Isomers in *fac*-[ReBr(CO)$_3$(L$_c$)$_2$] (L$_c$ = *cis*-3,4-Dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,3-diazaphosphole) arising from Chirality of Phosphorus Ligands: Separation and *X*-Ray Structural Studies†

Graziano Baccolini, Luigi Busetto,* and Antonella Roncarolo
Facolta' di Chimica Industriale, Universita' di Bologna, Viale Risorgimento 4, 40 136 Bologna, Italy
Vincenzo Giulio Albano
Istituto Chimico 'G. Ciamician,' Universita' di Bologna, Via Selmi 2, 40 126 Bologna, Italy
Franceso Demartin
Istituto di Chimica Strutturistica Inorganica, Via C. Venezian 21, 20 133 Milano, Italy

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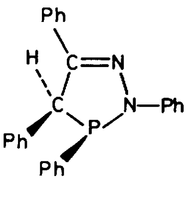
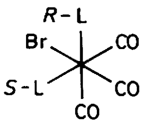
Reaction of *cis*-[ReBr(CO)$_4$(L$_c$)] with chiral L$_c$ (*cis*-3,4-dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,3-diazaphosphole) afforded *fac*-[ReBr(CO)$_3$(L$_c$)$_2$] which, owing to the racemic nature of L$_c$ (*R*,*S*-L), should be a mixture of three predictable diastereoisomers: *fac*-[ReBr(CO)$_3$(*R*-L)(*S*-L)] [*meso*-(**A**) or *meso*-(**B**)] and the enantiomeric pair *fac*-[ReBr(CO)$_3$(*R*,*S*-L)$_2$]. Two of these forms, *meso*-(**A**) and the enantiomeric pair, have been separated by column chromatography and their nature unambiguously attributed by *X*-ray studies. *fac*-[ReBr(CO)$_3$(*R*-L)(*S*-L)] crystallizes in the monoclinic space group $P2_1/n$, with a = 19.481(4), b = 13.204(3), c = 20.083(8) Å, β = 110.56(3)°, and Z = 4; R' = 0.046. *fac*-[ReBr(CO)$_3$(*R*,*S*-L)$_2$]·C_6H_{14}·C_7H_{16} crystallizes in the monoclinic space group $P2_1/n$, with a = 12.191(3), b = 20.939(4), c = 21.713(5) Å, β = 93.93(3)°, and Z = 4; R' = 0.048. Attempts to separate or detect spectroscopically isomers of *fac*-[ReBr(CO)$_3$(L)$_2$] (L = racemic PMeEtPh) failed, indicating that interligand interactions are the determining factors in achieving the separation.

In previous papers we have described the thermal substitution reactions of Group 6A and 7A metal carbonyls with diastereoisomeric L$_c$ and L$_t$ diazaphosphole ligands (L$_t$ and L$_c$ = *trans*- and *cis*-3,4-dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,3-diazaphosphole respectively) having large and different cone angles but practically identical electronic properties.[1] The most striking result obtained in this field is the high selectivity in forming disubstituted complexes when at least one of the co-ordinated diazaphospholes is the bulky L$_t$ ligand. In these cases *only* complexes in which the diazaphospholes are mutually *trans* have been obtained in reactions leading to disubstituted carbonyl complexes. Another consequence, which may be attributed to the different steric demands of the *cis*- and *trans*-diazaphosphole ligands, has been observed by comparing the i.r. spectra of *cis*-[ReBr(CO)$_4$(L$_t$)] and *cis*-[ReBr(CO)$_4$(L$_c$)] in cyclohexane solution. Whereas *cis*-[ReBr(CO)$_4$(L$_t$)] exhibits the expected four CO absorptions, *cis*-[ReBr(CO)$_4$(L$_c$)] shows eight ν(CO) bands.[1c] This 'CO frequencies doubling' was attributed to conformational isomers about the Re–P(L$_c$) bond which may arise from the lower steric hindrance of the *cis* diazaphosphole. In order to test the existence of the conformers in disubstituted *fac*-[ReBr(CO)$_3$(L$_c$)$_2$], we have first separated the facial diastereoisomers arising from the reaction of racemic L$_c$(*R*,*S*-L)[2] with *cis*-[ReBr(CO)$_4$(L$_c$)].

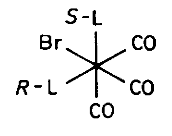


L$_c$ (*R*,*S*-L)

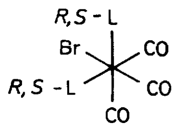
The resulting four possible *fac* stereoisomers, namely *meso*-(A), *meso*-(B), and an enantiomeric pair, are shown below. It should be noted that isomer (A) can be converted into (B) either by mutual exchange of *R*-L and *S*-L or by swapping the bromide ligand with the carbonyl group *trans* to it.



meso-(**A**)



meso-(**B**)



enantiomeric pair

In this work we report the separation and *X*-ray single-crystal structure determinations of both the *meso*-(A) and the enantiomeric pair of isomers. To the best of our knowledge no example of this type of isomerism has been reported.

Experimental

All reactions were carried out under an atmosphere of oxygen-free nitrogen and all solvents were dried according to established procedures. Infrared spectra were recorded on a Perkin-Elmer model 983G spectrometer using 0.5-mm cells. The diazaphosphole ligands L$_c$ and L$_t$,[2] *fac*-[ReBr(CO)$_3$(L$_c$)$_2$] (1),[1c] and [Re$_2$Br$_2$(CO)$_6$(thf)$_2$] (thf = tetrahydrofuran)[3] were prepared by published methods. The phosphine PMeEtPh was purchased from Strem Chemicals. Column chromatography was performed with silica gel of particle size 0.05—0.2 mm.

Separation of fac-[ReBr(CO)$_3$(L$_c$)$_2$] (1) *Isomers*.—Crude *fac*-[ReBr(CO)$_3$(L$_c$)$_2$], obtained[1c] from *cis*-[ReBr(CO)$_4$(L$_c$)] and L$_c$, was chromatographed on a silica gel column. Elution with n-hexane–benzene–diethyl ether (32:2:1) gave two different facial complexes (**I**) (R_f 0.14) and (**II**) (R_f 0.11) in a *ca.* 2:1 ratio. Crystallization from dichloromethane–n-hexane–heptane gave white crystals for both (**I**) and (**II**) (m.p. 195—197 and 170—175 °C, respectively). Refluxing (**II**) in chloroform

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Summary of crystal data and intensity collection parameters

	Isomer (I)	Isomer (II)
Formula	$C_{55}H_{42}BrN_4O_3P_2Re$	$C_{55}H_{42}BrN_4O_3P_2Re\cdot C_6H_{14}\cdot C_7H_{16}$
M	1 135.03	1 321.4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	19.481(4)	12.191(3)
b/Å	13.204(3)	20.939(4)
c/Å	20.083(8)	21.713(5)
β/°	110.56(3)	93.93(3)
U/Å^3	4 837(5)	5 530(4)
Z	4	4
D_c/g cm^{-3}	1.559	1.587
$F(000)$	2 256	2 680
μ(Mo-K_α)/cm^{-1}	34.76	30.52
Scan mode	ω	ω
θ range/°	3—25	3—25
ω scan width/°	1.3 + 0.35tanθ	1.4 + 0.35tanθ
Quadrants in the reciprocal space explored	$\pm h,k,l$	$\pm h,k,l$
Measured reflections	8 460	9 698
Unique observed reflections [with $I > 3\sigma(I)$]	3 313	4 445
R	0.043	0.041
R'	0.046	0.048
Goodness of fit	1.150	1.395
Minimum relative transmission factor	0.92	0.77

Table 2. Selected bond distances (Å) and angles (°)

	Isomer (I)	Isomer (II)
Re–Br	2.622(1)	2.616(1)
Re–P(1)	2.481(3)	2.477(2)
Re–P(2)	2.497(3)	2.480(2)
Re–C(1)	1.898(13)	2.12(2)*
Re–C(2)	1.926(12)	1.940(10)
Re–C(3)	1.956(14)	1.946(11)
C(1)–O(1)	1.153(12)	0.77(3)*
C(2)–O(2)	1.150(12)	1.149(10)
C(3)–O(3)	1.124(13)	1.136(11)
P(1)–N(11)	1.695(9)	1.734(7)
N(11)–N(12)	1.412(11)	1.416(9)
N(12)–C(13)	1.289(12)	1.299(10)
C(13)–C(14)	1.497(13)	1.522(11)
C(14)–P(1)	1.871(10)	1.867(8)
P(1)–C(111)	1.830(11)	1.825(9)
P(2)–N(21)	1.730(9)	1.725(7)
N(21)–N(22)	1.401(11)	1.399(9)
N(22)–C(23)	1.282(12)	1.285(10)
C(23)–C(24)	1.487(14)	1.538(11)
C(24)–P(2)	1.866(11)	1.879(8)
P(2)–C(211)	1.847(12)	1.811(9)
Br–Re–P(1)	85.30(7)	96.61(6)
Br–Re–P(2)	90.56(7)	83.64(6)
Br–Re–C(2)	85.0(3)	91.7(3)
Br–Re–C(1)	88.8(4)	85.7(3)
P(1)–Re–P(2)	95.6(1)	92.3(1)
P(1)–Re–C(1)	98.4(3)	88.0(7)
P(1)–Re–C(3)	86.8(4)	91.3(3)
P(2)–Re–C(2)	90.7(3)	89.8(3)
P(2)–Re–C(1)	89.1(4)	101.6(5)
C(1)–Re–C(2)	91.3(5)	83.6(8)
C(1)–Re–C(3)	91.3(5)	88.8(6)
C(2)–Re–C(3)	86.7(5)	88.2(4)

* Value affected by Br–CO disorder (see text).

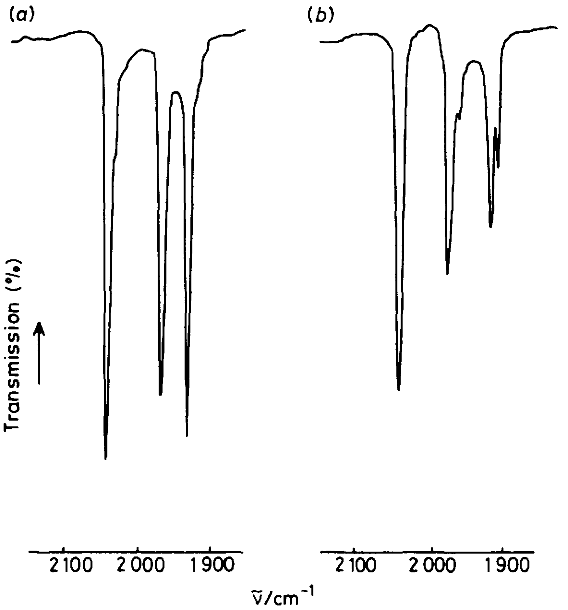

Figure 1. I.r. spectra of *fac*-[ReBr(CO)$_3$(L$_c$)$_2$] in cyclohexane: (*a*) isomer (**I**), (*b*) isomer (**II**)

gave, after 15 min, an isomeric mixture of (**I**) and (**II**) in a *ca.* 2:1 ratio.

Preparation of fac-[ReBr(CO)$_3$(L$_c$)$_2$] *from* [Re$_2$Br$_2$(CO)$_6$(thf)$_2$].—The diazaphosphole ligand L$_c$ (0.53 mmol, 0.200 g) was added to a suspension of the thf adduct [Re$_2$Br$_2$(CO)$_6$(thf)$_2$] (0.095 mmol, 0.080 g) in toluene (20 cm^3) and the mixture stirred for 2 d at room temperature. Filtration of the solution to eliminate traces of the thf adduct was followed by addition of n-heptane (20 cm^3). The colourless powder precipitated was subsequently filtered off, dried under vacuum, chromatographed, and crystallized as described above. The two facial isomers (**I**) and (**II**) were obtained in a 1:2 ratio. Crystals of (**II**) suitable for *X*-ray determination were obtained from this reaction. No *mer* isomers were detected in this reaction.

Preparation of [ReBr(CO)$_3$(PMeEtPh)$_2$].—Stoicheiometric amounts of [ReBr(CO)$_5$] and PMeEtPh were dissolved in chloroform and refluxed for *ca.* 12 h. The reaction course was followed by t.l.c. A small portion of the reaction mixture was chromatographed on silica gel plates. Elution with n-hexane–diethyl ether–benzene (32:1:2) gave the title complex [R_f 0.25; i.r.: ν(CO) at 2 030, 1 955, and 1 890 cm^{-1} (cyclohexane)]. Small amounts of [ReBr(CO)$_4$(PMeEtPh)] [R_f 0.4; i.r.: ν(CO) at 2 100w, 2 010m, 1 995vs, 1 950m, and 1 935s cm^{-1} (cyclohexane)] were also obtained. The separation of the facial isomers was attempted but proved unsuccessful.

Crystal Structure Determinations.—The crystal data together with some experimental details for both isomers (**I**) and (**II**) are summarized in Table 1. The diffraction data were collected at room temperature on an Enraf-Nonius CAD 4 diffractomer and reduced to F_o values which were corrected for absorption by the empirical method described in ref. 4. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares using the Enraf-Nonius SDP package of crystallographic programs. The hydrogen atoms were introduced in calculated positions and not refined. Crystals of isomer (**II**) contained partially disordered molecules of n-hexane and

Table 3. Positional parameters with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) Isomer (**I**)							
Re	0.237 85(2)	0.038 67(4)	0.064 11(3)	C(134)	0.151 3(8)	−0.020(1)	−0.387 0(8)
Br	0.096 05(6)	0.022 3(1)	0.034 21(6)	C(135)	0.203 4(8)	0.048(1)	−0.364 6(8)
P(1)	0.204 7(2)	0.133 9(2)	−0.049 4(2)	C(136)	0.219 8(7)	0.087(1)	−0.293 7(7)
P(2)	0.240 9(2)	−0.131 3(2)	0.010 6(2)	C(141)	0.071 9(6)	0.100 1(9)	−0.171 5(6)
O(1)	0.404 5(4)	0.050 5(6)	0.111 0(4)	C(142)	0.018 6(6)	0.042(1)	−0.162 5(6)
O(2)	0.245 3(4)	−0.056 5(7)	0.206 11(4)	C(143)	−0.055 2(7)	0.067(1)	−0.196 2(7)
O(3)	0.238 3(5)	0.241 4(7)	0.139 8(5)	C(144)	−0.072 5(7)	0.148(1)	−0.240 2(7)
N(11)	0.273 9(4)	0.161 7(7)	−0.079 1(4)	C(145)	−0.019 8(7)	0.207(1)	−0.250 1(7)
N(12)	0.261 8(5)	0.135 9(7)	−0.150 5(5)	C(146)	0.053 7(6)	0.183 7(9)	−0.215 6(6)
N(21)	0.239 8(4)	−0.143 7(7)	−0.075 5(4)	C(211)	0.311 4(6)	−0.223 8(9)	0.060 3(6)
N(22)	0.179 9(4)	−0.198 0(7)	−0.121 0(4)	C(212)	0.327 6(7)	−0.235(1)	0.130 4(7)
C(1)	0.341 4(6)	0.045 8(9)	0.091 4(6)	C(213)	0.374 7(8)	−0.313(1)	0.168 0(8)
C(2)	0.245 8(5)	−0.023 2(8)	0.153 4(6)	C(214)	0.402 5(7)	−0.380(1)	0.131 6(7)
C(3)	0.235 0(6)	0.169(1)	0.109 7(6)	C(215)	0.385 9(7)	−0.372(1)	0.061 5(7)
C(13)	0.200 0(6)	0.090 0(9)	−0.179 1(6)	C(216)	0.339 4(7)	−0.291(1)	0.024 5(7)
C(14)	0.153 2(5)	0.069 4(8)	−0.135 4(5)	C(221)	0.295 2(5)	−0.119 7(8)	−0.103 8(5)
C(23)	0.136 8(6)	−0.228 3(8)	−0.089 3(6)	C(222)	0.360 0(6)	−0.078 7(9)	−0.060 8(6)
C(24)	0.152 1(6)	−0.200 7(8)	−0.013 7(5)	C(223)	0.416 0(6)	−0.059 7(9)	−0.087 5(6)
C(111)	0.157 3(5)	0.255 4(8)	−0.057 7(5)	C(224)	0.405 9(7)	−0.080(1)	−0.156 8(7)
C(112)	0.099 7(6)	0.269 1(9)	−0.032 6(6)	C(225)	0.341 7(6)	−0.122(1)	−0.200 6(6)
C(113)	0.058 9(7)	0.357(1)	−0.047 7(7)	C(226)	0.285 9(6)	−0.142 1(9)	−0.173 5(6)
C(114)	0.074 5(7)	0.432(1)	−0.087 1(7)	C(231)	0.068 5(5)	−0.282 1(8)	−0.133 2(5)
C(115)	0.130 7(6)	0.421 2(9)	−0.111 7(6)	C(232)	0.008 6(6)	−0.283 5(9)	−0.111 7(6)
C(116)	0.173 9(6)	0.333 6(9)	−0.097 3(6)	C(233)	−0.055 1(7)	−0.338(1)	−0.151 1(7)
C(121)	0.342 4(6)	0.209 5(9)	−0.040 2(6)	C(234)	−0.056 7(6)	−0.383(1)	−0.211 3(7)
C(122)	0.347 9(6)	0.267(1)	0.017 6(6)	C(235)	−0.000 0(7)	−0.382(1)	−0.235 4(6)
C(123)	0.416 5(7)	0.312(1)	0.057 0(7)	C(236)	0.064 6(6)	−0.329(1)	−0.195 5(6)
C(124)	0.472 8(8)	0.296(1)	0.034 3(8)	C(241)	0.155 9(6)	−0.290(1)	0.036 6(6)
C(125)	0.467 8(8)	0.242(1)	−0.021 1(7)	C(242)	0.135 8(7)	−0.272(1)	0.094 8(7)
C(126)	0.402 8(7)	0.196(1)	−0.062 8(6)	C(243)	0.145 7(8)	−0.353(1)	0.143 9(8)
C(131)	0.180 6(6)	0.054 9(9)	−0.253 0(6)	C(244)	0.170 5(8)	−0.441(1)	0.130 4(8)
C(132)	0.126 7(7)	−0.016(1)	−0.280 3(7)	C(245)	0.189 7(8)	−0.463(1)	0.074 0(8)
C(133)	0.112 6(7)	−0.057(1)	−0.350 8(7)	C(246)	0.179 2(6)	−0.381(1)	0.024 4(6)
(*b*) Isomer (**II**)							
Re	0.162 35(3)	0.248 47(3)	−0.002 98(2)	C(134)	0.420 5(9)	0.320 0(6)	−0.355 9(5)
Br	−0.034 2(1)	0.202 69(8)	−0.031 40(7)	C(135)	0.315 2(9)	0.334 6(6)	−0.362 2(5)
Br′	0.351 3(7)	0.300 1(4)	0.027 4(4)	C(136)	0.251 7(9)	0.337 0(6)	−0.311 4(5)
P(1)	0.160 0(2)	0.329 6(1)	−0.086 1(1)	C(141)	0.360 2(8)	0.386 6(5)	−0.120 5(4)
P(2)	0.220 9(2)	0.163 0(1)	−0.072 7(1)	C(142)	0.451 5(9)	0.381 2(6)	−0.079 1(5)
O(1)	0.368 7(6)	0.303 6(4)	0.042 8(3)	C(143)	0.517(1)	0.435 1(6)	−0.066 5(6)
O(2)	0.202 1(7)	0.160 3(4)	0.110 2(3)	C(144)	0.494(1)	0.489 3(7)	−0.093 7(6)
O(3)	0.044 1(7)	0.337 3(4)	0.084 0(4)	C(145)	0.407(1)	0.497 2(7)	−0.135 6(6)
N(11)	0.072 3(6)	0.321 6(4)	−0.151 9(3)	C(146)	0.339 6(9)	0.444 1(6)	−0.149 2(5)
N(12)	0.126 7(6)	0.322 4(4)	−0.207 4(3)	C(211)	0.226 6(8)	0.082 6(5)	−0.042 0(5)
N(21)	0.342 7(6)	0.168 8(4)	−0.108 4(3)	C(212)	0.143 0(9)	0.061 4(5)	−0.006 6(5)
N(22)	0.332 5(6)	0.170 1(4)	−0.173 0(4)	C(213)	0.147(1)	−0.001 6(6)	0.018 2(6)
C(1)	0.315 5(9)	0.286 4(5)	0.031 4(5)	C(214)	0.233(1)	−0.038 8(6)	0.006 2(6)
C(2)	0.184 2(8)	0.190 7(5)	0.066 7(5)	C(215)	0.315(1)	−0.019 5(7)	−0.027 3(6)
C(3)	0.089 8(9)	0.307 0(5)	0.050 8(5)	C(216)	0.310 3(9)	0.042 3(6)	−0.050 9(5)
C(13)	0.232 9(7)	0.326 0(5)	−0.198 1(4)	C(221)	0.448 0(8)	0.179 4(5)	−0.079 9(4)
C(14)	0.283 6(7)	0.331 1(5)	−0.132 3(4)	C(222)	0.535 6(8)	0.195 1(5)	−0.116 7(5)
C(23)	0.231 9(8)	0.165 9(5)	−0.194 6(4)	C(223)	0.639(1)	0.206 4(6)	−0.085 4(5)
C(24)	0.140 9(8)	0.157 5(5)	−0.149 6(4)	C(224)	0.654(1)	0.203 8(6)	−0.023 3(5)
C(111)	0.141 0(8)	0.412 6(5)	−0.063 7(4)	C(225)	0.571 1(9)	0.185 7(6)	0.011 7(5)
C(112)	0.190 7(9)	0.434 2(5)	−0.007 0(5)	C(226)	0.466 9(8)	0.173 0(5)	−0.017 0(5)
C(113)	0.180 3(9)	0.498 3(5)	0.008 8(5)	C(231)	0.206 4(8)	0.167 2(5)	−0.261 9(5)
C(114)	0.124(1)	0.539 6(6)	−0.029 8(6)	C(232)	0.099 3(9)	0.180 4(5)	−0.285 3(5)
C(115)	0.079 8(9)	0.518 9(5)	−0.086 1(5)	C(233)	0.078(1)	0.184 5(6)	−0.348 7(6)
C(116)	0.088 0(8)	0.454 9(5)	−0.103 4(5)	C(234)	0.159(1)	0.176 2(6)	−0.388 0(6)
C(121)	−0.041 7(8)	0.329 7(5)	−0.158 9(4)	C(235)	0.263(1)	0.164 2(6)	−0.365 6(6)
C(122)	−0.100 4(8)	0.341 6(5)	−0.107 9(5)	C(236)	0.288 9(9)	0.159 8(6)	−0.301 6(5)
C(123)	−0.211 4(9)	0.352 1(6)	−0.114 3(5)	C(241)	0.072 3(8)	0.098 9(5)	−0.161 3(5)
C(124)	−0.265(1)	0.350 3(7)	−0.171 5(6)	C(242)	0.119 4(9)	0.041 6(6)	−0.177 5(5)
C(125)	−0.209(1)	0.337 2(7)	−0.222 1(6)	C(243)	0.054(1)	−0.012 6(7)	−0.191 8(6)
C(126)	−0.095 6(9)	0.326 4(6)	−0.217 1(5)	C(244)	−0.054(1)	−0.009 3(7)	−0.189 2(7)
C(131)	0.301 7(8)	0.325 1(5)	−0.252 4(5)	C(245)	−0.105(1)	0.044 8(7)	−0.173 4(7)
C(132)	0.413 6(9)	0.310 7(5)	−0.246 0(5)	C(246)	−0.043(1)	0.100 8(6)	−0.159 9(6)
C(133)	0.472 8(9)	0.3083 3(6)	−0.298 8(5)				

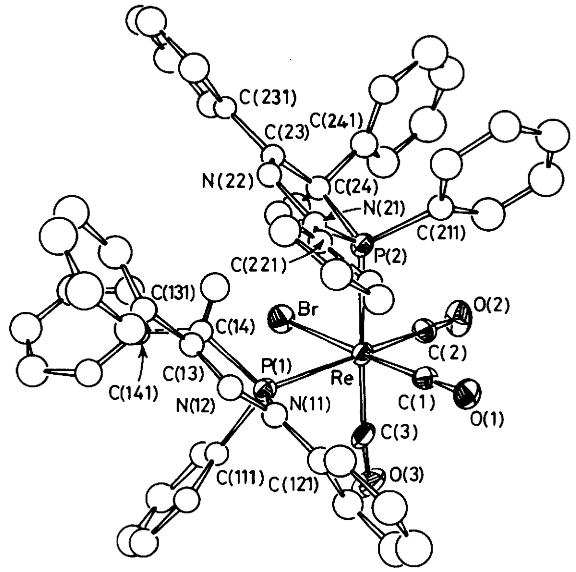

Figure 2. ORTEP drawing of isomer (**I**) showing the pseudo-mirror relationship between the L_c ligands of opposite configuration. These ligands are referred to as L_c(a) and L_c(b) (see text), with reference to P(1) and P(2), respectively

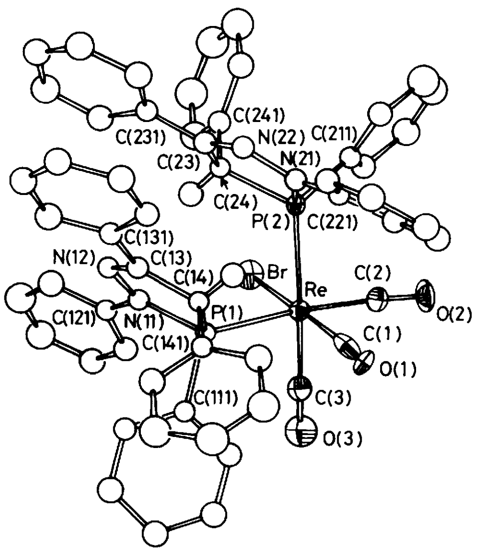

Figure 3. ORTEP drawing of isomer (**II**) showing the rotational relationship between the L_c ligands of equal configuration

n-heptane trapped in the crystal lattice in a molar ratio with the complex molecules of *ca.* 1:1:2. Moreover, a 10% disorder between the bromine atom and the carbonyl *trans* to it is also present; as a result the Re–C(1) and C(1)–O(1) distances are anomalous and affected by higher estimated standard deviations. Selected bond distances and angles are summarized in Table 2. The atomic co-ordinates for both isomers are listed in Table 3.

Results and Discussion

We have already described the synthesis of *fac*-$[ReBr(CO)_3(L_c)_2]$ (**1**) achieved by stepwise carbonyl substitution, in $[ReBr(CO)_5]$ by the racemic mixture of the diastereoisomeric L_c form of the diazaphosphole[1c] in refluxing $CHCl_3$. In order to separate the crude complex (**1**) into the facial isomers arising from the chirality of L_c (see above), we have carried out a careful t.l.c. analysis on samples of the *fac* derivative. This study has revealed two components, (**I**) and (**II**), which have been isolated in a 2:1 ratio by scaling up the separation in a silica gel column eluted with n-hexane–benzene–diethyl ether (32:2:1). Infrared analysis on component (**I**) in cyclohexane solution (Figure 1) shows three strong bands of similar intensity in the carbonyl stretching region (2 041, 1 969, and 1 932 cm^{-1}) which are typical for the C_s symmetry of a facial complex ($2A' + A''$).[5] As indicated in Figure 1 component (**II**) shows three main bands (2 044, 1 979, and 1 918 cm^{-1}) attributable to a *fac* geometry, together with two weaker absorptions (1 962 and 1 910 cm^{-1}). Repeated crystallization of this complex does not substantially alter the appearance of the spectra or the relative intensities of the five bands. This observation, together with the i.r. pattern which is the expected one for a mixture of two *fac* isomers, suggests the presence of conformational isomerism about Re–P bonds or within the ligands themselves detectable only in the case of isomer (**II**). The same hypothesis was put forward for *cis*-$[ReBr(CO)_4(L_c)]$ in which the observed 'CO frequencies doubling' was attributed to conformers.[1c] Two additional facts further illustrate the *fac* and isomeric nature of derivatives (**I**) and (**II**). At first (**I**) and (**II**) are obtained as expected, without formation of *mer* isomers, from $[Re_2Br_2(CO)_6(thf)_2]$ and L_c at room temperature.[6] In this case, (**II**) is the prevalent form [(**I**):(**II**) = 1:2]. Secondly (**II**) isomerizes to (**I**) affording, after a few minutes in refluxing $CHCl_3$, an isomeric mixture of (**I**) and (**II**) in a 2:1 ratio which is not representative of the true thermodynamic equilibrium composition. A concomitant formation of *mer* isomers was also observed in accordance with previous observations on *fac*⟶*mer* thermal isomerization reactions.[1c,7]

At this point it was necessary to define the type of isomerism present in the two isolated *fac* forms, in order to clarify whether (**I**) and (**II**) are two of the diastereoisomers depicted above or rotamers of restricted rotation. Unequivocal information has been obtained by *X*-ray crystallographic investigations on both complexes. Suitable crystals of (**I**) and (**II**) were obtained by crystallization from dichloromethane–n-hexane–n-heptane of the products prepared from *cis*-$[ReBr(CO)_4(L_c)]$ and $[Re_2Br_2(CO)_6(thf)_2]$, respectively.

The crystals of (**I**) and (**II**) contain discrete monomeric molecules. The crystal packing is normal in (**I**) while in (**II**), besides a slight orientational disorder, solvent molecules are present and the approximate composition of the crystal is $[ReBr(CO)_3(L_c)_2]\cdot C_6H_{14}\cdot C_7H_{16}$. Figures 2 and 3 show isomers (**I**) and (**II**), respectively, and have been drawn using similar orientations of the molecules and the same atom labelling. The symmetry of co-ordination around the rhenium atom in (**I**) is C_s but the diazaphosphole ligands do not actually match this symmetry because they are rotated differently around their Re–P axes with respect to each other. On inspecting Figure 2 it can be seen that L_c(a) and L_c(b) (see Figure 2) can become the mirror images of each other. Therefore these ligands have opposite absolute configurations and the molecule as a whole is an achiral *meso* isomer. The configurations of the chiral centres in L_c(a), based on the sequence priority rules,[8] are *S* at C(14) and *S* at P(1). These sterically demanding ligands are oriented in such a way as to face their flat sides. (The diazaphosphole rings and the phenyl groups bonded to the sp^2 hybridized ring atom can be considered roughly planar.) The phenyl groups bonded to the chiral centres P(1) and C(14) are oriented away from their counterparts bonded to P(2) and C(24). The hydrogen atoms bonded to C(14) and C(24), on the other hand, are pointing towards each other and their contact would be a very short one if it was not alleviated by rotation of the ligands around the

Re–P axes. As for intermolecular packings, a mirror operation relating contiguous ligands would not be very efficient in fitting one ligand into the other and a good packing is achieved only by taking advantage of the conformational degrees of freedom.

Inspection of Figure 3 shows that $L_c(a)$ and $L_c(b)$ in isomer **(II)** have the same chirality and these ligands are related by an idealized two-fold axis bisecting the P–Re–P angle. In this isomer the L_c ligands are still facing their flat surfaces, as in **(I)**, but the hydrogen atoms bonded to C(14) and C(24) are now pointing away from each other. The local C_2 operation relating the bulky diazaphosphole ligands dominates the molecule and the ability of the polar Re–Br interaction in determining an ordered crystal packing is heavily shielded. This is the reason why *ca.* 10 molecules in 100 are found rotated in the crystal causing partial Br–CO disorder. The molecule of **(II)** is asymmetric but the crystal is centric because it is built up of the racemic mixture.

Bond distances and angles for **(I)** and **(II)** are reported in comparative form in Table 2. Bond distances are strictly comparable, but some significant differences are present in the angles as a consequence of the configurational and conformational differences between the two isomers. An analysis of these values does not afford strong evidence for different stabilities of the two species, nevertheless the following facts should be pointed out. (*i*) The Re–P distances are strictly equivalent in **(II)** [2.477(2), 2.480(2) Å] and slightly but significantly different in **(I)** [2.481(3), 2.497(3) Å]. An explanation is that the rotational relationship between the ligands in **(II)** is very effective in producing good interligand contacts. (*ii*) The Re–P distances are slightly shorter in **(II)** than in **(I)** [average values 2.479(2) and 2.489(3) Å, respectively]. (*iii*) The shorter Re–P distance in **(II)** is accompanied by a lower P–Re–P angle [92.3(1) against 95.6(1)°]. (*iv*) The phenyl rings in **(II)** bonded to C(13) and C(23) are almost parallel and partially superimposed so that a graphite-type interaction is established between the rings with an interplanar distance of 3.56 Å. This interaction also explains the concerted deviation from orthogonality of the Br–Re–P angles [96.61(6) and 83.64(6)°] as an adjustment necessary for improving the ring overlap. These values indicate a better optimization of the bonded and non-bonded interactions in **(II)**. The same factors may be responsible for the easy preparation of good crystals in the case of *cis*-$[Mo(CO)_4(L_c)_2]$ in which the ligands have been found to be bonded in the same way as in **(II)**, still in a racemic crystal.[1b] Therefore **(II)** should be enthalpically favoured with respect to **(I)**. The different interligand interactions found in the solid state may also operate in solution and could be responsible for the observed slight differences in the ν(CO) absorptions between the *meso* and racemic forms. The fact that isomer **(II)** in solution partially converts into **(I)** (see above) suggests that what we have called isomer **(I)** could actually be a mixture of isomer **(A)** and **(B)**, at least in solution. Our inability to separate *meso*-**(B)** is not clear, but it may be ascribed to a fortuitous equivalence in both i.r. spectra and R_f values of the two *meso* forms. If this is true, either steric factors are responsible for favouring the crystallization of only one *meso* derivative or the crystals of **(B)** are indistinguishable from those of **(A)**.

In conclusion we have isolated and fully characterized two of the three predictable *fac* diastereoisomers of $[ReBr(CO)_3(L_c)_2]$ arising from the chirality of L_c. In this respect it should be pointed out that, using the commercial chiral phosphine PMeEtPh, it was impossible both to achieve such a separation and even to detect differences in the i.r. spectra of their *fac* isomers. This observation might indicate the necessity of using bulky phosphorus ligands in order to isolate diastereoisomeric forms of the resulting overcrowded molecules.

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References

1 (*a*) G. Baccolini and L. Busetto, *Synth. React. Inorg. Met.-Org. Chem.*, 1979, **9**, 263; (*b*) G. Baccolini, L. Busetto, and E. Foresti, *J. Chem. Soc., Dalton Trans.*, 1981, 1544; (*c*) G. Baccolini, L. Busetto, L. Contessa, V. G. Albano, and F. Demartin, *Phosphorus Sulfur*, 1984, **19**, 319.

2 G. Baccolini and P. E. Todesco, *J. Org. Chem.*, 1975, **40**, 2318.

3 D. Vitali and F. Calderazzo, *Gazz. Chim. Ital.*, 1972, **102**, 587.

4 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

5 L. F. Wuyts and G. P. Van der Kelen, *Inorg. Chim. Acta*, 1977, **23**, 19.

6 F. Calderazzo, I. P. Marani, D. Vitali, I. Bernal, J. D. Korp, and J. L. Atwood, *J. Organomet. Chem.*, 1978, **160**, 207.

7 M. Freni, V. Valenti, and D. Giusto, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2635; E. W. Abel and S. P. Tyfield, *Can. J. Chem.*, 1969, **47**, 4627; A. M. Bond, R. Colton, and M. E. McDonald, *Inorg. Chem.*, 1978, **17**, 2842.

8 R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 385; *J. Org. Chem.*, 1970, **35**, 2849.

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