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Synthesis and solid-state isomerisation reactions of *diag*- and *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2

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Abstract

Reaction of *diag*- or *lat*- (i.e. *trans* or *cis*)(η^5-C_5H_4R)Re(CO)$_2X_2$ (R = Me, *t*-Bu, $SiMe_3$; X = Br, I) with isocyanides, phosphites and triphenyl phosphine proceeded rapidly at room temperature (r.t.) in the presence of Me_3NO to give (η^5-C_5H_4R)Re(CO)(L)X_2 (L = $CNC_6H_3Me_2$, $P(OMe)_3$, $P(O^iPr)_3$, $P(OPh)_3$, PPH_3) in good yields (typically > 75%) with the diagonal isomer as the dominant (> 90%) product. The *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 isomer were readily converted into the lateral isomer in excellent yield (> 70%) by directly heating solid *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 under nitrogen below its melting point. Solution phase isomerisation in $CHCl_3$ or C_6D_6 (r.t., visible light irradiation) also proceeded from the *diag* to the *lat* isomer. The solid-state reaction between *diag*-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]Br_2 and excess NaI surprisingly gave *diag*-(η^5-C_5H_4Me)Re(CO)$_2I_2$ in quantitative yield, revealing both Re–P and Re–Br bond cleavage. The new complexes, *diag*- and *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2, have been fully characterized by elemental analysis and IR and NMR spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of cyclopentadienyl half-sandwich rhenium complexes has been developed over the past three decades [1]. In this time many cyclopentadienyl four-legged piano stool rhenium complexes have been prepared, and the solution isomerization behavior and the chemical reactivity of these complexes have been studied [3–8]. However, it is only since 1976 that King and Reimann successfully separated the *diagonal* and *lateral* (i.e. *trans* and *cis*) isomers of (η^5-C_5H_5)Re(CO)$_2Br_2$ [2].

The carbonyl substitution reactions of cyclopentadienyl dicarbonyldihalides rhenium complexes have been little exploited. Indeed as far as we aware, the King and Reimann description of the reaction of *diag*-(η^5-C_5H_5)Re(CO)$_2Br_2$ with different phosphites, $P(OR)_3$, and isocyanides is the only example of the CO replacement on these complexes reported to date. The method used to prepare *lat*-(η^5-C_5H_5)Re(CO)(L)Br_2 by refluxing *diag*-(η^5-C_5H_5)Re(CO)$_2Br_2$ with three equivalents of phosphites in toluene gave modest results (yields were only 35–45%) [2]. The reactions of the pentamethylcyclopentadienyl rhenium complexes Cp*Re(CO)$_2X_2$ (X = Cl, Br, I) with $P(OMe)_3$ in refluxing toluene were studied by Klahn et al and it was found that Cp*Re(CO)$_2$[$P(OMe)_3$], not the carbonyl substitution product, was the dominant product [9]. Cp*Re(CO)(PMe_3)X_2 (X = Cl, Br, I) and *cis*-Cp*Re(CO)(L)I_2 (L = $P(OMe)_3$, $P(OPh)_3$, PMe_3, PMe_2Ph) have rather been prepared indirectly by oxidative-addition of X_2 to the dinitrogen complexes Cp*Re(CO)(L)N_2 [10], or by Me_3NO induced decarbonylation of cationic [*cis*-Cp*Re(CO)$_2$(L)I]$^+$ [11].

Recently the first thermal solid-state isomerization reaction of (η^5-C_5H_4R)Re(CO)$_2Br_2$ (R = Me) was reported by us [4] but work on related complexes (R = *t*-

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Bu, $SiMe_3$, etc.) indicated that the reaction may not be general. To further explore the generality of this unusual solid-state reaction [12] the substituted complexes (η^5-C_5H_4R)Re(CO)(L)X_2, have been considered for study. Trimethylamine *N*-oxide has been shown to be a valuable synthetic reagent in the preparation of substituted metal carbonyl complexes [13] and its use for preparing new rhenium complexes seemed feasible. Thus, we decided to study the carbonyl substitution reactions of (η^5-C_5H_4R)Re(CO)$_2X_2$ using Me_3NO as a decarbonylating reagent. The results of this study are described below. The solid-state and solution *diag–lat* isomerization reactions of the new complexes are also reported.

2. Experimental

The diagonal and lateral (η^5-C_5H_4R)Re(CO)$_2Br_2$ (R = Me, *t*-Bu, $SiMe_3$) complexes were prepared by the literature methods [4]. 2,6-dimethylphenylisocyanide, phosphites and phosphines were used as supplied by Fluka or Merck. Trimethylamine *N*-oxide dihydrate (Aldrich) was used as received. All reactions were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by conventional methods, distilled under nitrogen, and used immediately. Melting points were recorded on a Kofler hot stage melting point apparatus. IR spectra were measured on a Midac FTIR spectrometer, usually in KBr cells (solutions). NMR spectra were measured on a Bruker AC 200 spectrometer operating at 200 MHz. Microanalysis were carried out at the CSIR, Pretoria, South Africa.

2.1. Preparation of *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2

Diag- or *lat*-(η^5-C_5H_4R)Re(CO)$_2X_2$ (100 mg, 0.174–0.208 mmol) (R = Me, *t*-Bu, $SiMe_3$; X = Br, I) and 1.1 equivalents of ligand L (L = $CNC_6H_3Me_2$, $P(OMe)_3$, $P(O^iPr)_3$, $P(OPh)_3$, PPh_3) were dissolved in 15 ml CH_2Cl_2 under nitrogen. $Me_3NO\cdot 2H_2O$ (two to five equivalents) was added to the above magnetically stirred solution. The reactions were monitored by IR spectroscopy and were complete within 30 min. Solvent was removed by vacuum rotatory evaporation to leave a red residue, which was dissolved in CH_2Cl_2 and chromatographed on a silica gel column (2 × 50 cm) prepared in hexane. Successive elution with 1:1 CH_2Cl_2/hexane gave first *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 from a red band, then a small amount (< 5%) of *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 from a brown band. The yields, as well as the spectroscopic and analytical data for *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 are listed in Tables 1 and 2.

Similar reactions with triethyl phosphine, triisopropyl phosphine, tributyl phosphine and pyridine resulted in decomposition of starting materials.

2.2. Thermal solid-state isomerization of *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2

Solid *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 (50 mg) in a 25 ml round-bottom flask was heated under nitrogen in an oil bath at temperatures at least 10–15°C below their melting points for 0.5–6 h. No decomposition was observed. The solid residues were then dissolved in CH_2Cl_2 and chromatographed on a silica gel column. The composition of the new lateral isomers was confirmed by IR and NMR spectroscopy. The yields, as well as the spectroscopic and analytical data for the *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 complexes are listed in Tables 1–3.

The *lat*-(η^5-C_5H_4R)Re(CO)(PPh_3)X_2 complex decomposed on a silica gel column and purification of the complex was achieved by recrystalization from a mixture of dichloromethane and hexane at −15°C.

2.3. Thermal solid-state halogen exchange reaction of *diag*-(η^5-C_5H_4Me)Re(CO)$_2Br_2$ with excess NaI

Diag-(η^5-C_5H_4Me)Re(CO)$_2Br_2$ (200 mg, 0.416 mmol) and NaI (1.25 g, 8.31mmol) were dissolved in acetone in a 25 ml round-bottom flask. The solvent was then removed by rotatory evaporation, and the residue was dried under vacuum (0.1 mmHg) at 25°C and heated under nitrogen in an oil bath at 100–105°C for 18 h. After column separation (silica gel, 1:1 CH_2Cl_2/hexane), red microcrystaline *diag*-(η^5-C_5H_4Me)Re(CO)$_2I_2$ (239 mg, 100% yield) was obtained. IR (ν_{co}, CH_2Cl_2): 1982 cm^{-1}, 2043 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.44 ppm (s, 3H, CH_3); 5.59 ppm (t, 2H, Cp); 5.71 ppm (t, 2H, Cp).

2.4. Thermal solid-state reaction of *diag*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2 with excess NaI

Diag-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]Br_2 (80 mg, 0.105 mmol) and NaI (314 mg, 2.10 mmol) were dissolved in acetone in a 25 ml round-bottom flask. The solvent was then removed by rotatory evaporation, and the residue was dried under vacuum (0.1 mmHg) at 25°C and heated under nitrogen in an oil bath at 125–130°C for 16 h. After column separation (silica gel, 1:1 CH_2Cl_2/hexane), *diag*-(η^5-C_5H_4Me)Re(CO)$_2I_2$ (30 mg, 0.052 mmol, 49.5% yield) was obtained as the only carbonyl product. IR (ν_{co}, CH_2Cl_2): 1982 cm^{-1}, 2043 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.44 ppm (s, 3H, CH_3); 5.59 ppm (t, 2H, Cp); 5.71 ppm (t, 2H, Cp).

Table 1
IR and NMR spectroscopic data for *diag*- and *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 complexes

Complex	ν^a_{co} (cm^{-1})	^{1}H-NMR[b] (ppm)		
		Cp ring	R	L
diag-(η^5-C_5H_4Me)Re(CO)($CNC_6H_3Me_2$)Br_2	1974	4.72 (t, 2H); 4.90 (t, 2H)	1.82 (s, 3H)	2.35 (s, 6H);6.63 (m, 3H)
diag-(η^5-C_5H_4Me)Re(CO)[$P(OMe)_3$]Br_2	1969	4.71 (t, 2H); 4.90 (t, 2H)	1.80 (s, 3H)	3.48 (d, 9H)
diag-(η^5-C_5H_4Me)Re(CO)[$P(O^iPr)_3$]Br_2	1963	4.73 (t, 2H); 4.93 (t, 2H)	1.84 (s, 3H)	1.24 (s, 9H);1.27 (s,9H);4.84 (m, 3H)
diag-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]Br_2c	1989	4.53 (t, 2H);4.65 (t, 2H)	1.64 (s, 3H)	6.88–7.56 (m, 15H)
diag-(η^5-C_5H_4Me)Re(CO)(PPh_3)Br_2	1963	4.75 (t, 2H); 5.00 (t, 2H)	1.82 (s, 3H)	6.95–7.69 (m, 15H)
diag-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]I_2	1976	4.63 (t, 2H); 4.73 (t, 2H)	1.82 (s, 3H)	6.75–7.59 (m, 15H)
diag-(η^5-C_5H_4Me)Re(CO)(PPh_3)I_2	1948	4.81 (t, 2H);5.09 (t, 2H)	2.00 (s, 3H)	6.64–7.64 (m, 15H)
diag-(η^5-C_5H_4t-Bu)Re(CO)($CNC_6H_3Me_2$)Br_2	1975	4.84 (t, 2H); 5.10 (t, 2H)	1.15 (s, 9H)	2.46 (s, 6H);6.68 (m, 3H)
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(OMe)_3$]Br_2	1971	4.56 (t, 2H); 5.28 (t, 2H)	1.18 (s, 9H)	3.53 (d, 9H)
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(O^iPr)_3$]Br_2	1960	4.62 (t, 2H);5.35 (t, 2H)	1.19 (s, 9H)	1.28 (d, 18H);4.89 (m, 3H)
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(OPh)_3$]Br_2	1992	4.44 (t, 2H); 4.92 (t, 2H)	1.06 (s, 9H)	6.76–7.58 (m, 15H)
diag-(η^5-C_5H_4t-Bu)Re(CO)(PPh_3)Br_2	1963	4.75 (t, 2H); 5.31 (t, 2H)	1.20 (s, 9H)	6.96–7.79 (m, 15H)
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)($CNC_6H_3Me_2$)Br_2	1976	4.83 (t, 2H);5.21 (t, 2H)	0.18 (s, 9H)	2.41 (s, 6H);6.63 (m, 3H)
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(OMe)_3$]Br_2	1971	4.67 (t, 2H); 5.38 (t, 2H)	0.27 (s, 9H)	3.45 (d, 9H)
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(O^iPr)_3$]Br_2	1963	4.70 (t, 2H); 5.47 (t, 2H)	0.28 (s, 9H)	1.26 (d, 18H);4.87 (m, 3H)
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(OPh)_3$]Br_2	1993	4.51 (t, 2H);5.08 (t, 2H)	0.16 (s, 9H)	6.76–7.57 (m, 15H)
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)(PPh_3)Br_2	1956	4.90 (t, 2H); 5.44 (t, 2H)	0.26 (s, 9H)	6.64–7.96 (m, 15H)
lat-(η^5-C_5H_4Me)Re(CO)($CNC_6H_3Me_2$)Br_2	1959	4.72 (m, 1H); 4.78 (m, 2H); 4.90 (m, 1H)	1.76 (s, 3H)	2.14 (s, 6H);6.63 (m, 3H)
lat-(η^5-C_5H_4Me)Re(CO)[$P(OMe)_3$]Br_2	1938	4.82 (m, 2H);4.94 (m, 1H); 4.95 (m, 1H)	1.76 (s, 3H)	3.47 (d, 9H)
lat-(η^5-C_5H_4Me)Re(CO)[$P(O^iPr)_3$]Br_2	1932	4.97 (m, 4H)	1.82 (s, 3H)	1.12 (s, 9H);1.15 (s, 9H);4.81 (br, 3H)
lat-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]Br_2c	1959	4.62 (d, 1H); 4.72 (d, 1H); 4.77 (d, 1H); 5.07 (d, 1H)	1.73 (s, 3H)	6.75–7.55 (m, 15H)
lat-(η^5-C_5H_4Me)Re(CO)(PPh_3)Br_2	1926	4.51 (m, 1H); 4.71 (m, 1H);4.92 (m, 1H); 4.99 (m, 1H)	1.90 (s, 3H)	6.75–7.55 (m, 15H)
lat-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]I_2	1950	4.43 (m, 2H); 4.69 (m, 1H);5.05 (m, 1H)	1.99 (s, 3H)	6.75–7.59 (m, 15H)
lat-(η^5-C_5H_4Me)Re(CO)(PPh_3)I_2	1922	4.35 (m, 1H); 4.68 (m, 1H);4.91 (m, 1H); 5.00 (m, 1H)	2.12 (s, 3H)	6.64–7.64 (m, 15H)

Table 1 (Continued)

Complex	ν_a^{co} (cm^{-1})	^{1}H-NMR[b] (ppm)		
		Cp ring	R	L
lat-(η^5-C_5H_4t-Bu)Re(CO)($CNC_6H_3Me_2$)Br_2	1957	4.98 (m, 2H); 5.11 (m, 1H);5.15 (m, 1H)	1.07 (s, 9H)	2.16 (s, 6H);6.62 (m, 3H)
lat-(η^5-C_5H_4t-Bu)Re(CO)[P(OMe)$_3$]Br_2	1933	4.86 (m, 1H); 5.03 (m, 1H);5.23 (m, 1H); 5.35 (m, 1H)	1.17 (s, 9H)	3.46 (d, 9H)
lat-(η^5-C_5H_4t-Bu)Re(CO)[P(O^{i}Pr)$_3$]Br_2	1930	5.10 (m, 1H); 5.16 (m, 1H);5.25 (m, 1H); 5.49 (m, 1H)	1.22 (s, 9H)	1.12 (s, 9H);1.15 (s, 9H);4.79 (br, 3H)
lat-(η^5-C_5H_4t-Bu)Re(CO)[P(OPh)$_3$]Br_2	1953	4.94 (m, 1H); 5.03 (m, 1H);5.11 (m, 1H); 5.57 (m, 1H)	1.11 (s, 9H)	6.76–7.55 (m, 15H)
lat-(η^5-C_5H_4t-Bu)Re(CO)(PPh_3)Br_2	1924	4.89 (m, 1H); 4.97 (m, 1H);5.04 (m, 1H); 5.52 (m, 1H)	1.14 (s, 9H)	6.96–7.79 (m, 15H)
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)($CNC_6H_3Me_2$)Br_2	1958	5.07 (m, 2H); 5.21 (m, 1H);5.26 (m, 1H)	0.23 (s, 9H)	2.15 (s, 6H);6.62 (m, 3H)
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)[P(OMe)$_3$]Br_2	1935	5.07 (m, 1H); 5.17 (m, 1H);5.32 (m, 1H); 5.39 (m, 1H)	0.28 (s, 9H)	3.45 (d, 9H)
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)[P(O^{i}Pr)$_3$]Br_2	1931	5.25 (m, 1H); 5.31 (m, 1H);5.35 (m, 1H); 5.62 (m, 1H)	0.32 (s, 9H)	1.11 (s, 9H);1.14 (s, 9H);4.77 (br, 3H)
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)[P(OPh)$_3$]Br_2	1952	4.98 (m, 1H); 5.13 (m, 1H);5.21 (m, 1H); 5.64 (m, 1H)	0.21 (s, 9H)	6.82–7.40 (m, 15H)
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)(PPh_3)Br_2	1924	4.86 (m, 2H); 5.07 (m, 1H);5.67 (m, 1H)	0.28 (s, 9H)	7.35–7.80 (m, 15H)

[a] Recorded in CH_2Cl_2.
[b] Recorded in C_6D_6, relative to TMS: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.
[c] [12]e.

3. Results and discussion

3.1. Synthesis and characterization of diag- and lat-(η^5-C_5H_4R)Re(CO)(L)X_2

The initial approach to the preparation of monocarbonyl substitution products of (η^5-C_5H_4R)Re(CO)$_2X_2$ was attempted using the King method, i.e. refluxing (η^5-C_5H_4R)Re(CO)$_2X_2$ and ligands, L, in benzene or toluene [12](e). Indeed, the desired products (η^5-C_5H_4R)Re(CO)(L)X_2 were obtained. However, we found that the product selectivity, not unexpectedly, was poor. The product was obtained as a mixture of diagonal and lateral isomers, and the [*diag*]/[*lat*] ratio varied from reaction to reaction. Further, some unwanted side products, which were not characterized, were formed [9]. Catalytic carbonyl substitution using a PdO catalyst was attempted. This catalyst has previously been successfully used to catalyze reactions between Re(CO)5X and group 15 donor ligands [14]. Numerous reactions (varying temperature, time, etc.) indicated that PdO did not catalyse the carbonyl substitution reactions of (η^5-C_5H_4R)Re(CO)$_2X_2$.

Attempts to use Me_3NO as a decarbonylating agent were then undertaken. In the presence of excess Me_3NO, reactions of either *diag*- or *lat*-(η^5-C_5H_4R)Re(CO)$_2X_2$ (X = Br, I) with isocyanides, phosphites and triphenyl phosphine in CH_2Cl_2 at room temperature (r.t.) rapidly gave *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 in good yields. Usually, a few percent of *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 was also found in the product. Detailed studies indicated that these lateral isomers were formed by isomerization of the diagonal products (see below).

All the diagonal isomers of (η^5-C_5H_4R)Re(CO)(L)X_2 have a red color and the lateral isomers are brown in colour. They all dissolve in organic solvents such as dichloromethane, chloroform, benzene and toluene, but the lateral isomers have lower solubility.

Reaction of (η^5-C_5H_4R)Re(CO)$_2X_2$ with L = PEt_3, P^iPr_3, P^tBu_3 or pyridine resulted in extensive decomposition and no new monosubstituted neutral products were formed. (No attempt was made to analyse the reaction solution). This finding most certainly relates to the stronger basic properties of these ligands [2].

The identification of the diagonal and lateral isomers of (η^5-C_5H_4R)Re(CO)(L)X_2 was based on IR and NMR spectroscopy and X-ray single crystal structures. The proton patterns of the cyclopentadienyl ring resonances of the diagonal isomers occur as two 'pseudo'

Table 2
Analytical data for *diag*- and *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 complexes

Complex	Yield (%)	m.p. (°C)	Analysis (%)			
				C	H	N
diag-(η^5-C_5H_4Me)Re(CO)($CNC_6H_3Me_2$)Br_2	92	154–156	Calc.	32.89	2.76	2.40
			Found	32.82	2.64	2.32
diag-(η^5-C_5H_4Me)Re(CO)[$P(OMe)_3$]Br_2	75	114–116	Calc.	20.81	2.79	
			Found	20.69	2.68	
diag-(η^5-C_5H_4Me)Re(CO)[$P(O^iPr)_3$]Br_2	84	108–110	Calc.	29.06	4.27	
			Found	29.01	3.93	
diag-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]Br_2	89	164–166	Calc.	39.33	2.90	
			Found	39.39	2.68	
diag-(η^5-C_5H_4Me)Re(CO)(PPh_3)Br_2	70	186–188	Calc.	41.97	3.10	
			Found	42.06	2.88	
diag-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]I_2	60	—[a]	Calc.	35.02	2.59	
			Found	35.03	2.44	
diag-(η^5-C_5H_4Me)Re(CO)(PPh_3)I_2	84	176-169	Calc.	37.10	2.74	
			Found	36.96	2.61	
diag-(η^5-C_5H_4t-Bu)Re(CO)($CNC_6H_3Me_2$)Br_2	96	142–144	Calc.	36.43	3.54	2.24
			Found	36.35	3.31	2.19
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(OMe)_3$]Br_2	75	123–125	Calc.	25.21	3.58	
			Found	24.97	3.28	
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(O^iPr)_3$]Br_2	75	126–128	Calc.	32.44	4.87	
			Found	32.42	4.64	
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(OPh)_3$]Br_2	61	124–126	Calc.	41.75	3.50	
			Found	41.43	3.26	
diag-(η^5-C_5H_4t-Bu)Re(CO)(PPh_3)Br_2	76	172–174	Calc.	44.40	3.73	
			Found	44.41	3.69	
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)($CNC_6H_3Me_2$)Br_2	95	144–146	Calc.	33.65	3.45	2.18
			Found	33.50	3.30	2.12
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(OMe)_3$]Br_2	76	—[a]	Calc.	22.68	3.49	
			Found	22.70	3.57	
diag–(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(O^iPr)_3$]Br_2	75	106–108	Calc.	30.05	4.76	
			Found	30.16	4.64	
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(OPh)_3$]Br_2	84	124–126	Calc.	39.47	3.44	
			Found	39.20	3.44	
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)(PPh_3)Br_2	63	155–157	Calc.	41.92	3.65	
			Found	42.17	3.69	
lat-(η^5-C_5H_4Me)Re(CO)($CNC_6H_3Me_2$)Br_2	—	192–194	Calc.	32.89	2.76	2.40
			Found	32.60	2.48	2.34
lat-(η^5-C_5H_4Me)Re(CO)[$P(OMe)_3$]Br_2	—	116–118	Calc.	20.81	2.79	
			Found	20.51	2.78	
lat-(η^5-C_5H_4Me)Re(CO)[$P(O^iPr)_3$]Br_2	—	178–180	Calc.	29.06	4.27	
			Found	29.02	4.06	
lat-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]Br_2	—	183–185	Calc.	39.33	2.90	
			Found	39.38	2.69	
lat-(η^5-C_5H_4Me)Re(CO)(PPh_3)Br_2	—	200–202	Calc.	41.97	3.10	
			Found	42.00	2.87	
lat-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]I_2	—	189–191	Calc.	35.02	2.59	
			Found	35.00	2.46	
lat-(η^5-C_5H_4Me)Re(CO)(PPh_3)I_2	—	227–229	Calc.	37.10	2.74	
			Found	37.01	2.63	
lat-(η^5-C_5H_4t-Bu)Re(CO)($CNC_6H_3Me_2$)Br_2	—	194–196	Calc.	36.43	3.54	2.24
			Found	36.31	3.27	2.19
lat-(η^5-C_5H_4t-Bu)Re(CO)[$P(OMe)_3$]Br_2	—	154–156	Calc.	25.21	3.58	
			Found	32.44	4.87	
lat-(η^5-C_5H_4t-Bu)Re(CO)[$P(O^iPr)_3$]Br_2	—	170–172	Calc.	32.50	4.50	
lat-(η^5-C_5H_4t-Bu)Re(CO)[$P(OPh)_3$]Br_2	—	158–160	Calc.	41.75	3.50	
			Found	41.82	3.46	
lat-(η^5-C_5H_4t-Bu)Re(CO)(PPh_3)Br_2	—	190–192	Calc.	44.40	3.73	
			Found	43.90	3.62	
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)($CNC_6H_3Me_2$)Br_2	—	179–181	Calc.	33.65	3.45	2.18
			Found	33.41	3.27	2.15
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(OMe)_3$]Br_2	—	143–145	Calc.	22.68	3.49	
			Found	22.46	3.43	

Table 2 (Continued)

Complex	Yield (%)	m.p. (°C)	Analysis (%)			
				C	H	N
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)[P(O^{i}Pr)$_3$]Br_2	—	159–161	Calc.	30.05	4.76	
			Found	30.11	4.61	
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)[P(OPh)$_3$]Br_2	—	137–139	Calc.	39.47	3.44	
			Found	39.16	3.43	
lat-(η^5-$C_5H_4SiMe_3$)Re(CO)(PPh_3)Br_2	—	187–189	Calc.	41.92	3.65	
			Found	41.89	3.45	

[a] Due to fast isomerization in solutions, the pure diagonal isomers of these complexes were not obtained.

triplet peaks while those of the lateral isomers usually comprise of four multiplet peaks. The diagonal isomers were also observed to have higher carbonyl stretching frequencies than the lateral isomers. The structures of *diag*- and *lat*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br_2, the first structures of cyclopentadienyl monocarbonyl substituted dihalogen rhenium complexes, were successfully determined by X-ray single crystal diffraction and unambiguously confirmed our assignments [15].

3.2. Solid-state diag–lat isomerization of (η^5-C_5H_4R)Re(CO)(L)X_2

It was found that all the diagonal isomers of (η^5-C_5H_4R)Re(CO)(L)X_2 underwent thermal solid-state isomerization reactions to give the corresponding lateral isomers in good yields ($>70\%$) within a few hours (Table 3). It should be noted that the reaction temperatures reported here (Table 3) are not the minimum temperatures needed for solid-state isomerization reactions. The isomerization is unidirectional, i.e. from the diagonal to the lateral isomer; the lateral isomers remained unchanged under the same reaction conditions. Unlike the thermal isomerization reactions of (η^5-C_5H_4R)Re(CO)$_2$$Br_2$ in which the isomerization process is strongly influenced by the cyclopentadienyl ring substituent R and the solid-state isomerization is only observed for (η^5-C_5H_4R)Re(CO)$_2$$Br_2$ (R = Me [4], iPr), all (η^5-C_5H_4R)Re(CO)(L)X_2 underwent thermal solid-state *diag*-to-*lat* isomerization. In these reactions the different cyclopentadienyl ring substituent R, ligand L and halogen X have no influence on the direction of the solid-state isomerization process. More importantly, our study indicates that thermal solid-state *diag–lat* isomerization is a common reaction for a wide range of cyclopentadienyl four-legged piano stool rhenium complexes. Reaction of *diag*-(η^5-C_5H_4Me)Re(CO)$_2$$Br_2$ and excess NaI in the solid-state, under typical isomerisation conditions, gave quantitative formation of *diag*-(η^5-C_5H_4Me)Re(CO)$_2$$I_2$. This methodology also offers a convenient method for the preparation of cyclopentadienyl dicarbonyldiiodide rhenium complexes. Reaction of a solid mixture of *diag*-(η^5-C_5H_4Me)Re(CO)-[P(OPh)$_3$]Br_2 and excess NaI, surprisingly gave *diag*-(η^5-C_5H_4Me)Re(CO)$_2$$I_2$ (50% yield) instead of the expected *diag*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]I_2. The above reactions indicate that both Re–Br and Re–P(OPh)$_3$ bonds can be broken during the solid-state halogen exchange processes. These are remarkable results in that:

1. The diagonal iodo isomer has formed in the solid-state. Previously we had not been able to interconvert the iodo *diag–lat* isomers in the solid-state [16] as a melt formed prior to isomerisation. However the preference for the diagonal isomer is expected from a consideration of the melting points of the isomers.
2. The yield is near quantitative in the phosphite–iodide exchange reaction and implies no CO is lost when the ligand exchange occurs.
3. This is the first time we have observed the replacement of a neutral ligand by another neutral ligand (phosphite by CO) in the solid-state.

Any mechanism will need to take the above information into consideration. In a previous paper [17] we proposed that isomerisation was achieved by a flexing of the four ligands relative to the cyclopentadienyl ring followed by a turnstile process as shown in Fig. 1. For this new set of compounds it appears that both the ring and the L ligand will provide the pivots for the 3-fold rotation of the Br and CO ligands. This is entirely consistent with the original proposal.

Presumably during the flexing process all metal–ligand bonds are weakened (even the ring–Re bonds [18]) and in the presence of appropriate ligands e.g. iodide/iodine atom, substitution can take place. This would lead to the unusual results obtained above. Clearly further studies will be needed to assess both the generality of the reaction and the mechanism of the ligand exchange.

3.3. Solution phase diag–lat isomerization of (η^5-C_5H_4R)Re(CO)(L)X_2

Both *diag*- and *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 are stable in solution in the dark, even in the presence of

Table 3
Thermal solid-state *diag–lat* isomerization of *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2

Complex	Reaction temperature (°C)	Reaction time (h)	Yield (%)[a]
diag-(η^5-C_5H_4Me)Re(CO)($CNC_6H_3Me_2$)Br_2	140–145	1.0	86
diag-(η^5-C_5H_4Me)Re(CO)[$P(OMe)_3$]Br_2	100–105	2.0	96
diag-(η^5-C_5H_4Me)Re(CO)[$P(O^iPr)_3$]Br_2	95–100	6.0	81
diag-(η^5-C_5H_4Me)Re(CO)[$P(OPh)_3$]Br_2	145–150	5.0	80
diag-(η^5-C_5H_4Me)Re(CO)(PPh_3)Br_2	145–150	2.0	72
diag-(η^5-C_5H_4Me)Re(CO)(PPh_3)I_2	145–150	2.0	70
diag-(η^5-C_5H_4t-Bu)Re(CO)($CNC_6H_3Me_2$)Br_2	130–135	1.0	94
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(OMe)_3$]Br_2	105–110	2.0	82
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(O^iPr)_3$]Br_2	105–110	2.0	70
diag-(η^5-C_5H_4t-Bu)Re(CO)[$P(OPh)_3$]Br_2	108–110	2.0	85
diag-(η^5-C_5H_4t-Bu)Re(CO)(PPh_3)Br_2	140–145	2.0	85
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)($CNC_6H_3Me_2$)Br_2	130–135	1.0	76
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(O^iPr)_3$]Br_2	90–95	2.0	70
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)[$P(OPh)_3$]Br_2	105–110	2.0	71
diag-(η^5-$C_5H_4SiMe_3$)Re(CO)(PPh_3)Br_2	130–135	0.5	75

[a] Yield after isomer separation.

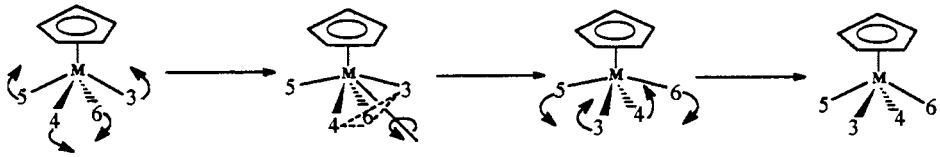

Fig. 1. Combined Berry–turnstile isomerization mechanism for $CpML_4$ complexes.

excess ligand, L. Only a few percent ($< 5\%$) of the lateral isomer forms when the chloroform or benzene solutions of *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2, covered with aluminum foil, were kept at r.t. for 4 weeks. No isomerisation was observed for *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 under these conditions. However, the solution isomerization of (η^5-C_5H_4R)Re(CO)(L)X_2 proceeds readily on irradiation with visible light in $CHCl_3$ or more slowly in C_6H_6.

As with the thermal solid-state isomerization reaction, only the *diag*-to-*lat* isomerization was observed for solutions of (η^5-C_5H_4R)Re(CO)(L)X_2. No isomerization was observed for *lat*-(η^5-C_5H_4R)Re(CO)(L)X_2 under the same irradiation conditions. A mechanism for the solution photochemical *cis–trans* isomerism of (η^5-C_5Me_5)Re(CO)$_2X_2$ (X = Cl, Br, I) has been reported and a carbonyl dissociation–association process has been proposed [19]. A similar mechanism may apply here although a dissociative–associative process involving X groups seems more likely.

4. Conclusions

With the assistance of Me_3NO, reaction of *diag*- or *lat*-(η^5-C_5H_4R)Re(CO)$_2X_2$ (R = Me, *t*-Bu, $SiMe_3$; X = Br, I) with isocyanides, phosphites and triphenyl phosphine proceeded rapidly at r.t. to give *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 (L = $CNC_6H_3Me_2$, $P(OMe)_3$, $P(O^iPr)_3$, $P(OPh)_3$, PPh_3) in good yields. Solid-state *diag–lat* isomerization reactions were observed for all the monocarbonyl substituted rhenium complexes (η^5-C_5H_4R)Re(CO)(L)X_2, prepared in this study, indicating that the solid-state isomerization reaction is a common phenomenon for cyclopentadienyl four-legged piano stool rhenium complexes. The direction of the isomerisation reaction was also found to be different from their parent complexes (η^5-C_5H_4R)Re(CO)$_2X_2$ in which *lat*-to-*diag* solution isomerization occurred. *diag*-(η^5-C_5H_4R)Re(CO)(L)X_2 completely isomerized into the corresponding lateral isomers in chloroform or dichloromethane on irradiation with visible light at r.t.

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