The Synthesis and Properties of the Transannularly Bonded Electron-rich Olefin Derived from 1,4,8,11-Tetra-azacyclotetradecane; *X*-Ray Crystal Structure of the Chelating *cis*-Dicarbenerhodium(I) Salt Obtained Therefrom

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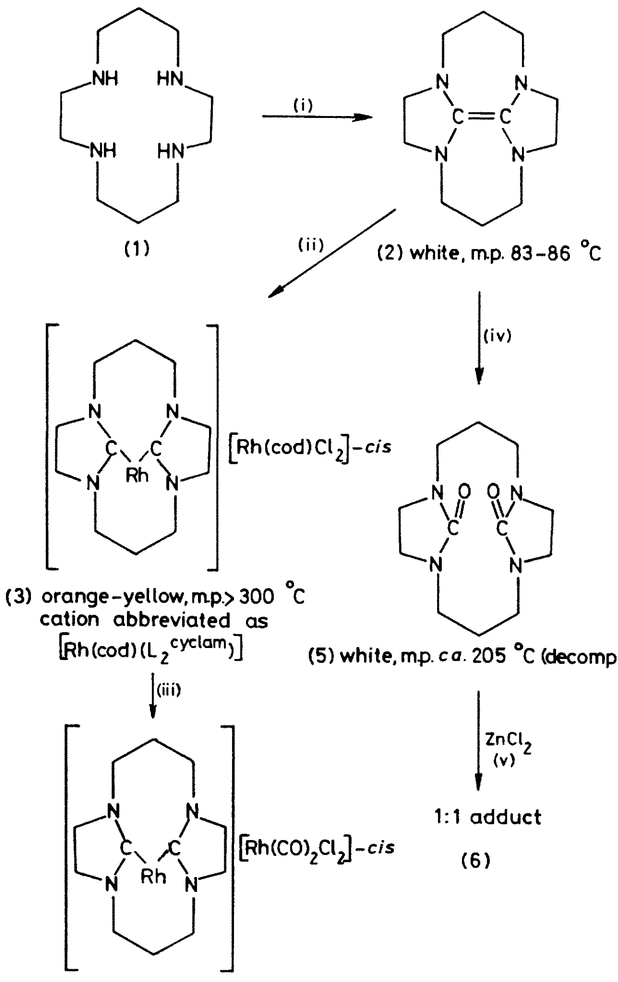
Summary Reaction of 1,4,8,11-tetra-azacyclotetradecane with HC(OMe)$_2$NMe$_2$ yields the olefin (abbreviated as L$_2^{\text{cyclam}}$), formed by filling the macrocyclic cavity with a transannularly bound C=C bond, this being cleaved by (a) insertion therein of a Rh$^{\text{I}}$ moiety upon treatment with [{Rh(cod)Cl}$_2$] (cod = cyclo-octa-1,5-diene) to furnish [Rh(cod)(L$_2^{\text{cyclam}}$)] [Rh(cod)Cl$_2$] (**3**), or (b) oxidation to give a bis(urea), *X*-ray analysis of the chelating dicarbenerhodium(I) complex, obtained from (**3**) and CO, to R = 0·0357, R' = 0·0716, shows Rh–C(carb, av) 2·02 and Rh–(cod)$_{\text{av}}$ 2·20 Å, and C(carb)–Rh–C(carb′) = 78·1(2)°

ELECTRON-RICH olefins, such as [$\overline{\text{MeNCH}_2\text{CH}_2\text{N(Me)C}}$=]$_2$ (abbreviated as L$_2^{\text{Me}}$), are conveniently prepared from the acetal of *N,N*-dimethylformamide and an *N,N′*-dialkyldiamine, such as MeN(H)CH$_2$CH$_2$N(Me)H, they have an extensive transition metal chemistry, *e.g.*, they often give rise to carbene–metal complexes, such as *trans*-$[RhCl(L^{Me})(PPh_3)_2]$.[1] We now report some developments which may lead to significant extensions of this area of chemistry. These are (i) that the secondary diamine may be incorporated within a macrocycle, whence (ii) the derived olefin may form as a consequence of a transannular elimination reaction, and then (iii) give rise to a dicarbene-metal chelate complex effectively by insertion of a metal atom [with appended ligand(s)] into the C=C bond. Further features of considerable potential relate (iv) to alternative reactions of the olefins, *e.g.*, oxidation to a bis(urea) which, indirectly, are novel methods of functionalising the macrocycle.



SCHEME. *Reagents and conditions*: (i) $HC(OMe)_2NMe_2$, EtOH, 90 °C, 2 h, followed by removal of volatiles by distillation and crystallisation (n-pentane); (ii) $[\{Rh(cod)Cl\}_2]$, PhMe, 130 °C, 3 h (cod = cyclo-octa-1,5-diene); (iii) CO through CH_2Cl_2 solution, 15 min, 20 °C; (iv) O_2 through n-pentane solution at 20 °C; (v) EtOH, 20 °C.

Items (i)—(iv) are here illustrated for the case of 1,4,8,11-tetra-azacyclotetradecane ('cyclam'), (**1**), as the macrocycle, and a sequence of reactions (see Scheme) giving rise to the olefin (**2**) (abbreviated as L_2^{cyclam}), the *cis*-dicarbene-rhodium(I) chelate complexes (**3**) and (**4**) containing the cation $[Rh(cod)(L_2^{\text{cyclam}})]^+$ (cod = cyclo-octa-1,5-diene), the bis(urea) (**5**), and its 1:1-adduct with $ZnCl_2$, (**6**). Compounds (**1**)—(**5**) have been characterised by elemental analyses, i.r. and ^1H and ^{13}C n.m.r. spectra, and for the case of the title compound, by details of its molecular structure.

Crystal data: $C_{22}H_{32}Cl_2N_4O_2Rh_2$, $M = 558{\cdot}4$, space group *Pnma*, orthorhombic, $a = 19{\cdot}485(2)$, $b = 13{\cdot}511(2)$, $c = 9{\cdot}889(1)$ Å, $U = 2603{\cdot}4$ Å, $Z = 4$, $D_c = 1{\cdot}42$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 13{\cdot}6$ cm^{-1}.

Data were measured on a Hilger and Watts Y290 diffractometer with monochromated Mo-K_α radiation, and 2328 reflections with $F_o > 6\sigma(F_o)$ were used in the analysis. Anisotropic full matrix refinement of non-hydrogen atoms gave $R = 0{\cdot}0357$, $R' = 0{\cdot}0716$.†

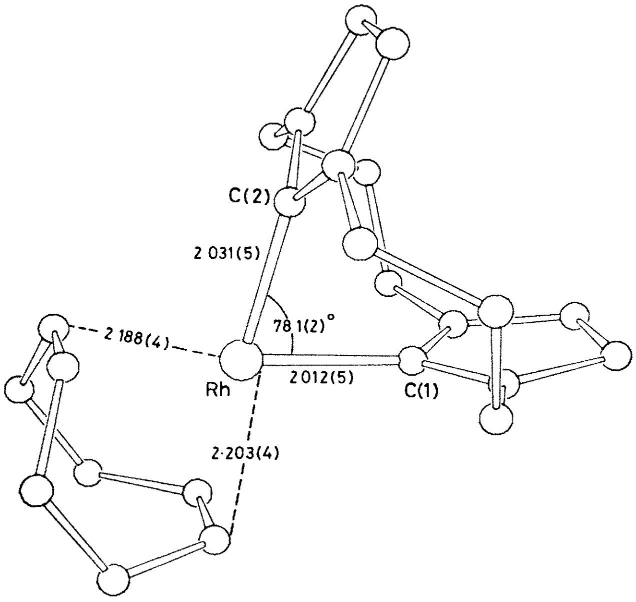


FIGURE. Molecular structure of the cation of $[Rh(cod)(L_2^{\text{cyclam}})][Rh(CO)_2Cl_2]$ (**4**), showing important lengths (Å) and an angle.

The crystallographic mirror plane is coincident with the co-ordination plane of the cation, and at right angles to the co-ordination plane of the anion bisecting the *cis* Rh–Cl bonds. The structure of the cation is shown in the Figure. The chelating Rh–C_{carbene} bond lengths are 2·012(5) and 2·031(5) Å and are constrained by the framework of the ligand to a narrow bite angle C(1)–Rh–C(2) of 78·1(2)°. The N–C_{carbene} bond lengths are unexceptional at 1·336(5) and 1·324(5) Å. The cyclo-octadiene ligand is not skewed and has idealised C_{2v} point-group symmetry with Rh–C bond lengths of 2·188(4) and 2·203(4) Å.

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† The atomic co-ordinates for this work are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] M. F. Lappert, R. W. McCabe, J. J. MacQuitty, P. L. Pye, and P. I. Riley, *J. Chem. Soc., Dalton Trans.*, 1980, 90; and references therein.