Phase-Dependent Diagonal and Lateral Isomerism of the Rhenium Complexes (η^5-C_5H_4Me)Re(CO)$_2$Br$_2$

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Received July 18, 1995[⊗]

The new diagonal and lateral monosubstituted cyclopentadienyl dibromodicarbonylrhenium complexes (η^5-C_5H_4R)Re(CO)$_2$Br$_2$ (R = Me, Et, tBu, Si(CH$_3$)$_3$, C$_6$H$_{11}$) have been synthesized and fully characterized by elemental analysis and IR and NMR spectroscopy. All the lateral complexes are completely converted to the corresponding diagonal isomers upon refluxing in toluene. Interestingly, *diag*-(η^5-C_5H_4Me)Re(CO)$_2$Br$_2$ isomerizes to the corresponding lateral isomer in almost quantitative yield upon heating at 106−110 °C in the solid state. A DSC study of *diag*-(η^5-C_5H_4Me)Re(CO)$_2$Br$_2$ shows that the solid state *diag* to *lat* isomerization proceeds exothermically. This is the first example of an organometallic complex that undergoes a phase-dependent reversible isomerization reaction under only thermal conditions.

Introduction

In the extensive organometallic chemistry of ring-substituted cyclopentadienyl transition metal complexes there is much evidence to indicate that ring substitution can considerably influence not only the physical properties but also, and more importantly, the catalytic selectivities and activities of such complexes.[1−3] To further explore these type of complexes, we have commenced a thorough investigation of the little studied substituted cyclopentadienyl four-legged piano stool rhenium complexes of the type (η^5-C_5H_4R)Re(CO)$_2$X$_2$ (R = ring substituent, X = halogen). The unsubstituted parent complex CpRe(CO)$_2$Br$_2$ was first synthesized by Nesmeyanov *et al.* in 1969.[4] Complexes of the type CpMX$_2$Y$_2$ exist as two nonequivalent stereoisomers that are commonly referred to as *cis* and *trans*, or more precisely, *lateral* and *diagonal*, isomers. It was not until 1975 that a simple and reproducible chromatographic technique for the separation of *lat*-CpRe(CO)$_2$Br$_2$ (Figure 1a) and *diag*-CpRe(CO)$_2$ Br$_2$ (Figure 1b) was reported by King *et al.*[5] Later, the diagonal and lateral Cp*Re(CO)$_2$Br$_2$ complexes were synthesized by Sutton *et al.*[6] The only other report on related complexes involving substituents on the cyclopentadienyl ring (η^5-C_5H_4R)Re(CO)$_2$Br$_2$ (R = Me, I, COOMe) contained preliminary information, without comment on the separation, characterization, and stereochemistry of the diagonal and lateral isomers, of the new complexes.[7] Here we report the syntheses of a range of complexes, *diag*- and *lat*-(η^5-C_5H_4R)Re(CO)$_2$Br$_2$ (R = Me, Et, tBu, Si(CH$_3$)$_3$, C$_6$H$_{11}$). Of significance has been the finding of unusual solid and solution state isomerization reactions for these new complexes. Previously only mention has been made of the solution state isomerization of the lateral to diagonal isomers of CpRe(CO)$_2$Br$_2$ and Cp*Re(CO)$_2$Br$_2$.[5,6] A tantalizing comment on the solid state isomerization of (η^5-C_5H_5)Mo(CO)$_2$(PBu$_3$)I appeared in the literature some years ago.[8]

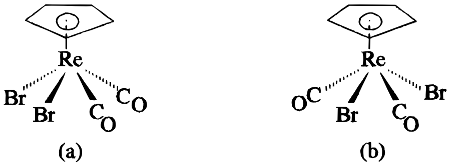

Figure 1. (a) Lateral and (b) diagonal isomers of (η^5-C_5H_5)Re(CO)$_2$Br$_2$.

A literature survey revealed that most isomerization reactions of organometallic compounds are unidirectional. Reversible isomerization reactions have been observed for a few organometallic complexes, and this has been achieved by changing the reaction conditions from that of a thermal reaction to a photochemical reaction[9] or by changing the reaction medium from a polar solvent to a nonpolar solvent.[10] A unique phase-dependent isomerization reaction has been reported for *trans*-[Pt(Me$_2$S)(Py)Cl$_2$], which isomerizes into the *cis* isomer on heating in the solid state. In the presence of excess ligand (Me$_2$S), a reverse *cis* to *trans* solution isomerization reaction occurs.[11] As far as we are aware, no organometallic complex has been reported to undergo a completely reversible phase-dependent isomerization reaction. Here we report an example of this phenom-

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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Table 1. Spectroscopic and Analytical data for $(\eta^5$-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ Complexes

			^{1}H NMR^b (ppm)		analysis (%)		
compound	mp (°C)	$\nu_{co}{}^a$ (cm^{-1})	Cp ring	R		C	H
diag-$(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$	116−118	2064, 1998	5.50 (t, 2H), 5.65 (t, 2H)	2.32 (s, 3H)	calcd found	19.97 19.94	1.47 1.30
diag-$(\eta^5$-C$_5$H$_4$Et)Re(CO)$_2$Br$_2$	93−95	2064, 1999	5.46 (t, 2H), 5.68 (t, 2H)	1.23 (t, 3H) 2.63 (q, 2H)	calcd found	21.83 21.64	1.83 1.71
diag-$(\eta^5$-C$_5$H$_4$tBu)Re(CO)$_2$Br$_2$	95−97	2062, 1998	5.21 (t, 2H), 5.76 (t, 2H)	1.40 (s, 9H)	calcd found	25.25 25.13	2.50 2.38
diag-$[\eta^5$-C$_5$H$_4$Si(CH$_3$)$_3$]Re(CO)$_2$Br$_2$	92−94	2062, 2000	5.23 (t, 2H), 5.94 (t, 2H)	0.38 (s, 9H)	calcd found	22.27 22.21	2.43 2.32
diag-$(\eta^5$-C$_5$H$_4$C$_6$H$_{11}$)Re(CO)$_2$Br$_2$	122−124	2064, 1997	5.38 (t, 2H), 5.70 (t, 2H)	1.21−2.48 (m, 11H)			
lat-$(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$	158−160 dec	2050, 1978	5.80 (t, 2H), 5.91 (t, 2H)	2.32 (s, 3H)	calcd found	19.97 19.90	1.47 1.36
lat-$(\eta^5$-C$_5$H$_4$Et)Re(CO)$_2$Br$_2$	94−96	2052, 1976	5.84 (t, 2H), 5.91 (t, 2H)	1.26 (t, 3H) 2.67 (q, 2H)	calcd found	21.83 21.54	1.83 1.63
lat-$(\eta^5$-C$_5$H$_4$tBu)Re(CO)$_2$Br$_2$	115−117	2048, 1976	5.96 (t, 2H), 6.11 (t, 2H)	1.31 (s, 9H)	calcd found	25.25 25.18	2.50 2.36
lat-$[\eta^5$-C$_5$H$_4$Si(CH$_3$)$_3$]Re(CO)$_2$Br$_2$	109−111	2050, 1978	5.96 (t, 2H), 6.28 (t, 2H)	0.34 (s, 9H)	calcd found	22.27 22.20	2.43 2.31
lat-$(\eta^5$-C$_5$H$_4$C$_6$H$_{11}$)Re(CO)$_2$Br$_2$	133−135	2052, 1978	5.87 (t, 2H), 5.89 (t, 2H)	121−2.60 (m, 11H)			

[a] Recorded in CH$_2$Cl$_2$. [b] Recorded in CDCl$_3$, relative to TMS. s, singlet; t, triplet; q, quintet; m, multiplet.

enon, which is shown by $(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$, and also report a study of the influence of the ring substituent on the *diag*−*lat* isomerism of related complexes.

Experimental Section

The ligands ethylcyclopentadiene and *tert*-butylcyclopentadiene and the complex CpRe(CO)$_3$ were prepared by the literature methods.[12−14] All reactions were carried out under dry N$_2$ in either a Schlenk apparatus or a flask connected to a double manifold providing low vacuum or nitrogen. Solvents were dried by conventional methods, distilled under nitrogen, and used immediately. Differential scanning calorimetry was obtained on 5−15-mg samples under flowing nitrogen at a constant heating rate of 10 °C/min on a Du Pont 910 DSC instrument. Melting points were recorded on a Kofler hot-stage melting point apparatus. Infrared spectra were measured on a Perkin-Elmer 580B IR spectrometer, usually in KBr cells (solutions). NMR spectra were measured on a Bruker AC200 spectrometer operating at 200 MHz. Microanalyses were carried out at the CSIR, Pretoria, South Africa.

Synthesis of $(\eta^5$-C$_5$H$_4$R)Re(CO)$_3$ (R = Me, Et, tBu). A 100-ml round-bottom flask was charged with freshly distilled monosubstituted cyclopentadiene (3−7 mL), Re$_2$(CO)$_{10}$ (0.32−1.00 g, 0.049−1.53 mmol), and a magnetic stirrer bar and was fitted with a reflux condenser and a N$_2$ inlet/oil bubbler. The reaction mixture was stirred, heated, and kept at 210 °C for 2 h. At this point, gas evolution had ceased. The flask was then allowed to cool to room temperature. IR spectroscopy and silica gel TLC showed that no Re$_2$(CO)$_{10}$ remained. The reaction mixture was then chromatographed on a silica gel column prepared in hexane. For R = Me and Et, elution with hexane gave first unreacted monosubstituted cyclopentadiene and then the product as a colorless crystalline solid. For R = tBu, elution with hexane gave unreacted *tert*-butylcyclopentadiene, followed by a mixture containing $(\eta^5$-C$_5$H$_4$tBu)Re(CO)$_3$ and a small amount of *tert*-butylcyclopentadiene polymer which could not easily be separated by column chromatography. This mixture was used as such in further reactions. $(\eta^5$-C$_5$H$_4$Me)Re(CO)$_3$: 96% yield, IR (cm^{-1}, CH$_2$Cl$_2$) ν_{co}: 1922, 2020. ^{1}H NMR (ppm, CDCl$_3$): 2.23 (s, 3H), 5.21−5.25 (m, 4H). $(\eta^5$-C$_5$H$_4$Et)Re(CO)$_3$: 75% yield, IR (cm^{-1}, CH$_2$Cl$_2$) ν_{co}: 1920, 2022. ^{1}H NMR (ppm, CDCl$_3$): 1.15 (t, 3H), 2.48 (q, 2H), 5.25 (m, 4H). $(\eta^5$-C$_5$H$_4$tBu)Re(CO)$_3$: ~90% yield. IR (cm^{-1}, CH$_2$Cl$_2$) ν_{co}: 1922, 2018. ^{1}H NMR (ppm, CDCl$_3$): 1.22 (s, 9H), 5.19 (t, 2H), 5.34 (t, 2H).

Synthesis of $[\eta^5$-C$_5$H$_4$Si(CH$_3$)$_3$]Re(CO)$_3$. To a stirred solution of $(\eta^5$-C$_5$H$_5$)Re(CO)$_3$ (0.60 g, 1.79 mmol) in 45 mL of THF at −65 °C was added *n*-C$_4$H$_9$Li (2.3 mL of 1.6 M solution, 3.68 mmol) in hexane. After stirring at −40 to −50 °C for 120 min, (CH$_3$)$_3$SiCl (2.5 mL, 19.7 mmol) was added, and the reaction mixture was allowed to warm to 20 °C. Solvent was then removed under reduced pressure, and the product was purified by column chromatography (hexane eluent). $[\eta^5$-C$_5$H$_4$Si(CH$_3$)$_3$]Re(CO)$_3$ was obtained as white needles (0.63 g, 87% yield). IR (cm^{-1}, CH$_2$Cl$_2$) ν_{co}: 1924, 2022. ^{1}H NMR (ppm, CDCl$_3$): 0.24 (s, 9H), 5.39−5.43 (m, 4H).

Syntheses of Diagonal and Lateral $(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$ Complexes. A solution of Br$_2$ (220 mg, 1.38 mmol) in 2 mL of trifluoroacetic acid was added dropwise at 25 °C to a solution of $(\eta^5$-C$_5$H$_4$Me)Re(CO)$_3$ (484 mg, 1.38 mmol) in 3 mL of trifluoroacetic acid. After the reaction mixture was stirred for an additional 40 min at room temperature, the reaction was quenched by pouring it into 100 mL of water at 25 °C. The resulting brown precipitate, which contained unreacted $(\eta^5$-C$_5$H$_4$Me)Re(CO)$_3$ and both isomers of $(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$, was filtered and dried at 25 °C (0.1 mmHg). This solid was dissolved in dichloromethane and chromatographed on a 2 × 60 cm silica gel column prepared in hexane. Successive elution with hexane, hexane/dichloromethane (1:1), and dichloromethane gave unreacted $(\eta^5$-C$_5$H$_4$Me) Re(CO)$_3$ (261 mg, 54% recovery), *diag*-$(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$ (142 mg, 21% conversion, 46% yield) from a red band, and *lat*-$(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$ (71 mg, 11% conversion, 23% yield) from a brown band, respectively. The complexes, diagonal and lateral $(\eta^5$-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$, were characterized by elemental analysis and by IR and NMR spectroscopy (Table 1).

Syntheses of Diagonal and Lateral $(\eta^5$-C$_5$H$_4$Et)Re(CO)$_2$Br$_2$ Complexes. A solution of Br$_2$ (350 mg, 2.19 mmol) in 3 mL of trifluoroacetic acid was added dropwise at 25 °C to a solution of $(\eta^5$-C$_5$H$_4$Et)Re(CO)$_3$ (780 mg, 2.14 mmol) in 5 mL of trifluoroacetic acid. After the reaction mixture was stirred for an additional 1 h at room temperature, the reaction was quenched by pouring it into 100 mL of water at 25 °C. The resulting brown precipitate, which contained unreacted $(\eta^5$-C$_5$H$_4$Et)Re(CO)$_3$ and both isomers of $(\eta^5$-C$_5$H$_4$Et)Re(CO)$_2$Br$_2$, was filtered and dried at 25 °C (0.1 mmHg). This solid was dissolved in dichloromethane and chromatographed on a 2 × 60 cm silica gel column prepared in hexane. Successive elution with hexane, hexane/dichloromethane (1:1), and dichloromethane gave unreacted $(\eta^5$-C$_5$H$_4$Et)Re(CO)$_3$ (350 mg, 45% recovery), *diag*-$(\eta^5$-C$_5$H$_4$Et)Re(CO)$_2$Br$_2$ (180 mg, 17% conver-

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sion, 31% yield) from a red band, and *lat*-(η^5-C_5H_4Et)Re$(CO)_2Br_2$ (108 mg, 10% conversion, 18% yield) from a brown band, respectively. The complexes, diagonal and lateral (η^5-C_5H_4Et)Re$(CO)_2Br_2$, were characterized by elemental analysis and by IR and NMR spectroscopy (Table 1).

Syntheses of Diagonal and Lateral (η^5-C_5H_4tBu)Re$(CO)_2Br_2$ Complexes. A solution of Br_2 (170 mg, 1.06 mmol) in 2 mL of trifluoroacetic acid was added dropwise at 25 °C to a solution of the impure (η^5-C_5H_4tBu)Re$(CO)_3$ (prepared from 0.49 mmol $Re_2(CO)_{10}$) in 3 mL of trifluoroacetic acid. After the reaction mixture was stirred for an additional 40 min at room temperature, the reaction was quenched by the addition of 100 mL of water. The resulting sticky brown precipitate, which contained unreacted (η^5-C_5H_4tBu)Re$(CO)_3$ and both isomers of (η^5-C_5H_4tBu)Re$(CO)_2Br_2$, was washed with water (2 × 50 mL) and dried at 25 °C (0.1 mmHg). This precipitate was dissolved in dichloromethane and chromatographed on a 2 × 60 cm silica gel column prepared in hexane. Successive elution with hexane, hexane/dichloromethane (1:1), and dichloromethane gave unreacted impure (η^5-C_5H_4tBu)Re$(CO)_3$, *diag*-(η^5-C_5H_4tBu) Re$(CO)_2Br_2$ (45 mg, 18% conversion, based on $Re_2(CO)_{10}$) from a red band, and *lat*-(η^5-C_5H_4tBu)Re$(CO)_2Br_2$ (97 mg, 38% conversion, based on $Re_2(CO)_{10}$) from a brown band, respectively. The complexes, diagonal and lateral (η^5-C_5H_4tBu)Re$(CO)_2Br_2$, were characterized by elemental analysis and by IR and NMR spectroscopy (Table 1).

Syntheses of Diagonal and Lateral [η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_2Br_2$ Complexes. A solution of Br_2 (230 mg, 1.44 mmol) in 5 mL of $CHCl_3$ was added dropwise at 0 °C to a solution of [η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_3$ (530 mg, 1.30 mmol) in 15 mL of $CHCl_3$. After the reaction mixture was stirred for an additional 60 min at 0 °C, the reaction was stopped and the solvent was removed under reduced pressure. The resulting dark red solid was dissolved in dichloromethane and chromatographed on a silica gel column prepared in hexane. Successive elution with hexane, hexane/dichloromethane (1:1), and dichloromethane gave unreacted [η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_3$ (300 mg, 57% recovery), *diag*-[η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_2Br_2$ (55 mg, 7.8% conversion, 18% yield) from a red band, and *lat*-[η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_2Br_2$ (66 mg, 9.4% conversion, 22% yield) from a brown band, respectively. The complexes, diagonal and lateral [η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_2Br_2$, were characterized by elemental analysis and by IR and NMR spectroscopy (Table 1).

Solution Isomerization of *lat*-(η^5-C_5H_4R)Re$(CO)_2Br_2$ (R = Me, Et, tBu, $Si(CH_3)_3$). A solution of 20−200 mg of *lat*-(η^5-C_5H_4R)Re$(CO)_2Br_2$ complex (R = Me, Et, tBu, $Si(CH_3)_3$) in 15 mL of toluene was refluxed under nitrogen for 2−5 h. Silica gel TLC showed that the reaction yield was ~95%. Removal of solvent at 25 °C (0.1 mmHg) gave a red solid shown to be the corresponding diagonal isomer by its υ_{co} frequency in dichloromethane solution and ^1H NMR spectrum.

Solid State Isomerization of *diag*-(η^5-C_5H_4Me)Re$(CO)_2Br_2$. Solid *diag*-(η^5-C_5H_4Me)Re$(CO)_2Br_2$ (20−100 mg) was heated in a 25-mL round-bottom flask at 106−110 °C under nitrogen for 2−5 h. The color of the solid changed gradually from red to brown. No decomposition was observed after the heating process. Silica gel TLC and IR and NMR spectroscopy confirmed that the brown solid was *lat*-(η^5-C_5H_4Me)Re$(CO)_2Br_2$.

Molten State Isomerization of *diag*-(η^5-C_5H_4R)Re$(CO)_2Br_2$ (R = Et, tBu, $Si(CH_3)_3$). Solid *diag*-(η^5-C_5H_4Et)Re$(CO)_2Br_2$ or *diag*-(η^5-C_5H_4tBu)Re$(CO)_2Br_2$ (5−20 mg) was sealed into a capillary tube under N_2 and heated in an oil bath at 100 °C for 5 h or at 120 °C for 10 h, respectively. At these temperatures, the complexes were in the homogeneous molten state. No decomposition was observed after the heating process. Silica gel TLC and IR and NMR spectroscopy confirmed that the products contained the lateral isomers. ^1H NMR spectra of the products showed that 65% and 30% of the lateral isomers had formed for the ethyl and *tert*-butyl-substituted complexes, respectively.

About 10% of *diag*-[η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_2Br_2$ complex isomerized into the lateral isomer when heated at 110 °C for 3 h in the molten state, but some decomposition occurred during the process.

Results and Discussion

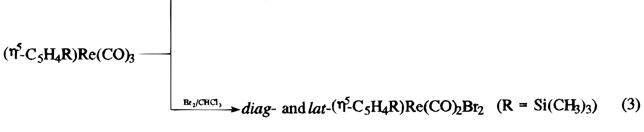
Syntheses of (η^5-C_5H_4R)Re$(CO)_3$ (R = Me, Et, tBu, $Si(CH_3)_3$, C_6H_{11}) Complexes. Direct reaction of $Re_2(CO)_{10}$ with monosubstituted cyclopentadiene gave (η^5-C_5H_4R)Re$(CO)_3$ (R = Me, Et, tBu) in good yield (75%−96%, eq 1). This constituted a distinct improvement over the literature methods.[15,16] The (η^5-C_5H_4R)Re$(CO)_3$ complexes have good solubility in organic solvents, which makes it difficult to separate them from the reaction mixture of the monosubstituted cyclopentadiene and its polymer[17] by traditional sublimation or recrystallization methods. We found that (η^5-C_5H_4Me)Re$(CO)_3$ and (η^5-C_5H_4Et)Re$(CO)_3$ could be easily separated by column chromatography as a colorless crystalline solid; (η^5-C_5H_4tBu)Re$(CO)_3$ could be separated from most of the corresponding *tert*-butylcyclopentadiene polymer by the same method. The product was, however, always contaminated with some *tert*-butylcyclopentadiene polymer, which had the same solubility as that of the product and was difficult to remove by column chromatography. However, the small amount of diene polymer in the product did not have any influence on the subsequent bromination reaction.

$$\mathrm{Re_2(CO)_{10} + C_5H_5R \xrightarrow{170-210\ ^\circ C}} \\ (\eta^5\text{-}\mathrm{C_5H_4R})\mathrm{Re(CO)_3} \quad (\mathrm{R = Me, Et, tBu}) \quad (1)$$

[η^5-$C_5H_4Si(CH_3)_3$]Re$(CO)_3$ was synthesized in good yield by following the procedures used to synthesize [η^5-$C_9H_6Si(CH_3)_3$]Re$(CO)_3$.[18] Reaction of $Re_2(CO)_{10}$ with cyclohexylcyclopentadiene gave (η^5-$C_5H_4C_6H_{11}$)Re$(CO)_3$ in good yield (monitored by IR spectroscopy). However, it was difficult to separate the product from the cyclohexylcyclopentadiene polymer even by repeated column chromatography.

In summary, our results show that direct reaction of $Re_2(CO)_{10}$ with monosubstituted cyclopentadiene provides a good route for the preparation of monosubstituted cyclopentadienyltricarbonylrhenium complexes and that column chromatography is an effective separation method for most of these complexes.

Syntheses of Diagonal and Lateral (η^5-C_5H_4R)Re$(CO)_2Br_2$ (R = Me, Et, tBu, $Si(CH_3)_3$, C_6H_{11}) Complexes. The reaction of (η^5-C_5H_4R)Re$(CO)_3$ with bromine in trifluoroacetic acid at room temperature was carried out by the procedure used for the syntheses of the unsubstituted analogue [5] (eq 2) and gave *diag*- and *lat*-(η^5-C_5H_4R)Re$(CO)_2Br_2$ complexes which were sepa-



$$(\eta^5\text{-}\mathrm{C_5H_4R})\mathrm{Re(CO)_3} \xrightarrow{\mathrm{Br_2/CF_3COOH}} \textit{diag-}\text{ and }\textit{lat-}(\eta^5\text{-}\mathrm{C_5H_4R})\mathrm{Re(CO)_2Br_2} \quad (\mathrm{R = Me, Et, tBu}) \quad (2)$$

$$(\eta^5\text{-}\mathrm{C_5H_4R})\mathrm{Re(CO)_3} \xrightarrow{\mathrm{Br_2/CHCl_3}} \textit{diag-}\text{ and }\textit{lat-}(\eta^5\text{-}\mathrm{C_5H_4R})\mathrm{Re(CO)_2Br_2} \quad (\mathrm{R = Si(CH_3)_3}) \quad (3)$$

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Table 2. Bond Angle 2θ between Two CO Groups for the (η^5-C_5H_4R)$Re(CO)_2Br_2$ Complexes

complex	I_{as}/I_s	2θ
diag-(η^5-C_5H_5)$Re(CO)_2Br_2$	2.50	115 (120)[a]
diag-(η^5-C_5H_4Me)$Re(CO)_2Br_2$	2.44	115
diag-(η^5-C_5H_4Et)$Re(CO)_2Br_2$	2.25	113
diag-(η^5-$C_5H_4C_6H_{11}$)$Re(CO)_2Br_2$	2.25	113
diag-($\eta^5$$C_5H_4$tBu)$Re(CO)_2Br_2$	2.26	113
diag-[η^5-$C_5H_4Si(CH_3)_3$]$Re(CO)_2Br_2$	2.20	112
lat-(η^5-C_5H_5)$Re(CO)_2Br_2$	0.658	78 (78)[a]
lat-(η^5-C_5H_4Me)$Re(CO)_2Br_2$	0.649	78
lat-(η^5-C_5H_4Et)$Re(CO)_2Br_2$	0.646	78
lat-(η^5-$C_5H_4C_6H_{11}$)$Re(CO)_2Br_2$	0.635	78
lat-($\eta^5$$C_5H_4$tBu)$Re(CO)_2Br_2$	0.706	80
lat-[η^5-$C_5H_4Si(CH_3)_3$]$Re(CO)_2Br_2$	0.713	80

[a] Reported data.

rated by a chromatographic technique. Surprisingly, [η^5-$C_5H_4Si(CH_3)_3$] $Re(CO)_3$ lost the ring substituent $Si(CH_3)_3$ and formed (η^5-C_5H_5)$Re(CO)_3$ quantitatively when dissolved in trifluoroacetic acid. However, reaction of [η^5-$C_5H_4Si(CH_3)_3$]$Re(CO)_3$ with bromine in chloroform gave *diag*- and *lat*-[η^5-$C_5H_4Si(CH_3)_3$]$Re(CO)_2Br_2$ in good yield (eq 3). Monitoring of the bromination reaction by TLC revealed that a new yellow product assumed to be {[η^5-$C_5H_4Si(CH_3)_3$] Re $(CO)_3Br$}Br[19] formed rapidly and decomposed slowly to form *diag*-[η^5-$C_5H_4Si(CH_3)_3$]$Re(CO)_2Br_2$, *lat*-[η^5-$C_5H_4Si(CH_3)_3$]$Re(CO)_2Br_2$, [η^5-$C_5H_4Si(CH_3)_3$]$Re(CO)_3$, and a red product which has as yet not been characterized.

Reaction of the mixture of (η^5-$C_5H_4C_6H_{11}$)$Re(CO)_3$ and the cyclohexylcyclopentadiene polymer with bromine in trifluoroacetic acid or in THF indeed gave *diag*- and *lat*-(η^5-$C_5H_4C_6H_{11}$)$Re(CO)_2Br_2$ complexes, which were separated by column chromatography, but the yield was low (~10%). The complexes were characterized by IR and ^1H NMR spectroscopy, and the data are given in Table 1.

Characterization of Diagonal and Lateral (η^5-C_5H_4R)$Re(CO)_2Br_2$ (R = Me, Et, tBu, $Si(CH_3)_3$) Complexes. The new complexes were characterized by IR and NMR spectroscopy and by elemental analysis. In every instance, correct intensity ratios as well as the requisite number of adsorption bands were observed in the NMR spectrum. The identification of the diagonal and lateral isomers was based on the angles between their two carbonyl groups (Table 2) which were estimated from the relationship $\tan^2\theta = I_{as}/I_s$, where 2$\theta$ is the angle between the two carbonyl bonds, I_{as} is the height of the asymmetric υ_{co} band, and I_s is the height of the symmetric υ_{co} band.[20]

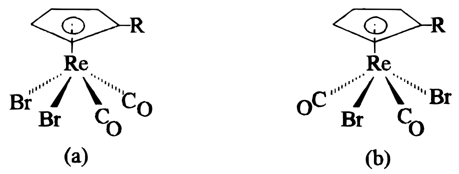

Figure 2. (a) Lateral and (b) diagonal isomers of (η^5-C_5H_4R)$Re(CO)_2Br_2$.

Table 3. *Diag*−*Lat* Isomerization of (η^5-C_5H_4Me)$Re(CO)_2Br_2$ in Different Solvents

complex	solvent	reaction time[a] (h)	product[b] (%)	
			diag	*lat*
lat-(η^5-C_5H_4Me)$Re(CO)_2Br_2$	$CHCl_3$	6.0	17	83
	benzene	4.5	79	21
	toluene	1.0	>95[c]	<5
	C_6H_5Cl	2.0	>95[c]	<5
diag-(η^5-C_5H_4Me)$Re(CO)_2Br_2$	$CHCl_3$	6.0	100	0
	benzene	4.5	100	0
	toluene	1.0	>95[c]	<5
	C_6H_5Cl	2.0	>95[c]	<5

[a] The solution was heated under reflux. [b] Calculated from the integration of peaks in the ^1H NMR spectrum. [c] From silica gel TLC.

Solution Isomerization of *lat*-(η^5-C_5H_4R)$Re(CO)_2Br_2$ (R = Me, Et, tBu, $Si(CH_3)_3$). The (η^5-C_5H_4R)$Re(CO)_2Br_2$ complexes have solution isomerization behavior similar to the unsubstituted (R = H) analogue. The *lat*-(η^5-C_5H_4R)$Re(CO)_2Br_2$ isomers were stable in solution at room temperature over a period of hours and ~5% of the reactants isomerized to the corresponding diagonal isomers over a period of days. They were readily converted into the corresponding diagonal isomers when refluxed in toluene. In refluxing toluene, an equilibrium was established and our preliminary results showed that the equilibrium constant $K = [diag]/[lat]$ was larger than 20 and independent of the R group. The *lat*-(η^5-C_5H_4R)$Re(CO)_2Br_2$ complexes were slightly more difficult to isomerize than the unsubstituted analogue. For example, unsubstituted *lat*-(η^5-C_5H_5)$Re(CO)_2Br_2$ completely changed into the diagonal isomer in boiling chloroform after a few minutes,[5] whereas only 17% of the lateral (η^5-C_5H_4Me)$Re(CO)_2Br_2$ complex isomerized to the corresponding diagonal isomer after 6 h in refluxing chloroform. The *diag*-(η^5-C_5H_4R)$Re(CO)_2Br_2$ complexes were stable to isomerization in solution even at temperatures as high as 130 °C. The polarity of the solvent did not change the lateral to diagonal solution isomerization direction. *diag*- and *lat*-(η^5-C_5H_4Me)$Re(CO)_2Br_2$ were heated under reflux in $CHCl_3$, benzene, toluene and C_6H_5Cl for the same period of time. In all cases, the lateral complex isomerized into the diagonal isomer, while the reverse isomerization reaction did not take place (Table 3).

Solid State Isomerization of *diag*-(η^5-C_5H_4Me)-$Re(CO)_2Br_2$. Surprisingly, the *diag*-(η^5-C_5H_4Me)$Re(CO)_2Br_2$ isomerized into the corresponding lateral isomer in almost quantitative yield when it was heated in the solid state at 106−110 °C under nitrogen for 2−5 h. Thus, a completely reversible isomerization takes place at the same temperature (110 °C), the direction of the isomerization being dependent on the phase of the complex. By contrast, no isomerization occurred when solid *diag*-(η^5-C_5H_5)$Re(CO)_2Br_2$ was heated at temperatures as high as 150 °C. A similar negative result for the isomerization of solid *diag*-Cp*$Re(CO)_2Br_2$ under photochemical conditions was reported by Hill *et al.*[21] A DSC plot of powdered *diag*-(η^5-C_5H_4Me)$Re(CO)_2Br_2$ (Figure 3b) shows that one exothermic peak beginning at 118 °C and one endothermic peak at 171 °C were observed. The exotherm corresponded to the *diag* to *lat* isomerization of the complex. This was verified by the color change from red to brown (the latter color corresponding to that of the lateral isomer), and

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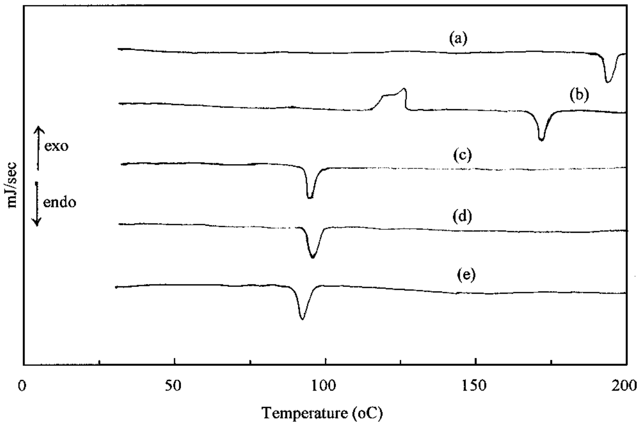

Figure 3. DSC curves for *diag*-(η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ complexes (a) R = H, $\Delta H_f = +1.0$ kJ/mol; (b) R = Me, $\Delta H_{iso} = -0.44$ kJ/mol, $\Delta H_f = +2.2$ kJ/mol; (c) R = Et, $\Delta H_f = +0.21$ kJ/mol; (d) R = tBu, $\Delta H_f = +0.21$ kJ/mol; (e) R = Si(CH$_3$)$_3$, $\Delta H_f = +0.20$ kJ/mol.

by the IR and ^{1}H NMR spectra recorded on the cooled sample after completion of the exotherm. The IR and ^{1}H NMR spectra indicated complete conversion to the lateral isomer. This DSC result suggests that the solid state *diag* to *lat* isomerization of the (η^5-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$ complex proceeds under thermodynamic control. The endothermic peak at 171 °C correlated with the melting point of the lateral isomer obtained after isomerization of the diagonal isomer. For comparison, the DSC curve of unsubstituted *diag*-(η^5-C$_5$H$_5$)Re(CO)$_2$Br$_2$ is also given in Figure 3; here only one endothermic peak corresponding to the melting peak of starting material was observed.

Molten State Isomerization of *diag*-(η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ (R = Et, tBu, Si(CH$_3$)$_3$). When *diag*-(η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ (R = Et, tBu, Si(CH$_3$)$_3$) was heated at a temperature below its melting point (in the solid state), no isomerization was observed. DSC curves reveal only one endothermic peak for these complexes (Figure 3c−e) which corresponds to the melting point of starting material. However, diagonal to lateral isomerization, a reversed direction to that of the solution isomerization, occurred for these complexes in the molten state. Further, if *lat*-(η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ was heated in the molten state, lateral to diagonal isomerization occurred.

The ratio of *lat* to *diag* isomers for the R = Et complex in the molten state was found to be independent of the direction of the isomerization reaction and reached an equilibrium value of 65/35 as determined by NMR spectroscopy. Raising the heating temperature or increasing reaction time did not improve the reaction yield substantially. It is to be noted that in all cases the isomerization reaction was carried out at a temperature higher than the melting points of both the diagonal and lateral isomers and that a homogeneous melt was observed under a microscope. For R = Si(CH$_3$)$_3$, the *diag*-[η^5-C$_5$H$_4$Si(CH$_3$)$_3$]Re(CO)$_2$Br$_2$ complex decomposed slowly in the molten state. It appears that a *diag*−*lat* equilibrium is set up in the homogeneous melt, which is dependent on the R group (R = Et, $K = [lat]/[diag] = 1.85$; R = tBu, $K = 0.42$; and R = Si(CH$_3$)$_3$, $K = 0.11$). Molten state isomerization thus provides an alternative method to the preparation of *lat*-(η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$, and our data indicate that the reversible isomerization is a general phenomenon for the monosubstituted (η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ complexes. The mechanism of such bidirectional isomerization is not as yet clear. Solvation effects clearly play a role in the isomerization reaction and overcome the thermodynamic constraints for the *diag* to *lat* isomerization reaction observed in the absence of solvents. The limited solvent study data suggest that the reaction is faster in nonpolar solvents, which means that a nondissociative mechanism is involved.

Solid state studies to investigate the latter isomerization are needed to establish the expected intramolecular nature of the reaction (unit cell volume changes, mode of Br-CO interconversion, etc.). Both lateral and diagonal conformations of (η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ must be sterically and/or electronically favored in the different phases (Figure 2).

Conclusion

The diagonal and lateral monosubstituted cyclopentadienyl four-legged piano stool rhenium complexes (η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ (R = Me, Et, tBu, Si(CH$_3$)$_3$, C$_6$H$_{11}$) were synthesized for the first time, and their structures were determined by elemental analysis and by IR and NMR spectroscopy. Similar to the unsubstituted analogue, the lateral (η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ complexes isomerized to the corresponding diagonal isomers upon refluxing in solution. Quite different from the parent complex (η^5-C$_5$H$_5$)Re(CO)$_2$Br$_2$, the reverse *diag* to *lat* isomerization was observed for the monosubstituted ring complexes (η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ in the solid state or molten state. Our results showed that the different ring-substituted complexes had different *diag* to *lat* isomerization behavior. The diagonal (η^5-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$ complex isomerized to the corresponding lateral isomer in almost quantitative yield when heated in the solid state and the isomerization proceeded exothermically. This is the first example of an organometallic complex that undergoes a nearly quantitative phase-dependent reversible isomerization reaction under only thermal condition. The diagonal (η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ (R = Et, tBu, Si(CH$_3$)$_3$) complexes isomerized incompletely into the corresponding lateral isomers in the molten state, and the results revealed that the larger the ring substituent, the more difficult the *diag* to *lat* isomerization reaction. Solid state studies (single-crystal and powder X-ray diffraction) to explore the reasons for this unusual behavior are underway and should provide further information on the isomerization reaction.

Acknowledgment. We express our thanks to the FRD and the University of the Witwatersrand for financial support.

OM950548S