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# Synthesis and vibrational spectra of thiobutyrolactone and thiono-benzonaphthopyranones and their cyclopentadienyl ruthenium complexes ☆

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**Abstract**

The preparation of the thiobutyrolactone complexes [Cp(dppx)Ru-**1**]PF$_6$ with dppx = dppm (**1a**) and dppe (**1b**) is described. Raman spectra of the polycrystalline solids and the CH$_2$Cl$_2$ solutions were recorded by means of the scanning multichannel technique and charge-coupled device detection. The results are reported with complementary IR data. Vibrational assignments are proposed for the compounds and the carbon–sulfur stretching vibrations have been assigned by means of polarized Raman measurements. Likewise, spectra of thiono-benzonaphthopyranones **2–4** and their complexes were recorded. Assignments are given for the lactones themselves and their ruthenium complexes.

*Keywords:* Thionolactones; Thiobutyrolactone; Synthesis; Thiono-benzonaphthopyranones; Raman spectroscopy; Biaryls

## 1. Introduction

The typical reactivity of a functional group in an organic molecule experiences dramatic changes when this group is coordinated to a transition metal [3]. Such changes can in principle arise from an interaction of the ground-state properties of the substrate molecule or from a modification of the transition states along the reaction path. Ground-state properties such as bond strengths can be conveniently probed by vibrational spectroscopy, combined with normal coordinate analysis. For large molecules, however, the problem of unambiguous assignment of the observed vibrational bands is not trivial.

We have investigated the transition metal activation of molecules containing a C=S group such as CS$_2$ [4–6], dithioesters [7–9], thioaldehydes [10,11], or thiono-lactones [12]. The typical reactivity of these species—nucleophilic attack at carbon—can be exploited for the stereoselective ring opening of thiono-benzonaphthopyranones [13] and thus opens up a promising enantioselective route to configurationally stable biaryls [14,15].

For a better understanding of how a transition metal influences the properties of thiono-lactones we have begun a systematic study of the vibrational spectra of some complexes of type A (Fig. 1), where the ring represents either γ-thiobutyrolactone or a thiono-benzonaphthopyranone. The vibrational behaviour of the carbonyl group in organic compounds is well described in the literature, whereas there are relatively few publications about its sulfur analog [16–18]. A vibrational analysis of a benzonaphthopyranone—the parent compound of a new class of axially prostereogenic bridged

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☆ Part L of the series "Novel concepts in directed biaryl synthesis"; for Part IL, see Ref. [1]. Part XIII of the series "Coordination chemistry of the C=S function"; for Part XII, see Ref. [2].

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biaryls [19]—has already been undertaken [20]. The group frequencies have been discussed and assignments have been made based on a normal coordinate analysis of 6-H-benzo[b]naphtho[1,2-d]pyran-6-one. The data were compared with those obtained by a semiempirical AM1 calculation. Recently the influence of aluminum trichloride on the vibrations of such a lactone-bridged biaryl has been reported [1,21].

By comparing the spectra of the thiono-lactone complexes with those of the carbonyl compounds mentioned above, the position of the C=S-stretching vibration can be assigned. The most intense vibrational modes of these aromatics lie in the same spectral region [22,23]. For comparison we examined the non-aromatic cyclic γ-thiobutyrolactone (**1**). Assignments are based on vibrational data of similar compounds [24–27].

## 2. Experimental details

IR spectra of Nujol mulls were recorded using a Bruker model IFS 25 spectrometer and a Perkin–Elmer model 283 double-beam spectrometer with a resolution of 4 $cm^{-1}$. Raman spectra were excited with the 647 and 676 nm lines of a krypton ion laser (Spectra Physics model 2025). In order to avoid fluorescence, the 1064 nm line of a Nd-doped yttrium aluminum garnet laser (MBB Medilas 2) was applied for some of the compounds. The samples recorded were in the crystalline state as well as dissolved in dichloromethane ($CH_2Cl_2$). The rotating-sample technique was used for Raman measurements of solutions [28]. In the visible region, the scattered light was dispersed by means of a Spex model 1404 double monochromator and detected with a cooled charge-coupled device camera system (Photometrics model RDS 2000). For excitation in the near-IR region, a Jarrell–Ash model 25-103 double monochromator was used, equipped with an InGaAs photodiode and a lock-in-amplifier (EG & G Princeton Applied Research model 5210) [29].

$C_4H_6OS$ [30] and the thiono-benzonaphthopyranone complexes [12] were prepared as described in the literature.

### *2.1. Preparation of [Cp(dppx)RuSC$_4$H$_6$O]PF$_6$ (dppx ≡ dppm (1a) or dppe (1b)); general procedure*

To a solution of 0.50 mmol of CpRu(dppx)Cl and 1.00 mmol of $NH_4PF_6$ in acetone (10 ml), γ-thiobutyrolactone (2.5 mmol) was added. The mixture was refluxed for 12 h and then allowed to cool to room temperature. The solvent was removed in vacuum and the resulting residue was extracted with $CH_2Cl_2$. Further purification was done by chromatography on silica gel (eluent $CH_2Cl_2 \rightarrow CH_2Cl_2$ : acetone (20 : 1)). After concentration to 2 ml the product was precipitated by the addition of ether. The orange solid was filtered off and dried in vacuo.

#### *2.1.1. 1a (dppm)*

This compound was obtained from 270 mg (0.46 mmol) CpRudppmCl, 150 mg (0.92 mmol) $NH_4PF_6$, and 235 mg (2.30 mmol) $C_4H_6OS$ (yield, 319 mg, 0.40 mmol (87%); melting point (m.p.), 89°C (decomposition)). Anal. Found: C, 50.67; H, 4.42. $C_{34}H_{33}F_6OP_3RuS$ Calc.: C, 51.20; H, 4.17%, $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.51–7.10 (20H, m, Ph); 4.70 (5H, s, cp); 3.81 (2H, t, C(S)OC$H_2$, $J_{HH} = 6.99$ Hz); 2.42 (2H, t, C(S)C$H_2$, $J_{HH} = 7.71$ Hz); 1.53 (2H, m, C(S)CH$_2$C$H_2$). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 220.2 (s, C=S); 136.8 (vt, P–C(1), $N = 44$ Hz); 133.0 (vt, P–C(1), $N = 46$ Hz); 131.3 (vt, P–C(2,6), $N = 12$ Hz); 130.62 (vt, P–C(2,6), $N = 11$ Hz); 130.5 (s, P–C(4)); 130.4 (s, P–C(4)); 130.0 (vt, P–C(3,5), $N = 10$ Hz); 128.6 (vt, P–C(3,5), $N = 10$ Hz); 81.8 (s, cp); 79.6 (s, C(S)O$C$H$_2$); 49.9 (t, P–CH$_2$–P, $^1J_{PC} = 25$ Hz); 42.8 (s, C(S)$C$H$_2$); 24.4 (s, C(S)CH$_2$$C$H$_2$). $^{31}P$ NMR ($CDCl_3$, 161 MHz): $\delta$ 7.9 (s).

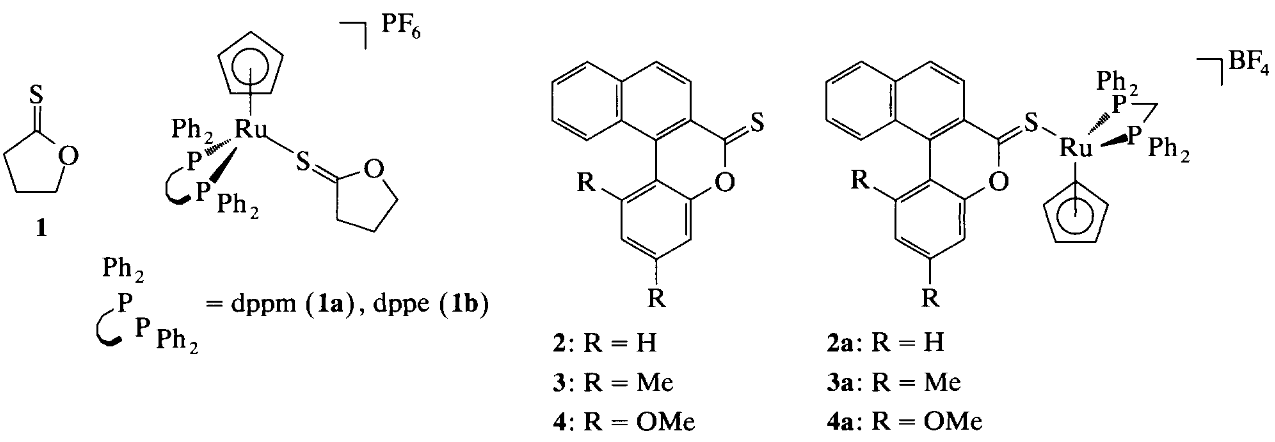

Fig. 1. Molecules studied in this paper; **1**: γ-Thiobutyrolactone; **1a**: [Cp(dppm)Ru-1]PF$_6$; **1b**: [Cp(dppe)Ru-1]PF$_6$; **2**: Thionolactone H, H; **3**: Thionolactone Me, Me; **4**: Thionolactone OMe, OMe; **2a**: [Cp(dppm)Ru-2]BF$_4$; **3a**: [Cp(dppm)Ru-3]PF$_6$; **4a**: [Cp(dppm)Ru-4]BF$_4$.

Table 1
Most characteristic Raman bands [a] of **1** and their tentative assignment: vs, very strong: s, strong: m, medium: w, weak: vw, very weak

| Approximate description | Raman ($cm^{-1}$) Measured | Raman ($cm^{-1}$) Calculated [24] | Assignment |
|---|---|---|---|
| $CH_{2c}$ | 1480 w | 1470 | $\beta$(CH) |
| $CH_{2b}$ | 1459 w | 1446 | $\beta$(CH) |
| $CH_{2a}$ | 1417 w | | $\beta$(CH) |
| $OCH_{2c}$ | 1378 w | 1356 | $\gamma$(CH) |
| OCS | 1319 vs | | $\nu$(OCS) |
| $CH_2$ | 1305 m | | $\gamma$(CH) |
| $CH_2OCS$ [25] | 1233 m | | $\nu$(OCS) |
| $CH_2OCS$ [25] | 1023 vw | | |
| COC [24] | 476 s | | $\delta$(COC) |

[a] A complete set of vibrational frequencies can be obtained from the authors upon request.

### 2.1.2. *1b (dppe)*

This compound was obtained from 220 mg (0.37 mmol) CpRudppeCl, 119 mg (0.74 mmol) $NH_4PF_6$, and 189 mg (1.85 mmol) $C_4H_6OS$ (yield, 255 mg, 0.31 mmol (85%); m.p., 87°C (decomposition)). Anal. Found: C, 51.70; H, 4.45. $C_{35}H_{35}F_6OP_3RuS$ Calc.: C, 51.79; H, 4.35%. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.66–7.11 (20H, m, Ph); 4.67 (5H, s, cp); 4.04 (2H, t, C(S)O$CH_2$, $J_{HH}$ = 7.06 Hz); 2.36 (2H, t, C(S)$CH_2$, $J_{HH}$ = 7.76 Hz); 1.65 (2H, m, C(S)$CH_2$–$CH_2$). $^{13}C$ NMR ($CDCl_3$, 100 MHz); $\delta$ 220.4 (t, C=S, $^3J_{PC}$ = 5 Hz); 139.7 (vt, P–C(1), $N$ = 44 Hz); 132.3 (vt, P–C(2,6), $N$ = 10 Hz); 130.8 (vt, P–C(2,6), $N$ = 10 Hz); 130.4 (s, P–C(4)); 130.1 (s, P–C(4)); 128.7 (vt, P–C(3,5), $N$ = 10 Hz); 128.5 (vt, P–C(3,5), $N$ = 10 Hz); 83.0 (s, cp); 79.7 (s, C(S)O$CH_2$); 42.8 (s, C(S)$CH_2$); 28.0 (vt, P–$CH_2$–$CH_2$–P, $N$ = 46.26 Hz); 24.3 (s, C(S)$CH_2CH_2$). $^{31}P$ NMR ($CDCl_3$, 161 MHz): $\delta$ 78.9 (s).

## 3. Results and discussion

### 3.1. *γ-Thiobutyrolactone*

The Raman and IR spectra of butyrolactone have already been reported and the bands at 1770 $cm^{-1}$ and 1140 $cm^{-1}$ have been assigned to the stretching vibration of the C=O and C–O group respectively [31]. Replacing the oxygen by sulfur leads to a red shift of the C=X mode (Table 1). Approximations according to [24] were used to determine the deformation modes of the single methylene fragments between 1400 and 1500 $cm^{-1}$. Although we observe the same characteristic band patterns, the wavenumbers determined are about 10–20 $cm^{-1}$ higher than those reported in [24]. Comparable compounds containing a similar $CH_2$–O–C=S unit are generally believed to give rise to $\nu$(C=S) at about 1230 $cm^{-1}$ [18,25]. However, we observe that the band at 1319 $cm^{-1}$ has a much higher intensity in the Raman spectrum and a higher polarization ratio than that at 1230 $cm^{-1}$. We therefore assume that this band arises mainly from the $\nu$(C=S) vibration, although the C–S oscillator of course cannot be regarded as uncoupled from the rest of the molecule. Coordination of the γ-butyrolactone to Cp(dppx)Ru–Cl results in a general decrease in band intensities throughout the spectrum; they are superimposed by the bands of the other ligands. The $a_1$ and $b_2$ modes of the phosphanes and their phenyl groups dominate the spectrum [32,33]. The C=S-stretching vibration shifts from 1319 $cm^{-1}$ to slightly lower wavenumbers (Table 2). This is in accordance with earlier observations of dithioester complexes of tungsten [8]. In the Raman spectra of the solids we found an asymmetric doublet centered at around 1310 $cm^{-1}$, which could not be resolved in solution. By exchange of dppm for dppe no influence on this vibration is expected; it can therefore be assumed to give rise to the band at 1306 $cm^{-1}$. In the spectra of the free thiolactone this band has the highest intensity. The other modes of the lactone cannot be found in spectra of the complexes **1a** and **1b**. From the position of the stretching vibration, conclusions concerning the bonding can be drawn. Replacing the oxygen of a carbonyl group by sulfur yields a thione. The associated shift of the vibrations can be estimated [34,35] by regarding the C=X groups as isolated from the molecular framework. For isostructural compounds, identical ratios of $\nu$(C=O) to $\nu$(C=S) are to be

Table 2
Most characteristic Raman and IR bands [a] of **1a** and **1b** and their tentative assignments *, obscured by solvent bands: vs, very strong: s, strong: m, medium: w, weak: vw, very weak

| 1a Raman ($cm^{-1}$) Solid | 1a Raman ($cm^{-1}$) In $CH_2Cl_2$ | 1a IR ($cm^{-1}$), Nujol | 1b Raman ($cm^{-1}$) Solid | 1b Raman ($cm^{-1}$) In $CH_2Cl_2$ | 1b IR ($cm^{-1}$) Nujol | Assignment [19,20] |
|---|---|---|---|---|---|---|
| 1586 s | | | 1587 s | 1584 s | | $k(a_1)\nu$(CC) |
| 1573 m | | 1576 vw | 1574 m | 1572 m | | $l(b_2)\nu$(CC) |
| 1315 w | | | 1310 m | 1308 wm | 1304 s | $\nu$(OCS) |
| 1305 w | 1307 vw | 1309 m | 1306 m | 1305 m | | $CH_2$ twisting |
| 1098 m | | | 1100 m | 1098 wm | 1093 ms | $q(a_1)$ X-sens. |
| 1001 vs | | 1000 vw | 1006 vs | 1003 v | 1008 vw | $p(a_1)$ ring breathing |

[a] A complete set of vibrational frequencies can be obtained from the authors upon request.

Table 3
Most characteristic Raman and IR bands [a] of **2–4** and their tentative assignment; mode numbering and description according to [20]: arom, aromatic ring system; lac, lactone bridge; ip, in plane; oop, out of plane; exo, exocyclic; endo, endocyclic; vs, very strong; s, strong; m, medium; w, weak; vw, very weak

| **2** | | | **3** | | | **4** | | | Assignment | |
|---|---|---|---|---|---|---|---|---|---|---|
| Raman (cm$^{-1}$) | | IR (cm$^{-1}$), Nujol | Raman (cm$^{-1}$) | | IR (cm$^{-1}$), Nujol | Raman (cm$^{-1}$) | | IR (cm$^{-1}$), Nujol | | |
| Solid | In $CH_2Cl_2$ | | Solid | In $CH_2Cl_2$ | | Solid | In $CH_2Cl_2$ | | | |
| 1396 vs | 1397 vs | | 1396 vs | 1396 vs | 1396 w | 1399 s | 1399 s | 1396 m | $\upsilon_{21}$ | $\delta(\text{arom})_{\text{in}} + \upsilon(\text{CC})_{\text{arom}}$ |
| 1376 s | 1376 s | 1377 s | 1371 vs | 1372 s | 1376 vs | 1370 s | 1374 sh | 1376 vs | $\upsilon_{23}$ | $\delta(\text{arom})_{\text{ip}} + \upsilon(\text{CC})_{\text{arom}}$ |
| 1368 m | 1370 sh | | | | | 1360 m | 1360 m | 1358 wm | | |
| 1345 w | | | 1347 vw | | 1355 sh | 1353 m | | 1354 m | $\upsilon_{24}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| | | | | | | 1335 m | 1335 m | | | |
| 1310 m | 1312 m | 1309 w | 1307 m | 1307 m | 1306 w | 1307 vw | 1307 vw | 1306 w | | $\upsilon(\text{OCS})$ |
| 1301 vw | | | 1297 w | 1299 w | | | | | $\upsilon_{25}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1275 ms | 1275 m | 1274 w | 1281 w | 1281 w | 1284 s | 1283 w | 1286 w | 1284 s | $\upsilon_{26}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1262 w | 1267 w | 1262 w | 1256 vs | 1256 vs | 1253 s | 1260 w | 1260 w | | $\upsilon_{27}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1249 vs | 1252 vs | 1248 w | 1246 vs | 1248 m | | 1247 vs | 1253 s | 1252 s | $\upsilon_{28}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1228 m | 1226 m | | | | 1230 vw | 1231 m | 1235 w | 1230 w | $\upsilon_{29}$ | $\delta(\text{arom})_{\text{ip}}$ |
| 1203 m | 1202 w | | 1204 vs | 1206 m | 1199 w | 1203 m | 1201 m | 1199 m | $\upsilon_{30}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1114 w | 1114 w | | | | | | | | $\upsilon_{35}$ | $\upsilon(\text{CC})_{\text{arom}} + \upsilon(\text{C–O})_{\text{endo}}$ |
| 1087 m | 1089 m | 1082 w | 1087 w | 1086 w | 1089 w | 1083 m | 1082 w | 1089 w | $\upsilon_{36}$ | $\upsilon(\text{CC})_{\text{arom}} + \upsilon(\text{C–O})_{\text{endo}}$ |
| 966 w | 967 vw | | 968 w | | | 964 w | 963 w | | $\upsilon_{43}$ | $\upsilon(\text{CC})_{\text{arom}} + \upsilon(\text{C–O})_{\text{endo}}$ |

[a] A complete set of vibrational frequencies can be obtained from the authors upon request.

expected. In the case of γ-thiobutyrolactone, this ratio has a value of 1.34. Thus the C=S vibration of the uncoordinated thiono-benzonaphthopyranones are expected to appear at 1288 cm$^{-1}$ for **2**, 1284 cm$^{-1}$ for **3**, and 1291 cm$^{-1}$ for **4**. This will be discussed in the following section.

### 3.2. *Thiono-biaryllactones*

The vibrational frequencies of the uncoordinated thiono-benzonaphthopyranones are almost the same as the analogous oxygen compounds (Tables 3 and 4). The vibrational assignment is based on results reported previously from a normal coordinate analysis of the unsubstituted biaryl lactone [20]. On the basis of this publication by our group the band at about 1310 cm$^{-1}$ could be assigned to the C=S-stretching vibration. The observed wavenumber for this band is approximately 20 cm$^{-1}$ higher than estimated. This confirms that the thiocarbonyl group cannot be regarded as isolated from the rest of the molecule. The interactions of the conju-

Table 4
Most characteristic Raman and IR bands [a] of **2a–4a** and their tentative assingment; mode numbering and description according to [20]: arom, aromatic ring system; lac, lactone bridge; ip, in plane; oop, out of plane; exo, exocyclic; endo, endocyclic; vs, very strong; s, strong; m, medium; w, weak; vw, very weak

| **2a** | | | **3a** | | | **4a** | | | Assignment | |
|---|---|---|---|---|---|---|---|---|---|---|
| Raman (cm$^{-1}$) | | IR (cm$^{-1}$), KBr | Raman (cm$^{-1}$) | | IR (cm$^{-1}$), Nujol | Raman (cm$^{-1}$) | | IR (cm$^{-1}$), KBr | | |
| Solid | In $CH_2Cl_2$ | | Solid | In $CH_2Cl_2$ | | Solid | In $CH_2Cl_2$ | | | |
| 1391 s | 1390 s | 1395 vs | 1395 s | 1397 s | 1392 m | 1393 m | 1390 m | 1399 vs | $\upsilon_{21}$ | $\delta(\text{arom})_{\text{ip}} + \upsilon(\text{CC})_{\text{arom}}$ |
| 1370 m | 1370 m | 1374 w | 1370 m | 1372 s | 1372 s | 1368 s | 1370 s | 1370 w | $\upsilon_{23}$ | $(\text{arom})_{\text{ip}} + \upsilon(\text{CC})_{\text{arom}}$ |
| 1305 s | 1303 s | | 1300 m | 1303 s | 1300 m | 1300 m | 1298 m | 1306 vw | | $\upsilon(\text{OCS})$ |
| 1282 sh | | | 1280 s | 1281 vs | 1277 w | | | 1285 s | $\upsilon_{26}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1274 s | 1274 s | 1279 w | 1264 s | 1265 vs | 1260 vw | 1259 s | 1260 s | 1262 w | $\upsilon_{27}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1256 m | 1254 s | 1257 m | 1248 m | 1248 s | | | | | $\upsilon_{28}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1227 vw | | 1230 vs | | | | | | | $\upsilon_{29}$ | $\delta(\text{arom})_{\text{ip}}$ |
| | | 1220 s | 1215 sh | 1214 s | 1214 vs | | | | | |
| 1208 vw | | 1210 s | 1208 s | 1208 vs | | | | 1210 s | $\upsilon_{30}$ | $\upsilon(\text{CC})_{\text{arom}} + \delta(\text{arom})_{\text{ip}}$ |
| 1109 vw | | | | | | | | | $\upsilon_{35}$ | $\upsilon(\text{CC})_{\text{arom}} + \upsilon(\text{C–O})_{\text{endo}}$ |
| 1080 m | 1078 wm | 1083 s | 1086 w | 1087 m | 1093 s | 1071 s | 1070 m | 1083 s | $\upsilon_{36}$ | $F_2(BF_4)$ |
| | | 995 m | | | 997 w | | | 995 w | | $a_1$ (P–Ph) |
| 964 vw | 960 vw | | 968 vw | 973 w | 970 w | | | | $\upsilon_{43}$ | $\upsilon(\text{CC})_{\text{arom}} + \upsilon(\text{C–O})_{\text{endo}}$ |

[a] A complete set of vibrational frequencies can be obtained from the authors upon request.

gated system with the lactone bridge results in a shift to higher wavenumbers [20].

Normally the vibrational modes of the phenyl groups of phosphines dominate the Raman and the IR spectra [33]. The lactones, however, are extremely strong scatterers and the band intensity is very high compared with the phenyl modes of the ruthenium complex fragment. Therefore we did not find any bands of the CpRu(dppm) parts.

The C=S stretching vibration is the only mode that is shifted upon coordination to a metal, and even this shift is limited to only 3–5 $cm^{-1}$. By contrast, Bringmann et al. [21] have reported that the coordination of biaryllactones to $AlCl_3$ results in large shifts in the vibrations. In the light of these results the small shift in the C=S vibration is rather surprising. Further work must give an explanation for this almost negligible shift. These investigations will include a normal coordinate analysis of **1**, **1a** and **1b** and a complete assignment.

## Supplementary material available

Tables containing the complete set of vibrational modes and assignments can be obtained from the authors.

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