3,3″-Bis(saccharin-6-ylmethyl)-1,1′:3′,1″-terphenyl – Precursor of A New Tetradendate Bis-bridging Ligand

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

The title compound (H_2tpsac) was synthesized from 6-bromosaccharin and 3,3″-bis(bromomethyl)-*m*-terphenyl. The ability of tpsac to serve as a tetradentate bis-bridging ligand was demonstrated by the formation of the dinuclear ruthenium(I,I) complexes $[Ru_2(CO)_5(\mu,\mu\text{-tpsac})]_2$, $[Ru_2(CO)_4(\mu,\mu\text{-tpsac})]_n$, $[Ru_2(CO)_4(PPh_3)_2(\mu,\mu\text{-tpsac})]$, and $[Ru_2(CO)_5(PPh_3)(\mu,\mu\text{-tpsac})]$. An X-ray crystal structure analysis of $[Ru_2(CO)_4(PPh_3)_2(\mu,\mu\text{-tpsac})]$ showed the head-to-tail (or 1,1) arrangement of the two saccharinate coordination sites.

Key words: Ruthenium Complexes, Saccharin, Ligands

Introduction

Dinuclear rhodium(II,II) carboxylates and amidates of the type $Rh_2(\mu\text{-L})_4$ (L = bidentate ligand) are efficient catalysts for intramolecular and intermolecular carbenoid reactions of diazo compounds [1]. While experimental evidence and computational results nowadays corroborate the mechanistic hypotheses of short-lived rhodium-carbene intermediates and their chemical and stereochemical mode of interaction with substrate molecules, it is still not clear which role is played by ligand dynamics in the catalytic process and to which extent it affects the catalyst's lifetime under the reaction conditions. The mentioned complexes $Rh_2(\mu\text{-L})_4$ have a paddlewheel structure with the chelating ligands in equatorial positions; in a rhodium-carbene complex, the carbene ligand occupies the available axial coordination site at one rhodium center, similar to the coordination of neutral Lewis base ligands such as water, amines and nitriles (for the first X-ray crystal structure determination of a $Rh_2(t\text{BuCOO})_4$ complex bearing an axial NHC ligand, see ref. [2]; for a related Ru(I,I)-NHC complex, see ref. [3]). It has generally been assumed that the tetrabridged dinuclear framework of a rhodium-carbene remains intact during carbenoid reactions, and recent computational work seems to support this assumption (see, for example, refs. [4 – 6]). On the other hand, in order to explain the enantioselectivity observed for alkyne cyclopropenation with ethyl diazoacetate, Corey and co-workers have proposed a mechanism that involves the complete dissociation of one carboxylate ligand followed by [2+2] cycloaddition of the alkyne to the resulting tribridged rhodium-carbene complex [7, 8].

We have recently synthesized a variety of dinuclear tetracarbonyldiruthenium(I,I) carboxylate and amidate complexes, $Ru_2(CO)_4(\mu\text{-L})_2$, and have studied them as alternative catalysts for carbene transfer reactions with diazo compounds [9 – 13]. These diruthenium complexes have the typical sawhorse structure [14] with the two bidentate ligands in *cis*-configuration. Examples are shown in Fig. 1. With the unsymmetrical amidate ligands, which coordinate by an N–C=O moiety, head-to-tail (or 1,1, *e. g.* **1** and **3**) and head-to-head (or 0,2, *e. g.* **2** and **4**) complexation is possible. Our investigations on saccharinato- (**1** and **2** [12]) and 2-pyridinolato- (**3** and **4** [3, 10]) tetracarbonyldiruthenium(I,I) complexes have shown that the mutual conversion of the (1,1) and (0,2) arrangements of the equatorial bidentate ligands can occur smoothly at room

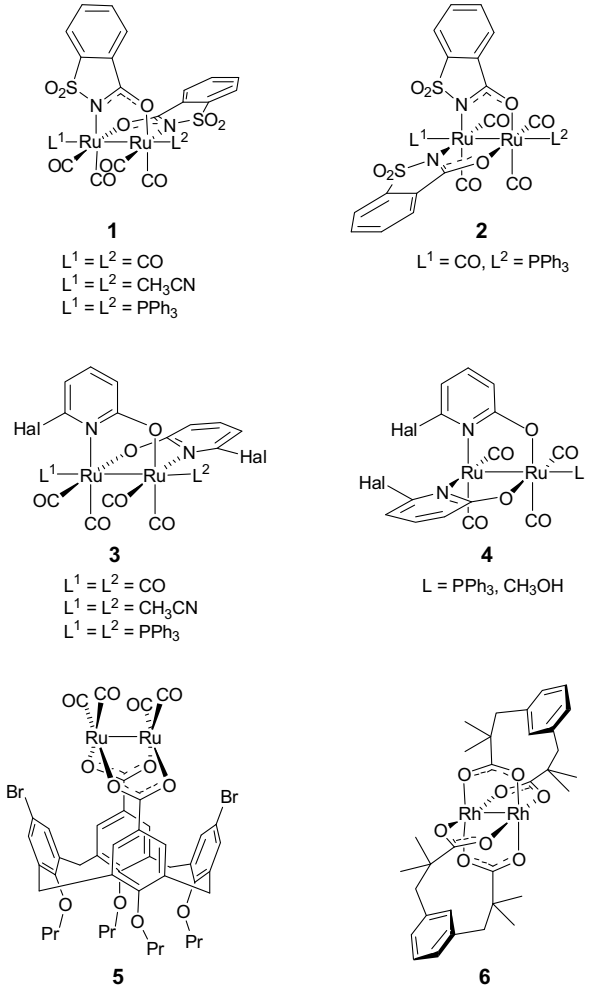


Fig. 1. Dinuclear Ru(I,I) and Rh(II,II) complexes relevant to this study.

temperature during exchange of the axial ligands. For 6-halogenopyridin-2-olato complexes $[Ru_2(CO)_4(\mu\text{-HalpyO})_2(L_{1/2})]$, solvent- and temperature-dependent equilibria between (1,1) and (0,2) species could be observed in solution by NMR spectroscopy [3] in the temperature range where carbenoid reactions with these complexes as catalysts are usually performed.

It is obvious that the presence of constitutional equilibria in the catalytically active complexes can be an obstacle to the design of catalysts, particularly with respect to the diastereo- and enantioselectivity of the envisaged catalyzed reactions. Additionally, complete dissociation of a chelating ligand from the dinuclear core may facilitate degradation of the catalyst. Intramolecular bridging of two carboxylato or amidato moieties has been envisaged to alleviate this problem; this would prevent a dissociating ligand to leave the complex completely, and it could enhance the structural stability of the complex with respect to $(1,1)/(0,2)$ isomerization in the case of the unsymmetrical amidato ligands. In fact, a number of dirhodium complexes with tethered dicarboxylato ligands have become known recently [15 – 23]. We have prepared bis(calixarenedicarboxylato)dirhodium complexes and analogous (calixarenedicarboxylato)tetracarbonyldiruthenium complexes such as **5** (Fig. 1) [17]. Both types of complexes were active catalysts for carbenoid reactions of diazo compounds (cyclopropanation, intramolecular C–H insertion) [11, 13, 17], although a significant advantage over simple dirhodium tetracarboxylates could not be seen. Taber's first dirhodium complex with a tethered dicarboxylate ligand was highly efficient and effective in an intramolecular carbenoid C–H insertion [15]. Complex $Rh_2(esp)_2$ (**6**) performed exceptionally effective and versatile in catalytic C–H bond amination reactions under oxidative conditions [21, see also 23], and it was better suited than simple dirhodium tetracarboxylates for the cyclopropanation of mono- and *cis*-disubstituted olefins [24].

As far as we know, dinuclear complexes containing two tethered saccharin moieties as briding ligands have not been reported. For the design of a suitable ligand, we considered the solid-state structure of the diruthenium complex **1** ($L^1 = L^2 = CH_3CN$) [12], where the distance between the C-6 ring positions of the two *cis*-oriented saccharin ligands is 8.16 Å. We speculated that this distance could be bridged with a 1,1′:3′,1″-terphenyl-3,3″-dimethyl structural moiety, more rigid

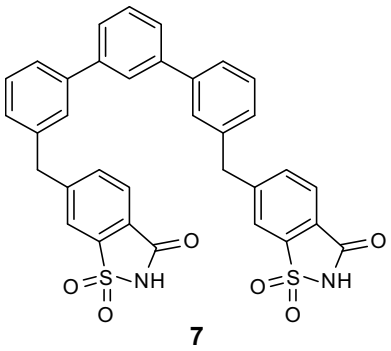


Fig. 2. The title compound **7**.

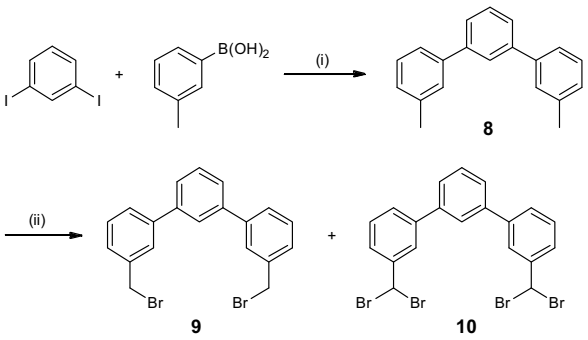
than a linear alkyl chain but still flexible enough to accommodate the new bis-saccharinate ligand in a rather unstrained complex geometry. We report here on the synthesis of the ligand precursor **7** (Fig. 2) and tetracarbonyldiruthenium(I,I) complexes derived from it.

Results and Discussion

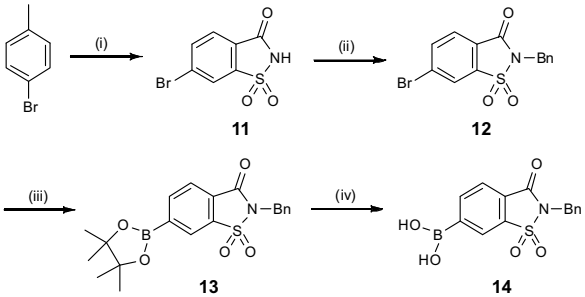
Synthesis of bis-saccharin 7 (H_2tpsac)

Bis-saccharin **7** was assembled in a convergent manner from 3,3″-bis(bromomethyl)-*m*-terphenyl (**9**) and saccharin building blocks **13** or **14**. At first, terphenyl **8** [25] was prepared from 1,3-diiodobenzene and 3-methylphenylboronic acid by a Suzuki-Miyaura reaction (Scheme 1). The conversion of **8** into the dibromide **9** was achieved by photochemical bromination with NBS in dichloromethane. Tetrabromide **10** was formed as a minor by-product (**9**:**10** ≈ 11) which could not be removed easily by crystallization or chromatography. However, it was possible to use this mixture for the subsequent coupling reaction. The usual thermally activated Wohl-Ziegler bromination (NBS and dibenzoyl peroxide in CCl_4 [20]) gave a significantly higher amount of the tetrabromide **10** (> 20% yield) even when NBS was added in small portions.

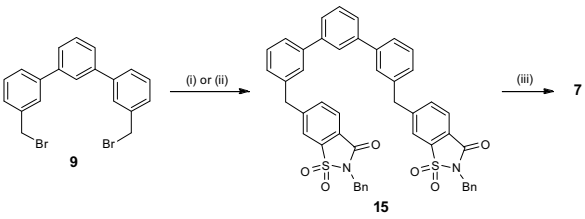
The saccharin building blocks **13** and **14** were obtained from 6-bromosaccharin (**11**) [26] as shown in Scheme 2. *N*-Protection with NaH/benzyl bromide in DMF [27] gave **12**, which was converted into (*N*-benzylsaccharin-6-yl)boronic acid pinacol ester (**13**) by Pd-catalyzed boration. The boration of unprotected 6-bromosaccharin (**11**) under the same conditions has been described in a patent [28], but the product was



Scheme 1. (i) $Pd(PPh_3)_4$ (cat.), Na_2CO_3, 1,4-dioxane/H_2O, 90 °C, 12 h, 88% yield; (ii) *N*-bromosuccinimide, CH_2Cl_2, hν, mixture of **9** (46%) and **10** (4%).



Scheme 2. (i) ref. [26], 3 steps, overall yield 22%; (ii) 1. NaH, DMF; 2. BnBr, r. t., 2 d, then 80 °C, 3 h, 84% yield; (iii) bis(pinacolato)diboron (1.32 equiv.), KOAc (3.92 equiv.), $PdCl_2$(dppf)·CH_2Cl_2 (3 mol-%), 1,4-dioxane, 90 °C, 12 h, 73% yield; (iv) $NaIO_4$, 2 M HCl, acetone/H_2O, r. t., 12 h, 96% yield; Bn = benzyl.



Scheme 3. (i) **13** (2.2 equiv.), $PdCl_2$(dppf)·$CHCl_3$ (cat.), Cs_2CO_3 (2 equiv.), THF/H_2O, 80 °C, 12 h, 48% yield; (ii) **14** (2.6 equiv.), $Pd(PPh_3)_4$ (cat.), Na_2CO_3 (7 equiv.), toluene/EtOH/H_2O, 90 °C, 12 h, 76% yield; (iii) 1. $HCOONH_4$, Pd/C, EtOH, reflux, 12 h; 2. 1 M HCl_{aq}; 84% yield.

obtained with insufficient purity. Boronic acid ester **13** could be cleaved with sodium periodate/HCl [29] to give the (*N*-benzylsaccharin-6-yl)boronic acid **14** almost quantitatively.

The terphenyl/saccharin conjugate **15** was obtained by Suzuki-Miyaura coupling of dibromide **9** and either dioxaborolane **13** or boronic acid **14** (Scheme 3). With the boronic acid and standard reaction conditions ($Pd(PPh_3)_4$, Na_2CO_3, toluene/EtOH/H_2O) a significantly better yield of **15** (76%) was obtained. *N*-Deprotection of **15** was achieved by transfer hydrogenation [30] and furnished the ligand precursor H_2tpsac (**7**).

Tetracarbonyldiruthenium(I,I) complexes with the tpsac ligand

Based on our previous experience with the synthesis and structures of diruthenium(I,I) saccharinate com-

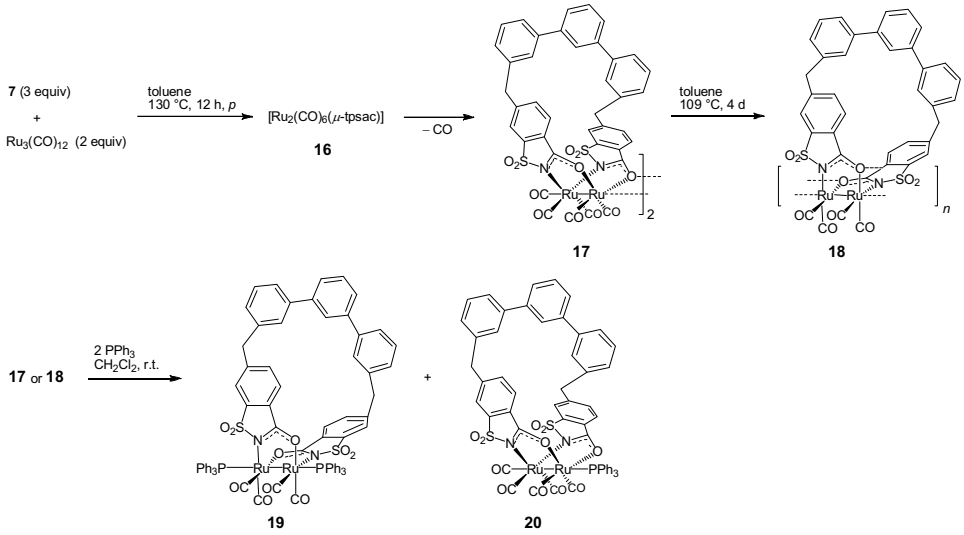
plexes such as **1** and **2** [12], we wondered whether similar complexes could be obtained with the bis-saccharin H_2tpsac (**7**). Two coordination patterns could be expected – the tetradentate ligand tpsac could either coordinate intramolecularly with both N−C=O moieties at the same diruthenium core to form a discrete 1 : 1 complex, or it could coordinate with each N−C=O moiety at a different Ru_2 core giving rise to oligo- or polymeric chains or supramolecular macrocyclic structures. We were pleased to find that the intramolecular coordination motif was realized. This is remarkable, because the tpsac ligand is a conformationally flexible ligand for which the two amidate coordination sites do not appear to be as much pre-organized as, *e. g.*, in calix[4]arenedicarboxylates (compare structure **5**, Fig. 1).

When H_2tpsac was heated with $Ru_3(CO)_{12}$ in toluene under reflux conditions, a brown solid of unknown constitution was obtained which was insoluble in common organic solvents including DMSO and acetonitrile. However, when the reaction was performed at 130 °C in a closed pressure Schlenk tube (so that evolved carbon monoxide could not escape), a yellow solution was formed; after completion of the reaction and work-up, a yellow solid was isolated which after removal of most of the solvent *in vacuo* turned light-brown. The structure of the dimeric complex $[Ru_2(CO)_5(\mu,\mu\text{-tpsac})]_2$ (**17**) is tentatively assigned to this solid, based on the presence of an IR absorption indicating an axial CO ligand ($\nu = 2096\,cm^{-1}$) in addition to the absorptions caused by equatorial CO ligands ($\nu = 2040, 2013, 1946\,cm^{-1}$), the solubility in hot chloroform, and the subsequent transformations. Unfortunately, a correct elemental analysis could not be obtained, because the solid strongly retained some toluene even when kept at 150 °C/0.001 mbar for one hour. An analogous structure has been postulated for the saccharinato complex $[Ru_2(CO)_5(\mu,\mu\text{-sac})_2]_2$ [12], and the structure of the related complex $[Ru_2(CO)_5(\mu,\mu\text{-6-fluoropyridin-2-olate})_2]_2$ was proven by XRD analysis [31]. Notably, the anticipated precursor to **17**, the hexacarbonyl complex $[Ru_2(CO)_6(\mu,\mu\text{-tpsac})]$ (**16**), could neither be isolated nor observed directly, in contrast to the analogous saccharinato complex $[Ru_2(CO)_6(\mu,\mu\text{-sac})_2]$ [12]. It appears that **16** loses one or even both axial CO ligands very easily, and that a clean reaction yielding complex **17** is only possible in the presence of a carbon monoxide atmosphere.

Heating of complex **17** in refluxing toluene for four days yielded a greenish-gray solid which was identified as the dinuclear complex $[Ru_2(CO)_4(\mu,\mu\text{-tpsac})]_n$ (**18**). The polymeric structure is maintained by head-to-tail dimerization across the Ru–O bonds and requires the dinuclear repeating unit to exist in the head-to-tail (1,1) arrangement of the bis-saccharinato ligand. Because of its polymeric nature, **18** is only soluble in certain donor solvents, such as in hot DMSO. In addition to an elemental analysis, the structural assignment is supported by the absence of an IR absorption for axial CO ligands and by the typical absorption pattern of an $M_2(CO)_4$ unit [14, 32, 33] ($\nu = 2046$ vs, 1995 s, 1962 vs cm^{-1}).

As expected, the axial Ru···O coordination in the dimeric complex **17** and in the polymeric complex **18** could be cleaved by the action of better donor ligands. Thus, complex **17** reacted with two equivalents of triphenylphosphane (relative to a monomeric Ru_2^{2+} complex unit) in dichloromethane to give a yellow solid, the ^{31}P NMR spectrum of which displayed signals at δ_P ($CDCl_3$) = 14.4 and 23.6 ppm in a 10:1 ratio. While the major signal is attributed to the bis-PPh_3 complex $[Ru_2(CO)_4(PPh_3)_2(\mu,\mu\text{-tpsac})]$ (**19**), the minor signal is likely to belong to the mono-PPh_3 complex $[Ru_2(CO)_5(PPh_3)(\mu,\mu\text{-tpsac})]$ (**20**). The presence of an axial CO ligand in **20** was indicated by a rather weak absorption at 2085 cm^{-1} in the IR spectrum of the mixture of **19** and **20**. These observations and interpretations are in agreement with those for the analogous diruthenium complexes containing two saccharinate ligands, which in contrast to **19**/**20** could be separated [12]. While the tpsac ligand in complex **19** adopts the head-to-tail arrangement (*vide infra*), the mono-PPh_3 complex **20** is likely to have the head-to-head constitution, with the PPh_3 ligand occupying the sterically less congested axial position, in agreement with the known molecular structure of the analogous complex $[Ru_2(CO)_5(PPh_3)(\mu\text{-sac})_2]$ [12].

Treatment of the coordination polymer **18** with two equivalents of triphenylphosphane in $CDCl_3$ gave the monomeric complex $[Ru_2(CO)_4(PPh_3)_2(\mu,\mu\text{-tpsac})]$ (**19**) almost quantitatively. The ^{31}P NMR spectrum showed, besides the signal of **19** (δ_P = 14.4 ppm), the presence of a very minor second species (δ_P = 22.3 ppm), which could be the mono-PPh_3 complex $[Ru_2(CO)_4(PPh_3)(\mu,\mu\text{-tpsac})]$ (**20**) (however, note the small difference in δ_P values compared with **20** obtained from **17**) or the analogous complex



Scheme 4. Formation of dinuclear Ru(I,I) complexes **16**–**20**.

$[Ru_2(CO)_4(PPh_3)(\mu,\mu\text{-tpsac})]$ with no axial CO ligand (Scheme 4).

It should be noted that the ^1H and ^{13}C NMR spectra of the tpsac complexes reported here in all cases show more signals than expected from their composition. This is likely due to the presence of the *m*-terphenyl-3,3″-dimethyl bridge, which can exist in different diasteroisomeric conformations that are stable on the NMR time scale. Due to signal overlap and partial line broadening, a detailed interpretation was not undertaken.

Single crystals of $[Ru_2(CO)_4(PPh_3)_2(\mu,\mu\text{-tpsac})]$ (**19**, prepared from **18**) were obtained, which were suited for an X-ray crystal structure determination. Fig. 3 shows the molecular structure of **19**. The two amidate coordination sites of the tpsac ligand are in *cis*-position and assume a head-to-tail constitution; furthermore the complex has a crystallographic C_2 symmetry in the solid state. Characteristic bond geometry data are provided in Table 1. While the bond lengths agree well with the data reported for $[Ru_2(CO)_4(PPh_3)_2(\mu\text{-sac})_2]$ (**1**, Fig. 1) featuring two non-tethered saccharinato ligands [12], bond angles and torsion angles in part assume different values to accommodate the steric requirements imposed by the terphenyl bridge. Thus, the N–Ru–O bond angle is 85.3° in **19** and 88.5° in **1** ($L^1 = L^2 = PPh_3$, Fig. 1), and the C6–C6′ distance is 7.58 Å in the bridged complex **19** compared to 8.16 Å in the unbridged complex **1**. In the terphenyl bridge, the outer phenyl rings are tilted against the central ring by about 40°.

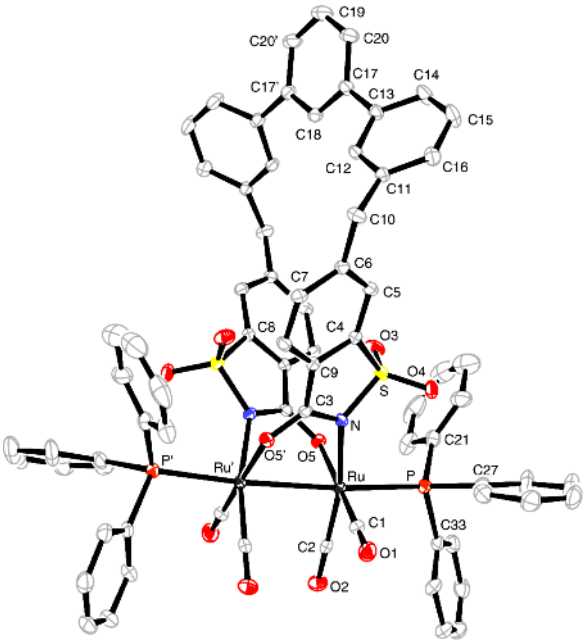
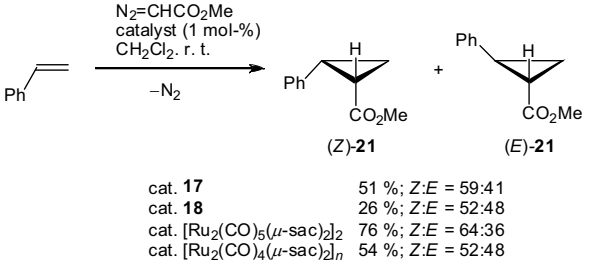


Fig. 3 (color online). Solid-state structure of the C_2-symmetrical complex **19**. Displacement ellipsoids are shown at the 20 % probability level.

The catalytic activity of the new complexes **17** and **18** was tested on the cyclopropanation of styrene with methyl diazoacetate to give methyl 2-

Distances		Angles		Torsion angles	
Ru–Ru′	2.7504(13)	C1–Ru–Ru′	94.0(2)	N–Ru–Ru′–O5′	–24.1(4)
Ru–P	2.462(2)	C2–Ru–Ru′	88.6(2)	C1–Ru–Ru′–C1′	–117.3(4)
Ru–C1	1.814(7)	P–Ru–Ru′	172.08(5)	C1–Ru–Ru′–C2′	–30.2(4)
Ru–C2	1.860(7)	C1–Ru–C2	87.2(3)	Ru–N–C3–O5′	–5.5(8)
Ru–O5	2.117(4)	C1–Ru–O5	175.6(2)		
Ru–N	2.170(4)	C1–Ru–N	90.9(2)		
C3–N	1.334(7)	C2–Ru–O5	96.1(2)		
C3–O5′	1.259(6)	O5–Ru–N	85.3(2)		

Table 1. Selected bond lengths (Å), angles (deg), and torsion angles (deg) for **19** with estimated standard deviations in parentheses.



Scheme 5. Comparison of catalysts for carbenoid cyclopropanation of styrene. Reaction conditions: the catalyst was suspended in styrene/CH_2Cl_2, and the diazoacetate dissolved in CH_2Cl_2 was gradually added; styrene : diazoester = 10 : 1.

phenylcyclopropane-1-carboxylates (*Z*)- and (*E*)-**21** (Scheme 5). It is known that the diazo compound is able to cleave the Ru···O bonds maintaining the coordination dimer and polymer. The comparison with the results obtained by us for closely related untethered bis(saccharinato) catalysts [12] shows that the yields with **17** and **18** as catalysts are lower, and the diastereomeric ratio is more or less the same. Thus, the tethered bis-sacharinato ligand of **17** and **18** offers no advantage in this case.

Conclusion

The ability of the new tetradentate bis-saccharinato ligand tpsac to bridge a tetracarbonyldiruthenium core by μ,μ-coordination of the two amidate units has been demonstrated. Several complexes of the type $[Ru_2(CO)_4(\mu,\mu\text{-tpsac})L^1L^2]$ were synthesized. All of them have the two bridging amidate groups in *cis*-position, but depending on the axial ligands L^1 and L^2, they exist either in the head-to-tail or the head-to-head constitution. Although equilibria between the two constitutions were not observed directly, it is obvious that in spite of the terphenyl bridge, constitutional changes can occur smoothly during the synthesis of the different complexes.

Experimental Section

General information

$Ru_3(CO)_{12}$ (ABCR) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (ChemPur) were purchased and used as supplied; $PdCl_2(dppf)\cdot CHCl_3$ was prepared as described [34]. Solvents were dried by known procedures and stored under argon, most reactions were carried out using a standard Schlenk technique. Column chromatography was performed using silica gel 60 (Macherey-Nagel, 0.063 – 0.2 mm). Petroleum ether with a b. p. range of 40 – 60 °C was used.

NMR spectra were recorded using a Bruker DRX 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz; ^{31}P: 161.98 MHz). The ^{1}H and ^{13}C spectra were referenced to the residual proton signal of the solvent; ^{1}H: $\delta(CHCl_3) = 7.26$, $\delta((CH_3)_2SO) = 2.50$, $\delta(CH_2Cl_2) = 5.31$ ppm; ^{13}C: $\delta(CDCl_3) = 77.0$, $\delta((CD_3)_2SO) = 39.5$, $\delta(CD_2Cl_2) = 53.7$ ppm. The ^{31}P NMR spectra were referenced to 85 % H_3PO_4 as an external standard ($\delta_P = 0$ ppm). IR spectra were recorded on KBr pellets with a Bruker Vector 22 FTIR instrument. Mass spectra: ESI(+): Waters Micromass ZMD instrument; CI(+): Finnigan-MAT SSQ-7000, 100 eV, methane as reagent gas. Elemental analyses were obtained with an elementar Hanau vario MICRO cube analyzer. Melting points were determined with a Büchi B-540 instrument at a heating rate of 2 °C min^{-1} (if not stated otherwise). Differential scanning calorimetry (DSC): Perkin Elmer DSC 7 calorimeter.

*3,3″-Dimethyl-1,1′:3′,1″-terphenyl (**8**)*

A solution of 1,3-diiodobenzene (4.02 g, 12.2 mmol) and 3-methylphenylboronic acid (3.62 g, 26.6 mmol) in 1,4-dioxane (20 mL) was prepared in a thick-walled Schlenk tube, and an aqueous solution of Na_2CO_3 (2 M, 30 mL) and $Pd(PPh_3)_4$ (0.43 g, 0.36 mmol) were added. The mixture was stirred at 90 °C overnight. After cooling, the solvent was evaporated and the residue was extracted with 2 × 30 mL of diethyl ether. The combined ether phases were extracted with hydrochloric acid (2 M, 10 mL) and water (20 mL). After drying (Na_2SO_4) and evaporation of the solvent, the residue was worked up by column chromatography over silica gel (140 g, petroleum ether) to give **8** as a clear viscous

oil (2.80 g, 88 %) (lit. [25]: m. p. 54 °C). – $C_{20}H_{18}$ (258.4): calcd. C 92.98, H 7.02; found C 93.17, H 7.02. ^{1}H and ^{13}C NMR data fully agreed with the reported ones [25].

*3,3″-Bis(bromomethyl)-1,1′:3′,1″-terphenyl (**9**)*

A solution of terphenyl **8** (1.96 g, 7.6 mmol) and *N*-bromosuccinimide (3.00 g, 16.9 mmol) in dichloromethane (50 mL) was placed in a round-bottom glass flask and irradiated for 4 d with an electrical light bulb (Osram, Krypton 60 W). After extraction with saturated aqueous $NaHCO_3$ solution (10 mL) and water (2 × 10 mL), the reaction solution was dried (Na_2SO_4), the solvent was evaporated, and the remaining oil was stirred in diethyl ether (2 mL) and petroleum ether (10 mL) until crystallization took place. The colorless solid obtained after drying (22 °C/0.001 mbar) consisted of dibromide **9** (1.56 g, 46 % yield) and tetrabromide **10** (0.16 g, 4 % yield). This mixture was used without separation for the subsequent transformation. The NMR data of **9** were in agreement with lit. [25]. 3,3″-Bis(dibromomethyl)-1,1′:3′,1″-terphenyl (**10**) was identified by the following NMR data: ^{1}H NMR ($CDCl_3$): δ = 6.74 (s, 2 H, $CHBr_2$), 7.47–7.50 (m, 2 H, H_{aryl}), 7.60–7.64 (m, 7 H, H_{aryl}), 7.78 (s, 1 H, H_{aryl}), 7.82 (s, 2 H, H_{aryl}) ppm. – ^{13}C NMR ($CDCl_3$): δ = 40.8, 125.3, 125.6, 126.1, 126.7, 128.7, 129.2, 129.5, 140.9, 141.5, 142.5 ppm.

*6-Bromobenzo[d]isothiazol-3(2H)-one 1,1-dioxide (6-bromosaccharin) (**11**)*

This compound was prepared from 4-bromotoluene *via* 2-chlorosulfonyl-4-bromotoluene and 2-aminosulfonyl-4-bromotoluene as described in ref. [26], but without complete purification of the intermediate products, in 22 % overall yield. Crystallization from ethanol-water gave colorless long needles, m. p. 227–228 °C (lit. [26]: 216–217 °C). – IR (KBr): ν = 3407 br m, 3096 br m, 2659 w, 1737 vs (C=O), 1705 vs (C=O), 1587 s, 1344 vs, 1331 vs, 1268 m, 1248 m, 1177 vs, 1143 m, 1123 m, 1076 m, 886 m, 854 m cm^{-1}. – ^{1}H NMR ($CDCl_3$/[D_6]DMSO = 9/1): δ = 7.73 (d, ^3J = 8.1 Hz, 1 H, H_{aryl}), 7.87 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1 H, H_{aryl}), 7.96 (d, ^4J = 1.5 Hz, 1 H, H_{aryl}), 8.50 (br s, 1 H, NH) ppm. – ^{13}C NMR ($CDCl_3$/[D_6]DMSO = 9/1): δ = 123.5, 125.9, 126.5, 129.1, 136.9, 140.7, 159.5 (NC=O) ppm. – MS (CI+): *m/z* (%) = 264 (100)/262 (94, $[M + H]^+$, $^{81/79}$Br). – $C_7H_4BrNO_3S$ (262.1): calcd. C 32.08, H 1.54, N 5.34; found C 32.19, H 1.55, N 5.32.

*2-Benzyl-6-bromobenzo[d]isothiazol-3(2H)-one 1,1-dioxide (N-benzyl-6-bromosaccharin) (**12**)*

6-Bromosaccharin (**11**, 0.42 g, 1.6 mmol) was dissolved in dry DMF (10 mL), sodium hydride (80 % in mineral oil, 53 mg, 1.8 mmol) was gradually added, and the mixture was stirred until gas evolution had ceased. After addition of benzyl bromide (0.22 mL, 1.9 mmol), the reaction mixture was stirred at r. t. for two days, then at 80 °C for 3 h. Water (5 mL) was added, and the mixture was extracted with ethyl acetate (3 × 15 mL). The organic phase was washed with aq. HCl (1 M, 5 mL), saturated aqueous $NaHCO_3$ solution (5 mL) and brine (5 mL), then dried with Na_2SO_4. After filtration the solvent was evaporated, and the residue was stirred in petroleum ether (10 mL), yielding product **12** as a colorless solid (0.47 g, 84 %), m. p. 160–162 °C. – IR (KBr): ν = 3091 w, 3073 w, 1746 vs (C=O), 1587 m, 1454 m, 1392 m, 1334 vs, 1319 s, 1278 s, 1241 s, 1169 vs, 1076 m, 1043 m, 947 m, 846 m, 747 m, 698 m, 669 m, 592 m, 522 m cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 4.89 (s, 2 H, NCH_2), 7.30–7.38 (m, 3 H, H_{phenyl}), 7.49 (d, J = 7.1 Hz, 2 H, H_{phenyl}), 7.88 (d, J = 8.1 Hz, 1 H, H_{aryl}), 7.93 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1 H, H_{aryl}), 8.05 (d, ^4J = 1.5 Hz, 1 H, CH_{aryl}) ppm. – ^{13}C NMR ($CDCl_3$): δ = 42.9 (NCH_2), 124.2, 126.0, 126.4, 128.3, 128.68, 128.71, 129.8, 134.1, 137.6, 139.1, 158.1 (C=O) ppm. – MS (CI+): *m/z* (%) = 354 (100)/352 (90) $[M + H]^+$, $^{81/79}$Br; 289 (18)/287 (18) [M – SO_2]$^+$. – $C_{14}H_{10}BrNO_3S$ (352.2): calcd. C 47.74, H 2.86, N 3.98; found C 47.72, H 2.87, N 3.93.

*2-Benzyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (**13**)*

In a thick-walled Schlenk tube, a solution of *N*-benzyl-6-bromosaccharin (**12**, 0.99 g, 2.8 mmol) and bis(pinacolato)diboron (0.94 g, 3.7 mmol) in dry 1,3-dioxane (30 mL) was prepared, and potassium acetate (1.08 g, 11.0 mmol) was added. After degassing and saturation with argon $PdCl_2$(dppf)·CH_2Cl_2 (70 mg, 86 μmol) was added, and the mixture was kept with stirring at 90 °C overnight. After cooling the solvent was replaced by ethyl acetate, the solution was passed over a plug of silica gel to remove a polar impurity, and the solid obtained after evaporation of the solvent was treated with boiling petroleum ether for 10 min to remove last traces of ethyl acetate. The solid was filtered off and dried at r. t./0.001 mbar for 1 h to leave a light-beige powder (0.81 g, 73 %), m. p. 169.9–170.3 °C. – IR (KBr): ν = 2978 w, 1732 vs (C=O), 1400 m, 1364 s, 1339 vs, 1276 m, 1239 m, 1189 s, 1146 m, 1134 m, 1091 m, 845 m, 703 m, 691 m, 593 m, 525 m cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 12 H, 4 CH_3), 4.90 (s, 2 H, CH_2), 7.30–7.38 (m, 3 H, H_{phenyl}), 7.51 (dd, ^3J = 6.6 Hz, 2 H, H_{phenyl}), 8.01 (d, J = 7.6 Hz, 1 H, H_{aryl}), 8.21 (d, J = 7.1 Hz, 1 H, H_{aryl}), 8.34 (s, 1 H, H_{aryl}) ppm. – ^{13}C NMR ($CDCl_3$): δ = 24.9 (CH_3), 42.7 (NCH_2), 85.1, 124.2, 126.9, 128.2, 128.7, 128.8, 129.0, 134.5, 137.1, 140.4, 159.0 (C=O) ppm. – MS (CI+): *m/z* (%) = 400 (100) $[M + H]^+$. – $C_{20}H_{22}BNO_5S$ (399.3): calcd. C 60.16, H 5.55, N 3.51; found C 60.02, H 5.39, N 3.42.

*(2-Benzyl-1,1-dioxido-3-oxo-2,3-dihydrobenzo[d]isothiazol-6-yl)boronic acid [(N-benzylsaccharin-6-yl)boronic acid] (**14**)*

Sodium periodate ($NaIO_4$, 0.81 g, 3.8 mmol) and boronic acid ester **13** (0.50 g, 1.3 mmol) were stirred in acetone/water (3/1, 30 mL) until a homogeneous solution was formed. After addition of 2 M hydrochloric acid (0.4 mL), the solution was stirred overnight. The colorless precipitate was filtered off with suction and washed with a small amount of cold acetone. The solid was discarded, and to the combined filtrates water was added until the solution became turbid. It was then left overnight in an open vessel (hood!) to allow acetone to evaporate. The formed precipitate of colorless needles was collected and dried at r. t./0.001 mbar for 1 h. Yield of **14**: 0.38 g (96 %), m. p. 180–181 °C. – IR (KBr): ν = 3553 s, 3358 br s, 3078 w, 2915 w, 1743 vs (C=O), 1453 m, 1427 s, 1350 vs, 1320 vs, 1285 vs, 1180 s, 1154 s, 1126 m, 1061 m, 958 m, 688 s, 599 m, 513 m cm^{-1}. – ^1H NMR (CD_3OD): δ = 4.88 (s, 2 H, NCH_2), 7.26–7.35 (m, 3 H, H_{phenyl}), 7.45 (d, J = 7.1 Hz, 2 H, H_{phenyl}), 8.01 (d, J = 3.8 Hz, 1 H, H_{aryl}), 8.23 (d, J = 4.1 Hz, 1 H, H_{aryl}), 8.29 (s, 1 H, H_{aryl}) ppm. – ^{13}C NMR (CD_3OD): δ = 43.3 (NCH_2), 125.0, 126.7, 129.0, 129.1, 129.4, 129.6, 136.5, 138.5, 140.9, 160.6 (C=O) ppm. – MS (CI+): *m/z* (%) = 274 (100) $[M - B(OH)_2 + 2\ H]^+$, 184 (17) $[M - B(OH)_2 - Bn + 2\ H]^+$. – $C_{14}H_{12}BNO_5S$ (317.1): calcd. C 53.02, H 3.81, N 4.42; found C 52.99, H 3.82, N 4.40.

*6,6′-((1,1′ : 3′,1″-Terphenyl)-3,3″-diylbis(methylene))bis(2-benzylbenzo[d]isothiazol-3(2H)-one 1,1-dioxide [3,3″-bis-(N-benzylsaccharin-6-ylmethyl)-1,1′ : 3′,1″-terphenyl] (**15**)*

Method A: A suspension of boronic acid ester **13** (0.50 g, 1.3 mmol), bis(bromomethyl)terphenyl **9** (0.25 g, 0.6 mmol, contaminated with a small amount of tetrabromide **10**, see above) and Cs_2CO_3 (0.86 g, 2.6 mmol) in THF (35 mL) and water (4 mL) was prepared in a thick-walled Schlenk tube, degassed, and saturated with argon. After addition of $PdCl_2(dppf)\cdot CHCl_3$ (76 mg, 89 μmol, 14.8 mol-% based on **9**), the mixture was kept with stirring at 80 °C overnight. After cooling the solvent was evaporated, the black residue was dissolved in dichloromethane (50 mL), and this solution was extracted with water (40 mL) to which 2 M aqueous HCl was added to facilitate the phase separation. The organic phase was washed with water (2 × 40 mL) to remove traces of acid, then dried with Na_2SO_4. A brown oil (0.53 g) was left after evaporation of the solvent, which was pre-purified by passing it through a short silica gel column (elution with ethyl acetate). Further separation was achieved by column chromatography on silica gel [140 g, elution with cyclohexane/ethyl acetate (4/1] to yield 0.23 g (48 %) of **15** as a colorless solid. – M. p. 138–144 °C (from THF/diisopropyl ether). – IR (KBr): ν = 3032 w, 2933 w, 1732 vs (C=O), 1600 m, 1338 s, 1324 s, 1261 s, 1171 s, 698 m, 595 m, 518 m cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 4.22 (s, 4 H, $ArCH_2Ar$), 4.89 (s, 4 H, NCH_2), 7.16 (d, J = 8.1 Hz, 2 H), 7.28–7.36 (m, 6 H), 7.41–7.57 (m, 13 H), 7.65–7.67 (m, 2 H), 7.72–7.75 (m, 3 H), 7.95 (d, J = 8.1 Hz, 2 H) (all arom. H) ppm. – ^{13}C NMR ($CDCl_3$): δ = 42.0, 42.6, 121.0, 125.3, 126.2, 126.4, 127.9, 128.1, 128.2, 128.61, 128.62, 129.3, 129.5, 134.5, 134.9, 138.1, 138.7, 141.3, 141.9, 149.7, 158.8 (C=O) ppm. – MS (CI+): *m/z* (%) = 801 (100) $[M]^+$. – $C_{48}H_{36}N_2O_6S_2$ (800.9): calcd. C 71.98, H 4.53, N 3.50; found C 71.79, H 4.63, N 3.45.

Method B: In a thick-walled Schlenk tube, boronic acid **14** (1.40 g, 2.6 mmol), bis(bromomethyl)terphenyl **9** (0.70 g, 1.7 mmol, contaminated with a small amount of tetrabromide **10**) and 2 M aqueous Na_2CO_3 (5.9 mL, 11.8 mmol) were mixed with toluene (40 mL) and ethanol (2 mL). The mixture was degassed and saturated with argon, then $Pd(PPh_3)_4$ (0.290 g, 0.25 mmol, 9.6 mol-% based on **14**) was added, and the mixture was kept with stirring at 90 °C overnight (a homogeneous phase was formed). After cooling dichloromethane (30 mL) was added, the solution was extracted with 3 × 20 mL of water, and the organic phase was dried with Na_2SO_4. After evaporation of the solvent, a foam remained which was separated by column chromatography on silica gel (140 g, elution with cyclohexane/ethyl acetate (5/1)), yielding 1.00 g (75 %) of **15** as an off-white solid.

*6,6′-((1,1′ : 3′,1″-Terphenyl)-3,3″-diylbis(methylene))bis-(benzo[d]isothiazol-3(2H)-one 1,1-dioxide [bis(saccharin-6-ylmethyl)-1,1′ : 3′,1″-terphenyl] (H_2tpsac, **7**)*

Benzyl-protected bis-saccharin **15** (0.20 g, 0.25 mmol), ammonium formate (0.310 g, 5 mmol) and palladium on coal (Pd/C 10 %, 0.10 g, 0.09 mmol) in ethanol (30 mL) were kept overnight with stirring at reflux temperature. The catalyst was filtered off, the solvent was evaporated, and the residual solid was suspended in 1 M aqueous HCl (30 mL) and exposed to ultrasonic irradiation for 5 min. The colorless jelly-like solid was filtered off with suction, washed with water and dried for 2 h at 140 °C/0.001 mbar. A colorless solid (0.13 g, 84 %) was obtained. A DSC measurement indicated a glass transition at T_g = 119 °C. – IR (KBr): ν = 3436 br s, 3285 br s, 3057 br m, 2677 br w, 1735 vs (C=O), 1600 s, 1482 m, 1338 vs, 1248 s, 1171 vs, 1137 s, 1115 m, 886 m, 788 m, 716 m, 597 m, 521 m cm^{-1}. – ^1H NMR ($CDCl_3$/[D_6]DMSO (9/1)): δ = 4.16 (s, 4 H, $ArCH_2Ar$), 7.12 (d, J = 7.6 Hz, 2 H), 7.35 (t, J = 7.6 Hz, 2 H), 7.41–7.48 (m, 7 H), 7.60–7.66 (m, 5 H), 7.81 (d, J = 8.1 Hz, 2 H) (all H-arom.) ppm. – ^{13}C NMR ($CDCl_3$/[D_6]DMSO (9/1)): δ = 41.3 ($ArCH_2Ar$), 120.2, 124.5, 125.3, 125.4, 125.69, 125.74, 127.3, 127.6, 128.8, 128.9, 134.1, 138.6, 139.7, 140.7, 141.1, 149.0, 160.2 (C=O) ppm. – MS (CI+): *m/z* (%) = 621 (100)

$[M + H]^+$. – $C_{34}H_{24}N_2O_6S_2$ (620.7): calcd. 65.79, H 3.90, N 4.51; found C 65.68, H 4.02, N 4.50.

*$[Ru_2(CO)_5(\mu,\mu\text{-tpsac})]_2$ (**17**)*

$Ru_3(CO)_{12}$ (0.10 g, 0.16 mmol), H_2tpsac (**7**, 0.15 g, 0.24 mmol) and dry toluene (30 mL) were placed in a thick-walled Schlenk tube and kept with stirring at 130 °C overnight. The solution was allowed to come to r. t., and petroleum ether (30 mL) was added. The formed yellow precipitate was isolated and stirred in refluxing cyclohexane for 1 h. The solvent was evaporated, and the residue was dried at 150 °C/0.001 mbar. A light-brown solid (0.12 mg) was obtained, which still contained some toluene that could not be removed even after longer drying at 150 °C/0.001 mbar. The complex decomposed above 380 °C (heating rate 10 °C min^{-1}). NMR spectra indicate the presence of two or more species. – IR (KBr): ν = 2926 w, 2851 w, 2096 s (CO_{ax}), 2040 vs (CO_{eq}), 2013 vs (CO_{eq}), 1946 s (CO_{eq}), 1614 s (C=O, sac), 1577 s (C=O, sac), 1376 m, 1322 m, 1163 s, 959 m cm^{-1}. – ^{1}H NMR ($CDCl_3$, 325 K): δ = 3.99–4.20 (m, 8 H, CH_2), 7.06–7.72 (m, 36 H, H_{aryl}) ppm. – ^{13}C NMR ($CDCl_3$, 325 K): δ = 42.1–42.2, 120.8–122.4, 124.2–129.4, 133.8–134.9, 138.6–139.2, 140.8–143.3, 148.4–148.6, 172.0, 175.5, 176.2, 178.5, 179.4, 194.1 – 199.3 ppm.

*$[Ru_2(CO)_4(\mu,\mu\text{-tpsac})]_n$ (**18**)*

In a round-bottom flask fitted with a reflux condenser, complex **17** (55 mg) was heated for 4 d in toluene at 109 °C (50 mL). After cooling and evaporation of the solvent *in vacuo*, the residue was dried at 150 °C/0.001 mbar for 1 h. A greenish-grey solid of complex **18** was left (47 mg, 45 % yield based on $Ru_3(CO)_{12}$), which turned yellow in contact with toluene or dichloromethane. Decomp. > 220 °C (heating rate 10 °C min^{-1}). – IR (KBr): ν = 3059 w, 2926 w, 2046 vs (CO_{eq}), 1995 s (CO_{eq}), 1963 vs (CO_{eq}), 1614 s (C=O, sac), 1577 s (C=O, sac), 1311 m, 1156 s, 957 m cm^{-1}. – The NMR spectra indicate the presence of more than one species. – ^{1}H NMR ([D$_6$]DMSO, 350 K): δ = 4.05–4.30 (m, 4 H, CH_2), 7.05–8.02 (m, 18 H, CH_{ar}) ppm. – ^{13}C NMR ([D$_6$]DMSO, 350 K): δ = 40.4, 40.5, 119.9–121.1, 123.6–128.9, 133.8–134.2, 139.7–141.6, 148.8–149.3, 175.9–177.2, 197.0 – 200.1 ppm. – $C_{38}H_{22}N_2O_{10}Ru_2S_2$ (932.9): C 48.93, H 2.38, N 3.00; found C 48.79, H 2.38, N 2.84.

*$[Ru_2(CO)_4(PPh_3)_2(\mu,\mu\text{-tpsac})]$ (**19**) and $[Ru_2(CO)_5(PPh_3)(\mu,\mu\text{-tpsac})]$ (**20**)*

A mixture of complex **17** (1 equiv.), triphenylphosphane (2 equiv.) and dichloromethane (1 mL for 8 μmol) was stirred until a clear solution was formed. The solvent was evaporated, and the residue was extracted while hot with two portions of cyclohexane (1 mL for 6 μmol) in order to remove residual PPh_3 (control by TLC). The yellow solid was dried at 100 °C/0.001 mbar for 1 h. A ^{31}P NMR spectrum suggested the presence of complexes **19** and **20** in a 10 : 1 molar ratio. – Decomp. > 220 °C (heating rate 10 °C min^{-1}). – IR (KBr): ν = 3058 w, 2924 w, 2085 w (CO_{ax}, **20**), 2034 vs (CO_{eq}), 1996 m (CO_{eq}), 1963 s (CO_{eq}), 1952 s (CO_{eq}), 1610 s (C=O, sac), 1571 s (C=O, sac), 1481 m, 1435 m, 1322 m, 1164 m, 695 m cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.85–4.09 (m, 4 H, CH_2, **19** + **20**), 6.87–7.77 (m, 52 H, H_{aryl}, **19** + **20**) ppm. – ^{31}P NMR ($CDCl_3$): δ = 14.4 (**19**), 23.6 (**20**) ppm.

When complex **18** was allowed to react with two molar equivalents of triphenylphosphane in $CDCl_3$ solution (NMR tube), complex **19** was formed almost exclusively, with only traces of **20** detectable. ^{31}P NMR: δ = 14.4 (**19**), 22.3 (slightly different from value given above for **20**).

*X-Ray structure determination of $[Ru_2(CO)_4(PPh_3)_2(\mu,\mu\text{-tpsac})]$ (**19**)*

Suitable yellow crystals were obtained by slow evaporation of a toluene–dichloromethane solution at 7 °C.

Table 2. Crystal structure data for $[Ru_2(CO)_4(PPh_3)_2(\mu,\mu$-tpsac)] (**19**).

Formula	$C_{74}H_{52}N_2O_{10}P_2Ru_2S_2$
M_r	1457.38
Crystal size, mm^3	$0.23 \times 0.23 \times 0.19$
Crystal system	monoclinic
Space group	$C2/c$
a, Å	18.232(5)
b, Å	20.782(5)
c, Å	18.252(4)
α, deg	90
β, deg	118.89(3)
γ, deg	90
V, Å^3	6055(2)
Z	4
D_{calcd}, g cm^{-3}	1.60
μ(Mo K_α), cm^{-1}	6.9
F(000), e	2960
hkl range	±21, ±24, ±21
θ range, deg	2.34–24.41
Refl. measured/unique/R_{int}	23 399/4955/0.1003
Param. refined/restraints	416/0
$R(F)/wR(F^2)$[a] ($I > 2\sigma(I)$)	0.0510/0.1103
$R(F)/wR(F^2)$[a] (all reflexions)	0.0928/0.1223
GoF (F^2)[b]	0.876
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.26/ – 0.39

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$; [b] GoF = $[\sum w(|F_o| - |F|_c)^2/(N_{obs} - N_{param})]^{1/2}$.

Data collection was performed at 190 K on an image-plate diffractometer (Stoe IPDS) using monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods and refined (F^2 values) using a full-matrix least-squares method. Hydrogen atom positions were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. Software for structure solution and refinement: SHELX-97 [35, 36]; molecule plot: ORTEP-3 [37]. Further details are provided in Table 2.

CCDC 882161 contains the supplementary crystallographic 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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