

## Efficient catalytic reduction of ketones with formic acid and ruthenium complexes

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### Abstract

The ruthenium complex  $(\eta^5\text{-C}_4\text{Ph}_4\text{COHOC}_4\text{Ph}_4\text{-}\eta^5)(\mu\text{-H})(\text{CO})_2\text{Ru}_2$  and its phenyl ring-substituted derivatives were found to act as efficient catalysts in reduction reactions of aldehydes and ketones to alcohols, using formic acid as H source. Excess formic acid accelerates the reaction, and the corresponding formate esters were isolated as sole products. Turnover numbers of up to 8000 (alcohols) and 11 000 (formate esters) were attained, with yields in the order of 90%. Alkenes are not reactive, however, double bonds conjugated to a carbonyl group are selectively reduced under the reaction conditions. The reaction is compatible with a variety of ketones, but with aliphatic aldehydes the reaction is not selective, inasmuch as aldol condensation products are formed.

**Keywords:** Ruthenium; Carbonyl; Catalytic reduction

### 1. Introduction

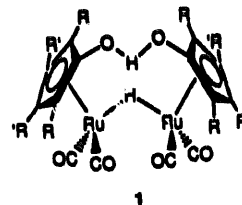
The organo-ruthenium complex **1** ( $\text{R} = \text{R}' = \text{Ph}$ ), along with other ring-substituted derivatives, exhibits an interesting spectrum of catalytic activity [1]. It was found to be catalytically reactive in hydrogenation of ketones, aldehydes, alkenes and alkynes at moderate pressures [1b], and in water-gas shift type reductions ( $\text{CO} + \text{H}_2\text{O}$ ) of ketones, aldehydes [1c] and nitro aromatic compounds [1e]. Complex **1**, in the presence of catalytic quantities of water, was also found to be catalytically reactive in transalkylation of aliphatic amines [1d].

In a recent paper, an extremely efficient Tishchenko type reaction using formic acid as a promoter and **1** as catalyst has been demonstrated [2]. The reaction is carried out at moderate temperatures, neutral non-aqueous conditions, and in an open vessel. Complex **1** is a fairly stable compound which can be handled with no special precautions. Presently, **1** may probably be considered as the best catalyst for the Tishchenko type disproportionation of aldehyde to esters.

Formic acid is a convenient source of hydrogen for reduction of various substrates. Thus,  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyzes the reduction of ketones and aldehydes to

alcohol under moderate conditions [3] with turnover number of ca. 800.

With triethylammonium formate and  $\text{Ru}(\text{Cl})_2(\text{PPh}_3)_3$  [4] or  $\text{RuCl}_2(\text{m-SPPH}_2)_2$  [5], aldehydes were selectively reduced to alcohols at room temperature in the presence of various unsaturated functional groups. However, a heterogeneous Pd/C-triethylammonium formate system is selective towards the reduction of double bonds in the presence of an aldehyde function [6].



### 2. Results and discussion

Using formic acid as a promoter in the Tishchenko type reaction [2] led us to investigate the catalytic activity of **1** in the reduction of organic unsaturated substrates using formic acid as H source.

First, we have examined the reaction of **1** and formic acid in the absence of unsaturated substrate at 100°C in a closed reactor. No change in pressure was recorded during 24 h. Thus, **1** does not decompose formic acid to

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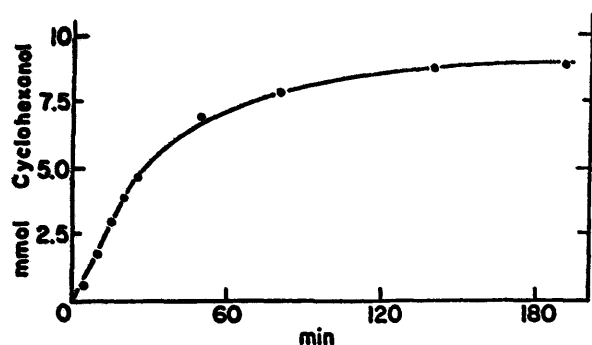


Fig. 1.

carbon dioxide and hydrogen, a thermodynamically favored reaction. Any reducing properties of this system must therefore be attributed to a hydrogen transfer process from formic acid to a substrate, mediated by a ruthenium hydride complex.

The results of a preliminary reduction experiment of cyclohexanone with formic acid and **1** in toluene are displayed in Fig. 1. It is evident that using stoichiometric quantities of cyclohexanone and formic acid, and a catalyst to cyclohexanone ratio of 1 : 400, gave rise to a

high conversion (above 80%) with 100% selectivity at a reasonable time.

In order to demonstrate a synthetically efficient reaction, it is desirable to conduct it without a solvent, if possible. Therefore, various liquid carbonyl compounds were mixed with a 10% molar excess of formic acid and heated in an open vessel at 100°C in the presence of the catalyst **1**. Rather large quantities (0.1–0.2 mol) of the substrates were used in order to demonstrate the preparative aspect of the reduction reaction.

Since the product, an alcohol, is formed in the presence of formic acid, some esterification takes place. In order to obtain an ester-free alcohol as a product, a small quantity of sodium formate and water were added at the outset of the reaction. The results of our reduction experiments are presented in Table 1. The scope of the reduction reaction was examined with a variety of ketones, all of which were found to be reduced by formic acid. The relative reactivity of the various carbonyl substrates may be judged from the initial turnover frequency values (Table 1). Entries 1–5 represent simple cyclic and acyclic ketones all reacting at similar rates except for cyclohexanone, which is somewhat more

Table 1  
Reduction of ketones and aldehydes with formic acid and **1**

Entry	Ketone (mol)	Alcohol (% yield)	TF (h <sup>-1</sup> ) initial <sup>a</sup>	TN (time, h) <sup>b</sup>
1	Cyclohexanone (0.18)	Cyclohexanol (100)	3800	7200 (3)
2	Diethyl ketone (0.20)	3-Pentanol (92)	2760	7400 (6.6)
3	5-Methyl-3-heptanone (0.10)	5-Methyl-3-heptanol (92)	2160	3680 (15)
4	Ethylbenzyl ketone (0.15)	Ethylbenzyl carbinol (93)	2700	5590 (6.6)
5	2-Pentanone (0.15)	2-Pentanol (98)	2340	5880 (3)
6	Acetophenone (0.15)	1-Phenylethanol (93)	2700	5600 (4.8)
7	Benzaldehyde (0.20)	Benzyl alcohol (99)	20563	8000 (0.5)
8	Ethylacetoacetate (0.10)	Ethyl-3-hydroxy propionate (97)	1754	3900 (5)
9	Benzalacetophenone (0.05)	Benzylacetophenone (90); 1,3-diphenyl propan-1-ol (10)	2250	2000 (2.5)
10	Methyl vinyl ketone (0.021)	2-Butanone (96)	760	810 (5.5)

Reactants: 0.025 mmol catalyst **1**. Molar ratio formic acid:carbonyl substrate:water:sodium formate 1.1:1:0.1:0.2. Reaction conditions: oil bath temperature 100°C.

<sup>a</sup> Mol alcohol/mol **1**/h formed after 1 h reaction time.

<sup>b</sup> Mol alcohol/mol **1** formed after the designated reaction time.

Table 2  
Reduction of ketones and aldehydes with excess formic acid and **1**

Entry	Ketone (mol)	Formate ester (% yield)	TF(h <sup>-1</sup> ) initial <sup>a</sup>	TN (time, h) <sup>b</sup>
1	Cyclohexanone	Cyclohexyl formate (97)	10940	3100 (0.66)
2	5-Methyl-3-heptanone	5-Methyl-3-heptyl formate (96)	3120	3070 (3.0)
3	Phorone	2,6-Dimethyl-4-heptanone (88)	7240	2820 (1.2)
4	2,6-Dimethyl-4-heptanone	2,6-Dimethyl-4-heptyl formate (95)	3060	3040 (3.0)
5	4-Methylcyclohexanone	<i>trans</i> -4-Methylcyclohexyl formate (64); <i>cis</i> -4-methylcyclohexyl formate (26)	4980	2880 (1.0)
6	4- <i>tert</i> -Butylcyclohexanone	<i>trans</i> -4- <i>tert</i> -Butyl cyclohexyl formate (61); <i>cis</i> -4- <i>tert</i> -butyl cyclohexylformate (29)	4780	2880 (1.0)
7	Ethylacetoacetate	Ethyl 3-formyloxybutyrate (80)	4180	2560 (1.3)

Reaction conditions: 0.044 mol ketone; 0.220 mol HCOOH;  $1.38 \times 10^{-5}$  mol **1**. Reaction temperature 100°C.

<sup>a</sup> Mol alcohol/mol **1**/h formed after 1 h reaction time.

<sup>b</sup> Mol alcohol/mol **1** formed after the designated reaction time.

Table 3  
Initial reduction rates of cyclohexanone with formic acid and **1** in various solvents

Solvent	Toluene	THF	1,4-Dioxane	Sulfolane	Acetonitrile
Initial rate <sup>a</sup>	12.1	4.0	4.3	3.6	1.2

Reaction conditions: [cyclohexanone] = [formic acid] = 0.4 M; [catalyst] = 10<sup>-3</sup> M. Temperature 65°C. <sup>a</sup> Rate × 100 mmol min<sup>-1</sup>.

reactive (entry 1). Benzaldehyde (entry 7) is particularly reactive with initial TF of over 20000 and a total turnover number of 8000. All yields are 90% or better. Although somewhat slower, ethyl acetoacetate (entry 8) was reduced to the corresponding  $\beta$ -hydroxy ester (97%). Benzalacetophenone and methyl vinyl ketone possessing a conjugated double bond were reduced at the double bonds with high selectivity (in the presence of excess formic acid the carbonyl was reduced as well). Ethyl cinnamate as well as simple alkenes are unreactive. Thus, in the presence of non-conjugated double bonds, ketones and aldehydes may be selectively reduced to the alcohols while, when conjugated, the double bond is reduced in preference to the conjugated carbonyl group.

When the ester is the desired product, the reaction is carried out with a 4–5 fold molar excess of formic acid relative to the carbonyl substrate. In most cases the final reaction mixture consists of a water phase and an ester phase. From Table 2 it is evident that the reduction of ketones to formate esters can be driven practically to completion. Phorone (entry 3), a cross-conjugated ketone, is being selectively reduced first at the two double bonds yielding 2,6-dimethyl-4-heptanone which, after isolation, is further reduced to the formate ester (entry 4).

In the reduction of the 4-substituted cyclohexanones (entries 5 and 6) the *trans* and *cis* isomeric alcohols were obtained in a ratio of ca. 2:1 respectively in both cases. Cyclohexanol isomers were identified by the <sup>1</sup>H-NMR spin multiplicity of the C-1 hydrogen atom. Since, in the presence of excess formic acid, the rate of esterification is fast, (no alcohol is observed) it must be the kinetic picture that is being observed. Thus, under the above conditions, the reaction is not diastereoselective.

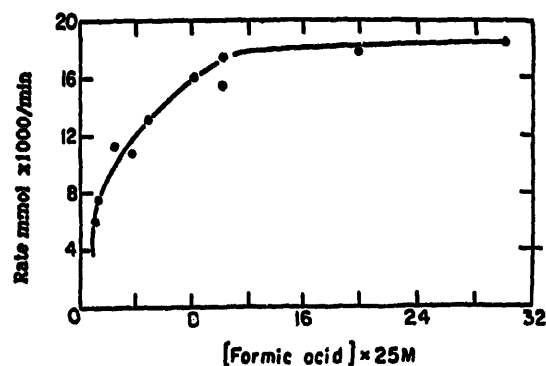


Fig. 2.

Furthermore, comparing the initial TF values of the first entries in Tables 1 and 2, it is evident that the formate esters are formed substantially faster than the alcohols. This is attributed to the higher concentration of formic acid and was verified by examining the dependence of the reaction rate on the concentration of formic acid in toluene as solvent (Fig. 2), which is zero order above 0.25 M. Linear regression analysis on the region below 0.25 M (Fig. 2) gave a reaction order of 0.48, indicating that the reaction proceeds via ionization of formic acid.

Under the standard reaction conditions, isobutyraldehyde and decanal gave the corresponding alcohols and formate esters, but these were accompanied by substantial amounts of aldol condensation products of the aldehydes. Thus, the reduction reaction is synthetically useful only with aromatic aldehydes (entry 7, Table 1) or those having no  $\alpha$  hydrogen atoms.

The effect of solvent on the reaction rate was examined. From Table 3 it is clear that ligand solvents slow down the reaction by a maximum rate factor of 10, implying competitive metal coordination of solvent and ligand molecules at some point in the reaction cycle (vide infra).

The structure reactivity relationship with respect to the complex catalyst was also studied. The syntheses of complexes **2**, **3** and **5** are given in the experimental section. From Table 4 it is evident that electron donating groups on phenyls accelerate the reaction. Although small, the effect is consistent. Usually such a structure reactivity relationship implies the involvement of oxidative addition of a substrate to the metal in the rate determining step.

In addition to its present catalytic activity, complex **1** had previously been found to catalytically reduce ke-

Table 4  
Initial reduction rates of cyclohexanone with formic acid and various complexes

Complex	R'	R	Initial rate <sup>a</sup>
<b>1</b> <sup>b</sup>	Phenyl	Phenyl	19
<b>2</b>	p-Methoxyphenyl	Phenyl	25
<b>3</b>	p-Fluorophenyl	Phenyl	17
<b>4</b> <sup>b</sup>	p-Chlorophenyl	Phenyl	11
<b>5</b>	p-Chlorophenyl	p-Chlorophenyl	9

Reaction conditions: [cyclohexanone] = [formic acid] = 0.4 M in toluene; [catalyst] = 10<sup>-3</sup> M. Temperature 75°C.

<sup>a</sup> Rate × 100 mmol min<sup>-1</sup>. <sup>b</sup> See Ref. [1a].

**Table 5**  
Comparative reduction data of cyclohexanone under various conditions

Entry	Conditions	Yield (%)	TF (h <sup>-1</sup> ) initial	TN (time, h)
1 <sup>a</sup>	Formic acid	97	10940	3100 (0.66)
2 <sup>b</sup>	H <sub>2</sub> , 500 psi, 145°C	97	652	3100 (10.5)
3 <sup>c</sup>	CO, 500 psi, H <sub>2</sub> O, 105°C	2		13 (8.0)
4 <sup>d</sup>	Formic acid + (CPD)Ru(CO) <sub>3</sub> <sup>e</sup>	97	39	3100 (6.0)

<sup>a</sup> Taken from Table 1, entry 1.

<sup>b</sup> Cyclohexanone, 44.2 mmol; catalyst 1, 0.0138 mmol; toluene, 13 ml.

<sup>c</sup> Cyclohexanone, 44.2 mmol; catalyst 1, 0.0138 mmol; THF, 11.5 ml, H<sub>2</sub>O 1.55 ml.

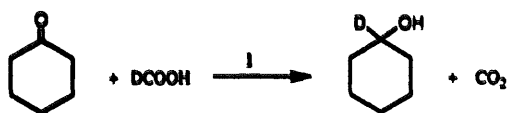
<sup>d</sup> Reaction conditions identical with those of entry 1.

<sup>e</sup> ( $\eta^4$ -2,3,4,5-tetraphenylcyclopentadienone)tricarbonyl Ru(0).

tones and aldehydes under hydrogenation as well as water–gas shift type reaction conditions [1]. Entries 1–3 in Table 5 provide comparative data for the three reduction methods using reaction conditions as similar as possible, cyclohexanone as a substrate, and 1 as catalyst. Hydrogenation (entry 2), although reaching the yield and TN of the formic acid reduction (entry 1), is slower by a factor of ca. 17. The WGS type reduction (entry 3, Table 1) is extremely slow relative to the reduction with formic acid. Replacing catalyst 1 with (CPD)Ru(CO)<sub>3</sub> (entry 4) gave a final high TN using reaction conditions identical to those of entry 1, but the reaction is slower, mostly due to an induction period where the (CPD)Ru(CO)<sub>3</sub> is converted to 1.

It may therefore be concluded that, from the practical point of view, the reduction of ketones using formic acid as H source and 1 as the loaded catalyst, as described in this work, is by far the method of choice.

Reduction of cyclohexanone with DCOOH proceeded as described below:

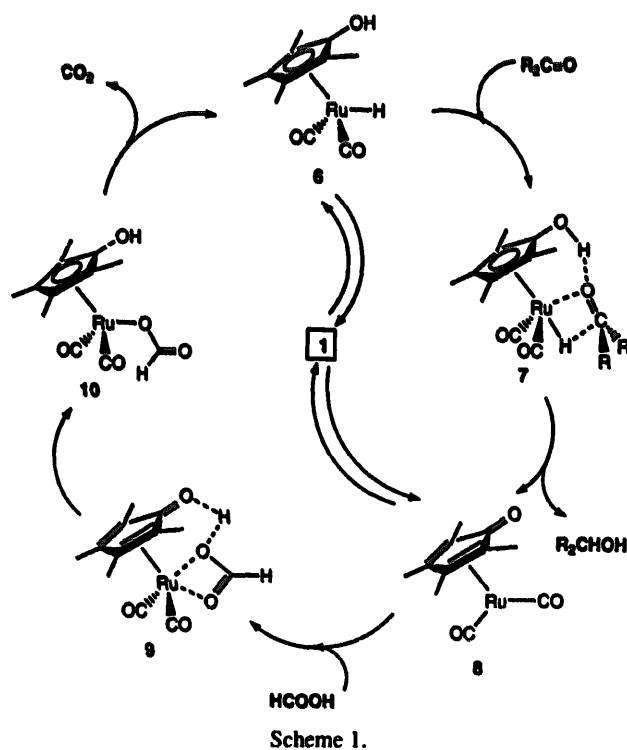


giving 95% D incorporation into the carbinol C atom of cyclohexanol (NMR). Thus, H transfer from formic acid to the carbonyl is regiospecific inasmuch as the acidic proton of formic acid binds selectively to the oxygen atom of the C=O group.

On the basis of the experimental evidence in hand, we propose a catalytic cycle presented in Scheme 1. The reduction cycle originates with the thermal dissociation equilibrium [7] of the charged catalyst 1, thereby generating 6 and 8. While the presence and structure of 6 have been demonstrated in previous studies [2], those of the coordinately unsaturated complex 8 were inferred. The results of Table 3 (solvents study) may be

accounted for since 8 is capable of reversibly coordinating a ligand solvent molecule, thereby retarding the reaction. The regiospecific transfer of the H atoms from 6 to C=O is accounted for by the structure of the intermediate 7. Possibly, an Ru–alkoxide intermediate may lie on the reaction path 7 → 8. Complex 9 (18e) represents a coordination mode of formic acid which is also in accord with the regiospecific requirement of H atom delivery. Oxidative addition of O–H of formic acid is being completed with the generation of the ruthenium formate complex 10 which, by beta elimination of CO<sub>2</sub>, regenerates 6.

The regeneration of 6 may occur as described above via 10, similar to the thermal decomposition of CpRe(NO)(PPh<sub>3</sub>)(O<sub>2</sub>CH) to the corresponding hydride and CO<sub>2</sub> [8], or directly from 9 by a concerted process. A question may be raised as to the stability of 10 or similar derivatives. Attempts to isolate 10 failed. Never-



theless, a stable hydrochloride complex ( $\eta^5\text{-C}_4\text{-Ph}_4\text{COH}(\text{CO})_2\text{RuCl}$ ) was prepared by the action of HCl gas on **1**, and structurally characterized by X-ray crystallography [9]. Thus, a strong acid does oxidatively add to the Ru atom of **1**. Evidently complexes of carboxylic acids, such as formic acid, are unstable and do not survive the isolation conditions. However, the occurrence of **10** as a transient intermediate in the catalytic cycle presented in Scheme 1 is plausible.

Regarding the rate determining step of the above catalytic cycle, the only species observed during the reaction is **6**, implying its slow disappearance vs. its fast formation (**10**  $\rightarrow$  **6**). The transformation **8**  $\rightarrow$  **9** may be safely considered to be a fast one due to the coordinate unsaturation of **8**. Since at high concentration of formic acid the reaction is zero order in the acid, it is likely that the slow step lies along the reaction path **6**  $\rightarrow$  **8**.

### 3. Experimental

#### 3.1. General

IR spectra were recorded on a Nicolet 1600 FT spectrophotometer.  $^1\text{H-NMR}$  spectra were obtained with Bruker AC 200E and AM 360B spectrometers in  $\text{CDCl}_3$  solution with TMS as internal standard. Chemical shifts are reported in ppm ( $\delta$ ). GC spectra were recorded with Varian 3300, 3700 and 4600 instruments using 20% SE-30 on GasChrom Q. Mass spectra were obtained with a DUPONT 21-491B mass spectrometer.

The reaction conditions for the reduction of alcohols and aldehydes are given in Tables 1 and 2. Commercial ketones, aldehydes and formic acid were used without purification.

All the alcohols (Table 1) were identified by spiking GC reaction samples with authentic samples. The formate esters (Table 2) were identified as described above, except for the following ones.

##### 3.1.1. 4-Methylcyclohexyl formate

Two signals in the ratio 0.4:1 assigned to the *trans* and *cis* isomers respectively were observed in the GC spectrum of the product. IR ( $\text{CH}_2\text{Cl}_2$ ):  $1716\text{ cm}^{-1}$ ; MS:  $m/z$  97 ( $\text{M}^+-\text{HCO}_2$ ) (3%), 81 (100%);  $^1\text{H-NMR}$ : 0.86–1.97 (m, 12H), 4.76 (quint. 0.71H,  $J = 12\text{ Hz}$ ), 5.1 (quint. 0.29H,  $J = 4\text{ Hz}$ ), 8.02 (s, 0.71H), 8.06 (s, 0.29H).

##### 3.1.2. 4-tert-Butylcyclohexyl formate

Two signals in the ratio 0.47:1 assigned to the *trans* and *cis* isomers respectively were observed in the GC spectrum of the product. B.p.  $81\text{--}84^\circ\text{C}/1.5\text{ mm Hg}$ ; Anal. Found: C, 71.80; H, 11.05.  $\text{C}_{11}\text{H}_{20}\text{O}_2$ . Calc.: C, 71.74; H, 10.87. IR ( $\text{CH}_2\text{Cl}_2$ ):  $1717\text{ cm}^{-1}$ ; MS:  $m/z$  139 ( $\text{M}^+-\text{HCO}_2$ ) (17%), 82 (88%), 57 (100%);  $^1\text{H-NMR}$ : 0.7 (s, 9H), 0.9 (m, 9H), 4.7 (quint. 0.68H, 10

Hz), 5.2 (quint. 0.32H, 4 Hz), 8.02 (s, 0.68H), 8.07 (s, 0.32H).

##### 3.1.3. Ethyl 3-formyloxybutyrate

B.p.  $92^\circ\text{C}/29\text{ mm Hg}$ ; IR ( $\text{CH}_2\text{Cl}_2$ ):  $1725, 1731\text{ cm}^{-1}$ ; MS:  $m/z$  139, 115 ( $\text{M}^+-\text{HCO}_2$ ) (19%), 69 (100%);  $^1\text{H-NMR}$ : 1.27 (t + d, 6H), 2.58 (d, 2H,  $J = 6\text{ Hz}$ ), 4.13 (q, 2H), 5.4 (sext. 1H), 8.01 (s, 1H).

##### 3.1.4. 5-Methyl-3-heptyl formate

IR ( $\text{CH}_2\text{Cl}_2$ )  $1716\text{ cm}^{-1}$ ; MS:  $m/z$  113 ( $\text{M}^+-\text{HCO}_2$ ) (2%), 83 (100%), 55 (10%);  $^1\text{H-NMR}$ : 0.9–1.58 (m, 16H), 5.0 (quint. 1H), 9.09 (s, 1H).

##### 3.1.5. 2,6-Dimethyl-4-heptyl formate

IR ( $\text{CH}_2\text{Cl}_2$ ):  $1718\text{ cm}^{-1}$ ; MS:  $m/z$  113 ( $\text{M}^+-\text{HCO}_2$ ) (2%), 111 (95%), 69 (100%);  $^1\text{H-NMR}$ : 0.93 (d, 12H), 1.3–1.7 (m, 4H), 2.16 (ddd, 2H, 5,6,11 Hz), 5.18 (quint. 1H), 7.28 (s, 1H). After basic hydrolysis, the isolated alcohol was compared with an authentic sample.

#### 3.2. Preparation of complexes

##### 3.2.1. $[3,4\text{-}(4\text{-MeO-C}_6\text{H}_4)_2\text{-}2,5\text{-Ph}_2(\eta^5\text{-C}_4\text{CO})\text{H}(\text{OCC}_4\text{-}\eta^5)3,4\text{-}(4\text{-MeO-C}_6\text{H}_4)_2\text{-}2,5\text{-Ph}_2(\mu\text{-H})(\text{CO})_4\text{-Ru}_2]$ (**2**)

Dodecacarbonyltriruthenium(0) (1.43 g; 2.24 mmol) and 2,5-diphenyl-3,4-bis(4-methoxyphenyl)cyclopentadienone [10] (3.20 g; 7.20 mmol) in benzene (20 ml) were heated under nitrogen in a closed stainless steel reactor at  $150^\circ\text{C}$  for 24 h. After cooling to room temperature the solvent was removed in vacuum, and the solid residue was flash chromatographed on silica in dichloromethane:ethyl acetate (95:5). A pale green crystalline product was obtained,  $[(3,4\text{-}(4\text{-MeO-C}_6\text{H}_4)_2\text{-}2,5\text{-Ph}_2(\eta^4\text{-C}_4\text{CO})\text{Ru}(\text{CO})_3)]$  (**6**) (72%), m.p.  $191^\circ\text{C}$  dec. IR( $\text{CH}_2\text{Cl}_2$ ): 2080, 2005,  $1630\text{ cm}^{-1}$ .

Anal. Found: C, 65.10; H, 3.92.  $\text{C}_{34}\text{H}_{24}\text{O}_6\text{Ru}$ . Calc.: C, 64.86; H, 3.84. To a solution of complex **6** (1.26 g; 2 mmol) in acetone (40 ml) was added a saturated solution of sodium carbonate (2 ml). After stirring at room temperature for 45 min, the acetone was evaporated in vacuum, and the residue extracted with methylene chloride, dried ( $\text{MgSO}_4$ ), and the organic solvent removed in vacuum. The residue was flash chromatographed on a silica column in pet ether (60/80):methylene chloride 1:3. An orange solid was obtained (75%), m.p.  $210^\circ\text{C}$ , dec. IR( $\text{CH}_2\text{Cl}_2$ ): 2030, 2000, 1970,  $1510\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.12–6.52 (m, 36H), 3.68 (s, 12H), –18.47 (s, 1H).

Anal. Found: C, 65.48; H, 4.19.  $\text{C}_{66}\text{H}_{50}\text{O}_{10}\text{Ru}_2$ . Calc.: C, 65.77; H, 4.18.

##### 3.2.2. $[3,4\text{-}(4\text{-F-C}_6\text{H}_4)_2\text{-}2,5\text{-Ph}_2(\eta^5\text{-C}_4\text{CO})\text{H}(\text{OCC}_4\text{-}\eta^5)3,4\text{-}(4\text{-F-C}_6\text{H}_4)_2\text{-}2,5\text{-Ph}_2(\mu\text{-H})(\text{CO})_4\text{-Ru}_2]$ (**3**)

The reaction of dodecacarbonyltriruthenium(0) with 2,5-diphenyl-3,4-bis(4-fluorophenyl)cyclopentadienone

[11] was carried out as described above. A gray solid was obtained, [(3,4-(4-F-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-2,5-Ph<sub>2</sub>(η<sup>4</sup>-C<sub>4</sub>CO)-Ru(CO)<sub>3</sub>)] (7) (81%), m.p. 189°C dec. IR(CH<sub>2</sub>Cl<sub>2</sub>): 2090, 2035, 2020, 1640 cm<sup>-1</sup>.

Anal. Found: C, 63.76; H, 3.15. C<sub>32</sub>H<sub>18</sub>F<sub>2</sub>O<sub>4</sub>Ru. Calc.: C, 63.47; H, 3.00.

Complex 3 was obtained from 7 as described above (85%), m.p. 189°C dec. IR(CH<sub>2</sub>Cl<sub>2</sub>): 2040, 2010, 1980, 1520 cm<sup>-1</sup>. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): 7.86–6.35 (m, 36H), –17.9 (s, 1H).

Anal. Found: C, 63.76; H, 3.15. C<sub>62</sub>H<sub>38</sub>F<sub>2</sub>O<sub>6</sub>Ru<sub>2</sub>. Calc.: C, 63.47; H, 3.00.

### 3.2.3. [(4-Cl-C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>(η<sup>5</sup>-C<sub>4</sub>CO)H(OCC<sub>4</sub>-η<sup>5</sup>)(4-Cl-C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>(μ-H)(CO)<sub>4</sub>Ru<sub>2</sub>] (5)

Dodecacarbonyltriruthenium(0) (0.575 g; 0.9 mmol) and bis(4-chlorophenyl)acetylene [12] (1.482 g; 6 mmol) in benzene (20 ml) were heated at 150°C under nitrogen in a stainless steel reactor for 24 h. After cooling the solvent was removed in vacuum, and the residue was flash chromatographed on silica in dichloromethane:ethyl acetate (95:5). A beige crystalline material was obtained, [(4-Cl-C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>(η<sup>4</sup>-C<sub>4</sub>CO)Ru(CO)<sub>3</sub>] (8) (65%), m.p. 200°C, dec. IR(CH<sub>2</sub>Cl<sub>2</sub>): 2090, 2025, 2020, 1650 cm<sup>-1</sup>.

Anal. Found: C, 54.14; H, 2.38. C<sub>32</sub>H<sub>16</sub>Cl<sub>4</sub>O<sub>4</sub>Ru. Calc.: C, 54.33; H, 2.28.

Complex 5 (yellow) was obtained from 8 as described above (80%), m.p. 252°C, dec. IR(CH<sub>2</sub>Cl<sub>2</sub>):

2040, 2015, 1970, 1500 cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.37–6.92 (m, 32H), –15.87 (s, 1H).

Anal. Found: C, 54.48; H, 2.63. C<sub>62</sub>H<sub>34</sub>Cl<sub>8</sub>O<sub>6</sub>Ru<sub>2</sub>. Calc.: C, 54.72; H, 2.52.

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