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Preliminary communication

ROUTES TO OPTICALLY ACTIVE ELECTRON-RICH OLEFINS ($L^\star_2$) AND SOME DERIVED CARBENEMETAL COMPLEXES; X-RAY STRUCTURES OF $[Co(CO)(L^\star)(NO)(PPh_3)]$ AND *cis*-$[Rh(Cl)(COD)(L'^\star)]$ [$L^\star$ = (S)-$\overline{CN(Me)CH(Me)CH_2N}Me$, $L'^\star$ = (S)-$\overline{CN(CH_2CH_2CH_2)CHCH_2N}Me$, COD = 1,5-$C_8H_{12}$]*

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Summary

Optically active electron-rich olefins $L^\star_2$ are obtained from readily available chiral starting materials [(S)-α-amino-acids, (R)- or (S)-terpene derivatives, or *cis* + *trans*-(±)-cyclohexane-1,2-diamine], and are converted into carbenemetal (Rh^I or Co^I) complexes with retention of optical integrity.

Electron-rich olefins $[:\overline{CN(R)CH_2CH_2N}R]_2$, ($L^R{}_2$), are useful as (i) strong reducing agents [1, 2], (ii) convenient precursors to a variety of carbene-transition-metal complexes [1, 3], (iii) catalysts for benzoin-type C—C coupling [4], and (iv) chemiluminescent materials [5]. We now describe (a) three alternative routes to optically active electron-rich olefins of types (I), (II) (where $R^\star$ represents an optically active substituent), and (III); (b) the preparation of some carbenemetal complexes (of cobalt, having four different unidentate ligands around the tetrahedral Co atom, and rhodium(I)) derived therefrom; and (c) X-ray data on two of these complexes, one of which was obtained as a preferred conformer. Our longer term objectives are to examine olefins such as I—IV as sources of (a) optically active carbenoids (we note that L^R is a masked carbonyl group) and (b) diastereoisomeric transition metal complexes having a chiral metal centre; the latter may in suitable cases provide (c) asymmetric homogeneous catalysts.

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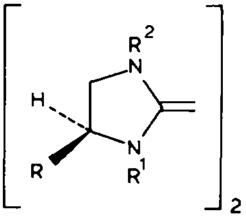
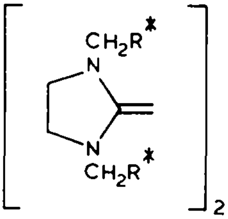

(I)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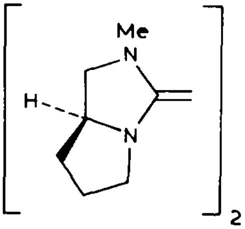
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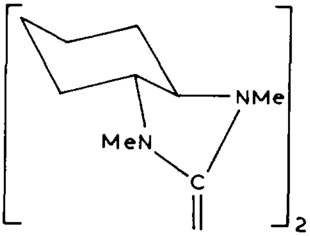
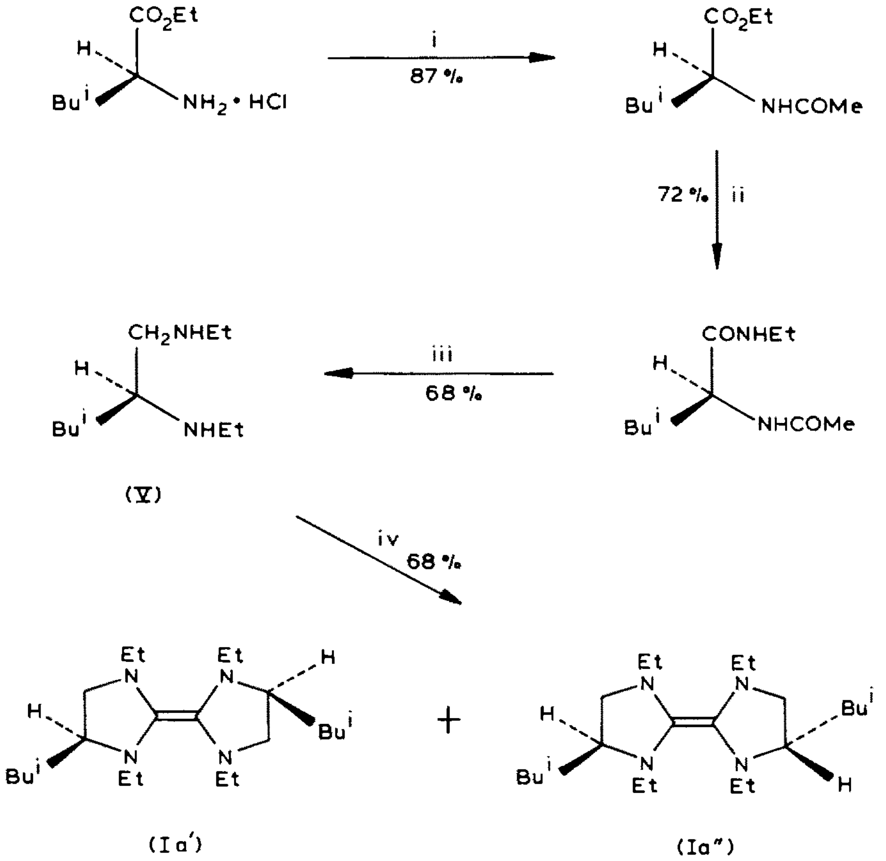

(III)

α-Amino-acids provided a readily available source of chiral starting material for the synthesis of optically active electron-rich olefins of type I (e.g., olefins Ia, R = Bu^i, R^1 = R^2 = Et; Ib, R = R^1 = R^2 = Me; or IV; derived from (*S*)-leucine, (*S*)-alanine, or (*S*)-proline, respectively). Typically, bis[(*S*)-1,3-diethyl-4-isobutylimidazolidinylid-2-ene] (Ia) was prepared from (*S*)-leucine ethyl ester hydrochloride in four steps (see Scheme 1) and is an air-sensitive, chemiluminescent, viscous oil (b.p. 110—116°C/0.1 torr). The ^{13}C NMR spectrum (220 MHz) of olefin Ia indicates an approximately equal mixture of the two geometric isomers Ia′ and Ia″. Compounds Ia were obtained in good overall yield and in high optical purity, checked by NMR at the diamine stage (V) by use of the optically active reagent $PhC(OMe)CF_3C(=O)Cl$ [6].

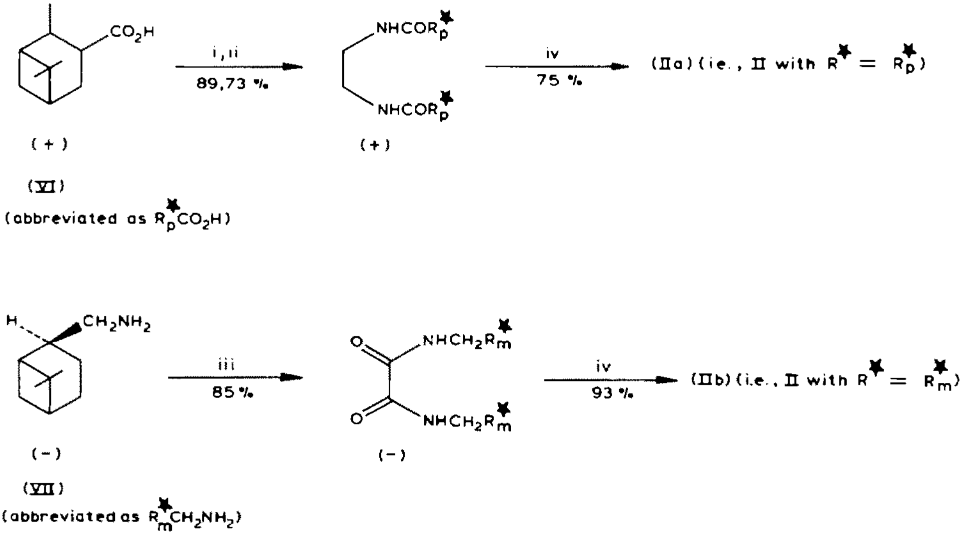
Compounds II, bearing chiral substituents $R^{\star}$, were obtained using the available terpene derivatives (+)-3-pinanecarboxylic acid (VI) or (—)-*cis*-myrtanylamine (VII), Scheme 2.

The two separated enantiomers of compound III were obtained from the available mixture of *cis*- and *dl*-*trans*-1,2-diaminocyclohexane by successive separation of the *cis*- and *trans*-isomers, resolution of the latter [7], conversion into the (+)- and (—)-*trans*-*N*,*N*′-dimethyldiaminocyclohexanes (via the *N*,*N*′-bisformyl derivatives), and their reactions with $CH(OMe)_2NMe_2$ (cf., iv in Scheme 1).

Optically active olefins such as Ia, Ib, IIa, IIb, III, and IV, (collectively abbreviated as $L^{\star}_2$) were converted into the optically active carbenemetal complexes by standard procedures [1, 3]. Typical of such complexes are *trans*-$[RhCl(L^{\star})(PPh_3)_2]$ (VIII, $L^{\star}_2$ = Ia; IX, $L^{\star}_2$ = IIb); *cis*-$[RhCl(COD)(L^{\star})]$ (X, $L^{\star}_2$ = IV, XI, $L^{\star}_2$ = III); and $[Co(CO)(L^{\star})(NO)(PPh_3)]$ (XII, $L^{\star}_2$ = Ib). X-ray crystallography confirmed that for X, XI [8], and XII, each was obtained with complete retention of configurational integrity of the $L^{\star}$ ligand as compared with the starting organic precursor, e.g. the (*S*)-α-amino acid. Furthermore in



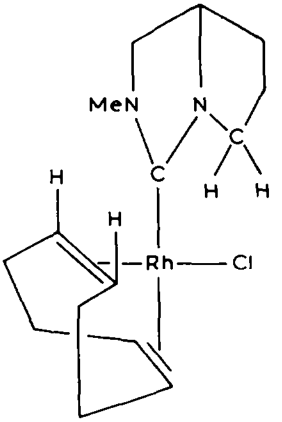
SCHEME 1. Reagents and conditions: i, $(MeCO)_2O$, $NaOH/H_2O$, $-10^\circ C$; ii, $EtNH_2$, EtOH, 20°C, 7d; iii, $Li[AlH_4]$, THF, reflux, 24 h; iv, $CH(OMe)_2NMe_2$, 90°C, 1 h, distillation.



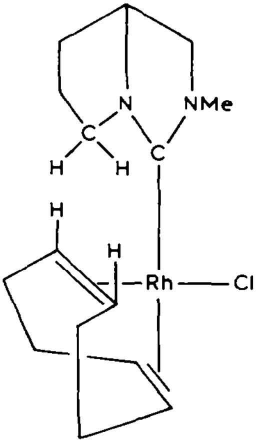
SCHEME 2. Reagents: i, $SOCl_2$, reflux; ii, $H_2NCH_2CH_2NH_2$, NC_5H_5, 0°C; iii, $(CO_2Et)_2$, 20°C, 2 h; iv, cf., iii and iv in Scheme 1.

one case, X, it was clear that a preferred conformer (Xa rather than the diastereoisomer Xb) had crystallised, presumably because (i) there is restricted rotation about the C_{carb}—Rh bond [1] and (ii) steric preference.

The olefins I—IV (as well as their *N,N'*-diamide and -diamine precursors) and the metal complexes VIII—XII have been characterised by microanalysis, optical rotation, IR and ^{1}H and ^{13}C NMR spectroscopy.



(Xa)



(Xb)

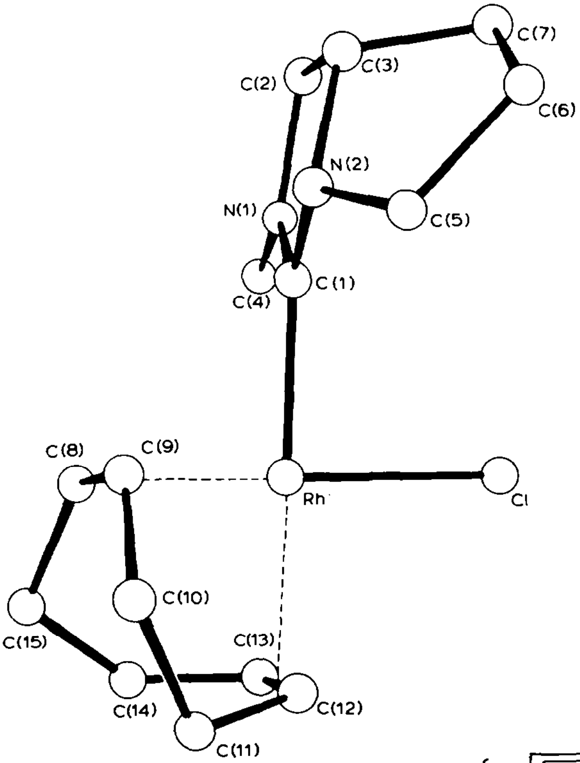


Fig. 1. The molecular structure of *cis*-[RhCl(COD){(*S*)-$\overline{\text{CN}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{CHCH}_2\text{NMe}}$}], (Xa). Bond lengths: Rh—Cl 2.368(2), Rh—C(1) 2.004(4), Rh—C(8) 2.118(7), Rh—C(9) 2.101(8), Rh—C(12) 2.227(6), Rh—C(13) 2.206(5) Å; bond angle: Cl—Rh—C(1) 87.5(3)°.

For both crystal structures, data were measured on a Hilger and Watts Y290 diffractometer using Mo-K_α radiation. The structures were solved by heavy atom methods and refined by least squares using reflections with $I > 3\sigma(I)$, see Figs. 1 and 2.

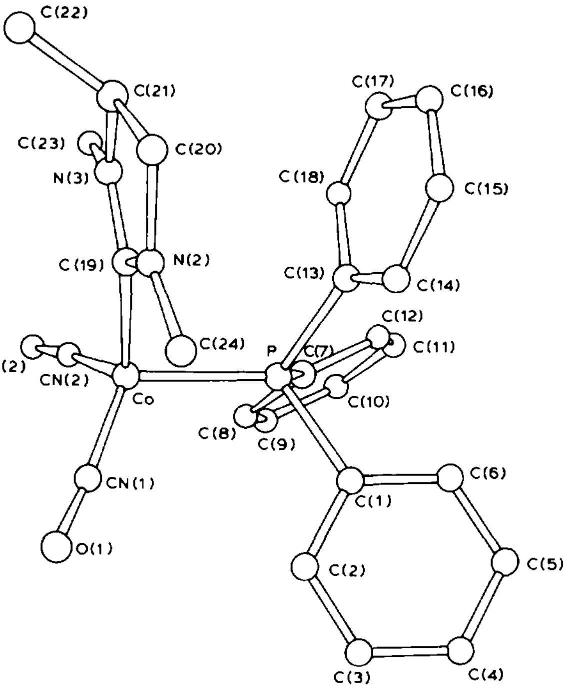


Fig. 2. The molecular structure of $[\mathrm{Co(CO)}\{(S)\text{-}\overline{\mathrm{CN(Me)CH(Me)CH_2N}}\mathrm{Me}\}\mathrm{(NO)(PPh_3)}]$, (XII). The atoms labelled CN(1) and CN(2) were each refined as 50% carbon and 50% nitrogen atoms. Bond lengths: Co—P 2.227(4), Co—C(19) 1.974(15), Co—CN(1) 1.708(21), Co—CN(2) 1.689(13), CN(1)—O(1) 1.14(2), CN(2)—O(2) 1.15(2) Å; bond angles: P—Co—C(19) 96.5(4), P—Co—CN(1) 113.0(6), P—Co—CN(2) 110.0(6)°.

Crystal data for complex Xa. $C_{15}H_{24}ClN_2Rh$, monoclinic, $P2_1$, *a* 10.133(1), *b* 11.336(2), *c* 7.286(1) Å, β 111.16(1)°, $Z = 2$. A refinement (1705 reflections) corresponding to the (*S*)-configuration of the carbene ligand converged at $R = 0.029$, $R' = 0.038$ compared to $R = 0.035$, $R' = 0.053$ for the alternative.

Crystal data for complex XII. $C_{25}H_{27}CoN_3O_2P$, monoclinic, $P2_1$, *a* 9.179(8), *b* 15.063(11), *c* 9.306(9) Å, β 113.20(6)°, $Z = 2$. A refinement (1574 reflections) corresponding to the (*S*)-configuration of the carbene ligand converged at $R = 0.085$, $R' = 0.115$ compared to $R = 0.087$, $R' = 0.119$ for the alternative. There appeared to be no significant differences between the two Co—X—O groups (X = C or N) and it is assumed that the crystal contains an equal mixture of the two configurations at the chiral Co atom.

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