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Neutral and cationic 1,4-diphospha-2-rhoda-3-thia-[4]-ferrocenophane

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Abstract

A mixed bidentate ferrocenyl ligand $Fe(\eta^5-C_5Me_4P(S)Ph_2)(\eta^5-C_5Me_4PPh_2)$ (abbreviated {P,P=S}) was synthesised and used for complexation with $[RhCl(CO)_2]_2$. The neutral [4]-ferrocenophane {P,P=S}Rh(CO)Cl **2** and the unusual dimeric cationic species $[\{P,P{=}S\}Rh(CO)(\mu\text{-}Cl)(CO)Rh\{P,P{=}S\}]^+$ **3** were obtained and characterized by crystal structure analysis. During investigations on the catalytic properties of **2** in carbonylation, some aspects of its behavior towards iodomethane were elucidated. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocenophane; Heterobimetallic; Iron–rhodium; Oxidative addition

1. Introduction

Many of the transition metal centers that play an important role in catalysis contain bidentate ligands in their coordination sphere. The control of the reactivity and the selectivity of the catalyst has been largely improved during the last few years [1]. A particular bidentate ligand can be used in order to tune the electronic and steric properties of a given complex. Casey recently developed the model of the natural bite angle of a diphosphine to tentatively rationalize the selectivities observed in the hydroformylation of alkenes with rhodium-diphosphine ligand, as a function of the geometry imposed by the ligand [2]. Thus it was attractive to develop a class of bidentate ligands in which two cyclopentadienyl ligands with a coordinating heteroatom group are linked in a metallocenic entity. In this class of compounds, ferrocenyl compounds such as dppf [3] or dppomf [4] are common ligands used for complexation due to their air-stability. They lead to various species offering a great variety of properties. For example, the rhodium derivatives are efficient catalysts for olefin hydroformylation or hydrogenation [3].

Recent reports have highlighted the catalytic potential of diphosphinemonoxide and diphosphine monosulfide ligands. Those are mixed-donor ligands, [P,P=E] (E = O, S), which offer the opportunity to exhibit either unidentate coordination or chelation, the latter forming monomeric, mononuclear or dinuclear derivatives. Among these ambivalent ligands the diphosphinesulfide $Ph_2PCH_2P(S)Ph_2$ promotes the rhodium-catalysed carbonylation of methanol [5].

In a previous paper [4] we reported the preparation of several mixed-donor diphosphine ligands based on the ferrocenyl moiety, for which the coordination chemistry has not yet been studied. We made the hypothesis that the synthesis of the related rhodium derivatives using diphosphinesulfide $Ph_2PC_5Me_4FeC_5Me_4P(S)Ph_2$ produces [4]-ferrocenophane. Beside the potential utility of ferrocenyl-rhodium complexes for catalytic applica-

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tions, it was of interest to investigate the chemistry and conformational behaviour of [4]-ferrocenophanes which have remained largely unexplored [6].

2. Result and discussion

2.1. Preparative results

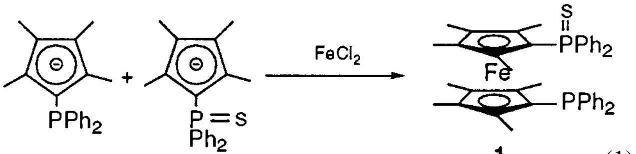
The dissymetrical complex Fe(η^5-$C_5Me_4P(S)Ph_2$)(η^5-$C_5Me_4PPh_2$) **1** containing simultaneously a phosphorus (III) and a phosphorus (V) atom was previously prepared by action of elementary sulfur on the 1,1′-diphenylphosphinooctamethylferrocene. The absence of any differentiation for the two initial phosphorus sites leads to the formation of several products. After chromatography of the mixture the dissymetric 1-diphenylthiophosphino-1′-diphenylphosphinooctamethylferrocene (**1**) was isolated in very low yield (13%) [4].

In order to improve the yield, we have examined the preparation of the ferrocenyl compound by reaction of the two suitably substituted cyclopentadienyl salts, $C_5Me_4PPh_2Li$ and $C_5Me_4P(S)Ph_2Li$, on $FeCl_2$.

The 1,2,3,4-tetramethylcyclopenta-1,3-diene was obtained in four steps from butanone via 3,4-dimethylhexane-2,5-diones and trimethylcyclopentenones [4]. The two last steps consist of the action of methyllithium on trimethylcyclopentenones and the dehydration of the tetramethylcyclopentenol formed in the presence of hydrochloric acid. This preparation is a convenient alternative to the procedures generally described in the literature [4,8].

$C_5Me_4HPPh_2$ was readily obtained by the successive action of butyllithium and chlorodiphenylphosphine on tetramethylcyclopentadiene, whereas $C_5Me_4HP(S)Ph_2$ required the supplementary addition of elemental sulfur [9]. Suitable cyclopentadienyl salts, $C_5Me_4PPh_2Li$ and $C_5Me_4P(S)Ph_2Li$, were further obtained by reaction of one equivalent of butyllithium.

Finally, successive additions of $C_5Me_4P(S)Ph_2Li$ and $C_5Me_4PPh_2Li$, at −78°C, to a suspension of $FeCl_2$ in THF led to the formation of the dissymetric species **1** (60%, Eq. (1)) with only a small amount of the symmetric ones (diphosphine and bis(phosphinesulfide)).

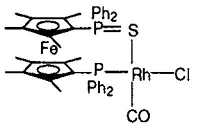


1 (1)

Dichloromethane solutions of **1** and $[RhCl(CO)_2]_2$ reacted immediately on mixing at room temperature (r.t.) to produce a mixture of two products, **2** and **3**, which were separated by recrystallisation. However, when the reaction was repeated, it was not possible to obtain a reproducible ratio of products presumably owing to small variations in the reaction conditions (ratio of reactants, concentrations, conditions of mixing). In addition, when a dichloromethane solution of **2** and **3** was allowed to stand for a number of days, the evolution of the **2**/**3** ratio was observed. It has been shown previously that the coordination behaviour of rhodium(I) may be subject to change, depending on the experimental conditions. Thus, complexes formed by mixing $[RhCl(CO)_2]_2$ with $Ph_2PCH_2P(S)Ph_2$ (dppmS) in methanol are mononuclear RhCl(CO)dppmS, whereas neutral dimers $[RhCl(CO)dppmS]_2$ are isolated in dichloromethane [5,10].

Complexes **2** and **3** are air-stable. Their very similar spectral parameters do not allow clear differentiation of their structures. Both complexes **2** and **3** involve [P,S] chelation as indicated by the ^{31}P-NMR and IR data. In ^{31}P-NMR the doublet at 34.0 ppm ($^1J = 176$ Hz) for **2** and 32.6 ppm ($^1J = 180$ Hz) for **3** are indicative of a phosphorus–rhodium bonding interaction (the free ligand δ value is -24.8 ppm). In contrast the δ(P=S) at 43.2 ppm for **2** and **3**, are close to, but definitely distinct from, that of the free ligand (41.3 ppm). Rhodium complexation of the thiophosphoryl ligand is also consistent with a lowering P=S stretching frequency observed in the IR spectra (632 cm^{-1} for **2** and **3**; 647 cm^{-1} for **1**).

Since the spectroscopic data alone could not allow the nature of the complexes to be unequivocally assigned, X-ray structural investigations have been carried out on complexes **2** and **3**. Compound **2** is the neutral [4]-ferrocenophane whereas **3** shows an unusual structure consisting of a dimeric cationic species with two anionic counterparts (vide infra).



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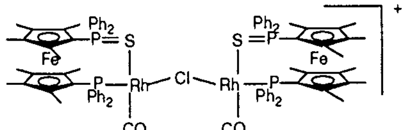


3

The structural studies indicate that **2** should be a precursor to **3**. In fact, compound **2**, which was exclusively obtained from the 1:1 reaction between **1** and $[RhCl(CO)_2]_2$ in toluene instead of dichloromethane, further reacts with $[RhCl(CO)_2]_2$ to yield cationic **3** with $[RhCl_2(CO)_2]^-$ as anion. The presence of $[RhCl_2(CO)_2]^-$ in the anionic part greatly complicates the IR spectra in the CO absorption. In addition, **3** associated with BF_4^- was prepared by treatment of **2** with $AgBF_4$. Hence **2** shows a ν(C=O) band at 1987 cm^{-1} and **3** presents a single ν(C=O) band at 2000 cm^{-1} consistent with a pseudo-centrosymmetric arrangement for the two CO ligands.

2.2. Molecular structure

Crystals of **2** contain two independent heteronuclear (Rh, Fe) complex molecules (A and B) (Figs. 1 and 2) and three $CHCl_3$ solvent molecules. In each molecule, rhodium atom is bonded to the S and P atoms of the two functional substituents $–PPh_2$ and $–PPh_2S$ attached to different ferrocenyl cyclopentadiene rings, one chlorine and one terminal CO ligand to give a square-planar arrangement typical of 16 electron Rh(I) complexes. In the two independent molecules, the corresponding bond lengths and bond angles are equal within experimental error. It is well known that, in square-planar transition metal complexes containing different ligands, the metal–ligand distances are sensitive to the mutual arrangement of the ligands. Baker et al. [5] have reported the structure of $RhCl(CO)(Ph_2PCH_2PSPh_2)$, with the ligand mutual arrangement similar to that observed in **2**. The Rh–S bond distances 2.435(3) and 2.420(3) Å in **2** are longer than the Rh–S bond length in $RhCl(CO)(Ph_2PCH_2PSPh_2)$ (2.403(2) Å). The Rh–C bond lengths with the carbonyl group (in both molecules, 1.80(2) Å) are comparable within experimental error (1.826(8) Å) and the Rh–P bond lengths (2.216(3) and 2.219(3) Å) are also consistent with that in $RhCl(CO)(Ph_2PCH_2PSPh_2)$ (2.220(2) Å). At the same time, although the S=P bond lengths (1.994(4) and 2.001(4) Å) are comparable (2.005(3) Å), the Rh–S–P angles (110.9(2) and 112.4(1)°) are significantly increased compared to 98.6°. The Rh–Cl bond lengths of 2.395(3) and 2.375(3) Å have normal values for a terminal chlorine ligand in Rh(I) complexes [11].

The ferrocene fragments adopt a staggered conformation in both molecules. The P–C(Cp)···C(Cp)–P pseudo-torsional angles are 29.7° in the first molecule and −26.0°, in the second one. Two Cp rings in the ferrocene moieties of each molecule are almost parallel: the corresponding dihedral angles are 2.5 and 3.3°.

The P(1) and P(3) atoms are displaced from the least-squares plane of the corresponding Cp ring opposite from Fe atom by −0.327 and 0.338 Å, respectively (P(1)–C(1) and P(3)–C(6′) bend off are 9.4 and 9.6°). Inversely, P(2) and P(4) atoms are displaced by 0.304 and −0.268 Å (P(2)–C(6) and P(4)–C(1′) bend off are 8.7 and 10.8°). Spatial hindrance within the portions of the complex results in the reduction of the bond angles between the bonds with ipso atoms of phenylsubstituents on phosphorus. Bond angles C(12)–P(1)–C(18) and C(24′)–P(3)–C(30′) are reduced to 93.9(6) and 96.0(5)°. Intrachelate angles at P(1) (118.4(4)°), P(2)(118.5(4)°, P(3) (117.1(4)°, and P(4) (118.1°) are increased compared to the tetrahedral value.

One side of the Rh coordination plane is eclipsed by a ferrocene fragment. The Rh and Fe atoms are separated by 4.364 and 4.366 Å in molecules A and B, respectively.

Crystals of **3** are composed of the tetraheteronuclear (2Rh,2Fe) complex cation, the $[RhCl_2(CO)_2]^-$ complex anion, the Cl^- anion and toluene molecules in the ratio of 1:0.5:0.5:2. In the molecule of the cation, a two-fold axis passes through the bridging Cl(1) atom (Fig. 3).

The geometry of each moiety of the cation is similar to that of **2**. In each moiety, the rhodium atom is also coordinated by the two functional substituents $–PPh_2$ and $–PPh_2S$ attached to different ferrocenyl cyclopentadiene rings, a single bridging chlorine atom and one CO ligand to give square-planar coordination. The coordination planes of the Rh atoms are tilted to one another by 76.6°.

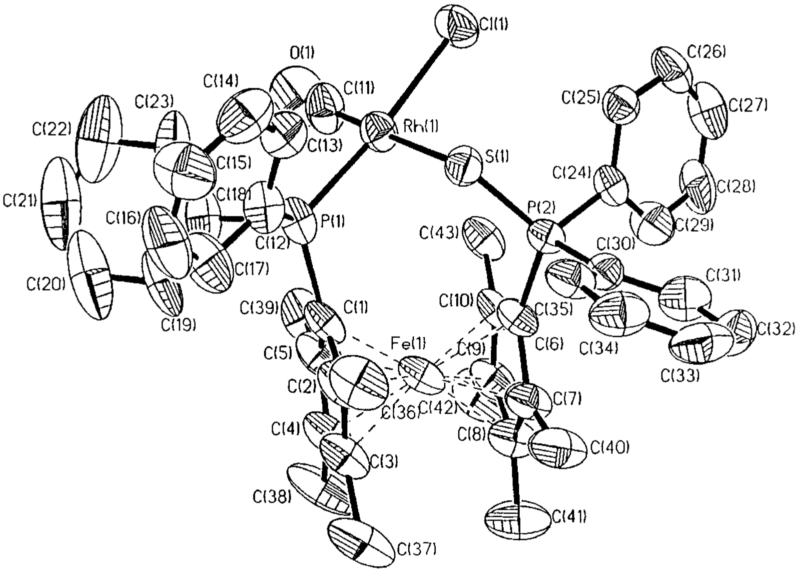


Fig. 1. The molecular structure of **2**A and atom numbering scheme.

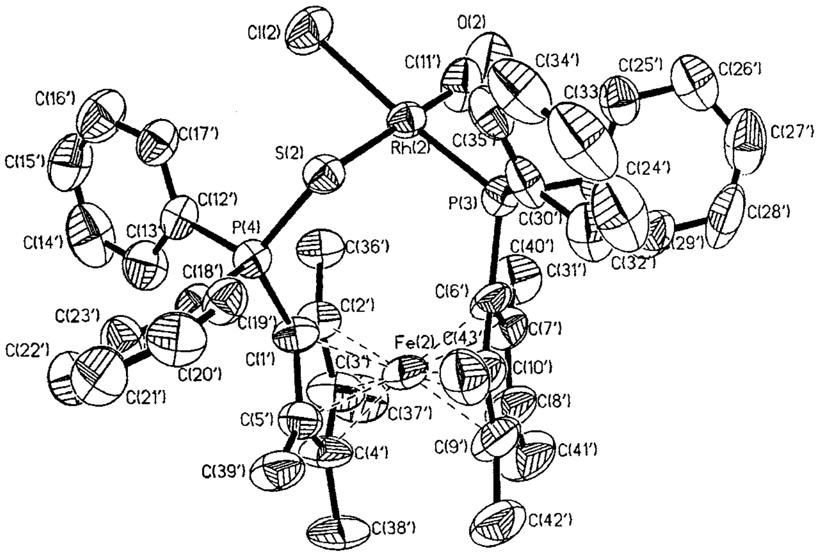


Fig. 2. The molecular structure of **2B** and atom numbering scheme.

The occurrence of one bridging ligand Cl(1) between the two Rh atoms is a peculiar feature of the structure. The Rh(1)–Cl(1) bond length is 2.435(2) Å, the Rh(1)Cl(1)Rh(**1**A) bond angle (87.86(9)°) is less than 90°. The difference is small but significant. The decrease in the angle found cannot be explained by steric hindrance in the complex because no short interatomic contacts between the two parts of the complex are observed. It can probably be explained by a weak secondary interaction between the Rh atoms. The corresponding Rh···Rh distance is 3.378 Å.

The Cambridge Crystallographic Database contains only one example of a binuclear Rh compound where two Rh atoms are combined through only one bridging ligand Cl with the structure $(CO)_2ClRh(\mu\text{-}Cl)Rh(CO)(Me_4\text{-phoran})$ [11]. In this neutral molecule, the Rh–Cl bond lengths 2.454 and 2.372 Å are different but their mean value (2.413 Å) is close to the value found in **3**. The angle at bridging Cl atom (89.4°) is close to 90° than in our case and the Rh···Rh distance is some what longer 3.393 Å (3.378 Å for **3**). The difference in the Rh···Rh distance for these two structures is significant and can result from a weaker Rh···Rh interaction in the case of the neutral complex as compared to the present cationic species.

The Rh–S, Rh–C(43) and Rh–P(1) bond distances are equal to 2.422(2), 1.833(8) and 2.241(2) Å, respectively. The Rh–S and Rh–C bond distances are comparable, respectively with those in **2**, whereas the Rh–P bond length is longer than those in **2** (2,216(3) and 2,219(3) Å); this lenghtening may be considered as a significant one caused by the ionic nature of the complex.

The S(1)–P(2) bond length is 2.010(3) Å and the Rh(1)–S(1)–P(2) angle is 108.12(9)°. In other transition metal complexes containing the M–S=PR3 fragment [12] these values vary within the range of 1.99–2.04 Å and 102.5–116.6° with the mean values 2.016 Å and 108.8° exactly corresponding to those observed in **3**.

The ferrocenyl has an almost ideal staggered conformation, the P(1)–C(1)···C(6)–P(2) pseudo-torsional angle being equal to 28.5°. The two Cp rings are nearly parallel, and the dihedral angle between them is 4.5°. The P(1) atom attached to the first Cp ring (C(1)···C(5)) is displaced from its least squares plane by −0.289 Å (P(1)–C(1) bend off is 8.7°), whereas the displacement of P(2) attached to the second Cp ring(C(6)–C(10)) is 0.265 Å (P(2)–C(6) bend off is 8.4°). Internal stress in **3** resembles that in **2**. The bond angle C(19)–P(1)–C(25) are reduced to 97.8(3)°. The intrachelate angles (116.1(3)° at P(1) and 118.3(3)° at P(2)) are increased compared to tetrahedral values. At the same time, the angle at the sulfur atom has a normal value.

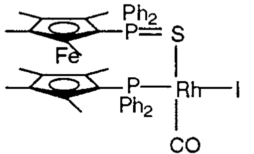
For each half of the cation, one side of the Rh coordination plane is screened by the ferrocenyl fragment (Fe···Rh distance is 4.331 Å). The other side of the Rh coordination plane is significantly eclipsed by the phenyl rings at P(1) and P(1a) atoms. Although these phenyl rings can rotate around P–C bonds in some range, the space between the phenyl rings is of rather restricted size. This fact may be important for the specific catalytic activity of the compound.

The $Rh(CO)_2Cl_2^-$ anion exhibits an usual *cis* configuration with expected metric parameters [13].

2.3. Reactivity with iodomethane

The oxidative addition of iodomethane is often examined for rhodium(I) complexes because it represents a good test for evaluating the nucleophilicity of the metal centres. Moreover, this reaction is the rate-determining step for methanol carbonylation to acetic acid catalysed by $[RhI_2(CO)_2]-$ [5,14]. As the complex **2** presents some similarities with the procatalyst published recently by Baker et al. [5] containing a thiophosphine ligand, we examined the reactivity of **2** and **3** with CH_3I. In addition it was interesting to observe how the ferrocenyl fragment, which in **2** eclipses the rhodium coordination plane, can move to allow the reaction with CH_3I.

The reaction of methyl iodide with **2** in dichloromethane solution results in the quantitative formation of the iodo-substituted rhodium complex **4**. The identity of the reaction products has been established by X-ray structure analysis for **4** [15] and by ^{1}H-NMR (sealed tube) for the byproduct CH_3Cl. Compund **4** is stable at r.t. but reacts with an excess of MeI (neat or in concentrated solution) to give the ferrocenic compound **5** of formula $[Fe(\eta^5\text{-}C_5Me_4P(S)Ph_2)(\eta^5\text{-}C_5Me_4PPh_2Me)]^+$ for the cationic part, involving the decomposition of the bimetallic species **4**. The structure of the cationic part of **5** has been established by the observation of the NMR data. ^{31}P-NMR spectrum shows two singlets at 38.8 and 22.7 ppm whereas ^{1}H-NMR shows a doublet at 3.24 ppm indicating the decoordination of the rhodium fragment and formation of a methyl-phosphonium salt. A series of infrared spectra recorded during and after the reaction of **4** with MeI diplays an evolution of the eliminated rhodium fragment, initially formulated as $[Rh_2(CO)_2I_4]^{2-}$ (ν(C=O) 2058 cm^{-1}; litt: 2058 (KBr)[16]). This anion is unstable in solution and forms $[Rh_2(CO)_2I_2]^-$ whose infrared absorption frequencies are observed at 2059 and 1988 cm^{-1}. The structure of **5** is supported by the spectroscopic identification of the product of the direct reaction of methyl iodide on the ferrocenyl precursor **1**.



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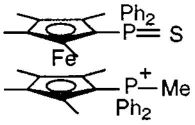

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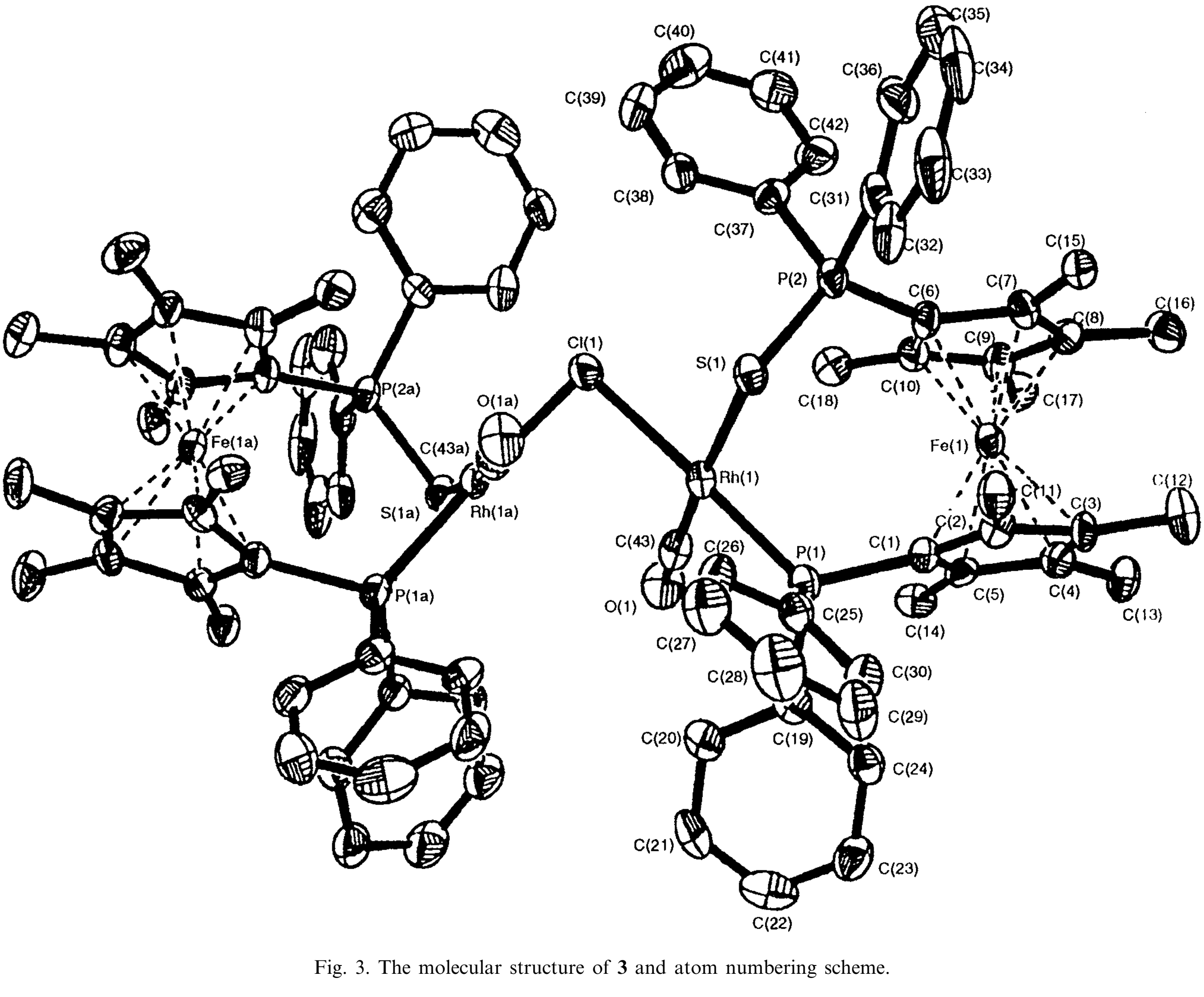
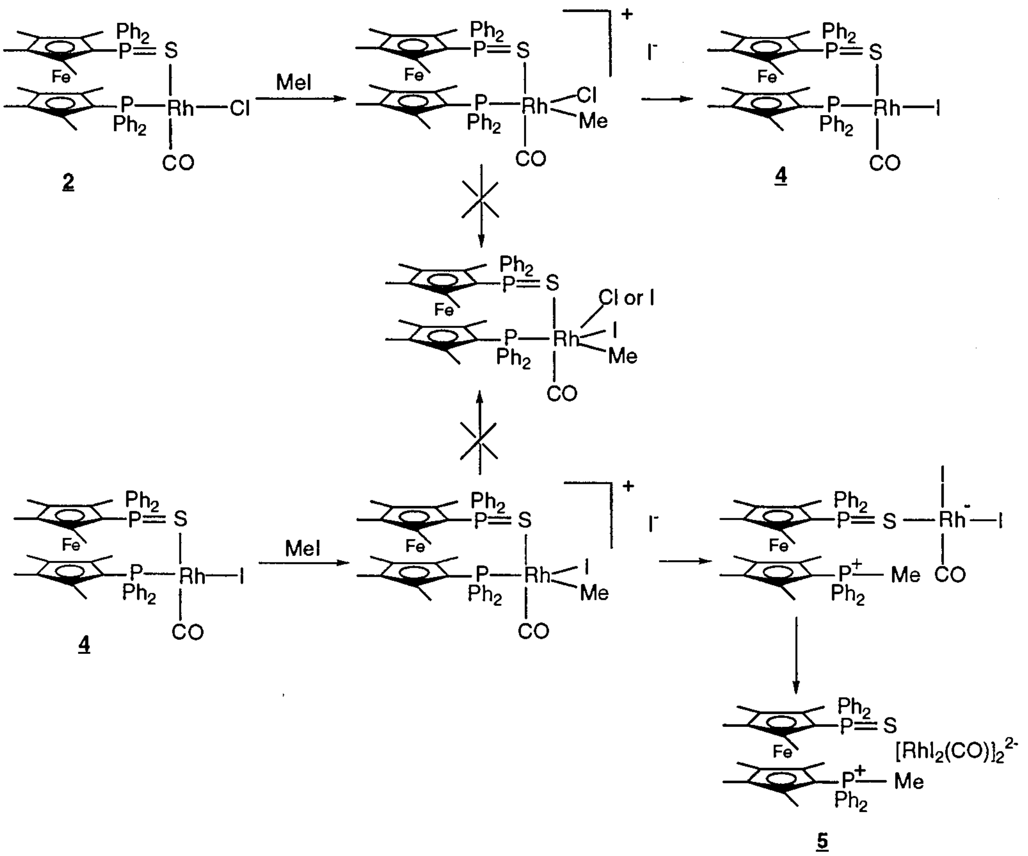


Fig. 3. The molecular structure of **3** and atom numbering scheme.



Scheme 1.

It is widely accepted that iodomethane reacts with square planar rhodium(I) complexes by a stepwise mechanism: a classical S_N^2 attack at the carbon atom followed by coordination of the resulting iodide anion [17]. A nucleophilic attack by **2** on iodomethane would lead to the intermediate shown in Scheme 1, with a five-coordinate rhodium centre. The coordination of iodide to this complex is hindered by the ferrocenic portion of the molecule. Instead, it appears that reductive elimination of chloromethane occurs, either by a concerted process on attack of I^- or by a stepwise process with the resulting vacant site stabilised by coordination of solvent. Compound **4** is the expected thermodynamic product given that C–Cl bonds are stronger than C–I bonds ($\Delta H_f = -81.9$ kJ mol^{-1} (MeCl), -12.3 kJ mol^{-1} (MeI)) [18] and that Rh–I bonds would be expected to be at least as strong as, if not stronger than, Rh–Cl bonds. A simple substitution of chloride by iodide present in the iodomethane, due to hydrolysis or photolysis seems unlikely given that the near-quantitative isolated yield of **4**. Nor is there any evidence that the complete oxidative addition process ever occurs. Compound **5** could form either by the migration of a methyl group from rhodium to phosphorus [19], or by the direct quaternisation of the phosphine group while it has been momentarily displaced from the coordination sphere of rhodium.

These reactivity studies show that complex **2** cannot be a precursor to an active species for the carbonylation of methanol like the complex of Baker et al. We are currently investigating the reactivity of complexes **2** and **3**, but in reactions other than the methanol carbonylation.

3. Experimental

3.1. General considerations

The tetramethylcyclopentadiene was prepared by reacting a mixture of trimethylcyclopent-2-enone [7] with MeLi followed by dehydration of intermediate alcohol by simple ice-acidified water hydrolysis and was isolated as the C_2 isomer [8f].

The phosphine $C_5Me_4HPPh_2$ was prepared following a method similar to the synthesis of $C_5Me_3H_2PPh_2$ [7] and $C_5Me_4HP(S)Ph_2$ following [9]. All manipulations were performed under argon using standard Schlenk tube techniques.

3.2. Preparation of **1**

A solution of $C_5Me_4HP(S)Ph_2$ (2.19 g, 6.5 mmol) in 20 ml of THF was treated with BuLi (7.2 mmol) at −40°C over 30 min. Stirring was continued at r.t. for 3 h. The solution, now containing $[C_5Me_4P(S)Ph_2Li]$, was added dropwise, at −78°C, to a suspension of $FeCl_2$ (0.93g,6.5 mmol) in 15 ml of THF. Immediatly after the end of the addition, a solution of $[C_5Me_4PPh_2Li]$ (2.2g, 6.5 mmol) in 40 ml of THF at −78°C was also added. The cold bath was then removed and the mixture was allowed to warm to r.t., and stirred for 18 h.

The mixture was then treated with diethyl ether and the combined organic extracts were washed with water before being dried with $MgSO_4$. After filtration, the solvent was removed and the brown residue was chromatographied on a silica column with 2:1 toluene–hexane as eluent.

Three successive orange fractions were observed: The firstone contained dppomf, the second contained the expected product and the last one the disulfured compound. The solvent was removed from the second fraction and gave **1** as a yellow powder (60% yield). The analytical and spectroscopic data of the isolated product were identical to those described in Ref. [4].

3.3. Preparation of **2**

A solution of 0.13 mmol (50 mg) of $[RhCl(CO)_2]_2$ in 5 ml of toluene was added, at r.t., to a solution of 0.26 mmol (180 mg) of **1** in 25 ml of toluene. After 2 h of stirring, a precipitate was observed. After filtration, an orange powder was obtained. The yield was essentially quantitative.

This powder was recrystallised from a mixture of toluene and chloroform and gave orange crystals suitable for crystal structure determination. Anal. Calc. for $C_{43}H_{44}ClFeOP_2RhS{\cdot}CHCl_3$: C, 52.48; H, 4.47; Rh, 10.45. Found: C, 52.68; H, 4.70; Rh,9.73. IR (CH_2Cl_2, cm^{-1}): ν(CO)1986.7. ^{31}P-NMR ($CDCl_3$): 33.97 (d, $J_{P–Rh} = 176$ Hz), 43.16 (s). ^{1}H-NMR ($CDCl_3$): δ 1.60 (6H, s), δ 1.69 (6H, s), δ 1.71 (6H, s), δ 1.72 (6H, s), δ 7.24 (m), δ 7.40 (m), δ 7.46 (m), δ 7.68 (m).

3.4. Preparation of **3**

(a) A solution of 0.025 mmol (100 mg) of $[RhCl(CO)_2]_2$ in 2 ml of toluene was added to a mixture of 0.05 mmol (450 mg) of **2** in 30 ml of toluene. After 2 h of stirring, a precipitate was formed which was isolated by filtration and was obtained as a red powder (quantitative yield). ^{31}P-NMR ($CDCl_3$): 32.61 (d, $J_{P–Rh} = 180$ Hz), 43.23 (s). ^{1}H-NMR ($CDCl_3$): δ 1.63 (6H, s), δ 1.77(6H, s), δ 1.80 (6H, s), δ 1.81 (6H, s), δ 6.96 (m),δ 7.26 (m), δ 7.39 (m), δ 7.53 (m), δ 7.71(m).

(b) **2** (0.029 mmol, 25 mg) was dissolved in 15 ml of CH_2Cl_2. To this orange solution was added a solution of $AgBF_4$ (0.015 mmol, 3 mg) in 3 ml of methanol. After 2 h of stirring, the solvent was removed under reduced pressure, giving a red powder. We obtained **3** quantitatively with BF_4^- as an anion. IR (CH_2Cl_2, cm^{-1}): ν(CO)2000.

3.5. Reaction of **1** with 0.5 equivalent of $[RhCl(CO)_2]_2$ in CH_2Cl_2

A solution of 1.3 mmol (0.5 g) of $[RhCl(CO)_2]_2$ in 10 ml of CH_2Cl_2 was added, at r.t., to a solution of 2.6 mmol (1.8 g) of **1** in 30ml of CH_2Cl_2. After 1 h of stirring, the solvent was removed in vacuo and the mixture was purified in air by recrystallization in toluene–CH_2Cl_2. This purification gave red crystals of **3** (40%) suitable for X-ray analysis and a solution that, after evaporation, yielded to an orange–red powder of **2** (60%). Anal. Calc. for $C_{87}H_{88}Cl_{2.5}Fe_2O_3P_4Rh_{2.5}S_2$, $2(C_7H_8)$, 5 H_2O: C, 57.74; H, 5.42; S, 3.05. Found: C, 57.78; H, 5.00; S, 3.04.

3.6. Reaction of **2** with MeI

3.6.1. Preparation of **4**

1.5 ml of a solution of iodomethane in CH_2Cl_2 (0.023 M) was added to a solution of (0.23 mmol, 200 mg) **2** in 15 ml of CH_2Cl_2. After 2 h of stirring, the solvent was evaporated to dryness: a brown, pure, powder was so obtained. IR (CH_2Cl_2,cm^{-1}): ν(CO) 1981.3. ^{31}P-NMR($CDCl_3$): 32.11 (d, $J_{P–Rh} = 176$ Hz), 42.13 (s). ^{1}H-NMR ($CDCl_3$): δ 1.54 (6H, s), δ 1.64 (6H, s), δ 1.70 (12H, s), δ7.20 (m), δ 7.38 (m), δ 7.64 (m).

3.6.2. Preparation of **5** (neat iodomethane)

Compound **2** (0.43 mmol, 370 mg) was dissolved in 5 ml of iodomethane. The orange solution became dark red immediately. The solvent was removed under reduced pressure and a red powder was obtained. Anal. Calc. for $C_{43}H_{47}P_2S_1Fe_1I_1$: C, 61.46; H, 5.59;S, 3.81. Found: C, 61.22; H, 6.23; S, 3.40. ^{31}P-NMR ($CDCl_3$): 38.78 (s), 22.81 (s).^{1}H-NMR ($CDCl_3$): δ 1.41 (6H, s), δ 1.57(6H, s), δ 1.70 (6H, s), δ 1.85 (6H, s), δ 3.26 (3H, d, $J_{P–H} = 13.4$ Hz), δ 7.44 (m).

3.7. X-ray crystallography

Compound **2** consists of two independent complex molecules and three partially rotationally disordered solvent molecules. The refined position of the solvent molecules is not completely occupied. Two of the molecules ($C(1'')HCl_3$ and $C(2'')CHCl_3$) have a site occupation factor equal to 0.8 and the third molecule ($C(3'')HCl_3$) has a factor equal to 0.4. In the structure, the highest peaks of residual electron density are located in the vicinity of these solvent molecules.

The structure of **3** is composed of a complex tetranuclear cation, two types of anions and a solvent toluene molecule. The cation and both anions occupy special positions on the two-fold axes, the toluene molecule is in a general position. The anions share the same position with the half site occupation factor (s.o.f. is 0.25 for Rh(2) and Cl(3) and 0.5 for Cl and CO ligands). Since the size of the chloro anion is significantly smaller than that of $[RhCl_2(CO)_2]^-$ one can expect that the empty space around Cl^- anion is filled by a small molecules. Most likely these are water molecules, which are disordered in the space. Such a suggestion is supported by a number of highest peaks of residual electron density in the vicinity of chlorine and carbonyl ligands anion. The water molecules are, probably, hydrogen-bonded to the Cl^- anion and fix the anion in its position. However, we failed to successfully refine the electron density peaks identified as oxygen which are located at a suitable distance from Cl^-.

The structures were solved and refined using SHELXS86 [20] and SHELXL96 [21] software. Software SHELXTL-PLUS [22] was used for graphics and prepara-

Table 1
Crystallographic data for **2** and **3**

Compound	**2**	**3**
Empirical formula	$C_{86}H_{88}Cl_2Fe_2O_2P_4Rh_2S_{2.3}(CHCl_3)$	$C_{50.50}H_{52}Cl_{1.25}FeO_{1.50}P_2Rh_{1.25}S$
Formula weight	852.98	1005.72
Colour, habit	Dark red, block	Dark red, prism
Crystal size (mm)	0.46 × 0.54 × 0.32	0.12 × 0.14 × 0.22
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12$
Unit cell dimensions		
a (Å)	20.241(5)	18.6380(3)
b (Å)	25.948(4)	19.6650(3)
c (Å)	18.163(5)	12.8810(2)
α (°)	90	90
β (°)	99.50(3)	90
γ (°)	90	90
V (Å^3)	9409(4)	4721.1(1)
Z	4	4
$F(000)$	4248	2066
$D_{calc.}$ (g cm^{-3})	1.474	1.415
Absorption coefficient (mm^{-1})	1.110	0.961
Diffractometer	Enraf–Nonius CAD-4	Siemens SMART
Temperature (K)	293(2)	150.0(2)
Radiation (λ, Å)	Mo–K$_\alpha$ (0.71073)	Mo–K$_\alpha$ (0.71073)
Scan mode	ω	ω
Scan step/speed (°)	–	0.3
Min/max scan speed (deg min^{-1})	1.2/8	–
Time per step (s)	–	30
Scan range in ω	$1.1 + 0.35 \tan\theta$	–
θ range for data collection	2.04–25.07°	1.51–28.00°
Index ranges	$0 \leq h \leq 23$, $-30 \leq k \leq 0$, $-21 \leq l \leq 20$	$-21 \leq h \leq 25$, $-26 \leq k \leq 26$, $-18 \leq l \leq 14$
Reflections collected	13957	36061
Independent reflections	13062 [$R_{int} = 0.0551$]	11384 [$R_{int} = 0.0785$]
Absorption correction	Empirical (ψ-curve)	Empirical (SHELXTL-PLUS)
Max transmission	0.735	0.596
Min transmission	0.614	0.463
Solution method	Direct (SHELX-86)	Direct (SHELX-86)
Refinement method	Full-matrix least-squares on F^2 (SHELXL-93)	Full-matrix least-squares on F^2 (SHELXL-93)
Treatment of hydrogen atoms	Found from difference map with $U = 1.5$Uiso(C)	Placed in calculated positions and refined using riding model
Data/restraints/parameters	13040/0/950	10543/4/543
Goodness-of-fit on F^2	1.089	1.170
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0670$, $wR_2 = 0.1978$	$R_1 = 0.0648$, $wR_2 = 0.1534$
R indices (all data)	$R_1 = 0.1364$, $wR_2 = 0.2387$	$R_1 = 0.1021$, $wR_2 = 0.1874$
Absolute structure parameter		$-0.02(3)$
Extinction coefficient	0.00000(7)	0.0003(2)
Largest diff. peak and hole (e A^{-3})	1.453 and -0.714	2.021 and -0.855

tion of material for publication (see Table 1 for crystallographic data).

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 116611 for compound **2** and CCDC 116612 for compound **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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