

Synthesis, nucleophilic attack on, and rearrangement of cationic ruthenafurans: X-ray crystal structures of $[\text{Ru}(\text{CO})_2\{\text{C}(\text{Ph})\text{NHCMe}_3\}(\text{CH}_2\text{CO}_2\text{Et})(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$ and $[\text{Ru}(\text{CO})_2\{\text{C}(\text{Me})=\text{CHC}(\text{O})\text{OEt}\}(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$

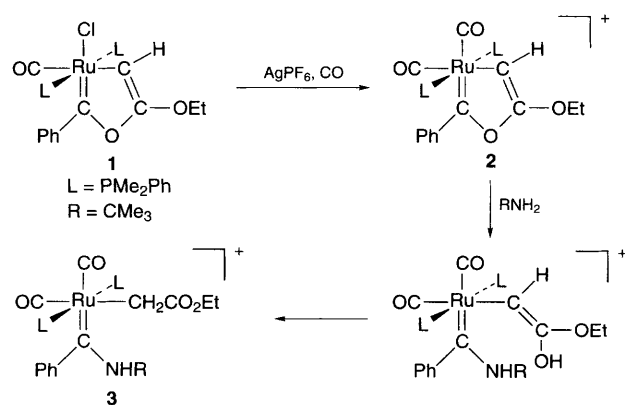
Paul D. Morran, Roger J. Mawby,* Giles D. Wilson and Madeleine H. Moore

Department of Chemistry, University of York, York, UK YO1 5DD

The methyl-substituted ruthenafuran **5** rearranges at room temperature by dismantling and reassembly of the five-membered ring, yielding **7** and then **8**: the conversion is catalysed by Me_3CNH_2 ; in contrast Me_3CNH_2 attacks **2**, the phenyl analogue of **5**, to give a stable non-cyclic aminocarbene complex **3**.

We have recently reported the synthesis of a range of novel ruthenium carbene complexes in which the metal–carbene unit forms part of a ruthenafuran ring.¹ The carbene atom in these complexes does not appear to be susceptible to nucleophilic attack: thus, for example, complex **1** (see Scheme 1), obtained from $[\text{Ru}(\text{CO})_2\text{PhCl}(\text{PMe}_2\text{Ph})_2]$ and $\text{EtOC}\equiv\text{CH}$, does not react with amines. In contrast, the cationic complex **2**, prepared by treating **1** with AgPF_6 in propanone solution under CO, reacted with Me_3CNH_2 to yield the non-cyclic aminocarbene complex **3**: similar products were formed with NH_3 and other primary amines. The X-ray crystal structure of the PF_6^- salt of **3**,[†] obtained by crystallisation from propanone–ethanol, is shown in Fig. 1. The carbene carbon atom and those atoms to which it is attached are essentially coplanar (maximum deviation 0.03 Å), but this plane is twisted out of that defined by Ru, C(17) and C(28) by 28°, and the phenyl substituent is itself twisted out of the carbene plane by 82°, evidently by steric constraints. The metal–carbene bond $\text{Ru}-\text{C}(17)$ [2.140(6) Å] is much longer than the corresponding bond in **1** [1.935(4) Å],¹ reflecting decreased back-donation from the metal, but significant π donation from nitrogen to carbon is suggested by the shortness of $\text{N}(1)-\text{C}(17)$ [1.290(8) Å]. Similar effects have been observed in other aminocarbene complexes of ruthenium(II).² The proximity of N(1) and O(1) suggests that the hydrogen attached to N(1) is also hydrogen-bonded to O(1).

A plausible mechanism for the conversion of **2** into **3** is shown in Scheme 1. Nucleophilic attack results in ring-opening and proton transfer from nitrogen to oxygen, followed by tautomerisation of the hydroxyvinyl ligand.



Scheme 1

An attempt to convert **4**, the methyl analogue of **1**, into the cationic complex **5** (see Scheme 2) by treatment with AgPF_6 under CO instead yielded $[\text{Ru}(\text{CO})_3\text{Me}(\text{PMe}_2\text{Ph})_2]^+$ **6**, also

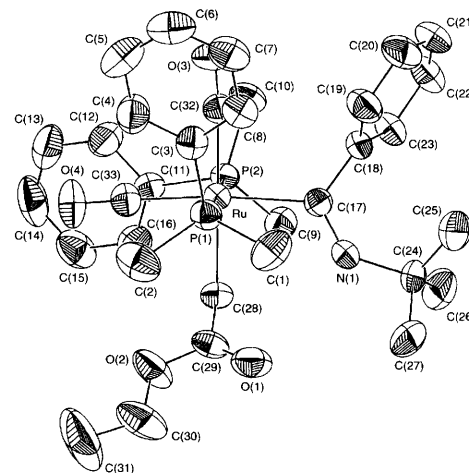
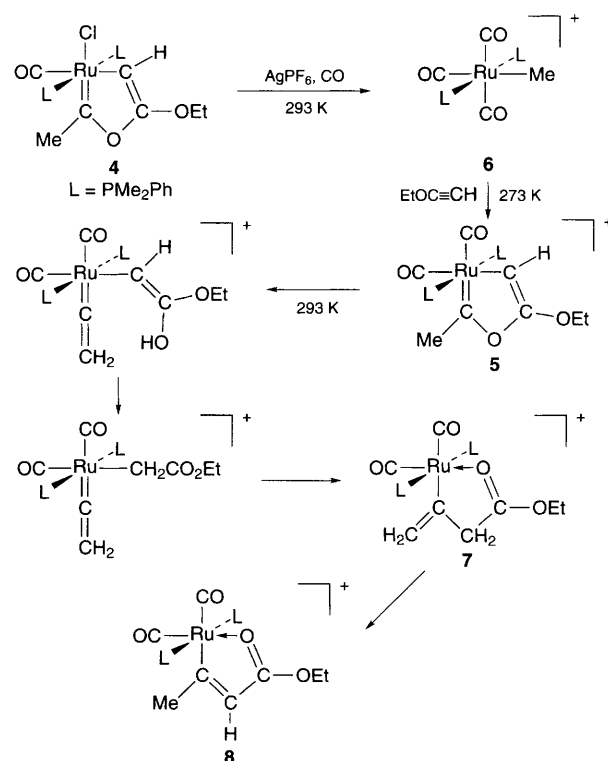


Fig. 1 Crystal structure of **3**



Scheme 2

accessible by similar treatment of $[\text{Ru}(\text{CO})_2\text{MeCl}(\text{PMe}_2\text{Ph})_2]$. Complex **5** is almost certainly an intermediate in the conversion of **4** into **6**, since **5** was formed when an excess of $\text{EtOC}\equiv\text{CH}$ was added to a CD_3COCD_3 solution of **6** at 273 K. When this solution was warmed to room temperature, **5** was not re-converted into **6**: instead the metallacycle rearranged to give a new cyclic complex **7** which itself rearranged more slowly to **8** (see Scheme 2).

The structure of **8** (see Fig. 2) was established by an X-ray study† of its PF_6^- salt, obtained by crystallisation from methylbenzene–propanone. The geometry around the metal is somewhat distorted from a regular octahedron, most notably where the constraints of the five-membered ring reduce the $\text{C}(19)\text{—Ru—O}(3)$ angle to $78.4(2)^\circ$. The ring is essentially planar, the largest torsion angle being 2° , and the other angles within it range from $111.3(4)^\circ$ for $\text{C}(22)\text{—O}(3)\text{—Ru}$ to $121.6(5)^\circ$ for $\text{O}(3)\text{—C}(22)\text{—C}(21)$. The fact that the torsion angle $\text{C}(23)\text{—O}(4)\text{—C}(22)\text{—C}(21)$ is only 3° suggests that there may be some π interaction between $\text{O}(4)$ and the ring. Various features indicate (see Fig. 3) that **8** is best regarded as a hybrid of resonance structures **8A** and **8B**. Although **8B** is clearly the minor contributor, its significance is shown by the fact that $\text{Ru—C}(19)$ [$2.086(6)$ Å] is actually shorter than the formal double bond to the carbene ligand in **3**, by the relatively small difference in bond lengths between $\text{C}(19)\text{—C}(21)$ [$1.353(9)$ Å] and $\text{C}(21)\text{—C}(22)$ [$1.420(9)$ Å], and by the unusually large chemical shift for the metal-bound carbon atom (δ 227.5). In contrast, the corresponding C—C bonds within the ring in $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CHC}(\text{O})\text{OMe}\}(\text{PMe}_2\text{Ph})_2][\text{HgCl}_3]$ show a much more marked difference in length, and the chemical shift for the metal-bound carbon atom (δ 203.1) is more normal.³ A further sign of the strong π interaction between the metal and $\text{C}(19)$ in **8** is the unusually long bond $[\text{Ru—C}(17), 1.978(7)$ Å] to the carbonyl ligand *trans* to $\text{C}(19)$: the bond to the other carbonyl ligand $[\text{Ru—C}(18), 1.844(7)$ Å] is appreciably shorter.

Complex **7** could not be isolated, but was assigned the structure shown in Scheme 2 on the basis of NMR evidence: in

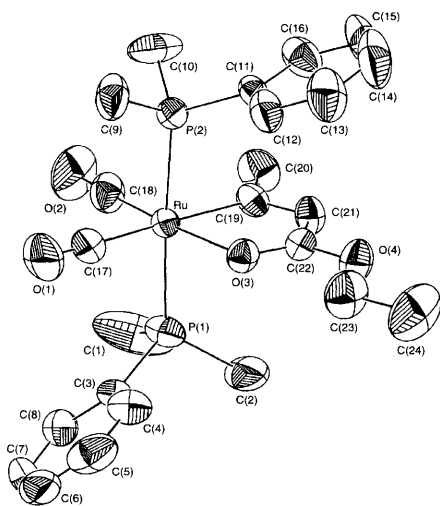


Fig. 2 Crystal structure of **8**

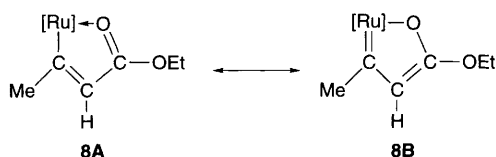


Fig. 3 Resonance structures for **8**

the ^1H spectrum, for example, resonances with the expected splitting patterns were observed for the two inequivalent vinyl protons at δ 5.73 and 5.25 and for the CH_2 group within the ring at δ 2.83. The mechanism proposed for the conversion of **5** into **7** involves an initial proton transfer from the methyl group in **5** to the oxygen in the metallafuran ring, resulting in cleavage of the ring and formation of vinylidene and hydroxyvinyl ligands. Tautomerisation of the latter (*cf.* Scheme 1) is followed by migration of the resulting alkyl ligand onto the α -carbon of the vinylidene unit and ring closure to generate **7**. There are several examples of this type of migration in the literature.^{4–8} Conversion of **7** into **8** involves a 1,3-hydrogen shift. Overall, the effect of the rearrangement **5** \rightarrow **8** is to interchange the positions of two non-adjacent atoms in the original metallacycle, in the process completely separating the carbon and oxygen atoms of the carbonyl ligand used in its construction.

Two other points are of interest. Firstly, **2** cannot rearrange by this mechanism since no proton is available for the initial step. Secondly, whereas amines attack **2** to give amino-carbene complexes (see Scheme 1), Me_3CNH_2 simply catalyses the rearrangement of **5** to **8**, presumably by assisting both the initial proton transfer and the final 1,3-shift which converts **7** into **8**.

We thank the EPSRC for a grant to P. D. M. and Johnson Matthey PLC for a loan of ruthenium chloride.

Footnote

† Crystal data for **3** and **8**: For both compounds, crystallographic measurements were made at 293 K on a Rigaku AFC6S diffractometer using $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71070$ Å. The structures were solved by heavy-atom Patterson methods,⁹ and expanded using Fourier techniques.¹⁰ Refinement was carried out using SHELXL93.¹¹

For **3**: $\text{C}_{33}\text{H}_{44}\text{F}_6\text{NO}_4\text{P}_3\text{Ru}$, $M = 826.67$, orthorhombic, space group $P2_12_12_1$, $a = 15.347(5)$, $b = 21.964(5)$, $c = 11.109(3)$ Å, $Z = 4$, $D_c = 1.466$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 6.13$ cm^{-1} , $U = 3745(2)$ Å³, 4415 unique reflections out of 4999 measured, $F(000) = 1696$. $R1 = 0.0390$ ($wR2 = 0.0910$) for $I > 4\sigma(I)$.

For **8**: $\text{C}_{24}\text{H}_{31}\text{F}_6\text{O}_4\text{P}_3\text{Ru}$, $M = 691.47$, monoclinic, space group $P2_1/c$, $a = 8.928(4)$, $b = 20.293(5)$, $c = 17.088(5)$ Å, $\beta = 103.40(3)^\circ$, $Z = 4$, $D_c = 1.525$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 7.44$ cm^{-1} , $U = 3012(2)$ Å³, 5287 unique reflections out of 5829 measured, $F(000) = 1400$. $R1 = 0.0490$ ($wR2 = 0.1230$) for $I > 4\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- M. P. Waugh, P. D. Morran, R. J. Mawby, F. C. F. Körber, A. J. Reid and C. D. Reynolds, *J. Chem. Soc., Chem. Commun.*, 1995, 941.
- M. A. Gallop and W. R. Roper, *Adv. Organomet. Chem.*, 1986, **25**, 121.
- J. R. Crook, B. Chamberlain, R. J. Mawby, F. C. F. Körber, A. J. Reid and C. D. Reynolds, *J. Chem. Soc., Dalton Trans.*, 1992, 843.
- R. Wiedemann, P. Steinert, M. Schäfer and H. Werner, *J. Am. Chem. Soc.*, 1993, **115**, 9864.
- R. G. Beevor, M. J. Freeman, M. Green, C. E. Morton and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1985, 68.
- A. Höhn and H. Werner, *J. Organomet. Chem.*, 1990, **382**, 255.
- H. E. Selnau and J. S. Merola, *J. Am. Chem. Soc.*, 1991, **113**, 4008.
- M. Schäfer, J. Wolf and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1991, 1341.
- Fan Hai-Fu, SAPI91, Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan, 1991.
- P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF Program System, Technical Report of the Crystallographic Laboratory, University of Nijmegen, The Netherlands, 1992.
- G. M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.

Received, 4th August 1995; Com. 5/05228I