C–C Bond Formation and C–H Bond Cleavage in Redox Reactions of Ruthenium Complexes

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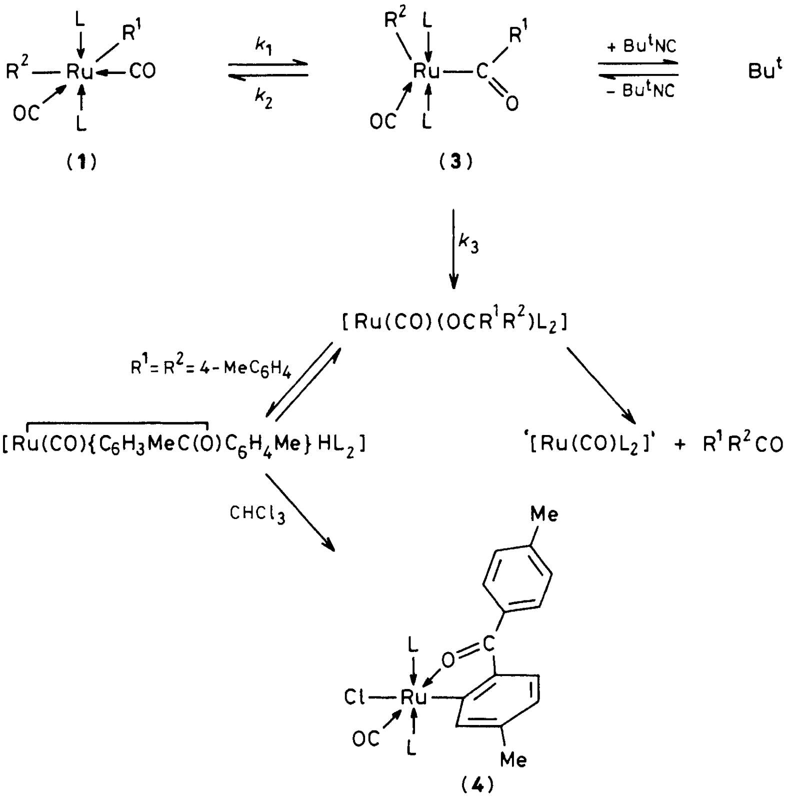
Complexes $[Ru(CO)_2R^1R^2(PMe_2Ph)_2]$ decompose intramolecularly in $CHCl_3$ to yield ketones R^1R^2CO; the complex $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ (**1a**) also yields $[\overline{Ru(CO)\{C_6H_3MeC(O)}C_6H_4Me\}Cl(PMe_2Ph)_2]$ (**4**).

Since the early discovery by Chatt and Davidson[1] of an equilibrium between $[Ru(RH)(Me_2PCH_2CH_2PMe_2)_2]$ (RH = arene) and $[Ru(R)(H)(Me_2PCH_2CH_2PMe_2)_2]$, oxidative addition to ruthenium(0) and reductive elimination from ruthenium(II) complexes have received much less attention than the corresponding reactions of the iso-electronic rhodium(I) and rhodium(III) complexes. Here we report examples of reductive elimination by C–C bond formation and an apparent oxidative addition by C–H bond cleavage.

Complexes $[Ru(CO)_2R^1R^2(PMe_2Ph)_2]$ (**1a**—**c**) (see Scheme 1) decompose in $CHCl_3$ or $CDCl_3$ solution at 298 K to yield ketones R^1R^2CO. Decomposition is intramolecular, since (**1c**) yields *only* $(4\text{-}MeOC_6H_4)(4\text{-}MeC_6H_4)CO$, and the disappearance of (**1a**) follows simple first-order kinetics. As shown in Scheme 1, where L = PMe_2Ph, complexes (**1a**—**c**) react with Bu^tNC to form $[Ru(CO)(CNBu^t)(COR^1)R^2(PMe_2Ph)_2]$, (**2a**—**c**), by a two-step mechanism, the first step involving formation of the acyl species $[Ru(CO)(COR^1)R^2(PMe_2Ph)_2]$ (**3a**—**c**).[2] We believe that these are the species from which ketone elimination occurs, so that the overall first-order rate constant for decomposition is $k_1k_3/(k_2 + k_3)$. At 298.3 K in $CHCl_3$ solution the rate constant for decomposition of (**1a**) is $2.30 \times 10^{-6}\,s^{-1}$, and the value of k_1 is known[2] to be $2.02 \times 10^{-4}\,s^{-1}$, giving a value for the ratio $k_3/(k_2 + k_3)$ of 1.14×10^{-2}.

Complex (**2a**) also decomposes in $CHCl_3$ solution to yield ketone: the decomposition is inhibited by free Bu^tNC, indicating (see Scheme 1) that reductive elimination must be preceded by loss of isonitrile, despite the fact that one might expect both the steric effect and the π-acceptor ability of the isonitrile to promote reductive elimination. Possibly there are electronic factors favouring elimination from a five- rather than a six-co-ordinate species [as there are, apparently, for elimination from three- rather than four-co-ordinate palladium(II)].[3,4] Alternatively the acyl ligands in intermediates (**3a**—**c**) may actually be bound to ruthenium through both carbon *and* oxygen,[5,6] and this may lower the activation energy for attack by R^2.



L = PMe_2Ph

a; $R^1 = R^2 = 4\text{-}MeC_6H_4$
b; $R^1 = R^2 = Me$
c; $R^1 = 4\text{-}MeOC_6H_4$, $R^2 = 4\text{-}MeC_6H_4$

Scheme 1

In an attempt to trap the ruthenium product of the reaction, decomposition of (**1a**) was carried out in $CHCl_3$ at 308 K in the presence of $PhC\equiv CPh$. Removal of $CHCl_3$ under reduced pressure and treatment of the residue with an ethanol–propanone mixture yielded red crystals of $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$ (**4**), the structure of which was determined by *X*-ray crystallography.[7] Subsequent experiments showed that (**4**) was formed even if $PhC\equiv CPh$ was not present, and that the yield of (**4**) increased (and that of ketone decreased) with increasing temperature. We believe that the ketone, while still bound to Ru^0, adds oxidatively to yield $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}H(PMe_2Ph)_2]$ and that subsequent reaction with $CHCl_3$ replaces hydride by chloride [complete separation of ketone and Ru^0 species evidently does *not* occur prior to oxidative addition, since decomposition of (**1b**) in the presence of $(4\text{-}MeC_6H_4)_2CO$ does not yield (**4**)]. It may be that {as in the case of $[Ru(RH)(Me_2PCH_2CH_2PMe_2)_2]$[1]} the oxidative addition is reversible, and that replacement of hydride by chloride is needed to keep the ruthenium in the +2 state. This would explain why no Ru^{II} product could be isolated when (**1a**) was allowed to decompose in propanone, although $(4\text{-}MeC_6H_4)_2CO$ was still formed.

We thank the S.E.R.C. for a maintenance grant (to D. R. S.).

Received, 2nd August 1983; Com. 1041

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