Activation of C−S Bonds in Organosulfur Compounds Containing α,β-Unsaturated Ketone Systems by Carbonylruthenium and -iron Complexes

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Vinylidenetetraruthenium clusters have been obtained from the reactions between $[Ru_3(CO)_{12}]$ and $[CH_3C(O)CH{=}C(SCH_3)_2]$ or $[(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}]$ by cleavage of the S–C sp^2 bonds in these ligands. An excess of $[CH_3C(O)CH{=}C(SCH_3)_2]$ afforded the dinuclear complex $[Ru_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2]$, which was then converted into the vinylidene cluster $[Ru_4(CO)_{10}(\mu\text{-}SCH_3)_2\{\mu_4,\eta^3{:}\kappa\text{-}C,C,O\text{-}C{=}CHC(O)CH_3\}]$ in the presence of more of the carbonylruthenium complex. However, the carbonyliron complex led to the formation of the dinuclear compounds $[Fe_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2]$ and $[Fe_2(CO)_5\{\mu,\eta^4{:}\kappa\text{-}C,O,S,S\text{-}(SCH_2CH_2S)C{=}CHC(O)CH{=}CHC_5H_4\}Fe(C_5H_5)]$. All of the new complexes exhibit a pentametallacycle group as a consequence of the rupture of the S–C bonds, as well as the presence of the C(O)R substituent in these ligands. The compounds have been characterised by analytical and spectroscopic data and the crystal structures of some of them have been solved by X-ray diffraction.

Introduction

The chemistry of transition metals with organosulfur ligands is being widely developed due to its importance in a variety of applications such as hydrodesulfurisation processes, bioinorganic chemistry and synthetic procedures.[1] The activation of S−C bonds is known in the synthesis of sulfur cluster compounds.[2] We have previously reported[3] that the reaction between $Ru_3(CO)_{12}$ and $S(C{\equiv}CSiMe_3)_2$ affords two compounds $[Ru_3(CO)_9(\mu,\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3,\eta^2\text{-}C{\equiv}CSiMe_3)]$ and $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4,\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ by cleavage of one or two of the S−C bonds in the sulfide ligand.

On the other hand, although clusters containing vinylidene ligands bonded to several metals have been considered as models in processes that imply the formation of hydrocarbons, as far as we know not many homopolynuclear derivatives have been prepared.[4]

Finally, in spite of the use of carbonyliron and -ruthenium compounds containing α,β-unsaturated ketone systems as precursors in organic syntheses,[5] there are few reports on the coordination chemistry of these multifunctional ligands with transition metals.[6]

Taking all of the above into account we are interested in exploring the chemistry of carbonylruthenium and -iron complexes and some organosulfur ligands, which have an α,β-unsaturated ketone group in common, in order to prepare some vinylidene clusters. Here, we report on the preparation of some dinuclear and cluster compounds containing pentametallacycle and thiolate groups. These compounds have been characterised by analytical and spectroscopic data and the structures of some of them have been confirmed by X-ray diffraction.

Results and Discussion

Treatment of $[Ru_3(CO)_{12}]$ and $[CH_3C(O)CH{=}C(SCH_3)_2]$ (1:1 stoichiometry) in the presence of $ONMe_3$ in toluene at 85 °C afforded the new compound $[Ru_4(CO)_{10}(\mu\text{-}SCH_3)_2\{\mu_4,\eta^3{:}\kappa\text{-}C,C,O\text{-}C{=}CHC(O)CH_3\}]$ (**1**) (Scheme 1) which was isolated in 35% yield as orange crystals after purification by column chromatography on silica gel, followed by recrystallisation from hexane at −20 °C. Compound **1** was characterised by analytical and spectroscopic data. The ν(CO) pattern in the carbonyl region is similar to that observed for the vinylidene derivatives $[Ru_4(CO)_{10}(\mu_4,\eta^2\text{-}C{=}CH\mathit{i}Pr)(OR)(PPh_2)]$ (R = H, Et).[7] On the other hand, ^1H NMR resonances at δ = 4.50

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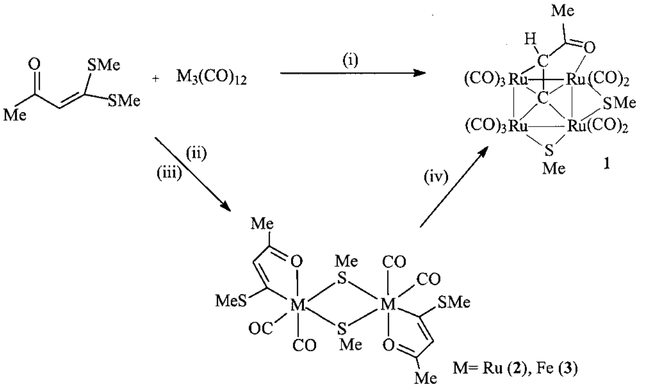
[C(O)CH=C], 2.70 and 2.20 (SCH_3) and 2.00 ppm [$C(O)CH_3$] are shifted in comparison with those of the ligand {δ = 6.02 [C(O)CH=C], 2.46 and 2.43 (SCH_3), 2.18 ppm [$C(O)CH_3$]}. A single-crystal X-ray diffraction study on compound **1** confirmed the formation of a vinylidenetetraruthenium compound by rupture of the two S−C bonds in the ligand. Examples of activation of the S−C bonds in the synthesis of clusters are known. Thus, the thioketene $C_6H_6Me_4C_2S$ derivative in its reaction with [$Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$] generates a heteronuclear compound bearing a terminal vinylidene ligand[8] and the triosmium cluster [$Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}SPh)\{\mu_3,\eta^2\text{-}(CCH_2CH_2C)\}$] has been isolated from cyclobutenyl thioether.[2a] We have also previously reported the synthesis of ruthenium clusters by thermolysis of [$Ru_3(CO)_{12}$] and $S(C{\equiv}CSiMe_3)_2$.[3]



Scheme 1. (i) $ONMe_3$, toluene, 85 °C, 1:1 stoichiometry; (ii) $ONMe_3$, toluene, 85 °C, 3:1 stoichiometry; (iii) $ONMe_3$, THF, room temp., 1:1 stoichiometry; (iv) [$Ru_3(CO)_{12}$], $ONMe_3$, toluene, 85 °C

Although several clusters with vinylidene ligands have been reported, as far as we know only a few examples of homotetrametallic compounds containing a μ_4-C=CRR′ or μ_4-C=CR_2 group have been described. Compounds [$Ru_4(CO)_{10}(\mu_4,\eta^2\text{-}C{=}CH\mathit{i}Pr)(OR)(PPh_2)$] (R = H, Et),[7] have been obtained in moderate yield by reaction of [$Ru_4(CO)_{11}(PPh_2C{\equiv}CR)$] in wet THF, while the complexes [$Fe_4(CO)_{12}\{\mu_4,\eta^2\text{-}C{=}C(OMe)R\}$] (R = OMe, Me)[9a] have been synthesised in high yield by methylation of the anionic clusters [$Fe_4(CO)_{12}\{CC(O)(OMe)\}$]$^-$ or [$Fe_4(CO)_{12}\{CC(O)(Me)\}$]$^-$, the former cluster being the precursor for [$Fe_4(CO)_{12}\{\mu_4,\eta^2\text{-}C{=}C(OMe)H\}$].[9b] The reaction between [$Os_4(CO)_{12}(\mu_3\text{-}S)$] and PhC≡CH affords the cluster [$Os_4(CO)_{12}(\mu_3\text{-}S)\{\mu_4,\eta^2\text{-}C{=}C(Ph)H\}$].[9c] The known compound [$Ru_2(CO)_6(\mu\text{-}SCH_3)_2$][10] was also obtained from this reaction in trace amounts along with compound **1**.

The same reaction, carried out with an excess of the ligand, yielded the new compound [$Ru_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2$] (**2**) in 45% yield. Compound **2** exists as a mixture of two isomers (*syn*/*anti*) in a 20:80 ratio, as determined from ^1H NMR spectroscopic data, that could be separated by chromatography. The major isomer gave suitable crystals for X-ray diffraction studies (Figure 2). The two IR bands observed at 2028, 1970 (*anti*) and 2044, 1988 cm^{-1} (*syn*) are expected for compounds of the type [$Ru(CO)_2L_2]_2$.[11] In the ^1H NMR spectrum, in addition to the resonance corresponding to the CH_3 group [δ = 2.12 (*anti*) and δ = 2.12 ppm (*syn*)], two more signals appear in this region at δ = 2.39 and 2.42 (*anti*), δ = 2.33 and 2.41 ppm (*syn*) that are indicative of the presence of two inequivalent SCH_3 groups. The FAB$^+$ mass spectrum of compound **2** reveals a molecular ion at *m*/*z* = 638 in agreement with this formulation. Conversion of the dinuclear compound **2** to the cluster **1** occurred on heating the former at 85 °C in toluene (Scheme 1).

The compound [$Ru_4(CO)_{10}(\mu\text{-}SCH_3)_2\{\mu_4,\eta^3{:}\kappa\text{-}C,C,O\text{-}C{=}CHC(O)CH_3\}$] (**1**) contains two crystallographically independent molecules in the asymmetric unit. The discussion will be limited to only one of these molecules. An ORTEP illustration of compound **1** is given in Figure 1. Selected interatomic distances and angles are shown in Table 1.

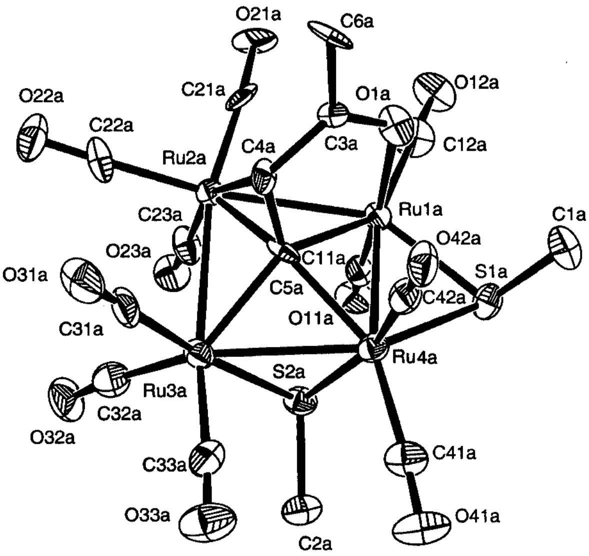


Figure 1. Molecular structure of compound **1**

Table 1. Selected distances [Å] and angles [°] for compound **1**

Ru(1)−Ru(2)	2.8306(14)	Ru(2)−C(5)	2.002(16)
Ru(2)−Ru(3)	2.923(2)	Ru(2)−C(4)	2.206(14)
Ru(1)−Ru(4)	2.7869(19)	Ru(3)−C(5)	2.137(13)
Ru(3)−Ru(4)	2.8009(14)	Ru(1)−C(5)	2.210(13)
Ru(1)−O(1)	2.108(10)	Ru(4)−C(5)	2.135(15)
Ru(1)−S(1)	2.368(4)	O(1)−C(3)	1.281(17)
Ru(3)−S(2)	2.403(4)	C(4)−C(5)	1.43(19)
Ru(4)−S(2)	2.424(4)	C(3)−C(4)	1.45(2)
Ru(4)−Ru(1)−Ru(2)	90.72(5)	C(3)−O(1)−Ru(1)	114.5(8)
Ru(4)−Ru(3)−Ru(2)	88.56(4)	O(1)−C(3)−C(4)	119.0(12)
Ru(1)−Ru(2)−Ru(3)	86.80(5)	C(3)−C(4)−C(5)	115.0(12)
Ru(1)−Ru(4)−Ru(3)	90.08(5)		

The four ruthenium atoms form a distorted rectangular geometry with three similar distances [Ru(1)−Ru(4) 2.7869(19), Ru(1)−Ru(2) 2.8306(14), Ru(3)−Ru(4) 2.8009(14) Å] and one that is slightly longer [Ru(2)−Ru(3) 2.923(2) Å] but still within the normal range found for other ruthenium clusters.[3,12] Although compounds

$[Ru_4(CO)_{10}(\mu_4,\eta^2\text{-}C{=}CH\textit{i}Pr)(OR)(PPh_2)]$ (R = H, Et)[7] and $[Fe_4(CO)_{12}\{\mu_4,\eta^2\text{-}C{=}C(OMe)R\}]$ (R = OMe, Me)[9a] show a butterfly geometry, a rhombus frame has been observed in the compound $[Os_4(CO)_{12}(\mu_3\text{-}S)\{\mu_4,\eta^2\text{-}C{=}C(Ph)H\}]$.[9c]

The breaking of two S−C sp² bonds in $[CH_3C(O)CH{=}C(SCH_3)_2]$ affords two methylthiolate ligands that are joined to three Ru atoms of the cluster framework. The remaining vinylidene group is coordinated to the four metal atoms at the C-α atom while the C-β atom is only attached to the Ru(2) atom. It is worth noting that the presence of the $C(O)CH_3$ group as a substituent on the C=CHR ligand allows the formation of a pentametallacycle. The cluster shell is completed by ten terminal carbonyl ligands. Most of the vinylidene tetranuclear cluster show a μ_4-η^2 coordination mode, such as has been observed in compound **1**. However, in the clusters $[Fe_4(CO)_{12}\{\mu_4,\eta^2\text{-}C{=}C(OMe)R\}]$ (R = OMe, Me)[9a] this ligand only acts towards the C-α atom.

The Ru−S distances [2.368(4), 2.335(4), 2.403(4) and 2.424(4) Å] are similar to the values reported for other thiolate-bridged complexes, $[Ru_3(CO)_9(\mu,\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3,\eta^2\text{-}C{\equiv}CSiMe_3]$ [2.4353(7) and 2.4337(7) Å][3] and $[Ru_3(CO)_9(\mu\text{-}SEt)(\mu_3,\eta^2\text{-}C{\equiv}CPh)]$ [2.424(2) and 2.4116(2) Å].[13] The C(4)−C(5) distance [1.43(19) Å] for compound **1** is similar to those observed in $[Ru_4(CO)_{10}(\mu_4,\eta^2\text{-}C{=}CH\textit{i}\text{-}Pr)(OH)(PPh_2)]$ [1.415 Å],[7] $[Ru_5(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ [1.435(5) Å],[12] $[Ru_3H_2(\mu_3,\eta^2\text{-}C{=}C(CH_3)(C_6H_5)(CO)_9]$[14] [1.379(8) Å], and $[Os_4(CO)_{12}(\mu_3\text{-}S)\{\mu_4,\eta^2\text{-}C{=}C(Ph)H\}]$[9c] [1.446(16) Å]. The C(3)−O(1) distance of 1.281(17) Å is slightly longer than expected for a C=O bond [1.20 Å], which is indicative of the existence of a σ-bond between the oxygen atom of the ketone group and the Ru(1) atom.

This arrangement of the four Ru−Ru bonds is consistent with an electron count of 64 electrons achieved when the two methylthiolate ligands as well as the vinylidene $C{=}CHC(O)CH_3$ group each contribute six electrons.

The molecular structure of the *anti* isomer of $[Ru_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2]$ (**2**) is illustrated in Figure 2 and selected bond lengths and angles are given in Table 2. Compound **2** crystallises in the space group $P\bar{1}$ and is centrosymmetric. The cleavage of one $C{-}SCH_3$ bond in the disulfide ligand leads to the $C(SCH_3)CHC(O)CH_3$ group that acts as a three-electron donor making a pentaruthenacycle around each Ru atom. Both metal units are linked through two bridging methylthiolate ligands. The intramolecular distance between the ruthenium atoms [3.634(2) Å] suggests that there is no bonding interaction, while the Ru−S distances [2.4599(10) and 2.4352(11) Å] are slightly longer than those observed for compound **1**. The C(12)−Ru−S(1) [177.63(8)°] and C(1)−Ru−S′(1) [168.00(7)°] angles are indicative of a *cis* position for the two CO ligands. The equatorial plane of the octahedron seems to consist of the S(1), S′(1), C(1) and C(12) atoms. The remaining CO ligand and O(1) atom are located in the apical positions. The distances Ru−O(1) [2.1109(18) Å] and O(1)−C(3) [1.270(3) Å] are similar to those reported in the related compounds $[RuCl\{o\text{-}C_6H_3\text{-}CH_3C(O)C_6H_4CH_3\}(CO)(PMe_2Ph)]$,[15] $[RuCl\{o\text{-}C_6H_4\text{-}C(O)C_6H_4CH_3\}(CO)(PPh_3)]$,[16] and $[RuCl\{{=}C(CH_2Ph)\text{-}OC(O)H\}(P\textit{i}Pr_3)]$.[17]

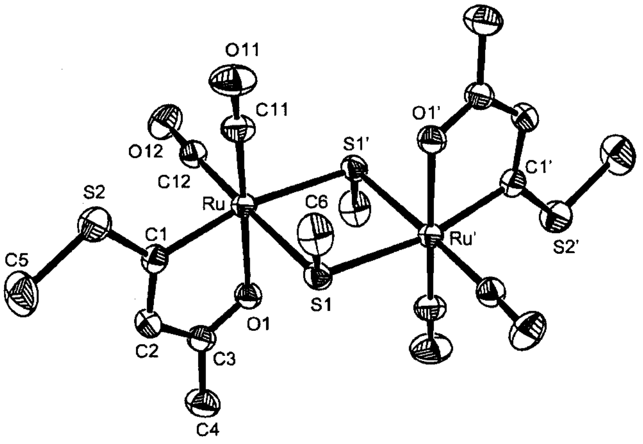


Figure 2. View of the *anti* isomer of compound **2**

Table 2. Selected interatomic distances [Å] and angles [°] for compound **2**

C(1)−C(2)	1.372(4)	C(11)−Ru	1.854(3)
C(1)−Ru	2.055(2)	C(12)−Ru	1.894(3)
C(3)−O(1)	1.270(3)	S(1)−Ru	2.4352(11)
C(2)−C(3)	1.411(4)	Ru−S(1)′1	2.4599(10)
O(1)−Ru	2.1109(18)	Ru−Ru′	3.634(2)
O(1)−C(3)−C(2)	119.9(2)	C(12)−Ru−S(1)	177.63(8)
C(2)−C(1)−Ru	113.16(18)	C(1)−Ru−S(1′)	168.00(7)
C(1)−C(2)−C(3)	115.4(2)	S(1)−Ru−S(1′)	84.13(4)
C(3)−O(1)−Ru	112.77(16)	O(1)−Ru−C(11)	173.24(8)
C(1)−Ru−O(1)	78.57(9)		

We have previously reported[6b] that the reaction of $[Fe_2(CO)_9]$ and $C_6H_5CH{=}CHC(O)CH{=}C(SCH_2CH_2S)$, in diethyl ether at room temperature, affords the compound $[Fe_2(CO)_5\{\mu,\eta^4{:}\kappa\text{-}C,O,S,S\text{-}(SCH_2CH_2SC{=}CHC(O)\text{-}CH{=}CHC_6H_5\}]$ by rupture of one S−C bond. On the other hand, taking into account that treatment of $Ru_3(CO)_{12}$ with $[CH_3C(O)CH{=}C(SCH_3)_2]$ yields the new cluster **1**, reported here, we were interested to know whether the use of $[Fe_3(CO)_{12}]$ instead of $[Fe_2(CO)_9]$, in the presence of $ONMe_3$ under mild conditions, leads to an iron cluster by reaction with $[CH_3C(O)CH{=}C(SCH_3)_2]$. Unfortunately, in this case, the reaction carried out by heating in toluene affords the expected vinylidene compound in trace amounts only, with $[Fe_2(CO)_6(\mu\text{-}SCH_3)_2]$ being the main product. However, the dinuclear compound $[Fe_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2]$ (**3**) was obtained at room temperature in THF in 25% yield (Scheme 1). The spectroscopic data are similar to those shown for compound **2**. In the FAB⁺ mass spectrum peaks analogous to those observed in **2** corresponding to the molecular ion and the loss of CO groups were found.

Compound **3** was not converted into a vinylidene cluster on reaction with more carbonyliron compound, showing a different behaviour from that observed in the analogous ruthenium case.

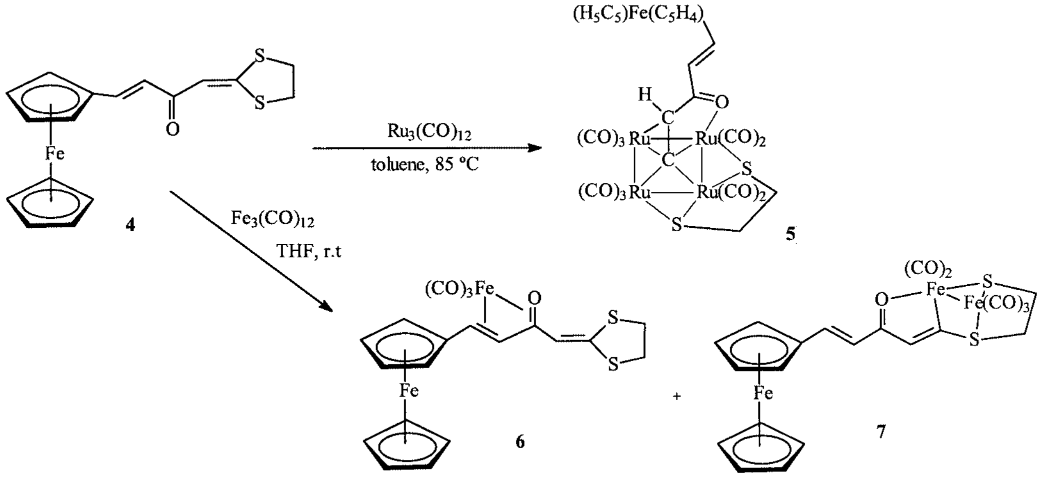
Following our research interest to synthesize vinylidene derivatives we decided to prepare [$(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}$] (**4**), which is similar to the ligand studied before with an α,β-unsaturated ketone system. The presence of one more C=C bond in the chain as well as the active redox ferrocenyl group could lead to differences in its reactivity. Compound **4** was prepared according to the procedure described in the literature for other analogous compounds[19] and was characterised by analytical and spectroscopic techniques (see Exp. Sect.).

Treatment of [$Ru_3(CO)_{12}$] with [$(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}$] in the presence of $ONMe_3$ in toluene at 85°C afforded the tetraruthenium compound [$Ru_4(CO)_{10}\{\mu_3\text{-}(SCH_2CH_2S)\}\{\mu_4,\eta^3{:}\kappa\text{-}C,C,O\text{-}(C{=}CHC(O)CH{=}CHC_5H_4)Fe(C_5H_5)\}$] (**5**) (Scheme 2), as was inferred from the presence of the molecular ion peak in the FAB^+ mass spectrum (*m*/*z* = 1041) as well as from the analytical data. The ν(CO) pattern in the carbonyl region is similar to that observed for compound **1** and other related derivatives [$Ru_4(CO)_{10}(\mu_4,\eta^2\text{-}C{=}CH\textit{i}Pr)(OR)(PPh_2)$] (R = H, Et).[7] In the ^1H NMR spectrum resonances that appear at δ = 4.07 [C(O)CH=C] and 3.29, 2.42, 2.26 ppm [SCH_2CH_2S] are shifted in comparison with those of the ligand [δ = 6.77 ppm for C(O)CH=C; δ = 3.43, 3.35 ppm for SCH_2CH_2S]. It was found that the same chemical shift occurs as was observed in **1** for the [C(O)CH=C] resonance.

Finally, the reaction carried out between [$Fe_3(CO)_{12}$] and [$(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}$] with $ONMe_3$ in THF at room temperature for 2 h yielded three compounds after chromatographic workup (Scheme 2). The first band, that appeared as traces from the column, gave an orange solid which was identified by IR and ^1H NMR spectroscopic data as the known compound [$Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S)$].[20] The second band afforded the main compound [$Fe(CO)_3\{(C_5H_5)Fe\{\eta^4{:}\kappa\text{-}(C{=}C,C{=}O)\text{-}C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}\}$] (**6**) in 23% yield; its structure was confirmed by X-ray diffraction. A small amount of [$Fe_2(CO)_5\{\mu,\eta^4{:}\kappa\text{-}C,O,S,S\text{-}SCH_2CH_2SC{=}CHC(O)CH{=}CHC_5H_4\}Fe(C_5H_5)$] (**7**) was obtained from the third band of the column. We have observed that if the reaction time is increased to 48 h, compound **7** is the main product of this reaction.

Compound **6** is formed by coordination of the $Fe(CO)_3$ fragment towards both the ketone group and the C=C bond of the ligand. The IR spectrum in the carbonyl region is similar to that found in the analogous compound [η^4-{(3*E*)-4-phenyl-1-(1,3-dithiolan-2-ylidene)butene-2-one}$Fe(CO)_3$] recently prepared by us.[6b] The ^1H NMR spectrum of compound **6** shows, as a prominent feature, two signals at δ = 5.71 and 3.38 ppm ($^3J_{H,H}$ = 8.7 Hz), corresponding to the protons of the coordinated CH=CHC(O) group which are shifted upfield with respect to the free ligand. A view of compound **6** with the atom numbering scheme is shown in Figure 3. Selected interatomic distances and angles are presented in Table 3. The coordination geometry of Fe(2) can be described as a distorted trigonal bipyramid with the atoms C(20), C(30) of the carbonyl groups and the C(2)−C(3) double bond in the equatorial positions, while the O(1) atom and the C(10) atom of the carbonyl group are located in the apical positions. The ferrocene unit is not affected much by the coordination of the $Fe(CO)_3$ moiety and the distances and angles are in the usual range found in many other ferrocene derivatives. The enone moiety and the 1,3-dithiolane ring shows only slight deviations from the analogous fragment present in [$Fe(CO)_3\{\eta^4\text{-}H_5C_6CHCHC(O)CHC(SCH_2CH_2S)\}$].[6b] The comparison of the Fe−CO distance of the carbonyl group *trans* to the oxygen atom of the enone and the rest of the carbonyl groups suggests a *trans* influence.

Finally, the breaking of only one S−C bond in [$(C_5H_5)Fe\{(C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}$] generated [$Fe_2(CO)_5\{\mu,\eta^4\text{-}SCH_2CH_2SC{=}CHC(O)CH{=}CHC_5H_4\}Fe(C_5H_5)$] (**7**). The analogous compound [{(3*E*)-4-phenyl-1-(1,3-dithiolan-2-ylidene)butene-2-one}$Fe_2(CO)_5$], whose structure has been confirmed by X-ray diffraction, was formed in a similar manner.[6b] The ν(CO) pattern is similar in both compounds. In the FAB^+ spectrum, a peak observed at *m*/*z* = 609 corresponding to the molecular ion



Scheme 2

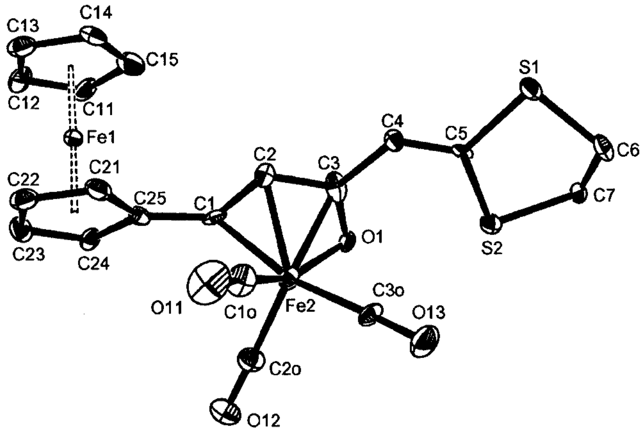


Figure 3. Structure of compound **6**

Table 3. Selected distances [Å] and angles [°] for compound **6**

Fe(1)−Cp(1)	1.632	Fe(2)−C(2)	2.043(10)
Fe(1)−Cp(2)	1.633	Fe(2)−C(3)	2.086(10)
Fe(2)−C(10)	1.742(13)	O(1)−C(3)	1.324(12)
Fe(2)−C(20)	1.805(12)	C(1)−C(2)	1.415(14)
Fe(2)−C(30)	1.799(11)	C(2)−C(3)	1.403(14)
Fe(2)−O(1)	2.036(6)	C(3)−C(4)	1.453(14)
Fe(2)−C(1)	2.162(10)	C(4)−C(5)	1.353(14)
Cp(1)−Fe(1)−Cp(2)	178.26	C(20)−Fe(2)−C(3)	139.3(4)
C(10)−Fe(2)−C(20)	90.7(5)	C(30)−Fe(2)−C(2)	128.8(4)
C(20)−Fe(2)−C(30)	99.2(4)	C(30)−Fe(2)−C(3)	96.2(4)
C(10)−Fe(2)−O(1)	159.8(4)	O(1)−C(3)−C(2)	114.5(8)
C(20)−Fe(2)−O(1)	104.8(4)	O(1)−C(3)−C(4)	121.5(9)
C(30)−Fe(2)−O(1)	90.3(4)	C(4)−C(5)−S(1)	120.7(8)
C(10)−Fe(2)−C(1)	98.2(4)	C(4)−C(5)−S(2)	125.1(7)
C(10)−Fe(2)−C(2)	95.6(4)	C(1)−C(2)−C(3)	118.4(9)
C(10)−Fe(2)−C(3)	122.5(5)	C(2)−C(3)−C(4)	24.0(9)
C(20)−Fe(2)−C(1)	91.4(4)	C(5)−S(1)−C(6)	95.5(5)
C(20)−Fe(2)−C(2)	130.46(12)		

and the analytical data are in agreement with this formulation. The ^1H NMR spectrum exhibits two doublet resonances at $\delta = 7.12$ and 6.47 ppm assigned to the uncoordinated double bond, with a value of $^3J_{H,H} = 15.7$ Hz similar to that observed in compound **5**. Additionally a singlet signal that appears at $\delta = 2.35$ ppm [C(O)CHC] is strongly shifted to a higher field than that observed in the free ligand ($\delta = 6.79$ ppm). The compounds **6** and **7** are obtained in similar yield to those prepared by us using $[Fe_2(CO)_9]$ and analogous ligands.

Conclusion

Compounds $[CH_3C(O)CH{=}C(SCH_3)_2]$ and $[(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C\ (SCH_2CH_2S)\}]$ act as precursors of vinylidene groups by activation of the two S−C bonds in their reactions with $[Ru_3(CO)_{12}]$ but not with $[Fe_3(CO)_{12}]$. This has allowed the formation of new homonuclear vinylideneruthenium clusters, which is important when one considers the scarcity of literature reports on these complexes.

The cleavage of only one S−C bond from $[CH_3C(O)CH{=}C(SCH_3)_2]$ as well as the presence of the ketone group led to the compounds $[M_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2]$ (M = Ru, Fe) containing two metallacycles.

The presence of SCH_2CH_2S instead of two SCH_3 groups in the ligand $[(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}]$ seems to drive the formation of the compound $[Fe_2(CO)_5\{\mu,\eta^4\text{-}SCH_2CH_2SC{=}CHC(O)CH{=}CHC_5H_4\}Fe(C_5H_5)]$.

Experimental Section

General Remarks: All reactions were carried out under argon using Schlenk techniques. Solvents were dried according to standard methods. IR spectra were recorded with a Perkin−Elmer 1650 FTIR spectrophotometer using NaCl cells. ^1H NMR spectra were recorded with a Bruker AMX-300 instrument in $CDCl_3$. Elemental analyses were performed with a Perkin−Elmer 240-B microanalyser. FAB mass spectra were carried out with a WG AutoSpec spectrometer, using 3-nitrobenzyl alcohol as the matrix. $[CH_3C(O)CH{=}C(SCH_3)_2]$[19] was synthesised according to literature methods.

Synthesis of $[Ru_4(CO)_{10}(\mu\text{-}SCH_3)_2\{\mu_4,\eta^3{:}\kappa\text{-}C,C,O\text{-}C{=}CHC(O)CH_3\}]$ (1): An excess of $ONMe_3$ (0.103 g, 1.38 mmol) was added to a solution of $[Ru_3(CO)_{12}]$ (0.300 g, 0.46 mmol) and $[CH_3C(O)CH{=}C(SCH_3)_2]$. (0.076 g, 0.46 mmol) in toluene (30 mL). The mixture was stirred at 85 °C for 24 h to give an orange-brown solution. The solvent was removed under vacuum, and the residue was chromatographed on silica gel 100. Elution with hexane afforded $[Ru_2(CO)_6(\mu\text{-}SMe)_2]$ in low yield. A second band using *n*-hexane/toluene (4:1) gave compound **1** as the main product (0.136 g, 35% yield). Crystals of **1** were obtained from *n*-hexane at −20 °C. IR (THF): $\tilde{\nu} = 2080$ (m), 2044 (vs), 2026 (s), 2012 (s), 1986 (m), 1969 (sh), 1955 (w) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 4.50$ [s, 1 H, C*H*C(O)], 2.70 (s, 3 H, SCH_3), 2.20 (s, 3 H, SCH_3), 2.00 [s, 3 H, $C(O)CH_3$] ppm. FAB^+: *m*/*z* = 846 [M^+], 818−566 [M^+ − *n* CO, *n* = 1−10]. $C_{16}H_{10}O_{11}Ru_4S_2$ (846.64): calcd. C 22.70, H 1.19; found C 22.83, H 1.44.

Synthesis of $[Ru_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2]$ (2): $ONMe_3$ (0.092 g, 1.23 mmol) was added to a solution of $[Ru_3(CO)_{12}]$ (0.250 g, 0.39 mmol) and $[CH_3C(O)CH{=}C(SCH_3)_2]$ (0.200 g, 1.23 mmol) in toluene (30 mL). The mixture was stirred at 85 °C for 24 h. Removal of the solvent and chromatography on silica gel gave the first band of compound **1** in trace amounts, eluted with *n*-hexane/toluene (4:1). A second band using toluene/THF (5:1) afforded $[Ru_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CHC(O)CH_3\}_2]$ (**2**) as the main product (0.75 g, 45% yield). Crystals of **2** were obtained by diffusion of hexane in THF at 0 °C. IR (toluene): *anti* isomer: $\tilde{\nu} = 2028$ (s), 1970 (s) cm^{-1}; *syn* isomer: $\tilde{\nu} = 2044$ (s), 1988 (s) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.62$ [s, 1 H, C*H*C(O)], 2.42 (s, 3 H, SCH_3, *anti* isomer), 2.41 (s, 3 H, SCH_3, *syn* isomer), 2.39 (s, 3 H, SCH_3, *anti* isomer), 2.39 (s, 3 H, SCH_3, *syn* isomer), 2.12 [s, 3 H, $C(O)CH_3$] ppm. FAB^+: *m*/*z* = 638 [M^+]. $C_{16}H_{20}O_6Ru_2S_4$ (638.71): calcd. C 30.11, H 3.13; found C 30.73, H 3.31.

Synthesis of $[Fe_2(CO)_4(\mu\text{-}SCH_3)_2\{\eta^2{:}\kappa\text{-}C,O\text{-}C(SCH_3)CH(CO)CH_3\}_2]$ (3): A solution of $[CH_3C(O)CH{=}C(SCH_3)_2]$ (0.068 g, 0.42 mmol) in THF (10 mL) was slowly added to a solution of $[Fe_3(CO)_{12}]$ (0.210 g, 0.42 mmol) and $ONMe_3$ (0.031 g, 0.42 mmol) in THF. The resulting mixture was stirred at room temperature for 2.5 h. The solvent was then evaporated under vacuum to dryness and the residue chromatographed on silica gel 100. An orange band of $[Fe_2(CO)_6(\mu\text{-}SCH_3)_2]$ (trace) was obtained using *n*-hexane as the eluent. Further elution with *n*-hexane/THF (10:3) yielded a red band. The solvent was removed under vacuum and recrystallisation of the residue in THF/*n*-hexane at −20 °C yielded compound **3** (29 g, 25.9% yield). IR (THF): $\tilde{\nu}$ = 2017 (s), 1969 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.69 [s, 1 H, C*H*C(O)], 2.52 (s, 3 H, SCH_3), 2.35 (s, 3 H, SCH_3) 2.08 [s, 3 H, C(O)CH_3] ppm. FAB$^+$: *m*/*z* = 549.0 [M$^+$], 520.0 [M$^+$ − CO], 492.0 [M$^+$ − 2 CO], 436.0 [M$^+$ − 4 CO] ppm. $C_{16}Fe_2H_{20}O_6S_4$ (548.26): calcd. C 35.05; H 3.68; found C 34.88, H 3.62.

Synthesis of $[(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}]$ (4): This compound was prepared according to a procedure described for other analogous compounds.[17] Sodium hydroxide (0.125 g, 3.12 mmol) in EtOH (20 mL) was added to a solution of 1-(1,3-dithiolan-2-ylide)acetone (0.500 g, 3.12 mmol) in EtOH (30 mL). After 40 min of stirring, $[(C_5H_5)Fe(C_5H_5CHO)]$ (0.067 g, 3.12 mmol) in EtOH (10 mL) was added. The mixture was stirred for 24 h affording a red precipitate. The solid compound was purified by column chromatography using *n*-hexane as the eluent (0.3 g, 27% yield). ^1H NMR ($CDCl_3$): δ = 7.52 [d, $^3J_{H,H}$ = 15.6 Hz, 1 H, *H*C=CHC(O)], 6.79 [s, 1 H, C(O)C*H*C], 6.39 [d, $^3J_{H,H}$ = 15.6 Hz, 1 H, HC=C*H*C(O)], 4.50 (t, $^3J_{H,H}$ = 1.8 Hz, 2 H, C_5H_4), 4.42 (t, $^3J_{H,H}$ = 1.8 Hz, 2 H, C_5H_4), 4.14 (s, 5 H, C_5H_5), 3.43 and 3.35 (m, 4 H, SCH_2CH_2S) ppm. FAB$^+$: *m*/*z* = 356 [M$^+$]. $C_{17}FeH_{16}OS_2$ (356.28): calcd. C 57.31; H 4.53; found C 56.90, H 4.59.

Reaction of $Ru_3(CO)_{12}$ and $[(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}]$: The reaction was carried out according to the same procedure as for compound **1**, but leaving the reaction for 48 h. Chromatography on silica gel 100 afforded two compounds. Elution with hexane gave $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ in a small amount, while hexane/toluene (5:3) gave the cherry-coloured compound **5** as the main product (0.100 g, 28% yield). IR (THF): $\tilde{\nu}$ = 2078 (m), 2045 (vs), 2028 (s), 2008 (s), 1974 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.30 [d, $^3J_{H,H}$ = 15.5 Hz, 1 H, *CH*CH*C*(O)], 6.13 [d, $^3J_{H,H}$ = 15.5 Hz, 1 H, CH*CHC*(O)], 4.50 (m, 4 H, C_5H_4), 4.10 (s, 5 H, C_5H_5), 4.07 [s, 1 H, C(O)C*H*C], 3.29 (m, 2 H, SCH_2), 2.42 (m, 1 H, SCH_2), 2.26 (m, 1 H, SCH_2) ppm. FAB$^+$: *m*/*z* = 1041 [M$^+$], 985 [M$^+$ − 2 CO], 957 [M$^+$ − 3 CO], 901 [M$^+$ − 5 CO], 873 [M$^+$ − 6 CO], 789 [M$^+$ − 9 CO], 761 [M$^+$ − 10 CO]. $C_{27}FeH_{16}O_{11}Ru_4S_2$ (1040.66): calcd. C 31.16, H 1.55; found C 31.53, H 1.67.

Reaction of $Fe_3(CO)_{12}$ and $[(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}]$: A solution of $[(C_5H_5)Fe\{C_5H_4CH{=}CHC(O)CH{=}C(SCH_2CH_2S)\}]$ (0.156 g, 0.44 mmol) in THF (5 mL) was slowly added to a mixture of $[Fe_3(CO)_{12}]$ (0.220 g, 0.44 mmol) and $ONMe_3$ (0.033 g, 0.44 mmol) in the same solvent (15 mL). The resulting mixture was stirred at room temperature for 2 h. Then the solvent was evaporated under vacuum to dryness and the residue chromatographed on silica gel 100. Using *n*-hexane as the eluent, an orange band of $[Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (trace) was obtained. Further elution with a mixture of *n*-hexane/toluene (10:1) yielded a red band of **6** (0.050 g, 23.0% yield). Subsequent elution with *n*-hexane/toluene (1:2) gave a red-brown band of compound **7** in trace amounts. Applying the same procedure and increasing the reaction time to 48 h, compound **7** was obtained in a 17.8% yield.

6: IR (THF): $\tilde{\nu}$ = 2052 (s), 1990 (s), 1975 (s), 1604 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.72 [s, 1 H, C(O)CHC], 5.71 [d, $^3J_{H,H}$ = 8.7 Hz, 1 H, *CH*CH*C*(O)], 4.42 (s, 1 H, C_5H_4), 4.20 (s, 2 H, C_5H_4), 4.16 (s, 1 H, C_5H_4), 4.13 (s, 5 H, C_5H_5), 3.38 [m, 5 H, SCH_2CH_2S and CHC*H*C(O)] ppm. FAB$^+$: *m*/*z* = 440 [M$^+$ − 2 CO], 412 [M$^+$ − 3 CO], 356 [M$^+$ − Fe − 3 CO]. $Fe_2S_2O_4C_{20}H_{16}$ (495.91): calcd. C 48.42, H 3.25; found C 48.12, H 3.61.

7: IR (THF): $\tilde{\nu}$ = 2052 (s), 2009 (vs), 1991 (s), 1975(sh), 1959 (w), 1946 (sh), 1647 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.12 [d, $^3J_{H,H}$ = 15.7 Hz, 1 H, *CH*CH*C*(O)], 6.47 [d, $^3J_{H,H}$ = 15.7 Hz,1 H,CHC*H*C(O)], 4.45 (m, 2 H, C_5H_4), 4.34 (m, 2 H, C_5H_4), 4.15 (s,

Table 4. Crystal data, data collection and structure refinement for the complexes

	1	**2**	**6**
Empirical formula	$C_{16}H_9O_{11}Ru_4S_2$	$C_{16}H_{20}O_6Ru_2S_4$	$C_{20}H_{16}Fe_2O_4S_2$
Formula mass	845.63	638.70	496.15
T [K]	160(2)	180(2)	180(2)
Crystal size [mm]	0.45 × 0.20 × 0.17	0.45 × 0.40 × 0.37	0.20 × 0.15 × 0.06
Colour	orange	orange	dark red
Crystal form	parallelepiped	parallelepiped	platelet
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1$	$P\bar{1}$	$P21/c$
a [Å]	9.680(2)	7.994(2)	6.2660(10)
b [Å]	15.217(3)	8.845(2)	30.673(6)
c [Å]	15.746(3)	8.961(2)	10.125(2)
α [°]	90	76.27(3)	90
β [°]	89.927(2)	69.58(3)	98.10(3)
γ [°]	90	82.62(3)	90
V [Å^3]	2319.4(8)	576.1(2)	1926.6(6)
Z	4	1	4
μ [mm^{-1}]	2.789	1.701	1.747
2θ range [°]	3.3−52.1	3.77−24.41	2.9−48.4
Reflections measured	18095	4381	7916
Reflections unique	8666	1631	2008
R	0.0358	0.0208	0.0863
R_w	0.0429	0.0518	0.1458
Goodness of fit	0.987	1.167	1.082

2 H, C_5H_4), 4.13 (s, 5 H, C_5H_5), 3.14 (m, 1 H, SCH_2CH_2S), 2.35 [s, 1 H, C(O)CHC], 2.20 (m, 3 H, SCH_2CH_2S) ppm. FAB^+: m/z = 609 [$M^+ + 1$], 580 [$M^+ - CO$], 552 [$M^+ - 2\ CO$], 524 [$M^+ - 3\ CO$], 496 [$M^+ - 4\ CO$], 468 [$M^+ - 5\ CO$]. $C_{22}Fe_3H_{16}O_6S_2$ (608.02): calcd. C 43.46, H 2.65; found C 42.38, H 2.58.

X-ray Crystallographic Studies: For all the compounds data have been collected at low temperature with an STOE Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and using a graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Crystal data and structure refinement parameters for compounds **1**, **2** and **6** are listed in Table 4. Final unit cell parameters have been obtained by using a least-squares refinement of a set of 5000 well-measured reflections, and crystal decay was monitored during data collection. No significant fluctuations of the intensity were observed. Structures were solved by Direct Methods using SIR92,[20] and subsequent difference Fourier maps refined by least-squares procedures on F^2 by using SHELXL-97[21] included in the package WINGX.[22] Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[23] All hydrogen atoms were located on a difference Fourier map and refined by using a riding model with an isotropic thermal parameter fixed at 20% higher than those of the carbon atoms to which they are connected. For all structures all non-hydrogen atoms were anisotropically refined and in the last cycles of refinement a weighting scheme was applied, where weights have been calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Drawings of the molecules were performed using the program ORTEP32[24] with 50% probability displacement ellipsoids for non-hydrogen atoms. The structure of compound **1** has been solved in the monoclinic cell (space group $P2_1$) with $\beta = 90°$ and may be emulated by an orthorhombic system of space group $P2_12_12$, all attempts to solve this structure in this system failed. We observed some characteristic warning signs of the presence of twinning in the data, notably a very low value for $E^2 - 1$ (= 0.63), lower than the expected value of 0.74 for the non-centrosymmetric case. Consequently, **1** was solved in the monoclinic system $P2_1$ by using the following twin law which allows to simultaneously refine general and racemic twinning: TWIN 1.00 0.00 0.00 0.00 − 1.00 0.00 0.00 0.00 − 1.00 −4. Application of this specific instruction led to a stable model which could be refined without any constraints or restraints and converged nicely. CCDC-183656 (**1**), -186787 (**2**), and -186357 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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