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Ruthenium Complexes of Thiocinnamaldehydes: Synthesis, Structure, and [4+2]-Cycloaddition Reactions**

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Dedicated to Professor Dr. Dr. h. c. mult. Siegfried Hünig on the occasion of his 85th birthday

Abstract: Ruthenium hydrogensulfido complexes [CpRu(P−P)(SH)] ((P−P)= $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC_2H_4PPh_2$ (dppe)) were obtained from the corresponding chloro complexes by Cl/SH exchange. Condensation with a range of cinnamaldehydes gave thiocinnamaldehyde complexes $[CpRu(P{-}P)(S{=}CH{-}CR^2{=}CHR^1)]PF_6$ ($R^1 = C_6H_4X$, R^2 = H, Me, X = H, OMe, NMe_2, Cl, NO_2) as highly-colored crystalline compounds. The thiocinnamaldehyde complexes undergo [4+2]-cycloaddition reactions with vinyl ethers $CH_2{=}CHOR^3$ (R^3 = Et, Bu) and styrenes $H_2C{=}CHC_6H_4Y$ (Y = H, Me, OMe, Cl, Br, NO_2) to give complexes of 2,4,5-trisubstituted 3,4-dihydro-2*H*-thiopyrans as mixtures of two diastereoisomers. The rate of addition of *para*-substituted styrenes $H_2C{=}CHC_6H_4Y$ to [CpRu(dppm)(S=CH−CH=CHPh)]PF_6 increases in the series Y = NO_2, Br, Cl, H, Me, OMe, indicating that the cycloaddition is dominated by the HOMO(dienophile)–LUMO(diene) interaction. The strained dienophiles norbornadiene and norbornene also add, giving ruthenium complexes of 3-thia-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-dienes and 3-thia-tricyclo[6.2.1.$0^{2,7}$]undec-4-enes, respectively. Addition reactions with acrolein, methacrolein, methyl vinyl ketone, acrylic ester, or ethyl propiolate finally yielded ruthenium complexes of 3,4-disubstituted 3,4-dihydro-2*H*-thiopyrans and 4*H*-thiopyrans, respectively.

Keywords: cycloaddition · half-sandwich complexes · ruthenium · S ligands · thioaldehydes · thiopyrans

Introduction

α,β-Unsaturated thiocarbonyl compounds (thioaldehydes, thioketones, dithioesters) are valuable diene equivalents in cycloaddition reactions.[2–6] Their high reactivity in hetero-Diels–Alder (HDA) reactions originates from an unusually small HOMO–LUMO gap which allows for rapid addition reactions of both electron-poor and -rich dienophiles.[3] While α,β-unsaturated dithioesters and thioketones are isolable compounds[6] or easily accessible from their Diels–Alder dimers,[4,6] the corresponding α,β-unsaturated thioaldehydes are difficult to obtain (a notable exception are mesomerically stabilized amino-substituted derivatives,[7,8] which can be seen as vinylogous thioformamides). Thioacetals of α,β-unsaturated aldehydes or ketones have been introduced as synthetic equivalents; the Lewis acid promoted ring opening and addition to olefins involves a thienium ion intermediate.[9–13] Very recently, thiocinnamaldehyde has been produced from cinnamaldehyde and $(Me_2Al)_2S$ and trapped as its Diels–Alder dimer.[14]

Thioaldehydes can be stabilized as ligands in transition-metal complexes.[6] While this as expected attenuates their otherwise high reactivity, the coordinated C=S group is still susceptible to a range of nucleophilic addition and cycloaddition reactions.[15] Surprisingly, there are only a few examples of complexes of α,β-unsaturated thioaldehydes with the metals tungsten,[16–18] iron,[19,20] cobalt,[19–21] and iridium.[22]

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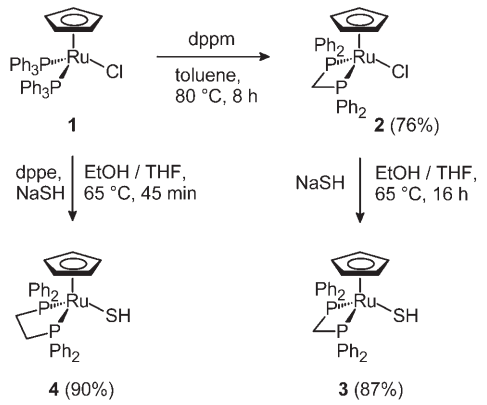
[**] The Coordination Chemistry of the C=S Function, Part 20; for Part 19 see: S. Dilsky, W. A. Schenk, *Z. Naturforsch. B* **2004**, *59*, 1093–1102.

The reactivity of these compounds has not yet been addressed.

The cationic ruthenium thiobenzaldehyde complexes $[CpRu(PR'_3)_2(S{=}CHR)]^+$ are easily accessible and stable compounds which are nevertheless sufficiently reactive to undergo nucleophilic addition and cycloaddition reactions.[23,24] Here we report the synthesis and reactions of analogous complexes of thiocinnamaldehydes. A preliminary account of this work was included in a recent review.[24]

Results

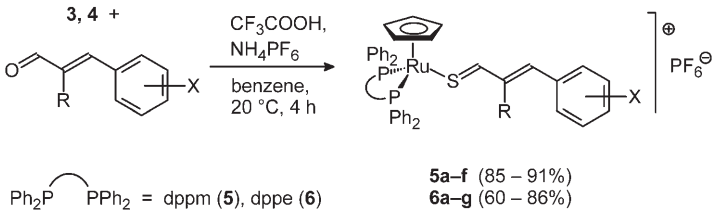
Synthesis of thiocinnamaldehyde ruthenium complexes: As a promising synthetic route we chose the condensation of Ru–SH complexes with cinnamaldehydes, which has some precedent in the synthesis of thioaldehyde complexes of tungsten.[16,18,25,26] Beginning with the universal starting material **1**,[27] exchange of the monodentate phosphine ligands for bis(diphenylphosphino)methane (dppm) gave **2**,[28] which was subsequently transformed in high yield into the hydrogensulfido complex **3** by reaction with NaSH. The synthesis of the corresponding 1,2-bis(diphenylphosphino)ethane (dppe) complex **4** could even be carried out as a one-pot reaction (Scheme 1).



Scheme 1. Synthesis of ruthenium-SH complexes (dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PC_2H_4PPh_2$).

Compounds **3** and **4** are yellow crystalline, slightly air-sensitive compounds. A characteristic feature of their ^{1}H NMR spectra is the high-field ($\delta = -4.0$ ppm) triplet resonance of the SH group. In that, **3** and **4** are similar to the well-known complex $[CpRu(PPh_3)_2(SH)]$.[29] The reactions of **3** and **4** with a range of cinnamaldehydes in the presence of trifluoroacetic acid, ammonium hexafluorophosphate, and magnesium sulfate (as an absorbent for the water formed during the reaction) were accompanied by a conspicuous color change to deep purple. After chromatographic purification, the thiocinnamaldehyde complexes **5a–f** and **6a–g** were obtained in very good yields (Scheme 2).

Complexes **5a–f** and **6a–g** are highly-colored crystalline compounds. Due to their ionic nature they are soluble only



Scheme 2. **a**: R = X = H; **b**: R = H, X = 2-OMe; **c**: R = H, X = 4-OMe; **d**: R = H, X = 4-NMe_2; **e**: R = H, X = 4-Cl; **f**: R = Me, X = H; **g**: R = H, X = 2-NO_2.

in polar media, such as dichloromethane or acetone. The presence of the end-on-coordinated thioaldehyde function was inferred from downfield ^{1}H ($\delta = 9.5$ ppm) and ^{13}C NMR ($\delta = 205$ ppm) spectroscopic resonances, the latter being split into triplets due to coupling with the two equivalent phosphorus nuclei. The ^{1}H NMR spectra of **5d** and **6d** exhibited broadened signals at ambient temperature. Upon cooling, decoalescence set in, and at 200 K separate signals for two isomeric forms in a ratio of 65:35 (**5d**) and 95:5 (**6d**) were observed. We attribute this to a hindered rotation around the formal single bond adjacent to the C=S group of the 4-dimethylamino-thiocinnamaldehyde ligand.

X-ray structure determinations of [CpRu(dppe)(S=CH–CH=CHC$_6$H$_4$NMe$_2$)]PF$_6$ (6d) and 4-dimethylamino-cinnamaldehyde: A deep blue crystal of **6d**·$CDCl_3$ suitable for structure determination was obtained from $CDCl_3$. Figure 1 shows the cation portion of that structure.

The geometry of the cation of **6d** is very similar to that of the related complex $[CpRu(dppe)(S{=}CHC_6H_4OMe)]PF_6$.[23,24] This includes the length of the Ru–S bond and the orientation of the thioaldehyde ligand with the C–H bond pointing towards the Cp ring. The unsaturat-

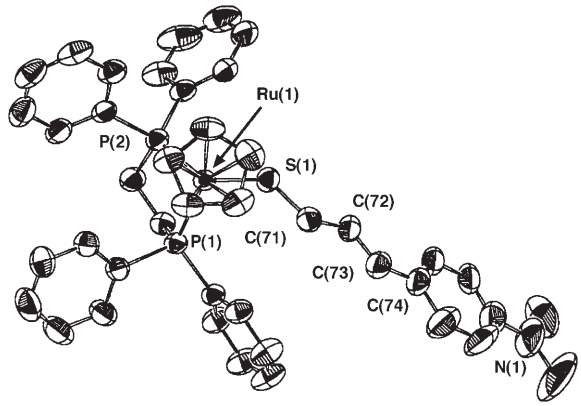


Figure 1. Structure of the cation of [CpRu(dppe)(S=CH–CH=CHC$_6$H$_4$NMe$_2$)]PF$_6$ (**6d**), hydrogen atoms omitted for clarity. Space group $P2_1/n$; selected distances [pm] and angles [°] (standard deviations in parentheses): Ru–P(1) 228.47(13), Ru–P(2) 229.26(12), Ru–S(1) 232.00(13), S(1)–C(71) 165.5(5), C(71)–C(72) 139.3(6), C(72)–C(73) 135.8(6), C(73)–C(74) 144.0(7), P(1)-Ru-P(2) 83.02(4), P(1)-Ru-S(1) 86.73(5), P(2)-Ru-S(1) 90.73(4), Ru-S(1)-C(71) 112.0(2), S(1)-C(71)-C(72) 124.2(4), C(71)-C(72)-C(73) 121.0(5), C(72)-C(73)-C(74) 127.2(5).

ed ligand is tilted out of the pseudo-mirror plane of the [CpRuP$_2$] framework, approaching one of the phenyl groups of the dppe ligand. The most conspicuous feature is the succession of bond lengths along the Ru–S=C–C=C–C chain. While the Ru–S distance is the same as in the thiobenzaldehyde complex, the C=S double bond is 2 pm longer. The adjacent C–C bond is much shorter than the central C–C single bond in butadiene (147.6 pm)[30] to which it might reasonably be compared. The next formal double bond is fairly long. The entire thiocinnamaldehyde ligand is almost perfectly planar, including even the dimethylamino group in the *para* position. The structure of 4-dimethylamino-cinnamaldehyde was determined for comparison (Figure 2).

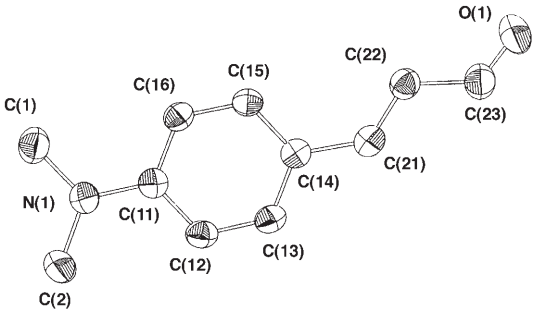


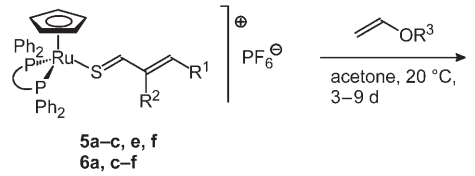
Figure 2. Structure of 4-dimethylamino-cinnamaldehyde, hydrogen atoms omitted for clarity. Space group *Pbca*; selected distances [pm] and angles [°] (standard deviations in parentheses): C(14)–C(21) 144.7(2), C(21)–C(22) 134.1(2), C(22)–C(23) 144.2(2), C(23)–O(1) 121.8(2), C(14)-C(21)-C(22) 128.12(14), C(21)-C(22)-C(23) 120.88(15), C(22)-C(23)-O(1) 124.90(18).

As expected the unsaturated aldehyde adopts an almost planar transoid structure. The largest deviation from coplanarity is manifested in the dihedral angle C(21)-C(22)-C(23)-O(1) of 10.6(3)°. The lengths of the formal single and double bonds in this molecule conform exactly to their expected values. Almost identical geometric parameters have previously been found in the structures of the closely related 4-nitro-cinnamaldehyde[31] and 4-hydroxy-3-methoxy-cinnamaldehyde.[32]

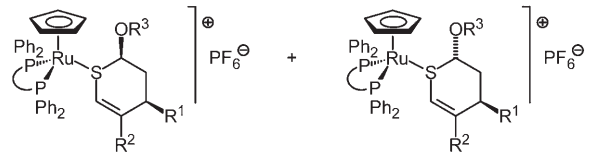
[4+2]-Cycloaddition reactions with vinylethers: To test the reactivity of the thiocinnamaldehyde complexes towards electron-rich dienophiles, the compounds **5a–f** and **6a–f** were treated with a large excess of ethylvinylether or butylvinylether. Monitoring the progress of the reaction by ^{31}P NMR spectroscopy revealed the slow disappearance of the starting materials (except for **5d** and **6d** which were unreactive and **6g** which decomposed too rapidly) whilst one or two AB systems began to appear, signaling the possible formation of diastereomeric products. Chromatographic workup gave the cycloadducts **7a–f** and **8a–f** in generally good yields (Table 1).

The cycloadducts are brownish-orange or -red crystalline materials that are readily soluble in polar organic solvents. Their ^{1}H NMR spectra are fairly complex but nevertheless allow an unambiguous assessment of the constitution of the

Table 1. Products from the [4+2]-cycloaddition reactions with vinylethers.



5a–c, e, f
6a, c–f



endo-**7**, **8** *exo*-**7**, **8**

	$Ph_2P–PPh_2$	R^1	R^2	R^3	Yield [%]	*endo*/*exo*
7a′	dppm	Ph	H	Bu	78	84:16
7b	dppm	2-$MeOC_6H_4$	H	Et	88	74:26
7c	dppm	4-$MeOC_6H_4$	H	Et	82	*endo* only
7e	dppm	4-ClC_6H_4	H	Et	66	*endo* only
7f	dppm	Ph	Me	Et	90	*endo* only
8a	dppe	Ph	H	Et	73	>90:<10
8a′	dppe	Ph	H	Bu	81	82:18
8c	dppe	4-$MeOC_6H_4$	H	Et	65	>90:<10
8e	dppe	4-ClC_6H_4	H	Et	73	>90:<10
8f	dppe	Ph	Me	Et	74	*endo* only

newly-formed 3,4-dihydro-2*H*-thiopyran rings. We begin with the signal at $\delta = 3.0$ ppm whose assignment to H4 follows known precedence[33–37] and is further supported by the observation, in the H,H-COSY spectra, of weak crosspeaks with the signals of the aryl group R^1. H4 is coupled to three vicinal protons, establishing the regioselectivity of the cycloaddition as shown in Table 1. For this six-membered ring system, two conformers of both diastereoisomers have to be taken into consideration (Figure 3).

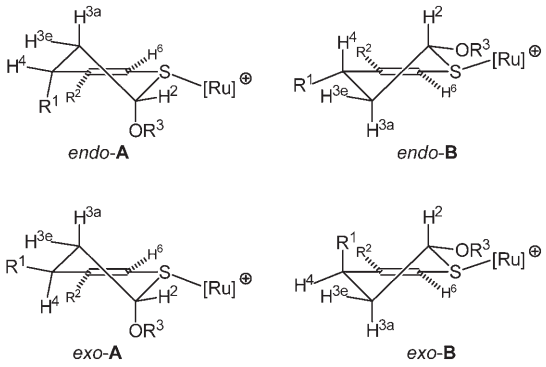


Figure 3. Conformers of *endo* and *exo* adducts **7** and **8**.

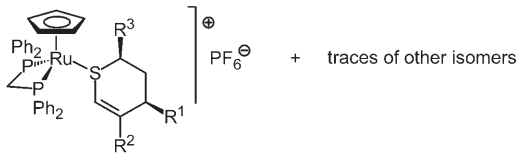
In the major products, the only H,H coupling exceeding $J = 8$ Hz is the geminal coupling between H3a and H3e. This immediately rules out conformer **B** of the *endo* adduct and both conformers of the *exo* adduct. All of those would contain pairs of protons in antiperiplanar positions which

should give rise to another large H,H coupling in the range of $J = 8$–13 Hz. A careful inspection of the ^{1}H NMR spectra of the raw materials revealed additional signals which in the cases of **7a′**, **7b**, **8a**, and **8a′** could be assigned to the respective *exo* adducts. In these, H4 exhibits a large ($J = 13$ Hz) coupling to one of the methylene protons and thus has to be assigned an axial position, while the small couplings of the H-2 signal hint at an equatorial site for that proton. Thus conformer **A** can also be identified as the predominant one of the *exo* adducts.

[4+2]-Cycloaddition reactions with styrenes: Styrenes, in particular those bearing electron-withdrawing substituents, added less readily to the thiocinnamaldehyde complexes. Thus the reactions of the sterically more hindered dppe complexes **6** were too slow and accompanied by decomposition. As a consequence, pure cycloaddition products could not be obtained. The dppm complexes **5**, however, reacted readily with a series of styrenes to give ruthenium-coordinated 2,4-diaryl-3,4-dihydro-2*H*-thiopyrans (Table 2).

Table 2. Products from the [4+2]-cycloaddition reactions with styrenes.

5a,c,e,f



endo-**9**

	R^1	R^2	R^3	Yield [%]
9a	Ph	H	Ph	79
9b	Ph	H	4-MeC_6H_4	87
9c	Ph	H	4-$MeOC_6H_4$	79
9d	Ph	H	4-ClC_6H_4	73
9e	Ph	H	4-BrC_6H_4	83
9f	Ph	H	4-$O_2NC_6H_4$	83
9g	4-$MeOC_6H_4$	H	4-MeC_6H_4	70
9h	4-ClC_6H_4	H	4-MeC_6H_4	65
9i	Ph	Me	4-MeC_6H_4	70

The reactions were monitored by ^{31}P NMR spectroscopy. In addition to the signals of the main product, two or even three small AB systems also began to appear. We have not been able to fully identify these side products, but it is reasonable to assume that besides the expected two diastereoisomeric 2,4-diaryl-3,4-dihydro-2*H*-thiopyrans the corresponding 3,4-diaryl-3,4-dihydro-2*H*-thiopyrans were also formed. After chromatographic separation the main products were isolated in generally good yields as yellow crystalline materials. Their ^{1}H NMR spectra are distinctly different from those of the vinylether adducts **7** and **8**. The H2 signal at $\delta = 3.8$ ppm consistently exhibits one large and one small coupling indicating that this proton resides in an axial position. The H4 signal at $\delta = 2.3$ ppm was unfortunately observed only as a broad multiplet. However, its large ($J = 2.4$–2.8 Hz) allylic coupling to H6 could be seen in the signal of that proton. This value is near the upper limit for that type of coupling and indicates that the C4–H4 bond is almost parallel to the p orbitals of the C5–C6 π bond,[38] which means that H4 is also axial. Thus the addition of styrenes also gives predominantly *endo* diastereoisomers that prefer the all-equatorial conformation **B** (Figure 3, R^3 instead of OR^3).

The rate of reaction of **5a** with the *para*-substituted styrenes $H_2C{=}CHC_6H_4Y$ (Y=OMe, Me, H, Cl, Br, NO_2) was determined to gain some insight into the electronic character of this [4+2]-cycloaddition. Reactions were carried out at 37.5 °C under pseudo-first-order conditions with a large excess of the respective styrene (Table 3 and Figure 4).

Table 3. Rates of addition of the *para*-substituted styrenes $H_2C{=}CHC_6H_4Y$ to **5a** at 37.5 °C (c (styrene) = 0.60 mol L^{-1}).

Y	OMe	Me	H	Cl	Br	NO_2
σ_p^{+}[a]	−0.78	−0.31	0.00	0.11	0.15	0.79
k [10^{-5} s^{-1}]	3.10	1.39	1.04	0.97	0.76	0.59
k_2 [10^{-5} L mol^{-1} s^{-1}]	5.17	3.21	1.73	1.61	1.26	0.98
k_2(rel)	2.99	1.86	1.00	0.93	0.73	0.57
log[k_2(rel)]	0.48	0.27	0.00	−0.03	−0.14	−0.25

[a] Values taken from reference [39].

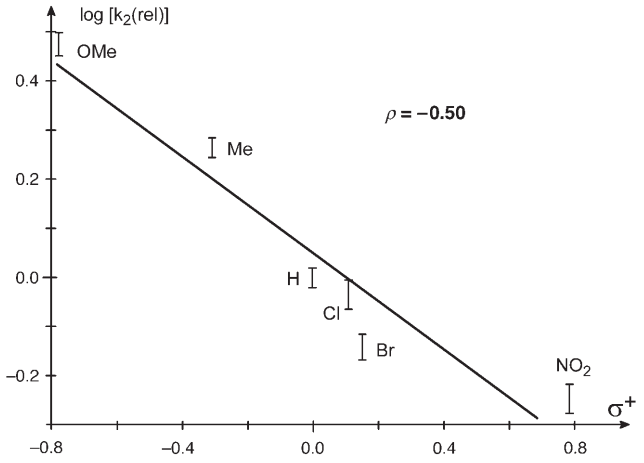


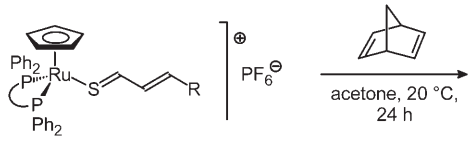
Figure 4. Hammett plot of log[k_2(rel)] for the addition of *para*-substituted styrenes $H_2C{=}CHC_6H_4Y$ to **5a**.

The rate of reaction covers a fivefold range and it increases with electron-releasing substituents at the aromatic ring. This implies that the energy of the transition state is dominated by the incipient interaction of the HOMO of the dienophile with the LUMO of the coordinated thiocinnamaldehyde.

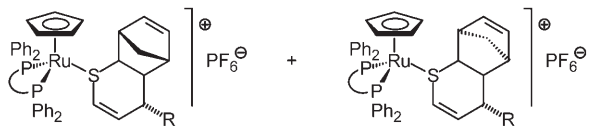
[4+2]-Cycloaddition reactions with norbornadiene and norbornene: The thiocinnamaldehyde complexes did not react

with simple olefins, such as 1-hexene, cyclohexene, or cyclopentene. A clean addition, however, was observed with the strained olefins norbornadiene and norbornene. Thus, treatment of **5a**,**b**,**d** or **6a**,**b**,**d** with a large excess of norbornadiene at room temperature gave the expected complexes of 3-thia-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-dienes **10a–c** and **11a–c** as mixtures of two diastereoisomers (Table 4).

Table 4. Products from the [4+2]-cycloaddition reactions with norbornadiene.



5a,b,d
6a,b,d



exo-**10, 11** *endo*-**10, 11**

$Ph_2P–PPh_2$	dppm			dppe		
R		Yield [%]	*endo*/*exo*		Yield [%]	*endo*/*exo*
Ph	**10a**	87	90:10	**11a**	90	75:25
2-$MeOC_6H_4$	**10b**	82	82:18	**11b**	87	77:23
4-$Me_2NC_6H_4$	**10c**	89	86:14	**11c**	78	89:11

The constitution of the major isomers was unambiguously deduced by ^{1}H NMR spectroscopy combined with H,H-COSY and NOE spectroscopic measurements, taking *exo*-**10a** as a typical example: we begin with the pair of doublets at $\delta = 0.90$ and 1.57 ppm. The latter exhibits a strong Overhauser correlation with the ddd signal at $\delta = 2.97$ ppm and is thus assigned to H11 (Figure 5).

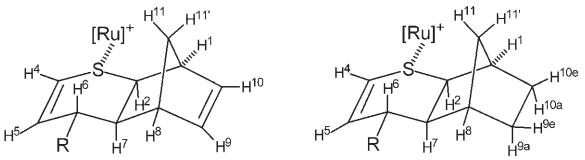
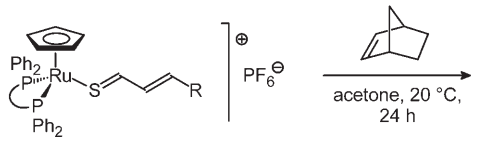


Figure 5. Atom numbering schemes for the norbornadiene adducts *exo*-**10a–c** and *exo*-**11a–c** (left) and the norbornene adducts *exo*-**12a–c** and *exo*-**13a–c** (right).

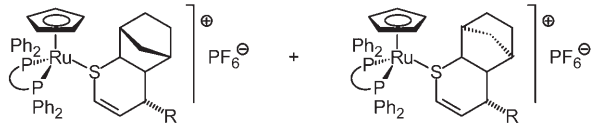
The signal at $\delta = 2.97$ ppm in turn has Overhauser correlations with the *ortho* protons of the phenyl group and one olefinic signal at $\delta = 6.01$ ppm, and therefore can be assigned to H6. A large ^3J(H,H) coupling shows that H6 and its coupling partner H7 ($\delta = 1.84$ ppm) reside in axial positions. H7 is connected through a large coupling with the doublet at $\delta = 2.88$ ppm, belonging to H2. The two narrow unresolved multiplets at $\delta = 1.80$ and 2.30 ppm arise from the bridgehead protons. The former shows a distinct Overhauser correlation with the cyclopentadienyl ligand and must therefore be assigned to H1. Crosspeaks in the H,H-COSY spectrum connect H1 to H10 ($\delta = 5.82$ ppm) and H8 to H9 ($\delta = 5.95$ ppm). Finally, the signals of H4 and H5 can be assigned by their chemical shift, the fairly large allylic coupling between H4 and H6, and the Overhauser correlation between H5 and H6. The ^{1}H NMR spectra of the other *exo* isomers are, as expected, very similar. Many of the signals of the minor isomers were hidden beneath those of the *exo* adducts. Taking the available evidence together (and assuming that a minor substituent change at the aryl group would not completely change the stereochemical course of the cycloaddition), it is nevertheless safe to assume that the minor isomers have the *endo* structure shown in Table 4. Further support for this assignment comes from a comparison with the ^{1}H and ^{13}C NMR spectra of the uncoordinated 6-phenyl-3-thia-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene[14] and the corresponding 6-phenyl-3-thia-tricyclo[6.2.1.$0^{2,7}$]undec-4-ene.[13]

The reaction of norbornene with the thiocinnamaldehyde complexes gave completely analogous products with even better selectivity for the *exo* addition (Table 5).

Table 5. Products from the [4+2]-cycloaddition reactions with norbornene.



5a,b,d
6a,b,d



exo-**12, 13** *endo*-**12, 13**

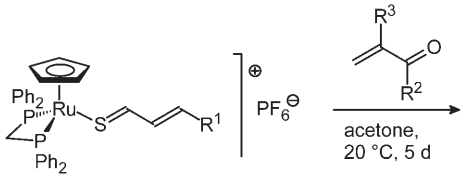
$Ph_2P–PPh_2$	dppm			dppe		
R		Yield [%]	*endo*/*exo*		Yield [%]	*endo*/*exo*
Ph	**12a**	91	93:7	**13a**	90	88:12
2-$MeOC_6H_4$	**12b**	76	91:9	**13b**	81	89:11
4-$Me_2NC_6H_4$	**12c**	88	96:4	**13c**	81	91:9

The ^{1}H NMR spectra could not always be fully assigned due to the serious overlap of the many aliphatic signals. Nevertheless, the similarity of the characteristic resonances of H6, H7, H11, and H11′ to those of the norbornadiene adducts leaves no doubt that the two groups of cycloadducts have analogous stereochemistry.

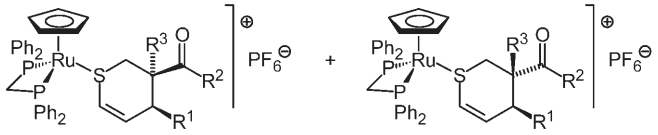
[4+2]-Cycloaddition reactions with α,β-unsaturated carbonyl compounds: The reaction of **5a**,**b** with acrolein, methacrolein, ethyl acrylate, and methylvinylketone proceeded smoothly to give the cycloadducts **14a–e** in generally good yields as mixtures of two diastereoisomers (Table 6).

The outcome of this reaction with regard to regio- and diastereoselectivity as shown in Table 6 has some precedence

Table 6. Products from the [4+2]-cycloaddition reactions with α,β-unsaturated carbonyl compounds.



5a,b



	endo-**14**				*exo*-**14**
	R^1	R^2	R^3	Yield [%]	*endo*/*exo*
14a	Ph	H	H	88	62:38
14b	Ph	H	Me	83	90:10
14c	2-MeOC_6H_4	H	Me	81	69:31
14d	Ph	Me	H	76	77:23
14e	Ph	OEt	H	81	95:5

in the cycloaddition chemistry of α,β-unsaturated thioketones and -amides.[33,34,43] The assignment of the ^{1}H NMR spectrum of the methylvinylketone adduct **14d** may serve as an example. In the major isomer, the CH_2 group next to sulfur shows the expected large geminal coupling and a large vicinal coupling to H3, which establishes an axial position for the latter. H3 gives rise to a ddd signal with a large coupling to H2a, a medium one to H4 (indicating an equatorial position of that proton), and a small one to H2e which, due to a slight broadening of the H2 signals, is not resolved in the ^{1}H NMR spectrum but can still be seen in the H,H-COSY spectrum. H4 appears as an unresolved multiplet, but the vicinal coupling ^3J(H4,H5) = 5.1 Hz can be seen in the signal of H5. In the minor isomer, H4 produces a large coupling to H3 and a very small one to H5, establishing axial positions for H3 and H4. Thus it is clear that the major isomer has the *endo* and the minor isomer the *exo* configuration (Figure 6).

[4+2]-Cycloaddition reactions with ethyl propiolate: Three representative thiocinnamaldehyde complexes were treated with a large excess of ethyl propiolate. The addition was quite slow but produced the expected 4*H*-thiopyran complexes **15a–c** in reasonable yields (Table 7).

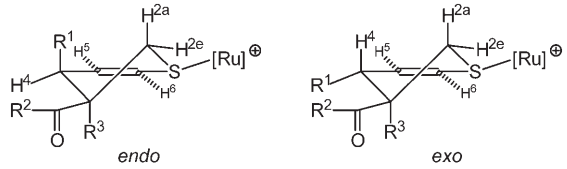
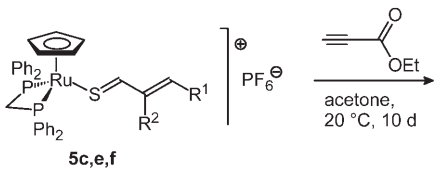
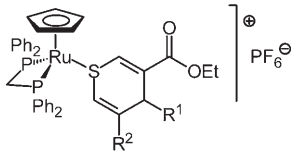


Figure 6. Atom numbering schemes for the *endo* and *exo* adducts of **14a–e**.

Table 7. Products from the [4+2]-cycloaddition reactions with ethyl propiolate.



5c,e,f



15a–c

	R^1	R^2	Yield [%]
15a	4-C_6H_4OMe	H	62
15b	4-C_6H_4Cl	H	51
15c	Ph	Me	65

The direction of the cycloaddition is immediately evident from the NMR signal of H4, which couples with only one olefinic proton. Other noteworthy spectroscopic features are a long-range coupling between H2 and H6 and the apparent, if sometimes broad, singlet in the ^{31}P NMR spectrum. The stereogenic center at C^4 is too far removed from the phosphine ligand to lead to a significant shift difference of the two diastereotopic P nuclei.

Discussion

The synthesis of the thiocinnamaldehyde complexes via the condensation reaction (Scheme 2) exploits the high nucleophilicity of the Ru−SH group, a result of the antibonding interaction of the p orbital at sulfur and one of the d orbitals out of the occupied t_{2g} set at ruthenium.[40] The deep color of the products **5** and **6** arises from an intense absorption with a broad maximum around 510 nm which tails out all the way into the NIR region of the spectrum. Thus it appears that the already fairly small HOMO–LUMO separation of α,β-unsaturated thiocarbonyl compounds[41] is further lowered by coordination to the electron-rich ruthenium complex. The structure of **6d** points to some degree of electron delocalization along the unsaturated C−C−C chain (Figure 7). It is tempting to also invoke the planarity of the dimethylamino group as an indication of this delocalization. On the other hand, the nitrogen in 4-dimethylamino-cinnamaldehyde is also planar, although there are no further indications of delocalization within this molecule.

The Diels–Alder addition of vinyl ethers to the thiocinnamaldehyde complexes is slow as a result of the steric hindrance by the ruthenium complex. It is nevertheless complete and gives the expected 2,4,5-trisubstituted 3,4-dihydro-2*H*-thiopyrans in good yields with high regio- and good diastereoselectivities. The preference for the *endo* adducts is in line with previous results obtained with α,β-unsaturated thi-

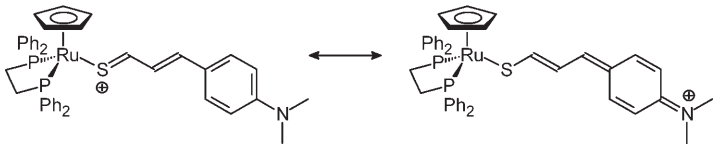


Figure 7. Electron delocalization within the cation of **6d**.

oketones,[42,43] dithioesters,[44,45] or thioamides.[33] The fact that the diastereoselectivity is even higher than in most of the previous cases[33,42–45] is certainly due to the restrictions imposed by the bulky ruthenium complex. In the products, the dihydropyran should be able to undergo a rapid ring inversion like its oxo analogue.[46] This would have to be accompanied by a rapid inversion at sulfur which, for thioether complexes, is a facile process.[47] Nevertheless, the observed NMR data, in particular the large diaxial couplings, indicate that only the conformer with both the alkoxy and the aryl groups in axial positions is present in solution. Obviously the preference of the alkoxy group for the axial position at C2 dominates the conformational equilibrium regardless of the presence of the large ruthenium complex.

The addition of styrenes gives a largely analogous result with perhaps slightly lower regioselectivity, the only difference being the fact that now the conformer with both substituents in equatorial positions is thermodynamically favored. The decrease of the rate of addition with the increasing Hammett substituent constant σ^+ shows that this is a Diels–Alder addition with "inverse electron demand".[48] Nevertheless, highly electrophilic dienophiles, such as α,β-unsaturated aldehydes, ketones, and esters as well as ethyl propiolate add readily to the thiocinnamaldehyde complexes. Obviously, for dienophiles with very low LUMO energies the reaction is dominated by the HOMO(diene)–LUMO(dienophile) interaction.

3,4-Dihydro-2*H*-thiopyrans belong to a well-known class of heterocycles.[49,50] However, due to a lack of suitable synthetic procedures there are only a few known examples which bear hydrogen substituents at the 5- and 6-positions. The isomeric 3,6-dihydro-2*H*-thiopyrans have previously been obtained as $[W(CO)_5]$ or $[CpRu(PR_3)_2]^+$ complexes by Diels–Alder addition of dienes to the corresponding thiobenzaldehyde complexes.[23,51] Thus the use of transition-metal-stabilized thioaldehydes as starting materials provides suitable alternatives for the synthesis of six-membered sulfur heterocycles. In this context it should be mentioned that the cleavage of thioether ligands from halfsandwich ruthenium complexes can be achieved under mild conditions.[52–54]

Conclusion

The work presented here shows that ruthenium complexes of thiocinnamaldehydes are readily accessible and undergo [4+2]-cycloadditions with a range of electron-rich and -poor dienophiles. Thus the thiocinnamaldehyde ruthenium complexes described here can serve as protected forms of thiocinnamaldehydes. The ruthenium complex does not significantly change the electronic character of the heterodiene but exerts a pronounced steric effect. We may therefore expect that by introducing chiral, enantiomerically pure phosphine ligands at the ruthenium complex, we should be able to obtain enantiomerically enriched Diels–Alder adducts. Work along these lines is forthcoming from our laboratory.

Experimental Section

All preparations were carried out in an inert atmosphere by using standard Schlenk techniques. $[CpRu(PPh_3)_2Cl]$,[27] [CpRu(dppm)Cl],[28] and NaSH[55] were prepared by following published procedures. The cinnamaldehydes and dienophiles were vacuum-distilled or recrystallized prior to use; other starting materials were employed as received from commercial sources. Chromatographic separations were performed by using a silica (Merck, grain size 0.062–0.20 mm) column of 20 cm length and 2 cm diameter. Elemental analyses were carried out by the microanalytical laboratory of the Institut für Anorganische Chemie. Melting or decomposition points were determined by differential scanning calorimetry (DSC). UV spectra were recorded by using a Hewlett–Packard HP 8452 A diode array spectrophotometer. Samples were measured as dilute solutions in 1.00 mm quartz cells. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded by using Jeol JNM-LA 300 or Bruker AMX 400 instruments. The assignment of the ^{13}C NMR spectra was routinely checked by recording DEPT 135 spectra. H,H-COSY spectra were consulted to elucidate the complicated coupling patterns in the ^1H NMR spectra of the cycloadducts. The ^1H and ^{13}C NMR spectroscopic signals of the chelate phosphine ligands dppm and dppe are very similar for all compounds and have therefore been omitted from the lists of spectral data. All PF_6^- salts exhibited a septet at $\delta = -144.1$ ppm ($^1J(P,F) = 710$ Hz) in their ^{31}P NMR spectra.

[CpRu(dppm)(SH)] (3): A solution of [CpRu(dppm)Cl] (0.35 g, 0.60 mmol) and NaSH (0.24 g, 2.50 mmol) in THF (15 mL) and EtOH (10 mL) was heated under reflux for 16 h. The mixture was evaporated in vacuo to 10 mL, toluene (15 mL) was added, and the resulting mixture further evaporated to 10 mL. The precipitated solids were filtered off and the filtrate evaporated to 5 mL. Addition of hexane (20 mL) and cooling to 0 °C caused the product to crystallize. Yield 0.30 g (87 %); yellow crystalline powder; m.p. 83 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -3.98$ (t, $^3J(P,H) = 10.5$ Hz, 1 H; RuSH), 4.60 (dt, $^2J(H,H) = 14.1$, $^2J(P,H) = 11.4$ Hz, 1 H; CH_2), 4.83 (s, 5 H; Cp), 4.90 ppm (dt, $^2J(H,H) = 14.1$, $^2J(P,H) = 9.7$ Hz, 1 H; CH_2); ^{31}P NMR (162 MHz, C_6D_6, 25 °C, H_3PO_4): $\delta = 18.2$ ppm (s); elemental analysis (%) calcd for $C_{30}H_{28}P_2RuS$ (583.6): C 61.74, H 4.84; found: C 61.49, H 4.88.

[CpRu(dppe)(SH)] (4): A solution of $[CpRu(PPh_3)_2Cl]$ (0.30 g, 0.41 mmol), dppe (0.20 g, 0.50 mmol), and NaSH (35 mg, 0.61 mmol) in THF (10 mL) and EtOH (7 mL) was heated under reflux for 45 min. The volatiles were removed in vacuo and the residue extracted with benzene (20 mL). The mixture was filtered and the clear filtrate evaporated to 5 mL. Addition of hexane (20 mL) and cooling to 0 °C caused the product to crystallize. Yield 0.22 g (90 %); yellow crystalline powder; m.p. 59 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -4.56$ (t, $^3J(P,H) = 8.1$ Hz, 1 H; RuSH), 2.23 (m, 2 H; CH_2), 2.77 (m, 2 H; CH_2), 4.67 ppm (s, 5 H; Cp); ^{31}P NMR (162 MHz, C_6D_6, 25 °C, H_3PO_4): $\delta = 85.7$ ppm (s); elemental analysis (%) calcd for $C_{31}H_{30}P_2RuS$ (597.7): C 62.30, H 5.06; found: C 62.76, H 5.14.

General procedure for the synthesis of thiocinnamaldehyde complexes 5a–f and 6a–g: Trifluoroacetic acid (5.0 μL, 0.40 mmol) was added to a suspension of RuSH complex **3** or **4** (0.40 mmol), the respective cinnamaldehyde (1.20 mmol), NH_4PF_6 (0.10 g, 0.61 mmol), and $MgSO_4$ (0.10 g, 0.83 mmol) in THF (10 mL). After stirring for 4 h, the mixture was evaporated to 3 mL, and the crude product precipitated by adding diethyl ether (10 mL) and hexane (30 mL). The deep purple solid was dissolved

in acetone (5 mL) and chromatographed by using dichloromethane/acetone 20:1 as an eluent. The deep purple band was collected and evaporated to a few milliliters, and the product precipitated by adding diethyl ether.

Compound 5a: Yield 0.30 g (88%); deep purple crystalline powder; m.p. 116°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 5.01$ (s, 5H; Cp), 6.80 (m, 2H; CH), 9.21 ppm (d, $^3J(H,H) = 10.4$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 84.6$ (s; Cp), C(β) signal obscured by phenyl resonances, 142.0 (s; PhCH), 206.8 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 9.2$ ppm (s); elemental analysis (%) calcd for $C_{39}H_{35}F_6P_3RuS$ (843.8): C 55.52, H 4.18; found: C 56.13, H 4.28.

Compound 5b: Yield 0.30 g (85%); deep purple crystalline powder; m.p. 118°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.85$ (s, 3H; OMe), 5.05 (s, 5H; Cp), 6.80 (m, 2H; CH), 9.11 ppm (d, $^3J(H,H) = 10.4$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 55.6$ (s; OMe), 85.1 (s; Cp), C(β) signal obscured by phenyl resonances, 140.4 (s; PhCH), 212.6 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 9.3$ ppm (s); elemental analysis (%) calcd for $C_{40}H_{37}F_6OP_3RuS$ (873.8): C 54.98, H 4.27, S 3.67; found: C 54.96, H 4.36, S 3.48.

Compound 5c: Yield 0.32 g (91%); deep purple crystalline powder; m.p. 127°C (decomp); ^{1}H NMR (300 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 3.83$ (s, 3H; OMe), 5.35 (s, 5H; Cp), 6.78 (d, $^3J(H,H) = 16.0$ Hz, 1H; PhCH), 7.01 (dd, $^3J(H,H) = 16.0$, $^3J(H,H) = 12.0$ Hz, 1H; SCCH), 9.68 ppm (d, $^3J(H,H) = 12.0$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 55.3$ (s; OMe), 83.7 (s; Cp), 114.7 (s; C(β)), 143.8 (s; PhCH), 208.5 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (121.5 MHz, [D$_6$]acetone, 25°C, H_3PO_4): $\delta = 10.2$ ppm (s); elemental analysis (%) calcd for $C_{40}H_{37}F_6OP_3RuS$ (873.8): C 54.98, H 4.27, S 3.67; found: C 54.88, H 4.44, S 3.70.

Compound 5d: Yield 0.30 g (85%); dark blue crystalline powder; m.p. 133°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, −53°C, TMS): $\delta = 3.02$ (s, 6H; NMe_2), 5.00 (s, 5H; Cp), 6.73 (d, $^3J(H,H) = 14.0$ Hz, 1H; PhCH), 6.81 (dd, $^3J(H,H) = 14.3$, $^3J(H,H) = 11.2$ Hz, 1H; SCCH), 9.18 ppm (d, $^3J(H,H) = 10.8$ Hz, 1H; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, −53°C, H_3PO_4): $\delta = 11.3$ ppm (s); elemental analysis (%) calcd for $C_{41}H_{40}F_6NP_3RuS$ (886.8): C 55.53, H 4.55, N 1.58, S 3.62; found: C 55.26, H 4.45, N 1.77, S 3.36.

Compound 5e: Yield 0.30 g (85%); deep purple crystalline powder; m.p. 123°C (decomp); ^{1}H NMR (300 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 5.39$ (s, 5H; Cp), 6.73 (d, $^3J(H,H) = 15.0$ Hz, 1H; PhCH), 7.07 (dd, $^3J(H,H) = 15.0$, $^3J(H,H) = 11.0$ Hz, 1H; SCCH), 9.56 ppm (d, $^3J(H,H) = 11.0$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 84.9$ (s; Cp), C(β) signal obscured by phenyl resonances, 140.9 (s; PhCH), 206.4 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (121.5 MHz, [D$_6$]acetone, 25°C, H_3PO_4): $\delta = 9.3$ ppm (s); elemental analysis (%) calcd for $C_{39}H_{34}ClF_6OP_3RuS$ (878.2): C 53.34, H 3.90, S 3.65; found: C 53.76, H 4.36, S 3.50.

Compound 5f: Yield 0.28 g (81%); deep purple crystalline powder; m.p. 113°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.96$ (s, 3H; Me), 5.06 (s, 5H; Cp), 6.50 (s, 1H; CH), 9.05 ppm (s, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 13.6$ (s; Me), 85.6 (s; Cp), C(β) signal obscured by phenyl resonances, 143.0 (s; PhCH), 212.4 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 9.1$ ppm (s); elemental analysis (%) calcd for $C_{40}H_{37}F_6P_3RuS$ (857.8): C 56.01, H 4.35, S 3.74; found: C 57.03, H 4.87, S 3.60.

Compound 6a: Yield 0.28 g (82%); deep purple crystalline powder; m.p. 190°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 4.93$ (s, 5H; Cp), 6.70 (dd, $^3J(H,H) = 15.3$, $^3J(H,H) = 11.4$ Hz, 1H; SCCH), 6.92 (d, $^3J(H,H) = 15.3$ Hz, 1H; PhCH), 9.25 ppm (d, $^3J(H,H) = 11.4$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 85.5$ (s; Cp), C(β) signal obscured by phenyl resonances, 144.0 (s; PhCH), 210.9 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 80.1$ ppm (s); elemental analysis (%) calcd for $C_{40}H_{37}F_6P_3RuS$ (857.8): C 56.01, H 4.35; found: C 56.33, H 4.10.

Compound 6b: Yield 0.29 g (82%); deep purple crystalline powder; m.p. 150°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.86$ (s, 3H; OMe), 4.91 (s, 5H; Cp), 6.80 (m, 2H; CH), 9.09 ppm (d, $^3J(H,H) = 10.8$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 55.5$ (s; OMe), 84.3 (s; Cp), C(β) signal obscured by phenyl resonances, 139.2 (s; PhCH), 212.1 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 80.3$ ppm (s); elemental analysis (%) calcd for $C_{41}H_{39}F_6OP_3RuS$ (887.8): C 55.47, H 4.43, S 3.61; found: C 55.85, H 4.57, S 3.44.

Compound 6c: Yield 0.31 g (86%); deep purple crystalline powder; m.p. 178°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.78$ (s, 3H; OMe), 4.90 (s, 5H; Cp), 6.64 (dd, $^3J(H,H) = 15.0$, $^3J(H,H) = 11.0$ Hz, 1H; SCCH), 6.88 (d, $^3J(H,H) = 15.0$ Hz, 1H; PhCH), 9.18 ppm (d, $^3J(H,H) = 11.0$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 55.6$ (s; OMe), 85.1 (s; Cp), 121.1 (s; C(β)), 140.7 (s; PhCH), 212.7 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 79.6$ ppm (s); elemental analysis (%) calcd for $C_{41}H_{39}F_6OP_3RuS$ (887.8): C 55.47, H 4.43, S 3.61; found: C 55.51, H 4.62, S 3.42.

Compound 6d: Yield 0.29 g (81%); dark blue crystalline powder; m.p. 144°C (decomp); ^{1}H NMR (400 MHz, CD_2Cl_2, −80°C, TMS): $\delta = 3.02$ (s, 6H; NMe_2), 5.83 (s, 5H; Cp), 6.74 (d, $^3J(H,H) = 14.4$ Hz, 1H; PhCH), 6.84 (dd, $^3J(H,H) = 14.8$, $^3J(H,H) = 11.2$ Hz, 1H; SCCH), 8.40 ppm (d, $^3J(H,H) = 12.0$ Hz, 1H; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, −80°C, H_3PO_4): $\delta = 79.8$ ppm (s); elemental analysis (%) calcd for $C_{42}H_{42}F_6NP_3RuS$ (900.8): C 56.00, H 4.70, N 1.55, S 3.56; found: C 55.77, H 4.61, N 1.51, S 3.66.

Compound 6e: Yield 0.27 g (77%); deep purple crystalline powder; m.p. 120°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 4.93$ (s, 5H; Cp), 6.61 (dd, $^3J(H,H) = 15.0$, $^3J(H,H) = 11.0$ Hz, 1H; SCCH), 6.94 (d, $^3J(H,H) = 15.0$ Hz, 1H; PhCH), 9.28 ppm (d, $^3J(H,H) = 11.0$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 85.9$ (s; Cp), C(β) signal obscured by phenyl resonances, 142.4 (s; PhCH), 210.8 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 80.4$ ppm (s); elemental analysis (%) calcd for $C_{40}H_{36}ClF_6OP_3RuS$ (892.2): C 53.85, H 4.07, S 3.59; found: C 53.33, H 4.02, S 3.47.

Compound 6f: Yield 0.28 g (80%); deep purple crystalline powder; m.p. 185°C (decomp); ^{1}H NMR (300 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 1.87$ (s, 3H; Me), 5.21 (s, 5H; Cp), 6.71 (s, 1H; CH), 9.44 ppm (s, 1H; CHS); ^{13}C NMR (100 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 13.4$ (s; Me), 86.3 (s; Cp), C(β) signal obscured by phenyl resonances, 144.3 (s; PhCH), 216.1 ppm (t, $^3J(P,C) = 7$ Hz; CHS); ^{31}P NMR (162 MHz, [D$_6$]acetone, 25°C, H_3PO_4): $\delta = 80.1$ ppm (s); elemental analysis (%) calcd for $C_{41}H_{39}F_6P_3RuS$ (871.8): C 56.49, H 4.51, S 3.68; found: C 56.57, H 4.73, S 3.41.

Compound 6g: Yield 0.22 g (60%); violet crystalline powder; m.p. 136°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 5.07$ (s, 5H; Cp), 6.69 (dd, $^3J(H,H) = 15.0$, $^3J(H,H) = 11.0$ Hz, 1H; SCCH), 7.01 (d, $^3J(H,H) = 15.0$ Hz, 1H; PhCH), 9.15 ppm (d, $^3J(H,H) = 11.0$ Hz, 1H; CHS); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 87.7$ (s; Cp), C(β) signal obscured by phenyl resonances, 139.8 (s; PhCH), 207.2 ppm (t, $^3J(P,C) = 6$ Hz; CHS); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): $\delta = 80.6$ ppm (s); elemental analysis (%) calcd for $C_{40}H_{36}F_6NO_2P_3RuS$ (902.8): C 53.22, H 4.02, N 1.55, S 3.55; found: C 53.51, H 4.45, N 1.69, S 3.08.

General procedure for the synthesis of 3,4-dihydro-2*H*-thiopyran complexes 7a–f, 8a–f, and 9a–i: The dienophile (ca. 16 mmol) was added to a solution of the respective thiocinnamaldehyde complex **5** or **6** (0.20 mmol) in acetone (5 mL). After stirring for 2–9 d a color change from purple to brown was observed; at this point the starting material had been consumed (^{31}P NMR). The mixture was then evaporated to dryness and the crude product dissolved in dichloromethane (5 mL) and precipitated by adding diethyl ether (10 mL) and hexane (30 mL). The solid was redissolved in acetone (5 mL) and chromatographed by using dichloromethane/acetone 20:1 as the eluent. The brownish fraction was collected and evaporated to a few milliliters, and the product precipitated by adding diethyl ether and hexane.

Compound 7a′: Yield 0.15 g (78%); grey crystalline powder; m.p. 125°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 0.66 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 0.75–1.15 (m, 4H; C_2H_4), 2.21 (dt, ^2J(H,H) = 8.8, ^3J(H,H) = 6.2 Hz, 1H; OCH_2), 2.25 (ddd, ^2J(H,H) = 14.5, ^3J(H,H) = 4.8, ^3J(H,H) = 4.2 Hz, 1H; H3a), 2.35 (ddd, ^2J(H,H) = 14.5, ^3J(H,H) = 6.8, ^3J(H,H) = 2.2 Hz, 1H; H3e), 2.73 (dt, ^2J(H,H) = 8.8, ^3J(H,H) = 6.2 Hz, 1H; OCH_2), 3.30 (m, 1H; H4), 4.00 (m, 1H; H2), 5.04 (s, 5H; Cp), 5.08 (d, ^3J(H,H) = 10.0 Hz, 1H; H6), 5.96 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 4.3 Hz, 1H; H5); *exo* isomer: δ = 0.78 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 1.94 (ddd, ^2J(H,H) = 13.5, ^3J(H,H) = 13.5, ^3J(H,H) = 1.2 Hz, 1H; H3a), 3.00 (dt, ^2J(H,H) = 9.8, ^3J(H,H) = 6.6 Hz, 1H; OCH_2), 3.15 (dt, ^2J(H,H) = 9.8, ^3J(H,H) = 6.6 Hz, 1H; OCH_2), 3.55 (ddd, ^3J(H,H) = 12.8, ^3J(H,H) = 3.0, ^3J(H,H) = 3.0 Hz, 1H; H4), 4.09 (m, 1H; H2), 4.90 (d, ^3J(H,H) = 10.0 Hz, 1H; H6), 5.04 (s, 5H; Cp), 5.84 ppm (d, ^3J(H,H) = 10.0 Hz, 1H; H5), other signals obscured by *endo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 13.6 (s; CH_3), 18.8 (s; CH_2), 31.0 (s; CH_2), 33.7 (s; C3), 36.7 (s; C4), 69.2 (s; OCH_2), 81.4 (s; Cp), 87.5 (s; C2), 119.6 ppm (s; C6), C5 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *endo* isomer: δ = 7.0, 7.6 ppm (AB system, ^2J(P,P) = 90 Hz); *exo* isomer: δ = 6.8, 7.5 ppm (AB system, ^2J(P,P) = 90 Hz); elemental analysis (%) calcd for $C_{45}H_{47}F_6OP_3RuS$ (943.9): C 57.26, H 5.02, S 3.40; found: C 57.28, H 5.10, S 3.15.

Compound 7b: Yield 0.17 g (88%); brown powder; m.p. 139°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 0.67 (t, ^3J(H,H) = 6.8 Hz, 3H; CH_3), 2.21 (m, 2H; H3a, H3e), 2.30 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 2.82 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 6.8 Hz, 1H; OCH_2), 3.68 (m, 1H; H4), 3.79 (s, 3H; OMe), 3.85 (m, 1H; H2), 5.02 (s, 5H; Cp), 5.13 (d, ^3J(H,H) = 10.0 Hz, 1H; H6), 5.90 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 4.4 Hz, 1H; H5); *exo* isomer: δ = 0.85 (t, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 2.01 (ddd, ^2J(H,H) = 13.4, ^3J(H,H) = 13.4, ^3J(H,H) = 2.0 Hz, 1H; H3a), 2.18 (m, 1H; H3e), 3.03 (dt, ^2J(H,H) = 10.0, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 3.20 (dt, ^2J(H,H) = 10.0, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 3.78 (s, 3H; OMe), 4.07 (m, 1H; H2), 4.30 (m, 1H; H4), 4.87 (d, ^3J(H,H) = 10.4 Hz, 1H; H6), 5.06 (s, 5H; Cp), 5.82 ppm (d, ^3J(H,H) = 9.8 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 14.5 (s; CH_3), 30.6 (s; C4), 31.4 (s; C3), 55.1 (s; OMe), 81.3 (s; Cp), 86.1 (s; C2), 121.1 ppm (s; C6), C5 signal obscured by phenyl resonances; *exo* isomer: δ = 14.8 (s; CH_3), 29.7 (s; C4), 31.1 (s; C3), 55.2 (s; OMe), 81.3 (s; Cp), 86.6 ppm (s; C2), other signals obscured by *endo* isomer; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *endo* isomer: δ = 7.0, 7.8 ppm (AB system, ^2J(P,P) = 90 Hz); *exo* isomer: δ = 7.1, 7.6 ppm (AB system, ^2J(P,P) = 90 Hz); elemental analysis (%) calcd for $C_{44}H_{45}F_6O_2P_3RuS$ (945.9): C 55.87, H 4.80, S 3.39; found: C 56.57, H 4.45, S 3.17.

Compound 7c: Yield 0.16 g (82%); brownish-red powder; m.p. 179°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 0.75 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 2.20 (m, 2H; H3a, H3e), 2.42 (dq, ^2J(H,H) = 8.7, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 2.75 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 6.3 Hz, 1H; OCH_2), 3.13 (d, ^3J(H,H) = 3.9 Hz, 1H; H4), 3.71 (s, 3H; OMe), 3.99 (m, 1H; H2), 4.64 (dd, ^3J(H,H) = 11.0, ^4J(H,H) = 2.5 Hz, 1H; H6), 5.00 (s, 5H; Cp), 5.90 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 4.1 Hz, 1H; H5); ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 6.8, 7.7 ppm (AB system, ^2J(P,P) = 89 Hz); elemental analysis (%) calcd for $C_{44}H_{45}F_6O_2P_3RuS$ (945.9): C 55.87, H 4.80, S 3.39; found: C 55.81, H 4.50, S 3.23.

Compound 7e: Yield 0.13 g (66%); dark brown crystalline powder; m.p. 122°C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): δ = 0.68 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 2.24 (m, 2H; H3a, H3e), 2.29 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 7.3 Hz, 1H; OCH_2), 2.78 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 7.2 Hz, 1H; OCH_2), 3.39 (d, ^3J(H,H) = 3.9 Hz, 1H; H4), 3.90 (d, ^3J(H,H) = 2.4 Hz, 1H; H2), 5.06 (s, 5H; Cp), 5.16 (dd, ^3J(H,H) = 10.2, ^4J(H,H) = 2.5 Hz, 1H; H6), 5.97 ppm (dd, ^3J(H,H) = 10.1, ^3J(H,H) = 4.2 Hz, 1H; H5); ^{13}C NMR (75 MHz, [D$_6$]acetone, 25°C, TMS): δ = 14.2 (s; CH_3), 33.4 (s; C4), 36.1 (s; C3), 65.1 (s; OCH_2), 81.2 (s; Cp), 86.8 (s; C2), 121.1 (s; C6), 141.6 ppm (s; C5); ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 7.0, 7.5 ppm (AB system, ^2J(P,P) = 90 Hz); elemental analysis (%) calcd for $C_{43}H_{42}ClF_6OP_3RuS$ (950.3): C 54.35, H 4.45, S 3.37; found: C 55.09, H 4.56, S 3.18.

Compound 7f: Yield 0.17 g (90%); brownish-orange powder; m.p. 122°C (decomp); ^{1}H NMR (300 MHz, CD_3CN, 25°C, TMS): δ = 0.50 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 1.49 (s, 3H; Me), 1.97 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 6.9 Hz, 1H; OCH_2), 2.25 (m, 1H; H3a), 2.46 (m, 1H; H3e), 2.74 (dq, ^2J(H,H) = 8.9, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 3.38 (m, 1H; H4), 4.15 (m, 1H; H2), 4.89 (d, ^4J(H,H) = 1.3 Hz, 1H; H6), 5.31 ppm (s, 5H; Cp); ^{13}C NMR (75 MHz, CD_3CN, 25°C, TMS): δ = 14.8 (s; CH_3), 24.6 (s; Me), 34.6 (s; C3), 41.9 (s; C4), 65.6 (s; OCH_2), 82.4 (s; Cp), 88.1 (s; C2), 116.5 ppm (s; C6), C5 signal obscured by phenyl resonances; ^{31}P NMR (121.5 MHz, CD_3CN, 25°C, H_3PO_4): δ = 8.2, 8.7 ppm (AB system, ^2J(P,P) = 91 Hz); elemental analysis (%) calcd for $C_{44}H_{45}F_6OP_3RuS$ (929.9): C 56.83, H 4.88, S 3.45; found: C 56.35, H 4.96, S 3.69.

Compound 8a: Yield 0.14 g (73%); brown crystalline powder; m.p. 131°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 0.87 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 1.93 (m, 1H; H3a), 2.10 (m, 1H; H3e), 2.84 (m, 1H; OCH_2), 2.92 (m, 1H; H4), 2.99 (m, 1H; OCH_2), 3.47 (d, ^3J(H,H) = 6.9 Hz, 1H; H2), 4.33 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 2.5 Hz, 1H; H6); 4.92 (s, 5H; Cp), 5.77 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 3.5 Hz, 1H; H^5); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 14.7 (s; CH_3), 34.9 (s; C4), 39.8 (s; C3), 64.2 (s; OCH_2), 82.2 (s; Cp), 84.5 (s; C2), 119.6 ppm (s; C6), C5 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 74.3, 74.5 ppm (AB system, ^2J(P,P) = 26 Hz); elemental analysis (%) calcd for $C_{44}H_{45}F_6OP_3RuS$ (929.9): C 56.83, H 4.88, S 3.45; found: C 56.70, H 4.65, S 3.20.

Compound 8a′: Yield 0.16 g (81%); grey crystalline powder; m.p. 127°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 0.74 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 1.00 (tq, ^3J(H,H) = 7.2, ^3J(H,H) = 6.6 Hz, 2H; CH_2), 1.14 (tt, ^3J(H,H) = 6.6, ^3J(H,H) = 6.6 Hz, 2H; CH_2), 1.94 (ddd, ^2J(H,H) = 15.0, ^3J(H,H) = 6.8, ^3J(H,H) = 6.4 Hz, 1H; H3a), 2.13 (ddd, ^2J(H,H) = 15.0, ^3J(H,H) = 6.4, ^3J(H,H) = 2.2 Hz, 1H; H3e), 2.65 (dt, ^2J(H,H) = 8.8, ^3J(H,H) = 6.8 Hz, 1H; OCH_2), 2.89 (dt, ^2J(H,H) = 8.4, ^3J(H,H) = 6.8 Hz, 1H; OCH_2), 3.04 (m, 1H; H4), 3.44 (d, ^3J(H,H) = 7.2 Hz, 1H; H2), 4.37 (dd, ^3J(H,H) = 9.8, ^4J(H,H) = 1.6 Hz, 1H; H6), 4.91 (s, 5H; Cp), 5.81 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 3.6 Hz, 1H; H^5); *exo* isomer: δ = 0.82 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 4.27 (d, ^3J(H,H) = 10.6 Hz, 1H; H6), 5.00 (s, 5H; Cp), 5.71 ppm (d, ^3J(H,H) = 10.6 Hz, 1H; H5), other signals obscured by *endo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 14.8 (s; CH_3), 20.0 (s; CH_2), 31.2 (s; CH_2), 35.1 (s; C4), 38.3 (s; C3), 64.0 (s; OCH_2), 82.8 (s; Cp), 85.6 (s; C2), 119.7 ppm (s; C6), C5 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *endo* isomer: δ = 74.1, 74.4 ppm (AB system, ^2J(P,P) = 26 Hz); *exo* isomer: δ = 73.6, 75.5 ppm (AB system, ^2J(P,P) = 26 Hz); elemental analysis (%) calcd for $C_{46}H_{49}F_6OP_3RuS$ (957.9): C 57.68, H 5.16, S 3.35; found: C 57.37, H 4.93, S 3.47.

Compound 8c: Yield 0.12 g (65%); brown powder; m.p. 126°C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): δ = 0.90 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 1.95 (m, 2H; H3a, H3e), 2.84 (m, 1H; H4), 2.93 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 3.06 (dq, ^2J(H,H) = 8.9, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 3.54 (dd, ^3J(H,H) = 5.8, ^4J(H,H) = 1.8 Hz, 1H; H2), 4.33 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 1.8 Hz, 1H; H6), 4.95 (s, 5H; Cp), 5.75 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 3.3 Hz, 1H; H5); ^{13}C NMR (75 MHz, CD_2Cl_2, 25°C, TMS): δ = 15.0 (s; CH_3), 35.7 (s; C4), 38.2 (s; C3), 55.5 (s; OMe), 64.1 (s; OCH_2), 83.2 (s; Cp), 84.4 (s; C2), 114.0 ppm (s; C6), C5 signal obscured by phenyl resonances; ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): *endo* isomer: δ = 74.5, 74.7 ppm (AB system, ^2J(P,P) = 25 Hz); *exo* isomer: δ = 78.1, 83.0 ppm (AB system, ^2J(P,P) = 23 Hz); elemental analysis (%) calcd for $C_{45}H_{47}F_6O_2P_3RuS$ (959.9): C 56.31, H 4.94, S 3.34; found: C 55.97, H 5.00, S 2.93.

Compound 8e: Yield 0.14 g (73%); brownish-green crystalline powder; m.p. 124°C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): δ = 0.81 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 1.94 (m, 1H; H^{3a}), 2.11 (m, 1H; H3e), 2.75 (dq, ^2J(H,H) = 8.8, ^3J(H,H) = 7.3 Hz, 1H; OCH_2), 3.14 (dq, ^2J(H,H) = 9.0, ^3J(H,H) = 7.2 Hz, 1H; OCH_2), 3.26 (d, ^3J(H,H) = 3.9 Hz, 1H; H4), 3.54 (d, ^4J(H,H) = 2.1 Hz, 1H; H2), 4.71 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 2.4 Hz, 1H; H6), 5.20 (s, 5H; Cp), 5.88 ppm (dd, ^3J(H,H) =

10.1, ^3J(H,H) = 3.9 Hz, 1H; H5); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C, TMS): δ = 14.9 (s; CH_3), 34.9 (s; C4), 37.7 (s; C3), 64.7 (s; OCH_2), 83.2 (s; Cp), 84.6 (s; C2), 120.6 (s; C6), 141.9 ppm (s; C5); ^{31}P NMR (121.5 MHz, [D_6]acetone, 25 °C, H_3PO_4): *endo* isomer: δ = 73.9, 74.3 ppm (AB system, ^2J(P,P) = 26 Hz); *exo* isomer: δ = 79.3, 84.2 ppm (AB system, ^2J(P,P) = 22 Hz); elemental analysis (%) calcd for $C_{44}H_{44}ClF_6OP_3RuS$ (950.3): C 54.80, H 4.60, S 3.33; found: C 54.90, H 4.38, S 3.56.

Compound 8f: Yield 0.14 g (74%); brownish crystalline powder; m.p. 152 °C (decomp); ^{1}H NMR (300 MHz, [D_6]acetone, 25 °C, TMS): δ = 0.71 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 1.36 (s, 3H; Me), 2.07 (m, 2H; H3a, H3e), 2.50 (dq, ^2J(H,H) = 9.1, ^3J(H,H) = 7.1 Hz, 1H; OCH_2), 2.90 (dq, ^2J(H,H) = 8.9, ^3J(H,H) = 7.0 Hz, 1H; OCH_2), 3.19 (m, 1H; H4), 3.52 (dd, ^3J(H,H) = 5.5, ^4J(H,H) = 1.3 Hz, 1H; H2), 4.29 (d, ^4J(H,H) = 1.3 Hz, 1H; H6), 5.22 ppm (s, 5H; Cp); ^{13}C NMR (75 MHz, [D_6]acetone, 25 °C, TMS): δ = 14.7 (s; CH_3), 23.0 (s; Me), 35.0 (s; C3), 41.3 (s; C4), 65.0 (s; OCH_2), 83.7 (s; Cp), 86.1 (s; C2), 125.4 ppm (s; C6), C5 signal obscured by phenyl resonances; ^{31}P NMR (121.5 MHz, [D_6]acetone, 25 °C, H_3PO_4): δ = 73.2, 74.9 ppm (AB system, ^2J(P,P) = 26 Hz); elemental analysis (%) calcd for $C_{45}H_{47}F_6OP_3RuS$ (943.9): C 57.26, H 5.02, S 3.40; found: C 56.98, H 4.89, S 3.22.

Compound 9a: Yield 0.15 g (79%); greenish-yellow powder; m.p. 149 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.90 (m, 2H; H3a, H3e), 2.24 (m, 1H; H4), 3.72 (dd, ^3J(H,H) = 10.4, ^2J(H,H) = 2.4 Hz, 1H; H2), 4.30 (s, 5H; Cp), 4.95 (dd, ^3J(H,H) = 10.4, ^4J(H,H) = 2.4 Hz, 1H; H6), 5.92 ppm (d, ^3J(H,H) = 10.4 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 41.4 (s; C3), 41.7 (s; C4), 54.9 (s; C2), 80.7 (s; Cp), 118.9 (s; C6), 137.4 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 3.9, 10.9 ppm (AB system, ^2J(P,P) = 86 Hz); elemental analysis (%) calcd for $C_{47}H_{43}F_6P_3RuS$ (947.9): calcd: C 59.55, H 4.57, S 3.38; found: C 59.25, H 4.50, S 3.26.

Compound 9b: Yield 0.17 g (87%); yellow crystalline powder; m.p. 98 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.90 (m, 2H; H3a, H3e), 2.22 (m, 1H; H4), 2.33 (s, 3H; Me), 3.80 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 2.8 Hz, 1H; H2), 4.31 (s, 5H; Cp), 4.95 (dd, ^3J(H,H) = 10.4, ^4J(H,H) = 2.8 Hz, 1H; H6), 5.91 ppm (d, ^3J(H,H) = 10.4 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.3 (s; Me), 41.5 (s; C3), 41.8 (s; C4), 54.7 (s; C2), 80.7 (s; Cp), 119.0 (s; C6), 137.3 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 4.0, 10.9 ppm (AB system, ^2J(P,P) = 86 Hz); elemental analysis (%) calcd for $C_{48}H_{45}F_6P_3RuS$ (961.9): C 59.93, H 4.72, S 3.33; found: C 60.66, H 4.70, S 2.71.

Compound 9c: Yield 0.15 g (79%); yellow crystalline powder; m.p. 160 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.87 (m, 2H; H3a, H3e), 2.25 (m, 1H; H4), 3.65 (dd, ^3J(H,H) = 10.4, ^4J(H,H) = 2.4 Hz, 1H; H2), 4.33 (s, 5H; Cp), 4.79 (s, 3H; OMe), 4.97 (dd, ^3J(H,H) = 10.8, ^4J(H,H) = 2.8 Hz, 1H; H6), 5.89 ppm (d, ^3J(H,H) = 10.8 Hz, 1H; H[5]); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 41.5 (s; C3), 41.9 (s; C4), 54.3 (s; C2), 55.5 (s; OMe), 80.8 (s; Cp), 114.6 (s; C6), 137.1 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 3.8, 11.1 ppm (AB system, ^2J(P,P) = 86 Hz); elemental analysis (%) calcd for $C_{48}H_{45}F_6OP_3RuS$ (977.9): C 58.95, H 4.64, S 3.28; found: C 59.96, H 4.64, S 2.85.

Compound 9d: Yield 0.14 g (73%); yellow powder; m.p. 120 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.87 (m, 2H; H3a, H3e), 2.35 (m, 1H; H4), 3.84 (m, 1H; H2), 4.40 (s, 5H; Cp), 5.02 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 2.8 Hz, 1H; H[6]), 5.90 ppm (dd, ^3J(H,H) = 10.4, ^3J(H,H) = 2.2 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 41.4 (s; C4), 41.7 (s; C3), 55.0 (s; C2), 80.9 (s; Cp), 119.4 (s; C6), 136.8 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 3.7, 9.9 ppm (AB system, ^2J(P,P) = 86 Hz); elemental analysis (%) calcd for $C_{47}H_{42}ClF_6P_3RuS$ (982.4): C 57.47, H 4.31, S 3.26; found: C 57.23, H 4.20, S 2.96.

Compound 9e: Yield 0.17 g (83%); yellow crystalline powder; m.p. 146 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.86 (m, 2H; H3a, H3e), 2.34 (m, 1H; H4), 3.84 (d, ^3J(H,H) = 7.4 Hz, 1H; H2), 4.40 (s, 5H; Cp), 5.02 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 2.4 Hz, 1H; H6), 5.90 ppm (dd, ^3J(H,H) = 10.4, ^3J(H,H) = 2.0 Hz, 1H; H[5]); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 41.4 (s; C4), 41.6 (s; C3), 55.2 (s; C2), 81.0 (s; Cp), 119.4 (s; C6), 136.7 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 3.6, 9.8 ppm (AB system, ^2J(P,P) = 87 Hz); elemental analysis (%) calcd for $C_{47}H_{42}BrF_6P_3RuS$ (1026.8): C 54.98, H 4.12, S 3.12; found: C 54.81, H 3.98, S 2.81.

Compound 9f: Yield 0.16 g (83%); yellow powder; m.p. 134 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.94 (m, 2H; H3a, H3e), 2.72 (m, 1H; H4), 4.20 (dd, ^3J(H,H) = 10.8, ^4J(H,H) = 3.2 Hz, 1H; H2), 4.57 (s, 5H; Cp), 5.20 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 2.8 Hz, 1H; H6), 5.90 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 2.0 Hz, 1H; H5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 3.7, 8.1 ppm (AB system, ^2J(P,P) = 87 Hz); elemental analysis (%) calcd for $C_{47}H_{42}F_6NO_2P_3RuS$ (992.9): C 56.86, H 4.26, S 3.23; found: C 56.65, H 4.42, S 2.96.

Compound 9g: Yield 0.14 g (70%), greyish-yellow powder; m.p. 141 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.89 (m, 2H; H3a, H3e), 2.24 (m, 1H; H4), 2.33 (s, 3H; Me), 3.63 (dd, ^3J(H,H) = 11.0, ^4J(H,H) = 2.8 Hz, 1H; H2), 3.70 (s, 3H; OMe), 4.30 (s, 5H; Cp), 4.91 (dd, ^3J(H,H) = 10.0, ^4J(H,H) = 2.6 Hz, 1H; H6), 5.88 ppm (d, ^3J(H,H) = 10.3 Hz, 1H; H5); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C, TMS): δ = 21.6 (s; Me), 41.8 (s; C3), 42.8 (s; C4), 55.3 (s; C2), 55.8 (s; OMe), 81.9 (s; Cp), 119.8 (s; C6), 138.2 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 3.9, 10.9 ppm (AB system, ^2J(P,P) = 87 Hz); elemental analysis (%) calcd for $C_{49}H_{47}F_6OP_3RuS$ (992.0): C 59.33, H 4.78, S 3.23; found: C 59.09, H 4.87, S 2.98.

Compound 9h: Yield 0.13 g (65%), brownish powder; m.p. 143 °C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): δ = 1.95 (m, 2H; H3a, H3e), 2.30 (m, 1H; H4), 2.37 (s, 3H; Me), 3.63 (dd, ^3J(H,H) = 11.6, ^4J(H,H) = 3.1 Hz, 1H; H[2]), 4.37 (s, 5H; Cp), 5.03 (dd, ^3J(H,H) = 9.9, ^4J(H,H) = 2.7 Hz, 1H; H6), 5.85 ppm (d, ^3J(H,H) = 10.0 Hz, 1H; H5); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C, TMS): δ = 21.4 (s; Me), 41.6 (s; C3), 41.8 (s; C4), 55.0 (s; C2), 81.3 (s; Cp), 120.4 (s; C6), 136.8 ppm (s; C5); ^{31}P NMR (121.5 MHz, CD_2Cl_2, 25 °C, H_3PO_4): δ = 4.8, 10.9 ppm (AB system, ^2J(P,P) = 87 Hz); elemental analysis (%) calcd for $C_{48}H_{44}ClF_6OP_3RuS$ (996.4): C 57.86, H 4.45, S 3.22; found: C 57.34, H 4.22, S 2.86.

Compound 9i: Yield 0.14 g (70%); yellow powder; m.p. 144 °C (decomp); ^{1}H NMR (300 MHz, [D_6]acetone, 25 °C, TMS): δ = 1.23 (s, 3H; Me), 2.25 (m, 2H; H3a, H3e), 2.34 (s, 3H; Me), 2.83 (m, 1H; H4), 3.71 (dd, ^3J(H,H) = 12.1, ^4J(H,H) = 2.8 Hz, 1H; H2), 4.51 (s, 5H; Cp), 4.93 ppm (s, 1H; H6); ^{13}C NMR (75 MHz, [D_6]acetone, 25 °C, TMS): δ = 21.2 (s; Me), 24.4 (s; Me), 42.6 (s; C3), 47.2 (s; C4), 54.1 (s; C2), 81.9 (s; Cp), 115.8 ppm (s; C6), C5 signal obscured by phenyl resonances; ^{31}P NMR (121.5 MHz, [D_6]acetone, 25 °C, H_3PO_4): δ = 3.8, 10.4 ppm (AB system, ^2J(P,P) = 86 Hz); elemental analysis (%) calcd for $C_{49}H_{47}F_6P_3RuS$ (976.0): C 60.30, H 4.85, S 3.29; found: C 59.89, H 4.87, S 3.17.

Kinetic experiments: Reactions were carried out under pseudo-first-order conditions by using a large excess of the dienophile. For every kinetic run, a 1.00 mm quartz cell was filled with 0.35 mL of a 5.0×10^{-4} M stock solution of complex **5a** in acetone. The respective styrene (0.24 mmol) was added with a microliter syringe, and acetone was added to give a total volume of 0.40 mL. The cell was placed in a thermostatted cell holder equipped with a molybdenum thin-film temperature probe. The setup was calibrated against a certified mercury thermometer and was found to be accurate to within $\pm$0.2 K. 60 seconds were allowed to reach thermal equilibrium, and then about 30 spectra in the range λ = 350–705 nm were automatically recorded at regular intervals and over up to four halflifes. A wavelength with maximum change of absorbance was chosen (typically at λ = 510 nm) and the change of absorbance with time approximated by a single-exponential law by using the HP89531 A UV/VIS Operating Software provided by the manufacturer. The results conformed with the conventional data analysis using plots of $\ln\{A_t A_0^{-1}\}$ versus time, which were linear for at least three halflifes. Each entry in Table 3 represents the average of three individual runs.

General procedure for the cycloaddition reaction with norbornadiene and norbornene: The olefin (ca. 16 mmol) was added to a solution of the respective thiocinnamaldehyde complex **5** or **6** (0.20 mmol) in acetone (5 mL). After stirring for 24 h the mixture was evaporated to dryness and the crude product dissolved in dichloromethane (5 mL) and precipitated by adding diethyl ether (10 mL) and hexane (30 mL). The solid was then redissolved in acetone (5 mL) and chromatographed by using dichloro-

methane/acetone 20:1 as the eluent. The brownish fraction was collected and evaporated to a few milliliters, and the product precipitated by adding diethyl ether and hexane.

Compound 10a: Yield 0.16 g (87%); brownish-yellow powder; m.p. 90°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 0.90$ (d, $^2J(H,H) = 9.1$ Hz, 1H; H11′), 1.57 (d, $^2J(H,H) = 9.1$ Hz, 1H; H11), 1.80 (m, 1H; H1), 1.84 (dd, $^3J(H,H) = 11.0$, $^3J(H,H) = 8.2$ Hz, 1H; H7), 2.30 (m, 1H; H8), 2.88 (d, $^3J(H,H) = 8.2$ Hz, 1H; H2), 2.97 (ddd, $^3J(H,H) = 11.0$, $^3J(H,H) = 4.0$, $^4J(H,H) = 2.6$ Hz, 1H; H6), 5.06 (s, 5H; Cp), 5.51 (dd, $^3J(H,H) = 8.5$, $^4J(H,H) = 2.6$ Hz, 1H; H4), 5.82 (dd, $^3J(H,H) = 5.7$, $^3J(H,H) = 2.8$ Hz, 1H; H10), 5.95 (dd, $^3J(H,H) = 5.7$, $^3J(H,H) = 2.9$ Hz, 1H; H9), 6.01 ppm (dd, $^3J(H,H) = 8.5$, $^3J(H,H) = 4.0$ Hz, 1H; H5); *endo* isomer: $\delta = 1.03$ (d, $^2J(H,H) = 9.8$ Hz, 1H; H11′), 1.68 (d, $^2J(H,H) = 9.8$ Hz, 1H; H11), 2.00 (m, 1H; H1), 2.18 (d, $^3J(H,H) = 8.4$ Hz, 1H; H2), 5.51 (s, 5H; Cp), 6.33 ppm (dd, $^3J(H,H) = 9.4$, $^3J(H,H) = 3.0$ Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 44.1$ (s; C11), 45.6 (s; C1/8), 45.9 (s; C1/8), 46.9 (s; C6), 55.0 (s; C7), 65.3 (s; C2), 80.9 (s; Cp), 135.1 (s; C10), 140.5 (s; C5/9), 141.3 ppm (s; C5/9), C4 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *exo* isomer: $\delta = 6.0$, 6.9 ppm (AB system, $^2J(P,P) = 89$ Hz); *endo* isomer: $\delta = 6.8$, 7.9 ppm (AB system, $^2J(P,P) = 85$ Hz); elemental analysis (%) calcd for $C_{46}H_{43}F_6P_3RuS$ (935.9): C 59.04, H 4.63, S 3.43; found: C 58.76, H 4.65, S 3.28.

Compound 10b: Yield 0.16 g (82%); yellow crystalline powder; m.p. 171°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 0.90$ (d, $^2J(H,H) = 9.4$ Hz, 1H; H11′), 1.58 (d, $^2J(H,H) = 9.4$ Hz, 1H; H11), 1.75 (m, 1H; H1), 1.90–1.99 (m, 1H; H7), 2.27 (m, 1H; H8), 2.86 (d, $^3J(H,H) = 8.0$ Hz, 1H; H2), 3.30–3.37 (m, 1H; H6), 3.78 (s, 3H; OMe), 5.05 (s, 5H; Cp), 5.47 (dd, $^3J(H,H) = 8.4$, $^4J(H,H) = 2.8$ Hz, 1H; H4), 5.80 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.2$ Hz, 1H; H10), 5.95 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.0$ Hz, 1H; H9), 6.00 ppm (dd, $^3J(H,H) = 8.6$, $^3J(H,H) = 4.2$ Hz, 1H; H5); *endo* isomer: $\delta = 0.97$ (d, $^2J(H,H) = 9.2$ Hz, 1H; H11′), 1.52 (d, $^2J(H,H) = 9.2$ Hz, 1H; H11), 1.67 (m, 1H; H1), 2.34 (m, 1H; H8), 2.40 (d, $^3J(H,H) = 8.8$ Hz, 1H; H2), 3.88 (s, 3H; OMe), 5.15 (s, 5H; Cp), 5.42–5.46 (m, 1H; H4), 5.86 (dd, $^3J(H,H) = 5.4$, $^3J(H,H) = 3.0$ Hz, 1H; H10), 6.26 (dd, $^3J(H,H) = 5.4$, $^3J(H,H) = 4.0$ Hz, 1H; H9), 6.33 ppm (dd, $^3J(H,H) = 9.0$, $^3J(H,H) = 3.4$ Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 44.4$ (s; C11), 45.6 (s; C1/8), 45.7 (s; C1/8), 54.9 (s; OMe/C7), 55.1 (s; OMe/C7), 65.0 (s; C2), 80.8 (s; Cp), 134.7 (s; C10), 140.7 (s; C5/9), 141.2 ppm (s; C5/9), C4 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *exo* isomer: $\delta = 6.1$, 7.1 ppm (AB system, $^2J(P,P) = 89$ Hz); *endo* isomer: $\delta = 7.5$, 8.2 ppm (AB system, $^2J(P,P) = 89$ Hz); elemental analysis (%) calcd for $C_{47}H_{45}F_6OP_3RuS$ (965.9): C 58.44, H 4.70, S 3.32; found: C 58.47, H 4.61, S 3.31.

Compound 10c: Yield 0.16 g (81%); yellow crystalline powder; m.p. 153°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 0.88$ (d, $^2J(H,H) = 8.7$ Hz, 1H; H11′), 1.54 (d, $^2J(H,H) = 8.7$ Hz, 1H; H11), 1.75–1.83 (m, 2H; H1, H7), 2.29 (m, 1H; H8), 2.85–3.03 (m, 1H; H2, H6), 2.96 (s, 6H; NMe_2), 5.06 (s, 5H; Cp), 5.48 (dd, $^3J(H,H) = 8.4$, $^4J(H,H) = 2.4$ Hz, 1H; H4), 5.82 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.2$ Hz, 1H; H10), 5.93 ppm (m, 2H; H5, H9); *endo* isomer: $\delta = 1.00$ (d, $^2J(H,H) = 8.6$ Hz, 1H; H11′), 1.63 (d, $^2J(H,H) = 8.6$ Hz, 1H; H11), 1.98 (m, 1H; H1), 2.16 (d, $^3J(H,H) = 11.2$ Hz, 1H; H2), 2.97 (s, 6H; NMe_2), 5.10 (s, 5H; Cp), 5.85–5.88 (m, 1H; H10), 6.27 ppm (dd, $^3J(H,H) = 8.4$, $^3J(H,H) = 2.4$ Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 42.8$ (s; NMe_2), 44.3 (s; C11), 46.0, 46.1, 46.3 (all s; C1, C6, C8), 55.2 (s; C7), 65.4 (s; C2), 81.2 (s; Cp), 135.2 (s; C10), 140.8 (s; C5/9), 141.6 ppm (s; C5/9), C4 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *exo* isomer: $\delta = 6.1$, 6.9 ppm (AB system, $^2J(P,P) = 89$ Hz); *endo* isomer: $\delta = 6.8$, 8.0 ppm (AB system, $^2J(P,P) = 90$ Hz); elemental analysis (%) calcd for $C_{48}H_{48}F_6NP_3RuS$ (979.0): C 58.89, H 4.94, N 1.43, S 3.28; found: C 58.17, H 4.82, N 1.31, S 2.75.

Compound 11a: Yield 0.17 g (90%); grey powder; m.p. 136°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 1.12$ (d, $^2J(H,H) = 9.2$ Hz, 1H; H$^{11'}$), 1.56 (d, $^2J(H,H) = 9.2$ Hz, 1H; H11), 1.75 (dd, $^3J(H,H) = 9.2$, $^3J(H,H) = 8.4$ Hz, 1H; H7), 1.78 (m, 1H; H1), 2.30 (m, 1H; H8), 2.51 (d, $^3J(H,H) = 8.4$ Hz, 1H; H2), 2.70–2.74 (m, 1H; H6), 4.85 (s, 5H; Cp), 5.14 (dd, $^3J(H,H) = 8.4$, $^4J(H,H) = 3.0$ Hz, 1H; H4), 5.68 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.0$ Hz, 1H; H10), 5.84–5.89 (m, 1H; H9), 5.91 ppm (dd, $^3J(H,H) = 8.4$, $^3J(H,H) = 3.4$ Hz, 1H; H5); *endo* isomer: $\delta = 0.98$ (d, $^2J(H,H) = 8.8$ Hz, 1H; H11′), 1.63 (d, $^2J(H,H) = 8.8$ Hz, 1H; H11), 2.10 (m, 1H; H1), 4.58 (d, $^3J(H,H) = 9.2$ Hz, 1H; H^4), 5.07 (s, 5H; Cp), 5.33 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.2$ Hz, 1H; H10), 5.76–5.80 (m, 1H; H9), 6.10 ppm (dd, $^3J(H,H) = 8.8$, $^3J(H,H) = 3.3$ Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 44.0$ (s; C11), 46.0 (s; C1/8), 46.4 (s; C1/8), 46.8 (s; C6), 54.0 (s; C7), 61.9 (s; C2), 83.1 (s; Cp), 126.6 (s; C4), 135.1 (s; C10), 140.5 (s; C5/9), 140.7 ppm (s; C5/9); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *exo* isomer: $\delta = 71.3$, 74.9 ppm (AB system, $^2J(P,P) = 26$ Hz); *endo* isomer: $\delta = 71.0$, 72.9 ppm (AB system, $^2J(P,P) = 28$ Hz); elemental analysis (%) calcd for $C_{47}H_{45}F_6P_3RuS$ (949.9): C 59.43, H 4.78, S 3.38; found: C 59.54, H 4.93, S 3.69.

Compound 11b: Yield 0.17 g (87%); brownish powder; m.p. 139°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 1.11$ (d, $^2J(H,H) = 10.0$ Hz, 1H; H11′), 1.60–1.68 (m, 1H; H7), 1.75 (m, 1H; H1), 1.76 (d, $^2J(H,H) = 10.0$ Hz, 1H; H11), 2.25 (m, 1H; H8), 2.46 (d, $^3J(H,H) = 8.0$ Hz, 1H; H2), 3.13–3.20 (m, 1H; H6), 3.78 (s, 3H; OMe), 4.84 (s, 5H; Cp), 5.08 (dd, $^3J(H,H) = 8.8$, $^4J(H,H) = 2.8$ Hz, 1H; H4), 5.63 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 2.8$ Hz, 1H; H10), 5.86 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.2$ Hz, 1H; H9), 5.90 ppm (dd, $^3J(H,H) = 8.8$, $^3J(H,H) = 3.6$ Hz, 1H; H5); *endo* isomer: $\delta = 0.94$ (d, $^2J(H,H) = 8.8$ Hz, 1H; H11′), 1.60 (m, 1H; H1), 1.99 (d, $^2J(H,H) = 8.8$ Hz, 1H; H11), 2.39 (dd, $^3J(H,H) = 8.8$, $^3J(H,H) = 6.4$ Hz, 1H; H7), 3.87 (s, 3H; OMe), 4.13 (ddd, $^3J(H,H) = 6.0$, $^3J(H,H) = 3.6$, $^4J(H,H) = 2.8$ Hz, 1H; H6), 4.29 (d, $^3J(H,H) = 8.8$ Hz, 1H; H4), 5.10 (s, 5H; Cp), 5.33 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.2$ Hz, 1H; H10), 5.79 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 2.8$ Hz, 1H; H9), 6.12 ppm (dd, $^3J(H,H) = 9.2$, $^3J(H,H) = 3.2$ Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 44.1$ (s; C11), 45.9 (s; C1/8), 46.3 (s; C1/8), 46.9 (s; C6), 54.1 (s; OMe/C7), 54.8 (s; OMe/C7), 61.4 (s; C2), 82.9 (s; Cp), 125.2 (s; C4), 139.8 (s; C5/9), 140.5 ppm (s; C5/9), C10 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *exo* isomer: $\delta = 71.3$, 75.1 ppm (AB system, $^2J(P,P) = 26$ Hz); *endo* isomer: $\delta = 72.4$, 73.0 ppm (AB system, $^2J(P,P) = 28$ Hz); elemental analysis (%) calcd for $C_{48}H_{47}F_6OP_3RuS$ (979.9): C 58.83, H 4.83, S 3.27; found: C 58.06, H 4.84, S 3.07.

Compound 11c: Yield 0.16 g (78%); yellow powder; m.p. 139°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 1.11$ (d, $^2J(H,H) = 9.4$ Hz, 1H; H11′), 1.51 (dd, $^3J(H,H) = 9.0$, $^3J(H,H) = 9.0$ Hz, 1H; H7), 1.73 (d, $^2J(H,H) = 9.4$ Hz, 1H; H11), 1.78 (m, 1H; H1), 2.34 (m, 1H; H8), 2.49 (d, $^3J(H,H) = 8.0$ Hz, 1H; H2), 2.60–2.70 (m, 1H; H7), 2.94 (s, 6H; NMe_2), 4.84 (s, 5H; Cp), 5.09 (dd, $^3J(H,H) = 8.4$, $^4J(H,H) = 3.0$ Hz, 1H; H4), 5.67 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 3.2$ Hz, 1H; H10), 5.88 (dd, $^3J(H,H) = 5.8$, $^3J(H,H) = 3.2$ Hz, 1H; H9), 5.90 ppm (dd, $^3J(H,H) = 9.2$, $^3J(H,H) = 3.6$ Hz, 1H; H5); *endo* isomer: $\delta = 0.98$ (d, $^2J(H,H) = 8.8$ Hz, 1H; H11′), 1.65 (d, $^2J(H,H) = 8.8$ Hz, 1H; H11), 2.31 (m, 1H; H8), 2.94 (s, 6H; NMe_2), 4.53 (d, $^3J(H,H) = 9.2$ Hz, 1H; H4), 5.06 (s, 5H; Cp), 5.33 (dd, $^3J(H,H) = 6.2$, $^3J(H,H) = 3.2$ Hz, 1H; H10), 5.81 (dd, $^3J(H,H) = 5.6$, $^3J(H,H) = 2.8$ Hz, 1H; H9), 6.07 ppm (dd, $^3J(H,H) = 9.2$, $^3J(H,H) = 3.2$ Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 42.6$ (s; NMe_2), 44.0 (s; C11), 45.9, 46.1, 46.5 (all s; C1, C6, C8), 53.9 (s; C7), 65.0 (s; C2), 83.1 (s; Cp), 135.4 (s; C10), 140.5 (s; C5/9), 141.6 ppm (s; C5/9), C4 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *exo* isomer: $\delta = 71.1$, 74.9 ppm (AB system, $^2J(P,P) = 26$ Hz); *endo* isomer: $\delta = 71.1$, 73.1 ppm (AB system, $^2J(P,P) = 28$ Hz); elemental analysis (%) calcd for $C_{49}H_{50}F_6NP_3RuS$ (993.0): C 59.27, H 5.08, N 1.41, S 3.23; found: C 58.79, H 5.31, N 1.28, S 3.14.

Compound 12a: Yield 0.17 g (91%); brownish-yellow powder; m.p. 125°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *exo* isomer: $\delta = 0.44$ (d, $^2J(H,H) = 11.0$ Hz, 1H; H11′), 0.82–0.99 (m, 2H; H9a, H10a), 1.18–1.34 (m, 3H; H1, H9e, H10e), 1.50 (d, $^2J(H,H) = 11.0$ Hz, 1H; H11), 1.68 (dd, $^3J(H,H) = 9.4$, $^3J(H,H) = 9.0$ Hz, 1H; H7), 1.84 (m, 1H; H8), 2.73 (dd, $^3J(H,H) = 9.6$, $^3J(H,H) = 2.6$ Hz, 1H; H6), 2.75 (d, $^3J(H,H) = 9.3$ Hz, 1H; H2), 5.10 (s, 5H; Cp), 5.45 (dd, $^3J(H,H) = 8.5$, $^4J(H,H) =$

2.6 Hz, 1H; H4), 5.89 ppm (dd, ^3J(H,H) = 8.5, ^3J(H,H) = 4.1 Hz, 1H; H^5); *endo* isomer: δ = 5.51 ppm (s, 5H; Cp), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 28.5, 29.5 (both s; C9, C10), 34.7 (s; C11), 41.1, 41.4 (both s; C1, C8), 45.7 (s; C6), 56.8 (s; C7), 67.1 (s; C2), 81.2 (s; Cp), 126.8 (s; C4), 139.9 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *exo* isomer: δ = 6.3, 7.3 ppm (AB system, ^2J(P,P) = 89 Hz); *endo* isomer: δ = 6.2, 7.4 ppm (AB system, ^2J(P,P) = 82 Hz); elemental analysis (%) calcd for $C_{46}H_{45}F_6P_3RuS$ (937.9): C 58.91, H 4.84, S 3.42; found: C 58.82, H 4.88, S 3.37.

Compound 12b: Yield 0.15 g (71%); yellow powder; m.p. 142 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 0.45 (d, ^2J(H,H) = 10.0 Hz, 1H; H11′), 0.84–0.99 (m, 2H; H9a, H10a), 1.19–1.29 (m, 4H; H1, H9e, H10e, H11), 1.78 (m, 1H; H8), 1.79–1.84 (m, 1H; H7), 2.73 (d, ^3J(H,H) = 8.0 Hz, 1H; H2), 3.07–3.12 (m, 1H; H6), 3.77 (s, 3H; OMe), 5.05 (s, 5H; Cp), 5.40 (dd, ^3J(H,H) = 8.8, ^4J(H,H) = 2.4 Hz, 1H; H4), 5.89 ppm (dd, ^3J(H,H) = 8.8, ^3J(H,H) = 4.4 Hz, 1H; H^5); *endo* isomer: δ = 0.65 (d, ^2J(H,H) = 9.2 Hz, 1H; H11′), 2.66 (d, ^3J(H,H) = 8.2 Hz, 1H; H2), 3.90 (s, 3H; OMe), 5.14 (s, 5H; Cp), 6.31–6.35 ppm (m, 1H; H^5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 28.6, 29.5 (both s; C9, C10), 36.7 (s; C11), 41.1, 41.5 (both s; C1, C8), 45.6 (s; C6), 56.2. (s; OMe), 56.3 (s; C7), 68.2 (s; C2), 81.0 (s; Cp), 120.8 (s; C4), 140.2 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *exo* isomer: δ = 6.3, 7.5 ppm (AB system, ^2J(P,P) = 89 Hz); *endo* isomer: δ = 7.4, 8.5 ppm (AB system, ^2J(P,P) = 89 Hz); elemental analysis (%) calcd for $C_{47}H_{47}F_6OP_3RuS$ (967.9): C 58.32, H 4.89, S 3.31; found: C 58.04, H 4.77, S 3.16.

Compound 12c: Yield 0.17 g (88%); brownish powder; m.p. 122 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 0.44 (d, ^2J(H,H) = 9.6 Hz, 1H; H11′), 0.79–0.89 (m, 2H; H9a, H10a), 1.10–1.33 (m, 3H; H9e, H10e, H11), 1.32 (m, 1H; H1), 1.65 (dd, ^3J(H,H) = 9.2, ^3J(H,H) = 8.8 Hz, 1H; H7); 1.78 (m, 1H; H8), 2.70–2.76 (m, 2H; H2, H6), 3.02 (s, 6H; NMe_2), 5.07 (s, 5H; Cp), 5.40 (dd, ^3J(H,H) = 8.8, ^4J(H,H) = 2.6 Hz, 1H; H4), 5.77–5.81 ppm (m, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 28.2, 29.2 (both s; C9, C10), 34.4 (s; C11), 40.9, 41.1, (both s; C1, C8), 44.1 (s; NMe_2), 46.8 (s; C6), 56.4 (s; C7), 66.8 (s; C2), 80.9 (s; Cp), 139.2 ppm (s; C5), C4 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *exo* isomer: δ = 6.4, 7.3 ppm (AB system, ^2J(P,P) = 89 Hz); elemental analysis (%) calcd for $C_{48}H_{50}F_6NP_3RuS$ (981.0): C 58.77, H 5.14, N 1.43, S 3.27; found: C 58.49, H 5.26, N 1.30, S 3.00.

Compound 13a: Yield 0.17 g (90%); greyish-yellow powder; m.p. 134 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 0.68 (d, ^2J(H,H) = 10.6 Hz, 1H; H11′), 0.79–0.90 (m, 2H; H9a, H10a), 1.17–1.35 (m, 2H; H9e, H10e), 1.43 (dd, ^3J(H,H) = 10.5, ^3J(H,H) = 7.4 Hz, 1H; H7), 1.46 (d, ^2J(H,H) = 10.6 Hz, 1H; H11), 1.81 (m, 1H; H8), 2.39 (d, ^3J(H,H) = 7.4 Hz, 1H; H2), 2.51 (ddd, ^3J(H,H) = 10.5, ^3J(H,H) = 4.0, ^4J(H,H) = 3.0 Hz, 1H; H6), 4.86 (s, 5H; Cp), 5.04 (dd, ^3J(H,H) = 8.8, ^4J(H,H) = 3.0 Hz, 1H; H4), 5.82 ppm (dd, ^3J(H,H) = 8.8, ^3J(H,H) = 4.0 Hz, 1H; H5); *endo* isomer: δ = 1.95 (d, ^3J(H,H) = 8.8 Hz, 1H; H2), 5.06 (s, 5H; Cp), 6.07 ppm (dd, ^3J(H,H) = 9.2, ^3J(H,H) = 3.6 Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 28.8, 29.1 (both s; C9, C10), 34.4 (s; C11), 41.2, 41.5 (both s; C1, C8), 45.5 (s; C6), 56.4 (s; C7), 63.6 (s; C2), 83.1 (s; Cp), 126.4 (s; C4), 139.4 ppm (s; C5); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *exo* isomer: δ = 71.2, 75.0 ppm (AB system, ^2J(P,P) = 26 Hz); *endo* isomer: δ = 72.6, 75.0 ppm (AB system, ^2J(P,P) = 26 Hz); elemental analysis (%) calcd for $C_{47}H_{47}F_6P_3RuS$ (951.9): C 59.30, H 4.98, S 3.37; found: C 59.01, H 4.93, S 3.43.

13b: Yield 0.16 g (81%); brownish yellow powder; m.p. 140 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 0.68 (d, ^2J(H,H) = 10.4 Hz, 1H; H11′), 0.77–0.86 (m, 2H; H9a, H10a), 1.17–1.20 (m, 2H; H9e, H10e), 1.24 (m, 1H; H1), 1.48–1.54 (m, 2H; H7, H11), 1.74 (m, 1H; H8), 2.35 (d, ^3J(H,H) = 8.8 Hz, 1H; H2), 2.57–2.64 (m, 1H; H6), 3.77 (s, 3H; OMe), 4.85 (s, 5H; Cp), 4.98 (dd, ^3J(H,H) = 8.8, ^4J(H,H) = 2.2 Hz, 1H; H4), 5.80 ppm (dd, ^3J(H,H) = 8.8, ^3J(H,H) = 3.6 Hz, 1H; H5); *endo* isomer: δ = 0.85 (d, ^2J(H,H) = 10.8 Hz, 1H; H11′), 0.92–0.95 (m, 2H; H9a, H10a), 1.80 (m, 1H; H8), 2.21 (d, ^3J(H,H) = 9.2 Hz, 1H; H2), 3.90 (s, 3H; OMe), 4.31 (d, ^3J(H,H) = 9.3 Hz, 1H; H4), 5.08 (s, 5H; Cp), 6.12 ppm (dd, ^3J(H,H) = 9.2, ^3J(H,H) = 3.6 Hz, 1H; H5), other signals obscured by *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 29.0, 29.1 (both s; C9, C10), 34.5 (s; C11), 41.4, 41.5 (both s; C1, C8), 45.3 (s; C6), 55.4. (s; OMe), 55.5 (s; C7), 83.0 (s; Cp), 140.2 ppm (s; C5), C4 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *exo* isomer: δ = 71.4, 75.2 ppm (AB system, ^2J(P,P) = 26 Hz); *endo* isomer: δ = 72.3, 73.4 ppm (AB system, ^2J(P,P) = 28 Hz); elemental analysis (%) calcd for $C_{48}H_{49}F_6OP_3RuS$ (982.0): C 58.71, H 5.03, S 3.27; found: C 58.46, H 4.74, S 3.13.

Compound 13c: Yield 0.16 g (81%); greyish powder; m.p. 139 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 0.67 (d, ^2J(H,H) = 10.4 Hz, 1H; H11′), 0.78–0.86 (m, 2H; H9a, H10a), 1.17–1.24 (m, 2H; H9e, H10e), 1.26 (m, 1H; H1), 1.36 (dd, ^3J(H,H) = 10.4, ^3J(H,H) = 8.0 Hz, 1H; H7); 1.44 (d, ^2J(H,H) = 10.6 Hz, 1H; H11), 1.84 (m, 1H; H8), 2.37 (d, ^3J(H,H) = 8.0 Hz, 1H; H2), 2.43 (ddd, ^3J(H,H) = 10.4, ^3J(H,H) = 3.6, ^4J(H,H) = 2.8 Hz, 1H; H6), 2.93 (s, 6H; NMe_2), 4.84 (s, 5H; Cp), 4.99 (dd, ^3J(H,H) = 8.8, ^4J(H,H) = 2.8 Hz, 1H; H4), 5.79 ppm (dd, ^3J(H,H) = 8.8, ^3J(H,H) = 3.6 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *exo* isomer: δ = 28.8, 29.1 (both s; C9, C10), 33.4 (s; C11), 41.2, 41.5, (both s; C1, C8), 41.4 (s; NMe_2), 44.2 (s; C6), 56.5 (s; C7), 63.7 (s; C2), 85.9 (s; Cp), 139.2 ppm (s; C5), C4 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *exo* isomer: δ = 71.3, 75.0 ppm (AB system, ^2J(P,P) = 26 Hz); elemental analysis (%) calcd for $C_{49}H_{52}F_6NP_3RuS$ (995.0): C 59.15, H 5.27, N 1.41, S 3.22; found: C 58.90, H 5.05, N 1.28, S 2.97.

General procedure for cycloaddition reactions with α,β-unsaturated carbonyl compounds: The freshly distilled dienophile (ca. 16 mmol) was added to a solution of the thiocinnamaldehyde complex **5a**,**b** (0.20 mmol) in acetone (5 mL). After stirring for 5 d the mixture was evaporated to dryness and the crude product dissolved in dichloromethane (3 mL) and precipitated by adding diethyl ether (5 mL) and hexane (15 mL). The solid was redissolved in acetone (3 mL) and chromatographed by using dichloromethane/acetone 20:1 as the eluent. The dark yellow fraction was collected and evaporated to a few milliliters, and the product precipitated by adding diethyl ether and hexane.

Compound 14a: Yield 0.16 g (88%); yellow crystalline powder; m.p. 155 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *endo* isomer: δ = 2.07 (d, ^2J(H,H) = 13.0 Hz, 1H; H2e), 2.45 (dd, ^2J(H,H) = 13.0, ^3J(H,H) = 12.0 Hz, 1H; H2a), 3.68–3.76 (m, 2H; H3, H4), 5.04 (s, 5H; Cp), 5.38 (d, ^3J(H,H) = 10.6 Hz, 1H; H6), 5.80 (dd, ^3J(H,H) = 10.6, ^3J(H,H) = 3.2 Hz, 1H; H5), 9.09 ppm (s, 1H; CHO); *exo* isomer: δ = 2.39 (m, 1H, H2), 2.86 (m, 1H, H4), 3.05 (m, 1H, H3), 5.10 (s, 5H; Cp), 5.87 (d, ^3J(H,H) = 10.0 Hz, 1H; H5), 8.36 ppm (s, 1H; CHO), other signals obscured by the *endo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *endo* isomer: δ = 37.7 (s; C2), 40.1 (s; C4), 53.0 (s; C3), 81.8 (s; Cp), 123.9 (s; C6), 198.7 ppm (s; C=O), C5 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *endo* isomer: δ = 7.2 ppm (s); *exo* isomer: δ = 5.8, 7.2 ppm (AB system, ^2J(P,P) = 91 Hz); elemental analysis (%) calcd for $C_{42}H_{39}F_6OP_3RuS$ (899.8): C 56.06, H 4.39, S 3.56; found: C 56.28, H 4. 14, S 3.41.

Compound 14b: Yield 0.15 g (83%); yellow crystalline powder; m.p. 117 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *endo* isomer: δ = 0.85 (s, 3H; CH_3), 2.07/2.08 (AB system, ^2J(H,H) = 13.5 Hz, 2H; H2a, H2e), 3.41 (m, 1H; H4), 5.08 (s, 5H; Cp), 5.43 (dd, ^3J(H,H) = 10.2, ^4J(H,H) = 2.0 Hz, 1H; H6), 5.87 (dd, ^3J(H,H) = 10.2, ^3J(H,H) = 3.9 Hz, 1H; H5), 9.20 ppm (s, 1H; CHO); *exo* isomer: δ = 0.47 (s, 3H; CH_3), 1.85/2.27 (AB system, ^2J(H,H) = 12.5 Hz, 2H; H2a, H2e), 3.73 (m, 1H; H4), 4.38 (s, 5H; Cp), 5.40 (dd, ^3J(H,H) = 10.4, ^4J(H,H) = 2.0 Hz, 1H; H6), 5.82 (dd, ^3J(H,H) = 10.4, ^3J(H,H) = 3.7 Hz, 1H; H5), 8.95 ppm (s, 1H; CHO); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *endo* isomer: δ = 20.2 (s; CH_3), 42.9 (s; C2), 48.0 (s; C4), 65.6 (s; C3), 82.8 (s; Cp), 124.1 (s; C6), 201.6 ppm (s; C=O), C5 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): *endo* isomer: δ = 6.7, 7.6 ppm (AB system, ^2J(P,P) = 91 Hz); *exo* isomer: δ = 6.9 ppm (s); elemental analysis (%) calcd for $C_{43}H_{41}F_6OP_3RuS$ (913.8): C 56.52, H 4.52, S 3.51; found: C 56.21, H 4.42, S 3.43.

Compound 14c: Yield 0.15 g (81%); brownish powder; m.p. 123°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 0.87 (s, 3H; CH_3), 1.59/2.27 (AB system, ^2J(H,H) = 12.4 Hz, 2H; H2a, H2e), 3.73 (s, 3H; OMe), 3.81 (dd, ^3J(H,H) = 4.8, ^4J(H,H) = 2.0 Hz, 1H; H4), 5.10 (s, 5H; Cp), 5.39 (d, ^3J(H,H) = 10.0 Hz, 1H; H6), 5.73 (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 4.8 Hz, 1H; H5), 9.10 ppm (s, 1H; CHO); *exo* isomer: δ = 0.46 (s, 3H; CH_3), 1.81/2.39 (AB system, ^2J(H,H) = 12.8 Hz, 2H; H2a, H2e), 3.70 (s, 3H; OMe), 4.16 (dd, ^3J(H,H) = 3.0, ^4J(H,H) = 3.0 Hz, 1H; H4), 5.07 (s, 5H; Cp), 5.39 (d, ^3J(H,H) = 10.0 Hz, 1H; H6), 5.75 (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 4.8 Hz, 1H; H5), 8.89 ppm (s, 1H; CHO); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 19.7 (s; CH_3), 38.6 (s; C4), 41.3 (s; C2), 55.2 (s; OMe), 81.4 (s; Cp), 200.8 ppm (s; C=O), C3 signal not detected, C5 and C6 signals obscured by phenyl resonances; *exo* isomer: δ = 15.9 (s; CH_3), 35.8 (s; C4), 44.1 (s; C2), 55.0 (s; OMe), 81.7 (s; Cp), 200.4 ppm (s; C=O), C3 signal not detected, C5 and C6 signals obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *endo* isomer: δ = 6.8, 7.5 ppm (AB system, ^2J(P,P) = 91 Hz); *exo* isomer: δ = 7.1 ppm (s); elemental analysis (%) calcd for $C_{44}H_{43}F_6O_2P_3RuS$ (943.9): C 55.99, H 4.59, S 3.40; found: C 56.51, H 4.36, S 3.53.

Compound 14d: Yield 0.14 g (76%); red crystalline powder; m.p. 176°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 1.75 (d, ^2J(H,H) = 13.2 Hz, 1H; H2e), 1.78 (s, 3H; CH_3), 2.44 (dd, ^2J(H,H) = 13.2, ^3J(H,H) = 11.2 Hz, 1H; H2a), 2.95 (ddd, ^3J(H,H) = 11.2, ^3J(H,H) = 5.2, ^3J(H,H) = 2.4 Hz, 1H; H3), 3.86 (m, 1H; H4), 5.07 (s, 5H; Cp), 5.38 (d, ^3J(H,H) = 10.0 Hz, 1H; H6), 5.92 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 5.1 Hz, 1H; H5); *exo* isomer: δ = 1.34 (s, 3H; CH_3), 2.48 (dd, ^2J(H,H) = 13.0, ^3J(H,H) = 10.4 Hz, 1H; H2a), 2.82 (ddd, ^3J(H,H) = 10.4, ^3J(H,H) = 10.4, ^3J(H,H) = 2.4 Hz, 1H; H3), 3.53 (ddd, ^3J(H,H) = 10.0, ^3J(H,H) = 2.4, ^4J(H,H) = 2.4 Hz, 1H; H4), 5.03 (s, 5H; Cp), 5.29 (d, ^3J(H,H) = 10.4 Hz, 1H; H6), 5.76 ppm (dd, ^3J(H,H) = 10.4, ^3J(H,H) = 2.8 Hz, 1H; H5); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 29.0 (s; CH_3), 34.6 (s; C2), 40.5 (s; C4), 51.1 (s; C3), 81.4 (s; Cp), 123.9 (s; C6), 206.2 ppm (s; C=O), C5 signal obscured by phenyl resonances; *exo* isomer: δ = 29.8 (s; CH_3), 42.8 (s; C4), 53.4 (s; C3), 81.7 (s; Cp), 207.6 ppm (s; C=O), other signal obscured by *endo* isomer; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *endo* isomer: δ = 6.9 ppm (s); elemental analysis (%) calcd for $C_{43}H_{41}F_6OP_3RuS$ (913.8): C 56.52, H 4.52, S 3.51; found: C 56.78, H 4.33, S 3.30.

Compound 14e: Yield 0.15 g (81%); red crystalline powder; m.p. 103°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 1.03 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3), 1.68 (d, ^2J(H,H) = 13.2 Hz, 1H; H2e), 2.43 (dd, ^2J(H,H) = 13.0, ^3J(H,H) = 12.2 Hz, 1H; H2a), 2.83 (ddd, ^3J(H,H) = 12.0, ^3J(H,H) = 5.2, ^3J(H,H) = 2.1 Hz, 1H; H3), 3.83–3.91 (m, 3H; OCH_2, H4), 5.01 (s, 5H; Cp), 5.49 (d, ^3J(H,H) = 10.0 Hz, 1H; H6), 5.93 ppm (dd, ^3J(H,H) = 10.0, ^3J(H,H) = 5.6 Hz, 1H; H5); *exo* isomer: δ = 0.99 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 4.83 ppm (s, 5H; Cp), other signals obscured by *endo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *endo* isomer: δ = 13.9 (s; CH_3), 25.4 (s; C2), 40.7 (s; C4), 44.4 (s; C3), 61.0 (s; OCH_2), 81.5 (s; Cp), 124.4 (s; C6), 170.1 ppm (s; C=O), C5 signal obscured by phenyl resonances; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, H_3PO_4): *endo* isomer: δ = 7.3 ppm (s); elemental analysis (%) calcd for $C_{44}H_{43}F_6O_2P_3RuS$ (943.9): C 55.99, H 4.59, S 3.40; found: C 55.58, H 4.54, S 3.22.

General procedure for the cycloaddition reaction with ethyl propiolate: The alkyne (1.0 mL, 10.0 mmol) was added to a solution of the respective thiocinnamaldehyde complex **5c**,**e**,**f** (0.20 mmol) in acetone (5 mL). After stirring for 10 d the mixture was evaporated to dryness and the crude product dissolved in dichloromethane (5 mL) and precipitated by adding diethyl ether (10 mL) and hexane (30 mL). The solid was then redissolved in acetone (5 mL) and chromatographed by using dichloromethane/acetone 20:1 as the eluent. The brownish fraction was collected and evaporated to a few milliliters, and the product precipitated by adding diethyl ether and hexane.

Compound 15a: Yield 0.12 g (62%); brownish powder; m.p. 113°C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): δ = 1.19 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 3.73 (s, 3H; OMe), 4.04 (q of AB systems, ^3J(H,H) = 7.0 Hz, ^2J(H,H) not determined, 2H; CH_2), 4.39 (d, ^3J(H,H) = 5.2 Hz, 1H; H4), 5.01 (s, 5H; Cp), 5.08 (dd, ^3J(H,H) = 9.7, ^4J(H,H) = 2.8 Hz, 1H; H6), 5.88 (dd, ^3J(H,H) = 9.7, ^3J(H,H) = 5.3 Hz, 1H; H5), 6.31 ppm (d, ^4J(H,H) = 2.8 Hz, 1H; H2); ^{13}C NMR (75 MHz, CD_2Cl_2, 25°C, TMS): δ = 14.3 (s; CH_3), 39.1 (s; C4), 55.6 (s; OMe), 61.9 (s; OCH_2), 82.7 (s; Cp), 117.8 (s; C6), 163.5 ppm (s; C=O), other olefinic signals obscured by phenyl resonances; ^{31}P NMR (121.5 MHz, CD_2Cl_2, 25°C, H_3PO_4): δ = 6.6 ppm (s); elemental analysis (%) calcd for $C_{45}H_{43}F_6O_3P_3RuS$ (971.9): C 55.61, H 4.46, S 3.30; found: C 55.02, H 4.64, S 2.91.

Compound 15b: Yield 0.10 g (51%); maroon powder; m.p. 138°C (decomp); ^{1}H NMR (300 MHz, [D_6]acetone, 25°C, TMS): δ = 1.18 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 4.05 (q of AB systems, ^3J(H,H) = 7.1 Hz, ^2J(H,H) not determined, 2H; CH_2), 4.58 (d, ^3J(H,H) = 5.4 Hz, 1H; H4), 5.29 (s, 5H; Cp), 5.48 (dd, ^3J(H,H) = 9.9, ^4J(H,H) = 2.7 Hz, 1H; H6), 6.05 (dd, ^3J(H,H) = 9.9, ^3J(H,H) = 5.4 Hz, 1H; H5), 6.49 ppm (d, ^4J(H,H) = 2.7 Hz, 1H; H2); ^{13}C NMR (75 MHz, [D_6]acetone, 25°C, TMS): δ = 14.4 (s; CH_3), 39.8 (s; C4), 61.9 (s; OCH_2), 83.4 (s; Cp), 119.9 (s; C6), 141.6 (s; C5), 164.6 ppm (s; C=O), other olefinic signals obscured by phenyl resonances; ^{31}P NMR (121.5 MHz, [D_6]acetone, 25°C, H_3PO_4): δ = 6.5 ppm (s); elemental analysis (%) calcd for $C_{44}H_{40}ClF_6O_2P_3RuS$ (976.3): C 54. 31, H 4.13, S 3.28; found: C 54.44, H 4.30, S 2.88.

Compound 15c: Yield 0.125 g (65%); maroon powder; m.p. 116°C (decomp); ^{1}H NMR (300 MHz, [D_6]acetone, 25°C, TMS): δ = 1.19 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_3), 1.59 (s, 3H; CH_3), 4.04 (q of AB systems, ^3J(H,H) = 7.1 Hz, ^2J(H,H) not determined, 2H; CH_2), 4.26 (s, 1H; H4), 5.19 (s, 1H; H6), 5.27 (s, 5H; Cp), 6.52 ppm (d, ^4J(H,H) = 2.6 Hz, 1H; H2); ^{13}C NMR (75 MHz, [D_6]acetone, 25°C, TMS): δ = 14.4 (s; CH_3), 22.6 (s; CH_3), 45.3 (s; C4), 61.7 (s; OCH_2), 83.1 (s; Cp), 114.0 (s; C6), 163.5 (s; C=O), other olefinic signals obscured by phenyl resonances; ^{31}P NMR (121.5 MHz, [D_6]acetone, 25°C, H_3PO_4): δ = 6.9 ppm (s); elemental analysis (%) calcd for $C_{44}H_{40}ClF_6O_2P_3RuS$ (955.9): C 56.54, H 4.53, S 3.35; found: C 56.42, H 4.76, S 3.17.

X-ray structure determinations: An Enraf Nonius CAD4 instrument was used for data collection (graphite monochromator, $Mo_{K\alpha}$ radiation, λ = 0.71073 Å). The structures were solved by using Patterson (**6d**) or direct methods (4-dimethylamino-cinnamaldehyde) and refined with full-matrix least-squares against F^2 (SHELX-97).[56] Hydrogen atoms were included in their calculated positions and refined in a riding model. The details of the measurements are summarized in Table 8. CCDC-148939 (**6d**·$CDCl_3$) and -148289 (4-dimethylamino-cinnamaldehyde) contain the supplementary crystallograhic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 8. Details of the structure determinations of [CpRu(dppe)(S=CH–CH=CHC$_6$H$_4$NMe$_2$)]PF$_6$·CDCl$_3$ (**6d**·CDCl$_3$) and 4-dimethylamino-cinnamaldehyde.

	6d·CDCl$_3$	4-dimethylamino-cinnamaldehyde
empirical formula	$C_{42}H_{42}F_6NP_3RuS$·$CDCl_3$	$C_{11}H_{13}NO$
formula mass	1021.18	175.22
crystal color/habit	dark blue block	yellow plate
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	*Pbca*
a [Å]	12.689(6)	9.890(2)
b [Å]	14.742(3)	7.6091(15)
c [Å]	24.696(10)	25.428(5)
α [°]	90	90
β [°]	93.05(2)	90
γ [°]	90	90
V [Å^3]	4613(3)	1913.6(7)
Θ [°]	2.12–21.93	2.61–25.98
h	0 to 13	−12 to 12
k	0 to 15	−9 to 0
l	−25 to 25	−31 to 2
Z	4	8
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.405	0.078
crystal size [mm]	0.35×0.35×0.50	0.30×0.30×0.10
ρ_{calcd} [g cm^{-3}]	1.470	1.216
T [K]	293(2)	193(2)
reflections collected	5964	3993
independent reflections	5655	1879
parameter	606	171
R_1 [$I>2\sigma(I)$]	0.0347	0.0406
R_1 (overall)	0.0436	0.0536
wR_2 [$I>2\sigma(I)$]	0.0904	0.1021
wR_2 (overall)	0.1069	0.1126
goof on F^2	0.885	1.035
diff. peak/hole [e Å^{-3}]	0.392/−0.318	0.166/−0.141
CCDC	148939	148289

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