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Organometallic ruthenium, rhodium and iridium complexes containing a P-bound thiophene-2-(*N*-diphenylphosphino)methylamine ligand: Synthesis, molecular structure and catalytic activity

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ABSTRACT

Reaction of Ph_2PNHCH_2-C_4H_3S with $[Ru(\eta^6$-*p*-cymene$)(\mu$-Cl$)Cl]_2$, $[Ru(\eta^6$-benzene$)(\mu$-Cl$)Cl]_2$, $[Rh(\mu$-Cl$)(cod)]_2$ and $[Ir(\eta^5$-$C_5Me_5)(\mu$-Cl$)Cl]_2$ yields complexes $[Ru(Ph_2PNHCH_2$-$C_4H_3S)(\eta^6$-*p*-cymene$)Cl_2]$, **1**, $[Ru(Ph_2PNHCH_2$-$C_4H_3S)(\eta^6$-benzene$)Cl_2]$, **2**, $[Rh(Ph_2PNHCH_2$-$C_4H_3S)(cod)Cl]$, **3** and $[Ir(Ph_2PNHCH_2$-$C_4H_3S)(\eta^5$-$C_5Me_5)Cl_2]$, **4**, respectively. All complexes were isolated from the reaction solution and fully characterized by analytical and spectroscopic methods. The structure of $[Ru(Ph_2PNHCH_2$-$C_4H_3S)(\eta^6$-benzene$)Cl_2]$, **2** was also determined by single crystal X-ray diffraction. **1**–**4** are suitable precursors forming highly active catalyst in the transfer hydrogenation of a variety of simple ketones. Notably, the catalysts obtained by using the ruthenium complexes $[Ru(Ph_2PNHCH_2$-$C_4H_3S)(\eta^6$-*p*-cymene$)Cl_2]$, **1** and $[Ru(Ph_2PNHCH_2$-$C_4H_3S)(\eta^6$-benzene$)Cl_2]$, **2** are much more active in the transfer hydrogenation converting the carbonyls to the corresponding alcohols in 98–99% yields (TOF $\leq$ 200 h^{-1}) in comparison to analogous rhodium and iridium complexes.

1. Introduction

Aminophosphines and bis(phosphino)amines with P–NH and P–N–P skeletons, respectively, have been used as versatile ligands, and varying the substituents on both the P- and N-centers gives rise the changes in the P–N–P angle and the conformation around the P-centers [1]. Small variations in these ligands can cause significant changes in their coordination behavior and the structural features of the resulting complexes [2]. A large number of complexes with aminophosphine ligands have been employed in different catalytic reactions including allylic alkylation [3], amination [4], Heck [5] Sonogashira [6], Suzuki [7], hydroformylation [8] and hydrogenation [9]. Some aminophosphines and their derivatives have also found application as anticancer drugs [10], herbicides and antimicrobial agents, as well as neuroactive agents [11].

Transition-metal-catalyzed transfer hydrogenation of a wide variety of functional groups by different hydrogen donors is an interesting alternative to conventional hydrogenation [12]. Transfer hydrogenation of ketones by 2-propanol is convenient in large-scale synthesis since there is no need to employ a high hydrogen pressure or to use hazardous reducing agents [13]. Although very frequently ruthenium-based catalysts have been applied in the enantioselective hydrogenation of prochiral ketones [14–16], rhodium or iridium complexes have also been employed and found to be an efficient catalyst in some processes along with potential industrial applications [17,18]. Today, the asymmetric transfer hydrogenation [19–21] of prochiral ketones is one of the most attractive methods for synthesizing optically active secondary alcohols, which form an important class of intermediates for fine chemicals and pharmaceuticals [22].

As part of our continuing research program on the aminophosphine complexes we report here the synthesis of new ruthenium, rhodium and iridium complexes of Ph_2PNHCH_2-C_4H_3S. All the new complexes were isolated from the reaction solution and fully characterized by analytical and spectroscopic methods. Our report includes also the X-ray crystal structure of $[Ru(Ph_2PNHCH_2$-$C_4H_3S)(\eta^6$-benzene$)Cl_2]$ and pertinent features of this structure. In addition, metal complexes of this aminophosphine were tested as catalyst in the transfer hydrogenation of a variety of simple alkyl ketones.

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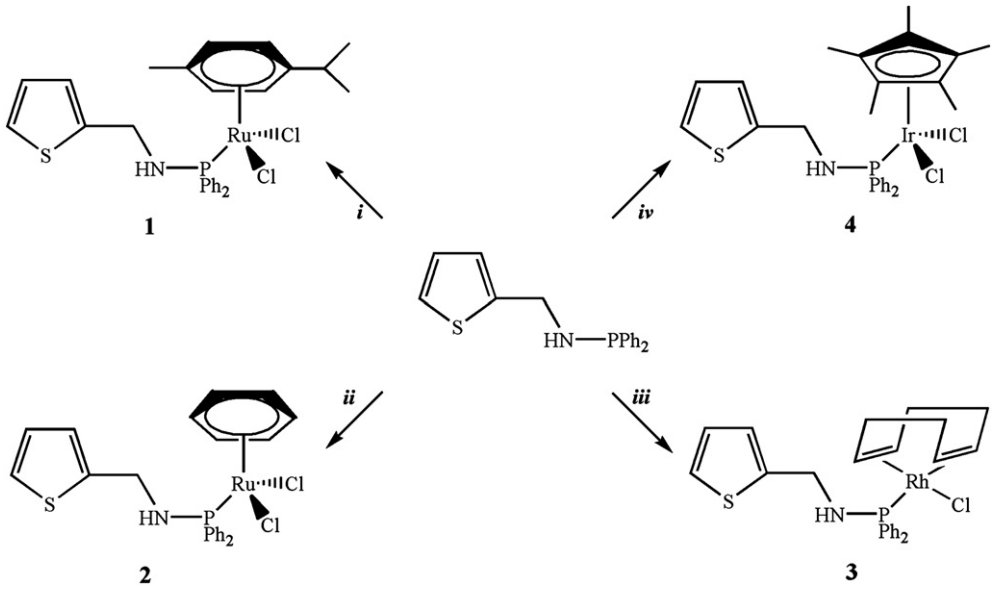


Scheme 1. The formation of complexes [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-*p*-cymene)Cl_2], **1**, [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-benzene)Cl_2], **2** [Rh(Ph_2PNHCH_2-C_4H_3S)(cod)Cl], **3** and [Ir(Ph_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], **4** from the reaction of Ph_2PNHCH_2-C_4H_3S and (i) 1/2 equiv. [Ru(η^6-*p*-cymene(μ-Cl)Cl]$_2$, (ii) 1/2 equiv. [Ru(η^6-benzene)(μ-Cl)Cl]$_2$, (iii) 1/2 equiv. [Rh(μ-Cl)(cod)]$_2$, (iv) 1/2 equiv. [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$, all in tetrahydrofuran.

2. Result and discussion

2.1. Synthesis of the complexes

Reaction of Ph_2PNHCH_2-C_4H_3S with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$, [Ru(η^6-benzene)(μ-Cl)Cl]$_2$, [Rh(μ-Cl)(cod)]$_2$ and [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ yields new complexes [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-*p*-cymene)Cl_2], **1**, [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-benzene)Cl_2], **2**, [Rh(Ph_2PNHCH_2-C_4H_3S)(cod)Cl], **3** and [Ir(Ph_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], **4**, respectively, as shown in Scheme 1. The complexes were isolated from the reaction solution as analytically pure substances and characterized by analytical and spectroscopic techniques following the procedures described elsewhere [23,24]. Some pertinent chemical shifts for ^{1}H and ^{31}P NMR, as well as coupling constants, of compounds **1**–**4** are summarized in Table 1.

As part of the characterization of the complexes we report herein the crystal structure of one representative example, namely complex **2**. Single crystals suitable for X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of the compound in dichloromethane over several days. The single crystal X-ray structure analysis of [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-benzene)Cl_2], **2** reveals a typical piano-stool geometry with the ruthenium atom being coordinated by a benzene, 2-thiophenemethylamine phosphine and two chloro ligands as shown in Fig. 1.

The distance between Ru and the centroid of the π-bonded benzene moiety is 1.698 (8) Å and the mean value of the Ru–C bond distances is 2.192 (19) Å. These dimensions agree well with those of the several related complexes, *e.g.* [CpRu(PPh_3)$_2$($NCCH_3$)]BF_4 [25] or [CpRu(PPh_3)$_2$(NCPh)]PF_6 [26]. Also bond lengths and angles in the compound **2** (see Table 2 and Supplementary materials) are similar to those of dichloro(η^6-*p*-cymene)(triphenylphosphine)-ruthenium(II)complex [27], which has the same classic *pseudo*-tetrahedral piano-stool structure.

In previously reported structures [28–30], a *trans* bond lengthening has been observed in the Ru-C bonds *trans* to P donors such as PPh_3. In the case of **2** with C1/C2 *trans* to P, the Ru–C1 and Ru–C2 bonds are longer than the other Ru–C bonds. A comparison of the P–Ru–Cl1 (84.6(2)), P–Ru–Cl2 (88.1(3)) and Cl1–Ru–Cl2 (88.1(2)) angles reveals that (η^6-benzene) group has similar steric hindrance; *i.e.*, the benzene ring is almost parallel to the plane of P, Cl1 and Cl2. No meaningful interactions between independent complexes are observed in the crystal packing (Fig. 2), the Cl···H–C distances ranging from 3.495 to 3.767 Å.

In summary, the 2-thiophenemethylamine phosphine, η^6-benzene, and two chloro ligands affords a classical pseudo-octahedral ruthenium(II) complex with typical Ru–P/Ru–Cl bond lengths and angles.

Table 1
Selected NMR data for complexes **1**–**4**.

Complexes	δ(^{1}H)			δ(^{31}P)
	CH_2	NH	Aromatics (Ph)	
1	3.81(dd, *J* 6.4; 6.8 Hz)	3.58 (m)	7.53–7.97	61.0
2	3.88(dd, *J* 6.2; 6.4 Hz)	3.56 (m)	7.46–7.96	61.7
3	3.98(dd, *J* 5.2; 6.8 Hz)	4.33 (m)	7.42–7.99	60.6[a]
4	3.94(dd, *J* 5.8; 6.4 Hz)	3.12 (m)	7.42–7.95	34.1

[a] $^1J(^{103}Rh - ^{31}P) = 158.8$ Hz.

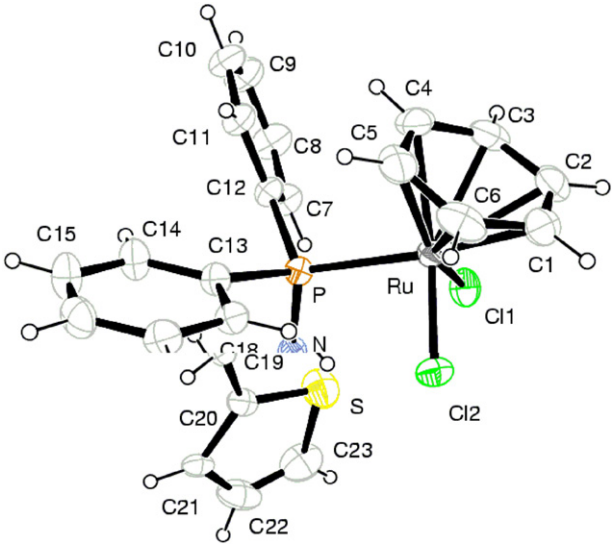


Fig. 1. Perspective view of the complex [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-benzene)Cl_2] (**2**)with the atom numbering scheme. Displacement ellipsoids are at the 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for (**2**).

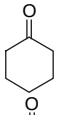
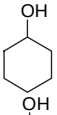
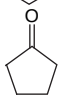
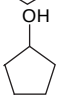
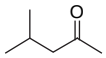
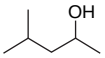
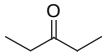
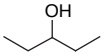
Bond lengths			
Ru–P	2.328(1)	P–N	1.654(3)
P–C(12)	1.817(4)	P–C(13)	1.827(4)
S–C(20)	1.693(4)	S–C(23)	1.699(6)
Ru–Cl1	2.410(2)	Ru–Cl2	2.413(2)
Ru–C(6)	2.176(3)	Ru–C(1)	2.256(2)
Ru–C(2)	2.260(3)		
Bond angles			
Ru–P–N	111.4(1)	Ru–P–C(12)	112.8(2)
Ru–P–C(13)	115.9(2)	N–P–C(12)	104.8(2)
N–P–C(13)	105.9(2)	C(12)–P–C(13)	105.2(2)
Cl(1)–Ru–Cl(2)	88.1(2)		
Cl(1)–Ru–P	84.6(2)	Cl(2)–Ru–P	88.1(3)

2.2. Catalytic transfer hydrogenation of ketones

The activity of Ru(II)-arene complexes is well known in the catalytic transfer hydrogenation of carbonyl compounds [31–33]. Complexes with sp^3-hybridized nitrogens and containing N–H bonds exhibit high catalytic activity. On the other hand, the presence of an N–H groups in the ligands possibly stabilizes a six membered ring, which is formed as transient by hydrogen bonding with the oxygen atom of ketone [34–37]. Hence, these kinds of ligands are attractive and also widely used in ruthenium, rhodium and iridium complexes for catalytic hydrogenations reactions [38,39]. Recently, we have reported that the novel half-sandwich complexes, based on the ligands with P–N and P–O backbone, are active catalysts in the reduction of aromatic ketones [40,41].

As part of our continuing research in this area [42–44], we report herein the results of catalytic activity tests using the complexes **1**–**4** in the transfer hydrogenation of a variety of simple alkyl ketones to the corresponding alcohols in i*so*-PrOH solution. In a typical experiment, 0.01 mmol of the complex and 1.0 mmol of ketone were added to a solution of NaOH in *iso*-PrOH (0.05 mmol of NaOH in 10 mL *iso*-PrOH) and refluxed at 82 °C. The reaction was followed by using GC. For alkyl ketones, heating is generally required to achieve high conversion. With a complex/NaOH ratio of 1/5, the complexes are highly active leading to a quantitative transformation of the ketone, with a moderate TOF. The results of catalytic tests are listed in Table 3.

Table 3
Transfer hydrogenation of various simple ketones with *iso*-PrOH catalyzed by [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-*p*-cymene)Cl_2], **1**, [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-benzene)Cl_2], **2**, [Rh(Ph_2PNHCH_2-C_4H_3S)(cod)Cl], **3** and [Ir(Ph_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], **4**[a].

Cat	Substrate	Product	Time	Conversion(%)[b]	TOF(h-1)[c]
1			30 min	97	194
2			30 min	98	196
3			2 h	99	50
4			2 h	98	49
1			30 min	98	196
2			30 min	97	194
3			2 h	98	49
4			2 h	99	50
1			2 h	99	50
2			2 h	98	49
3			3 h	98	33
4			3 h	99	33
1			4 h	99	25
2			4 h	98	25
3			7 h	98	14
4			7 h	97	14

[a] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 100:1:5.
[b] Determined by GC (three independent catalytic experiments).
[c] Referred at the reaction time indicated in column; TOF = (mol product/mol Ru(II)Cat.) × h^{-1}.

It is noteworthy that the complexes **1**, **2**, **3** and **4** display the different activity, when used with a complex/NaOH ratio of 1/5. Complexes **1** and **2** are the most active catalysts leading to quantitative transformation of ketones to the corresponding alcohol with a moderate TOF value of 200 h^{-1}. It should be pointed out that complexes **1** and **2** are more active catalysts than the corresponding

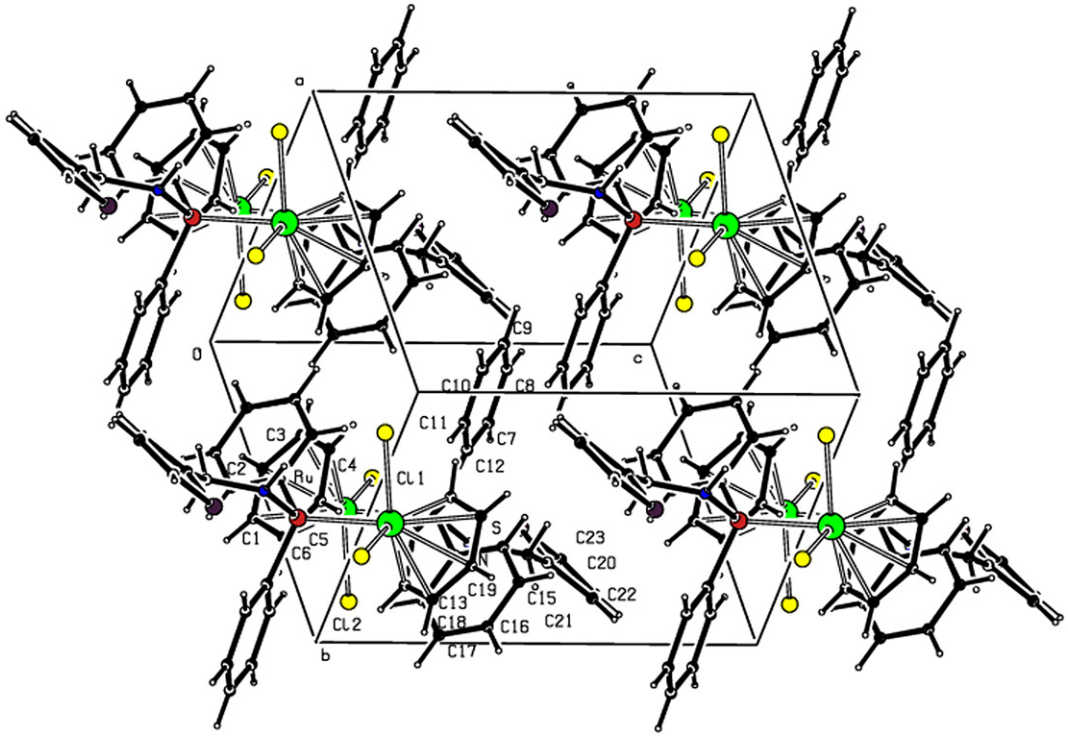


Fig. 2. Crystal packing of [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-benzene)Cl_2], **2**.

Table 4
Crystal data and structure refinement for (**2**).

Empirical formula	$C_{23}H_{22}NPCl_2SRu$	
Formula weight	547.4	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	$a = 9.226(6)$ Å	$\alpha = 94.05°$
	$b = 9.9280(16)$ Å	$\beta = 96.192(3)°$
	$c = 12.509(16)$ Å	$\gamma = 12.509°$
Volume	1136.13(12) Å^3	
Z	2	
Density (calculated)	1.60 Mg/m^3	
Absorption coefficient	1.098 mm$-^{1}$	
F(000)	552	
Crystal	block:yellow	
Crystal size	0.20 × 0.02 × 0.02 mm^3	
θ -range for data collection	2.1–26.4°	
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 12$, $-15 \le l \le 15$	
Reflections collected	24222	
Independent reflections	4654 [$R_{int} = 0.039$]	
Completeness to $\theta = 30.7°$	99.7%	
Max. and min. transmission	0.927 and 0.873	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4371/0/264	
Goodness-of-fit on F^2	1.061	
Final *R* indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.036$, $wR_2 = 0.097$	
R indices (all data)	$R_1 = 0.039$, $wR_2 = 0.101$	
Extinction coefficient	0.0219	
Largest diff. peak and hole	0.814 and −0.710 e Å^{-3}	

precursors: [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (41% maximum yield in 24 h) and [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ (37% maximum yield in 24 h) with a 1/14 complex/NaOH ratio [45]. From these preliminary results, it can be concluded that the η^6-*p*-cymene-ruthenium complex, **1** and η^6-benzene-ruthenium complex, **2** are more effective than those of the cod-Rh(I), **3** and Cp*-Ir(III), **4** complexes.

3. Conclusions

In summary, we have synthesized a series of selected transition-metal (Ru(II), Rh(I), Ir(III)) complexes with the thiophene-2-(*N*-diphenylphosphino)methylamine ligand. All the complexes were characterized using multi nuclear NMR, IR and microanalysis and also one representative structure was studied by single crystal X-ray diffraction analysis. We have found that these complexes are efficient homogeneous catalysts that can be readily employed in transfer hydrogenation of ketones to alcohols with high conversion. However, Ru(II)-aminophosphine complexes show higher catalytic activity in the transfer hydrogenation reaction than the analogous Rh(I) and Ir(III) complexes. Furthermore, the influence of arene ring in the catalytic transfer hydrogenation of ketones was also investigated and it was found that their catalytic activities were very similar.

4. Experimental

4.1. General remarks

All reactions and manipulations were performed under argon unless otherwise stated. Ph_2PCl and thiophene-2-methylamine were purchased from Fluka and used directly. Analytical grade and deuterated solvents were purchased from Merck. Solvents were dried using the appropriate reagents and distilled prior to use. The starting materials [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ [46,47], [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ [48], Rh(μ-Cl)(cod)]$_2$ [49], [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ [50] were prepared according to literature procedures. Infrared spectra were recorded as KBr pellet in the range 4000–400 cm^{-1} on a Mattson 1000 ATI UNICAM FT-IR spectrometer. ^{1}H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P-{^{1}H} NMR (162.0 MHz) spectra were recorded on a Bruker Avance 400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4, respectively. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded on a Gallenkamp Model apparatus with open capillaries.

4.2. GC analyses

GC analyses were performed on an HP 6890N Gas Chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). The GC parameters for transfer hydrogenation of ketones were as follows; initial temperature, 110 °C; initial time, 1 min; solvent delay, 4.48 min; temperature ramp 80 °C/min; final temperature, 200 °C; final time, 21.13 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

4.3. Transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a suspension of metal complexes Ru(II), Rh(I) or Ir(III) (0.005 mmol), NaOH (0.025 mmol) and alkyl ketone (0.5 mmol) in degassed *iso*-PrOH (5 mL) was refluxed until the reaction is completed. After this time a sample of the reaction mixture is taken, diluted with acetone and analyzed immediately by GC. Yields obtained are related to the residual unreacted ketone.

4.4. Procedure for the preparation of transition metal complexes

4.4.1. [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-*p*-cymene)Cl_2], (**1**)

Compound **1** was prepared according to the published procedure [23]. To a solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.30 mg, 0.49 mmol) in CH_2Cl_2, a solution (thf, 30 mL) of [Ph_2PNHCH_2-C_4H_3S], **1** (0.29 mg, 0.98 mmol) was added. The resulting reaction mixture was allowed to proceed with stirring at room temperature for 1 h. After this time, the solution was filtered and the solvent evaporated under vacuum, the solid residue thus obtained was washed with diethyl ether (3 × 15 mL) and then dried under vacuum. Following recrystallization from diethyl ether/CH_2Cl_2, a red crystalline powder was obtained. Yield 550 mg, 93.0%, m.p. = 180–182 °C.

4.4.2. Synthesis of [Ru(Ph_2PNHCH_2-C_4H_3S)(η^6-benzene)Cl_2], (**2**)

Compound **2** was prepared according to the published procedure [24]. A mixture of [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ (0.122 g, 0.244 mmol) and [Ph_2PNHCH_2-C_4H_3S] (0.145 g, 0.488 mmol) in 20 mL of tetrahydrofuran was stirred at room temperature for 2 h. The volume of the solvent was then reduced to 0.5 mL before addition of diethyl ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **2** as a red microcrystalline powder. Yield 245 mg, 92%, m.p. = 186–188 °C.

4.4.3. Synthesis of [Rh(Ph_2PNHCH_2-C_4H_3S)(cod)Cl], (**3**)

Compound **3** was prepared according to the published procedure [24]. A mixture of [Rh(μ-Cl)(cod)]$_2$ (0.123 g, 0.244 mmol) and [Ph_2PNHCH_2-C_4H_3S] (0.145 g, 0.488 mmol) in 20 mL of tetrahydrofuran was stirred at room temperature for 2 h. The volume of the solvent was then reduced to 0.5 mL before addition of diethyl ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **3** as a yellow microcrystalline solid. Yield 234 mg, 88%, m.p. = 214 °C (dec.).

4.4.4. Synthesis of [Ir(Ph_2PNHCH_2-C_4H_3S)(η^5-C_5Me_5)Cl_2], (**4**)

Compound **4** was prepared according to the published procedure [24]. A mixture of [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ (0.203 g, 0.244 mmol) and [Ph_2PNHCH_2-C_4H_3S] (0.145 g, 0.488 mmol) in 20 mL of tetrahydrofuran was stirred at room temperature for 2 h. The volume of the solvent was then reduced to 0.5 mL before addition of diethyl ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **4** as an orange microcrystalline solid. Yield 312 mg, 92%, m.p. = 204–206 °C.

4.5. X-ray diffraction structure analysis

For the crystal structure determination, the single crystal of the complex [Ru(Ph_2PNHCH_2–C_4H_3S)(η^6-benzene)Cl_2], **2** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å) and oscillation scans technique with $\Delta\omega = 5^\circ$ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. H atoms were positioned geometrically and refined using a riding model. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear software [51]. The structures were solved by direct methods using SHELXS-97 [52] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [52]. The crystal data and structure refinement details for compound **2** are given in Table 4. The final difference Fourier maps showed no peaks of chemical significance.

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Appendix A. Supplementary material

CCDC-808703 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: Fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk.

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