Synthesis, Properties, and *X*-Ray Crystal Structure of *trans*-Dichlorotetrakis-(1,3-diethylimidazolidin-2-ylidene)ruthenium(II), a Neutral Tetracarbenemetal Complex†

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Summary Oligocarbeneruthenium(II) complexes, having a high Ru–C_{carb} rotational barrier, have been obtained from $[RuCl_2(PPh_3)_3]$ and an electron-rich olefin $[=\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}]_2$ $(L^R)_2$ (R = Me or Et); these include (i) the unusual (*X*-ray determined) neutral *trans*-$[RuCl_2(L^R)_4]$, (R = Et), which with CO afford *trans*-$[Ru(CO)Cl_2(L^R)_3]$(R = Et) or *trans*-$[Ru(CO)Cl(L^R)_4]^+Cl^-$ (R = Me), (ii) the tri-μ-halogeno- $[Ru_2X_3(L^R)_6]^+X^-$ (X = Cl or I), and (iii) *trans*-$[RuCl(L^R)_4(PF_3)]^+Y^-$ (Y = Cl or BF_4) in which there is long-range F · · · H coupling (^6J).

We briefly report on the chemistry of some oligo(carbene)-ruthenium(II) complexes (see Scheme). The following are noteworthy: (i) the isolation of the first neutral tetracarbenemetal complexes, (II) and (III), and of a tricarbene complex, (VI); (ii) the details of the *X*-ray

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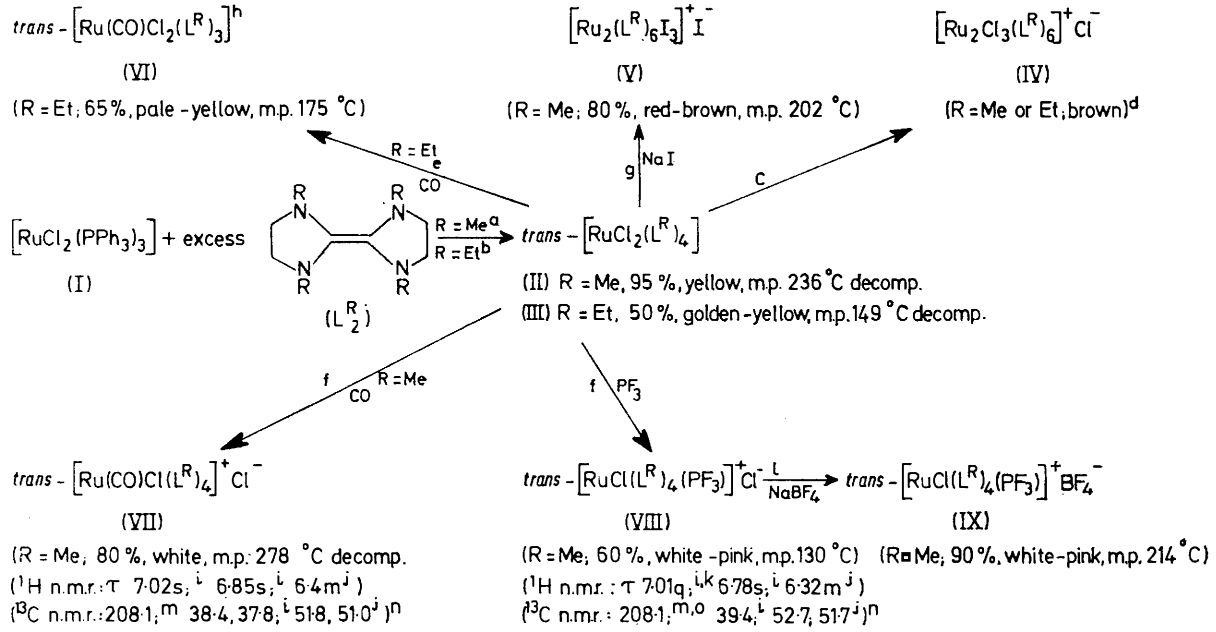
† No reprints available.



SCHEME. The synthesis of, and physical data for, oligocarbeneruthenium(II) complexes. [a] Xylene, 140 °C. [b] MeC_6H_{11}, 100 °C. [c] CH_2Cl_2, 40 °C. [d] Compound not isolated. [e] Toluene or MeC_6H_{11}, 100 °C. [f] $CHCl_3$, 60 °C (or toluene, 110 °C). [g] Acetone, 40 °C. [h] Isomerises *trans* → *cis*, $CHCl_3$, 30 °C. [i] N-CH_3. [j] N-CH_2CH_2N. [k] $^6J(^1H-^{19}F)$ *ca.* 1·5 Hz. [l] Acetone, 25 °C. [m] C_{carb}. [n] P.p.m., $Me_4Si = 0$. [o] ^2J ($^{13}C-^{31}P$) = 16·8 Hz.

crystal and molecular structure of one of the former, (III), showing the four carbene ligands arranged equatorially to the metal in a propeller-like arrangement (previously, *X*-ray data were available only on monocarbenemetal complexes[1]); (iii) the synthesis of cationic oligocarbene-binuclear [(IV) and (V)] and -mononuclear [(VII)—(IX)] ruthenium(II) complexes and their relationship to corresponding tertiary phosphine derivatives (*cf.*, ref. 2); (iv) qualitative differences between the two tetracarbeneruthenium(II) complexes, (II) and (III); (v) high barriers to rotation about the Ru–C_{carb} bonds; and (vi) evidence [$^6J(^1H-^{19}F)$] of long-range F · · · H through-space interaction in compounds (VIII) and (IX).

A few tetracarbenemetal complexes have been reported,[3,4] derived from co-ordinated isonitrile ligands; the cationic character (and also in one case the chelate effect of the carbene unit[3]) may[5] account for their stability (because of the metallo-carbonium ion nature of the carbenemetal bond). The neutral tetracarbeneruthenium(II) complexes, (II) and (III), are conveniently prepared in high (50—90%) yield and purity by the displacement of phosphine ligands from $[RuCl_2(PPh_3)_3]$ (I) with an excess of the electron-rich olefin L^R_2 (R = Me or Et) (see Scheme). Previously we found that L^R_2 affords compounds containing a maximum of three carbene ligands attached to a d^8 metal in a square-planar environment;[5] these were complex cations and their formation was encouraged by a strongly electronegative fourth ligand (CO or H^-). Here, the formation of the neutral octahedral complex may be favoured by the d^6 electronic configuration of Ru^{II}. The mutually *trans* arrangement of the four carbene ligands is unexpected because of the very high σ-donor:π-acceptor ratio of the carbene ligand and the electronegativity of the halide ion.

It is interesting that the reaction of (II) with NaI results in loss of a carbene fragment to form (V), a type of binuclear species well known for Ru^{II} with tertiary alkyl or aryl phosphines (but not Ph_3P).[2] The solution chemistry of the tetracarbene complexes (II) and (III) closely resembles (see Scheme) that of $[RuCl_2(PEtPh_2)_4]$.[2]

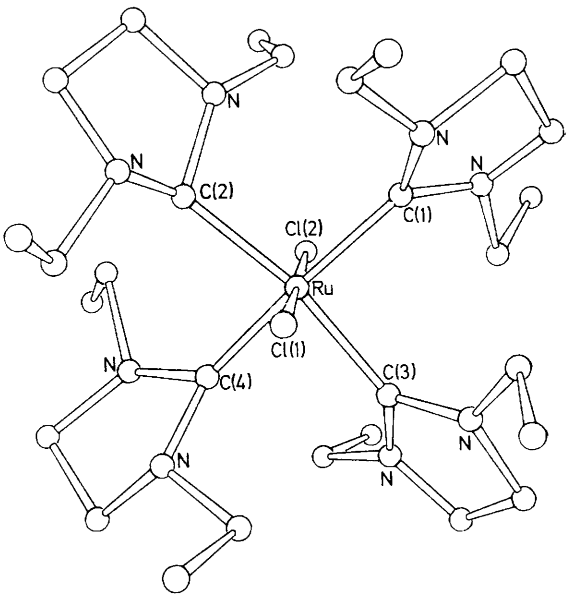


FIGURE. The molecular structure of $[RuCl_2\{\overline{CN(Et)CH_2CH_2N(Et)}\}_4]$. Pertinent bond lengths are Ru–Cl(1), 2·45(2); Ru–Cl(2), 2·44(2); Ru–C(1), 1·88(6); Ru–C(2), 2·07(5); Ru–C(3), 2·12(9); Ru–C(4), 2·00(7) Å.

There is, surprisingly, a significant difference between the chemistry of the Ru^{II} tetracarbene complexes (II) and (III) and this manifests itself most noticeably in their reaction with CO, whereby there is preferential loss of a carbene ligand from (III) but Cl^- is lost from (II), and is probably due to steric rather than electronic factors. This is the first example of a qualitative difference in chemical behaviour between two such similar carbene ligands.[6]

For octahedral compounds (VII)—(IX) which, unlike (II) and (III), have different axial ligands, the ^1H and ^{13}C n.m.r. spectra (see Scheme) indicate a high barrier to rotation around the $Ru–C_{carb}$ bond. For (VIII) and (IX) there is evidence for a through-space (direct) interaction of one set of *N*-Me protons with the F atoms of the PF_3 group as one of the singlets observed in (VII) is seen as a quartet, [$^6J(^1H–^{19}F)$ *ca.* 1·5 Hz].

The crystals of the tetracarbene complex (III) ($C_{28}H_{56}Cl_2N_8Ru$) are monoclinic $P2_1/c$, $a = 15{\cdot}04(1)$, $b = 13{\cdot}44(1)$, $c = 19{\cdot}43(1)$ Å, $\beta = 104{\cdot}8(1)°$, $Z = 4$; $R = 0{\cdot}15$ based on 974 independent reflections measured on a Hilger and Watts Y290 diffractometer with monochromated Mo-K_α *X*-rays. The limited data and relatively high *R* value are a consequence of considerable crystal decomposition during the data collection. Although the overall structure is reliably defined, the individual bond lengths have high e.s.d.'s and therefore it is intended to obtain further data.

The molecule (Figure) has four essentially planar carbene ligands equatorially co-ordinated to the ruthenium atom in a propeller-like arrangement with the plane of each carbene ligand at an angle of about 43° to the equatorial plane. There is therefore minimal possibility of π-bonding interaction between the metal and the carbene ligands.

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[1] *Cf.* J. A. Connor, *Organometallic Chem.*, 1975, **4**, 235, and earlier reviews.
[2] *Cf.* P. W. Armit, A. S. F. Boyd, and T. A. Stephenson, *J.C.S. Dalton*, 1975, **1663**.
[3] D. J. Doonan and A. L. Balch, *Inorg. Chem.*, 1974, **13**, 921.
[4] D. J. Doonan and A. L. Balch, *J. Amer. Chem. Soc.*, 1973, **95**, 4769.
[5] B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Dalton*, 1974, 1827.
[6] *Cf.* M. F. Lappert, *J. Organometallic Chem.*, 1975, **100**, 139.