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Preliminary Communication

Direct Synthesis of Dinuclear Carboxylate-Bridged Ruthenium(I) Complexes from the Substitution of the Formate Bridge in Compound $Ru_2(\mu_2\text{-}O_2CH)_2(CO)_4(PPh_3)_2$

Josep Soler and Josep Ros

Departament de Química, Universitat Autònoma de Barcelona,
08193-Bellaterra, Barcelona, Spain

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An easy method of preparation of $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4(PPh_3)_2$ compounds from the formate derivative $Ru_2(\mu_2\text{-}O_2CH)_2(CO)_4(PPh_3)_2$ is reported. Four carboxylate containing alkene groups complexes were prepared using this method. The new complexes were identified by elemental analyses, IR, ^{1}H-NMR, ^{31}P-NMR and ^{13}C-NMR spectroscopies.

Many dinuclear heteroatom-bridged ruthenimum(I) complexes have been prepared and studied in the last twenty years.[1] Since the works of G. R. Crooks *et al.*, the most common starting ruthenium compound for the synthesis of $Ru_2(\mu_2\text{-}X)_2(CO)_{6-n}L_n$ has been the $Ru_3(CO)_{12}$ cluster, whose reaction with carboxylic acids and subsequent addition of phosphines,[2,3] amines,[4] CO[5] or carboxylic acids[6] gives the known $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_{6-n}L_n$ complexes. Other studies have led to pyrazolate, diamide and dithiolate-bridged diruthenium(I) compounds.[7,8] The disubstituted $Ru_2(\mu_2\text{-}X)_2(CO)_4L_2$ complexes, typical products of these syntheses, have shown important catalytic activity in the hydroformilation of olefins and in the addition of carboxylic acids to alkynes.[9,10] Nevertheless, although they have been structurally studied,[11] there is no easy direct synthesis for their preparation. The common preparation method by fragmentation of the $Ru_3(CO)_{12}$ cluster averages a 65% yield of $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4L_2$ when L = phosphine. Very recently, K. B. Shiu *et al.* have published a new facile synthesis of dinuclear dicationic ruthenium(I) $Ru_2(CO)_4(MeCN)_4L_2^{2+}$ complexes by removal of the carboxylate bridge in $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4L_2$ compounds.[12] These dinuclear dicationic compounds have been used as a source of some $Ru_2(\mu_2\text{-}E\text{-}E)(CO)_4L_2$ complexes by reacting with HE-EH/NEt_3 mixtures (HE-EH = diamines and dithioles).[12] Our re-

TABLE I

Analytical, IR and NMR data on compounds **1–4**

Compound $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4(PPh_3)_2$	C, H Analyses Found (Calc.) Yield / %	IR $\upsilon(CO)/cm^{-1}$ (CH_2Cl_2)	^1H-NMR (250 Mz, $CDCl_3$)	$\{^1H\}^{31}P$-NMR (102 Mz, $CDCl_3$)	$\{^1H\}^{13}C$-NMR (62 Mz, $CDCl_3$)
1 R = $CH_2CH{=}CH_2$	C 60.77 (61.21) H 3.70 (3.72) 95.0%	2020 vs, 1977 m, 1943 vs	2.7, d, 2H; 5.4, m, 1H; 4.8, m, 2H; 7.17, m, 15H	11.52, s	41.9, 115.97, 126.09, 128.17, 129.52, 132.7, 133.7, 133.88, 141.14, 205.29
2 R = $CH{=}C(CH_3)_2$	C 57.85 (57.91) H 4.23 (4.28) 96.6%	2022 vs, 1978 m, 1949 vs	1.9, d, 3H; 2.17, d, 3H; 5.72, m, 1H; 7.3, m, 15H	11.68, s	23.52, 28.36, 113.34, 128.13, 129.13, 134.96, 143.13, 204.98
3 R = $CH_2CH_2CH{=}CH_2$	C 58.11 (57.91) H 4.25 (4.28) 98.1%	2023 vs, 1978 m, 1950 vs	1.8, dt, 2H; 2.04, t, 2H; 4.7, m, 2H; 5.5, dd, 1H; 7.4, m, 15H	11.48, s	29.61, 36.17, 124.88, 125.32, 126.47, 128.08, 133.08, 133.91, 205.23
4 R = $CH{=}CHCH{=}CHCH_3$	C 58.84 (58.87) H 4.11 (4.15) 94.8%	2022 vs, 1978 m, 1950 vs	1.74, d, 3H; 5.64, m, 1H; 5.77, d, 1H; 5.9, dd, 1H; 6.18, dd, 1H; 7.4, m, 15H	11.55 s	23.05, 125.48, 126.37, 128.18, 129.46, 130.53, 131.05, 204.56

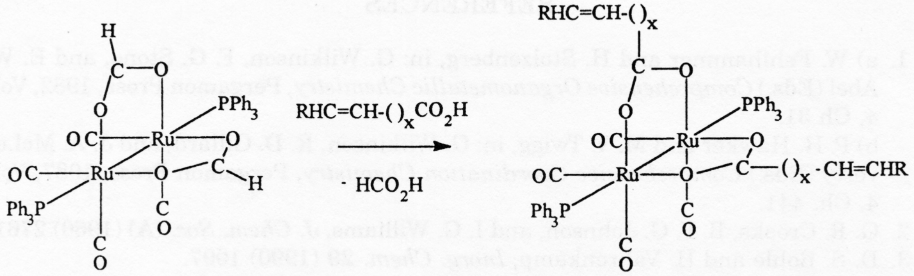

Figure 1.

cent interest in studying carboxylate-rutenium complexes prompted us to search for an easier method of synthesis of the $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4L_2$ complexes and other $Ru_2(\mu_2\text{-}X)_2(CO)_4L_2$ (with $L = PPh_3$) compounds.

In our investigations we have observed that, if the formate-bridged compound $Ru_2(\mu_2\text{-}O_2CH)_2(CO)_4(PPh_3)_2$ is reacted for two hours with an eightfold excess of a carboxylic acid (RCO_2H) in refluxing toluene, the formate bridge is completely substituted by the carboxylate bridge O_2CR (Figure 1). This simple method has allowed preparation of a new family of complexes of the type $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4(PPh_3)_2$ where R is an alkene-containing alkyl group ($R = CH_2CH{=}CH_2$ (**1**), $R = CH{=}C(CH_3)_2$ (**2**), $CH_2CH_2CH{=}CH_2$ (**3**) and $CH{=}CHCH{=}CHCH_3$ (**4**). All these complexes have been identified as dinuclear carboxylate ruthenium(I) compounds that have two bridging η^2-carboxylate groups and two PPh_3 ligands *trans* to the metal-metal bond providing a C_{2v} symmetry to the molecule (Table I). Three IR bands in the v(CO) region confirm this geometry and the ^{1}H- and ^{13}C-NMR of complexes **1–4** display signals of the carboxylic substituents whose C=C bonds do not interact with the ruthenium atoms. The $^{31}P\{^1H\}$ spectra of products show a singlet at *ca.* 11.5 ppm, which agrees with the presence of two equivalent PPh_3 ligands *trans* to the metal-metal bond.

The most outstanding features of this synthetic method are: availability of the formate precursor $Ru_2(\mu_2\text{-}O_2CH)_2(CO)_4(PPh_3)_2$ (93% yield from $Ru_3(CO)_{12}$), a short reaction time (2 hrs), quantitative formation of the carboxylate $Ru_2(\mu_2\text{-}O_2CR)_2(CO)(PPh_3)_2$ (>95% yield) and its application to alkene and, in general, to functionalized carboxylates. This last quality is very important because it is known that $Ru_3(CO)_{12}$ reacts with olefins and other organic groups.[1] For this reason, in spite of having alkene-containing carboxylate bridges, complexes **1–4** are coordinated only by the carboxylate group. Studies on the mechanism of substitution are in progress.

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SAŽETAK

Neposredna sinteza dinuklearnih kompleksa rutenija(I) s karboksilatnom skupinom u mostu zamjenom formiatnog mosta u spoju $Ru_2(\mu_2\text{-}O_2CH)_2(CO)_4(PPh_3)_2$

Josep Soler i Josep Ros

Opisana je jednostavna metoda priprave spojeva tipa $Ru_2(\mu_2\text{-}O_2CR)_2(CO)_4(PPh_3)_2$ iz $Ru_2(\mu_2\text{-}O_2CH)_2(CO)_4(PPh_3)_2$. Tom su metodom priređena četiri karboksilatna spoja koja sadrže alkenske skupine. Novi kompleksi identificirani su elementnom analizom i spektroskopskim metodama (IR, ^{1}H-NMR, ^{31}P-NMR i ^{13}C-NMR).