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Preliminary communication

Reactions of dicarboalkoxy(di-μ-methylene)bis(pentamethylcyclopentadienylrhodium); alkyl acrylates from a three-carbon coupling

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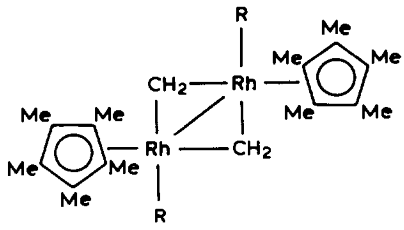
Abstract

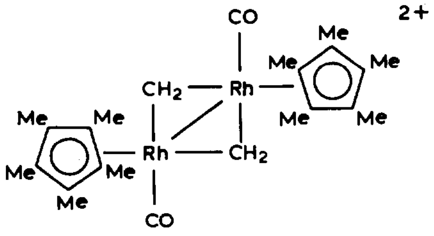
Decomposition of $[\{C_5Me_5Rh(\mu\text{-}CH_2)(COOR)\}_2]$ or of $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CO)\}_2]^{2+}$ (**2**) in alcohols (ROH) gave $CH_2{=}CHCOOR$ and CH_3COOR (R = Me, Et); production of the acrylate was maximised in the presence of oxidisers, especially $[Fe_4O(SO_4)_5]$. With reducers (Zn) **2** gave chiefly ethylene and $[\{C_5Me_5Rh(\mu\text{-}CO)\}_2]$.

In the preceding Communication we noted the possibility of producing acetone (and other carbonyl compounds) by in situ oxidation of propylene formed by the coupling of three C_1 ligands on complex **1** [1]. We here utilize the versatility of analogues of **1** to demonstrate the coupling of three C_1 ligands to acrylates.

The dicarboalkoxy complexes **3** and **4** are readily formed on dissolution of the dication $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CO)\}_2](BF_4)_2$ (**2**), in alcohols [2]. By contrast to the



(**1**, R = Me ;
3, R = CO_2Me ;
4, R = CO_2Et)



(**2**)

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Table 1

Products from decomposition of $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CO)\}_2](BF_4)_2$ (2) or $[\{C_5Me_5Rh(\mu\text{-}CH_2)(COOMe)\}_2]$ (3)

Conditions	Complex	Decomposition products (%) [a]						
		% [b]	CH_4	C_2H_4	C_2H_6	CH_3COOMe	$CH_2{=}CHCOOMe$	Other
Toluene (80 °C/18 h)	3	20	10	2	1	48	1	MeOH, 37
$[Fe_4O(SO_4)_5]$ MeOH/20 °C/72 h	3	62	1	2	–	36	60	
$[Fe_4O(SO_4)_5]$ [c] (EtOH/50 °C/48 h)	2	52	4	–	–	46 [c]	45 [c]	HCOOEt, 6
Na_2IrCl_6/MeOH (20 °C, 20 h)	3	26	1	6	–	77	17	
$PdCl_2$/MeOH (20 °C/18 h)	3	38	3	–	–	47	34	[d]
Zn/MeOH (20 °C/2 h)	2	68	18	62	18	–	–	[e]

[a] Products caculated as percentages of the total volatiles on the basis that each mole of complexes 2 or 3 has available 4 moles of C_1 for product formation. [b] Total amount of decomposition (%). [c] In ethanol the products were $CH_2{=}CHCOOEt$ and CH_3COOEt. [d] Methyl formate (9%) and dimethoxymethane (7%) were also formed; they may in part arise from oxidation of the methanol itself. [e] $[\{C_5Me_5Rh(CO)\}_2]$ (42%) was also isolated from this reaction.

reactions of **1**, where $FeCl_3$ or Na_2IrCl_6 were especially useful in promoting the C–C–C coupling [1,3], complexes **2–4** reacted best in the appropriate alcohol in the presence of the very insoluble basic ferric sulphate $[Fe_4O(SO_4)_5]$. Reaction of **2** in ethanol (50 °C, 48 h) gave very substantial amounts of ethyl acrylate (45%) and ethyl acetate (46%) (Table 1), identified by GC and GC/MS. Small amounts of methane and ethyl formate were also found. The total amount of decomposition was 52%.

A similar reaction took place between **3** and the basic ferric sulphate in methanol (20 °C, 72 h), giving methyl acrylate (60%) and methyl acetate (36%); the total extent of decomposition was 62%. Blank experiments showed that the basic ferric sulphate did not react at all with methanol or ethanol under these conditions.

Other oxidisers reacted analogously but less effectively. Thus there was less decomposition when **3** was treated with 6 equivalents of Na_2IrCl_6 (26%) or 3.5 equivalents of palladium chloride (38%) in methanol (20 °C, 20 h). The main products were methyl acetate (47%, Pd; 77%, Ir) but methyl acrylate (34%, Pd; 17%, Ir) was also formed.

Such products were also obtained when complex **3** was thermally decomposed (toluene, 80 °C, 18 h). The main products were methyl acetate, methanol and methane; however some methyl acrylate was also formed.

There have been numerous reports of the production of acetates involving a metal-promoted C–C bond formation; for example, from combination of a μ-CH_2 with a CO to give a coordinated ketene, followed by alcoholysis [4]. However, there does not seem to have any report so far of such a process in which three C_1 fragments are stitched together to produce an acrylate, as demonstrated here.

Complex **2** could also be reduced; thus, it reacted readily with zinc to give the blue dinuclear $[\{C_5Me_5Rh(\mu\text{-}CO)\}_2]$ (**5**) [5]. The other products were ethylene (60%

of the total CH_2 present), ethane, methane, and a little propylene. More methane and less ethane were formed when methanol was the solvent; in thf more ethane was produced. The major reaction path may well involve an initial 2-electron transfer from zinc giving the neutral $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CO)\}_2]$, in which the coupling of the methylenes takes place, (compare for example the formation of ethylene from $[Co_2(\mu\text{-}CH_2)_2(\mu\text{-dppm})(CO)_4]$ [6]).

$$[\{C_5Me_5Rh(\mu\text{-}CH_2)(CO)\}_2]^{2+} + Zn \rightarrow Zn^{2+} + [\{C_5Me_5Rh(\mu\text{-}CH_2)(CO)\}_2]$$

$$[\{C_5Me_5Rh(\mu\text{-}CH_2)(CO)\}_2] \rightarrow C_2H_4 + [\{C_5Me_5Rh(\mu\text{-}CO)\}_2]$$

Similar reactions were observed with other reducing agents; in no case was incorporation of the CO into the organic products observed.

These data show (i) that the C–C and C–C–C coupling reactions in dinuclear rhodium complexes are very dependent on oxidation state, and (ii) that the decompositions of complexes **2–4** obey very much the same rules as those found previously for **1**, namely that C–C–C couplings are promoted by oxidants [3].

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