Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 665 (2003) 167–175
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Double bond migration in *S*–allyl systems catalysed by $[RuClH(CO)(PPh_3)_3]$

Nikodem Kuźnik *, Stanisław Krompiec, Tadeusz Bieg, Stefan Baj, Krzysztof Skutil, Anna Chrobok

Faculty of Chemistry, Silesian University of Technology, Krzywoustego 6, 44-100 Gliwice, Poland

Received 25 July 2002; accepted 30 October 2002

Abstract

Reactions of *S*–allyl systems (allyl sulphides of R–S–allyl type, where R = Et, allyl, Ph, Me_3C, Ph_3C, as well as of allyl phenyl sulphoxide, allyl phenyl sulphone, 2,5-dihydro-1,1-dioxothiophene) with $[RuClH(CO)(PPh_3)_3]$ and other ruthenium compounds have been investigated. Double-bond migration was observed in the case of allyl trityl sulphide, allyl *t*-butyl sulphide and both sulphones, that is, where co-ordinating properties of sulphur were not too strong. High-yielded syntheses of (*E*)- and (*Z*)-R–S–$CH{=}CHCH_3$ (R = Me_3C, *Z*:*E* = 96:4 and Ph_3C, *Z*:*E* = 92:8), (*E*)–Ph–$S(O_2)$–$CH{=}CHCH_3$ and 2,3-dihydro-1,1-dioxothiophene from respective allyl systems are described. The binuclear Ru complex, formed in the model reaction of allyl phenyl sulphide with $[RuClH(CO)(PPh_3)_3]$ has been isolated and its structure has been resolved. The mechanism of the reaction between *S*–allyl systems and $[RuClH(CO(PPh_3)_3]$ is proposed.

Keywords: Isomerisation; *S*–allyl compounds; C–S bond cleavage; Ruthenium complexes

1. Introduction

S-(1-Propenyl), or generally, vinyl sulphides, sulphoxides and sulphones are attractive reagents in organic synthesis. Among other applications, they are used as reagents for addition to C=C [1–4] bond, cycloaddition [2+2] [5–7], cycloaddition [2+4] [8–10], dipolar addition [9,11], as well as donors of 1-propenyl fragment [12–15], what is of particular interest. It should be emphasised that unlike *S*-(1-propenyl), *S*–allyl systems are not propenyl donors [13,14]. *S*–(1-Propenyl) systems (vinyl systems generally) are easy to synthesise via catalytic isomerisation of respective *S*–allyl systems. Previously known reactions of the isomerisation of allyl sulphides were carried out in the presence of *t*-BuOK [16–18], KOH [18] or EtONa [19]. Allyl sulphones were transformed into vinyl sulphones using Et_3N [20], KOH [21], NaOH [22], NaH [23], NaOH–Bu_4NOH [24], Al_2O_3 [25]. In our paper, we demonstrated a possibility of the isomerisation of some allyl sulphides catalysed by ruthenium complexes [26]. To our best knowledge, in the literature there are no other reports of the isomerisations of *S*–allyl systems in the presence of transition metal complexes. This is certainly a consequence of very strong co-ordinating properties of sulphur atoms and the resulting tendency of S–C(allyl) bond cleavage. This, in turn, leads to transformation of the catalyst precursors into inactive complexes for the double-bond migration. The cleavage of C–O and C–S bonds by transition metal complexes (oxidative addition of *O*– and *S*–allyl compounds to low valent transition metal complexes) such as Ru has been studied intensively [27–29]. In this paper, however, the results of investigating the reactions between *S*–allyl systems and various ruthenium complexes (particularly $[RuClH(CO)(PPh_3)_3]$) are discussed. New methods of the synthesis of some vinyl sulphides and sulphones via isomerisation of respective *S*–allyl systems catalysed by $[RuClH(CO)(PPh_3)_3]$ are presented. The structure of the complex isolated from the products of the model reaction between allyl phenyl sulphide and

* Corresponding author. Tel.: +48-32-237-1707; fax: +48-32-237-2277.
E-mail address: nikodem@zeus.polsl.gliwice.pl (N. Kuźnik).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)02111-3

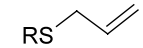
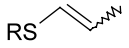
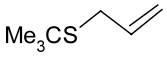
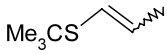
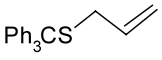
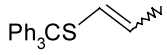
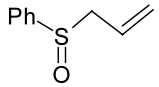
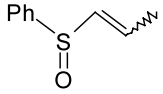
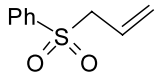
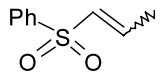
$[RuClH(CO)(PPh_3)_3]$ is described. Furthermore, the mechanism of the reaction between *S*–allyl systems and $[RuClH(CO)(PPh_3)_3]$ is discussed.

2. Results and discussion

The results of our investigation of the isomerisation of some sulphides, allyl phenyl sulphoxide, allyl phenyl sulphone and 2,5-dihydro-1,1-dioxothiophene catalysed by $[RuClH(CO)(PPh_3)_3]$ are presented in Table 1.

As it is shown in the Table 1, the isomerisation to 1-propenyl (vinyl) derivatives was successful for allyl sulphides with bulky groups (R), as well as for both sulphones. In the case of other allyl sulphides and allyl phenyl sulphoxide, practically no products of double-bond migration were observed. For *S*–allyl systems, which successfully undergo isomerisation no by-products were detected. Therefore, the conversion of allyl systems (ε) in the Table 1 was practically equal the yield of double-bond migration product (y). On the other hand, a decrease of Z/E ratio in the course of the isomerisation of allyl *t*-butyl sulphide and allyl trityl sulphide indicates that the $Z-E$ isomerisation is a consecutive reaction. However, double-bond migration is faster than $Z-E$ isomerisation. Therefore, it was possible to obtain 1-propenyl sulphides, which contained no more than 8% of the *E*-isomer (product) and less than 0.4% of allyl system (substrate). We have tried modifying several reaction conditions including: prolon-

Table 1
Isomerisation of S–allyl compounds catalysed by $[RuClH(CO)(PPh_3)_3]$

Allyl Compounds	t[°C]	τ[h]	[Ru]	Solv.	ε[%][a]	Isomerisation Structure	Product y[%][a]	Z/E
 R = Et, Allyl, Ph	60	6	3	B	0 – 3 [b]		c)	c)
	80	2	10	d)	0 – 3 [b]		c)	c)
	80	6	2	B	99.6 [e]		100	14.5 [f]
	80	3	2	B	99.7		100	24.0 [g]
	80	8	3	B	99.5		100	6.5
	80	6	2	THF	99.6		100	18.7
	80	3	2	THF	93		100	24.0
	80	10	2	i)	99.6		100	2.1
	20	168	100	h)	47		100	6.4
	80	3	2.0	B	76		100	20.0
	60	3	2.5	B	99.8		100	8.4
	60	2	2.5	B	99.6		100	13.0 [g]
	80	2	10	h)	99.8		100	2.5
	60	6	2	B	~3		c)	c)
	80	2	10	d)	< 3		c)	c)
	140	2	2	-	~3		c)	c)
	80	6	2	B	25		100	E [j,k]
	80	6	2	THF	10		100	E
	80	3	12	THF	67		100	E
	80	4	24	h)	74		100	E [g]
	80	6	2	B	45 [l]		100	
	80	6	2	THF	47		100	g)
	80	6	10	h)	48		100	

t, reaction temperature; τ, reaction time; [Ru], catalyst concentration in (%) mol; Solv., solvent (4 cm^3 per 1 mmol of substrate); ε, reagent conversion; y, yield of isomerisation product; B, benzene; (a) determined by ^{1}H-NMR; (b) an increase of the reaction temperature up to 140 °C or/and prolonging the reaction time up to 6 h, or an increase of catalyst concentration up to 10% mol does not improve the double-bond migration product yield; (c) not determined, but probably no other products formed; (d) reactions carried out in benzene and in THF, in both cases propene was released; (e) ~0.5% allyl sulphide in equilibrium [16]; (f) equilibrium composition: 29% (*Z*) and 71% (*E*) [16]; (g) also carried out on preparative scale, see Section 3; (h) the reactions carried out in benzene and in THF, in both cases propene release was not observed; (i) benzene+THF 1:1; (j) 100% (*E*); (k) equilibrium composition: 6% (*Z*) and 94% (*E*) [16]; (l) equilibrium conversion in accordance with [36]—42%.

gation of the reaction time, increasing the temperature up to 140 °C, changing the solvent (for $Cl_2C{=}CCl_2$, THF, xylene, 1,4-dioxane) and use of other ruthenium complexes as catalysts, like: $[RuClH(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, $[Ru(acac)_3]$, $[RuCl_2(NBD)]_x$, $[RuCl_2(p\text{-cymene})]_2$, $[Ru(CO)_3(PPh_3)_2]$, $[RuH_2(CO)(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, but it has not increased the isomerisation yield. It should be noted that the isomerisation of allyl trityl sulphide with $[RuClH(CO)(PPh_3)_3]$ occurred at ambient temperature (but the proportion of [Ru] to the substrate was 1:1). In this reaction, we did not observe any complexes, which were the products of insertion of $Ph_3C{-}S{-}$allyl into Ru–H bond. Such complexes, like $[Ru(C,S\text{–}CH_2CH_2CH_2SR)Cl(CO)(PPh_3)_2]$ were described by Hiraki et al. [30] as the products of insertion of $[RuClH(CO)(PPh_3)_3]$ to R–S–allyl, where R = Me, CH_2Ph or allyl (in a THF solution at 10–28 °C). It is important to indicate that we observed propene release in the reactions of the systems that did not isomerise (Et–S–allyl, Ph–S–allyl, $allyl_2S$, Ph–S(O)–allyl). Moreover, we demonstrated that the precursor, i.e. $[RuClH(CO)(PPh_3)_3]$, was transformed into an inactive complex (for isomerisation) in those reactions which did not lead to the migration of the double bond. This has been further proved by the observed impact of 'external' *S*–allyl systems (and similar solvents containing sulphur) on the isomerisation of 1-allyl-3,4-methylenedioxybenzene and allyl phenyl ether. Their double bond migration is successful (conditions: 0.1 M of the allyl system, 0.005 M $[RuClH(CO)(PPh_3)_3]$, 80 °C) in benzene (100% conversion of allylbenzene or allyl phenyl ether after 5 min), 1,1-dioxotetrahydrothiophene and allyl *t*-butyl sulphide. On the other hand, no double bond migration in similar conditions (molar 1:1 allyl system: solvent) in Et_2S, Ph–S–allyl, DMSO, $allyl_2S$, Ph–S(O)–allyl. *S*–Allyl systems which do not undergo isomerisation in the presence of $[RuClH(CO)(PPh_3)_3]$, if added to other usually easily isomerising allyl systems, i.e. allyl phenyl ether (**1**) and 1-allyl-3,4-methylenedioxybenzene (**2**) completely block their isomerisation by ruthenium complexes [31,32]. Also, the solvents with strong co-ordinating properties (Et_2S as $allyl_2S$, DMSO as Ph–S(O)–allyl) disable the double-bond migration both in (**1**) and (**2**).

On the other hand, addition of *S*–allyl systems which themselves easily undergo isomerisation (allyl *t*-butyl sulphide, allyl trityl sulphide and sulphones), as well as using 1,1-dioxotetrahydrothiophene as the solvent, blocks neither the isomerisation of (**1**) nor of (**2**).

Similar solvent behaviour had been previously observed in the reactions between various strong co-ordinating *S*– and *N*–allyl systems and $[Ru(acac)_3]$ [33]. To learn more about the reactions between S–allyl systems and $[RuClH(CO)(PPh_3)_3]$ we investigated thoroughly the reaction between allyl phenyl sulphide and the mentioned complex. The research has revealed that propene is released in the course of heating allyl phenyl sulphide with $[RuClH(CO)(PPh_3)_3]$ in boiling THF or benzene. Such release had previously been observed in the reactions of allyl methyl sulphide and allyl benzyl sulphide with $[RuClH(CO)(PPh_3)_3]$ [30] and $[RhH(CO)(PPh_3)_3]$ [34,35]. Moreover, we found that in both reactions (in THF and in benzene) coloured ruthenium complexes were formed (what was observed as coloured bands on preparative TLC plates); at the same time, in both discussed cases a yellow complex (**3**) constituted ~90% of the mass of the separated complexes. This complex (**3**) (from the reaction in benzene) was isolated using preparative TLC. An attempt to isolate this complex by means of column chromatography (on silica gel) failed. The structure of **3** was determined by an X-ray method (Fig. 1). The X-ray analysis result is fully consistent with its spectroscopy data (^1H and ^{13}C-NMR, IR) and elemental analysis. The separated complex (**3**) does not contain any hydride ligand, what was proved by spectroscopy data. Hiraki et al. in their investigations on the reaction of allyl alkyl sulphides (alkyl = Me, CH_2Ph, allyl) with $[RuClH(CO)(PPh_3)_3]$ had previously suggested the formation of binuclear complexes containing hydride ligand [30]. However, they had not separated the mixture of the formed complexes and had not evaluated their structure by X-ray. The structures of other complexes formed in the reaction between Ph–S–allyl and $[RuClH(CO)(PPh_3)_3]$ and seen on TLC plates were not analysed due to very low yields (1–3%; Table 2).

The determination of the structure of the complex (**3**) formed in the reaction between allyl phenyl sulphide and $[RuClH(CO)(PPh_3)_3]$ made it possible to present a more generalised proposal of the mechanism of the reaction between Q-allyl and $[RuClH(CO)(PPh_3)_3]$: see Fig. 3.

It has been assumed that the double-bond migration is a typical hydride mechanism. This assumption has strong support by our previous findings with deuterated species [31,32] as well as those made by other authors [37–39]. The reaction begins with dissociation of triphenylphosphine from $[RuClH(CO)(PPh_3)_3]$ to produce the active form [Ru]–H (**4**) [31]. Next, an is formed from [Ru]–H and Q–allyl. For clarity, the evident contribution of all π-olefin complexes produced in the consecutive reaction steps has not been shown on Fig. 2, however the proposed structures of the π-olefin complexes are depicted on Fig. 4. After that, by a typical 1,2-insertion of co-ordinated alkene to the Ru–H bond, complexes **5**, **6**, **7** or **8** and **10** are formed, respectively. It is our opinion that if the sulphur atom in the functional group Q has strong co-ordinating properties (like S atom in sulphides not shielded by a bulky group), functional group Q (via S atom) in complexes **8** and **10** interacts strongly with Ru atom. Consequently, this leads to C–Q (C–S) bond cleavage easily occurring in

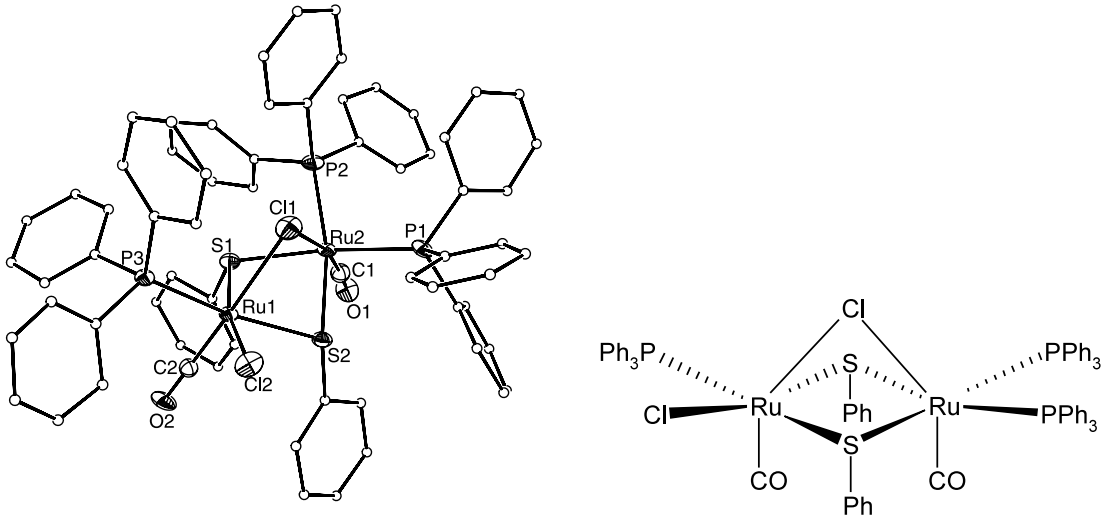


Fig. 1. Structure of chlorocarbonyl(triphenylphosphine)ruthenium (II)-μ-chloro-di(thiophenolato)-carbonyl-bis(triphenylphosphine)-ruthenium(II)—the yellow complex (**3**) isolated from the reaction between allyl phenyl sulphide and [$RuClH(CO)(PPh_3)_3$].

Table 2
Selected bond lengths (Å) and angles (°) for complex **3**

Bond lengths		Bong angles	
Ru1–C2	1.83(2)	Ru2–S2–Ru1	87.3(2)
Ru2–C1	1.82(2)	Ru1–S1–Ru2	88.8(2)
Ru1–S1	2.376(5)	O2–C2–Ru1	177.4(2)
Ru1–S2	2.439(5)	O1–C1–Ru2	176.5(2)
O1–C1	1.126(19)		
O2–C2	1.3(2)		

complex **8**. Propene is released and monomeric complex **9** is formed consecutively, dimerizing to binuclear complex **11**; as thiolate ligands are prone to co-ordinate in a bridging fashion [40]. This idea is based on the structure of the separated complex **3**. On the other hand, if Q does not have strong co-ordinating properties (for sulphones), complexes **5** and **6** (and in the case of sulphones—complex **8** as well) undergo β-elimination toward formation of double-bond migration product and [Ru]–H: product of (*Z*) configuration from complex **5**, and product of (*E*) configuration from complex **6** (for sulphides) or complex **8** (in the case of sulphone). This occurs when the sulphur atom present in Q is shielded by a bulky group disabling or, at least, limiting the co-ordination of Ru atom. One could imagine that a similar situation takes place when the sulphur is of 'sulphone' type (also having weak co-ordination properties). On the grounds of the proposed reaction mechanism, it is also possible to explain why an increase in the reaction temperature results in lowered double-bond migration product yield. In any case, the reactions presented in Fig. 3 are reversible with the exception of non-reversible transformations **8** and **10** into **9** (with propene release) and consequently into **11**. Thus, the isomerisation product may always be subjected to a non-reversible transformation (even if it occurs relatively slowly and most likely has higher activation energy, so is more temperature sensitive)—and even despite the fact that sulphur co-ordinates only weakly with Ru atom in complexes **8** and **10**.

Furthermore, we have observed that in the reaction between allyl phenyl selenide and [$RuClH(CO)(PPh_3)_3$]—under the same conditions as in the case of allyl phenyl sulphide propene is also released. At the same time, no double-bond migration products were observed—similarly to the case of Ph–S–allyl. Additionally, we have observed that the presence of Ph–S–allyl blocks the isomerisation of Ph–O–allyl and Ph–allyl—likewise in the presence of sulphides and sulphoxides (see Fig. 1). Basing on our previous research, we have found that Ph–O–allyl and other allyl ethers isomerise very easily to 1-propenyl ethers in the absence of sulphur compounds [31,32]. In our previous research in this field neither C–O bond cleavage was ever observed in ethers nor blocking of the catalytic activity of [Ru]–H by solvents containing an oxygen atom (like Et_2O, THF, MeCOMe) [31,32]. It turns out that the bond cleavage of Q–allyl in *S*– and *Se*–allyl systems results from a strong co-ordination of S or Se atoms to Ru. The co-ordination effect leads to the lengthening and weakening of C–Q bond what in consequence facilities C–Q bond cleavage. In the case of allyl ethers (O–allyl systems) the co-ordination of O atom to Ru is

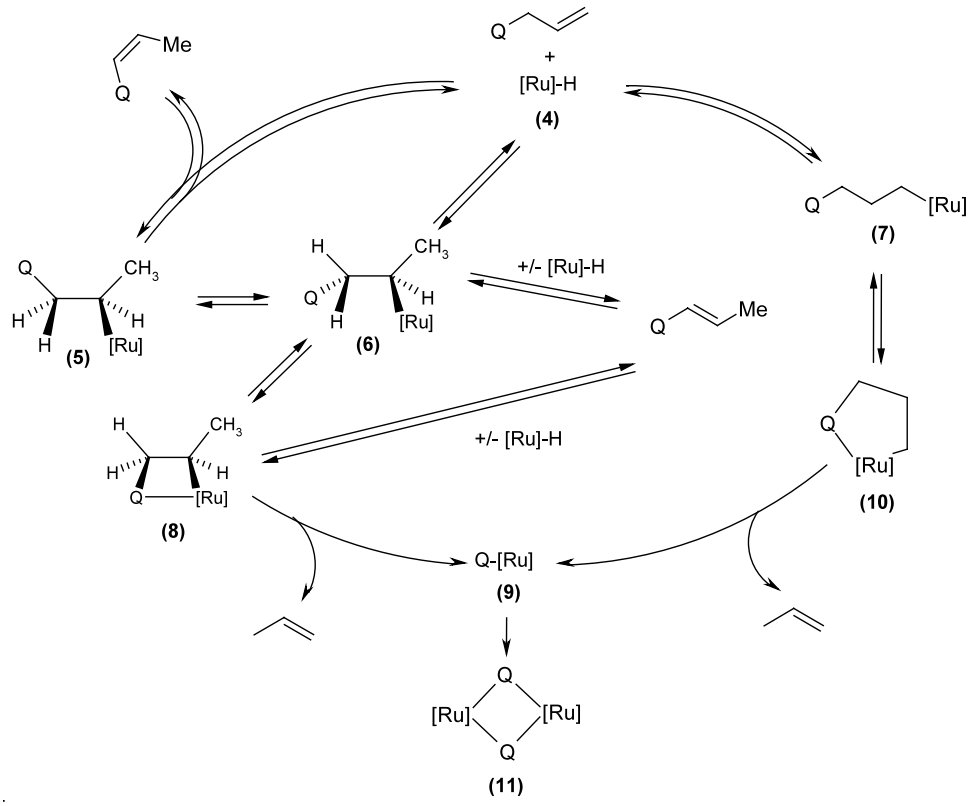


Fig. 2. Proposal of the mechanism of the reaction between *S*–allyl systems (Q–allyl) and $[RuClH(CO)(PPh_3)_3]$ in a benzene or THF solution. The above scheme does not take into account the step of [Ru]–H formation as well as the contribution of triphenylphosphine (also Cl and CO—non-liable under the conditions assumed) and a solvent in the co-ordination of Ru atom in all complexes.

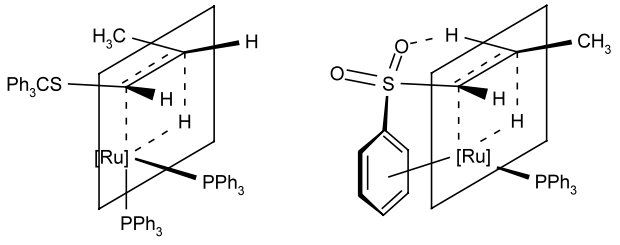


Fig. 3. Probable transition states of β-elimination resulting in (*Z*)-(1-propenyl) trityl sulphide **16** and (*E*)-(1-propenyl) phenyl sulphone **17**.

too weak to enable the C–O bond cleavage. Therefore, only fast double-bond migration is observed.

It should also be emphasised that the isomerisation of $Ph_3C–S–CH_2CH=CH_2$ and $Me_3C–S–CH_2CH=CH_2$ generally leads to 1-propenyl derivatives of (*Z*) configuration; whereas the isomerisation of allyl phenyl sulphone results solely in a product of (*E*) configuration. We claim that in the case of a sulphone (within the transition state of this reaction) the ruthenium atom is co-ordinated by the oxygen atom or by the benzene ring. Such co-ordination leads toward (*E*)-product. Fig. 3 depicts the most probable transition states during formation of the respective 1-propenyl products. In the case of bulky sulphones (**16**), the bulky PPh_3 ligands might locate on one side of the plane (Ru–H–C_{alkyl}–C_{alkyl}), while the other substituants may locate on the other side in order to reduce the steric hindrance. This might lead to the observed *Z* isomer. For sulphones (**17**) S=O...H interations might have important impact, as well as Ru–arene co-ordination, which is supported by our previous Quantum chemical calculations—Fig. 4. This should lead to *E* isomer.

Similar effect, i.e. the production of (*E*) isomers had been previously exclusively observed in the isomerisation of *N*-allyl-*N*-arylethanamides [41]. Quantum calculations performed are fully consistent with the explanation that such selectivity of the isomerisation of the above amides is caused by the co-ordination of the Ru atom by the arene ring and not merely by steric factors.

On the other hand, the formation of (*Z*) isomers in the isomerisation of sulphides is, in our opinion, a result of steric interactions. The interaction of such a bulky group like trityl or *tert*-butyl with other ligands co-ordinated by ruthenium atom leads to complex **5** being the product of [Ru]–H addition to C=C. As a result, β-elimination of [Ru]–H from complex **5** leads to (*Z*)-1-propenyle sulphide. Moreover, we claim that in the case of allyl trityl sulphide, steric hindrance disables the co-ordination of Ru atom by the benzene ring—which

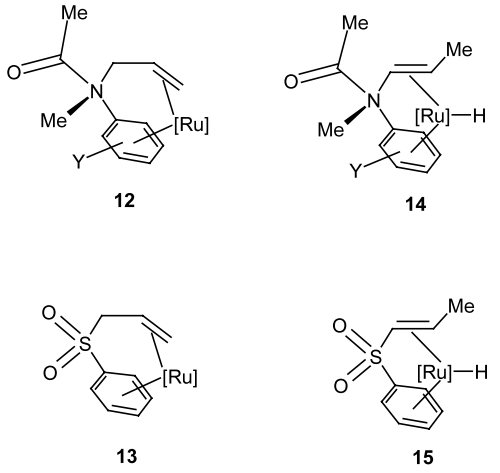


Fig. 4. The co-ordination of ruthenium to benzene ring might be an important factor to $Z-E$ regioselectivity. The co-ordination of N-alliloamides and N-(1-propenylo)amides is supported by quantum calculation [41].

would lead to the isomerisation product of (E) configuration (such as in the case of sulphone).

3. Experimental

All reactions were performed under dry argon atmosphere. Solvents were dried with appropriate drying agents (molecular sieves, CaH_2 or Na) and distilled prior to use. Infrared spectra were measured on a Karl Zeiss Jena M-80 spectrometer (in KBr). NMR spectra were obtained on a Varian Unity Inova 300 MHz spectrometer. MS analysis for $[Ru_2Cl_2(PhS)_2(CO)_2(PPh_3)_3]$ by ESJ–MS method was carried out in the Centre of Polymer Chemistry at the Polish Academy of Sciences in Zabrze. The mass spectra of the organic compounds were recorded on HPLC–MS Waters Integrity Systems with Termabeam Mass Detector (EI, 70 eV), Photodiode Array Detector on a cartridge column (Nova-Pak C18, 2 × 150 mm); methanol–water mixture (75:25; flow 0.25 ml min^{-1}) used as the solvent. Elemental analyses of ruthenium complexes were made by CP-AES method, on a Thermo Jamell Ash spectrometer, in the elemental analysis lab at Polish Chemical Reagents Co. (POCh) in Gliwice. Before the analysis, ruthenium complexes were mineralised in boiling 60% HNO_3. Elemental analyses of sulphides were carried out in the elemental analysis lab at Silesian University of Technology. GC of the gas products of the reaction between S–allyl systems and $[RuCl(H)(CO)(PPh_3)_3]$ was obtained by GC 505 (produced by INCO, Wrocław) equipped with flame-ionisation detector and argon as carrier gas. The composition of the carrier gas was analysed with a packed column (length: 2 m, diameter: 3 mm) filled with modified aluminium oxide, as well as on a capillary column Rt–Q-Plot (length: 15 m, diameter: 0.32 mm) produced by Restek. In the course of the analysis, a programmed increase of temperature was applied (from 80 to 180 °C).

3.1. Materials

Allyl trityl sulphide, t-butyl mercaptan, allyl phenyl sulphide, allyl phenyl sulphoxide, allyl phenyl sulphone, 2,5-dihydro-1,1-dioxothiophene (butadiene sulphone), allyl phenyl selenide-from Aldrich, $[RuCl_2(p\text{-cymene})]_2$ and $[RuH_2(CO)(PPh_3)_3]$ from STREM. Allyl t-butyl sulphide [42], $[RuClH(CO)(PPh_3)_3]$ [43,44], $[RuClH(PPh_3)_3]$ [45], $[RuCl_2(PPh_3)_3]$ [46], $[Ru(acac)_3]$ [47], $[RuCl_2(NBD)_x]$ [48], $[Ru(CO)_3(PPh_3)_2]$ [49], $[RuH_2(PPh_3)_4]$ [50] were synthesised as described in the literature.

3.2. Synthesis of allyl trityl sulphide

Triphenylmenanothiole (0.04 mol) was added to the solution of 0.05 mol of sodium methanolate in 150 cm^3 of methanol, stirred with a mechanical stirrer. The mixture was refluxed for 10 min, and next 0.08 mol of allyl bromide was added. Then the mixture was heated for 1 h; after that volatile fractions were evaporated on a rotary evaporator. The obtained precipitate was washed by water on a fritted funnel and crystallised from ethanol (with the addition of activated coal). Allyl trityl sulphide (10.3 g) was obtained (81%); m.p. = 74–75 °C. ^{1}H-NMR ($CDCl_3$) 2.81 (ddd, 2H, $J_1 = 7.3$ Hz; $J_2 = 1.4$ Hz; $J_3 = 1.0$ Hz); 4.97 (ddt, 1H, $J_1 = 10.5$ Hz; $J_2 = -1.8$ Hz; $J_3 = 1.0$ Hz); 5.05 (ddt, 1H, $J_1 = 17.2$ Hz; $J_2 = -1.8$ Hz; $J_3 = 1.4$ Hz); 5.67 (ddt, 1H, $J_1 = 17.2$ Hz; $J_2 = 10.0$ Hz; $J_3 = 7.3$ Hz); 7.17–7.43 (m, 15H). ^{13}C-NMR ($CDCl_3$, 75.4 MHz, 293 K) 35.56 (s); 66.95 (s); 117.63 (s); 126.54 (s); 127.93 (d); 129.59 (d); 133.10; 144.76. Anal. Calc. for $C_{22}H_{20}S$: C, 83.50; H, 6.37; S, 10.13%. Found: C, 83.47; H, 6.38; S, 10.15. MS m/z (%): 243 (100); 165 (72); 228 (11); 74 (7); 215 (6); 152 (5); 120 (5); 115 (4); 119 (4); 77 (3); 275 (1); 316 (1).

3.3. Isomerisation of S–allyl compounds in the presence of ruthenium or rhodium complexes

a) Allyl compounds were heated with a ruthenium complex (with or without a solvent) in high-pressure glass ampoules, which were put in a thermostat (± 0.1 °C). The proportions of the substrate, the catalyst and the solvent have been given in the description of Fig. 1 and Table 1. Before the reaction, oxygen had been removed from the reaction system and the system had been saturated with argon. After the reaction was completed, the composition of the reaction mixture was analysed by ^{1}H-NMR and/or by GC–MS method.
b) The post-reaction mixture consisting in: allyl compounds, solvent (benzene or THF) and catalyst was

refluxed with argon flow. The proportions of the substrate: catalyst; solvent have been given in the description of Fig. 1 and Table 1. The outlet gas from the reaction system was collected and analysed by GC.

3.4. Preparation of (*E*)- and (*Z*)-Me_3C–S–CH=$CHCH_3$

Allyl *t*-butyl sulphide (100 mmol), 2 mmol [RuClH(CO(PPh_3)$_3$] and 50 cm^3 benzene was refluxed for 3 h. Next, the reaction mixture was rectified with a 30 cm column packed with Fensky helixes under the pressure of 60 mmHg. The obtained distillate contained 0.4% of allyl sulphide and 4% of (*E*)- and 96% of (*Z*)-Me_3C–S–CH=$CHCH_3$ with the yield of 92%. B.p.: 60–62 °C. The spectroscopy data of both isomeric products were consistent with those quoted in literature (^{1}H and ^{13}C-NMR [51], MS [52]).

3.5. Preparation of (*E*)- and (*Z*)-Ph_3C–S–CH=$CHCH_3$

Allyl-trityl sulphide (10 mmol), 0.25 mmol [RuClH(CO(PPh_3)$_3$] and 40 cm^3 benzene were heated in 60 °C for 2 h, with vigorous stirring on a magnetic stirrer. Benzene was distilled off on a vacuum rotary evaporator, whereas the light-yellow residue was extracted three times with 30 cm^3 hexane. The extract (containing the product and some yellow Ru complex) was filtered, and then chromatographed by on a column containing 5 g silicagel (200–400 mesh). The product was eluted with hexane. After hexane evaporated, the residue contained 8% of (*E*)- and 92% of (*Z*)-Ph_3C–S–CH=$CHCH_3$ and it practically did not contain any allyl system with the yield of 95%. Anal. Calc. for $C_{22}H_{20}S$: C, 83.50; H, 6.37; S, 10.13%. Found: C, 83.46; H, 6.38; S, 10.16. ^{1}H-NMR ($CDCl_3$): (*E*) 1.56 (dd, 3H, $J_1 = 6.6$ Hz; $J_2 = 1.6$ Hz); 5.55 (dq, 1H, $J_1 = 15.38$; $J_2 = 1.65$); 5.86 (dq, 1H, $J_1 = 15.4$ Hz; $J_2 = 6.6$ Hz); 7.05–7.40 (m, 15H); (*Z*) 1.76 (dd, 3H, $J_1 = 6.6$ Hz; $J_2 = 1.7$ Hz); 5.51 (dq, 1H, $J_1 = 9.3$; $J_2 = 6.6$); 5.61 (dq, 1H, $J_1 = 9.3$ Hz; $J_2 = 1.7$ Hz); 7.05–7.40 (m, 15H). ^{13}C-NMR ($CDCl_3$, 75,4 MHz, 293 K): (*E*) 18.59 (s); 67.32 (s); 126.68 (s); 127.74 (s); 129.75 (s); 145.00 (s); (*Z*) 14.85 (s); 67.27 (s); 124.66 (s); 124.89 (s); 126.79 (s); 127.80 (s) 129.82 (s); 145.08 (s). MS *m*/*z* (%): 165 (100); 243 (94); 244 (49); 74 (11); 228 (10); 152 (9); 215 (7); 115 (6); 77 (5); 120 (5); 275 (1); 316 (1).

3.6. Preparation of (*E*)- Ph–$S(O_2)$–CH=$CHCH_3$

Allyl phenyl sulphone (100 mmol), 2 mmol [RuClH(CO(PPh_3)$_3$] and 50 cm^3 benzene were refluxed for 6 h. Benzene was distilled off on a vacuum rotary evaporator, and the residues were extracted two times with 50 cm^3 pentane. After the filtration of the catalyst (as well as triphenylphosphine and its oxide) the pentane solution was chromatographed on a column containing 5 g silicagel (200–400 mesh). After pentane evaporated, the residue contained 72% of (*E*)- Ph–$S(O_2)$–CH=$CHCH_3$ and 28% of allyl phenyl sulphone with the yield of 95%. Pure (*E*)- Ph–$S(O_2)$–CH=$CHCH_3$ was isolated from the mixture by preparative TLC method (the plates were developed with diethyl ether–chloroform mixture in the proportion of 1:1). M.p. = 70–71 °C (ethanol); 67–68 °C (ethanol) according to [53]. ^{1}H-NMR spectrum of the obtained product was consistent with the one described in literature [24].

3.7. Preparation of 1,2-dihydro-1,1-dioxothiophene

2,5-Dihydro-1,1-dioxothiophene (100 mmol), 2 mmol [RuClH(CO(PPh_3)$_3$] and 50 cm^3 benzene was refluxed for 6 h. Next, benzene was distilled off on a vacuum rotary evaporator, and the mixture of 2,5-dihydro-1,1-dioxothiophene and 2,3-dihydro-1,1-dioxothiophene (58:42) was rectified under the pressure of 0.5 mmHg (b.p. = 117–120 °C) with the yield of 90%. Pure 1,2-dihydro-1,1-dioxothiophene was isolated from the obtained mixture by preparative TLC method, with the yield of 93% (the plates were developed in chloroform). M.p. = 50–51 °C (recrystallised from Et_2O); 50–52 °C (recrystallised from Et_2O) according to [54]. The spectroscopy data were consistent with those given in the literature (^{1}H, ^{13}C-NMR and MS [55]).

3.8. Isolation of [$Ru_2Cl_2(PhS)_2(CO)_2(PPh_3)_3$]—(**3**)

[RuClH(CO)(PPh_3)$_3$] (1 mmol), 10 mmol allyl phenyl sulphide and 20 cm^3 benzene were refluxed in argon flow. The outlet gas was collected and analysed by GC. After the reaction, benzene was evaporated on a rotary evaporator, and 50 cm^3 pentane was added to the oily residue. The mixture was intensively shaken until a suspension of ruthenium complexes was obtained; then it was left for 24 h in the temperature of −10 °C. The orange–yellow precipitate was filtered off on a fritted funnel and washed three times with pentane. After drying under vacuum, the obtained yellow–orange ruthenium complexes mixture (also containing triphenylphosphine and its oxide) was separated with preparative TLC method. The plates were first developed in benzene and next in dichloromethane. Yellow complex **1** was extracted from the gel with acetone. The TLC analysis indicated that the extract does not contain any other ruthenium complexes. After acetone was evaporated on a rotary evaporator and dried under vacuum, 260 mg of **1** were obtained in the form of tiny, yellow crystals (bigger crystals take an orange colouring).

M.p.: within the temperature range of 60–140 °C it gradually changes the colour to red; in 153–155 °C

decomposes. Solubility: very good in CH_2Cl_2, $CHCl_3$, benzene, Et_2O; good in acetone; insoluble in hexane, cyclohexane. Stability in solutions: stable in CH_2Cl_2, acetone, less stable in $CHCl_3$, benzene, decomposes fast in Et_2O. Stability in solutions under increased temperature: after heating in benzene up to about 60 °C it partially decomposes into a red product. Anal. Calc. for $C_{68}H_{55}Cl_2O_2P_3Ru_2S_2$: C, 61.21; P, 6.96; Ru, 15.5; S, 4.81%. Found: C, 61.21; P, 6.60; Ru, 15.6; S, 4.60. ^{1}H-NMR: (ppm), (300 MHz, 293 K): (CD_2Cl_2): 2,12 (s); 6.5–7.8 (m); ($CDCl_3$): 2.14 (s); 5, 24 (s); 6.38–7.60 (m). ^{31}P-NMR: (CD_2Cl_2, 121.5 MHz, 293 K): 39.75 (dd, $J=12.2$; $J=15.9$ Hz); 43,32 (dd, $J=3.7$; $J=15.9$); 52.28 (dd, $J=12.2$ Hz; $J=3.7$ Hz); ^{13}C-NMR: ($CDCl_3$, 75.4 MHz, 293 K): 30.91 (s); 3.45 (s); 124.92 (s); 125.69 (s); 126.95 (s); 127.21 (s); 127.44 (s); 127.51 (s); 127.56 (s); 127.64 (s); 127.79 (s); 127.91 (s); 129.30 (d), $J=7.5$ Hz; 129.62 (d) $J=9.6$ Hz; 129,73 (d) $J=9.6$ Hz; 203.65 (s); 203.88 (t), $J=6.4$ Hz; IR (KBr): C=O: 1948, 1955 cm^{-1}, PPh_3: 1090, 1430, 1480 cm^{-1}, Ar: 3050, 1625, 1610, 1582, 750, 700 cm^{-1}.

3.9. X-ray of $[Ru_2Cl_2(PhS)_2(CO)_2(PPh_3)_3]$—(3)

All measurements of diffraction intensities were performed on a KUMA KM4 four-circle diffractometer [56], Mo–K_α radiation, $\omega/2\Theta$ scan mode. The structures were solved by direct methods using the program SHELXS-97 [57] and refined by full-matrix least-squares with the aid of the program SHELXL-97 [58]. Most of the non-hydrogen atoms were refined anisotropically, some of them were refined as restrained. The hydrogen positions were calculated according to the standard geometry, and refined as a riding model with isotropic thermal parameters. Software used to prepare material for publication ORTEP-3 [59].

Crystal data for **1**. The crystal chosen for X-ray analysis was a clear orange prism with the approximate dimensions $0.4\times0.2\times0.1$ mm. $Ru_2S_2P_3Cl_2O_2C_{68}H_{50}$ (MW = 1329.22 g mol^{-1}) crystallises in the monoclinic system, space group $P2_1/c$, with $a=11.71(1)$, $b=31.24(2)$, $c=18.23(2)$ Å, $\beta=94.09(3)^\circ$, $V=6652(2)$ Å^3, $Z=4$, μ(Mo–K_α) = 0.718 mm^{-1}, and $D_{calc}=1.437$ g cm^{-3} a total of 5581 reflections were collected to $2\Theta_{max}=48.5^\circ$ (h: $-10\rightarrow10$, k: $0\rightarrow20$, l: $0\rightarrow12$), of which 5581 were unique. The intensity decay of the reference reflections was 5.7%. In refinements, weights were used according to the scheme $w=1/[\sigma^2(F_o^2)+(0.123P)^2+15P]$, where $P=(F_o^2+2F_c^2)/3$. The refinement of 772 parameters converged to the final agreement factors $R=0.0754$, $R_w=0.2116$, and $S=1.011$ for 2621 observed reflections with $F>4\sigma(F_o)$. The electron density of the largest difference peak was found to be 1.62 e Å^{-3}, while that of the largest difference hole was 0.95 e Å^{-3}.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as deposition No. CCDC 175161. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] H. Su, Y. Hiwatari, M. Soenosawa, K. Sasuga, K. Shirai, T. Kumamoto, Bull. Chem. Soc. Jpn. 66 (1993) 2603.
[2] W.H. Chan, W.M. Lee, E.T.T. Chan, J. Chem. Soc. Perkin Trans. 1 8 (1992) 945.
[3] W.J. Bailey, E.W. Cummins, J. Am. Chem. Soc. 76 (1954) 1932.
[4] Y.R. Lee, N.S. Kim, B.S. Kim, Tetrahedron Lett. 38 (1997) 5671.
[5] W.E. Parham, J. Org. Chem. 29 (1964) 2211.
[6] S.M. Leibovitz, H.J. Johnson, Synth. Commun. 16 (1986) 1255.
[7] J.J. Eisch, J.E. Galle, L.E. Hallenbeck, J. Org. Chem. 47 (1982) 1608.
[8] B. Tinant, J. Feneau-Dupont, J.P. Declercq, P. Nshimyumukiza, Bull. Soc. Chim. Belg. 102 (1993) 635.
[9] N.S. Simpkins, Tetrahedron 46 (1990) 6951.
[10] O. Delucci, L. Pasquato, G. Madenn, Tetrahedron Lett. 25 (1984) 3643.
[11] P. Caramella, T. Bandiera, P. Grünanger, F. Marione Albini, Tetrahedron 40 (1984) 441.
[12] G. Bianchetti, D. Pocar, C. Torricelli, E. Arlandini, B. Gioia, Gazz. Chim. Ital. 111 (1981) 315.
[13] T. Asaki, T. Aoyama, T. Shioiri, Heterocycles 27 (1988) 343.
[14] M. Isobe, M. Kitamura, T. Goto, Chem. Lett. (1980) 331.
[15] H. Tohma, H. Watanabe, S. Takizawa, T. Maegawa, Y. Kita, Heterocycles 51 (1999) 1785.
[16] V. Svata, Collect. Czech. Chem. Commun. 43 (1978) 2619.
[17] H. Nishimura, J. Mizutani, J. Org. Chem. 40 (1975) 1567.
[18] C.C. Price, W.H. Snyder, J. Org. Chem. 27 (1962) 4639.
[19] D.S. Tarbell, W.E. Lovett, J. Am. Chem. Soc. 78 (1956) 2259.
[20] I. Sataty, C.Y. Meyers, Tetrahedron Lett. 47 (1974) 4161.
[21] H.J. Kuhn, R. Defoin, K. Gollnick, C. Krueger, Y.H. Tsay, Tetrahedron 45 (1989) 1667.
[22] L.A. Mukhamedova, L.I. Kursheva, M.A. Nechaeva, Khim. Geterotsikl. Soedin. 18 (1982) 478.
[23] T. Chou, H.-H. Tso, L.-J. Chang, Chem. Soc. Perkin Trans. 1, (1985) 515.
[24] T. Berranger, Y. Langlois, J. Org. Chem. 60 (1995) 1720.
[25] L. Horner, I. Ertel, H.-D. Ruprecht, O. Belovcký, Chem. Ber. 103 (1970) 1582.
[26] S. Krompiec, J. Suwinski, M. Gibas, J. Grobelny, Polish J. Chem. 70 (1996) 133.
[27] J.G. Planas, T. Marumo, Y. Ichikawa, M. Hirano, S. Komiya, J. Mol. Catal. A: Chem. 147 (1999) 137.
[28] S. Komiya, T. Kabasawa, K. Yamashita, M. Hirano, A. Fukuoka, J. Organomet. Chem. 471 (1994) C6.
[29] M. Hirano, N. Kurata, T. Marumo, S. Komiya, Organometallics 17 (1998) 501.
[30] K. Hiraki, Y. Fuchita, H. Kawabata, K. Iwamoto, T. Yoshimura, H. Kawano, Bull. Chem. Soc. Jpn. 65 (1992) 3027.
[31] S. Krompiec, Izomeryzacja alkenów i ich funkcyjnie podstawionych pochodnych katalizowana kompleksami rutenu, Zesz. Nauk. Pol. Śl. s. Chemia, Z 136 (1997).

[32] S. Krompiec, N. Kuźnik, T. Bieg, B. Adamus, J. Majnusz, M. Grymel, Polish J. Chem. 74 (2000) 1197.
[33] S. Krompiec, J. Suwiński, R. Grobelny, J. Mol. Catal. 89 (1994) 303.
[34] K. Osakada, K. Matsumoto, T. Yamamoto, A. Yamamoto, Organometallics 4 (1985) 857.
[35] K. Osakada, K. Matsumoto, T. Yamamoto, A. Yamamoto, Chem. Ind. (1984) 634.
[36] R.C. Krug, G.R. Tichelaar, F.E. Didot, J. Org. Chem. 23 (1958) 212.
[37] D.F. Ewing, B. Hudson, D.E. Webster, P.B. Wells, J. Chem. Soc. Dalton Trans. (1972) 1287.
[38] D. Bingham, D.E. Webster, P.B. Wells, J. Chem. Soc. Dalton Trans. (1974) 1519.
[39] B. Hudson, D.E. Webster, P.B. Wells, J. Chem. Soc. Dalton Trans. (1972) 1204.
[40] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
[41] S. Krompiec, M. Pigulla, T. Bieg, W. Szczepankiewicz, N. Kuźnik, M. Krompiec, M. Kubicki, J. Mol. Catal. A 189 (2002) 169.
[42] K. Oshima, H. Yamamoto, H. Nozaki, Bull. Chem. Soc. Jpn. 48 (1975) 1567.
[43] J.J. Levison, S.D.J. Robinson, Chem. Soc. A (1970) 2947.
[44] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45.
[45] M. Bianchi, U. Matteoli, P. Frediani, G. Menchi, C. Botteghi, M. Marchetti, J. Organomet. Chem. 252 (1983) 317.
[46] T.A. Stephenson, G. Wilkinson, J. Chem. Soc. A (1968) 2660.
[47] A. Johnson, G.W. Everett, J. Am. Chem. Soc. 94 (1972) 1419.
[48] E.W. Abel, M.A. Bennett, G. Wilkinson, J. Chem. Soc. A (1959) 3178.
[49] G.B. Szulpin, Organiceskije reakcji kataliziruemyje kompleksami metallow, Nauka, Moscow, 1988.
[50] R. Young, G. Wilkinson, Inorg. Synth. 17 (1977) 75.
[51] R. Virtanen, Acta Chem. Scand. Ser. B 40 (1986) 313.
[52] M.E. Alonso, G. Martin, A.W. Chitty, Phosphorus Sulfur 31 (1987) 147.
[53] W.E. Parham, H.G. Braxton, D.R. Theissen, J. Org. Chem. 27 (1962) 2415.
[54] H.E. Faith, M.P. Kautsky, B.E. Abreu, J. Org. Chem. 27 (1962) 2889.
[55] X.-F. Ren, E. Turos, C.H. Lake, M.R. Churchill, J. Org. Chem. 60 (1995) 6468.
[56] Kuma Diffraction, KUMA KM4 Software. User's Guide, ver. 5.0, Kuma Diffraction, Wroclaw, 1991.
[57] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[58] G.M. Sheldrick, SHELXL97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[59] L.J. Farrugia, Appl. Cryst. 32 (1997) 565.