Inorganica Chimica Acta, 132 (1987) 157–159

Reactivity of PPh_3 Towards $Ru_2Cl(O_2CR)_4$ (R = Me, Ph) in Alcoholic Medium: a Novel Decarbonylation Process Mediated by a Diruthenium Compound

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(Received March 11, 1987)

An interesting aspect of diruthenium(II, III) chemistry [1, 2] is the study of the reactivity of $Ru_2Cl(O_2CR)_4$ towards PPh_3. The reactivity patterns observed [3] in Ru_2 chemistry are quite different from other M_2 systems (M = Cr, Mo, Rh, Re, etc.). Earlier attempts [4–8] to prepare $Ru_2(O_2CMe)_4(PPh_3)_2$ lead to the formation of oxo-bridged diruthenium and triruthenium compounds. The change in reactivity is also dramatic on changing the bridging ligands, e.g. the product in the reaction between $Ru_2Cl(ArCONH)_4$ and PAr'_3 is $Ru_2(Ar')_2(ArCONH)_2[Ar'_2POC(Ar)N]_2$ [9, 10]. We have studied a similar reaction using $Ru_2Cl(O_2CR)_4$ but the products are monomeric and contain a carbonyl ligand. We report in this communication our preliminary observations which exemplify an unusual decarbonylation process involving for the first time a Ru–Ru multiple bonded species.

Results and Discussion

Under aerobic conditions when $Ru_2Cl(O_2CR)_4$ (R = Me [8], R = Ph [9]) was reacted with PPh_3 in boiling alcohol, $R'CH_2OH$ (R' = H, Me, Pr), a dark colored solution was obtained. Continuation of the reflux caused a change in the solution color to yellow along with the formation of yellow microcrystalline product (yield of isolated compounds: *ca.* 60% in MeOH, *ca.* 40% in EtOH and BuOH). The reaction rate which follows the order BuOH > EtOH > MeOH is also dependent on the $[PPh_3]:[Ru_2Cl(O_2CR)_4]$ ratio. The ratio was maintained in the range 4.0–6.0. When the reaction was conducted in Bu^tOH, MeCN or in toluene, the product is a purple compound showing a band at 563 nm (in $CHCl_3$ solvent) in the visible electronic spectra. For R = Me, the PMR spectra of the purple species show two methyl signals of equal intensity at 1.67 and 1.70 δ in $CDCl_3$. This compound is characterized as $Ru_2O(PPh_3)_2(O_2CMe)_4$ which can also be prepared by a known procedure [8] and was found to give identical PMR spectra.

The IR spectra of the yellow species from $R'CH_2OH$ medium show two bands at 1935 and 1915 cm^{-1} along with a relatively broad band at ~1990 cm^{-1} (Fig. 1) besides a weak band at 340 cm^{-1} and other usual IR bands of PPh_3 and carboxylato ligands. The product is a mixture of compounds containing two previously reported [11–13] monomeric carbonyl compounds, $RuH(CO)(PPh_3)_2(O_2CR)$ (1) and $RuCl(CO)(PPh_3)_2(O_2CR)$ (2). The IR bands at ~1990 and 1915 cm^{-1} are due to respective ν(Ru–H) and ν(CO) vibrations of 1, while bands at 1935 and 340 cm^{-1} of 2 are assignable [11, 12] to ν(CO) and ν(Ru–Cl), respectively. The intermediate species obtained from the reaction using $Ru_2Cl(O_2CMe)_4$ displays several relatively broad methyl signals in its PMR spectra indicating the presence of at least one paramagnetic species in the mixture. The presence of two methyl signals at 1.68 and 1.70 δ shows that the μ-oxo species is an intermediate. Relatively broad methyl signals at 2.10, 1.97 and 1.90 δ could be due to other intermediate species. When R = Ph, the phenyl region of the PMR spectra is again broad indicating the paramagnetic nature of the intermediate compound(s).

The present investigation raises questions regarding (i) whether decarbonylation is taking place from the bridging carboxylato ligands or (ii) whether the alcohol medium has any role in the process. We have observed that the formation of carbonyl compounds takes place only in alcoholic solvents $R'CH_2OH$ containing two β-H atoms. While aldehydes can undergo [14] decarbonylation, carboxylic acids are known [15] for the decarboxylation process forming CO_2. Experimental results clearly suggest that the source of CO is $R'CH_2OH$ and not the bridging carboxylato groups in $Ru_2Cl(O_2CR)_4$.

The mechanism for this reaction is of obvious interest to us considering the difference in reactivity of PPh_3 towards tetramidato [9, 10] and tetracarboxylatodiruthenium(II,III) compounds. PMR studies on the dark colored intermediate show that

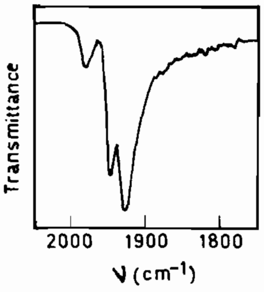

Fig. 1. Infrared spectrum (in KBr phase) of the yellow product obtained from BuOH medium showing carbonyl and Ru–H vibrations.

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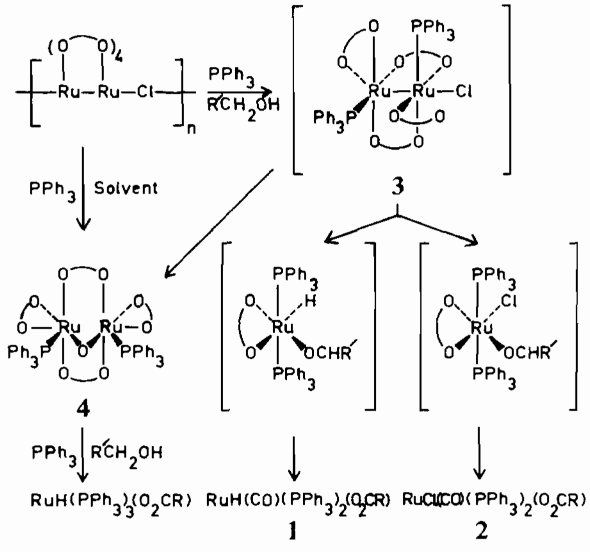
$Ru_2O(PPh_3)_2(O_2CR)_4$ and a paramagnetic species are possible intermediates. The electronic spectra of the transient intermediate show a band at 570 nm along with a shoulder at *ca.* 394 nm. The μ-oxo species display a band at *ca.* 561 nm with a shoulder in the range of 371–384 nm. A tentative mechanism, shown in Scheme 1, is similar to that proposed by Benedetti *et al.* [16] for a decarbonylation reaction involving a methoxy intermediate [17] which can undergo β-hydride transfer to form a hydridoaldehyde complex from which the formation of carbonyl species takes place after elimination of RH followed by an isomerization of the resulting isocarbonyl compound. The formation of an isocarbonyl intermediate and elimination of CH_4 was suggested [18] from $[CH_3CH{=}O{-}RuL_n]$ in the reaction between $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ and C_2H_5OH in the presence of KOH.



Scheme 1. A tentative mechanism for the decarbonylation process.

The μ-oxo species, $Ru_2O(PPh_3)_2(O_2CR)_4$, is not active in the decarbonylation process as is evidenced from the reaction between **4** and PPh_3 in alcohol medium. The product is yellow crystalline $RuH(PPh_3)_3(O_2CR)$ [8, 11]. A plausible intermediate for the process is believed to be similar to that involved in the formation of *ortho*-metallated diosmium and dirhodium compounds $M_2(L)_2(O_2CR)_2(C_6H_4PPh_2)_2$ ($M = Os$, $L = Cl$; $M = Rh$, $L = RCO_2H$) [19–21]. The proposed species **3** is paramagnetic and has non-equivalent R groups as is observed from the PMR spectra. While the methanol solution of **4** is known [8] to undergo a two-electron reduction at −0.99 V, the $Ru_2Cl(O_2CR)_4$ compounds display a reduction wave near 0.0 V *versus* SCE [22, 23]. The presence of PPh_3 in **3** enables the species to oxidize alcohol to aldehyde. The observed increase in the rate BuOH > EtOH > MeOH follows the oxidizing ability of **3**. The highly negative $E_{1/2}$ value of **4** makes this species inactive towards oxidation of alcohols. Further studies to establish the true identity of the reactive intermediate(s) are in progress.

Conclusions

Experimental results show that alcohols containing two β-H atoms undergo oxidation to the corresponding aldehyde in the presence of an active intermediate which is believed to be a paramagnetic diruthenium species containing PPh_3 in its coordination sphere. Quantitative formation of a μ-oxo species, $Ru_2O(PPh_3)_2(O_2CR)_4$, takes place in solvents lacking two β-H atoms.

Acknowledgement

We thank the Council of Scientific and Industrial Research, New Delhi, India for support.

References

1 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms', Wiley, New York, 1982.
2 F. A. Cotton and R. A. Walton, *Struct. Bonding (Berlin), 62,* 1 (1986).
3 A. R. Chakravarty, *Proc. Indian Natl. Sci. Acad., 52A,* 749 (1986).
4 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 28,* 2285 (1966).
5 A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* 786 (1974).
6 A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* 1570 (1972).
7 F. A. Cotton and J. G. Norman, Jr., *Inorg. Chim. Acta, 6,* 411 (1972).
8 R. W. Mitchell, A. Spencer ana G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* 846 (1973).
9 A. R. Chakravarty and F. A. Cotton, *Inorg. Chem., 24,* 3584 (1985).
10 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *J. Am. Chem. Soc., 106,* 6409 (1984).
11 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.,* 1912 (1973).
12 A. Dobson and S. D. Robinson, *Inorg. Chem., 16,* 1321 (1977).
13 M. F. McGuiggan and L. H. Pignolet, *Cryst. Struct. Commun., 7,* 583 (1978).
14 M. A. Bennett, M. I. Bruce and T. W. Matheson, in G. Wilkinson (ed.), 'Comprehensive Organometallic Chemistry', Vol. 4, Pergamon, Oxford, 1982, p. 691.
15 G. B. Deacon, S. J. Faulks and G. N. Pain, *Adv. Organomet. Chem., 25,* 237 (1986).
16 E. Benedetti, G. Brucci, G. Shrana and F. Salvetti, *J. Organomet. Chem., 37,* 361 (1972).
17 B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* 1546 (1977).
18 J. Chatt, B. L. Shaw and A. E. Field, *J. Chem. Soc.,* 2466 (1964).
19 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *J. Chem. Soc., Chem. Commun.,* 501 (1984).

20 A. R. Chakravarty, F. A. Cotton, D. A. Tocher and J. H. Tocher, *Organometallics, 4*, 8 (1985).

21 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem., 23*, 4697 (1984).

22 F. A. Cotton and E. Pedersen, *Inorg. Chem., 14*, 388 (1975).

23 T. Malinski, D. Chang, F. N. Feldmann, J. L. Bear and K. M. Kadish, *Inorg. Chem., 22*, 3225 (1983).