nonequivalent (diastereotopic) methoxy groups in the $P(O)(OCH_3)_2$ ligand even if free rotation occurs around either or both rhenium–phosphorus bonds. However, if the two groups lateral to the $P(O)(OCH_3)_2$ ligand have similar electronic properties then there might be an effective "pseudo plane of symmetry" through the phosphonate phosphorus, the rhenium atom, and the ligand diagonal to the phosphonate ligand even though there can never be a true geometric plane of symmetry in any of the isomers of IV. Indeed the fluorine NMR spectrum[13] of the manganese complex $C_5H_5Mn(CO)[PF_2N(CH_3)_2]_2$ (V) exhibits a simple doublet AX_2 pattern rather than a more complex AXY pattern indicating that a dialkylaminodifluorophosphine and a carbonyl ligand are electronically similar enough to create an effective pseudo plane of symmetry with a carbonyl group and a dialkylaminodifluorophosphine ligand on opposite sides. This suggests that a trialkyl phosphite and a carbonyl ligand could also be electronically similar enough to be on opposite sides of an effective pseudo plane of symmetry in a trialkyl phosphite metal carbonyl derivative. However, in all of the known dialkylaminodifluorophosphine metal halide[13] complexes of the types $C_5H_5Mo(CO)(PF_2NR_2)_2Cl$, $C_5H_5Fe(CO)(PF_2NR_2)I$, and $C_5H_5Fe(PF_2NR_2)_2I$ the halogen is so different from the other ligands that the fluorine NMR spectrum always exhibits nonequivalent R_2NPF_2 fluorines.



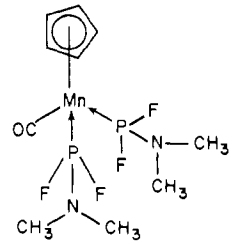
IVa



IVb



IVc



V

These considerations suggest that isomer B of $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$ with NMR equivalent methoxy groups in the $P(O)(OCH_3)_2$ ligand has structure IVb with the bromine diagonal to the $P(O)(OCH_3)_2$ ligand so that the electronically similar carbonyl and trimethyl phosphite ligands are on opposite sides of the effective pseudo plane of symmetry. Isomer A of $C_5H_5Re(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]Br$ with two doublet resonances for the methoxy groups of the $P(O)(OCH_3)_2$ is tentatively assigned structure IVa with the carbonyl group diagonal to the $P(O)(OCH_3)_2$ ligand since in the third and remaining alternative, IVc, the diagonal position of the two phosphorus atoms is likely to lead to sufficient phosphorus–phosphorus coupling to make the methoxy resonances of both the trimethyl phosphite and $P(O)(OCH_3)_2$ ligands triplets through virtual coupling rather than the observed doublets.

The reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with *tert*-butyl isocyanide in boiling benzene gives a brown monosubstituted derivative $C_5H_5Re(CO)[(CH_3)_3CNC]Br_2$ which does not isomerize in boiling toluene in contrast to the trialkyl phosphite derivatives discussed above. Since only one isomer of $C_5H_5Re(CO)[(CH_3)_3CNC]Br_2$ is available and since the elucidations of the stereochemistries of the trialkyl phosphite derivatives $C_5H_5Re(CO)[P(OR)_3]Br_2$ from the infrared ν(CO) and cyclopentadienyl proton NMR data require information on both isomers, the experimental data provide no indication of the stereochemistry of the *tert*-butyl isocyanide complex although its formulation as the diagonal isomer is more probable in view of its formation from *diag*-$C_5H_5Re(CO)_2Br_2$.

Reactions of *diag*-$C_5H_5Re(CO)_2Br_2$ with ligands more basic than the trialkyl phosphites and *tert*-butyl isocyanide appear to lead to complete destruction of the cyclopentadienylrhenium(III) system. Thus, the reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with methyldiphenylphosphine results not in carbonyl replacement but instead in reductive elimination of the elements of C_5H_5Br to give the known[17] rhenium(I) derivative *mer-cis*-$[CH_3P(C_6H_5)_2]_3Re(CO)_2Br$ (VI). A similar reaction of *diag*-$C_5H_5Re(CO)_2Br_2$ with dimethylphenylphosphine results in reductive elimination to give a rhenium(I) species tentatively assigned as $C_5H_5Re(CO)_2P(CH_3)_2C_6H_5$. Analogous reductive eliminations of C_5H_5X from the cyclopentadienylmolybdenum derivatives $C_5H_5Mo(CO)_3X$ by

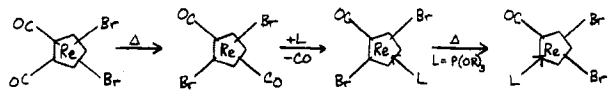
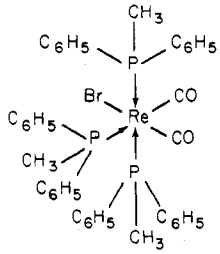


Figure 1. A summary of the stereochemistry of the $C_5H_5Re(CO)LBr_2$ reactions discussed in this paper. In this scheme L = $(RO)_3P$ or $(CH_3)_3CNC$ unless otherwise specified.

reaction with tertiary phosphines have been reported.[21]

Reactions of *diag*-$C_5H_5Re(CO)_2Br_2$ with stronger bases appear to lead to complete decomposition. Thus reactions of *diag*-$C_5H_5Re(CO)_2Br_2$ with excess liquid ammonia and with diethylamine or triethylamine in boiling benzene appear to lead to complete decomposition to give intractable reaction mixtures with infrared ν(CO) evidence of a low yield of $C_5H_5Re(CO)_3$ in the triethylamine reaction. Attempts to replace one or both bromine atoms in *diag*-$C_5H_5Re(CO)_2Br_2$ with organic groups by use of organometallic reagents such as thallium cyclopentadienide in boiling tetrahydrofuran, sodium cyclopentadienide in tetrahydrofuran at room temperature, dipotassium cyclooctatetraenediide in tetrahydrofuran at room temperature, and phenyllithium in benzene or diethyl ether at room temperature all led to extensive decomposition with the formation of no new organorhenium compounds in sufficient quantities for identification from experiments conducted with 0.5 to 1.0 g of *diag*-$C_5H_5Re(CO)_2Br_2$. There were some indications of very low-yield products in some of these reactions, but in order to obtain enough of these compounds for identification, use of at least 10 to 20 g of *diag*-$C_5H_5Re(CO)_2Br_2$ in a single reaction would be necessary; the high cost of rhenium presently precludes experiments on such a large scale. In any case, one characteristic of the cyclopentadienylrhenium(III) system appears to be its sensitivity to destruction by basic reagents including tertiary phosphines, amines, and organometallic derivatives of electropositive metals.



VI

Discussion

Simple steric considerations are sufficient to account for the stereochemistries of all of the adequately characterized reactions described in this paper which are summarized in Figure 1. The steric requirements (i.e., bulk) of the ligands of interest increase in the sequence CO < RNC < Br < $P(OR)_3$. The interligand repulsion energy in a given $C_5H_5ReX_2Y_2$ or $C_5H_5ReX_2YZ$ derivative will be minimized leading to the most stable isomer if the distance between the two bulkiest ligands is maximized by placing them in mutual diagonal positions. In $C_5H_5Re(CO)_2Br_2$ the two bulkiest ligands are the bromine atoms. The interligand repulsion energy of $C_5H_5Re(CO)_2Br_2$ will thus be minimized in the diagonal isomer thereby suggesting that *diag*-$C_5H_5Re(CO)_2Br_2$ should be more stable than the corresponding lateral isomer consistent with our observation of the thermal conversion of *lat*-$C_5H_5Re(CO)_2Br_2$ to *diag*-$C_5H_5Re(CO)_2Br_2$. The displacement of a carbonyl group in *diag*-$C_5H_5Re(CO)_2Br_2$ by an electron pair donor L to give the corresponding $C_5H_5Re(CO)LBr_2$ derivative can only occur in one way in the absence of any rearrangement since both carbonyl groups of *diag*-$C_5H_5Re(CO)_2Br_2$ are equivalent. The resulting carbonyl substitution product is then the corresponding diagonal isomer of $C_5H_5Re(CO)LBr_2$. If the entering ligand is a trialkyl phosphite, the two bulkiest ligands are trialkyl phosphite and one of the bromine atoms. Placement of these two ligands in relative diagonal positions leads to *lat*-$C_5H_5Re(CO)[P(OR)_3]Br_2$ thereby suggesting that this lateral isomer will be more stable than the corresponding diagonal isomer. This accounts for the observed thermal isomerization of the diagonal isomer of $C_5H_5Re(CO)[P(OR)_3]Br_2$ to the corresponding lateral isomer. If the entering ligand is *tert*-butyl isocyanide, the two bulkiest ligands in the resulting *diag*-$C_5H_5Re(CO)[(CH_3)_3CNC]Br_2$ are the two diagonal bromine atoms suggesting that this diagonal isomer will be more stable than the corresponding lateral isomer and hence resistant to thermal isomerization consistent with our observations. In this manner simple steric arguments can account for the thermal isomerization of *lat*-$C_5H_5Re(CO)_2Br_2$ to *diag*-$C_5H_5Re(CO)_2Br_2$, the thermal isomerization of *diag*-$C_5H_5Re(CO)[P(OR)_3]Br_2$ to *lat*-$C_5H_5Re(CO)[P(OR)_3]Br_2$, and the apparent stability of *diag*-$C_5H_5Re(CO)[(CH_3)_3CNC]Br_2$ to thermal isomerization under similar conditions.

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Registry No. *diag*-$CpRe(CO)_2Br_2$, 57194-43-1; *lat*-$CpRe(CO)_2Br_2$, 57195-35-4; *diag*-$CpRe(CO)[P(OEt)_3]Br_2$, 57139-10-3; *lat*-$CpRe(CO)[P(OEt)_3]Br_2$, 57194-44-2; *diag*-$CpRe(CO)[P(OPh)_3]Br_2$, 57139-11-4; *lat*-$CpRe(CO)[P(OPh)_3]Br_2$, 57194-45-3; *diag*-$CpRe(CO)[P(OMe)_3]Br_2$, 57139-12-5; *lat*-$CpRe(CO)[P(OMe)_3]Br_2$, 57194-46-4; $CpRe(CO)[P(OMe)_3][P(O)(OMe)_2]Br$ (isomer A), 57139-13-6; $CpRe(CO)[P(OMe)_3][P(O)(OMe)_2]Br$ (isomer B), 57194-47-5; $CpRe(CO)(t\text{-}BuNC)Br_2$, 57139-14-7; $CpRe(CO)_3$, 12079-73-1; $P(OEt)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; $P(OMe)_3$, 121-45-9; *mer-cis*-$[CH_3P(C_6H_5)_2]_3Re(CO)_2Br$, 49835-26-9.

References and Notes

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(3) Postdoctoral research associate, 1974–1975, on leave from the National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria, South Africa.
(4) In determining metal oxidation states, the cyclopentadienyl ring is regarded as a uninegative ligand in accord with the stability of $C_5H_5^-$.
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