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A new reaction of transition metal complexes with methyl formate

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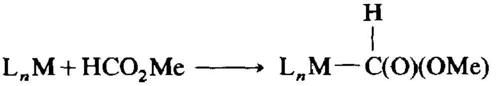
Abstract

The reactions of HCO_2Me and $ClCO_2Me$ with selected rhodium, iridium and palladium compounds have been investigated. The reactions formed $[Rh(HCO_2)(CO)_2]_2$, $[Rh(HCO_2)(cod)]_2$, $[Rh(Cl)(CO_2Me)(H)(PMe_3)_3]$, $[Rh(cp)(CO_2Me)(Cl)(PMe_3)_2]$, $[Pd(CO_2Me)(Cl)(PCy_3)_2]$, $[Ir(H)_2(PMe_3)_4]^+$ $(HCO_2)^-$, and $[Rh(\mu\text{-}CO)(PMe_3)_3]_2$. The reactions involving HCO_2Me provide a new method of synthesizing of the dimeric formate complexes.

Introduction

Methyl formate, HCO_2Me, is an important reagent in C_1 chemistry [1–4]. Its reactions with transition metal complexes are of interest because they give complexes with potential catalytic properties. The most interesting are the products of oxidative addition of HCO_2Me, i.e. the methoxycarbonyl complexes. They may be regarded as intermediates in hydroformylation, carbonylation, and hydroxyacylation of olefins. The methoxycarbonyl compounds can be obtained in a reaction of type (1):



$$L_nM + HCO_2Me \longrightarrow L_nM\overset{H}{\underset{|}{-}}C(O)(OMe) \qquad (1)$$

Such a reaction gave $[Ir(Cl)(H)(CO_2Me)(PMe_3)_3$ [5] and $[Rh(Cl)(H)(CO_2Me)(PMe_3)_3]$ [6,7] from $[Ir(Cl)(C_8H_{14})(PMe)_3]$ and $[Rh(Cl)(PMe_3)_3]$. The complexes containing methoxycarbonyl ligands could be of value in reactions with organic substrates, e.g. their reactions with olefins might produce esters. Formally, the methoxycarbonyl complexes can be regarded as the products of CO_2 insertion into

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M–Me bonds or of CO insertion into M–OMe bonds (eg. 2).

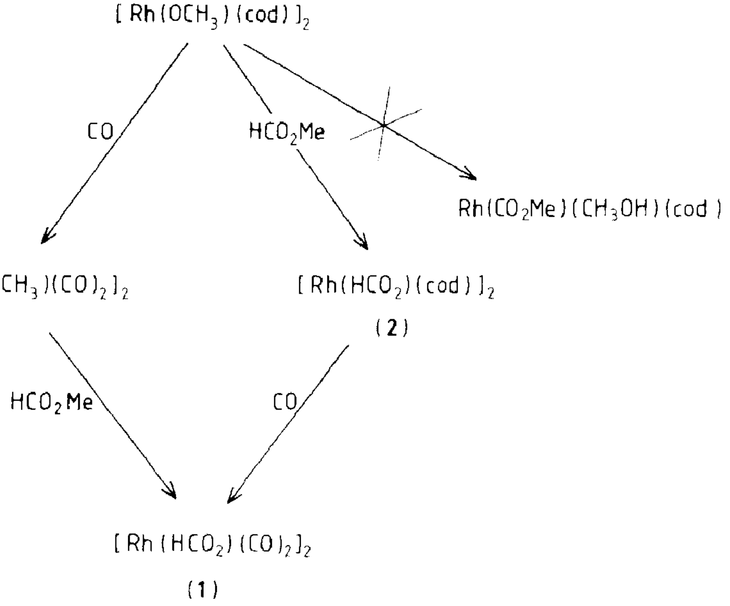
$$L_nM{-}OMe \xrightarrow{CO} L_nM{-}C(O)(OMe) \xleftarrow{CO_2} L_nM{-}Me \qquad (2)$$

Both reactions are important in C_1 chemistry, but they have been little studied. The reaction of $[Ir(OCH_3)(CO)(PPh_3)_2]$ with CO, yielding $[Ir(CO_2Me)(CO)_2(PPh_3)_2]$ [8] is an example of reaction between a methoxy complex and CO. However, insertion of CO_2 into a M–C bond usually produces the carboxylate M–OC(O)R complex, and, only rarely gives, the alkoxycarbonyl complex, MC(O)(OR) [9,10].

We present here the results of our studies of reactions between methyl formate and selected rhodium, iridium and palladium complexes. Our main goal was to examine the effect of the metal complex used on the course of the reaction with HCO_2Me and to find the most favourable conditions for formation of methoxycarbonyl complexes.

Results and discussion

The selected dimeric rhodium(I) compounds $[Rh(OCH_3)(cod)]_2$ and $[Rh(OCH_3)(CO)_2]_2$ were expected to react with HCO_2Me to give the methoxycarbonyl complexes and we thought that the presence of the methoxy ligand, a potential proton acceptor, might facilitate that reaction. However, the products obtained were the dimeric complexes with formate bridges (Scheme 1).



Scheme 1

The complex $[Rh(HCO_2)(CO)_2]_2$ (**1**) has been made previously by another route [11], but this is the first preparation of $[Rh(HCO_2)(cod)]_2$ (**2**). Complex **1** reacts with phosphines to give the monomeric complexes $Rh(HCO_2)(CO)L_2$ ($L = PPh_3$, PCy_3). The dimeric formate complexes could also be obtained by reaction of

[Rh(OH)(cod)]$_2$ with HCO$_2$Me; this reaction does not take place when [RhCl(cod)]$_2$ is used.

According to the previous reports the stable methoxycarbonyl complex **3** is formed by reaction of RhCl(PMe$_3$)$_3$ with HCO$_2$Me [6,7]. Our attemps to repeat that reaction failed, but we succeeded in making the methoxycarbonyl compound by the reaction of [RhCl(C$_2$H$_4$)$_2$]$_2$ with PMe$_3$ and HCO$_2$Me. Use of a similar procedure but with PPh$_3$ did not produce the methoxycarbonyl complex, implying that the presence of the strongly basic PMe$_3$ favours the coordination of HCO$_2$Me and stabilization of the product. This conclusion was supported by the results of reactions of rhodium and palladium complexes with ClCO$_2$Me, which gave the methoxycarbonyl complexes (Scheme 2).

$$\mathrm{ClCO_2Me} \xrightarrow{[\mathrm{Rh(cp)(PMe_3)_2}]} [\mathrm{Rh(cp)(CO_2Me)(Cl)(PMe_3)_2}] \qquad (4)$$

$$\mathrm{ClCO_2Me} \xrightarrow[{[\mathrm{Pd(PCy_3)_2}]}]{} [\mathrm{Pd(CO_2Me)(Cl)(PCy_3)_2}] \qquad (5)$$

Scheme 2

The oxidative addition of ClCO$_2$Me proceeds more readily than that of HCO$_2$Me, and the reaction is favoured by presence of the basic ligands such as PMe$_3$ or PCy$_3$. However, the presence of a strongly basic ligand in the coordination sphere of metal ion is not always sufficient to give rise to reaction of the metal complex with HCO$_2$Me to give the methoxycarbonyl compound. The reaction of [Rh(CO)(H)(PPh$_3$)$_3$] with PMe$_3$ and HCO$_2$Me unexpectedly gave the dimer with CO bridges,

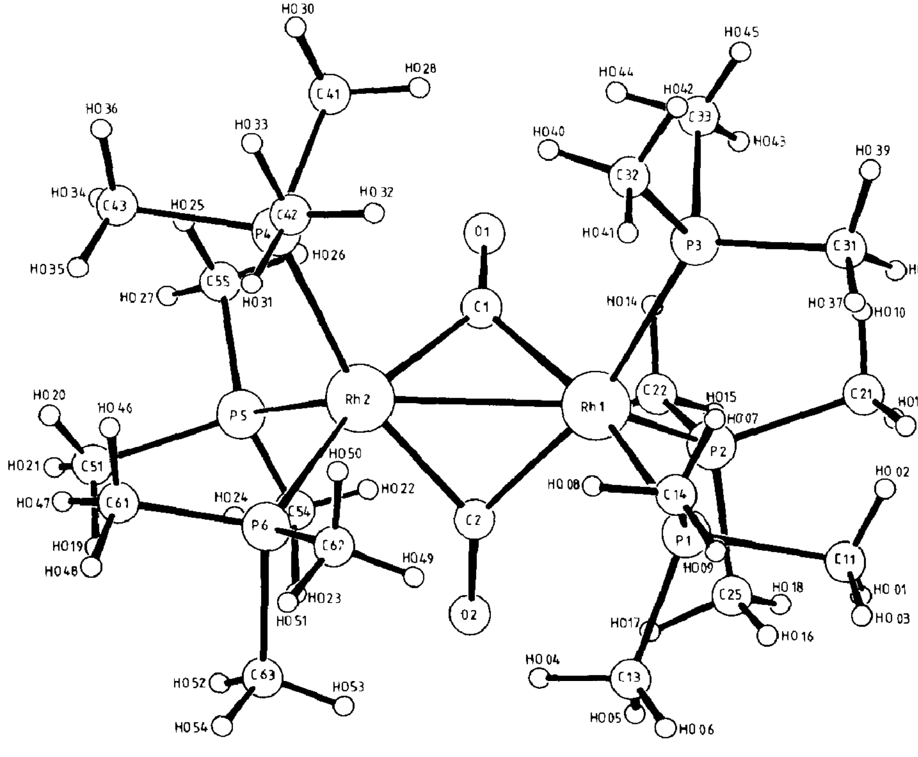


Fig. 1

$[Rh(\mu\text{-}CO)(PMe_3)_3]_2$, the structure of which (Fig. 1) was determined by X-ray diffraction *. The analogous reaction of the iridium compound $[Ir(CO)(H)(PPh_3)_3]$ produced the formate complex $[Ir(H)_2(PMe_3)_4]^+(HCO_2)^-$.

Conclusion

Transition metal compounds with strong basic ligands such as PMe_3 react readily with methyl formate (or the more reactive methyl chloroformate) to give stable methoxycarbonyl complexes.

Experimental

The complexes $[Rh(OCH_3)(CO)_2]_2$ [12], $[Rh(OCH_3)(cod)]_2$ [13] and $[Rh(OH)(cod)]_2$ [13] were prepared by published methods.

$[Rh(HCO_2)(CO)_2]_2$ (*1*)

Methyl formate (1 ml) was slowly added to a hexane solution (20 ml) of 0.2 g $[Rh(OCH_3)_2]_2$. The colour changed from green-yellow to brown, and a gold-brown complex separated. This was filtered off and dried in vacuum. Its IR and MS data were in agreement with those in the literature [11].

$[Rh(HCO_2)(cod)]_2$ (*2*)

Methyl formate (4 ml) was slowly added to a 0.2 g slurry of $[Rh(OCH_3)(cod)]_2$ or $[Rh(OH)(cod)]_2$ in 15 ml of ethyl ether. The mixture was boiled for 5–10 min under reflux until a clear solution was obtained. Cooling to −20 °C then gave dark-yellow precipitate. Filtration and drying yielding 0.11 g (51%) of **2**.

Found: C, 41.52; H, 5.16; $C_9H_{13}O_2Rh$ calc: C, 42.18; H, 5.08%. ^1H NMR ($CDCl_3$) δ: 1.9q (4); 2.85m (4); 4.25m (4); 7.83s (1) MS: 510, 465, 419, 307, 256, 208, 182, 168, 103, 79, 67, 44 IR (KBr), cm^{-1}: 3000w, 2940m, 2920m, 2880m, 2850m, 2840m, 1630s, 1595vs ($\nu_{as}(COO)$), 1480w, 1470w, 1375m, 1356s ($\nu_s(COO)$), 1320w, 960w, 760w.

$Rh(HCO_2)_2(CO)(PPh_3)_2$

Triphenylphosphine (0.15 g) was added to a slurry of 0.05 g $[Rh(HCO)_2(CO)_2]_2$ in hexane (50 ml) with slow stirring. The colour changed from dark to light yellow, and a bright yellow solid separated. This was filtered off, washed with ether, and dried. Yield 0.12 g (70%).

IR (KBr), cm^{-1}: 1970 ($\nu(C{\equiv}O)$); 1610 ($\nu_{as}(COO)$); 1290 ($\nu_s(COO)$) ^1H NMR ($CDCl_3$), δ: 7.08s (1); 7.42m (18); 7.72m (12).

$Rh(HCO_2)(CO)(PCy_3)_2$

The procedure used for $Rh(HCO_2)(CO)(PPh_3)_2$ was followed. $[Rh(HCO_2)(CO)_2]_2$ (0.055 g) and PCy_3 (0.18 g) were used. Yield 0.14 g (70%).

IR (KBr), cm^{-1}: 1948 ($\nu(C{\equiv}O)$), 1630 ($\nu_{as}(COO)$), 1300 ($\nu_s(COO)$) ^1H NMR (C_6D_6), δ: 1.22m, 1.74m, 2.18m, 8.9s.

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* The X-ray structure was determined by C. Kruger, MPI für Kohlenforschung. Details will be published elsewhere in the near future.

[Rh(PMe$_3$)$_3$(Cl)(H)(CO$_2$Me)] (3)

Trimethylphosphine (1 ml) was added to a slurry of 0.36 g $[(C_2H_4)_2RhCl]_2$ in 15 ml hexane at −78 °C, and the mixture was allowed to warm to room temperature during 12 h. The complex $(PMe_3)_3RhCl$ which separated was washed and dried, and again suspended in 15 ml of n-hexane, and 0.5 ml HCO_2Me was added at 25 °C. The mixture was stirred for 8 h, then the yellow solution filtrated and cooled to −15 °C. Yellow crystals were isolated in 50% yield. The IR and ^1H NMR data are in agreement with those in the literature [7].

[Rh(Cp)(CO$_2$Me)(PMe$_3$)$_2$]Cl (4)

A solution of 0.040 g of $CpRh(PMe_3)_2$ in 5 ml of pentane was treated with 0.1 ml of $ClCO_2Me$ at 25 °C. A white complex separated. IR (Nujol), cm^{-1}: ($\nu(CO_2Me)$) 1640 and 1043.

Pd(PCy$_3$)$_2$(Cl)(CO$_2$Me) (5)

To a solution of $Pd(PCy_3)_2$ (0.33 g) in 8 ml n-hexane, 0.1 ml of $ClCO_2Me$ was added at room temperature. The white precipitate was washed and dried. Yield 0.250 g (77%).

IR (KBr), cm^{-1}: ($\nu(CO_2Me)$) 1665/1040. ^1H NMR ($CDCl_3$), δ: 3.55 (s, OMe). Found: C, 59.83; H, 9.59; O, 4.18; $C_{38}H_{69}O_2$ calc: C, 59.82; H, 9.13; O, 4.20%.

[Ir(PMe$_3$)$_2$(H)$_2$]$^+$HCOO$^-$ (6)

Trimethylphosphine (1.5 ml) was added dropwise to a solution of 0.45 g of $Ir(H)(CO)(PPh_3)_3$ in 15 ml of toluene. The solution was stirred at room temperature for 30 min, and 1 ml HCO_2Me was then added and the the colourless solution was stirred overnight then concentrated to a volume of 5 ml, and pentane (ca. 15 ml) was added until a white solid separated. The precipitate was filtered off, washed with pentane, and dried. Yield: 0.045 g (18%).

IR (KBr), cm^{-1}: 2025 (Ir–H); 1611 ($\nu_{as}(COO)$): 1289 ($\nu_s(COO)$). ^1H NMR (CD_3CN), δ: −13.36t (1); −12.85t (1); 1.53d (18); 1.60t (1); 8.59s (1).

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