Spontaneous *N*-Aryl (rather than *P*-Aryl) Orthometallation in the System $[RuCl_2(PPh_3)_3]$–$[{=}CN(Ar)(CH_2)_2NAr]_2$ (Ar = C_6H_4Me-4); *X*-Ray Crystal and Molecular Structure of $[RuCl(PEt_3)_2\{CN(Ar)(CH_2)_2N(C_6H_3Me\text{-}4)\}]$, a Stereochemically Rigid 5-Co-ordinate Ru^{II} Complex, with a Short (2.2 Å) Ru . . . . H Contact†

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Summary A new type of electron-rich olefin reaction is observed by heating $[RuCl_2(PPh_3)_3]$ in boiling xylene with $[{=}CN(Ar)(CH_2)_2NAr]_2$ (Ar = C_6H_4Me-4) to yield the PPh_3 analogue (I) of the title compound (IV) [obtained from (I) + PEt_3]; the *X*-ray crystal structure shows that the latter has a significantly shorter Ru–C_{carb} [1·908(5) Å] than Ru–C_{aryl} [1·994(5) Å] bond, and (IV) and a related compound (III) provide the first examples of stereochemically rigid five-co-ordinate Ru^{II} complexes probably because of an exceptionally close Ru · · · · H contact.

Whereas $[RuCl_2(PPh_3)_3]$ reacts with an aliphatic electron-rich olefin $[{=}CN(R)(CH_2)_2NR]_2$ (R = Me or Et), $L^{Me}{}_2$ or

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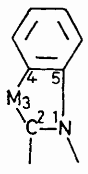
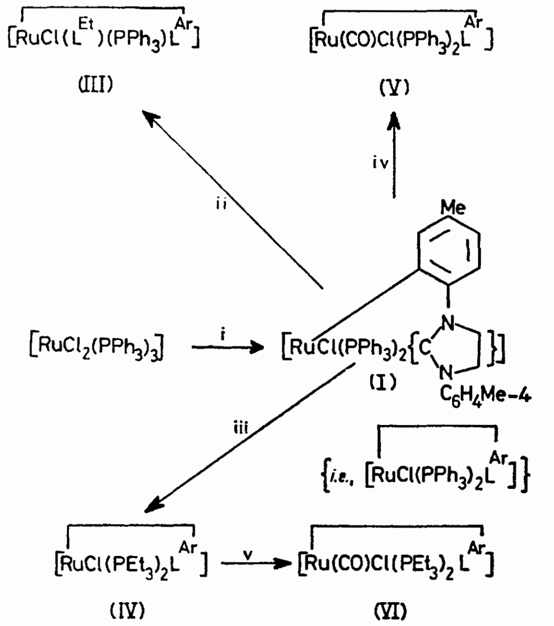
† No reprints available.

L^{Et}_2, in xylene at 140 °C to give the 6-co-ordinate tetracarbeneruthenium(II) complex *trans*-$[RuCl_2(L^R)_4]$,[1] we now find (Scheme) that under similar conditions L^{Ar}_2 (Ar = C_6H_4Me-4) yields $[L^{Ar} - H]^+Cl^-$ and the 5-co-ordinate monocarbeneruthenium(II) complex (I) containing the 3-ruthena-1-aza-4,5-benzocyclopentane nucleus [*cf.* (II)]. One or two triphenylphosphine ligands are displaced by treatment with respectively L^{Et}_2 or PEt_3 to give the 5-co-ordinate ruthenium(II) complexes (III) or (IV). However, the small ligand CO at 25 °C merely adds to (I) or (IV) to yield the appropriate 6-co-ordinate species. Satisfactory microanalyses and spectra (Scheme) were obtained for (I) and (III)—(VI); compounds (III) and (IV) both show invariant ^{13}C n.m.r. behaviour in solution between −90 and +30 °C [*n.b.* relative magnitudes of *cis* and *trans* $^2J(CP)$].



(II)



Scheme. (i) L^{Ar}_2 (Ar = C_6H_4Me-4) in xylene at 140 °C; (ii) L^{Et}_2 in toluene at 110 °C; (iii) PEt_3 in methylcyclohexane at 100 °C; (iv) CO in CH_2Cl_2 or toluene at 25 °C; (v) CO in toluene or methylcyclohexane at 25 °C. (I): 95%, red, m.p. > 340 °C; (III): 80%, orange–brown, m.p. 240 °C, δ (CD_2Cl_2 rel. to Me_4Si), 220.6d [C-2, *cf.* (II)] [^2J(CP) 9·1 Hz, *cis* to PPh_3], 158·2d (C-4) [^2J(CP) 14·4 Hz, *cis* to PPh_3], 213·4d [C_{carb} of L^{Et}] [^2J(CP) 88·5 Hz, L^{Et} *trans* to PPh_3]; (IV): 90%, red, δ ($CD_3C_6D_5$, 223·3*t* (C-2) [^2J(CP) 9·9 Hz] and 157·3t (C-4) [^2J(CP) 12·2 Hz]; (V): 90%, white, decomp. [to yield (I)] *ca.* 260 °C, δ ($CDCl_3$), 216·9t (C-2) [^2J(CP) 9·9 Hz], 202·4t (*C*O) [^2J(CP) 9·9 Hz], and 158·2t (C-4) [^2J(CP) 15·2 Hz]; (VI): 90%, white, m.p. 198 °C, δ ($CDCl_3$), 219·3t (C-2) [^2J(CP) 9·7 Hz], 201·2t (*C*O) [^2J(CP) 10·7 Hz], and 161.2t (C-4) [^2J(CP) 15·2 Hz].

The following are noteworthy: (a) a new type of transition-metal reaction of an electron-rich olefin, in which carbene–metal bond formation is accompanied by *ortho*-metallation; (b) *N*-aryl *ortho*-metallation occurs spontaneously, with L^{Ar}_2 acting also as a dehydrochlorinating reagent; (c) *N*-aryl *ortho*-metallation is preferred over *P*-aryl; (d) compounds (III) and (IV) are unique examples of 5-co-ordinate ruthenium(II) complexes which are stereochemically rigid in solution (*cf.* ref. 2); and (e) the details of the *X*-ray crystal and molecular structure of (IV) (see below), which show *inter alia* that there is an exceptionally close Ru · · · · H contact making the metal environment pseudo-octahedral, a rather short Ru–C_{carb} bond, and an extended coplanar fused tricyclic system with its pendant phenyl group (Figure). Structural data for a metallocycle (II) provide a direct probe into the nature of the M–C_{carb} [C(2) in (II)] bond, both C(2) and C(4) having sp^2-hybridised

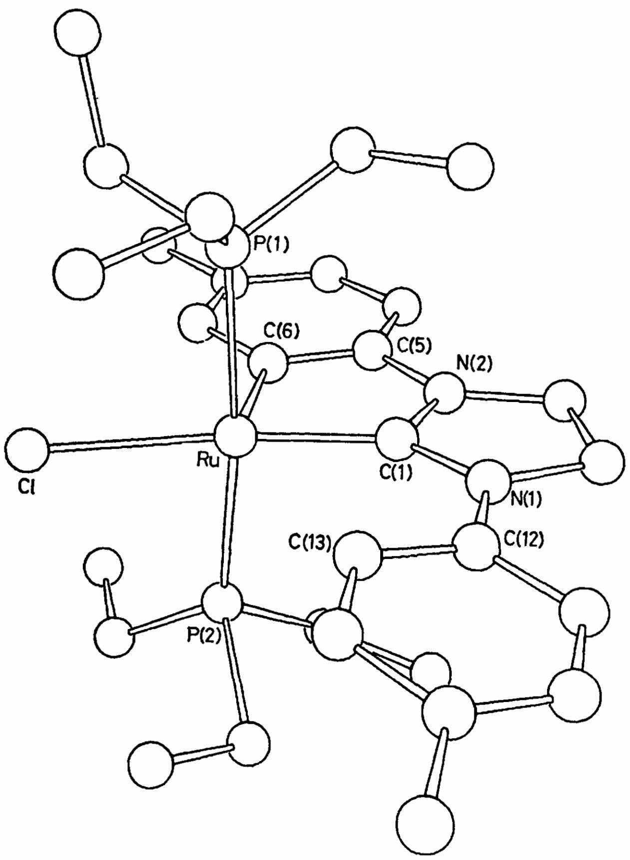


Figure. The molecular structure of $[RuCl(PEt_3)_2\{CN(C_6H_4Me\text{-}4)(CH_2)_2N(C_6H_3Me\text{-}4)\}]$, (IV). Pertinent bond lengths (Å) are Ru–Cl, 2·452(2); Ru–P(1), 2·354(2); Ru–P(2), 2·351(2); Ru–C(6), 1·994(5); Ru–C(1), 1·908(5); and Ru · · · · H(13), 2·2.

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‡ The atomic co-ordinates for this work are available on request 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.

C, without recourse to an external reference, whence we conclude that there is significant Ru $\cdots\cdot$ C_{carb} double bond character.

There is a single previous case of a metallocycle (II), $[\mathrm{PtCl_2(PEt_3)_2\{C(NHC_6H_3Cl\text{-}4)NHMe\}}]^+$, with Pt–C(2) = 1·985(16) and Pt–C(4) = 2·033(13) Å.[3] Point (c) contrasts with the $[\mathrm{Ru(H)Cl(PPh_3)_3}]$–olefin reaction,[4] which led to *P-ortho*-metallation [*cf.*, ref. 5 for a $\mathrm{Ru^{II}}$–$\mathrm{P(OPh)_3}$ reaction yielding an *O-ortho*-metallated product].

Crystal data: compound (IV): $C_{29}H_{47}ClN_2P_2Ru$, *M* 622·3, triclinic, space group $P\bar{1}$, $a = 12{\cdot}342(4)$, $b = 16{\cdot}387(6)$, $c = 9{\cdot}686(3)$ Å; $\alpha = 65{\cdot}41(2)$, $\beta = 117{\cdot}97(2)$, $\gamma = 103{\cdot}79(2)^\circ$; $Z = 2$.‡

The structure has been refined to a current R_F of 0·066 with Ru, Cl, and P anisotropic, based on 3035 reflections measured on a Hilger and Watts four-circle diffractometer with monochromated Mo-K_α radiation. The ethyl groups on P(2) are disordered and for clarity only one set of possible sites is shown in the Figure. The carbene ligand has a geometry similar to that seen in its complexes with $\mathrm{Pt^{II}}$,[6] except that the phenyl rings are coplanar with the carbene ring system. The Ru–C_{carb} bond is 1·908(5) Å, one of the shortest such bonds so far reported, and significantly shorter than the Ru–C bond [1·994(5) Å] to the metallated phenyl ring. The difference in *trans* ligand sites would not be expected to cause such an effect.

The calculated position for H(13) attached to C(13) assuming normal phenyl ring geometry (C–H, 1·08 Å) puts it in the vacant octahedral co-ordination site of the ruthenium with the very short Ru $\cdots\cdot$ H(13) distance of 2·2 Å. Similar short M $\cdots\cdot$ H interactions seen in dialkyldi-1-pyrazolyl borate complexes of molybdenum were suggested to be due to the formation of a 3-centre-2-electron bond with a hydrogen atom of the B–C–H ligand unit.[7] It appears that the favourable geometry in our *ortho*-metallated-carbene complex enables the ruthenium to achieve a formal 18e inert gas configuration by means of a similar Ru $\cdots\cdot$ H–C interaction.

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[1] P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Chem. Comm.*, 1976, 644.
[2] P. W. Armit, A. S. F. Boyd, and T. A. Stephenson, *J.C.S. Dalton*, 1975, 1663.
[3] K. W. Muir, R. Walker, J. Chatt, R. L. Richards, and G. H. D. Royston, *J. Organometallic Chem.*, 1973, **56**, C30.
[4] B. R. James, L. D. Markham, and D. K. W. Wang, *J.C.S. Chem. Comm.*, 1974, 439.
[5] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 639.
[6] Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 2427.
[7] F. A. Cotton, T. La Cour, and A. G. Stanislowski, *J. Amer. Chem. Soc.*, 1974, **96**, 754; and refs. therein.