Journal of Organometallic Chemistry, 472 (1994) 275–284

Synthesis and ring-opening reactions of cationic ruthenium biaryl thionolactone complexes *,**,‡

G. Bringmann, B. Schöner and O. Schupp

Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg (Germany)

W.A. Schenk and I. Reuther

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg (Germany)

K. Peters, E.-M. Peters and H.G. von Schnering

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70506 Stuttgart (Germany)

(Received November 1, 1993)

Abstract

The preparations of novel thionolactone-bridged configuratively labile biaryls and their $[Cp(R_3P)_2Ru]^+$-complexes are described. The dynamics of helimerization of these complexes and their reactivity towards nucleophiles have been investigated. Hydride transfer reagents lead to a cleavage of the thionolactone bridge to give the corresponding thiolate complexes, apparently *via* intermediate exothiolactolate ruthenium complexes. A similar lactolate analog is formed upon addition of a mild *S*-nucleophile.

Key words: Ruthenium; Crystal structure; Thionolactone; Ring opening; Fluxionality

1. Introduction

Organic thiocarbonyl compounds differ from their "true" carbonyl counterparts in two important characteristics. Because of the lower energy of the C–S π bond, they are much more reactive, but because of the low polarity of the C–S unit, they also react much less selectively. Thus, nucleophilic additions, for example, may occur either at the carbon (carbophilic addition) or at the sulfur (thiophilic addition) [3]. A promising strategy to circumvent this selectivity problem is to coordinate the C=S group *via* the sulfur atom to a transition metal, and thus redirect the nucleophilic attack to the carbon atom. Half-sandwich-type ruthenium complexes $[CpRu(PR_3)_2]^+$ are particularily suited for this purpose: the positive charge is largely expected to offset the decrease in reactivity brought about by steric hindrance. Indeed, we were recently able to demonstrate that thiobenzaldehyde complexes $[Cp(R_3P)_2Ru(\eta^1\text{-}S{=}CHR)]^+$, despite their substantial steric shielding, still react with dienes and with a variety of nucleophiles [2].

The well-documented ability of the $[CpRu(PR_3)_2]$ fragment to stabilize otherwise short-lived intermediates, such as thioaldehydes [2,4], sulfenes [5], sulfur monoxide [6] and many others [7], is an additional benefit in that it can provide important insights into reaction mechanisms. And finally, pseudotetrahedral complexes offer a number of ways of introducing an element of chirality into the system [8], and thus act as chiral auxiliaries in stereoselective reactions. It would be very attractive if these advantages could be incorporated into the concept of the atropisomer-selective ring opening of metal complexes **2** of stereochemically labile biaryl lactones **1** (Scheme 1) [9–11].

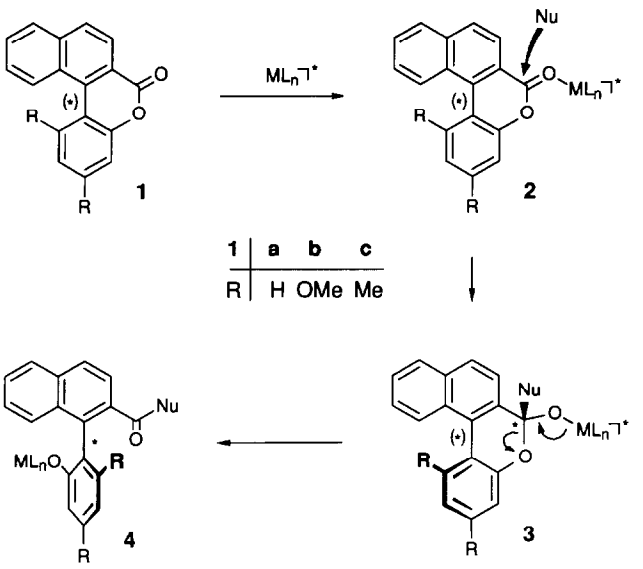
Correspondence to: Prof. Dr. W.A. Schenk or Prof. Dr. G. Bringmann.

* Novel concepts in directed biaryl synthesis, Part XXXV; for Part XXXIV, see Ref. 1.

** The coordination chemistry of the C=S function, Part XI; for Part X, see Ref. 2.

‡ Dedicated to Prof. Helmut Werner on the occasion of his 60th birthday.

0022-328X/94/$7.00
SSDI 0022-328X(93)24333-Z



Scheme 1. The directed, metal-assisted ring opening of "axially prostereogenic" biaryl lactones **1**, under simultaneous asymmetric induction at the axis. Configuratively stable stereogenic units are denoted by '*', and labile ones by '(*)'.

In terms of this concept, the $[CpRu(PR_3)_2]$-fragment would serve to activate the (thio)carbonyl group towards the attack by nucleophiles. In addition it would stabilize thio-analogs of the postulated [12] lactolate-type intermediates **3** of this stereochemically interesting ring-opening reaction to give **4**, as a key to a better understanding of the mechanism and its principles of stereocontrol. Furthermore, at a later stage, the use of *chiral* ruthenium complexes would perhaps allow the option of performing the cleavage of the bridge in a stereoselective manner. For this purpose, procedures for the mild demetalation of **4** (or its thio-analog) will have to be developed that give species in which the resulting metal-free biaryl is configuratively stable at the axis. In the field of "normal", *i.e.* lactone-bridged biaryls, the benzonaphtho-coumarins **1** [13] have proved to be very valuable substrates [14]. Here we describe the synthesis of the corresponding thiono-biaryl lactone substrates, their [CpRu(dppm)]- and [CpRu(dppe)]-complexes (dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PCH_2CH_2PPh_2$) and the chemical behavior of such complexes towards nucleophiles.

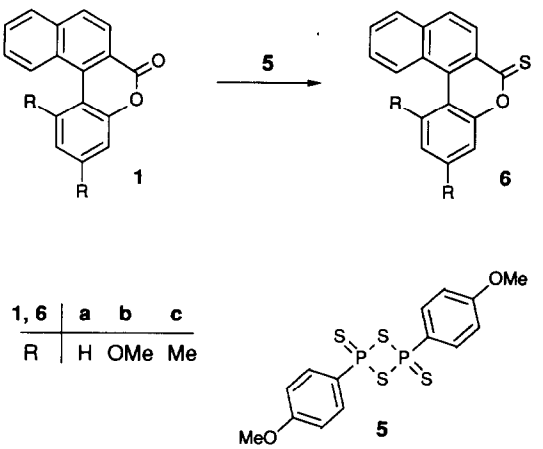
2. Preparation of the thionolactones and their metal complexes

To take advantage of the specific properties of ruthenium complexes, it was necessary to convert the hitherto utilized [13] oxolactones **1** into their thio-analogs **6**. For the required *O/S*-exchange of esters or lactones, use of the dithiophosphetane **5** (Lawesson's reagent) has proved to be the most effective and versatile method [15]. Thus, by reaction of **1** with a two-fold excess of **5** in refluxing toluene and subsequent recrystallization, the desired thionolactones **6** were obtained in good yields (greater than 75%) as orange-colored solids. As expected, these sulfur compounds are characterized by their typical infrared absorption at approximately 1200 cm^{-1} (C=S stretching) and, chemically, by their facile desulfurization reaction, regenerating the oxolactones **1**.

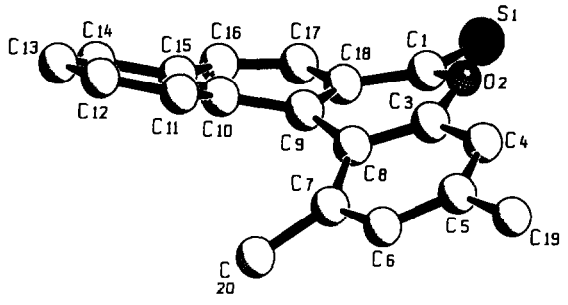
For an additional confirmation of the *O/S*-exchange, and in order to gain insight into the three-dimensional structure of such thionolactone-type bridged biaryls, an X-ray structure analysis of **6c** was performed, and this clearly revealed the expected helically twisted structure.

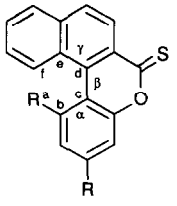
In considering the extent of the molecular distortion, two opposing effects exerted by the sulfur must be taken into account. First, the low tendency of the sulfur to form C=S double bonds would lead to a higher contribution by the mesomeric structure **7B** (Scheme 3), so that the compound is characterized by a higher double bond character in the endocyclic C–O bond and a higher positive charge within the ring system, both leading to a higher degree of planarization of the molecule. Second, the lower electronegativity of the sulfur than of oxygen should favor the mesomeric structure **7A**, which should result in a greater molecular distortion.

The crystal structure analysis shows that, surprisingly, the thionolactone **6c** is distorted to a significantly larger extent than the otherwise identically substituted oxolactone **1b**, and the distortion is even greater than that in the corresponding ethyl derivative **1** (R = Et).



Scheme 2. Generation of the thionolactone **6** by oxygen/sulfur-exchange of **1**.



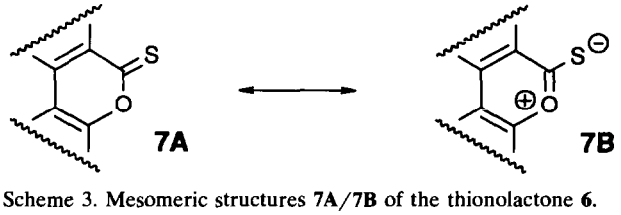


	α	β	γ	Σ
6c	12.1	33.4	18.1	63.6
1b	12.4	34.1	15.0	61.5
1 (R = Et)	14.5	34.0	14.2	62.7

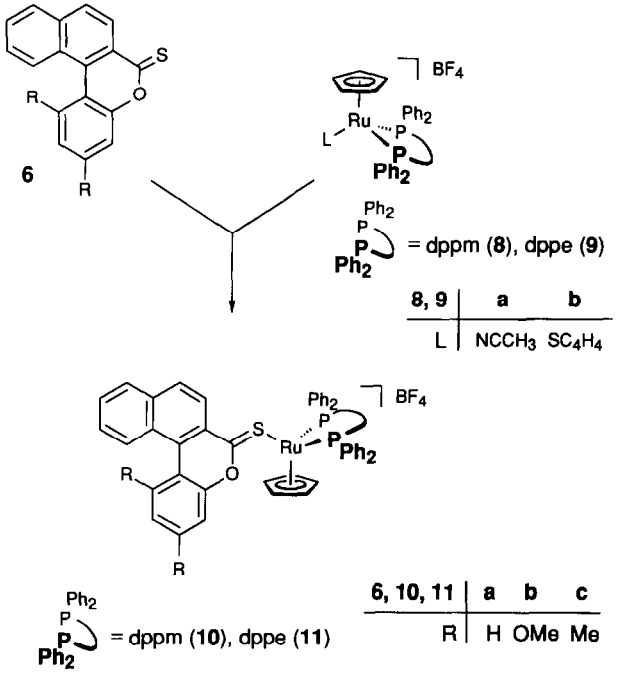
Fig. 1. Structure of **6c** in the crystal; selected bond lengths (Å) and bond angles (°): S1–C1 1.636(4), C1–O2 1.359(3), O2–C3 1.390(4), C8–C9 1.472(3); S1–C1–O2 116.6(2), C1–O2–C3 121.6(2).

With these novel thionolactone-bridged biaryls **6** in hand, we set out to prepare the required ruthenium complexes **10** and **11**. Initial attempts to use the acetonitrile complexes **8a/9a** [16] as starting materials were only partly successful. Even after 7 days refluxing in THF the substitution was not complete and work-up by column chromatography yielded less than 75% of the desired products **10/11**. The reagents of choice were found to be the labile thiophene complexes **8b/9b**, which were readily obtained from the corresponding chloro complexes, thiophene, and $AgBF_4$, as described for the related compound $[CpRu(CO)(PPh_3)(SC_4H_4)]BF_4$ [17]. Kinetic studies of this and similar complexes had previously shown that thiophene can be rapidly displaced by other ligands at 25°C [18]. Indeed, **8b/9b** and the thionolactones **6** gave excellent yields (greater than 95%) of **10** and **11** after 5 h at room temperature.

The complexes **10** and **11**, which were all obtained as deep purple powders, were unambiguously characterized by IR and NMR (^1H, ^{13}C and $^{31}P\{^1H\}$), and gave correct elemental analyses. A characteristic feature is the low-field ^{13}C signal of the C=S group, at 200



Scheme 3. Mesomeric structures **7A/7B** of the thionolactone **6**.

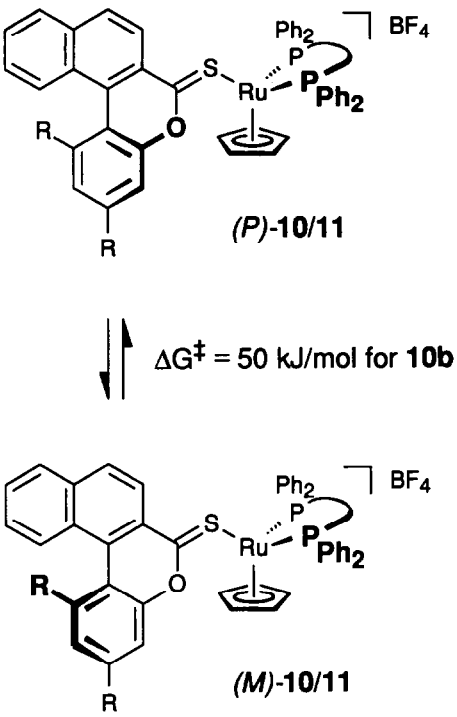


Scheme 4. Generation of the ruthenium thionolactone complexes **10** and **11**.

ppm, which is split by coupling with the two phosphorus nuclei at ruthenium. The ^{31}P-NMR spectra of the complexes turned out to be a useful tool for investigating the dynamic behavior of these compounds, especially with respect to the influence of the substituents R on the atropoisomerization barriers: at low temperatures, when the helimerization (*P*)-**10/11** ⇆ (*M*)-**10/11** (Scheme 5) is slow on the NMR timescale, the two phosphorus nuclei are diastereotopic, and give two different signals. At higher temperatures, because of a rapid helimerization process, the molecule appears as achiral, and the two phosphorus atoms are enantiotopic on the NMR timescale and thus isochronous. Thus, for **10/11 a** and **b** (*i.e.* R = H, OMe) at room temperature only one phosphorus signal is observed, suggesting that there is rapid isomerization at the axis.

By contrast, **10c** and **11c** (R = Me) exhibit AB-systems, showing that for this more hindered biaryl, the helimerization is slow even at room temperature. By temperature-dependent NMR measurements (see Fig. 2), the activation barrier was determined, as an example, for the methoxy-substituted representative **10b** as $\Delta G^{\#} = 50\ kJ\ mol^{-1}$.

By contrast, the ^{31}P NMR spectrum of the unsubstituted "parent compound" **10a** (R = H) does not give an AB-system, even at −70°C, demonstrating that there is a very low helimerization barrier and/or a small shift difference between the two (expected) signals.



Scheme 5. Helimerization equilibrium between (*P*)-**10/11** and (*M*)-**10/11**.

With this information on the structure and dynamics of the ruthenium thionolactone complexes acquired, we began an investigation of their reactivity towards nucleophiles.

3. Behavior of the ruthenium complexes towards nucleophiles

In initial investigations, we examined the reaction of the complexes **10/11** with simple hydride transfer reagents. Thus, treatment with an excess of $LiAlH_4$ (Scheme 6) yields a light yellow compound, whose ^1H NMR spectrum unambiguously proves the cleavage of the lactone bridge: in addition to the appearance of a signal from a benzylic CH_2-group, the distinct high-field shift of the *ortho*-substituents (R = OMe, Me) of the complexes **14/15 b** and **c**, is of particular value in stereochemical diagnosis. Whereas, in the still cyclic starting materials **10/11**, the two aromatic ring systems are oriented towards each other with a relatively small dihedral angle, they must be nearly orthogonal in the expected ring-opened products **14** and **15**, thus exposing the substituent R to the anisotropic ring current of the aromatic naphthalene system, an effect that specifically influences the *ortho*-substituent next to the biaryl axis, but not the substituent in the *para*-position. Thus the shift difference between the two substituents R is a helpful measure of the degree of orthogonality of the two aromatic halves. A further indication that the biaryl is no longer bridged is the configurative stability of the axis, which leads to a distinctly diastereotopic character ($\Delta\delta$ = 0.7–1.1 ppm) of the two benzylic protons, even for the least hindered derivatives **14a** and **15a** (R = H).

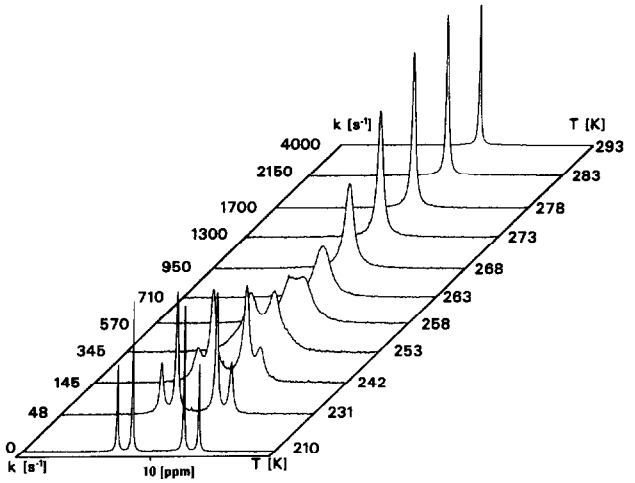
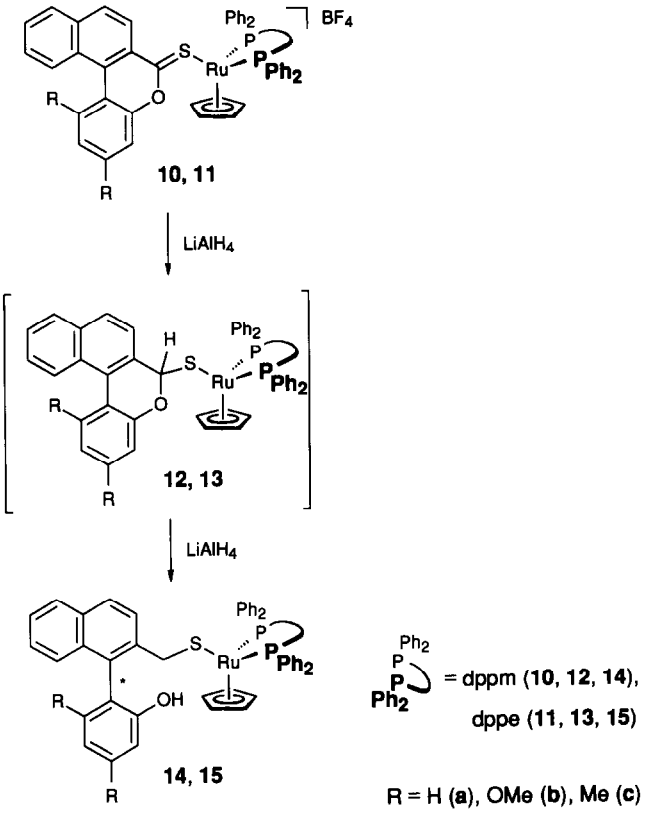


Fig. 2. Temperature-dependent ^{31}P NMR spectra of **10b**.

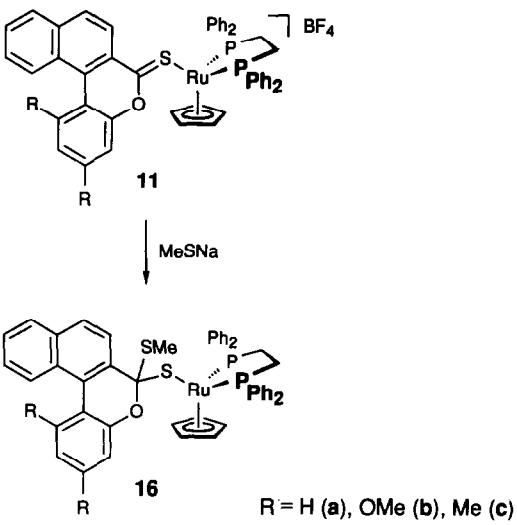


Scheme 6. Reaction of the thionolactone complexes **10/11** with a hydride transfer reagent.

Using a precisely stoichiometric amount of $LiAlH_4$ and rapid work-up, we detected by ^{31}P NMR spectroscopy, the formation of an intermediate, which further reacted to the isolable final product **14c**. Presumably this intermediate is the metal-coordinated thiolactolate **12c**. In the ring-opening reaction of the corresponding non-coordinated oxolactones **1**, the respective intermediate oxo-lactolates were postulated [9], but all attempts to detect them spectroscopically or chromatographically, or to isolate them, failed because of their very high tendency for ring-opening. By contrast, in **12**, the electronic pressure exerted by the exocyclic heteroatom, which in the case of the non-coordinated oxo-lactolate effects a rapid bridge cleavage, is apparently markedly lowered in this case. One reason for this is certainly the metal coordination, which lowers the electron density on the sulfur atom, which, moreover, itself has a lower tendency for ring-opening reactions involving regeneration of the C=S double bond. These effects should greatly stabilize such primary products. A further strong influence on the stability of **12** must be the size of the group R: large substituents should destabilize this cyclic intermediate, whereas, because of the lower ring strain, smaller ones should distinctly enhance its lifetime.

Attempts to prepare **12** by using less than stoichiometric amounts of $LiAlH_4$ or the milder *H*-nucleophile $KB(sBu)_3H$ ("*K-Selectride*"), failed. Nevertheless, these initial experiments seem far more promising than all previously available attempts at directed oxo-lactolate preparations.

In order to avoid a second attack by the nucleophile, such as occurred in the case of $LiAlH_4$, we tried using milder reagents. Thus, we treated **11** with NaSMe as an *S*-nucleophile (Scheme 7). Small highfield shifts, although much less marked than those for **14/15**, seemed initially to suggest a ring-opened biaryl product. However, the other spectroscopic data and the elemental analysis were in agreement with the assumption that the isolated ruthenium complex now was indeed the desired, still cyclic, primary product **16**. A further, stereochemically interesting, indication of the correct structure **16** of the isolated product was the formation of diastereomeric products in the case of **16b** and **16c** (R = OMe, Me). Addition of the thiolate to the heterocarbonyl group creates a new stereogenic element, the benzylic center in the bridge. As expected from comparison of the behavior of the oxolactones **1** with that of corresponding cyclic ethers [19], the isomerization barrier at the axis is distinctly enhanced by the sp^3-character of the bridge carbon atom, compared with that for thionolactone complexes **10/11**, and so the axis is a second (relatively) stable element of chirality, at least on the NMR time scale. Consequently, the



Scheme 7. Reaction of **11** with an *S*-nucleophile without subsequent cleavage of the C–O-bond.

observed formation of two diastereomeric products (in a 1:2 ratio for R = Me) can be regarded as further proof of the presence of the postulated lactolate-analog structure **16**.

The attempt to extend these reactions to the dppm derivatives **10** led to an interesting observation. As indicated by ^{31}P NMR spectroscopy, the initial product is still a thiolactolate complex **17** (Scheme 8), which is formed as a mixture of diastereomers (3:4 for **17c**, rapidly undergoing interconversion in the case of **17b**). In this case, however, the lactolate-analog compounds rearrange *via* a 1,3-metal shift [20,21], followed by extrusion of the thionolactone ligand **6**, to give the thiolate ruthenium complex [CpRu(dppm)SMe] (**19**) [22] (see Scheme 8). We assume that the lesser steric shielding of the metal center by the smaller dppm ligand allows the ruthenium fragment to migrate from the thiolate to the thioether function, a reaction which was not observed for the dppe complexes **16**. This mechanism seems more plausible than the conceivable reversal of the addition reaction, followed by substitution of the thionolactone by the strong nucleophile MeS^-.

This difference in behavior towards nucleophiles encourages us to investigate further addition reactions with other nucleophiles. Such investigations are aimed not only at a directed synthesis of metalla-lactolate analogs but also at finding new ways to bring about subsequent demetallation of the organic biaryl ligand without the risk of a simultaneous ring-opening reaction. Furthermore, investigations on the use of chiral (*e.g.* CHIRAPHOS-modified) ruthenium complexes, aiming at analogous stereoselective reactions, as well as the demetallation of the thus generated configuratively stable ligands, are in progress.

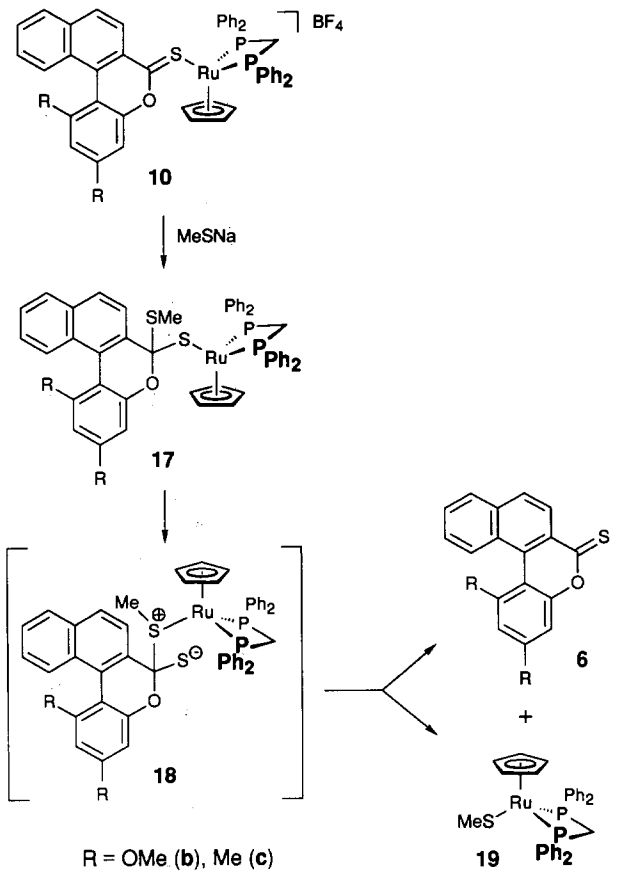
4. Experimental details

4.1. General

All reactions were performed under dry N_2 or Ar by use of standard Schlenk-tube techniques.

4.2. Spectroscopic data

IR spectra were recorded on a Bruker IFS 25 FT-IR-spektrometer and a Perkin Elmer 1420 spektrophotometer. ^1H and ^{13}C spectra were recorded on Bruker AMX 400, AC 200 or AM 250 spectrometers, and are referenced to internal $CHCl_3$ (^1H, δ 7.18 ppm; ^{13}C, δ 77.00 ppm), $CDHCl_2$ (^1H, δ 5.32 ppm; ^{13}C, δ 52.30 ppm) or C_6D_5H (^1H, δ 7.15 ppm, ^{13}C, δ 128.00 ppm). ^{31}P NMR spectra were obtained on the Bruker AMX 400 spectrometer and are referenced to external H_3PO_4. Melting points were determined by DTA and are uncorrected. For mass spectrometry (electron ionization, 70 eV) a Varian CH 7 instrument was used. Elemental analyses were performed by the microanalytical laboratory of the Institute of Inorganic Chemistry of the University of Würzburg.



Scheme 8. Behavior of the dppm complexes of type **10** towards *S*-nucleophiles.

Solvents and reagents were purified as follows: CH_2Cl_2 was distilled from P_2O_5, toluene, benzene, THF, ether and pentane were distilled from sodium.

4.3. Preparation of thionolactones (general procedure)

To a solution of 5 mmol of the corresponding oxolactone **1** in toluene (400 ml) were added 5 mmol of 2,4-bis(4-methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithia-diphosphetane (**5**). The mixture was refluxed for 10 h, then an additional 5 mmol of **5** were added and the mixture was refluxed for a further 10 h. It was then allowed to cool to room temperature and the solvent was removed *in vacuo*. The resulting solid was crystallized from CH_2Cl_2/petroleum ether.

4.4. Benzo[b]naphtho[1,2-d]pyran-6-thione (6a)

This compound was obtained from 1.00 g (4.06 mmol) of benzo[b]naphtho[1,2-d]pyran-6-on (**1a**) and 3.28 g (8.12 mmol) **5** as orange crystals (0.81 g, 3.09 mmol, 76%). m.p. 172°C. Anal. Found: C, 77.43; H, 3.77. $C_{17}H_{10}OS$ calc.: C, 77.85; H, 3.84%. IR(KBr): ν(C=S) 1180s cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.43 (1H, ddd, $J = 7.4$ Hz, $J' = 7.1$ Hz, $J'' = 1.8$ Hz, 2-H); 7.76–7.52 (4H, m, 3-, 4-, 10-, 11-H); 7.86 (1H, d, $J = 8.8$ Hz, 8-H); 7.95 (1H, d, $J = 7.6$ Hz, 9-H); 8.49 (1H, d, $J = 8.1$ Hz, 1-H); 8.79 (1H, d, $J = 8.9$ Hz, 7-H); 8.84 (1H, d, $J = 7.9$ Hz, 12-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 117.7–154.0 (16 signals); 199.3 (C=S). MS: *m/z* (%) 262(100) [M^+], 229(28) [$M^+ - SH$], 218(47) [$M^+ - CS$], 189 (50) [218 – CHO].

4.5. 1,3-Dimethoxy-benzo[b]naphtho[1,2-d]pyran-6-thione (6b)

This compound was obtained from 2.00 g (6.53 mmol) of 1,3-dimethoxy-benzo[b]naphtho[1,2-d]pyran-6-on (**1b**) and 5.28 g (13.06 mmol) **5** as orange crystals (1.60 g, 4.97 mmol, 76%). m.p. 219°C. Anal. Found: C, 70.51; H, 4.33. $C_{19}H_{14}O_3S$ calc.: C, 70.80; H, 4.38%. IR (KBr): ν(C=S) 1180s cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.78, (3H, s, OCH_3); 3.90 (3H, s, OCH_3); 6.51 (1H, d, $J = 2.4$ Hz, 2-H or 4-H), 6.77 (1H, d, $J = 2.4$ Hz, 4-H or 2-H); 7.45 (1H, ddd, $J = 7.8$ Hz, $J' = 7.2$ Hz, $J'' = 1.2$ Hz, 10-H or 11-H); 7.69 (1H, ddd, $J = 7.8$ Hz, $J' = 7.2$ Hz, $J'' = 1.2$ Hz, 11-H or 10-H); 7.83 (1H, d, $J = 8.3$ Hz, 9- or 12-H); 7.99 (1H, d, $J = 8.3$ Hz, 12- or 9-H); 8.65 (1H, d, $J = 8.8$ Hz, 7-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 55.3 (s, OCH_3); 56.2 (s, OCH_3); 93.2 ($COCH_3$); 97.3 ($COCH_3$); 124.8–162.3 (14 signals); 190.0 (C=S). MS: *m/z*(%) 322(100) [M^+], 278(35) [$M^+ - CS$], 263(29) [278 – CH_3].

4.6. 1,3-Dimethyl-benzo[b]naphtho[1,2-d]pyran-6-thione (6c)

This compound was obtained from 2.00 g (7.29 mmol) of 1,3-dimethyl-benzo[b]naphtho[1,2-d]pyran-6-

on (**1c**) and 5.90 g (14.58 mmol) **5** as orange crystals (1.63 g, 5.62 mmol, 77%). m.p. 210°C. Anal. Found: C, 78.37; H, 4.79. $C_{19}H_{14}OS$ calc.: C, 78.61; H, 4.86%. IR (KBr): ν(C=S) 1175s cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.22, (3H, s, CH_3); 2.49 (3H, s, CH_3); 7.13 (1H, s, 2-H or 4-H), 7.29 (1H, s, 4-H or 2-H); 7.55 (1H, ddd, $J = 7.8$ Hz, $J' = 7.8$ Hz, $J'' = 1.5$ Hz, 10-H or 11-H); 7.69 (1H, ddd, $J = 7.4$ Hz, $J' = 7.4$ Hz, $J'' = 1.3$ Hz, 11-H or 10-H); 7.83–8.00 (3H, m, 8-, 9-, 12-H); 8.71 (1H, d, $J = 8.7$ Hz, 7-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 21.6 (s, CH_3); 23.9 (s, CH_3); 114.4–173.3 (16 signals); 199.5 (C=S). MS: m/z(%) 290(100) [M^+], 246(16) [$M^+ - CS$], 229(91) [246 − OH], 215(17) [229 − CH_2].

4.7. Crystal structure determination of 6c

Suitable orange crystals were grown from CH_2Cl_2/petroleum ether. Measurements of diffraction intensities were performed on a Siemens R3m/V diffractometer using Mo–Kα radiation (0.7107 Å, graphite monochromator). Cell parameters were determined by least-squares refinement of 22 reflections. The structure was solved with Siemens SHELXTL PLUS by using direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and were included in the refinement with isotropic U_{eq}.

Crystal data for **6c**: formula $C_{19}H_{14}OS$, molecular weight 290.32, crystal size $0.4 \times 0.75 \times 0.1$ mm, triclinic, space group $P\bar{1}$, $a = 8.525(2)$ Å, $b = 11.687(3)$ Å, $c = 8.143(2)$ Å, $\alpha = 95.22(2)°$, $\beta = 114.73(2)°$, $\gamma = 98.94(2)°$, $V = 716.9(3)$ Å^3, $Z = 2$, $d_{calcd} = 1.345$ g cm^{-3}, $2\Theta_{max} = 55°$ (h: $-10 \rightarrow 9$, k: $-15 \rightarrow 15$, l: $0 \rightarrow 10$), μ(Mo–Kα) = 0.21 mm^{-1}, 3296 unique reflections measured, 3296 of which 2614 were considered observed [$F > 3\,\sigma(F)$], 191 refined parameters, $R = 0.058$, $R_w = 0.053$, final electron density 0.38 eÅ^{-3}.

Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Federal Republic of Germany, on quoting the depository number CSD-400413, the names of the authors, and the journal citation.

4.8. Preparation of [CpRu(PPh$_2$–(CH$_2$)$_n$–Ph$_2$P)(NCMe)]PF$_6$ (n = 1: 8a, n = 2: 9a; general procedure)

As previously described [16,23], 0.50 mmol of CpRu(PPh$_2$–(CH$_2$)$_n$–Ph$_2$P)Cl and 1.00 mmol of NH_4PF_6 were dissolved in methanol (15 ml), MeCN (2 ml) was added, and the mixture refluxed for 5 h. It was then allowed to cool to room temperature, the solvent was removed in vacuum, and the resulting residue was extracted with CH_2Cl_2 (5 ml). The extract was concentrated to 1 ml and the product precipitated by addition of ether. The yellow solid was filtered off, washed with ether, and dried *in vacuo*.

TABLE 1. Atomic parameters ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$)

Atom	x	y	z	U_{eq} [a]
S(1)	6135(1)	2913(1)	2233(1)	77(1)
C(1)	7680(3)	2868(2)	1550(4)	50(1)
O(2)	9280(2)	3592(2)	2615(2)	52(1)
C(3)	10540(3)	3857(2)	1965(3)	43(1)
C(4)	11886(3)	4828(2)	3007(4)	50(1)
C(5)	13086(3)	5233(2)	2356(4)	50(1)
C(6)	12831(3)	4711(2)	646(4)	52(1)
C(7)	11493(3)	3730(2)	−404(3)	45(1)
C(8)	10390(3)	3223(2)	363(3)	41(1)
C(9)	8996(3)	2143(2)	−425(3)	42(1)
C(10)	9072(3)	1133(2)	−1520(3)	45(1)
C(11)	10662(4)	937(2)	−1533(3)	51(1)
C(12)	10690(4)	−52(3)	−2544(4)	62(1)
C(13)	9128(5)	−896(3)	−3577(4)	70(2)
C(14)	7593(5)	−763(3)	−3533(4)	66(1)
C(15)	7516(4)	229(2)	−2472(3)	53(1)
C(16)	5991(4)	309(3)	−2225(4)	61(1)
C(17)	6029(3)	1162(3)	−970(4)	58(1)
C(18)	7570(3)	2080(2)	9(3)	46(1)
C(19)	14594(4)	6284(3)	3451(4)	70(1)
C(20)	11198(4)	3368(3)	−2353(4)	59(1)

[a] Equivalent U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

4.8.1. 8a

This compound was obtained from 215.0 mg (0.37 mmol) CpRu(PPh$_2$–(CH$_2$)–Ph$_2$P)Cl and 119.6 mg (0.73 mmol) NH_4PF_6. Yield 259.5 mg (0.35 mmol; 96%). m.p. 91°C (dec.). Anal. Found: C, 52.23; H, 4.14; N, 1.62. $C_{32}H_{30}F_6NP_3Ru$ calc: C, 52.18; H, 4.11; N, 1.90%. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.62 (3H, s, CH_3CN); 4.74 (5H, s, Cp); 6.92–7.60 (20H, m, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 3.3 (s, CH_3CN); 49.6 (t, P–CH_2–P, $J_{PC} = 24$ Hz); 80.0 (s, Cp); 127.4–133.6 (Ph, CN). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 10.1 (s).

TABLE 2. Bond lengths (pm)

S(1)–C(1)	163.6(4)	C(8)–C(9)	147.2(3)
C(1)–O(2)	135.9(3)	C(9)–C(10)	144.0(4)
C(1)–C(18)	144.8(4)	C(9)–C(18)	139.5(4)
O(2)–C(3)	139.0(4)	C(10)–C(11)	141.4(5)
C(3)–C(4)	138.9(3)	C(10)–C(15)	142.5(3)
C(3)–C(8)	138.7(4)	C(11)–C(12)	136.6(4)
C(4)–C(5)	137.8(5)	C(12)–C(13)	139.9(4)
C(5)–C(6)	138.1(4)	C(13)–C(14)	135.6(6)
C(5)–C(19)	151.9(3)	C(14)–C(15)	140.8(4)
C(6)–C(7)	139.5(3)	C(15)–C(16)	141.1(5)
C(7)–C(8)	141.8(4)	C(16)–C(17)	134.7(5)
C(7)–C(20)	150.8(4)	C(17)–C(18)	143.0(3)

TABLE 3. Bond angles (deg)

S(1)–C(1)–O(2)	116.6(2)	C(8)–C(9)–C(10)	124.0(3)
S(1)–C(1)–C(18)	127.1(2)	C(8)–C(9)–C(18)	117.4(2)
O(2)–C(1)–C(18)	116.2(3)	C(10)–C(9)–C(18)	118.6(2)
C(1)–O(2)–C(3)	121.6(2)	C(9)–C(10)–C(11)	122.9(2)
O(2)–C(3)–C(4)	114.3(3)	C(9)–C(10)–C(15)	118.5(3)
O(2)–C(3)–C(8)	121.7(2)	C(11)–C(10)–C(15)	118.3(3)
C(4)–C(3)–C(8)	123.9(3)	C(10)–C(11)–C(12)	121.1(2)
C(3)–C(4)–C(5)	118.3(3)	C(11)–C(12)–C(13)	119.9(4)
C(4)–C(5)–C(6)	118.8(2)	C(12)–C(13)–C(14)	120.6(3)
C(4)–C(5)–C(19)	120.4(3)	C(13)–C(14)–C(15)	121.3(3)
C(6)–C(5)–C(19)	120.7(3)	C(10)–C(15)–C(14)	118.5(3)
C(5)–C(6)–C(7)	123.2(3)	C(10)–C(15)–C(16)	119.5(3)
C(6)–C(7)–C(8)	117.9(3)	C(14)–C(15)–C(16)	121.9(3)
C(6)–C(7)–C(20)	117.3(3)	C(15)–C(16)–C(17)	121.2(2)
C(8)–C(7)–C(20)	124.5(2)	C(16)–C(17)–C(18)	120.3(3)
C(3)–C(8)–C(7)	116.7(2)	C(1)–C(18)–C(9)	121.0(2)
C(3)–C(8)–C(9)	115.8(3)	C(1)–C(18)–C(17)	118.8(3)
C(7)–C(8)–C(9)	127.3(2)	C(9)–C(18)–C(17)	119.9(3)

4.8.2. ***9a***

This compound was obtained from 200.0 mg (0.33 mmol) $CpRu(PPh_2–(CH_2)_2–Ph_2P)Cl$ and 108.5 mg (0.67 mmol) NH_4PF_6. Yield 237.5 mg (0.32 mmol; 95%). m.p. 97°C (dec.). Anal. Found: C, 53.22; H, 4.54; N, 1.87. $C_{33}H_{32}F_6NP_3Ru$ calc.: C, 52.81; H, 4.30; N, 1.87%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.44 (3H, s, CH_3CN); 4.64 (5H, s, Cp); 7.17–7.64 (20H, m, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 3.0 (s, CH_3CN); 28.2 (vt, $P–CH_2–CH_2–P$, $N = 45$ Hz); 81.6 (s, Cp); 127.4–133.6 (Ph, CN). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 79.9(s).

4.9. Preparation of [CpRu(PPh$_2$–(CH$_2$)$_n$–Ph$_2$P)(SC$_4$H$_4$)]BF$_4$ (n = 1: ***8b****, n = 2:* ***9b****; general procedure)*

As previously described [17] 1.00 mmol of $CpRu(PPh_2–(CH_2)_n–Ph_2P)Cl$ and 5.00 mmol of thiophene were dissolved in CH_2Cl_2 (60 ml). The solution was cooled to 0°C and 1.20 mmol of $AgBF_4$ was added and the mixture was stirred at 0°C for 30 min. A dark precipitate was removed by filtration and the product precipitated from the filtrate by addition of ether (20 ml). The solid was dried under vacuum. Recrystallization from CH_2Cl_2/Et_2O gave the yellow complex.

4.9.1. ***8b***

This compound was obtained from 520.0 mg (0.89 mmol) $CpRu(PPh_2–(CH_2)–Ph_2P)Cl$, 207.3 mg (1.06 mmol) $AgBF_4$ and 373.2 mg (4.44 mmol) thiophene. Yield 576.9 mg (0.80 mmol; 90%). m.p. 59°C (dec.). Anal. Found: C, 56.68; H, 4.52. $C_{34}H_{31}BF_4P_2RuS$ calc.: C, 56.60; H, 4.33%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.79 (5H, s, Cp); 6.56 and 6.88 (4H, AA'BB'-system, $N = 6.01$ Hz, thiophene); 7.34–7.71 (m, 20H, Ph). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 47.0 (t, $P–CH_2–P$, J_{PC} = 24 Hz); 81.6 (s, br, Cp); 129.5 (vt, $P–C_m$, $N = 11$ Hz); 129.7 (vt, $P–C_m$, $N = 11$ Hz); 130.8 (s, $S–C_b$, $S–C_{b'}$); 131.6 (m, $P–C_0$, $P–C_p$); 133.8 (vt, $P–C_i$, $N = 47$ Hz); 134.6 (vt, $P–C_i$, $N = 46$ Hz); 138.3 (t, $S–C_a$, $S–C_{a'}$, $J_{PC} = 3$ Hz). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 6.5 (s).

4.9.2. ***9b***

This compound was obtained from 315.0 mg (0.53 mmol) $CpRu(PPh_2–(CH_2)_2–Ph_2P)Cl$, 122.6. mg (0.63 mmol) $AgBF_4$ and 221.0 mg (2.63 mmol) thiophene. Yield 336.0 mg (0.46 mmol; 87%). m.p. 62°C (dec.). Anal. Found: C, 56.04; H, 4.88. $C_{35}H_{33}BF_4P_2RuS$ calc.: C, 57.15; H, 4.52%. ^{1}H-NMR (CD_2Cl_2, 200 MHz): δ 4.76 (5H, s, Cp); 6.73 and 5.75 (4H, AA'BB'-system, $N = 6.0$ Hz, thiophene); 7.14–8.03 (20H, m, Ph). ^{13}C-NMR (CD_2Cl_2, 50 MHz): δ 28.3 (vt, $P–CH_2–CH_2–P$, $N = 45$ Hz); 82.9 (t, Cp, $J_{PC} = 2$ Hz); 131.4 (s, $P–C_p$); 131.5 (s, $P–C_p$); 129.5 (vt, $P–C_m$, $N = 10$ Hz); 129.7 (vt, $P–C_m$, $N = 10$ Hz); 130.6 (s, $S–C_b$ and $S–C_{b'}$); 131.9 (vt, $P–C_0$, $N = 10$ Hz); 132.2 (vt, $P–C_0$, $N = 11$ Hz); 135.2 (vt, $P–C_i$, $N = 47$ Hz); 136.1 (vt, $P–C_i$, $N = 46$ Hz); 137.5 (s, $S–C_a$ and $S–C_{a'}$). ^{31}P-NMR (CD_2Cl_2, 162 MHz): δ 73.7 (s).

4.10. Preparation of the biaryl-ruthenium-complexes ***10,11*** *(general procedure)*

A 0.50 mmol solution of $[CpRu(PPh_2–(CH_2)_n–Ph_2P)(SC_4H_4)]BF_4$ ($n = 1$ **8a**, $n = 2$ **9a**) and 5.00 mmol of the thionolactone **6** in CH_2Cl_2 (20 ml) was stirred at room temperature for 12 h. The solution was filtered and then concentrated to 3 ml. The product was precipitated by addition of ether, filtered, washed with ether and pentane. [Particularly pure product can be obtained by chromatography on silica gel (eluent 1. CH_2Cl_2 → 2. THF/Et_2O 1/1).] Vacuum drying yielded a deep purple solid.

4.10.1. ***10a***

This compound was obtained from 364.4 mg (0.51 mmol) **8a** and 132.5 mg (0.51 mmol) **1a**. Yield 436.4 mg (0.49 mmol; 96%). m.p. 145°C. Anal. Found: C, 61.72; H, 4.16. $C_{47}H_{37}BF_4OP_2RuS$ calc.: C, 62.75; H, 4.15%. IR (nujol): ν(CS) 1232 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.03 (5H, s, Cp); 6.95–7.73 (26H, m, $P(C_6H_5)_2$, aryl–H); 7.86 (1H, d, $J = 8.2$ Hz, aryl–H); 8.11 (1H, d, $J = 8.9$ Hz, aryl–H); 8.34 (1H, d, $J = 8.0$ Hz, aryl–H); 8.69 (1H, d, $J = 8.3$ Hz, aryl–H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 49.2 (t, $P–CH_2–P$, $J = 24$ Hz); 81.4 (s, br, Cp); 152.8–117.2 (32 signals); 200.2 (t, C=S, $J_{PC} = 8$ Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 9.4 (s).

4.10.2. ***10b***

This compound was obtained from 523.0 mg (0.71 mmol) **8a** and 229.2 mg (0.71 mmol) **1b**. Yield 657.7 mg (0.68 mmol; 95%). m.p. 160°C. Anal. Found: C, 62.07;

H, 4.17. $C_{49}H_{41}BF_4O_3P_2RuS$ calc.: C, 61.32; H, 4.31%. IR (nujol): ν(CS) 1212 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.74 (3H, s, OMe); 3.96 (3H, s, OMe); 4.98 (5H, s, Cp); 6.49 (1H, d, $J = 2.2$ Hz, 2- or 4-H); 6.58 (1H, d, $J = 2.2$ Hz, 4- or 2-H); 6.93–6.98 (6H, m, $P(C_6H_5)_2$); 7.28–7.45 (15H, m, $P(C_6H_5)_2$ and 10- or 11-H); 7.58–7.61 (2H, m, 8-H and 11- or 10-H); 7.72 (1H, d, $J = 7.8$ Hz, 9-H); 7.83 (1H, d, $J = 8.5$ Hz, 12-H); 7.97 (1H, d, $J = 8.9$ Hz, 7-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 49.3 (t, P–CH_2–P, $J = 24$ Hz); 55.4 (s, OMe); 56.5 (s, OMe); 81.3 (s, br, Cp); 162.8–92.9 (44 signals); 199.7 (t, C=S, $J_{PC} = 8$ Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 9.5 (s).

4.10.3. 10c

This compound was obtained from 747.0 mg (1.04 mmol) **8a** and 300.0 mg (1.04 mmol) **1b**. Yield 911.0 mg (0.98 mmol; 95%). m.p. 208°C. Anal. Found: C, 63.39; H, 4.73. $C_{49}H_{41}BF_4OP_2RuS$ calc.: C, 63.44; H, 4.45%. IR (nujol): ν(CS) 1216 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.10 (3H, s, Me); 2.51 (3H, s, Me); 5.04 (5H, s, Cp); 6.84–7.45 (22H, m, $P(C_6H_5)$, 2-H, 4-H); 7.52 (1H, dd, $J = 7.3$ Hz, $J = 7.3$ Hz, 10- or 11-H); 7.65 (1H, dd, $J = 7.1$ Hz, $J = 7.1$ Hz, 11- or 10-H); 7.70 (1H, d, $J = 8.9$ Hz, 8-H); 7.76 (1H, d, $J = 8.5$ Hz, 9-H); 7.82 (1H, d, $J = 8.1$ Hz, 12-H), 8.01 (1H, d, $J = 8.8$ Hz, 7-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4 (s, Me); 23.5 (s, Me); 49.3 (dd, P–CH_2–P, $J(P_A–C) = J(P_B–C) = 24$ Hz); 81.4 (s, br, Cp); 113.3–153.4 (31 signals); 199.8 (d, C=S, $J_{PC} = 7$ Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta_A = 9.7$ ppm; $\delta_B = 9.3$ ppm; $J_{AB} = 86$ Hz.

4.10.4. 11a

This compound was obtained from 298.7 mg (0.41 mmol) **9a** and 106.5 mg (0.41 mmol) **1a**. Yield 259.8 mg (0.39 mmol; 97%). m.p. 136°C. Anal. Found: C, 62.86; H, 4.47. $C_{48}H_{39}BF_4OP_2RuS$ calc.: C, 63.10; H, 4.30%. IR (nujol): ν(CS) 1232 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 5.01 (5H, s, Cp); 6.94–7.85 (28H, m, $P(C_6H_5)_2$, aryl–H); 8.35 (1H, d, $J = 8.1$ Hz, aryl–H); 8.69 (1H, d, $J = 8.4$ Hz, aryl–H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.8 (vt, P–CH_2–CH_2–P, $N = 46$ Hz); 83.0 (s, br, Cp); 116.9–152.6 (42 signals); 198.1 (t, C=S, $J_{PC} = 7$ Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 77.0 (s).

4.10.5. 11b

This compound was obtained from 523.0 mg (0.71 mmol) **9a** and 229.2 mg (0.71 mmol) **1b**. Yield 657.7 mg (0.68 mmol; 95%). m.p. 122°C. Anal. Found: C, 61.33; H, 4.49. $C_{50}H_{43}BF_4O_3P_2RuS$ calc.: C, 61.67; H, 4.45%. IR (KBr): ν(CS) 1205 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.76 (3H, s, OMe); 3.95 (3H, s, OMe); 4.97 (5H, s, Cp); 6.44 (1H, d, $J = 2.3$ Hz, 2- or 4-H); 6.60 (1H, d, $J = 2.3$ Hz, 4- or 2-H); 6.95–7.02 (6H, m, $P(C_6H_5)_2$); 7.22–7.40 (12H, m, $P(C_6H_5)_2$); 7.42–7.50 (5H, m, $P(C_6H_5)_2$ and 10- or 11-H); 7.54 (1 H, d, $J = 8.9$ Hz, 8-H); 7.60 (1H, dd, $J = 8.5$ Hz, $J = 8.5$ Hz, 11- or 10-H); 7.71 (1H, d, $J = 8.9$ Hz, 7-H); 7.72 (1H, d, $J = 7.8$ Hz, 9-H); 7.84 (1H, d, $J = 8.5$ Hz, 12-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 27.7 (vt, P–CH_2–CH_2–P, $N = 46$ Hz); 55.4 (s, OMe); 56.4 (s, OMe); 82.8 (s, br, Cp); 93.1–162.6 (44 signals); 197.7 (t, C=S, $J_{PC} = 7$ Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 76.9 (s).

4.10.6. 11c

This compound was obtained from 340.0 mg (0.46 mmol) **9a** and 134.2 mg (0.46 mmol) **1c**. Yield 426.4 mg (0.45 mmol; 98%). m.p. 137°C. Anal. Found: C, 63.73; H, 4.69. $C_{50}H_{43}BF_4OP_2RuS$ calc.: C, 63.77; H, 4.60%. IR (KBr): ν(CS) 1204 cm^{-1}. 1H NMR ($CDCl_3$, 400 MHz): δ 2.11 (3H, s, Me); 2.48 (3H, s, Me); 5.01 (5H, s, Cp); 6.81–7.39 (22H, m, $P(C_6H_5)$, 4-, 2-H); 7.44–7.54 (2H, m, 10- and 11-H); 7.66 (1H, d, $J = 9.2$ Hz, 8-H); 7.75 (1H, d, $J = 8.9$ Hz, 7-H); 7.77 (1H, d, $J = 8.3$ Hz, 9-H); 7.81 (1H, d, $J = 8.2$ Hz, 12-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6 (s, Me); 23.6 (s, Me); 28.0 (dd, P–CH_2–CH_2–P, $^1J = 31$ Hz, $^2J = 15$ Hz); 28.3 (dd, P–CH_2–CH_2–P, $^1J = 30$ Hz, $^2J = 15$ Hz); 83.3 (s, br, Cp); 113.5–153.7 (41 signals); 198.3 (dd, C=S, $J(P_A–C) = J(P_B–C) = 7$ Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta_A = 77.4$ ppm; $\delta_B = 77.0$ ppm; $J_{AB} = 26$ Hz.

4.11. Reactions with H- and S-nucleophiles

4.11.1. Reaction with $LiAlH_4$

To a solution of 190.0 mg (0.205 mmol) of **10c** in THF (5 ml) 8.0 mg (0.210 mmol), an excess of $LiAlH_4$ (*ca.* 20 mg, 0.50 mmol) was added at −60°C. When allowed to warm to room temperature the purple mixture turned yellow. The solvent was removed under vacuum and the resulting solid was extracted with benzene (5 ml). The extract was concentrated to 1 ml, and the product was precipitated by addition of light petroleum. The yellow solid was filtered off, and recrystallized from benzene / light petroleum. Yield: 121.6 mg (0.144 mmol, 70%); light yellow powder. m.p. 160°C. Anal. Found: C, 69.44; H, 4.91. $C_{49}H_{44}OP_2RuS$ calc.: C, 69.73; H, 5.26%. ^1H NMR (C_6D_6, 400 MHz): δ 1.75 (3H, s, Me); 2.40 (3H, s, Me); 2.50 (1H, d, $J_{HH} = 9.7$ Hz, S–CH_2); 3.17 (1H, d, $J_{HH} = 9.7$ Hz, S–CH_2); 4.68 (5*H*, s, Cp); 6.77–7.63 (28H, m, $P(C_6H_5)_2$ and aryl–H); 8.99 (1H, s, OH). ^{13}C NMR (C_6D_6, 100 MHz): δ 20.3 (s, Me); 21.5 (s, Me); 39.2 (d, S–CH_2, $J = 7$ Hz); 49.0 (dd, P–CH_2–P, $J(P_A–C) = 21$ Hz, $J(P_B–C) = 24$ Hz); 80.5 (t, Cp, $J = 3$ Hz); 156.6–119.6 (46 signals). ^{31}P NMR (C_6D_6, 162 MHz): $\delta_A = 17.3$ ppm; $\delta_B = 13.3$ ppm; $J_{AB} = 95.7$ Hz.

4.11.2. Addition of NaSMe

A mixture of 97.0 mg (0.103 mmol) of **11c** and 21.7 mg (0.309 mmol) of NaSMe in acetone (5 ml) was stirred for 10 min at 0°C during which the purple mixture turned light red. The solvent was removed *in vacuo* and the residue was extracted with benzene. After precipitation with light petroleum the solid was filtered off and recrystallized from benzene/light petroleum. Yield: 60.1 mg (0.067 mmol, 65%); orange powder. m.p. (dec.) 97°C. Anal Found: C, 68.33; H, 5.24. $C_{51}H_{46}OP_2RuS_2$ calc.: C, 67.91; H, 5.14%.

Major isomer: ^{1}H NMR (C_6D_6, 400 MHz): δ 2.06 (3H, s, Me); 2.08 (3H, s, SMe); 2.35 (3H, s, Me); 4.13 (5H, s, Cp); 6.73–8.35 (28H, m, $P(C_6H_5)_2$, aryl-H). ^{13}C NMR (C_6D_6, 100 MHz): δ 15.3 (s, SMe); 21.5 (s, Me); 23.1 (s, Me); 25.4 (dd, $J = 16$ Hz, $J = 31$ Hz, P-CH_2-CH_2-P); 27.1 (dd, $J = 14$ Hz, $J = 31$ Hz, P-CH_2-CH_2-P); 80.3 (s, br, Cp); 101.5 (d, $J = 7$ Hz, O*C*(SMe)SRu). ^{31}P NMR (C_6D_6, 162 MHz): $\delta_A = 82.0$ ppm; $\delta_B = 80.0$ ppm; $J_{AB} = 24$ Hz.

Minor isomer: ^{1}H NMR (C_6D_6, 400 MHz): δ 1.61 (3H, s, SMe); 2.04 (3H, s, Me); 2.41 (3H, s, Me); 5.25 (5H, s, Cp); 6.73–8.35 (28H, m, $P(C_6H_5)_2$, aryl-H). ^{13}C NMR (C_6D_6, 100 MHz): δ 15.1 (s, SMe); 21.6 (s, Me); 23.2 (s, Me); 24.4 (dd, $J = 17$ Hz, $J = 31$ Hz, P-CH_2-CH_2-P); 28.3 (dd, $J = 16$ Hz, $J = 35$ Hz, P-CH_2-CH_2-P); 81.3 (s, Cp); 103.8 (d, $J = 7$ Hz, O*C*(SMe)-SRu). ^{31}P NMR (C_6D_6, 162 MHz): $\delta_A = 78.3$ ppm; $\delta_B = 77.5$ ppm; $J_{AB} = 25$ Hz.

Acknowledgments

We thank, for their help: R. Schedl (DTA), C.P. Kneis (elemental analysis), E. Ruckdeschel, Dr. D. Scheutzow, Dr. W. Buchner (NMR), Mrs. A. Linz and K. Manger (technical assistance). Generous financial support of the work by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich No. 347 "Selektive Reaktionen Metall-aktivierter Moleküle") and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 G. Bringmann, B. Schöner, O. Schupp, K. Peters, E.-M. Peters and H.G. von Schnering, *Liebigs Ann. Chem.*, (1994) 91.
2 W.A. Schenk, T. Stur and E. Dombrowski, *J. Organomet. Chem.*, submitted for publication.
3 H. Viola, H. Hartenhauer and R. Mayer, *Z. Chem., 28* (1988) 269; E. Schaumann, in E. Patai (ed.), *The Chemistry of Double-Bonded Functional Groups*, Vol. II, Part 2, Wiley, New York, 1989, p. 1269; K. Hartke, *Phosphorus, Sulfur, Silicon, 58* (1991) 223.
4 W.A. Schenk, T. Stur and E. Dombrowski, *Inorg. Chem., 31* (1992) 723.
5 W.A. Schenk and P. Urban, *J. Organomet. Chem., 411* (1991) C27; W.A. Schenk, P. Urban and E. Dombrowski, *Chem. Ber., 126* (1993) 679.
6 W.A. Schenk, U. Karl, M.R. Horn and S. Müssig, *Z. Naturforsch., B45* (1990) 239.
7 S.G. Davies, J.P. McNally and A.J. Smallridge, *Adv. Organomet. Chem., 30* (1990) 1.
8 G. Consiglio and F. Morandini, *Chem. Rev., 87* (1987) 762.
9 G. Bringmann, L. Göbel and O. Schupp, *GIT Fachz. Lab.*, (1993) 189.
10 G. Bringmann, O. Schupp, K. Peters, L. Walz and H.G. von Schnering, *J. Organomet. Chem., 438* (1992) 117, and references therein.
11 G. Bringmann, H. Bertagnolli, F. Bökman and O. Schupp, *J. Organomet. Chem.*, in press.
12 G. Bringmann, Ch.L.J. Ewers, L. Göbel, T. Hartung, B. Schöner, O. Schupp and R. Walter, in H. Werner, A.G. Griesbeck, W. Adam, G. Bringmann and W. Kiefer (eds.), *Selective Reactions of Metal-Activated Molecules, Vieweg*, Braunschweig, 1992, p. 183.
13 G. Bringmann, T. Hartung, L. Göbel, O. Schupp, Ch. L.J. Ewers, B. Schöner, R. Zagst, K. Peters, H.G. von Schnering and Ch. Burschka, *Liebigs Ann. Chem.*, (1992) 225.
14 G. Bringmann and T. Hartung, *Tetrahedron, 49* (1993) 7891.
15 M.P. Cava and M.I. Levinson, *Tetrahedron, 41* (1985) 5061.
16 G.S. Ashby, M.I. Bruce, I.B. Tomkins and R.C. Wallis, *Aust. J. Chem., 32* (1979) 1003; S.G. Davies and F. Scott, *J. Organomet. Chem., 188* (1980) C41.
17 J.W. Benson and R.J. Angelici, *Organometallics, 11* (1992) 922.
18 J.W. Benson and R.J. Angelici, *Organometallics, 12* (1993) 680.
19 G. Bringmann, T. Hartung, L. Göbel, O. Schupp, K. Peters and H.G. von Schnering, *Liebigs Ann. Chem.*, (1992) 769.
20 W.A. Schenk and M. Schmidt, *Z. Anorg. Allg. Chem., 416* (1975) 311.
21 E.W. Abel, K.G. Orrell and S.K. Bhargava, *Progr. Inorg. Chem., 32* (1984) 1.
22 W.A. Schenk and T. Stur, *Z. Naturforsch., B45* (1990) 1495.
23 T. Blackmore, M.I. Bruce and F.G.A. Stone, *J. Chem. Soc., A* (1971) 2376.