SHORT PAPER

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Microwave accelerated synthesis of cyclopentadienyl bis-phosphine ruthenium (II) thiolato complexes using focused microwave irradiation[†]

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The synthesis of cyclopentadienyl bis-phosphine ruthenium thiolato complexes of the type [RuCp(dppm)SR] from [RuCp(PPh_3)$_2$ Cl] using conventional heating and microwave irradiation using a focused monomode reactor is described and the protocols compared. A considerable decrease of the reaction time is observed under microwave conditions. Yields by both methods are comparable. Functionalities such as esters, carboxylic acids and amides on the thiolato ligands are tolerated under the reaction conditions.

Keywords: cyclopentadienyl bis phospine ruthenium (II) thiolato complexes

Introduction

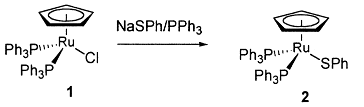
Over the last decade the application of microwave irradiation for the rate enhancement of organic reactions and solid state reactions has received considerable attention.[1] Not only are reaction times considerably shortened under conditions using microwave irradiation, but the energy that heats the sample is used much more efficiently and the amount of solvent used in the reaction can be minimised.

However, very few applications of microwave assisted synthetic methodology in co-ordination chemistry and organometallic chemistry have been reported to date. Pioneering work by Mingos did illustrate the applicability of MW heating in synthetic transition metal chemistry.[2] The synthesis of arene-cyclopentadienyl Fe(II) complexes using a domestic microwave oven[3] and the microwave mediated synthesis of Ru(II) pyridine complexes[4] and Rh (III) and Ru (II) terpyridyl complexes[5] have been described. These seem to represent only isolated examples.

As far as we are aware there have been no reports on the synthesis of organometallic compounds using a focused microwave reactor. It is worth noting that this type of microwave reactor is currently preferred over conventional multimode reactors because the reaction conditions may be more closely reproduced. In this paper we report a protocol for the synthesis of cyclopentadienyl bis-phosphine ruthenium thiolato-complexes, compounds generally considered to be air and moisture sensitive, using a focused microwave reactor.

Results and discussion

Initially starting from chloro complex **1**, we attempted the synthesis of bis-(triphenylphosphine)thiolato complexes **2** under microwave conditions in a focused microwave reactor. Bis-(triphenylphosphine)-thiolato complexes **2** have been synthesised thermally by reaction of chloro complex **1** with the appropriate sodium thiolate in an ethanol/THF mixture.[6–8] The reaction time for completion of the reaction is 2 h and additional PPh_3 is added to the reaction mixture to avoid formation of cubane type thiolate clusters[6–8] While the yield of compound **2** is excellent under thermal conditions under microwave irradiation (100 W, 60s, in diethylene glycol) a mixture of at least five compounds could be detected by NMR. The desired compound **2** was formed in 20% yield. The side products are presumably ruthenium clusters with bridged thiolate ligands, but these could not be adequately characterised due to difficulties in the separation procedure.[6–8]

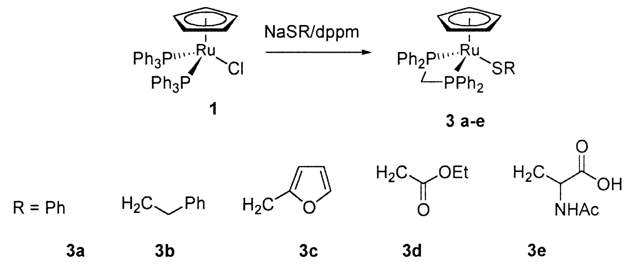


Thermal: EtOH/THF, 2h, 84 %

MW: diethylene glycol, 60s, 100W
20 % of **2** and 5 further products

Next we turned our attention to the more stable bis-diphenylphophinomethane (dppm) thiolato complexes **3a-e**, which contain a chelating phosphine ligand. Again under thermal conditions the reaction is complete after 2 h reflux in an ethanol/THF solvent mixture and the compounds are obtained in excellent yield. Since the thermally employed solvent mixture is unsuitable under our microwave conditions, due to safety considerations we choose diethylene glycol as a solvent of similar polarity, but with a higher boiling point. Ethylene glycol as a high boiling substitute was shown to be an effective choice for safe use under focused microwave conditions.

The thiolato complexes **3a–e** were formed in very good yield under microwave irradiation. Complete conversion of the starting material was achieved after microwave irradiation for 90–120 s at 100W (see Table 1 entries 1 and 4–7). A higher power setting of 200 W resulted in partial decomposition of the ruthenium starting material and products. A choice of thiolates was used to demonstrate the versatility of the new protocol. The amount of solvent required in the process was 1ml diethylene glycol per 1 mmol of material. This slight reduction of the solvent volume required in the process adds another environmentally friendly aspect to the microwave procedure.



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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

In order to obtain material of analytical purity a column chromatographic separation was still required to remove both PPh_3 and some undefined decomposition products.

To directly compare the efficiency of a focussed MW oven and a commercial household MW oven on our reaction, the reaction to yield **3a** was additionally performed in a conventional household oven. After 120 s at 100 W only 8 % conversion to the thiolato-complex **3a** was observed. After 10 min at 100 W a conversion of 35% was observed and the experiment was abandoned.

It is worth mentioning that the substitution process evidently tolerates functional groups such as esters **(3d)**, amides **(3e)** and carboxylic acids **(3e)**. Apparently the high stability of the ruthenium-sulfur bond favours exclusive formation of the thiolato-complexes over the COO-linkage isomer possible for **3e**, as indicated by the ^{31}P-NMR chemical shift and the missing signals corresponding to the SH functionality in both ^{1}H-NMR and IR spectra.[9]

Compounds **3a** and **3b** have been described in the literature.[7] Compounds **3c–e** are new compounds. The new thiolato-complexes are moderately air sensitive yellow powders, which are soluble in benzene, toluene, acetone and other polar solvents. In chlorinated solvents such as $CHCl_3$ or CH_2Cl_2 they decompose upon standing. They are insoluble in petroleum ether.

The spectroscopic data are in perfect agreement with their structure. The ^{31}P-NMR spectrum shows a singlet in the expected area.[6, 7] The thiolate α-CH signals in the ^{1}H and ^{13}C NMR spectrum are only marginally shifted in comparison to the free ligand. The coordination of the thiolate to the metal centre can be easily deduced from the ^{13}C NMR spectra of the complexes, which appears as a triplet and exhibit a $^{3}J_{PRuSC}$ coupling of 7 Hz to the α-C.

Conclusion

In conclusion we have shown that cyclopentadienyl bis-phosphine ruthenium thiolato-complexes can be obtained under microwave conditions in yields comparable to the thermal process. The reaction is compatible with functional groups such as esters, carboxylic acids and amides. The reaction times are dramatically enhanced under focussed microwave irradiation and cut from 2 h to 2 minutes. Methodology using focussed irradiation is clearly superior to the use of a conventional multimode oven. We hope that microwave conditions will find further applications in the field of organometallic and co-ordination chemistry.

Experimental

All thermal experiments were performed under an atmosphere of dry dinitrogen and solvents were dried using the typical procedures. Microwave irradiation was performed in a Labwell Microwell 10 reactor (focussed MW oven) and a Proline microchef ST44-950 W (household oven) in 10 ml pyrex glass tubes with a screw cap and rubber septum under an argon atmosphere. $[RuCp(PPh_3)_2Cl]$[10] and dppm[11] were prepared according to the literature procedures. All other reagents were used as purchased. The following analytical instruments were used: IR: Perkin-Elmer 283, Bruker IFS 25; NMR: Bruker AMX 400 (^{1}H, 400 MHz, TMS; ^{13}C, 100 MHz, TMS; ^{31}P, 162 MHz, H_3PO_4) and Jeol GSX-270. Signals of aryl groups and signals of the CH_2 group of the dppm ligand are uncharacteristic and have been omitted from the lists of spectral data. Melting or decomposition points were determined in closed capillaries in a copper block and are uncorrected.

Typical procedure for thermal reaction:

$[RuCp(dppm)(SCH_2CH_2Ph)]$ **(3a):** $[RuCp(PPh_3)_2Cl]$ **(1)** (726 mg, 1.00 mmol), $NaSCH_2CH_2Ph$ (192 mg 1.20 mmol) and dppm (461 mg, 1.20 mmol) in a a mixture of 20 ml THF and 15 ml ethanol were heated for 2h under reflux. The solvent was removed in vacuum and the residue purified by column chromatography (silica gel, eluent Et_2O/THF 2:1). The product was further purified by recrystallisation from toluene/petrolether.

Typical procedure for synthesis under focused microwave irradiation:

$[RuCp(PPh_3)_2Cl]$ **(1)** (73 mg, 0.10 mmol), $NaSCH_2CH_2Ph$ (20 mg, 0.12 mmol) and dppm (46 mg, 0.12 mmol) in diethylene glycol (1 ml) in a sealed tube were irradiated at 100 W for 120 s (up to 10 min in household MW oven). Every 20 s irradiation was discontinued and the reaction vessel was checked for safety considerations. The conversion was monitored by ^{1}H NMR. The solvent was removed in vacuum and the residue purified by column chromatography (silica gel, eluent Et_2O/THF 2:1). The product is further purified by recrystallisation from toluene/petrolether. The spectroscopical data were identical to those of the products of the thermal reactions. Yields and conversions are listed in Table 1.

[RuCp(dppm)(SPh)] **(3a):** Yield (thermal conditions) 82%, yield (MW conditions) 85% yellow powder. m.p. 118–120°C (dec.). ^{31}P NMR (C_6D_6): δ = 15.6 (s). ^{1}H NMR (C_6D_6): δ = 7.69–6.88 (m, 25H, Ar), 4.82 (s, 5H, Cp).

$[RuCp(dppm)(SCH_2CH_2Ph)]$ **(3b):** Yield (thermal conditions) 84%, yield (MW conditions) 85%, yellow powder. m.p. 163°C (dec.). $C_{38}H_{36}P_2RuS$ (679.79) calcd.: C 66.36 % H 5.28%, found: C 66.36 % H 5.26%. ^{31}P NMR (C_6D_6): δ =15.2 (s). ^{1}H NMR (C_6D_6): δ = 7.69–6.68 (m, 25H, Ar), 4.82 (s, 5H, Cp), 2.85 (AA'XX' system, N= 17.1 Hz, 2H, SCH_2), 2.65 (AA'XX'-system, N= 17.1 Hz, 2H, CH_2Ph).- ^{13}C NMR (C_6D_6): δ = 142.5–124.1 (m, Ar), 78.5 (s, Cp), 47.8 [t, *J*(PC)= 22 Hz, PCP], 41.5 (s, SC), 37.9 (s, CPh).

[RuCp(dppm){SCH2(C4H3O)}] **(3c):** Under thermal conditions 10% of the compound $[RuCp(dppm)(PPh_3)]Cl$ are formed as a side product:[11] Yield (thermal conditions) 74%, yield (MW conditions) 75%. m.p. 153–156°C (dec.). $C_{32}H_{35}OP_2RuS$ (630.71). no satisfactory elemental analysis could be obtained. ^{31}P NMR (C_6D_6): δ =15.8 (s). ^{1}H NMR (C_6D_6): δ = 7.99–6.86 (m, 21H, Ar), 6.07 (dd *J* = 2.9 and 1.9 Hz, 1H, Furyl), 5.91 (d, *J* = 3.0 Hz, 1H, H-3 Furyl), 4.84 (s, 5H, Cp), 2.87 (s, 2H, SCH_2). ^{13}C NMR (C_6D_6): δ = 141.7–124.3 (m, Ar), 110.3, 108.9 (Furyl), 79.9 (s, Cp), 46.2 [t, *J*(PC)= 22 Hz, PCP], 40.2 (t, *J* = 5 Hz, SC).

$[RuCp(dppm)SCH_2COOEt)]$ **(3d):** Yield (thermal conditions) 81%, yield (MW conditions) 85%, yellow powder. m.p. 151°C (dec.). $C_{34}H_{34}P_2O_2RuS$ (669.73) calcd.: C 60.88% H 5.12 %, found: C 60.36% H 5.24%. ^{31}P NMR (C_6D_6): δ = 15.6 (s). ^{1}H NMR (C_6D_6): δ = 7.78–6.88 (m, 20H, Ar), 5.04 (s, 5H, Cp), 4.30 (s, 2H, SCH_2), 3.93 [q, *J*(HCCH)= 6.8 Hz, 2H, OCH_2], 0.92 [t, *J*(HCCH)= 6.8 Hz, 3H, Me]. ^{13}C NMR (C_6D_6): δ = 174.8 (s, C=O), 142.6-126.3 (m, Ar),

Table 1 Conditions and yields for thermal and MW reactions for compounds **3a–e**

Entries	R in **3a–e**	Isolated yield/%, thermal conditions[a]	Conversion/% MW conditions	Isolated yield/% MW conditions
1	Ph **(3a)**	84	88[b,c]	85
2	Ph **(3a)**	See entry 1	8[e]	-
3	Ph **(3a)**	See entry 1	35[f]	-
4	CH_2CH_2Ph **(3b)**	84	88[b,d]	85
5	$CH_2C_4H_3O$ **(3c)**	74	75[b,d]	70[g]
6	CH_2COOEt **(3d)**	81	90[b,d]	85
7	$CH_2CH(NHAc)COOH$ **(3e)**	91	90[b,d]	88

[a]Conditions: THF/EtOH 2:1, 2 h reflux; [b]Monomode focused MW reactor at 100W in diethylene glycol using focused MW; [c]Reaction complete after 90 s at 100W; [d]Reaction complete after 120 s at 100W; [e]irradiation at 100W in standard household MW oven for 2 minutes; [f]irradiation at 100W in standard household MW oven for 10 minutes; [g]compound not analytically pure.

80.6 (s, Cp), 59.7 (s, OC), 48.6 (t, *J*(PC)= 22 Hz, PCP), 36.7 [t, *J*(PRuSC)= 7 Hz, SC], 14.2 (s, Me).

[RuCp(dppm){SCH2CH(NHAc)COOH}] **(3e):** [RuCp $(PPh_3)_2Cl$] 726 mg (1.00 mmol), NaACC 223 mg (1.20 mmol) and dppm (461 mg 1.20 mmol) were dissolved in a mixture of ethanol (15 ml) and THF (20 ml) and refluxed for 2 hours. The solvent was removed under reduced pressure and the residue was dissolved in 10 ml benzene and filtered through celite. The solvent was again removed under reduced pressure and the residue twice recrystallised from toluene/petroleum ether to give the product [RuCp (dppm) {$SCH_2CH(NHAc)COOH$}] as a yellow crystalline solid. After microwave irradiation, in diethylene glycol as a solvent, the work-up was done as described for the thermal experiment. Yield 91%, m.p.: 132°C (decomp.); $C_{35}H_{33}NO_3P_2RuS$ (710.73).- calc. C 59.15 % H 4.68% N 1.97%, found: C 59.00% H 4.99% N 1.71%; ^{31}P NMR {d^6-Acetone}: δ 15.4 (s); ^{1}H NMR {d^6-Acetone}: δ 7.67–6.87 (m, 20 H, Ar), 6.68 (d, *J* 7.4 Hz, 1H, NHAc); 5.22–4.84 (m, 2H, PCH_2P), 5.04 (s, 5H, Cp), 4.09 (dt, *J* 7.4 and 7.6 Hz, 1H, CHN), 1.78 (s, 3H, Me), 1.66 (d, *J* 7.6 Hz, 2H, SCH_2). ^{13}C NMR {d^6-Acetone}: δ 83.7 (Cp), no other signal detected due to low solubility.

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