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Preparation and properties of the dicarbonyl-thiolate complexes $[Ru(SR)_2(CO)_2(PR'_3)_2]$

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Abstract

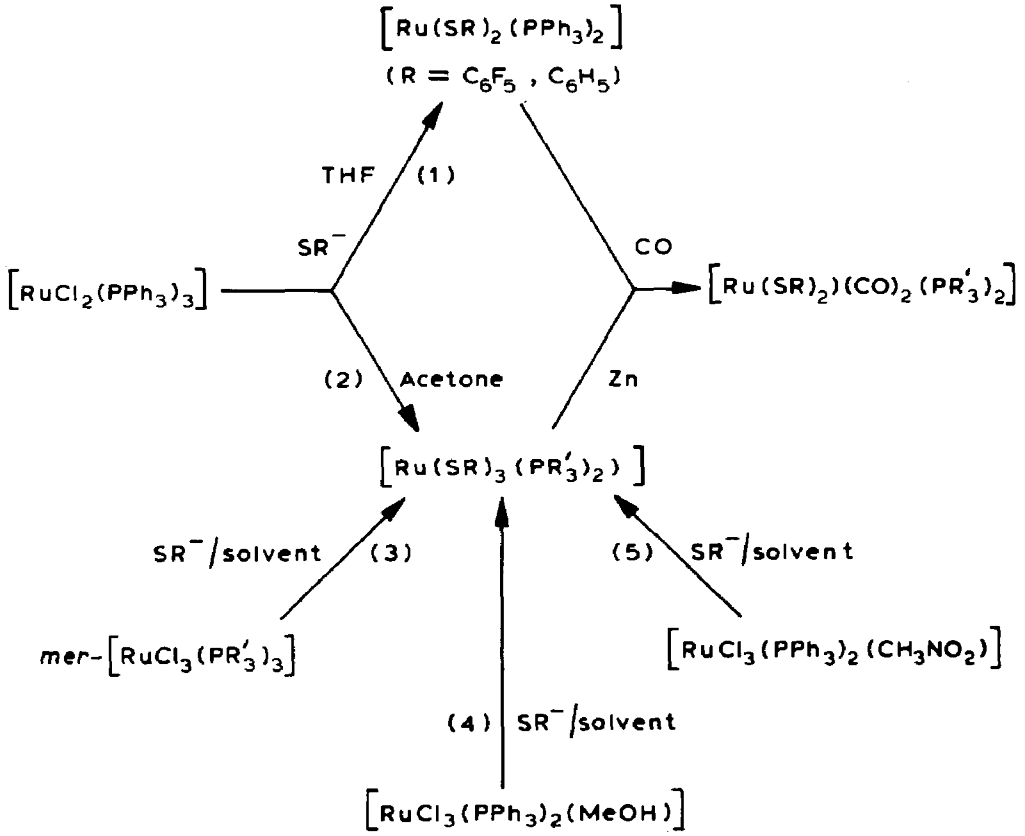
The preparations of the complexes $[Ru(SR)_2(CO)_2(PR'_3)_2]$ ($R = C_6F_5$, C_6F_4H, C_6FH_4, C_6H_5, CH_3 or Bu^t; $PR'_3 = PMe_2Ph$, PEt_2Ph or PPh_3) are described, together with spectroscopic data used to assign configurations.

We have been developing the chemistry of thiolate-phosphine complexes because the steric and electronic properties of thiolate ligands often produce new chemical features when compared, for example, with analogous complexes of halide ligands [1]. Thus we have recently found that thiolate complexes of ruthenium can show interaction of C–F or C–H bonds with the metal centre [2,3].

In this paper we describe the preparation of a series of thiolate-carbonyl complexes of ruthenium that should prove to be interesting starting materials for future reactions.

Preparation of complexes

The complexes $[Ru(SR)_n(PR'_3)_2]$ (**A**) ($n = 2$ or 3; $R = C_6F_5$, C_6F_4H, C_6FH_4, C_6H_5, CH_3, or Bu^t; $PR'_3 = PMe_2Ph$, PEt_2Ph, $PMePh_2$ or PPh_3) have been prepared by treatment of $[RuCl_2(PPh_3)_3]$ or *mer*-$[RuCl_3(PR'_3)_2]$ with $Pb(SR)_2$ or NaSR in acetone [2,3]. Reduction of **A** with amalgamated zinc under CO gives the series *cis*- or *trans*-$[Ru(SR)_2(CO)_2(PR'_3)_2]$ (**B**). An alternative synthesis of **B** involves direct treatment of the reaction mixture of $[RuCl_2(PPh_3)_3]$ or *mer*-$[RuCl_3(PR'_3)_3]$ in acetone with thiolate salts, then filtering off of the $PbCl_2$ or NaCl and addition of CO in situ (Scheme 1). The intense colour of the initially solution changes rapidly



Scheme 1. Solvents: acetone, tetrahydrofuran (thf) or ethanol (see Experimental).

with the formation of a yellow solution, from which the yellow complexes **B** can be isolated, the overall reaction being as in eq. 1.

$$\underset{\textbf{(A)}}{[\mathrm{Ru(SR)}_n(\mathrm{PR'_3})_2]} + 2\mathrm{CO} \xrightarrow{\mathrm{Zn}} \underset{\textbf{(B)}}{[\mathrm{Ru(SR)_2(CO)_2(PR'_3)_2}]} \quad (1)$$

($n = 2$ or 3)

It is well known that reaction of $[RuCl_2(PPh_3)_3]$ with CO in acetone or benzene gives isomers of $[RuCl_2(CO)_2(PPh_3)_2]$. Which isomer is formed depends on the reaction conditions [4]. Similarly we find that which isomers of the thiolate complexes are formed depends upon the method of preparation. In the following discussion, the reaction routes and the product configurations refer to Scheme 1 and to Fig. 1, respectively.

When a solution of $[Ru(SC_6F_5)_2(PPh_3)_2]$ in acetone is stirred under CO at room temperature (route 1), *cis*-$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$ (configuration I) can be isolated. This formulation is based on the spectroscopic details given below and the fact that the metathesis reaction is possible for *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ (configuration I) reacts with $Pb(SC_6F_5)_2$. If the reaction is carried out by route 3, the isomer with configuration III is obtained and if the reaction route is 4 or 5, isomer II is isolated.

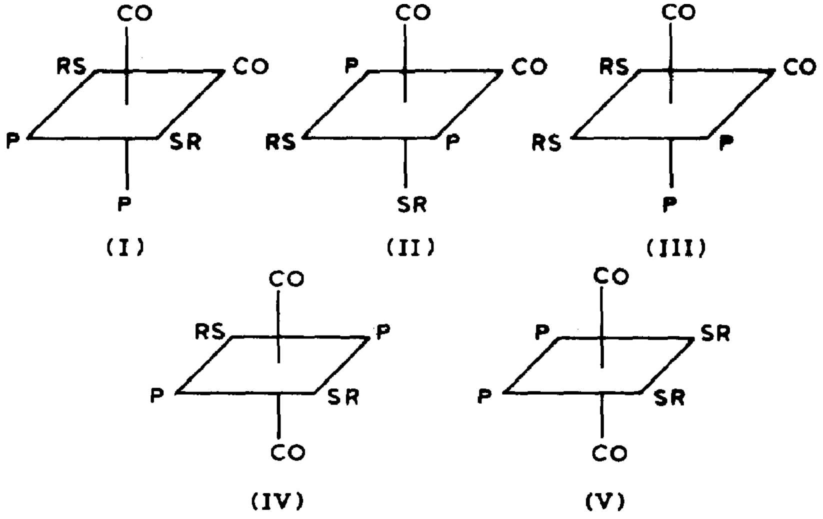


Fig. 1.

For the PMe_2Ph-, $PMePh_2$-, PEt_2Ph- and $PEtPh_2$-dicarbonyl derivatives the reactions were carried out, in all cases, by route 3. As before, it is also possible to obtain different isomers, also different configurations are obtained on changing the SR^- ligand, with the phosphine kept constant. In this paper we report our findings with PPh_3, PMe_2Ph, $PMePh_2$ and $PEtPh_2$, and work is in progress with other thiolates and phosphines.

The analytical and other physical properties of the compounds prepared are shown in Table 1.

The assignment of configurations has been made on the basis of IR and ^1H, ^{31}P and ^{19}F NMR spectroscopy, using methods well-established for the halide analogues [5,6].

IR spectra. All complexes show strong CO stretching absorbtions in the 1900–2100 cm^{-1} range (Table 2), complexes with *cis*-carbonyls showing two bands and those with *trans*-carbonyls only one.

For $[Ru(SR)_2(CO)_2(PR'_3)_2]$ (configuration I) the average $\nu(CO)$ varies with R in the sequence $C_6F_4H > C_6F_5 > C_6H_5$ and for $[Ru(SR)_2(CO)_2(PR'_3)_2]$ (configuration II) this variation is $Bu^t > CH_3 > C_6F_4H > C_6F_5 > C_6FH_4$.

A *trans*-influence is observed for $[Ru(SC_6F_5)_2(CO)_2(PR'_3)_2]$ (configuration I). As PR'_3 varies, $\nu(CO)$ decreases in the order $PMePh_2 > PPh_3 > PEt_2Ph$.

These effects are due to a combination of σ- and π-electronic fluctuations and are difficult to rationalise in detail.

NMR spectra. The ^1H NMR spectra of the complexes that contain methyl groups are shown in Table 3. The assignment of configuration of complexes of the type $[MCl_2(CO)_2(PR'_3)_2]$ (M = Ru or Os) from NMR and IR data has been described in detail [5,6]. When these methods are used for $[Ru(SR)_2(CO)_2(PPh_3)_2]$ (R = Me or Bu^t), the singlet ^1H and ^{31}P spectra and comparison with the halide analogues indicate that configuration II is most likely for these compounds, although configuration I cannot be completely excluded.

The complex $[Ru(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$ can be isolated in two different configurations in the solid state (see Table 2), but in solution both are transformed

Table 1

Elemental analyses for dicarbonylruthenium compounds

Compound [a]	Yield (%)	Analyses (Found (calcd.)(%))	
		C	H
$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$	62	55.5 (55.6)	2.9 (2.8)
$[Ru(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$	54	43.7 (43.3)	2.9 (2.7)
$[Ru(SC_6FH_4)_2(CO)_2(PPh_3)_2]$	33	64.3 (64.2)	4.3 (4.1)
$[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	67	45.8 (45.9)	3.1 (3.3)
$[Ru(SC_6F_4H)_2(CO)_2(PEt_2Ph)_2]$	70	46.3 (47.9)	4.0 (3.8)
$[Ru(SC_6F_5)_2(CO)_2(PMePh_2)_2]$	40	48.6 (50.2)	2.4 (2.7)
$[Ru(SC_6H_5)_2(CO)_2(PPh_3)_2]$	68	65.8 (66.7)	4.7 (4.4)
$[Ru(SCH_3)_2(CO)_2(PPh_3)_2]$	56	61.0 (61.9)	4.5 (4.6)
$[Ru(SBu^t)_2(CO)_2(PPh_3)_2]$	42	63.8 (64.4)	5.2 (5.6)

[a] All the isomers gave similar elemental analyses, all compounds are yellow.

into one isomer, for which a multiplet is observed in the ^1H NMR spectrum of the PMe_2Ph groups, characteristic of two mutually *trans*-phosphines [5,6]. The ^{31}P NMR spectrum is a singlet indicating that the two PMe_2Ph ligands are equivalent and the ^{19}F NMR pattern contains three groups of signals well-defined as one triplet for the *para*-fluorine, one doublet of doublets for the *ortho*-fluorine and one

Table 2

IR spectra of compounds $[Ru(SR)_2(CO)_2(PR'_3)]$

Compound	Configuration	$\nu(C{=}O)$ (cm^{-1}) [a]
$[Ru(SCH_3)_2(CO)_2(PPh_3)_2]$	II	2059, 1996
$[Ru(SBu^t)_2(CO)_2(PPh_3)_2]$	II	2060, 1998
$[Ru(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$	II	2017, 1975
$[Ru(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$	IV	1993
$[Ru(SC_6F_5)_2(CO)_2(PMePh_2)_2]$	II	2040, 1983
$[Ru(SC_6F_5)_2(CO)_2(PMePh_2)_2]$	I	2054, 1963
$[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	I	2020, 1960
$[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	III	2063, 1990
$[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	IV	1960 [b]
$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$	I	2048, 1990
$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$	II	2055, 1995
$[Ru(SC_6F_4H)_2(CO)_2(PPh_3)_2]$	II	2058, 1996
$[Ru(SC_6F_4H)_2(CO)_2(PPh_3)_2]$	I	2066, 2000
$[Ru(SC_6FH_4)_2(CO)_2(PPh_3)_2]$	II	2055, 1978
$[Ru(SC_6H_5)_2(CO)_2(PPh_3)_2$	I	2031, 1973

[a] KBr pellets. [b] In CH_2Cl_2 solution, 1968.

Table 3

NMR spectra of compounds $[Ru(SR)_2(CO)_2)PR'_3)_2]$

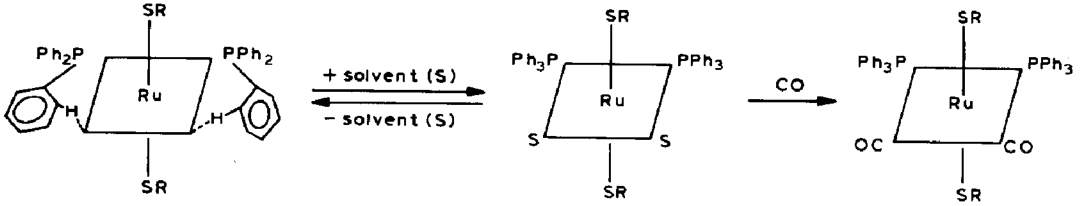
Compound [a]	δ(^{1}H) (ppm) [b]	δ(^{31}P) (ppm) [c]	δ(^{19}F) (ppm) [d]	^{3}J(FF); ^{4}J(FF) (Hz)
$[Ru(SCH_3)_2(CO)_2(PPh_3)_2]$				
(II)	1.48(s) (CH_3)	−118.2(s)	–	–
$[Ru(SBu^t)_2(CO)_2(PPh_3)_2]$				
(II)	0.8(s) (CH_3)	−101.43(s)	–	–
$[Ru(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$	1.78(m) [f] (CH_3)	−155.0(s)	−160.76(t)	
(II,IV) [e]			−165.38(m)	19.5; 7.3
			−131.58(dd)	
$[Ru(SC_6F_5)_2(CO)_2(PMePh_2)_2]$	2.43–2.1 [f] (CH_3)	−122.4(s)	−168.16(tt)	
(II)			−170.65(m)	19.5; 7.3
			−132.08(dd)	
$[Ru(SC_6F_5)_2(CO)_2(PMePh_2)_2]$	2.3(d) [g]	−153.0(s)	−164.0(tt)	
(I)	2.0(d) [g]		−168.20(m)	19.5; 7.3
			−132.20(dd)	
$[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	2.43–1.52(m) (CH_2)	−123.3(d) [h]	−163.90(tt)	
(I)	1.15–0.8(m) (CH_3)	−138.2(d) [h]	−168.48(m)	19.5; 7.3
			−133.33(dd)	
$[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	2.43–1.52(m) (CH_2)	−122.0(d) [h]	−168.5(m)	19.5
(III)	1.15–0.8(m) (CH_3)	−137.0(d) [h]	−131.9(m)	
$Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	2.20(n) (CH_2) [i]	−115.5(s)	−161.59(t)	
(IV)	0.93(q) (CH_3) [i]		−164.25(m)	19.5; 7.3
			−131.09(dd)	
$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$	–	−111.6(s)	−161.30(t)	
(II)			−163.58(m)	19.5; 7.3
			−133.0(dd)	
$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$	–	−122.3(s)	−164.09(t)	
(I)			−166.27(m)	19.5; 7.3
			−129.92(dd)	
$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$	–	−110.1(d) [j]	−161.25(m)	
(III)		−118.4(d) [j]	−165.35(m)	19.5; 7.3
			−132.25(dd)	
$[Ru(SC_6H_5)_2(CO)_2(PPh_3)_2]$	–	−145.88(s)	–	–
$[Ru(SC_6F_4H)_2(CO)_2(PPh_3)_2]$				
(II)	–	−114.4(s)	–	–

[a] Configurations in parentheses. [b] Rel. $SiMe_4$ in $CDCl_3$ solution; all compounds show a multiplet in the region δ 6.9–8.2 ppm due to Ph groups. [c] Rel. $P(OMe)_3$. [d] Rel. $CFCl_3$. [e] Isomer IV converts to II in solution. [f] Unresolved overlapping triplets, see text. [g] ^{2}J(PH) 9.1 Hz. [h] ^{2}J(PP) 27.9 Hz; [i] $^{3}J+^{5}J$ 9.1 Hz, $^{3}J+^{4}J$ 4.0 Hz see ref. 6 for details. [j] ^{2}J(PP) 27.8 Hz; s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, n = nontet, q = quintet, t = triplet, tt = triplet of triplets.

complicated signal for the *meta*-fluorine (integration 1/2/2). The solution IR spectrum shows two CO bands, therefore configuration II is most likely for $[Ru(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$ in solution. It is possible to obtain the I and II isomers of $[Ru(SC_6F_5)_2(CO)_2(PMePh_2)_2]$ by different routes (see experimental section). For isomer I, two doublets are observed in the ^{1}H NMR because there is no 'virtual coupling' between the *cis*-phosphines. The ^{19}F pattern corresponds to two equivalent SC_6F_5 groups.

Carbon monoxide reacts with $[Ru(SC_6F_5)_3(PEt_2Ph)_2]$ [2] to yield two different isomers of $[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$. That having configuration I has two doublets in its ^{31}P NMR spectrum (see Table 3). This type of AB pattern has been reported for similar halide derivatives [7]. Its ^{1}H spectrum consist of three groups of complicated signals and its ^{19}F spectrum has the characteristic splitting pattern of equivalent SC_6F_5 groups. The other isomer is assigned configuration III because two doublets arise in its ^{31} P NMR spectrum and very complicated splitting patterns occur both in the ^{1}H and in the ^{19}F NMR spectra. A third isomer of $[Ru(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ (configuration IV), is obtained starting from $[RuCl_2(CO)_2(PEt_2Ph)_2]$ and $Pb(SC_6F_5)_2$. Its ^{1}H resonance pattern is typical of *trans*-PEt groups with strong phosporus–phosphorus coupling and a plane of symmetry through the $P{-}CH_2$ bonds; similar patterns have been reported for $[OsCl_2(CO)_2(PEt_2Ph)_2]$ [6]. The presence of one ^{31}P resonance, equivalent SC_6F_5 groups (^{19}F spectrum) and one (C≡O) IR band are unequivocal proof of an all-*trans*-configuration.

Several routes can be used to obtain $[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$ (see Scheme 1), and therefore different configurations are possible, depending on the route chosen. The complex with configuration I is obtained by route 1. The starting material for this route, $[Ru(SC_6F_5)_2(PPh_3)_2]$ [3] has, in the solid state, *trans*-thiolates and *cis*-phosphines and an *ortho*-hydrogen of one phenyl group in each phosphine occupies a position in the coordination sphere around the ruthenium atom. Presumably, when $[Ru(SC_6F_5)_2(PPh_3)_2]$ is dissolved, the *ortho*-hydrogens leave their coordination positions and two carbon monoxide molecules occupy the vacant sites (see Scheme 2).



Scheme 2.

$[Ru(SC_6F_5)_2(CO)_2(PPh_3)_2]$ (configuration II) is obtained by both route 4 and route 5, whilst the analogue with configuration III is obtained by route 3. The latter assignment is based on the presence of two C≡O IR bands (Table 2), two doublets (1/1) in the ^{31}P NMR spectrum and a complicated splitting pattern in the ^{19}F NMR spectrum. It is noteworthy that if the reaction follows route 2 (Scheme 1) with SC_6F_5, SC_6F_4H, SC_6FH_4, or SC_6H_5, configuration II is favoured. We prefer the latter assignment on the basis of the singlet ^{31}P NMR spectra (equivalent phosphines) and the ^{19}F NMR spectral splitting pattern which indicates two equivalent fluorothiolate ligands.

Experimental

All manipulations involving air-sensitive materials were carried out by Schlenk or standard high-vacuum techniques. All solvents were degassed before use. The compounds $[Ru(SC_6F_5)_2(PPh_3)_2]$, $[Ru(SC_6F_5)_3(PR'_3)_2]$ ($R = CH_3$, Bu^t, C_6F_5, C_6F_4H, C_6FH_4 or C_6H_5; $PR'_3 = PPh_3$, PMe_2Ph, PEt_2Ph, or $PMePh_2$) were prepared by the reported methods [2,3].

The methods of preparation of complexes are general and typical examples are given here. Analytical data and spectra for the compounds prepared by these methods are given in Tables 1–3.

Spectra were determined using Pye–Unicam SP3-200s (IR) and Jeol FX90Q (NMR) instruments. Microanalyses were determined by Mr. C. Macdonald of the Nitrogen Fixation Laboratory.

Dicarbonylbis(pentafluorothiophenolato)bis(triphenylphosphine)ruthenium(II), [Ru-(SC$_6$F$_5$)$_2$(CO)$_2$(PPh$_3$)$_2$] (configuration I). A solution of $[Ru(SC_6F_5)_2(PPh_3)_2]$ (0.2 g; 0.019 mmol) in THF (50 cm^3) was stirred at room temperature under carbon monoxide. The initial blue-purple solution changed rapidly (ca. 20 min) to yellow, and it was then filtered. The yellow filtrate was evaporated to ca. 10 cm^3 and MeOH was added to yield yellow crystals, which were filtered off, washed with ether, and dried in a vacuum.

Dicarbonylbis(dimethylphenylphosphine)bis(pentafluorothiophenolato)ruthenium(II), [Ru(SC$_6$F$_5$)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] (configuration II). Lead pentafluorothiophenolate (0.45 g; 0.743 mmol) was added to a solution of *mer*-$[RuCl_3(PMe_2Ph)_3]$ (0.3 g; 0.496 mmol) in acetone (ca. 25 cm^3), the mixture was shaken at room temperature for ca. 2 h, and then the $PbCl_2$ formed was filtered off. Amalgamated Zn and carbon monoxide were added to the green solution and the mixture was shaken at room temperature. The yellow solution obtained was concentrated under reduced pressure and MeOH (ca. 10 cm^3) was added to yield yellow crystals, which were filtered off, washed with methanol and ether, and dried in a vacuum.

Dicarbonylbis(methylthiolato)bis(triphenylphoshpine)ruthenium(II), [Ru(SCH$_3$)$_2$-(CO)$_2$(PPh$_3$)$_2$]. Sodium methylthiolate (0.0401 g; 0.208 mmol) was added to a solution of $[RuCl_2(PPh_3)_3]$ (0.2 g; 0.208 mmol) in acetone (ca. 25 cm^3) and the mixture was shaken at room temperature for 12 h and then filtered. The resulting green-brown solution was shaken under carbon monoxide at room temperature until the colour changed to yellow. After concentration, MeOH (ca. 10 m^3) was added, to yield yellow crystals, which were filtered off, washed with methanol and ether, and dried in a vacuum.

Dicarbonylbis(diphenylmethylphosphine)bis(pentafluorothiophenolato)ruthenium(II), [Ru(SC$_6$F$_5$)$_2$(CO)$_2$(PMePh$_2$)$_2$] (configuration II). $RuCl_3 \cdot 3H_2O$ (0.3 g; 1.15 mmol) was dissolved in ethanol (30 cm^3) and methyldiphenylphosphine (1.2 g; 6 mmol) was added. The mixture was heated under reflux for ca. 5 min. The initial dark solution changed to green, lead pentafluorothiophenolate (0.9 g; 0.260 mmol) was added, and the mixture was shaken under a CO atmosphere. The green solution changed to yellow, and was evaporated to dryness. The residue was recrystallised from acetone MeOH (1/1) to yield yellow crystals, which were filtered off, washed with acetone, and dried in a vacuum.

Dicarbonylbis(methyldiphenylphosphine)bis(pentafluorothiophenate)ruthenium(II), [Ru(SC$_6$F$_5$)$_2$(CO)$_2$(PMePh$_2$)$_2$] (configuration I). $[RuCl_2(CO)_2(PMePh_2)_2]$ (configuration I) (0.2 g; 0.318 mmol) was dissolved in acetone 30 cm^3 and $Pb(SC_6F_5)_2$ (0.173 g; 0.318 mmol) was added under a CO atmosphere. The mixture was shaken ca. 10 h and then the $PbCl_2$ formed was filtered off. The yellow solution was evaporated to lower volume under reduced pressure and MeOH (10 cm^3) was added to yield yellow crystals, which were filtered off, washed with methanol and ether, and dried in a vacuum.

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