Reversible Cyclisation Reactions to Form Ruthenafurans: X-Ray Crystal Structure of [Ru(CO){C(Ph)OC(OEt)=CH}Cl(PMe$_2$Ph)$_2$]

Martin P. Waugh,[a] Paul D. Morran,[a] Roger J. Mawby,*[a] Fritjof C. F. Körber,[b] Amanda J. Reid[b] and Colin D. Reynolds[b]

[a] *Department of Chemistry, University of York, York, UK YO1 5DD*
[b] *School of Biomolecular Sciences, John Moores University, Byrom Street, Liverpool, UK L3 3AF*

Ruthenafurans [Ru(CO){C(R)OC(OEt)=CH}ClL$_2$] (L = PMe$_2$Ph, R = CH=CHOEt, CH=CHCMe$_3$, Me or Ph; L = PMe$_3$, R = CH=CHOEt or CH=CHPh) can be formed reversibly from [Ru(CO)$_2$RClL$_2$] and EtOC≡CH: the rate-determining forward step involves the formation of the intermediate [Ru(CO)(COR)ClL$_2$], which can be trapped when the reverse reaction occurs in the presence of Me$_3$CNC.

We report unusual and reversible cyclisation reactions in which metallafuran complexes are created. These complexes contain a bidentate ligand which has a carbene unit at one end and a vinyl group at the other.

Reaction of complexes [Ru(CO)$_2$ClHL$_2$] (L = PMe$_2$Ph or PMe$_3$) with alkynes XC≡CH (X = H, alkyl or aryl) is an effective route to vinyl complexes [Ru(CO)$_2$(CH=CHX)ClL$_2$].[1] We have found, however, that the complexes [Ru(CO)$_2$(CH=CHOEt)ClL$_2$] react with a further molecule of EtOC≡CH. This second reaction is fairly general: complexes [Ru(CO)$_2$RClL$_2$] (L = PMe$_2$Ph, R = CH=CHCMe$_3$, Me or Ph; L = PMe$_3$, R = CH=CHPh) all reacted with EtOC≡CH in C_6D_6 to yield products which appeared to be of the same basic type (for example, ^{13}C NMR spectra of the products all contained a resonance between δ 279 and 302). The use of EtOC≡CH was, however, crucial: for example, [Ru(CO)$_2$(CH=CHOEt)Cl(PMe$_2$Ph)$_2$] did not react with Me$_3$CC≡CH.

Isolation of the complexes was frustrated by the reversibility of the reactions by which they were formed, with slow polymerisation of free EtOC≡CH drawing the equilibrium back to [Ru(CO)$_2$RClL$_2$]. Thus pure [Ru(CO)$_2$MeCl(PMe$_2$Ph)$_2$] was obtained from an attempted recrystallisation of the product of its reaction with EtOC≡CH. In the case of [Ru(CO)$_2$PhCl(PMe$_2$Ph)$_2$] **1**, however, both the forward reaction and the reverse process were substantially slower, and red crystals of the product **2** were obtained from benzene–ethanol solution.

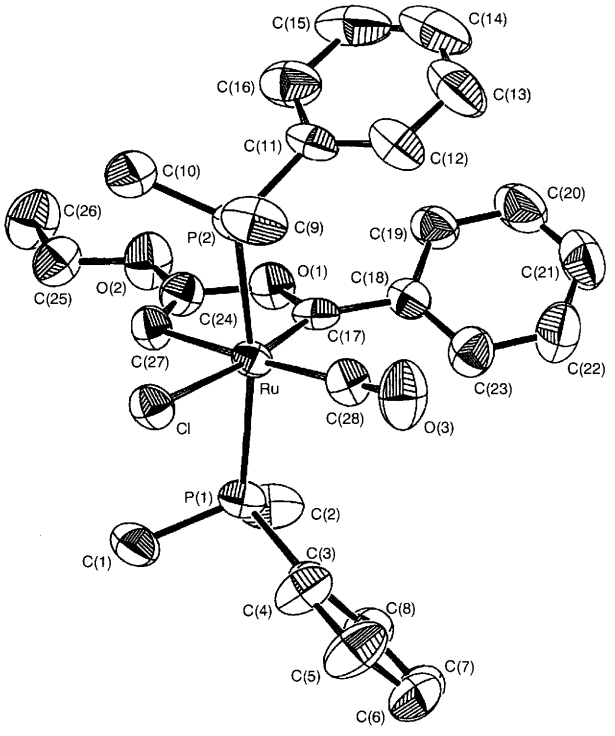

Fig. 1 Crystal structure of **2**

Elemental analysis revealed that the reaction stoichiometry was simply a 1 : 1 addition, and X-ray investigation† showed that **2** possesses the structure depicted in Fig. 1. The largest deviation from regular octahedral geometry around the metal is shown by the angle C(17)–Ru–C(27) [78.3(2)°], and this is also the smallest angle within the essentially planar metallafuran ring, the other angles ranging from 111.5(3) to 119.0(3)°. Despite the presence of the oxygen substituent on the carbene carbon atom, the bond to the carbene unit Ru–C(17) [1.935(4) Å] is significantly shorter than a normal Ru–C single bond to an sp^2 hybridised carbon atom [for comparison, the length of the bond to the vinyl group, Ru–C(27), is 2.106(4) Å], and it falls within the range of other ruthenium(II)–carbon bonds which have been ascribed double bond character, in complexes such as [Ru(CO){C(C$_6$H$_4$PPh$_2$)$_2$}Br$_2$],[2] [Ru(CO){CF(OCH$_2$CMe$_3$)}Cl$_2$(PPh$_3$)$_2$][3] and [Ru(CO){CN(C$_6$H$_4$Me)CH$_2$CH$_2$N(C$_6$H$_3$Me)}Cl(PEt$_3$)$_2$].[4] There is also, however, some shortening of the bond C(17)–O(1) [1.351(4) Å] relative to the other C–O bond within the ring [C(24)–O(1), 1.407(4) Å]. From the many features common to the NMR spectra of the products of the reactions of all the complexes [Ru(CO)$_2$RClL$_2$] with EtOC≡CH, including the extremely low-field resonance for the carbene carbon atom, it is evident that all are metallafuran complexes. A somewhat similar complex has been reported by Roper and Wright,[5] but the synthesis involved modification of a complex [Ru(CO)(CCl$_2$)Cl$_2$(PPh$_3$)$_2$] which already contained a carbene ligand.

A kinetic study was made of the reaction between **1** and EtOC≡CH in CHCl$_3$ solution (in which **2** is again formed), by monitoring the disappearance of the 2043 cm^{-1} band in the IR spectrum of **1**. Nine runs at 323.0 K, each with an initial concentration of **1** of *ca.* 5.8 × 10^{-3} mol dm^{-3}, but with initial EtOC≡CH concentrations varying from 5.87 × 10^{-2} to 1.73 × 10^{-1} mol dm^{-3}, gave first-order rate constants all between 4.00(2) × 10^{-4} and 4.12(2) × 10^{-4} s^{-1}, establishing that the reaction is zero order in HC≡COEt. Activation parameters, based on runs at nine temperatures between 313.0 and 329.0 K, were $\Delta H^{\ddagger}$ = 85.5(7) kJ mol^{-1} and $\Delta S^{\ddagger}$ = −46(2) J mol^{-1} K^{-1}.

A mechanism compatible with these results is shown in eqns. (1) and (2), where, under the conditions of the kinetic

$$[Ru(CO)_2PhCl(PMe_2Ph)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(CO)(COPh)Cl(PMe_2Ph)_2] \quad (1)$$

$$[Ru(CO)(COPh)Cl(PMe_2Ph)_2] + EtOC{\equiv}CH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ru(CO)\{C(Ph)OC(OEt){=}CH\}Cl(PMe_2Ph)_2] \quad (2)$$

runs, k_2[EtOC≡CH] is much greater than k_1, k_{-1} or k_{-2} {it is, of course, possible that cyclisation is preceded by formation of [Ru(CO)(COPh)(η^2-EtOC≡CH)Cl(PMe$_2$Ph)$_2$]}. The rate-determining step (k_1) involves combination of phenyl and carbonyl ligands, with a negative value for $\Delta S^{\ddagger}$ reflecting the formation of a three-membered ring in the activated state.

Intriguingly, there are several other examples in the literature[6–9] of reactions involving cyclisation by combination of an alkyl or aryl ligand, a carbonyl ligand and an alkyne which also appear to proceed *via* acyl intermediates, but in each case subsequent insertion of the alkyne into the metal–acyl bond and ring closure by coordination of the acyl oxygen yields M←O=C–C=C, not M=C–O–C=C.

We have previously shown[10] that **1** reacts with Me_3CNC in $CHCl_3$ in two competing processes, each first-order in **1** and zero-order in Me_3CNC. One yields the carbonyl substitution product $[Ru(CO)(CNCMe_3)PhCl(PMe_2Ph)_2]$, the other the benzoyl complex $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]Cl$. No intermediate was observed in the formation of the latter product, making a definite identification of the initial and rate-determining step impossible. From measurement of the overall rate constant (4.90×10^{-5} s^{-1}) at 298.3 K and of the relative amounts of the two products formed, the rate constant for formation of the benzoyl complex was estimated to be 2.72×10^{-5} s^{-1}, in excellent agreement with an extrapolated value of 2.66×10^{-5} s^{-1} for the rate constant for the reaction between **1** and EtOC≡CH at this temperature. Clearly combination of phenyl and carbonyl ligands is the first and rate-determining step for both reactions.

We have found no evidence for nucleophilic attack on the carbene carbon atom in **2**. Amines, PMe_2Ph and Me_3CNC failed to react with **2** at room temperature. At 323 K PMe_2Ph yielded $[Ru(CO)PhCl(PMe_2Ph)_3]$ by reformation and subsequent reaction of **1**, while Me_3CNC yielded $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]Cl$ and then $[Ru(CNCMe_3)_3(COPh)(PMe_2Ph)_2]Cl$ but no $[Ru(CO)(CNCMe_3)PhCl(PMe_2Ph)_2]$, proving that the acyl intermediate $[Ru(CO)(COPh)Cl(PMe_2Ph)_2]$ is trapped by the Me_3CNC before it can revert to **1**.

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Footnote

† *Crystal data*: $C_{28}H_{33}ClO_3P_2Ru$, M = 616.04, monoclinic, space group $P2_1/c$, a = 11.416(3), b = 14.044(4), c = 18.103(4) Å, β = 91.40(2)°, Z = 4, D_c = 1.412 g cm^{-3}, μ(Mo-Kα) = 7.56 cm^{-1}, U = 2902(1) $Å^3$, 3640 observed out of 5647 measured reflections [$I > 3.0\sigma(I)$], $F(000)$ = 1268. Data were measured on a Rigaku AFC6S diffractometer. The structure was solved by direct methods with full-matrix least squares refinement to give R = 0.033, R_w = 0.034. All crystallographic calculations were performed using the TEXSAN software package.[11] 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.

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