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One-pot synthesis of the new dianionic ligand $[Na]_2[C_5H_4CO_2(CH_2)_2NTs]$; preparation and structures of two rhodium derivatives

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Abstract

The new dianionic ligand $[Na]_2[C_5H_4CO_2(CH_2)_2NTs]$ (**1**) having an alkoxycarbonyl and an amide group in the same side chain has been prepared by a single step, high yield procedure. The synthesis of the related rhodium complexes $[Rh\{\eta^5\text{-}C_5H_4CO_2(CH_2)_2N(H)Ts\}(NBD)]$ (**3**) and $[Rh\{\eta^5\text{-}C_5H_4CO_2(CH_2)_2N(Me)Ts\}(NBD)]$ (**4**) is reported as well as their X-ray molecular structures.

Keywords: Cyclopentadienyl ligands; Oxazolidin-2-ones; Rhodium complexes; X-ray diffraction

1. Introduction

In the late 1980s, Bercaw and Shapiro [1] introduced the first complexes of a dianionic bridged amido-cyclopentadienyl ligand system $[\mathbf{A}]^{2-}$ (in Chart 1). Since then a variety of Cp/amide "constrained geometry" ligands, derived from the parent compound $[\mathbf{A}]^{2-}$, have become known and Chart 1 shows some representative examples [2].

All the dianionic ligands of the type reported in Chart 1 have been prepared with stepwise methods typically including purification of the intermediate products by distillation or sublimation. For instance, the synthesis of **A** can be accomplished using different routes: starting from the Cp fragment, from the amine NH_2R^2 or by introducing the amido linkage within the preformed half-sandwich complex. In any case at least three reaction steps are required [2a,b].

We have recently shown that the reaction of NaCp with aliphatic five-membered cyclic carbonates leads, in one step and high yields, to the selective formation of novel chiral and non-chiral hydroxy-functionalised alkoxycarbonylcyclopentadienides $Na[C_5H_4CO_2(CHR)_2OH]$ (R = H, Me, Ph) without formation of any by-product [3a–e]. These functionalised Cp ligands provided a valuable route to novel sandwich and half-sandwich metal complexes and among these the rhodium derivatives $[Rh\{\eta^5\text{-}C_5H_4CO_2(CHR)_2OH\}(L,L)]$ [R = H, Me, Ph; L,L = 2 CO, NBD] exhibited catalytic activity in the homogeneous hydroformylation and hydrogenation of hex-1-ene and styrene [3c–e].

In addition, the presence in the lateral chain of the Cp ligand of an hydroxyl functionality has been exploited to develop a new route for anchoring the rhodium complexes on the surface of polypropylenimine dendrimers DAB-*dendr*-$(NH_2)_n$ {n = 4, 8, 16, 32, 64} leading to

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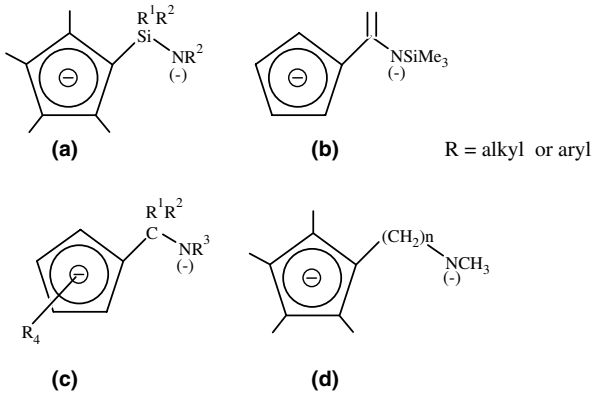


Chart 1.

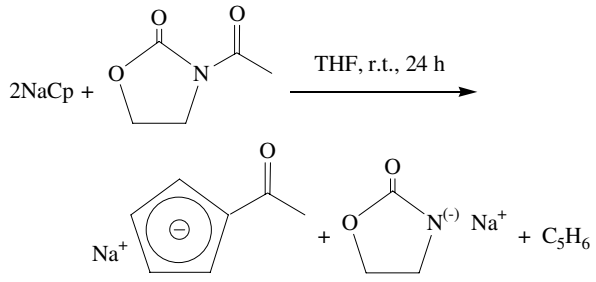
the quantitative formation of new, completely functionalised, organometallic macromolecules containing up to 64 peripheral alkoxycarbonylcyclopentadienyl complexes of rhodium(I) [4].

These results made us wonder if it were possible to apply the same procedure to five-membered cyclic oxazolidin-2-ones. In this paper, we report the reaction of NaCp with oxazolidin-2-ones and describe the one-step, high yield synthesis of the new dianionic cyclopentadienyl ligand $[Na]_2[C_5H_4CO_2(CH_2)_2NTs]$ (**1**) having an alkoxycarbonyl and an amide group on the same side chain. The synthesis and structure of related rhodium complexes is also described.

2. Results and discussion

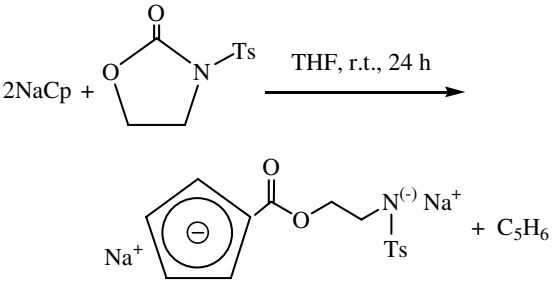
2.1. Synthesis and characterization of $[Na]_2[C_5H_4CO_2(CH_2)_2NTs]$ (1)

The initial observations that NaCp does not react with 3-methyl-oxazolidin-2-one or 3-trimethylsilyl-oxazolidin-2-one led us to consider systems with a nitrogen bearing an electron withdrawing group. In this direction, the first attempt with the commercially available 3-acetyl-oxazolidin-2-one resulted in the formation of the already known acetylcyclopentadienyl sodium $Na[C_5H_4COCH_3]$ [5] together with the oxazolidin-2-one sodium salt and cyclopentadiene with an overall reaction stoichiometry shown in Eq. (1) (see also Section 3).



(1)

This undesired result nevertheless indicated that a molecule in which the nitrogen atom is bound to a functional group not susceptible to undergo a nucleophilic attack by the Cp^- could be a promising candidate for our target molecule. Indeed, treatment of two equivalents of NaCp with one equivalent of 3-tosyl-oxazolidin-2-one in THF at room temperature for 24 h finally led to the one-step, high yield synthesis of the new dianionic cyclopentadienyl ligand $[Na]_2[C_5H_4CO_2(CH_2)_2NTs]$ (**1**) containing an alkoxycarbonyl and an amide group in the same side chain



(2)

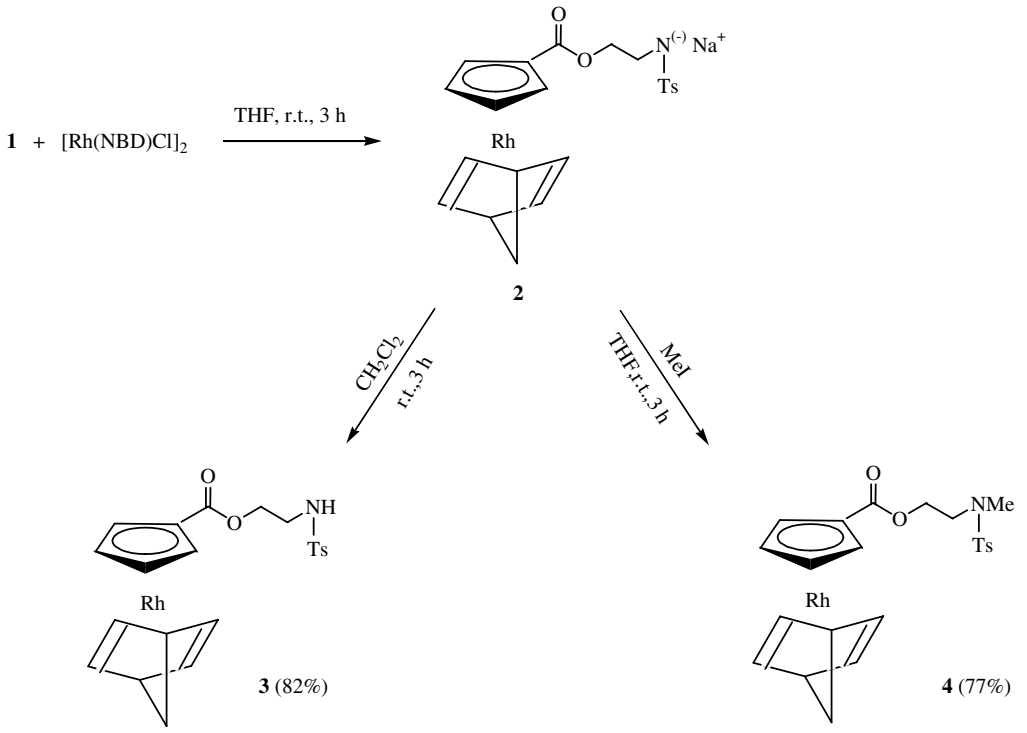
1 (91%)

The regioselective ring-opening reaction is likely to proceed via the formation of the 1-substituted cyclopentadiene intermediate $[Na][C_5H_5CO_2(CH_2)_2NTs]$ that, unlike what found with cyclic carbonates, is not intramolecularly deprotonated by the amide arm but by a second molecule of NaCp. After work-up, the dianionic ligand **1** was obtained in yields higher than 90% as an air- and moisture-sensitive beige solid soluble in THF.

The ^1H NMR spectrum in $[D_5]$Pyr showed for the Cp ring protons two AA′BB′ pseudotriplets at δ 7.36 and 6.60 whilst in the ^{13}C NMR the Cp signals were found in the range δ 113–109, very similar to what already reported for $Na[C_5H_4CO_2(CHR)_2OH]$ (R = H, Me, Ph) [3b–e]. The methylene protons of the anionic pendant side chain exhibited two triplets at δ 4.61 (CO_2CH_2) and 3.52 (CH_2N) with corresponding resonances in the ^{13}C NMR at δ 64.5 and 46.6. The IR spectra of **1** in THF showed a (C═O) broad band around 1635 cm^{-1}.

2.2. Synthesis and molecular structure of $[Rh\{\eta^5\text{-}C_5H_4CO_2(CH_2)_2N(H)Ts\}(NBD)]$ (3) and $[Rh\{\eta^5\text{-}C_5H_4CO_2(CH_2)_2N(Me)Ts\}(NBD)]$ (4)

In order to get further evidences of the dianionic nature of **1**, we reacted it with $[Rh(NBD)Cl]_2$ in THF at room temperature. The reaction readily led to the quantitative formation (established by NMR of the crude reaction mixture) of $[Na][Rh\{\eta^5\text{-}C_5H_4CO_2(CH_2)_2NTs\}(NBD)]$ (**2**) that for further treatment either with a proton acidic solvent such as dichloromethane or MeI, respectively, gave, after chromatography, the



Scheme 1.

neutral yellow, air-stable complexes [Rh{η^5-$C_5H_4CO_2$-$(CH_2)_2$N(H)Ts}(NBD)] (**3**) and [Rh{η^5-$C_5H_4CO_2$-$(CH_2)_2$N(Me)Ts}(NBD)] (**4**) (Scheme 1).

The two rhodium complexes **3** and **4** have been fully characterised by standard analytical/spectroscopic measurements. The NMR spectra in $CDCl_3$ of the complexes depicted in Scheme 1 showed the resonances for the C_5H_4- and NBD moieties, which are strictly comparable with those of the previously reported [Rh{η^5-$C_5H_4CO_2(CH_2)_2OH$}(NBD)] [3b].

Crystallization from CH_2Cl_2/Etp by the diffusion method yielded for both **3** and **4** single crystals that were characterised by X-ray diffraction. The molecular structures, as found in the crystals, are shown in Fig. 1 for **3** and Fig. 2 for **4**, relevant bond parameters are comparatively listed in Table 1. In order to make comparisons easier, the molecular drawings adopt almost equivalent points of view for the C_5H_4COO planar fragments.

Concerning **3**, the geometry of coordination around Rh is quite regular and the NBD molecule and C_5H_4COO fragment are mutually oriented in a quasi C_s symmetry. The side chain deprives the molecule of any symmetry and the crystal contains two randomly packed isomers of almost equivalent overall hindrance and shape. The disorder is seemingly generated by the fact that molecules of opposite configuration at the N(1) chiral centre fail to pack in an orderly way. In fact, the flexibility of the chain is able to confer comparable shape to the enantiomers.

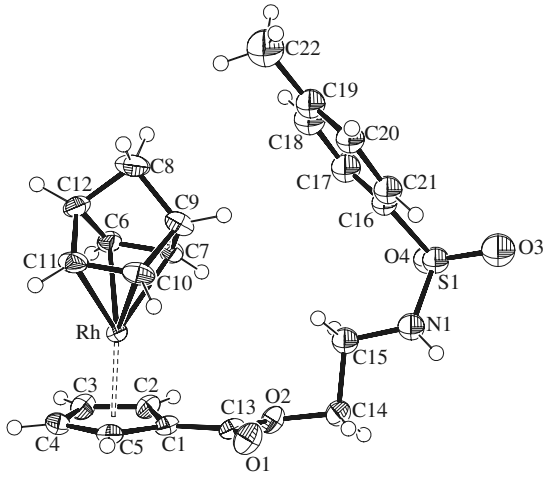


Fig. 1. Molecular structure of [Rh{$C_5H_4CO_2$ $(CH_2)_2$N(H)Ts}(NBD)] (**3**) showing the atomic numbering (thermal ellipsoids at 50% probability level). For the sake of clarity, only one image of the disordered side chain is shown.

The crystal of **4** contains an ordered packing of two isomers labelled **I** and **II** in Fig. 2. The coordination geometry around Rh, apart from a slightly different orientation of the NBD ligand, is substantially similar in the two isomers and **3**. However, significant differences are present in the side chains, starting from the point of attachment to the carboxylate oxygens. With reference to Fig. 2, C(14) is attached to the rear oxygen in molecule **I**, as in **3**, and to the front oxygen in molecule

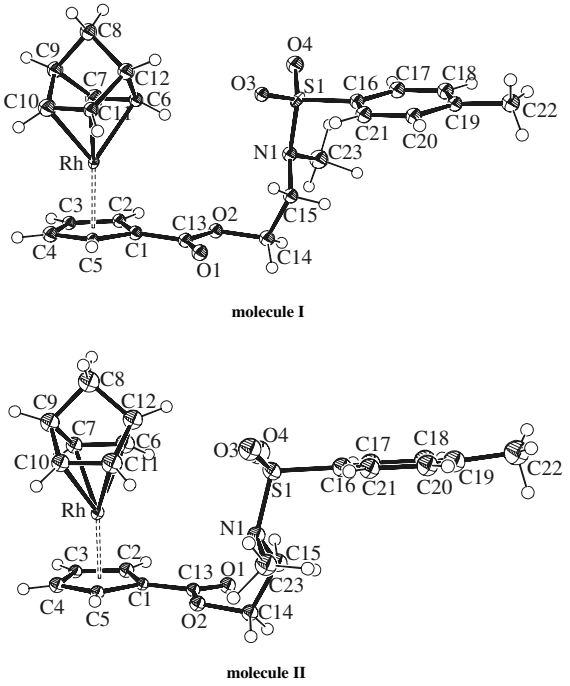


Fig. 2. Absolute structures of the two isomers (**I** and **II**) of [Rh{$C_5H_4CO_2(CH_2)_2N(CH_3)Ts$}(NBD)] (**4**) found in the crystal (thermal ellipsoids at 50% probability level).

II. A second relevant difference is that the absolute configuration at N(1) is *S* in **I** and *R* in **II**. In spite of these structural variations, the *p*-tolyl groupings are similarly oriented in **I** and **II**. Their positioning is quite different from that found in **3**. There is no spectroscopic evidence (NMR) of the persistence of isomeric forms in solution at least down to −80 °C.

Table 1
Significant bond distances (Å) for **3** and **4**

	3	**4**	
		I	**II**
Rh–C(1)	2.237(2)	2.263(5)	2.276(5)
Rh–C(2)	2.244(2)	2.193(6)	2.270(6)
Rh–C(3)	2.304(2)	2.271(5)	2.270(6)
Rh–C(4)	2.303(2)	2.293(6)	2.267(6)
Rh–C(5)	2.229(2)	2.262(5)	2.249(6)
Rh–C(6)	2.134(2)	2.106(6)	2.129(8)
Rh–C(7)	2.122(2)	2.091(7)	2.134(7)
Rh–C(10)	2.118(2)	2.105(7)	2.154(8)
Rh–C(11)	2.135(2)	2.126(6)	2.167(8)
C(1)–C(2)	1.430(3)	1.429(4)	1.425(4)
C(1)–C(5)	1.425(3)	1.427(4)	1.435(4)
C(2)–C(3)	1.420(3)	1.425(4)	1.423(4)
C(3)–C(4)	1.414(3)	1.424(4)	1.418(4)
C(4)–C(5)	1.421(3)	1.422(4)	1.423(4)
C(6)–C(7)	1.415(3)	1.413(5)	1.407(5)
C(7)–C(9)	1.533(3)	1.538(5)	1.535(5)
C(8)–C(9)	1.544(3)	1.540(5)	1.539(5)
C(8)–C(12)	1.541(3)	1.545(5)	1.547(5)
C(9)–C(10)	1.537(3)	1.536(5)	1.531(5)
C(10)–C(11)	1.407(3)	1.400(5)	1.390(5)
C(6)–C(12)	1.531(3)	1.534(5)	1.546(5)
C(11)–C(12)	1.535(3)	1.534(5)	1.543(5)
C(1)–C(13)	1.463(3)	1.465(4)	1.465(4)
C(13)–O(1)	1.210(3)	1.209(5)	1.212(4)
C(13)–O(2)	1.351(3)	1.355(6)	1.358(5)
C(14)–O(2)	1.445(3)	1.453(5)	1.450(5)
C(14)–C(15)	1.542(4)[a]	1.511(6)	1.523(6)
N(1)–C(15)	1.460(4)[a]	1.474(5)	1.479(5)
N(1)–S(1)	1.630(4)[a]	1.651(4)	1.655(4)
N(1)–C(23)		1.467(5)	1.467(5)
S(1)–O(3)	1.432(4)[a]	1.424(3)	1.435(3)
S(1)–O(4)	1.428(4)[a]	1.439(3)	1.431(4)
S(1)–C(16)	1.761(3)[a]	1.758(2)	1.758(3)

[a] Average value.

3. Experimental section

3.1. Materials and procedures for the syntheses

All reactions with organometallic reagents or substrates were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. The prepared derivatives were characterised by elemental analysis and spectroscopic methods. The IR spectra were recorded with a FT-IR spectrometer Perkin–Elmer Spectrum 2000. The NMR spectra were recorded using Varian Gemini XL 300 (^{1}H, 300.1; ^{13}C, 75.5 MHz), Varian MercuryPlus VX 400 (^{1}H, 399.9; ^{13}C, 100.6 MHz), Varian Inova 600 (^{1}H, 599.7, ^{13}C, 150.8 MHz) instruments. The spectra were referenced internally to residual solvent resonances and were recorded at 298 K for characterization purposes. EI-MS spectra were taken using a VG 7070E mass spectrometer. ESI-MS analysis were performed by direct injection of methanol solutions of the metal complexes using a WATERS ZQ 4000 mass spectrometer. GC–MS analyses were run on a chromatograph fitted with a 25-m capillary column (5% phenyl methyl silicone) and a quadrupolar detector working at 70 eV. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. The reagent 3-acetyl-oxazolidin-2-one (Aldrich) was recrystallised from Et_2O, 3-tosyl-oxazolidin-2-one was prepared according to the literature procedures [6]; $[Rh(NBD)Cl]_2$ was used as purchased, MeI was distilled under argon and stored on molecular sieves. Petroleum ether (Etp) refers to a fraction of b.p. 60–80 °C. Column chromatography were carried out on silica gel previously heated at about 200 °C while a slow stream of a dry nitrogen was passed through it [7]. Melting points were taken in sealed capillaries and were uncorrected.

3.1.1. Preparation of $[Na][C_5H_4C(O)CH_3]$

A mixture of NaCp (1.26 g, 14.3 mmol) and 3-acetyl-oxazolidin-2-one (0.93 g, 7.2 mmol) in THF (50

Table 2
Crystal data and details of structure refinement for complexes **3** and **4**

	3	**4**
Empirical formula	$C_{22}H_{24}NO_4SRh$	$C_{23}H_{26}NO_4SRh$
Formula weight	501.39	515.42
Temperature (K)	193	193
Wavelength (Å)	0.71069	0.71069
Crystallographic system	Monoclinic	Monoclinic
Space group	$P2_1/n$, no. 14	$P2_1$, no. 4
Unit cell dimensions		
a (Å)	19.7525(6)	9.2874(6)
b (Å)	5.7898(2)	6.0903(4)
c (Å)	20.2419(6)	37.184(2)
β (°)	117.296(1)	96.948(1)
Volume (Å^3)	2057.2(1)	2087.8(2)
Z	4	4
Crystal size (mm)	$0.18 \times 0.21 \times 0.34$	$0.15 \times 0.24 \times 0.40$
Maximum θ for data collection (°)	30	30
Number of reflections collected	21,735	26,940
Number of observed induced reflections	4913	6628
Number of parameters	230	238
Goodness-of-fit on F^2	1.00	1.17
Final R indices [$I > 2\sigma(I)$] (R_1 and wR^2)	0.033 and 0.084	0.056 and 0.119
R indices (all data) (R_1 and wR^2)	0.040 and 0.089	0.062 and 0.121
Largest difference peak and hole (e Å^{-3})	0.81 and −0.63	0.84 and −0.93

mL) was stirred at r.t. for 24 h to give a brownish solution along with a white precipitate. The reaction mixture was filtered. After evaporation of the solvent under reduced pressure 0.90 g (96%) of a light brown solid were obtained and identified as [Na][C_5H_4-C(O)CH_3] by comparison of the ^{1}H NMR spectra in D_2O with the literature data [5]. We here report the not previously described NMR spectra of [Na][C_5H_4-C(O)CH_3] in [D_5]Pyr. ^{1}H NMR (300.1 MHz, [D_5]Pyr): δ = 7.39 (m, 1H; Cp), 7.15 (m, 1H; Cp), 6.66 (m, 2H; Cp), 2.49 (s, 3H; Me); ^{13}C–{η^1H} NMR (75.5, [D_5]Pyr): δ = 187.6 (C═O), 117.1, 115.8, 113.6, 111.3 (CH; Cp), 26.3 (CH_3).

The NMR analysis of the white solid revealed to be the oxazolidin-2-one sodium salt while the GC–MS analysis of the volatiles showed the presence of $(C_5H_6)_2$.

3.1.2. Preparation of [Na]$_2$[$C_5H_4CO_2(CH_2)_2NTs$] (**1**)

To a solution of NaCp (4.74 g, 53.9 mmol) in THF (100 mL), solid 3-tosyl-oxazolidin-2-one was added (6.51 g, 27.0 mmol). The mixture was stirred for 24 h at room temperature and during this time it turned from an heterogeneous system (the oxazolidin-2-one is sparingly soluble in THF) to a slightly turbid solution filtered on a celite pad. After filtration, the volatiles were removed under vacuum and the residue kept under vacuum at 60 °C for 2 h. The resulting solid was washed with Et_2O to give 8.61 g (91%) of **1** as a beige solid.

^{1}H NMR (599.7 MHz, [D_5]Pyr): δ = 7.96 (AA′BB′, $^3J_{H,H}$ = 7.8 Hz, 2H; Ts) 7.36 (AA′BB′, $^3J_{H,H}$ = 2.7 Hz, 2H; Cp), 7.00 (AA′BB′, $^3J_{H,H}$ = 7.8 Hz, 2H; Ts), 6.60 (AA′BB′, $^3J_{H,H}$ = 2.7 Hz, 2H; Cp), 4.61 (t, $^3J_{H,H}$ = 5.9 Hz, 2H; CO_2CH_2), 3.52 (t, $^3J_{H,H}$ = 5.9 Hz, 2H; CH_2N), 2.14 (s, 3H; Me); ^{13}C{^{1}H} NMR (150.8 MHz, [D_5]Pyr): δ = 169.3 (C═O), 150.2 (*ipso*-C; Ts), 139.6 (*ipso*-C, Ts), 129.1 (CH, Ts), 127.4 (CH, Ts), 112.8 (CH, Cp), 111.3 (CH, Cp), 109.6 (*ipso*-C, Cp), 64.5 (CO_2C_2), 46.6 (CH_2N), 21.1 (CH_3). IR (THF, cm^{-1}) ν(C═O) 1635 (bs). Anal. Calcd. for $C_{15}H_{14}Na_2NO_4S$: C, 51.4; H, 4.03; Found: C, 51.7; H, 4.06%. The GC–MS (*m*/*z*, %) analysis of the volatiles showed the presence of $(C_5H_6)_2$: 132 ([M]$^+$, 17), 66 ([C_5H_6]$^+$, 100).

3.1.3. Preparation of [Rh{η^5-$C_5H_4CO_2(CH_2)_2N(H)Ts$}(NBD)] (**3**)

To a solution of **1** (0.84 g, 2.39 mmol) in THF (25 mL), solid [Rh(NBD)Cl]$_2$ (0.47 g, 1.02 mmol) was added. After stirring 3 h at room temperature, all the starting rhodium reagent has reacted as judged by TLC. The solvent was removed under vacuum and CH_2Cl_2 was added. The suspension was stirred for further 3 h and then first filtered on a celite pad and subsequently chromatographed on silica gel employing straight Et_2O as the eluting solvent. A yellow fraction was collected and identified as the title compound **3** (0.84 g, 82%). ^{1}H NMR (399.9 MHz, $CDCl_3$): δ = 7.78 (AA′BB′, $^3J_{H,H}$ = 8.0 Hz, 2H; Ts), 7.25 (d, $^3J_{H,H}$ = 8.0 Hz, 2H; Ts) 5.40 (AA′BB′, $^3J_{H,H}$ = 2.1 Hz, 2H; Cp), 5.31 (AA′BB′X, $^3J_{H,H}$ = 2.1 Hz, $J_{H,Rh}$ = 0.9 Hz, 2H; Cp), 5.14 (t, $^3J_{H,H}$ = 6.0 Hz, 1H; NHTs), 4.20 (t, $^3J_{H,H}$ = 5.4 Hz, 2H; CO_2CH_2), 3.32 (m, 8H; $H_{1,2,3,4,5,6}$, NBD, CH_2N overlapping peaks), 2.37 (s, 3H; CH_3), 0.99 (t, $^3J_{H,H}$ = 1.4 Hz, 2H; H_7, NBD); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 165.9 (C═O), 143.4 (*ipso*-C, Ts), 136.9 (*ipso*-C, Ts), 129.7 (CH, Ts), 126.9 (CH, Ts), 90.9 (d, $J_{C,Rh}$ = 4.6 Hz; *ipso*-C, Cp), 88.5 (d, $J_{C,Rh}$ = 4.0 Hz; CH, Cp), 85.9 (d, $J_{C,Rh}$ = 4.0 Hz; Cp), 62.1 (CO_2CH_2), 57.5 (d, $J_{C,Rh}$ = 6.5 Hz; C_7, NBD), 46.7 (d, $J_{C,Rh}$ = 2.4 Hz; $C_{1,4}$, NBD), 42.6 (CH_2N), 32.7 (d, $J_{C,Rh}$ = 10.5 Hz; $C_{2,3,5,6}$, NBD), 21.4 (CH_3). ^{1}H NMR (399.9 MHz, [D_8]Toluene): δ = 7.67 (AA′BB′, $^3J_{H,H}$ = 8.2 Hz, 2H; Ts), 6.78 (d, $^3J_{H,H}$ = 8.2 Hz, 2H; Ts) 5.45 (AA′BB′, $^3J_{H,H}$ = 2.2 Hz, 2H; Cp), 5.04 (AA′BB′X, $^3J_{H,H}$ = 2.2 Hz, $J_{H,Rh}$ = 0.9 Hz, 2H; Cp), 4.55 (t, $^3J_{H,H}$ = 6.0 Hz, 1H; NHTs), 3.91 (t, $^3J_{H,H}$ = 5.4 Hz, 2H; CO_2CH_2), 3.27 (m, 4H; $H_{2,3,5,6}$, NBD), 3.18 (m, 2H; $H_{1,4}$, NBD), 2.92 (m, 2H; CH_2N), 1.94 (s, 3H; CH_3), 0.88 (t, $^3J_{H,H}$ = 1.6 Hz, 2H; H_7, NBD). IR (THF, cm^{-1}): ν = 1712 (s) (C═O). ESI-MS [M]$^+$ + Na = 524 *m*/*z*. Anal. Calcd. for $C_{22}H_{24}NO_4RhS$: C, 52.8; H, 4.63; Found: C, 52.7; H, 4.64%. m.p. = 114 to 116 °C. R_f(Et_2O, SiO_2) = 0.39.

In a parallel experiment, the in situ generated [Na][Rh{$C_5H_4CO_2(CH_2)_2NTs$}(NBD)] (**2**) was analysed by NMR spectroscopy as follows: after 3 h a portion of the crude mixture was transferred with a cannula to a NMR tube. The solvent was removed under vacuum and after addition of [D_5]Pyr the tube was flame sealed under argon. NMR data for **2**: ^{1}H NMR (^{1}H, 399.9 MHz, [D_5]Pyr): δ = 8.09 (AA′BB′, $^3J_{H,H}$ = 8.4 Hz, 2H; Ts), 7.18 (AA′BB′, $^3J_{H,H}$ = 8.4 Hz, 2H; Ts), 5.70 (m, 2H; Cp), 5.35 (m, 2H; Cp), 4.64 (t, $^3J_{H,H}$ = 5.9 Hz, 2H; CO_2CH_2), 3.49 (t, $^3J_{H,H}$ = 5.9 Hz, 2H; CH_2N), 3.36 (m, 4H; $H_{2,3,5,6}$, NBD), 3.18 (m, 2H; $H_{1,4}$, NBD), 2.19 (s, 3H; Me), 0.85 (t, $^3J_{H,H}$ = 1.7 Hz, 2H; H_7, NBD); ^{13}C{^{1}H} NMR (100.6 MHz, [D_5]Pyr): δ = 166.2 (C═O), 141.1 (*ipso*-C, Ts), 129.4, 127.4 (Ts), 88.9 (d, $J_{C,Rh}$ = 5.0 Hz; *ipso*-C, Cp), 88.7 (d, $J_{C,Rh}$ = 4.5 Hz; CH, Cp), 86.7 (d, $J_{C,Rh}$ = 4.2 Hz; CH, Cp), 65.4 (CO_2C_2), 57.5 (d, $J_{C,Rh}$ = 6.9 Hz; C_7, NBD), 47.0 (d, $J_{C,Rh}$ = 2.9 Hz; $C_{1,4}$, NBD), 44.9 (CH_2NHTs), 32.6 (d, $J_{C,Rh}$ = 10.5 Hz; $C_{2,3,5,6}$, NBD), 21.1 (CH_3).

3.1.4. Preparation of [Rh{η^5-$C_5H_4CO_2(CH_2)_2N(Me)Ts$}(NBD)] (4)

To a solution of **1** (0.37 g, 1.1 mmol) in THF (25 mL), solid [Rh(NBD)Cl]$_2$ (0.20 g, 0.43 mmol) was added. After stirring 3 h at room temperature 0.2 mL of freshly distilled MeI was slowly added with a syringe. After 4 h, the solvent was removed under vacuum and CH_2Cl_2 was added. The suspension was first filtered on a celite pad and then chromatographed on silica gel using Et_2O/Etp (1:1) as the eluting solvent. A yellow fraction was collected and identified as the title compound (0.34 g, 77%). ^{1}H NMR (399.9 MHz, $CDCl_3$): δ = 7.68 (AA′BB′, $^3J_{H,H}$ = 8.1 Hz, 2H; Ts), 7.30 (AA′BB′, $^3J_{H,H}$ = 8.1 Hz, 2H; Ts), 5.46 (m, 2H; Cp), 5.34 (m, 2H; Cp), 4.35 (t, $^3J_{H,H}$ = 5.6 Hz, 2H; CO_2CH_2), 3.35 (t, $^3J_{H,H}$ = 5.6 Hz, 2H; CH_2N), 3.32 (m, 4H; $H_{2,3,5,6}$, NBD), 3.30 (m, 2H; $H_{1,4}$, NBD), 2.88 (s, 3H; NCH_3), 2.41 (s, 3H; CH_3), 0.99 (t, $^3J_{H,H}$ = 1.4 Hz, 2H; H_7, NBD); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 165.7 (C═O), 143.4 (*ipso*-C, Ts), 134.7 (*ipso*-C, Ts), 129.7 (CH, Ts), 127.3 (CH, Ts), 91.5 (d, $J_{C,Rh}$ = 4.0 Hz; *ipso*-C, Cp), 88.4 (d, $J_{C,Rh}$ = 4.0 Hz; CH, Cp), 86.0 (d, $J_{C,Rh}$ = 4.0 Hz; Cp), 61.9 (CO_2C_2), 57.5 (d, $J_{C,Rh}$ = 6.5 Hz; C_7, NBD), 49.1 (CH_2N), 46.7 (d, $J_{C,Rh}$ = 2.4 Hz; $C_{1,4}$, NBD), 36.0 (NCH_3), 32.6 (d, $J_{C,Rh}$ = 10.5 Hz; $C_{2,3,5,6}$, NBD), 21.5 (CH_3). ^{1}H NMR (399.9 MHz, [D_8]Toluene): δ = 7.55 (AA′BB′, $^3J_{H,H}$ = 8.2 Hz, 2H; Ts), 6.79 (AA′BB′, $^3J_{H,H}$ = 8.2 Hz, 2H; Ts), 5.53 (AA′BB′, $^3J_{H,H}$ = 2.2 Hz, 2H; Cp), 5.05 (AA′BB′X, $^3J_{H,H}$ = 2.2 Hz, $J_{H,Rh}$ = 0.8 Hz, 2H; Cp), 4.15 (t, $^3J_{H,H}$ = 5.6 Hz, 2H; CO_2CH_2), 3.29 (m, 4H; $H_{2,3,5,6}$, NBD), 3.18 (m, 2H; $H_{1,4}$, NBD), 3.05 (t, $^3J_{H,H}$ = 5.6 Hz, 2H; CH_2N), 2.56 (s, 3H; NCH_3), 1.94 (s, 3H; CH_3), 0.89 (t, $^3J_{H,H}$ = 1.6 Hz, 2H; H_7, NBD). IR (THF, cm^{-1}): ν = 1712 (s) (C═O). ESI-MS [M]$^+$ + Na═538 *m*/*z*. Anal. Calcd. for $C_{23}H_{26}NO_4RhS$: C, 53.6; H, 5.05; Found: C, 53.6; H, 5.04%. m.p. = 104 to 106 °C. R_f(Et_2O, SiO_2) = 0.50.

3.2. X-ray crystallography

Yellow crystals of **3** and **4** suitable for the X-ray diffraction studies were precipitated from a double layer CH_2Cl_2/Etp at −20 °C. Crystal data and details of structure refinement are reported in Table 2.

Diffraction intensities were collected on a Bruker AXS SMART 2000 CCD diffractometer. The data were collected using 0.3° wide ω scans, crystal-to-detector distance of 5.0 cm, and corrected for absorption using the SADABS routine [8]. Data collections nominally covered a full sphere of reciprocal space for both complexes with 10 s exposure time per frame. Both structures were solved by direct methods and refined on F^2 by full-matrix least-squares calculations using the SHELXTL/PC package [9]. The structure of **3** was found affected by disorder at the CH_2NHTs moiety, which could be refined using the Ts fragment taken from molecule **4** as a starting model for the two slightly displaced images. An occupation factor of ca. 0.5 was refined. Two independent isomeric molecules were found packed in an orderly way in the crystals of **4**. Thermal vibrations were treated anisotropically in **3**, except for the disordered moiety, while could be treated only isotropically in **4**, except for Rh and S atoms, due to the high correlation between parameters and consequent instability of the least squares calculations. The absolute configuration was assigned to the molecules in the crystal of **4**, as reported in Fig. 2, by using the Flack parameter (−0.0005 for the correct absolute structure) [10]. H atoms were experimentally located but geometrically positioned [C–H 0.93 and 0.97 Å for aromatic and aliphatic distances] and refined "riding" on their corresponding carbon atoms. The N–H distance in **3** was constrained to an average value of 0.89(1) Å in the two images. Refinement converged at a final R = 0.033 for **3** and R = 0.056 for **4**. Molecular graphics were prepared using ORTEP3 for WindowsNT [11].

CCDC-242972 (**3**) and CCDC-242973 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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