CARBENE COMPLEXES

XIX *. OPTICALLY ACTIVE ELECTRON-RICH OLEFIN-DERIVED CARBENE-TRANSITION-METAL COMPLEXES **. CRYSTAL STRUCTURES OF [RhCl(COD)(C₇H₁₂N₂)], [RhCl(COD)(C₉H₁₆N₂)], [RhCl(PPh₃)₂(C₉H₁₈N₂)] AND [Co(CO)(NO)(PPh₃)(C₆H₁₂N₂)]

ANTHONY W. COLEMAN, PETER B. HITCHCOCK, MICHAEL F. LAPPERT,
ROBIN K. MASKELL, and JOACHIM H. MÜLLER

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

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Summary

Several optically active electron-rich olefins $L_2^{\star}$ have been prepared from readily available chiral starting materials, such as (S)-α-amino-acids (e.g., (S)-leucine) or terpene derivatives (e.g., $(+)$- or $(-)$-3-pinanecarboxylic acid). The derived carbene-transition-metal complexes (17 monocarbene Rh^I, 1 bis(carbene) Rh^I, and a d^8 Co complex) have been prepared with retention of optical integrity; some of their chemical and spectroscopic properties are described. X-Ray structures of four transition-metal complexes bearing optically active carbene ligands $(L^{\star})$ derived from (S)-proline, (R)-$(-)$-*trans*-N,N'-dimethyl-1,2-diaminocyclohexane, (S)-leucine, or (S)-alanine, respectively are also reported: *cis*-[RhCl(COD)(PL$^{\star Me}$ *cis*-[RhCl(COD)(CyL$^{\star Me}$)], *trans*-[RhCl(Bu^{i}L$^{\star Me}$)(PPh₃)₂], and [Co(CO)(MeL$^{\star Me}$)-(NO)(PPh₃)].

Introduction

We have recently provided details relating to the synthesis and spectroscopic characterisation of 44 monocarbenerhodium(I) complexes of structure (A) [e.g., L_n = *trans*-(CO)₂Cl] derived from various electron-rich olefins of formula (B), (or six-membered ring analogues of (A) from the olefin [=CN(Me)(CH₂)₃NMe]₂) [1]. This study revealed that the carbene ligand in complexes (A) is extremely resistant to displacement from the inner coordination sphere of the metal, and that the synthetic strategy for obtaining such complexes (A) from electron-rich olefins (B) has close analogy with that used for tertiary phosphine complexes [Rh(L$_n$)(PR₃)] from PR₃.

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* For part XVIII, see ref. 1. No reprints available.
** Dedicated to Professor Lamberto Malatesta, in recognition of his outstanding contributions to organometallic chemistry.
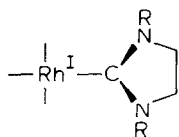
(A)

(abbreviated as $[Rh(L_n)L^R]$)
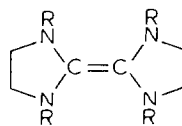
(B)

[abbreviated as L^R_2]

We have also published several preliminary communications on such compounds (A), dealing, inter alia, with (i) restricted rotation about their $Rh-C_{carb}$ bond [2], (ii) their role as electron-rich olefin metathesis catalysts [3], and (iii) their use as homogeneous catalysts for hydrogenation or hydrosilylation of various unsaturated organic substrates [4,5]. The X-ray structure of *trans*-[Rh(L^{Me}){N=C(CF$_3$)$_2$}(PPh$_3$)$_2$] (L^{Me} = 1,3-dimethylimidazolidin-2-ylidene) revealed that the coordination plane of the carbene ligand L^{Me} is approximately orthogonal to the coordination plane about the metal [6], which is a general feature of carbenemetal complexes [M(L$_n$)L^R] [7].

The olefins (B) are not only electron-rich carbenoids, e.g., to provide complexes (A), but have an otherwise extensive chemistry. Features of interest include their (a) powerful reducing properties [8], (b) chemiluminescence in air [9], and (c) catalytic activity for benzoin-type C–C coupling [10]. Compounds (B) are accessible only if the group R is relatively sterically undemanding, i.e., R is a primary alkyl or an unhindered aryl group [11].

We now describe (i) the preparation and spectroscopy of numerous optically active carbenerhodium(I) complexes related to (A) having an optically active carbene ligand L*$^{R,R'}$, (ii) synthetic approaches to their organic precursors L*$^{R,R'}_2$ (related to (B); R and R' may be the same or different and represent the hydrocarbyl substituents on the 2 (and 2′) and 5 (and 5′) nitrogen atoms), and (iii) the X-ray structures of three Rh^I complexes related to (A), of type [Rh(L$_n$)(L*^{R})], and a tetrahedral d^8 Co analogue. Some aspects of (i)–(iii) have already been briefly discussed [12]. The detailed procedures for preparing the optically active olefins (L*$^{R,R'}$)$_2$ used in the present study, and their physical properties, will be described in full in a future publication.

Our longer term objectives are to examine optically active electron-rich olefins related to (B) and derived carbenemetal complexes analogous to (A) as enantioselective reagents or catalysts. (The lack of lability of the M–C$_{carb}$ bond, and its rigidity, were regarded as useful attributes in this endeavour.) One goal was that of diastereoisomeric transition metal complexes having a chiral metal centre. Tetrahedral complexes having four different monohapto ligands were unknown at the outset of the present work; hence our report herein on [Co(CO)(MeL*^{Me})(NO)(PPh$_3$)] (where MeL*^{Me} represents =$\overline{CN(Me)CH(Me)CH_2NMe}$-($S$)).

The search for enantioselective reagents and catalysts continues, but we now consider that bidentate chelate carbene ligands will be required and research to that end are in progress.

Results and discussion

1. Synthetic approaches to optically active electron-rich olefins

The optically active carbene-metal precursors are the electron-rich olefins I–III, Fig. 1. The latter were obtained from readily available chiral starting materials. The
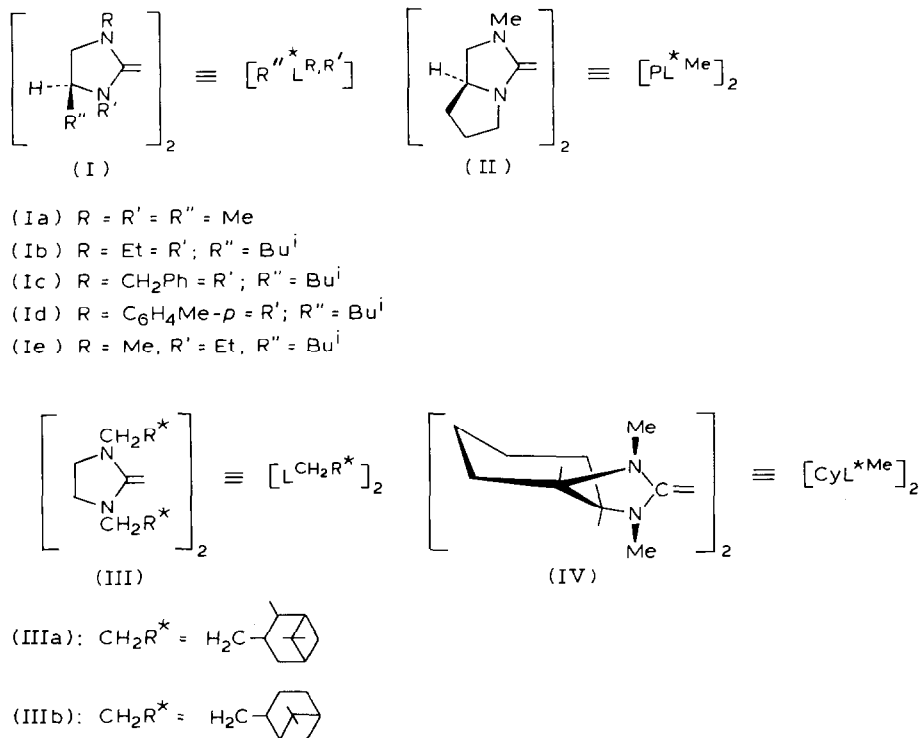
Fig. 1. Some optically active electron-rich olefins $L^{*R,R'}_2$ (or L^{*R}_2 if R = R'); R and R' denote the nature of the alkyl substituents at the nitrogen atoms; olefins I–IV are derived ultimately from (S)-R''CH(NH$_2$)COOH, (S)-proline, a chiral terpene amine R*CH$_2$NH$_2$, or (+)- or (−)-trans-1,2-diaminocyclohexane, respectively.

Olefins I and II were synthesised from naturally occurring (S)-α-amino-acids; e.g., olefins Ia, Ib, and II from (S)-alanine, (S)-leucine, or (S)-proline respectively. This is illustrated for the case of olefin II in Scheme 1.

Olefins III, bearing exocyclic chiral N-substituents, were obtained from available terpene derivatives; e.g., (+)-3-pinanecarboxylic acid or (−)-cis-myrtanylamine furnished olefins (IIIa) or (IIIb), respectively.

The point of departure for the electron-rich olefin IV was ultimately the commercially available mixture of cis- and dl-trans-1,2-diaminocyclohexanes. The chosen route required the following sequence: simultaneous separation of trans- from cis-isomer and resolution of the former, subsequent N,N'-dimethylation (via chloroformylation and reduction), and distillation with CH(OMe)$_2$NMe$_2$(cf., step iii in Scheme 1).

These (and other) methods of preparation, as well as the characterisation of the olefins I–IV, mentioned briefly above and in our preliminary communication [12], will be elaborated in a future publication.

2. Preparation of optically active carbenerhodium(I) complexes

Eighteen optically active carbenerhodium(I) complexes, V–XXII (Table 1), were prepared in good yields (70–90%) from a suitable Rh^I substrate and the appropriate optically active electron-rich olefin I–IV.
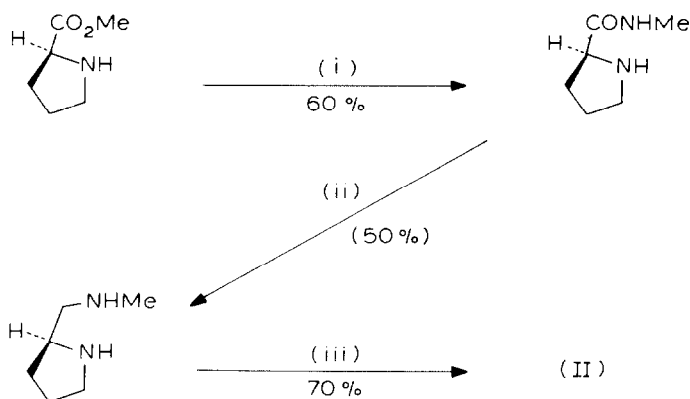
SCHEME 1. Synthetic sequence to the electron-rich olefin PL^{*Me}_2 (II) (see Fig. 1), from (S)-proline methyl ester. Reagents and conditions: (i), $MeNH_2$, EtOH, 20°C, 7 d; (ii), $Li[AlH_4]$, THF, reflux, 24 h; (iii), $CH(OMe)_2NMe_2$, 90°C, 1 h, distillation.

For example, di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) (with I–IV) was the source of complexes cis-[RhCl(COD)(L*)] (V–X), as illustrated in eq. 1. It is important in these reactions not to exceed the required 1/1 stoicheiometry, since an

$$\left[\{Rh(COD)(\mu\text{-Cl})\}_2\right] + Ib \xrightarrow[\substack{MeC_6H_{11},\\ 1\ h,\ reflux}]{} 2\ cis\text{-}\left[RhCl(COD)\{(S)\text{-}(Bu^iL^{*Et})\}\right] \qquad (1)$$
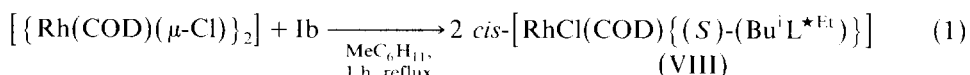$$(VIII)$$

excess of N-methyl- or N-ethyl-substituted electron-rich olefin L^R_2 (see **B**) has previously been shown to give products resulting from further ligand substitution, e.g., XXIII in eq. 2 [13,14].

$$\tfrac{1}{2}\left[\{Rh(COD)(\mu\text{-Cl})\}_2\right] + L^{Me}_2 \rightarrow cis\text{-}\left[Rh(COD)(L^{Me}_2)\right]^+Cl^- \qquad (2)$$
$$(XXIII)$$
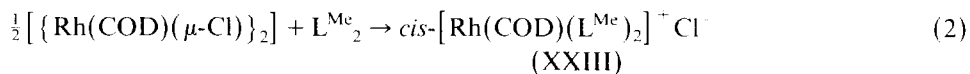
The reaction of tris(triphenylphosphine)chlororhodium(I) with the suitable optically active electron-rich olefins I–III gave the required carbenerhodium(I) complexes XI–XX (Table 1), e.g., eq. 3:

$$\left[RhCl(PPh_3)_3\right] + \tfrac{1}{2}(Ia) \xrightarrow[\substack{MeC_6H_{11}\\ 1\ h,\ reflux}]{} trans\text{-}\left[RhCl\{(S)\text{-}(MeL^{*Me})\}(PPh_3)_2\right] + PPh_3\,(3)$$
$$(XI)$$
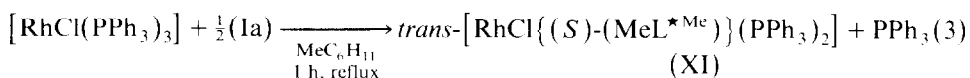
Although such reactions formally appear to be simple ligand substitutions, it is likely that they proceed via cleavage of the chloride-bridged dimer XXIV, as in eq. 4:

(XXIV)

$$trans\text{-}\left[RhCl(L^R)(PPh_3)_2\right] \qquad (4)$$

The reaction of bis(1,3-diethylimidazolidinylid-2-ene), (**B**, R = Et), with the chloride-bridged binuclear complex XXV has been reported to give the carbenerhodium(I) complex XXVI in good yield after 16 h at room temperature, eq. 5 [2]. Surprisingly,

TABLE 1

ANALYTICAL DATA FOR OPTICALLY ACTIVE CARBENERHODIUM(I) COMPLEXES [a]

Compound	Analytical data (Found (calcd.)(%))		
	C	H	N
cis-[RhCl(COD){(S)-(MeL*^{Me})}] (V)	46.7	6.8	7.9
	(46.9)	(6.7)	(7.8)
cis-[RhCl(COD){(S)-(Bu^{i}L*^{Me})}] (VI)	49.6	6.3	6.3
	(51.0)	(7.5)	(7.0)
cis-[RhCl(COD){(S)-(Bu^{i}L*^{Me,Et})}] (VII)	52.1	7.7	6.6
	(52.1)	(7.8)	(6.8)
cis-[RhCl(COD){(S)-(Bu^{i}L*^{Et})}] (VIII)	53.2	8.0	6.5
	(53.2)	(8.0)	(6.5)
cis-[RhCl(COD){(S)-(PL*^{Me})}] (IX)	48.7	6.5	7.6
	(48.6)	(6.5)	(7.6)
cis-[RhCl(COD)(CyL*^{Me})] [b] (X)	51.5	7.1	7.0
	(51.2)	(7.1)	(7.0)
trans-[RhCl{(S)-(MeL*^{Me})}(PPh$_3$)$_2$] (XI)	65.1	5.6	3.8
	(65.1)	(5.5)	(3.7)
trans-[RhCl{(S)-(Bu^{i}L*^{Me})}(PPh$_3$)$_2$] (XII)	64.8	5.8	3.4
	(66.1)	(5.9)	(3.4)
trans-[RhCl{(S)-(Bu^{i}L*^{Me,Et})}(PPh$_3$)$_2$] (XIII)	66.7	6.3	3.6
	(66.5)	(6.1)	(3.4)
trans-[RhCl{(S)-(Bu^{i}L*^{Et})}(PPh$_3$)$_2$] (XIV)	67.0	6.2	3.3
	(66.8)	(6.2)	(3.3)
trans-[RhCl{(S)-(Bu^{i}L*^{CH_2Ph})}(PPh$_3$)$_2$] (XV)	70.6	5.8	2.9
	(71.1)	(6.0)	(2.9)
trans-[RhCl{(S)-(Bu^{i}L *$^{C_6H_4Me-p,Me}$)}(PPh$_3$)$_2$] (XVI)	67.6	6.3	3.1
	(68.6)	(5.9)	(3.1)
trans-[RhCl{(S)-(PL*^{Me})}(PPh$_3$)$_2$] (XVII)	62.9	5.2	3.8
	(65.6)	(5.4)	(3.6)
trans-[RhCl(L^{CH_2pin*})(PPh$_3$)$_2$] [c] (XVIII)	70.3	7.2	2.7
	(70.9)	(7.0)	(2.7)
trans-[RhCl(L^{CH_2pin*})(PPh$_3$)$_2$] [d] (XIX)	69.1	6.8	2.8
	(70.9)	(7.0)	(2.7)
trans-[RhCl(L^{myr*})(PPh$_3$)$_2$] [e] (XX)	70.0	6.8	2.9
	(70.5)	(6.8)	(2.8)
[Rh(CO)Cl{(S)-(Bu^{i}L*^{Et})(PPh$_3$)] [f] (XXI)	59.2	6.3	4.6
	(59.0)	(6.1)	(4.6)
trans-[Rh(CO)Cl{(S)-(Bu^{i}L*^{Et})$_2$ (XXII)	51.6	8.4	10.4
	(52.0)	(8.4)	(10.6)

[a] The carbenemetal complexes were generally prepared in good yields (70–90%). [b] Carbene ligand derived from (−)-trans-N,N'-dimeth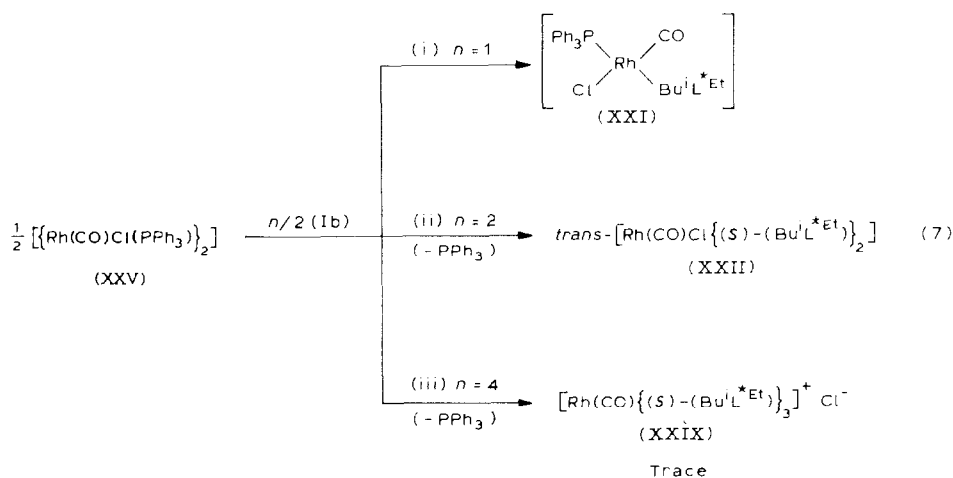yl-1,2-diaminocyclohexane. [c] Carbene ligand with N-substituents derived from (+)-3-pinanecarboxylic acid. [d] Carbene ligand with N-substituents derived from (−)-3-pinanecarboxylic acid. [e] Carbene ligand with N-substituents derived from (−)-cis-myrtanylamine. [f] For stereochemistry, see eq. 7.

$$\tfrac{1}{2}\left[\{Rh(CO)Cl(PPh_3)\}_2\right] + \tfrac{1}{2}(L^{Et})_2 \rightarrow \left[Rh(CO)Cl(L^{Et})(PPh_3)\right] \quad (5)$$
$$(XXV) \qquad\qquad (XXVI)$$

a similar experiment with the optically active olefin analogue Ib showed no observable reaction after 24 h. However, using a higher temperature (refluxing xylene), the required carbene complex XXI (Table 1) was obtained after only 1 h (eq. 7). Again it is essential to employ the correct 1/1 stoicheiometry, since excess of electron-rich

olefin leads to oligocarbene complexes such as XXVII and XXVIII (eq. 6) [2,15].

$$
\left[\text{Rh (Co) Cl}(\text{L}^{\text{Et}})(\text{PPh}_3) \right] \quad \longrightarrow
$$

(XXVI)

$$
\xrightarrow{\frac{1}{2}\text{L}^{\text{Et}}_2} \xrightarrow[(-\text{PPh}_3)]{} \quad trans-\left[\text{Rh (CO) Cl}(\text{L}^{\text{Et}})_2\right]
$$

(XXVII)

$$
\xrightarrow{\text{L}^{\text{Et}}_2} \xrightarrow[(-\text{PPh}_3)]{} \quad trans-\left[\text{RhCO}(\text{L}^{\text{Et}})_3\right]^+ \text{Cl}^-
$$

(6)

(XXVIII)

The optically active bis(carbene)rhodium(I) complex XXII was readily prepared from the Rh$^\text{I}$ precursor XXV and olefin Ib by heating for 2 h under reflux in xylene (eq. 7). However, attempts to prepare the cationic tris(carbene)rhodium(I) complex (XXIX) under similar conditions, using an excess of optically active electron-rich olefin Ib, proved unsuccessful (eq. 7). The isolated product, the bis(carbene)metal complex XXII, was separated from a minor impurity by fractional crystallisation. The latter is probably the cationic rhodium(I) complex XXIX, based on its spectral characteristics and comparison with those of [RhCO(L$^\text{Et}$)$_3$]$^+$ Cl$^-$ [2,14].

$$
\frac{1}{2}\left[\{\text{Rh(CO)Cl(PPh}_3)\}_2\right] \xrightarrow{n/2\,(\text{Ib})}
$$

(XXV)

(i) $n=1$

$$
\left[\begin{array}{c} \text{Ph}_3\text{P} \quad\quad \text{CO} \\ \quad\quad \text{Rh} \\ \text{Cl} \quad\quad \text{Bu}^i\text{L}^{*\text{Et}} \end{array}\right]
$$

(XXI)

(ii) $n=2$ $(-\text{PPh}_3)$ → $trans$-$[\text{Rh(CO)Cl}\{(S)-(\text{Bu}^i\text{L}^{*\text{Et}})\}_2]$ (7)

(XXII)

(iii) $n=4$ $(-\text{PPh}_3)$ → $[\text{Rh(CO)}\{(S)-(\text{Bu}^i\text{L}^{*\text{Et}})\}_3]^+ \text{Cl}^-$

(XXIX)

Trace

The preparation of complexes XXI, XXII, and XXIX, from the mononuclear species $trans$-[Rh(CO)Cl(PPh$_3$)$_2$], by direct ligand displacement, has met with very little success. In contrast, the analogous mono-, bis-, or tris-(carbene)rhodium(I) analogues XXVI–XXVIII, derived from L$^\text{Et}_2$, have been prepared by ligand substitution reactions with comparative ease [1,15]. It seems unlikely that the isobutyl group has any appreciable effect upon the nucleophilicity of the olefinic carbon–carbon double bond, since this is largely determined by the nature of the N-substituents. It is more probable that attack at the metal centre by the optically active electron-rich olefin Ib is in some way sterically impeded by the isobutyl group.

3. Physical and spectroscopic data for optically active carbene rhodium(I) complexes

The optically active carbenerhodium(I) complexes V–XXII are yellow crystalline solids, which are stable in air for long periods; analytical data are given in Table 1. Melting points, specific rotations, and selected IR spectroscopic data [$\nu(\text{CN}_2)$ and $\nu(\text{CO})$] are listed in Table 2.

IR spectra were recorded as Nujol mulls; however, for the carbonyl-containing

TABLE 2

MELTING POINTS, SPECIFIC ROTATIONS, AND SELECTED IR DATA ON THE OPTICALLY ACTIVE CARBENERHODIUM(I) COMPLEXES V–XXII

Compound	M.p. (°C)	Specific rotation [a] (°)	IR $[\nu_{asym}(CN_2)]$ [b] (cm^{-1})
V	168	+14.9[35]	1505s
VI	160	+33.8[35]	1510s
VII	95–99	+29.0[27]	1507s
VIII	115–117	+23.4[31]	1495s
IX	192	−59.7[35]	1515s
X	195 decomp.	−16.0[20] (C_6H_6) −8.6[20] ($CHCl_3$)	1512s
XI	240 [c]	+6.3[35]	1500s
XII	215 [c]	+10.4 [35]	1502s
XIII	218–222	−11.8[31]	1500w,1476s
XIV	246–248 [c]	+14.7[29]	1478s
XV	247–248 [c,d]	−7.7[31]	1489sh,1476s
XVI	280 [c]	+37.6[35]	1505s
XVII	225 [c]	[e]	1500s
XVIII	258–260 [c]	−12.7[31]	1478s
XIX	256–258 [c]	−8.6[31]	1476s
XX	257–260 [c]	[e]	1477s
XXI	144–145	+30.5[31]	1500s [f]
XXII	171.5–172	+64.5[31]	1500s [g]

[a] Specific rotation, $100\alpha/lc$; where α = observed rotation, l = cell path length = 1.0, and c = concentration (g dl^{-1}). Measurements were performed at 589 nm in dichloromethane, except for X, at the temperature indicated by the superscript. [b] Spectra recorded as Nujol mulls, unless otherwise stated. Abbreviations: br, broad; s, strong; sh, shoulder; vs, very strong; w, weak. [c] Melts with decomposition. [d] Softens at ca. 145°C. [e] Not recorded. [f] $\nu(CO)$ 1954s, 1927s cm^{-1}; [1960vs cm^{-1} (recorded as a solution in dichloromethane)]. [g] $\nu(CO)$ 1920s,br cm^{-1}; [1935s,br cm^{-1} (recorded as a solution in dichloromethane)].

complexes XXI and XXII, $\nu(CO)$ was also measured in solution, Table 2 (an intense singlet at 1920–1960 cm^{-1}). Each of complexes V–XXII exhibited a characteristically strong absorption in the region 1470–1510 cm^{-1}, assigned to $\nu_{asym}(CN_2)$ from the carbene ligand, cf. ref. 1.

The optically active carbene-analogues of Wilkinson's [RhCl(PPh$_3$)$_3$] reagent, complexes XI–XX, showed broad aromatic ^1H NMR resonances characteristic of coordinated triphenylphosphine ligands. The protons of the carbene ligands were generally ill-defined, particularly for those bearing terpene derived N-substituents. However, for complexes [RhCl(COD){(S)-Bu^{i}L$^{\star R,R'}$}] (VII: R = Me, R' = Et) and VIII: R = Et = R'), some of the peaks are assigned, Table 3. For each complex there was a pair of doublets at δ 0.8–1.0 ppm, characteristic of the magnetically distinct methyl groups of the isobutyl substituent. The olefinic protons of the cyclooctadiene ligand were inequivalent, owing to the asymmetry of each complex, and appeared as two broad singlets at δ 4.9–5.0 and 3.1–3.3 ppm. The low field signal is assigned to the olefinic protons *trans* to the carbene ligand, since protons *trans* to strong electron donor ligands generally appear at lower magnetic field than protons *trans* to chloride [15,16]. The ring methylene protons of the cyclooctadiene ligand appeared as a very broad multiplet at δ ca. 1.7–2.6 ppm.

TABLE 3

SELECTED ^{1}H NMR CHEMICAL SHIFTS (δ, ppm) AND COUPLING CONSTANTS (J, Hz) FOR THE OPTICALLY ACTIVE CARBENERHODIUM(I) COMPLEXES VII AND VIII

Compound	NCH_3	NCH_2CH$_3$	NCH$_2$CH_3	CH(CH_3)$_2$	Other resonances
cis -[RhCl(COD){ C, N, N, Me, Et, iBu, H }] ^{b}	3.49s	^{c}	1.30t (J 7 Hz)	0.88–0.98	4.96s,br ^{d}, 3.18s,br ^{e} 1.7–2.5m, br ^{f}
cis -[RhCl(COD){ C, N, N, Et, Et, iBu, H }] ^{g}	–	4.13q (J 7 Hz)	1.28t (J 7 Hz) 1.30t (J 7 Hz)	0.88–0.97	4.96s,br ^{d}, 3.22s,br ^{e}, 1.8–2.6m,br ^{f}

^{a} Spectrum recorded in CDCl$_3$ solution with Si(CH_3)$_4$ as internal standard ($\delta = 0$); abbreviations: s, singlet; t, triplet; q, quartet; m, multiplet; br, broad. ^{b} Spectrum recorded at 35°C. ^{c} Signal obscured by other resonances. ^{d} Olefinic protons of the cyclooctadiene ligand *trans* to the carbene ligand. ^{e} Olefinic protons of the cyclooctadiene ligand *trans* to chloride. ^{f} Ring methylene protons of the cyclooctadiene ligand. ^{g} Spectrum recorded at 55°C.

Chemical shifts and coupling constant data obtained from the ^{31}P NMR spectra of some of the optically active carbene(triphenylphosphine)rhodium(I) complexes are listed in Table 4. Each ^{31}P signal was observed as a sharp doublet, owing to coupling with the ^{103}Rh nucleus.

Carbon-13 NMR spectroscopic data for complexes cis-[RhCl(COD){(S)-(Bu^{i}L$^{\star R,R'}$)}] (VII: R = Me, R' = Et and VIII: R = Et = R') are shown in Table 5, together with assignments. The latter are based on analysis of similar data compiled on related but simpler complexes cis-[RhCl(COD)L^R] (R = Me, Et, CH$_2$Ph, Ph, or p-C$_6$H$_4$Me), which are provided in Table 6; (the syntheses of these compounds, except for R = CH$_2$Ph [17], and characterisation by other spectroscopic measurements, are described elsewhere [1]). The two pairs of olefinic carbon atoms of the COD ligand in such a Rh^I complex are magnetically inequivalent (one *trans* and the other *cis* to L^R) and each is split into a doublet in the ^{13}C NMR spectrum due to coupling with the ^{103}Rh nucleus. As yet it has not been possible to assign unambigu-

TABLE 4

^{31}P NMR CHEMICAL SHIFTS AND ^{31}P–^{103}Rh COUPLING CONSTANTS FOR SOME OPTICALLY ACTIVE CARBENE(TRIPHENYLPHOSPHINE)RHODIUM(I) COMPLEXES

Compound	$\delta(^{31}$P) ^{a}	$^1J(^{31}$P–^{103}Rh) ^{b}
XI	109.8d ^{c}	159
XII	110.1d ^{c}	159
XIII	110.0d ^{d}	161
XIV	109.3d ^{d}	159
XVII	109.3d ^{c}	159
XVIII	110.1d ^{d}	159
XX	109.8d ^{d}	159
XXI ^{e}	109.6d ^{d}	112

^{a} Chemical shifts in ppm relative to trimethyl phosphite. ^{b} Coupling constants measured in Hz. ^{c} Spectrum recorded in CH$_2$Cl$_2$. ^{d} Spectrum recorded in CDCl$_3$. ^{e} CO and Cl ligands are mutually *trans*.

TABLE 5

^{13}C NMR CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (J) FOR THE COMPLEXES cis-[RhCl(COD){(S)-Bu^{i}L*$^{R,R'}$}] (VII) (R = Me, R' = Et) AND (VIII) (R = Et = R')

Compound	$\delta(C_{carb})$ [a]	$^1J(^{103}Rh-^{13}C_{carb})$ (Hz)	$\delta[CH_2CH(CH_3)_2]$ [a]	$\delta[CH(CH_3)_2]$ [a]	$\delta[CH(CH_3)_2]$
VII	211.9d	47	41.3s	25.1s	23.8s, 21.5s
VIII	211.3d	46	41.3s	25.1s	23.8s, 21.5s

	$\delta(CH=CH)$ [a,b]	$^1J(^{103}Rh-^{13}C_{COD})$ (Hz)	$\delta(CH_2)$ [a,c]	Other resonances [a] (δ)
VII	98.7d	8	32.8s	13.4s [d]
	98.4d	8	28.7s	37.4s [e]
	68.4d	15		41.7s [f]
	68.0d	14		
VIII	98.5d	6	32.8s	13.3s [d]
	68.5d	15	28.8s	13.6s [d]
	67.9d	14		41.9s [f]
				45.0s [f]
				53.0s [g]
				56.5s [h]

[a] Spectra recorded in CDCl$_3$ solution; chemical shifts in ppm relative to Si(CH_3)$_4$. [b] Olefinic carbons of cyclooctadiene ligand. [c] Ring methylene carbons of cyclooctadiene ligand. [d] NCH$_2$CH$_3$. [e] NCH$_3$. [f] NCH$_2$CH$_2$. [g] NCH$_2$CHN. [h] NCH$_2$CHN.

ously which of the two olefinic signals is *trans* to the carbene ligand L^R. For the optically active carbenerhodium(I) complex VII, each olefinic signal appeared as a pair of doublets, and the same feature was observed for complexes VIII and X. This is attributed to the presence of two rotamers (C) and (D) which are not interconverting on the NMR time scale, due to restricted rotation about the Rh–C$_{carb}$ bond. The olefinic resonance at high field was found as a pair of doublets; however, that at low field sometimes showed only a doublet due to poor resolution. From the intensity of the latter signal it is likely that the corresponding carbon atoms are almost magnetically equivalent. (It was previously shown that in [Rh(CO)Cl(L^{CH_2R})(PPh$_3$)]

(C)   (D)
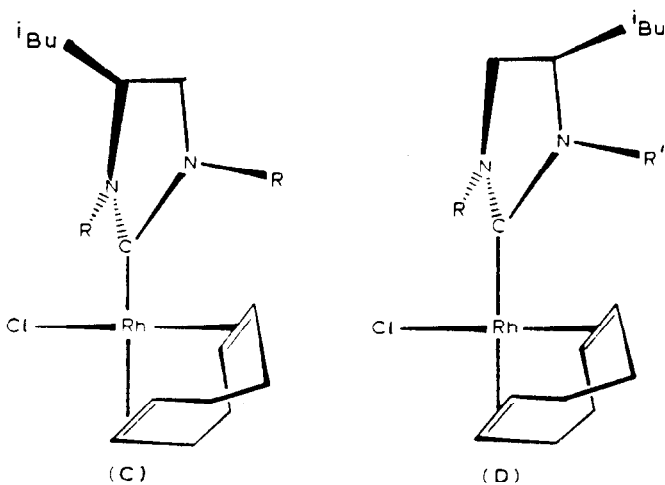
TABLE 6

^{13}C NMR CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (J) FOR SOME CARBENE-RHODIUM(I) COMPLEXES OF THE TYPE cis-[RhCl(COD)L^R]

R in cis-Rh^1 complex	δ(C$_{carb}$) ^{a}	$^1J(^{103}$Rh–^{13}C$_{carb}$)	δ(NCH$_2$CH$_2$N) ^{a}	δ(CH=CH) ^{a,b}	$^1J(^{103}$Rh–^{13}C$_{COD}$) (Hz)	δ(CH$_2$) ^{a,c}	Other resonances ^{a}
Me	212.3d	47	51.4s	98.6d	8	32.8s	37.1s ^{d}
				68.0d	14	28.7s	
Et	212.3d	46	47.6s	98.7d	6	33.0s	45.1s ^{e}
				68.3d	15	28.8s	13.8s ^{f}
CH$_2$Ph	213.0d	47	47.9s	99.3d	8	32.8s	136.3 ^{g}
				68.5d	14	28.6s	128.7 ^{g}
							128.2 ^{g}
							127.7 ^{g}
							54.8s ^{h}
Ph	212.7d	46	50.3s	97.6d	8	32.1s	141.7 ^{g}
				69.0d	15	28.4s	128.5 ^{g}
							125.9 ^{g}
							122.9 ^{g}
C$_6$H$_{11}$	219.4d	47	68.8s	99.1d / 99.0d	6.3	32.9s / 32.8s	35.5 ^{d} / 34.7 ^{d}
			67.8s	68.7d / 66.8d	14.7	28.7s / 28.6s	27.9,27.8 / 23.9
p-C$_6$H$_4$Me	212.9d	46	50.7s	97.7d	8	32.3s	140.0 ^{g}
				69.1d	14	28.5s	135.9 ^{g}
							129.5 ^{g}
							123.4 ^{g}
							21.0 ^{i}

^{a} Spectra recorded in CDCl$_3$; chemical shifts, δ, in ppm relative to Si(CH$_3$)$_4$. ^{b} Olefinic carbons of the cyclooctadiene ligand. ^{c} Ring methylene carbons of cyclooctadiene ligand. ^{d} NCH$_3$. ^{e} NCH$_2$CH$_3$. ^{f} NCH$_2$CH$_3$. ^{g} Aromatics. ^{h} NCH$_2$Ph. ^{i} p-C$_6$H$_4$CH$_3$.

(R = Me [2] or Ph [17]), the CH$_2$ protons appear as an AB doublet in the ^{1}H NMR spectrum at ambient temperature.)

Features of the ^{13}C NMR spectra of the complexes trans-[RhCl{(S)-Bu^{i}L$^{\star R,R'}$}(PPh$_3$)$_2$] (XIII: R = Me, R' = Et or XIV: R = Et = R') are shown in Table 7; there was no observable signals due to ^{13}C$_{carb}$. The latter resonance is, however, characteristically weak, because of the absence of a proton-induced nuclear Overhauser effect [18]. Furthermore, in complexes XIII or XIV, the ^{13}C$_{carb}$ nucleus is coupled to both ^{103}Rh and to two equivalent ^{31}P nuclei. It is not surprising, therefore, that this signal was lost in the baseline noise of the spectrum.

4. X-Ray structures of cis-[RhCl(COD)(L*)], (IX: L* = PL$^{\star Me}$ and X: L* = CyL$^{\star Me}$)

The molecular structures of complexes IX and X and atom numbering schemes are illustrated in Figs. 2 and 3, respectively. Bond lengths and angles are in Tables 8 and 9.

These two molecules show very similar structures, with the Cl$^-$ and carbene ligand L* cis to one another, and the carbene ligand plane approximately perpendicular to the square coordination plane of the Rh atom. The Rh–C$_{carb}$ bonds are almost identical, 2.004(4) and 2.003(5) Å for complexes IX and X, respectively. These values are similar to the M–C$_{carb}$ bond length of 2.009(13) Å in cis-

TABLE 7

^{13}C NMR CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (J) FOR THE COMPLEXES trans-[RhCl{(S)-Bu^{i}L$^{\star R,R'}$}(PPh$_3$)$_2$] (XIV: R = Et = R' AND XIII: R = Me, R' = Et)

Compound	CH$_2$CH(CH$_3$)$_2$	CH$_2$CH(CH$_3$)$_2$	CH(CH$_3$)$_2$
XIII	41.3s	25.1s	21.2s
			24.0s
XIV	41.8s	25.3s	21.2s
			24.0s
	NCHCH$_2$N	NCHCH$_2$N	Other resonances
XIII	58.2s	55.6s	13.8s ^{b}
			37.3s ^{d}
			43.0s ^{c}
XIV	58.3s	52.6s	12.2s ^{b}
			13.3s ^{b}
			43.2s ^{c}
			45.1s ^{c}

^{a} Spectra recorded in CDCl$_3$ solution; chemical shifts in ppm relative to Si(CH$_3$)$_4$. ^{b} NCH$_2$CH$_3$. ^{c} NCH$_2$CH$_3$. ^{d} NCH$_3$.

[PtCl$_2$(L^{Ph})(PEt$_3$)] [19] and 2.006(15) Å in trans-[Rh(L^{Me}){N=C(CF$_3$)$_2$}(PPh$_3$)$_2$] [6]. The Rh–Cl bonds are slightly different, 2.368(2) Å in IX and 2.384(2) Å in X. In both molecules the structure determination clearly indicates the retention of absolute configuration at the chiral centres of the carbene ligands.
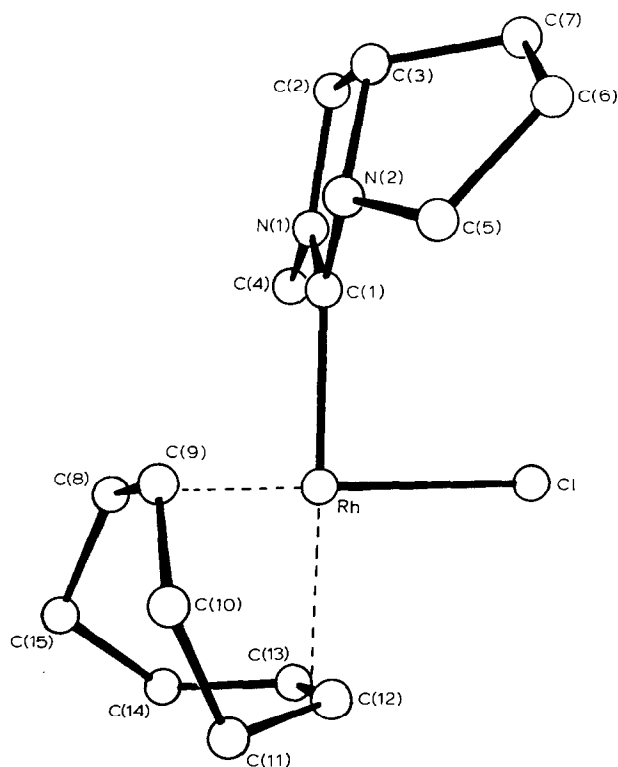
Fig. 2. The molecular structure and atom numbering scheme for cis-[RhCl(COD)(PL$^{\star Me}$)] (IX).
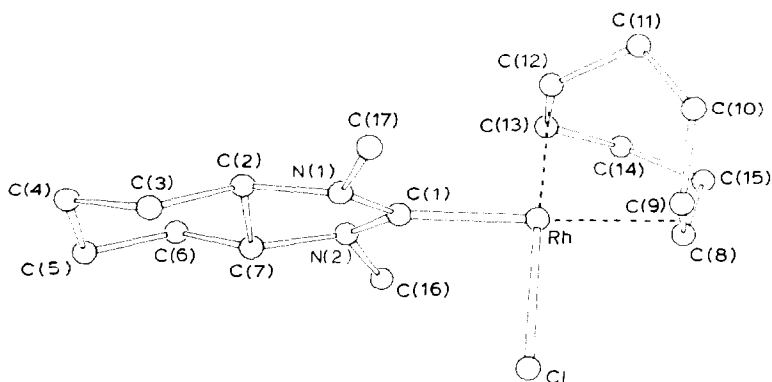
Fig. 3. The molecular structure and atom numbering scheme for cis-[RhCl(COD)(CyL*^{Me})] (X).

In complex IX, the carbene ligand could, in principle, adopt alternative orientations (C) and (D), with the carbene ligand rotated through 180° about Rh–C(1). Presumably the observed conformer (C) is preferred for steric reasons. In complex X, the carbene ligand has C_2 symmetry, and the two corresponding orientations of the carbene ligand are indistinguishable.

The Rh–C$_{COD}$ bonds have a similar pattern in both molecules, with two longer bonds trans to L* (2.227(6) and 2.206(5) Å in IX and 2.222(6) and 2.206(6) Å in X) and two shorter bonds trans to Cl$^-$ (2.118(7) and 2.101(8) Å in IX and 2.114(6) and 2.107(6) Å in X). The cyclooctadiene ligand itself has the usual slightly skewed conformation [20].

5. X-Ray structure of trans-[RhCl{ (S)-Bu^{i}L*^{Me} }(PPh$_3$)$_2$] (XII)

The molecular structure and atom numbering scheme for complex XII are shown in Fig. 4; Table 10 lists data on bond lengths and angles. Although the structure determination does not establish the absolute configuration of the molecule, it does show that both independent molecules in the same crystal have the same absolute configuration at C(3). Because of the low accuracy of the determination, caused by the small crystal size and resultant weak data, the molecular dimensions have high e.s.d.'s. However, the two molecules have a very similar conformation for the ligands, with the carbene plane perpendicular to the coordination plane of the Rh. The only difference between the independent molecules arises from a rotation of the isobutyl group about the C(6)–C(7) bond.

6. X-Ray structure of [Co(CO)(MeL*^{Me})(NO)(PPh$_3$)] (XXX)

The molecular structure and atom numbering scheme for complex XXX are in Fig. 5, and selected bond lengths and angles are in Table 11.

The structure determination shows that the carbene ligand has retained the chirality at C(21). However, whilst it had been hoped that the chiral carbene group would enforce a preferred configuration at the formally chiral Co atom, it was in practice impossible to distinguish the CO and NO groups which are disordered between the two sites. Since the overall steric requirements of linearly coordinated CO and NO are essentially identical there can be little thermodynamic preference for either absolute configuration at the Co atom. The presence in the crystal of both

TABLE 8

INTRAMOLECULAR DISTANCES AND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, AND SELECTED TORSION ANGLES, FOR cis-[RhCl(COD){(S)-PL*^{Me}}] (IX)

(a) Bonds (Å)

C(2)–C(3)	1.505(12)	Rh–Cl	2.368(2)
C(3)–C(7)	1.527(11)	Rh–C(1)	2.004(4)
C(5)–C(6)	1.559(13)	Rh–C(8)	2.118(7)
C(6)–C(7)	1.491(18)	Rh–C(9)	2.101(8)
C(8)–C(9)	1.389(11)	Rh–C(12)	2.227(6)
C(8)–C(15)	1.513(10)	Rh–C(13)	2.206(5)
C(9)–C(10)	1.518(11)	N(1)–C(1)	1.338(8)
C(10)–C(11)	1.537(10)	N(1)–C(2)	1.475(7)
C(11)–C(12)	1.532(12)	N(1)–C(4)	1.454(11)
C(12)–C(13)	1.363(11)	N(2)–C(1)	1.344(8)
C(13)–C(14)	1.499(12)	N(2)–C(3)	1.488(8)
C(14)–C(15)	1.520(12)	N(2)–C(5)	1.454(11)

(b) Angles (°)

C(1)–Rh–Cl	87.5(3)	C(3)–C(2)–N(1)	102.7(5)
C(8)–Rh–Cl	164.0(2)	C(2)–C(3)–N(2)	103.2(5)
C(8)–Rh–C(1)	93.7(4)	C(7)–C(3)–N(2)	102.9(5)
C(9)–Rh–Cl	157.5(2)	C(7)–C(3)–C(2)	118.2(8)
C(9)–Rh–C(1)	91.1(3)	C(6)–C(5)–N(2)	104.5(7)
C(9)–Rh–C(8)	38.5(3)	C(7)–C(6)–C(5)	106.4(8)
C(12)–Rh–Cl	93.4(2)	C(6)–C(7)–C(3)	104.2(7)
C(12)–Rh–C(1)	164.1(3)	C(9)–C(8)–Rh	70.1(4)
C(12)–Rh–C(8)	89.8(2)	C(15)–C(8)–Rh	112.7(5)
C(12)–Rh–C(9)	82.0(3)	C(15)–C(8)–C(9)	124.5(7)
C(13)–Rh–Cl	91.4(2)	C(8)–C(9)–Rh	71.4(4)
C(13)–Rh–C(1)	160.1(3)	C(10)–C(9)–Rh	110.7(5)
C(13)–Rh–C(8)	82.1(3)	C(10)–C(9)–C(8)	126.0(6)
C(13)–Rh–C(9)	97.3(3)	C(11)–C(10)–C(9)	113.1(7)
C(13)–Rh–C(12)	35.8(3)	C(12)–C(11)–C(10)	112.5(6)
C(2)–N(1)–C(1)	112.9(6)	C(11)–C(12)–Rh	110.2(4)
C(4)–N(1)–C(1)	124.9(5)	C(13)–C(12)–Rh	71.2(3)
C(4)–N(1)–C(2)	122.0(6)	C(13)–C(12)–C(11)	122.9(7)
C(3)–N(2)–C(1)	111.2(5)	C(12)–C(13)–Rh	72.9(3)
C(5)–N(2)–C(1)	122.9(6)	C(14)–C(13)–Rh	106.6(4)
C(5)–N(2)–C(3)	110.2(5)	C(14)–C(13)–C(12)	127.0(8)
N(1)–C(1)–Rh	124.8(4)	C(15)–C(14)–C(13)	114.0(7)
N(2)–C(1)–Rh	126.7(5)	C(14)–C(15)–C(8)	113.5(7)
N(2)–C(1)–N(1)	108.5(4)		

(c) Torsion angles (°)

C(2)–N(1)–C(1)–N(2)	6.2(8)	N(1)–C(2)–C(3)–C(7)	104.3(7)
C(4)–N(1)–C(1)–N(2)	−179.7(6)	N(2)–C(3)–C(7)–C(6)	−34.4(8)
C(1)–N(1)–C(2)–C(3)	2.0(8)	C(2)–C(3)–C(7)–C(6)	−147.2(8)
C(4)–N(1)–C(2)–C(3)	−172.4(6)	N(2)–C(5)–C(6)–C(7)	−10.3(10)
C(3)–N(2)–C(1)–N(1)	−12.1(8)	C(5)–C(6)–C(7)–C(3)	27.8(9)
C(5)–N(2)–C(1)–N(1)	−145.9(6)	C(15)–C(8)–C(9)–C(10)	1.8(12)
C(1)–N(2)–C(3)–C(2)	12.9(7)	C(9)–C(8)–C(15)–C(14)	−91.0(9)
C(1)–N(2)–C(3)–C(7)	−110.5(6)	C(8)–C(9)–C(10)–C(11)	44.0(11)
C(5)–N(2)–C(3)–C(2)	152.7(6)	C(9)–C(10)–C(11)–C(12)	34.0(9)
C(5)–N(2)–C(3)–C(7)	29.2(7)	C(10)–C(11)–C(12)–C(13)	−94.4(9)
C(1)–N(2)–C(5)–C(6)	122.1(8)	C(11)–C(12)–C(13)–C(14)	4.1(12)
C(3)–N(2)–C(5)–C(6)	−12.1(8)	C(12)–C(13)–C(14)–C(15)	44.4(11)
N(1)–C(2)–C(3)–N(2)	−8.4(7)	C(13)–C(14)–C(15)–C(8)	32.3(10)

TABLE 9

INTRAMOLECULAR DISTANCES AND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, AND SELECTED TORSION ANGLES, FOR cis-[RhCl(COD)[CyL*^{Me})] (X)

(a) Bonds (Å)

Rh–Cl	2.384(2)	C(2)–C(7)	1.514(8)
Rh–C(1)	2.003(5)	C(3)–C(4)	1.519(10)
Rh–C(8)	2.222(6)	C(4)–C(5)	1.529(11)
Rh–C(9)	2.206(6)	C(5)–C(6)	1.534(10)
Rh–C(12)	2.114(6)	C(6)–C(7)	1.485(9)
Rh–C(13)	2.107(6)	C(8)–C(9)	1.386(9)
N(1)–C(1)	1.342(7)	C(8)–C(15)	1.532(9)
N(1)–C(2)	1.472(8)	C(9)–C(10)	1.503(10)
N(1)–C(17)	1.425(9)	C(10)–C(11)	1.507(11)
N(2)–C(1)	1.372(8)	C(11)–C(12)	1.518(10)
N(2)–C(7)	1.472(7)	C(12)–C(13)	1.416(9)
N(2)–C(16)	1.443(8)	C(13)–C(14)	1.525(10)
C(2)–C(3)	1.538(9)	C(14)–C(15)	1.512(10)

(b) Angles (°)

C(1)–Rh–Cl	88.5(2)	C(7)–C(2)–N(1)	99.7(4)
C(8)–Rh–Cl	91.8(2)	C(7)–C(2)–C(3)	109.6(5)
C(8)–Rh–C(1)	166.2(2)	C(4)–C(3)–C(2)	105.5(6)
C(9)–Rh–Cl	91.1(2)	C(5)–C(4)–C(3)	114.1(6)
C(9)–Rh–C(1)	157.3(2)	C(6)–C(5)–C(4)	112.1(6)
C(9)–Rh–C(8)	36.5(2)	C(7)–C(6)–C(5)	106.2(6)
C(12)–Rh–Cl	165.7(2)	C(2)–C(7)–N(2)	100.0(4)
C(12)–Rh–C(1)	93.6(2)	C(6)–C(7)–N(2)	120.8(5)
C(12)–Rh–C(8)	89.5(2)	C(6)–C(7)–C(2)	110.2(5)
C(12)–Rh–C(9)	81.5(2)	C(9)–C(8)–Rh	71.1(3)
C(13)–Rh–Cl	154.9(2)	C(15)–C(8)–Rh	110.7(4)
C(13)–Rh–C(1)	92.4(2)	C(15)–C(8)–C(9)	124.4(5)
C(13)–Rh–C(8)	81.5(2)	C(8)–C(9)–Rh	72.4(4)
C(13)–Rh–C(9)	97.4(2)	C(10)–C(9)–Rh	107.5(4)
C(13)–Rh–C(12)	39.2(2)	C(10)–C(9)–C(8)	126.3(6)
C(2)–N(1)–C(1)	110.5(5)	C(11)–C(10)–C(9)	114.5(6)
C(17)–N(1)–C(1)	124.6(5)	C(12)–C(11)–C(10)	113.3(6)
C(17)–N(1)–C(2)	120.9(5)	C(11)–C(12)–Rh	113.5(4)
C(7)–N(2)–C(1)	108.5(5)	C(13)–C(12)–Rh	70.1(3)
C(16)–N(2)–C(1)	121.9(5)	C(13)–C(12)–C(11)	125.3(5)
C(16)–N(2)–C(7)	120.2(5)	C(12)–C(13)–Rh	70.7(3)
N(1)–C(1)–Rh	124.4(4)	C(14)–C(13)–Rh	110.5(4)
N(2)–C(1)–Rh	127.8(4)	C(14)–C(13)–C(12)	125.7(5)
N(2)–C(1)–N(1)	107.8(5)	C(15)–C(14)–C(13)	113.9(6)
C(3)–C(2)–N(1)	121.1(5)	C(14)–C(15)–C(8)	112.7(5)

(c) Torsion angles (°)

C(2)–N(1)–C(1)–N(2)	−9.2(6)	C(3)–C(2)–C(7)–N(2)	−162.7(5)
C(17)–N(1)–C(1)–N(2)	166.4(6)	C(3)–C(2)–C(7)–C(6)	69.0(6)
C(1)–N(1)–C(2)–C(3)	148.6(5)	C(2)–C(3)–C(4)–C(5)	54.0(7)
C(1)–N(1)–C(2)–C(7)	28.6(6)	C(3)–C(4)–C(5)–C(6)	−54.0(8)
C(17)–N(1)–C(2)–C(3)	−53.1(8)	C(4)–C(5)–C(6)–C(7)	55.3(7)
C(17)–N(1)–C(2)–C(7)	173.1(6)	C(5)–C(6)–C(7)–N(2)	−178.9(5)
C(7)–N(2)–C(1)–N(1)	−15.6(6)	C(5)–C(6)–C(7)–C(2)	−63.2(7)
C(16)–N(2)–C(1)–N(1)	162.0(5)	C(15)–C(8)–C(9)–C(10)	3.5(10)
C(1)–N(2)–C(7)–C(2)	32.3(5)	C(9)–C(8)–C(15)–C(14)	−92.9(7)
C(1)–N(2)–C(7)–C(6)	153.2(5)	C(8)–C(9)–C(10)–C(11)	46.3(10)
C(16)–N(2)–C(7)–C(2)	179.5(5)	C(9)–C(10)–C(11)–C(12)	29.5(9)
C(16)–N(2)–C(7)–C(6)	−59.7(8)	C(10)–C(11)–C(12)–C(13)	−90.2(8)

TABLE 9 (continued)

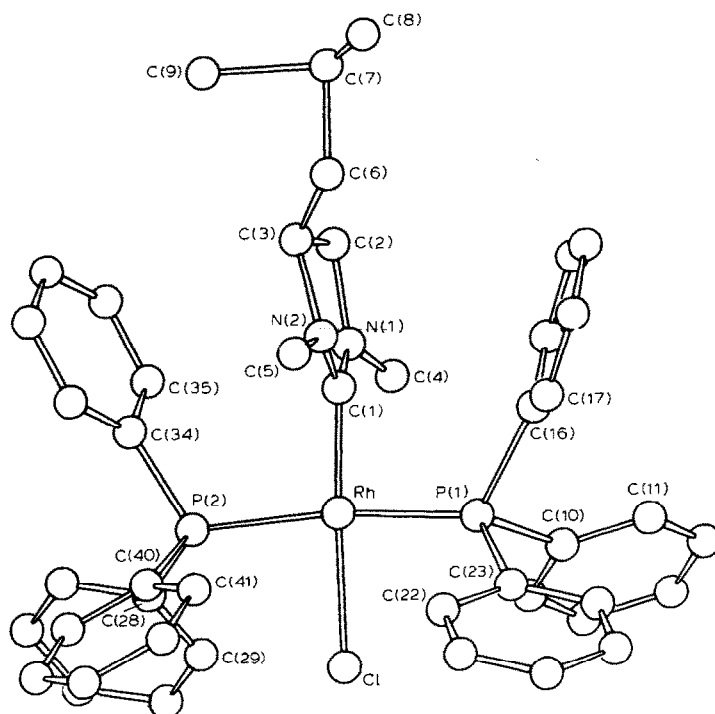| (c) Torsion angles (°)			
N(1)–C(2)–C(3)–C(4)	−175.3(5)	C(11)–C(12)–C(13)–C(14)	3.4(10)
C(7)–C(2)–C(3)–C(4)	−60.2(6)	C(12)–C(13)–C(14)–C(15)	43.9(9)
N(1)–C(2)–C(7)–N(2)	−34.6(5)	C(13)–C(14)–C(15)–C(8)	31.9(8)
N(1)–C(2)–C(7)–C(6)	−162.9(5)		

Fig. 4. The molecular structure and atom numbering scheme for one of the two independent molecules of trans-[RhCl{(S)-Bu^{i}L$^{\star Me}$}(PPh$_3$)$_2$] (XII). The other molecule differs only in the rotation of the terminal part of the isobutyl group about the C(6)–C(7) bond.

TABLE 10

SELECTED BOND LENGTHS AND ANGLES FOR trans-[RhCl{(S)-Bu^{i}L$^{\star Me}$}(PPh$_3$)$_2$] (XII)

(a) Bonds (Å)			
Rh–Cl	2.38(1)	Rh(A)–Cl(A)	2.43(1)
Rh–P(1)	2.20(1)	Rh(A)–P(1A)	2.37(2)
Rh–P(2)	2.29(2)	Rh(A)–P(2A)	2.27(1)
Rh–C(1)	1.92(3)	Rh(A)–C(1A)	1.95(3)
(b) Angles (°)			
Cl–Rh–P(1)	86.0(5)	Cl(A)–Rh(A)–P(1A)	89.4(5)
Cl–Rh–P(2)	86.3(4)	Cl(A)–Rh(A)–P(2A)	88.5(5)
C(1)–Rh–P(1)	90.7(11)	C(1A)–Rh(A)–P(1A)	95.1(12)
C(1)–Rh–P(2)	96.9(11)	C(1A)–Rh(A)–P(2A)	87.5(12)
C(1)–Rh–Cl	175.8(12)	C(1A)–Rh(A)–Cl(A)	172.7(13)
P(1)–Rh–P(2)	171.7(4)	P(1A)–Rh(A)–P(2A)	174.1(5)
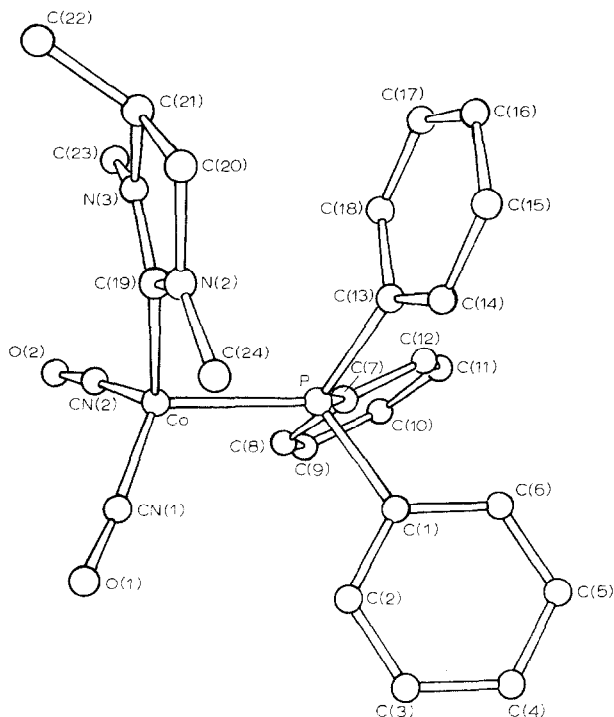
Fig. 5. The molecular structure and atom numbering scheme for [Co(CO){(S)-MeL*^{Mc}}(NO)(PPh$_3$)] (XXX). The CO and NO groups are disordered between the two positions shown.

configurations at the Co atom implies that there is either no kinetic or mechanistic control of the chirality at Co during the prepararation of the complex. or that any product formed rapidly racemises at the Co centre. In order to impose a preference for one or the other diastereoisomer it would be necessary to replace either the CO or NO ligand with some other ligand of significantly different shape; experiments along these lines are in hand.

The Co–P bond length of 2.227(4) Å is in good agreement with values in other tetrahedral complexes, e.g., 2.224(3) Å in [Co(CO)(NO)(PPh$_3$)$_2$] [21], where a similar CO/NO disorder was found. Likewise, the averaged Co–N/C and C/N–O distances of 1.70(2) and 1.15(3) Å are close to those observed in [Co(CO)(NO)(PPh$_3$)$_2$]. For comparison, the Co–N(O) bond lengths in [Co(NO)$_2$(PPh$_3$)$_2$][PF$_6$] [22] average 1.645(6) Å, and the Co–C(O) bond lengths in [Co$_2$(CO)$_6$(η-C$_4$H$_4$)] average 1.79(1) Å [23].

Experimental

General procedures

All experiments were performed under argon using freshly distilled, dry, degassed solvents.

^{1}H NMR spectra were recorded on Varian T60 (60 MHz) or Perkin–Elmer R32 (90 MHz) spectrometers, IR spectra were recorded on a Perkin–Elmer 597 (4000–200

TABLE 11

INTRAMOLECULAR DISTANCES AND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, AND SELECTED TORSION ANGLES, FOR [Co(CO){(S)-MeL*^{Me}}(NO)(PPh$_3$)] (XXX)

(a) Bonds (Å)

Co–P	2.227(4)	C(20)–C(21)	1.48(3)
Co–CN(1)	1.708(21)	C(20)–N(2)	1.47(3)
Co–C(19)	1.974(15)	C(21)–C(22)	1.51(3)
Co–CN(2)	1.689(13)	C(21)–N(3)	1.44(2)
P–C(1)	1.837(8)	C(23)–N(3)	1.48(2)
P–C(13)	1.846(7)	C(24)–N(2)	1.47(2)
P–C(7)	1.841(8)	CN(2)–O(2)	1.15(2)
C(19)–N(2)	1.33(2)	CN(1)–O(1)	1.14(2)
C(19)–N(3)	1.31(2)		

(b) Angles (°)

CN(1)–Co–P	113.0(6)	C(20)–N(2)–C(19)	113(2)
C(19)–Co–P	96.5(4)	C(24)–N(2)–C(19)	129(2)
C(19)–Co–CN(1)	109.6(8)	C(24)–N(2)–C(20)	118(2)
CN(2)–Co–P	110.0(6)	C(21)–N(3)–C(19)	115(2)
CN(2)–Co–CN(1)	114.8(6)	C(23)–N(3)–C(19)	126(1)
CN(2)–Co–C(19)	111.4(8)	C(23)–N(3)–C(21)	118(1)
C(1)–P–Co	118.3(4)	N(2)–C(19)–Co	124(1)
C(13)–P–Co	113.3(3)	N(3)–C(19)–Co	129(1)
C(13)–P–C(1)	102.6(5)	N(3)–C(19)–N(2)	107(1)
C(7)–P–Co	116.5(4)	N(2)–C(20)–C(21)	103(1)
C(7)–P–C(1)	98.5(5)	C(22)–C(21)–C(20)	115(2)
C(7)–P–C(13)	105.5(6)	N(3)–C(21)–C(20)	102(2)
C(2)–C(1)–P	119.1(4)	N(3)–C(21)–C(22)	115(2)
C(6)–C(1)–P	120.7(4)	O(2)–CN(2)–Co	174(2)
O(1)–CN(1)–Co	177(2)		

(c) Torsion angles (°)

C(21)–C(20)–N(2)–C(19)	6(2)	N(3)–C(19)–N(2)–C(20)	−3(2)
C(21)–C(20)–N(2)–C(24)	−178(2)	N(3)–C(19)–N(2)–C(24)	−178(2)
C(20)–C(21)–N(3)–C(19)	4(2)	N(2)–C(19)–N(3)–C(21)	0(2)
C(20)–C(21)–N(3)–C(23)	−169(2)	N(2)–C(19)–N(3)–C(23)	173(2)
C(22)–C(21)–N(3)–C(19)	−121(2)	N(2)–C(20)–C(21)–C(22)	121(2)
C(22)–C(21)–N(3)–C(23)	64(2)	N(2)–C(20)–C(21)–N(3)	−4(2)

cm^{-1}) spectrometer, as mulls between potassium bromide plates, or as dilute solutions in potassium bromide solution cells. A JEOL PFT 100 spectrometer was used for ^{13}C or ^{31}P NMR spectra at observing frequencies of 25 MHz or 40 MHz, respectively. Optical rotations were determined using a Perkin–Elmer 241 polarimeter. Melting points were recorded using an electrothermal melting point apparatus and are uncorrected.

The complexes [RhCl(PPh$_3$)$_3$] [24], *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] [25], [{Rh(CO)(μ-Cl)(PPh$_3$)}$_2$] [26], [{Rh(COD)(μ-Cl)}$_2$] [27], and [Co(CO)$_3$NO] [28] were obtained by literature procedures. The preparative details for the optically active electron-rich olefins, and their characterisation, will be published elsewhere.

Representative preparative procedures for the optically active carbenemetal complexes are given below.

Preparation of (+)$_{589}$-cis-(1,5-cyclooctadiene)[(S)-1,3-diethyl-4-isobutylimidazolidin-2-ylidene]chlororhodium(I) (VIII)

A solution of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) (0.64 g, 1.30 mmol) and bis[(S)-1,3-diethyl-4-isobutylimidazolidinylid-2-ene] (Ib) (0.47 g, 1.29 mmol) in methylcyclohexane (40 cm³) was refluxed for 1 h under argon. The reaction mixture was filtered. Addition of n-hexane to the yellow filtrate and cooling to −30°C gave a yellow microcrystalline solid, which, upon recrystallisation from toluene/n-hexane, gave yellow prisms of the title complex (VIII).

Preparation of (−)$_{589}$-cis-(1,5-cyclooctadiene)[(S)-1-methyl-3,4-pyrrolidylimidazolidin-2-ylidene]chlororhodium(I) (IX)

Bis[(S)-1-methyl-3,4-pyrrolidylimidazolidinylid-2-ene] (II) (0.26 g, 1.05 mmol) was added to a stirred suspension of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) (0.5 g, 1.01 mmol) in methylcyclohexane (15 cm³). The reaction mixture was refluxed for 1 h and filtered. Upon adding n-hexane to the yellow filtrate, yellow prisms of the title complex (IX) crystallised.

Preparation of (−)$_{589}$-trans-[(S)-1,3-dibenzyl-4-isobutylimidazolidin-2-ylidene]bis(triphenylphosphine)chlororhodium(I) (XV)

A stirred suspension of bis[(S)-1,3-dibenzyl-4-isobutylimidazolidinylid-2-ene] (Ic) (1.09 g, 1.78 mmol) and tris(triphenylphosphine)chlororhodium(I) (2.50 g, 2.70 mmol) in methylcyclohexane (50 cm³) was refluxed for 4 h under argon and then filtered whilst still hot. Cooling the filtrate to room temperature, and evaporating to dryness under reduced pressure, afforded a yellow oil. Trituration with n-hexane gave a yellow powder, which was crystallised from toluene/n-hexane to yield yellow microcrystals of the title complex (XV).

Preparation of (+)$_{589}$-trans-carbonylbis[(S)-1,3-diethyl-4-isobutylimidazolidin-2-ylidene]chlororhodium(I) (XXII)

Bis[(S)-1,3-diethyl-4-isobutylimidazolidinylid-2-ene] (Ib) (0.42 g, 1.15 mmol) was added to a stirred suspension of dicarbonylbis(triphenylphosphine)di-μ-chlorodirhodium(I) (0.49 g, 0.57 mmol) in xylene (25 cm³). The reaction mixture was refluxed for 2 h under argon, affording a yellow solution which was concentrated in vacuo. Addition of n-hexane, filtration, and cooling to −50°C gave pale yellow prisms of the title complex (XXII).

Preparation of [Co(CO)(MeL^{Mc})(NO)(PPh₃)] (XXX)*

Bis[(S)-1,3,4-trimethylimidazolidinylid-2-ene] (Ia) (1.5 mmol) was added to a solution of [Co(CO)₃NO] (0.52 g, 3 mmol) in methylcyclohexane (20 cm³). The solution was slowly heated (70°C, 1 h), then refluxed for 1 h, and cooled. The mixture was filtered, and the volatiles removed from the filtrate in vacuo. The resulting red oil was extracted with n-pentane (10 cm³). The extract was cooled to −50°C, to yield red crystals of dicarbonyl{(S)-1,3,4-trimethylimidazolidin-2-ylidene}nitrosylcobalt (XXXI) (0.35 g) as a low melting red solid. Analysis: Found: C, 38.9; H, 5.0; N, 16.7. $C_8H_{12}CoN_3O_3$ calcd.: C, 37.4; H, 4.70; N, 16.3%. IR(ν_{max}, cm⁻¹): 2025 and 1960 (CO), 1735 (NO), and 1505 (CN₂).

Triphenylphosphine (0.52 g, 2 mmol) was added to a solution of complex XXXI (2.0 mmol) in methylcyclohexane (20 cm³), and the solution was refluxed for 1 h. After cooling, n-hexane (10 cm³) was added; the mixture was then set aside at room temperature overnight to yield red-brown crystals of the title compounds (XXX).

m.p. 125°C. Analysis: Found: C, 60.9; H, 5.5; N, 8.6. $C_{25}H_{27}CoN_3O_2P$ calcd.: C, 61.1; H, 5.5; N, 8.6%. IR (ν_{max}, cm^{-1}): 1925 (CO), 1670 (NO), and 1495 (CN$_2$). {The procedure described here is similar to that used previously for [Co(CO)(L^{Et})-(NO)(PPh$_3$)] [29]}.

X-Ray structure determinations

In all cases the data were measured by an $\omega/2\theta$ step scan on a Hilger and Watts Y290 diffractometer using monochromated Mo-K_α radiation (λ 0.71069 Å) and a crystal sealed in a Lindemann glass capillary under argon. Structures were solved by heavy atom methods and refined by full matrix least squares with non-hydrogen atoms anisotropic unless otherwise stated. Scattering factors and dispersion corrections were taken from ref. 30. All calculations were done with the SHELX program system of G.M. Sheldrick. Tables of temperature factors, hydrogen atom positions, and final structure factors are available from one of the authors (P.B.H.)

[RhCl(COD)(CyL$^{\star Me}$*)] (X).* Crystal data: $C_{17}H_{28}ClN_2Rh$, $M = 398.8$, orthorhombic, space group $P2_12_12_1$, a 15.840(3), b 15.089(2), c 7.226(1) Å, U 1727.1 Å^3, $Z = 4$, D_c 1.53 g cm^{-3}, μ(Mo-K_α) 11.1 cm^{-1}.

Crystal size ca. $0.25 \times 0.20 \times 0.10$ mm. Data $+h + k + l$, $2 < \theta < 25°$, corrected for absorption. 1700 reflections with $I > 3\sigma(I)$ used in the refinement. The residuals before the inclusion of H atoms were $R = 0.0416$ (0.0440), $R' = 0.0721$ (0.0745), where the figures in parentheses are for the opposite absolute configuration. H atoms were held fixed at positions from a difference map with a common U_{iso} of 0.08 Å^2. Final residuals were $R = 0.0308$, $R' = 0.0513$, and the weighting scheme was $w = 0.15/[\sigma^2(F) + 0.009F^2]$.

[RhCl(COD)(PL$^{\star Me}$*)] (IX).* Crystal data: $C_{15}H_{24}ClN_2Rh$, $M = 370.8$, monoclinic, space group $P2_1$, a 10.133(1), b 11.336(2), c 7.286(1) Å, β 111.16(1)°, U 780.5 Å^3, $Z = 2$, D_c 1.58 g cm^{-3}, μ(Mo-K_α) 11.4 cm^{-1}.

Crystal size ca. $0.35 \times 0.32 \times 0.08$ mm. Data $+h + k \pm l$, $2 < \theta < 28°$, corrected for absorption. 1705 reflections with $I > 3\sigma(I)$ used in the refinement. Hydrogen atoms, except for H(6B), were located on a difference map and held fixed with isotropic temperature factors equivalent to those of the atoms they are bonded to. The final residuals were $R = 0.0292$ (0.0294), $R' = 0.0380$ (0.0384), and the weighting scheme was $w = 0.86/[\sigma^2(F) + 0.001F^2]$.

Trans-[RhCl(Bu^{i}L$^{\star Me}$*)(PPh$_3$)$_2$] (XII).* Crystal data: $C_{45}H_{48}ClN_2P_2Rh$, C_7H_8, $M = 909.4$, monoclinic, space group $P2_1$, a 12.050(2), b 18.787(3), c 21.393(3) Å, β 113.8l(2)°, U 4430.8 Å^3, $Z = 4$, D_c 1.36 g cm^{-3}, μ(Mo-K_α) 5.5 cm^{-1}.

Crystal size ca. $0.15 \times 0.05 \times 0.08$ mm. Data $+h + k \pm l$, $2 < \theta < 25°$. No absorption correction. 2831 reflections with $I > 3\sigma(I)$ used in the refinement. The structure was initially solved in space group $P2_1/c$ and refined to $R = 0.12$. However, the carbene ligand then had a chemically unreasonable geometry with a mirror plane through the ligand. A more intensive check on the diffraction intensities revealed that there were a few reflections of the type $h0l$ for l odd where there appeared to be some genuine intensity. The only one of these with $I > 3\sigma(I)$ was the 20–13 reflection with $I = 464$ and $\sigma(I) = 40$, but there were a further 15 reflections with $I > 2\sigma(I)$. It was therefore assumed that the structure was an ordered arrangement with two independent molecules in space group $P2_1$. The two independent molecules, excluding the isobutyl group, were refined with anisotropic temperature factors for Rh, P, and Cl only. The phenyl groups were refined as rigid bodies of

TABLE 12

FINAL ATOMIC COORDINATES ($\times 10^4$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR cis-[RhCl(COD)(CyL$^{\star Me}$)] (X)

	x	y	z
Rh	−1744.1(2)	−1914.9(3)	130.7(6)
Cl	−750(1)	−2885(1)	−1297(3)
N(1)	−376(3)	−564(3)	185(7)
N(2)	−376(3)	−1305(3)	2797(7)
C(1)	−773(3)	−1209(3)	1122(9)
C(2)	236(3)	−108(4)	1388(9)
C(3)	1054(4)	289(4)	598(11)
C(4)	1544(4)	625(5)	2262(11)
C(5)	1687(4)	−72(5)	3765(12)
C(6)	857(4)	−502(5)	4396(10)
C(7)	449(3)	−857(4)	2701(9)
C(8)	−2792(3)	−2869(4)	−325(9)
C(9)	−2733(4)	−2316(4)	−1850(9)
C(10)	−3271(5)	−1516(6)	−2230(11)
C(11)	−3384(4)	−906(5)	−596(12)
C(12)	−2640(4)	−916(4)	728(10)
C(13)	−2552(3)	−1489(4)	2269(8)
C(14)	−3163(4)	−2225(5)	2809(10)
C(15)	−3460(4)	−2782(5)	1196(10)
C(16)	−478(5)	−2089(4)	3916(10)
C(17)	−698(5)	−145(6)	1434(11)

idealised geometry (C–C 1.395 Å). Because of the high correlation, the two molecules were refined in alternate cycles. A difference map revealed the two isobutyl groups which were included in the refinement. No attempt was made to include H

TABLE 13

FINAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR cis-[RhCl(COD)[(S)-PL$^{\star Me}$}] (IX)

	x	y	z
Rh	−2046.7(3)	−13.3(0)	−4448.9(5)
Cl	−2612(2)	−1822(2)	−3281(3)
N(1)	−5174(5)	309(4)	−6065(7)
N(2)	−4424(5)	−306(5)	−8347(7)
C(1)	−4023(5)	−3(11)	−6440(7)
C(2)	−6500(6)	105(12)	−7748(10)
C(3)	−5987(7)	−439(6)	−9253(9)
C(4)	−5169(8)	698(9)	−4161(12)
C(5)	−3726(8)	−1228(9)	−9048(11)
C(6)	−4928(13)	−2125(8)	−10103(16)
C(7)	−6175(9)	−1766(7)	−9608(12)
C(8)	−1705(7)	1795(6)	−4856(10)
C(9)	−1361(7)	1118(7)	−6208(10)
C(10)	123(8)	794(8)	−6081(12)
C(11)	1085(7)	404(8)	−4010(12)
C(12)	274(6)	−261(6)	−2919(10)
C(13)	−257(7)	279(7)	−1662(9)
C(14)	−233(9)	1574(8)	−1228(12)
C(15)	−635(9)	2355(7)	−3044(13)

TABLE 14

FINAL ATOM COORDINATES ($\times 10^3$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR *trans*-[RhCl{(S)-Bu^{i}L$^{\star Me}$}(PPh$_3$)$_2$] (XII)

	x	y	z
Rh	45.4(4)	− 349.7(2)	− 497.1(3)
P(1)	− 127.1(8)	− 363.3(6)	− 486.1(4)
P(2)	219.7(12)	− 318.1(5)	− 508.4(6)
Cl	− 29.5(11)	− 235.0(6)	− 542.3(6)
N(1)	89(3)	− 500(2)	− 499(2)
N(2)	162(4)	− 454(2)	− 393(2)
C(1)	100(3)	− 441(2)	− 456(2)
C(2)	152(5)	− 570(3)	− 462(3)
C(3)	229(5)	− 533(3)	− 385(3)
C(4)	3(4)	− 507(2)	− 563(2)
C(5)	206(2)	− 413(1)	− 340(1)
C(6)	226(6)	− 574(3)	− 333(3)
C(7)	272(4)	− 658(3)	− 307(3)
C(8)	248(4)	− 676(2)	− 278(2)
C(9)	424(7)	− 632(4)	− 309(4)
C(10)	− 267(3)	− 384(2)	− 561(1)
C(11)	− 369(3)	− 420(2)	− 561(1)
C(12)	− 466(3)	− 435(2)	− 623(1)
C(13)	− 461(3)	− 413(2)	− 684(1)
C(14)	− 360(3)	− 377(2)	− 684(1)
C(15)	− 263(3)	− 362(2)	− 622(1)
C(16)	− 142(3)	− 442(2)	− 427(1)
C(17)	− 133(3)	− 424(2)	− 362(1)
C(18)	− 123(3)	− 477(2)	− 315(1)
C(19)	− 121(3)	− 549(2)	− 333(1)
C(20)	− 129(3)	− 566(2)	− 398(1)
C(21)	− 139(3)	− 513(2)	− 445(1)
C(22)	− 091(3)	− 242(2)	− 409(2)
C(23)	− 181(3)	− 291(2)	− 446(2)
C(24)	− 296(3)	− 286(2)	− 446(2)
C(25)	− 322(3)	− 232(2)	− 409(2)
C(26)	− 232(3)	− 183(2)	− 372(2)
C(27)	− 116(3)	− 188(2)	− 372(2)
C(28)	227(3)	− 288(2)	− 586(1)
C(29)	123(3)	− 269(2)	− 643(1)
C(30)	131(3)	− 250(2)	− 704(1)
C(31)	243(3)	− 250(2)	− 708(1)
C(32)	348(3)	− 269(2)	− 651(1)
C(33)	340(3)	− 288(2)	− 590(1)
C(34)	342(2)	− 380(1)	− 477(1)
C(35)	325(2)	− 443(1)	− 514(1)
C(36)	412(2)	− 497(1)	− 491(1)
C(37)	516(2)	− 488(1)	− 432(1)
C(38)	534(2)	− 425(1)	− 394(1)
C(39)	447(2)	− 371(1)	− 417(1)
C(40)	277(3)	− 238(1)	− 454(1)
C(41)	231(3)	− 220(1)	− 406(1)
C(42)	265(3)	− 156(1)	− 370(1)
C(43)	346(3)	− 111(1)	− 382(1)
C(44)	392(3)	− 129(1)	− 430(1)
C(45)	357(3)	− 193(1)	− 466(1)
Rh(A)	40.0(2)	− 150.2(2)	− 0.5(1)
P(1A)	− 140.3(11)	− 129.5(4)	16.0(7)

TABLE 14 (continued)

	x	y	z
P(2A)	217.5(9)	−178.7(7)	−7.7(6)
Cl(A)	−38.6(12)	−265.9(6)	−49.5(9)
N(1A)	88(3)	5(2)	−4(2)
N(2A)	171(3)	−37(2)	96(1)
C(1A)	107(3)	−56(2)	28(2)
C(2A)	150(3)	65(2)	45(2)
C(3A)	176(4)	39(2)	109(2)
C(4A)	34(3)	14(2)	−79(2)
C(5A)	168(6)	−96(3)	159(3)
C(6A)	299(6)	61(4)	166(3)
C(7A)	320(3)	142(2)	181(2)
C(8A)	311(7)	161(4)	134(4)
C(9A)	452(6)	152(3)	217(3)
C(10A)	−263(2)	−109(1)	−63(1)
C(11A)	−363(2)	−77(1)	−59(1)
C(12A)	−469(2)	−66(1)	−117(1)
C(13A)	−474(2)	−88(1)	−181(1)
C(14A)	−374(2)	−121(1)	−185(1)
C(15A)	−268(2)	−131(1)	−127(1)
C(16A)	−139(3)	−59(1)	71(1)
C(17A)	−140(3)	−69(1)	136(1)
C(18A)	−141(3)	−11(1)	176(1)
C(19A)	−141(3)	58(1)	151(1)
C(20A)	−140(3)	68(1)	87(1)
C(21A)	−139(3)	10(1)	47(1)
C(22A)	−93(2)	−253(1)	95(1)
C(23A)	−182(2)	−211(1)	47(1)
C(24A)	−304(2)	−227(1)	28(1)
C(25A)	−338(2)	−286(1)	56(1)
C(26A)	−249(2)	−328(1)	104(1)
C(27A)	−126(2)	−312(1)	124(1)
C(28A)	219(3)	−202(2)	−92(1)
C(29A)	110(3)	−231(2)	−139(1)
C(30A)	101(3)	−253(2)	−203(1)
C(31A)	201(3)	−247(2)	−220(1)
C(32A)	310(3)	−219(2)	−173(1)
C(33A)	319(3)	−196(2)	−109(1)
C(34A)	336(3)	−111(1)	18(2)
C(35A)	315(3)	−51(1)	−23(2)
C(36A)	399(3)	5(1)	−4(2)
C(37A)	503(3)	0(1)	57(2)
C(38A)	523(3)	−60(1)	98(2)
C(39A)	439(3)	−116(1)	78(2)
C(40A)	287(3)	−257(1)	42(2)
C(41A)	284(3)	−261(1)	106(2)
C(42A)	329(3)	−321(1)	147(2)
C(43A)	376(3)	−378(1)	123(2)
C(44A)	379(3)	−373(1)	58(2)
C(45A)	334(3)	−313(1)	18(2)
C(1S)	−112(5)	−558(3)	−772(3)
C(2S)	1(7)	−561(4)	−779(4)
C(3S)	65(7)	−490(5)	−752(4)
C(4S)	18(5)	−437(3)	−733(3)
C(5S)	−93(8)	−431(5)	−729(4)
C(6S)	182(5)	−516(3)	−743(3)
C(7S)	−161(7)	−507(4)	−753(3)

TABLE 15

FINAL ATOMIC COORDINATES ($\times 10^4$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR [Co(CO){(S)-MeL^{*Me}}(NO)(PPh$_3$)] (XXX)

	x	y	z
Co	−6042(2)	0(0)	−1759(2)
P	−3431(4)	90(3)	−1061(3)
C(1)	−2449(12)	−778(7)	−1743(14)
C(2)	−3365(12)	−1324(7)	−2980(14)
C(3)	−2634(12)	−1940(7)	−3597(14)
C(4)	−985(12)	−2009(7)	−2979(14)
C(5)	−68(12)	−1463(7)	−1743(14)
C(6)	−800(12)	−847(7)	−1125(14)
C(7)	−2700(12)	1065(6)	−1768(12)
C(8)	−3662(12)	1385(6)	−3246(12)
C(9)	−3117(12)	2062(6)	−3928(12)
C(10)	−1610(12)	2421(6)	−3132(12)
C(11)	−648(12)	2102(6)	−1654(12)
C(12)	−1193(12)	1424(6)	−972(12)
C(13)	−2301(11)	70(9)	1076(7)
C(14)	−1756(11)	−708(9)	1931(7)
C(15)	−1117(11)	−683(9)	3561(7)
C(16)	−1025(11)	121(9)	4337(7)
C(17)	−1571(11)	900(9)	3481(7)
C(18)	−2209(11)	874(9)	1851(7)
C(19)	−5983(15)	−125(13)	377(17)
C(20)	−5630(30)	−770(15)	2762(25)
C(21)	−6017(21)	184(18)	2808(19)
C(22)	−7438(27)	374(16)	3188(27)
C(23)	−6263(30)	1454(11)	998(24)
C(24)	−5453(32)	−1771(12)	669(29)
CN(1)	−6851(21)	−933(14)	−2818(21)
CN(2)	−6913(19)	962(11)	−2593(21)
N(2)	−5737(18)	−886(9)	1159(17)
N(3)	−6141(18)	488(9)	1298(16)
O(1)	−7466(20)	−1540(13)	−3534(21)
O(2)	−7528(24)	1582(12)	−3287(24)

atoms. The final residuals were $R = 0.115$ (0.115), $R' = 0.169$ (0.169) with a weighting scheme of $w = 1/[\sigma^2(F) + 0.067\ F^2]$. Since the residuals did not distinguish between the absolute configurations, the coordinates listed refer arbitrarily to both molecules with the (S)-configuration at C(3), as in the starting material.

[Co(CO)(MeL^{*Me})(NO)(PPh$_3$)] (XXX). Crystal data: C$_{25}$H$_{27}$CoN$_3$O$_2$P, M = 459.5, monoclinic, space group P2$_1$, a 9.179(8), b 15.063(11), c 9.306(9) Å, β 113.20(6)°, U 1182.6 Å^3, $Z = 2$, D_c 1.29 g cm^{-3}, μ(Mo-K$_\alpha$) 8.5 cm^{-1}.

Crystal size ca. 0.55 × 0.50 × 0.07 mm. Data $+h + k \pm l$, $2 < \theta < 25°$. No absorption correction. 1574 reflections with $I > 3\sigma(I)$ used in the refinement. All hydrogen atoms were included at calculated positions (C–H 1.08 Å). The C and H atoms of each phenyl group were refined as a rigid body (C–C 1.395 Å) as were the methyl groups. The remaining H atoms were constrained to ride on the corresponding carbon atom. The three types of H atoms were given common isotropic temperature factors which refined to $U = 0.096$, 0.133, and 0.106 Å^2, respectively. During the initial refinement, the molecule was assumed to have an ordered arrangement of the

carbonyl and nitrosyl groups and the residuals were $R = 0.0846$ (0.0857) and $R' = 0.1154$ (0.1191). However, the configuration with the lower R values, which also had an (S)-configuration for the carbene ligand as expected, did not show any significant difference between the M–X–O groups (X = C or N). The M–X distances were the same and both were linear. This suggested that the CO and NO groups were disordered and a further refinement was carried out assigning both the C and N site occupancies as 50% C and 50% N. This converged at $R = 0.0838$, $R' = 0.1150$. The weighting scheme was $w = 0.77/[\sigma^2(F) + 0.013\ F^2]$ and the 020 reflection, which appeared to have an anomalously high difference between $|F_0|$ and $|F_c|$, was omitted from the least squares throughout.

Final atom coordinates for the four complexes are in Tables 12–15.

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