Date: 23-04-12 11:49:03

Pages: 6

Dirhodium(II) Complexes of 2-(Sulfonylimino)pyrrolidine: Synthesis and Application in Catalytic Benzylic Oxidation

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A new class of dirhodium(II) tetraamidinates derived from 2-(sulfonylimino)pyrrolidines has been prepared through ligand substitution by using dirhodium(II) acetate, in which (3,1) geometric isomers are formed predominantly. Among these complexes, (3,1)-Rh₂(Msip)₄, exhibits good catalytic performance in benzylic oxidation. In the presence of (3,1)-

Introduction

Benzylic oxidation has emerged as an important transformative tool for the synthesis of fine chemicals.^[1,2] The combination of catalytic amounts of transition-metal complexes and excess peroxide has been shown to promote the transformation of arylalkanes into the corresponding carbonyl compounds under mild reaction conditions with high chemoselectivity and broad compatibility with a variety of sensitive functional groups.^[3] Within the family of neutral tetrabridged dirhodium(II) complexes, O,O- and N,O-ligated dirhodium(II) complexes have been extensively explored for their catalytic capabilities.^[4] Among them, N,Oligated dirhodium(II) caprolactamate, $Rh_2(cap)_4$ (cap = caprolactam anion), is the only catalyst so far reported to be highly efficient in the oxidation of benzylic, allylic and propargylic C-H bonds.^[5,6] Therefore, the development of other dirhodium(II) complexes for this catalytic oxidation is desired. Here we report the synthesis of a new class of N,N-ligated dirhodium(II) tetraamidinates derived from 2-(sulfonylimino)pyrrolidines and their application in catalytic benzylic oxidation. Notably, although neutral dirhodium(II) complexes ligated by monoanionic N-donor bidentate bridging ligands have been widely explored for numerous applications in electrochemistry, antitumor metallopharmaceuticals and supramolecular chemistry,^[7] their

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 $Rh_2(Msip)_4$ a variety of benzylic derivatives, including strongly electron-deficient arylalkanes such as 1-ethyl-4-nitrobenzene, are readily oxidized in water by the inexpensive oxidant T-HYDRO[®] (70 wt.-% aqueous *tert*-butyl hydroperoxide).

capabilities as catalysts have yet to be recognized in the literature.^[8] Moreover, to the best of our knowledge, studies on dirhodium(II) complexes ligated by cyclic sulfonylamid-ines have not been published.

Results and Discussion

The motivation for designing tetrakis[2-(sulfonylimino)pyrrolidine]dirhodium(II) complexes is the unique structural characteristics of *cis*-(2,2)-Rh₂(cap)₄, which we thought might afford interesting catalytic acitvity. We envisioned that replacement of the oxygen atom of caprolactam in Rh₂(cap)₄ by a functional group that could exert a steric effect, an electronic effect, or both might alter the catalytic activity of the complex (Figure 1). With this in mind we set out to prepare tetrasubstituted dirhodium complexes Rh₂(sip)₄ [sip = 2-(sulfonylimino)pyrrolidine anion] and examine their catalytic activity in the benzylic oxidation.



Figure 1. Design of dirhodium(II) tetrakis[2-(sulfonylimino)pyrrolidines].

Tetrasubstituted dirhodium complexes $Rh_2(sip)_4$ (**2a**–c) were prepared by heating a mixture of $Rh_2(OAc)_4$, an excess amount of 2-(sulfonylimino)pyrrolidines^[9] and chlorobenzene in a round-bottomed flask, fitted with a Soxhlet extraction apparatus containing a thimble charged with Na₂CO₃, and kept at reduced pressure in an oil bath at 140 °C for 32 h (Scheme 1).^[10] After facile purification by silica gel chromatography, $Rh_2(sip)_4$ complexes were ob-

Pages: 6

SHORT COMMUNICATION

tained in moderate to high yields. Four geometric isomers are possible: (4,0), (3,1), (2,2)-trans, and (2,2)-cis. The (3,1)-Rh₂(sip)₄ isomer was produced preferentially; in this isomer, the dirhodium(II) core is surrounded by four bridging 2-(sulfonylimino)pyrrolidine ligands such that three exocyclic nitrogen donor atoms (the nitrogen atom connected to the sulfonyl group) and one endocyclic nitrogen atom (in the pyrrolidine ring) are bonded to one of the rhodium atoms, while the second rhodium atom is bonded to three endocyclic and one exocyclic nitrogen atom. The geometric configuration of the (3,1)-Rh₂(sip)₄ isomers **2a**-c can be identified by analysis of the ¹H NMR spectra, which show three sets of peaks in a 2:1:1 ratio, indicating a pair of identical ligands as well as two different ones. The structure of (3,1)-Rh₂(Tsip)₄ (**2b**) was further confirmed by a singlecrystal X-ray diffraction analysis.[11]



Scheme 1. Preparation of (3,1)-Rh₂(sip)₄ complexes.

The crystal structure of (3,1)-Rh₂(Tsip)₄ (**2b**) gives an Rh–Rh bond length of 2.448 Å, which is in the range typical for Rh–Rh bonds in tetraamidinate compounds (2.389–2.570 Å).^[7] More interestingly, this length is very close to

the Rh–Rh bond length of Rh₂(cap)₄·2CH₃CN (2.442 Å).^[6] Rh–N bond lengths in the complex are within the range of 1.999–2.130 Å. Rh–Rh–N angles are in the range of 85.58–88.36°, and they maintain an overall octahedral arrangement of ligands around the Rh–Rh core. The sterically less hindered rhodium atom, which is bonded to only one exocyclic nitrogen atom bearing a bulky tosyl group and to three less hindered endocyclic nitrogen atoms, axially bonds with the oxygen atom of H₂O, with an Rh–O_{ax} bond length of 2.298 Å and an Rh–Rh–O_{ax} bond angle of 176.07°.

The strongly electron-deficient arylalkane 3a, which typically exhibits low reactivity toward benzylic oxidation, was used to examine the catalytic performance of the dirhodium(II) complexes Rh₂(sip)₄ (Table 1). Initial experiments demonstrated that water significantly facilitates the transformation (Entry 1 vs. Entry 4, Entry 2 vs. Entry 5, Entry 3 vs. Entry 6, Entry 9 vs. Entry 11).^[6] For example, when dichloromethane was used (Entry 1), treatment of 1-ethyl-4nitrobenzene (3a) (1.0 equiv.) with tert-butyl hydroperoxide (TBHP) (5.0 equiv.) at room temperature in the presence of 1 mol-% of $Rh_2(Msip)_4$ (2a) resulted in a yield of only 21% yield based on ¹H NMR analysis of the crude reaction mixture. In sharp contrast, by performing the same reaction in aqueous solution (Entry 4) furnished the corresponding oxidized products (4a + 5a + 6a) in 90% overall yield, with ketone 4a predominating.^[12] Reactions catalyzed by bulkier 2b or 2c gave slightly lower yields (Entries 5 and 6). The N,N-ligated dirhodium complex $Rh_2(dpf)_4$ (dpf = N,N'-diphenylformamidinate anion), in which ligands are acyclic amidines and the nitrogen atoms lack electron-withdrawing groups such as a sulfonyl group, was much less active for this transformation (Entry 7). Comparable yields were obtained by using Rh₂(cap)₄ under aqueous reaction condi-

Table 1. Oxidation of 1-ethyl-4-nitrobenzene with dirhodium(II) complexes.^[a]

		Rh ^{II} , tBuOOH solvent, temp., 20 h NO ₂ 3a	+ NO ₂ 4a	$\begin{array}{c} \begin{array}{c} \begin{array}{c} & \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} $	ЪН
Entry	Catalyst [mol-%]	Oxidant	Solvent	Temp [°C]	Yield [%] ^[b] of 4a/5a/6a/7a
1 ^[c]	2a [1.0]	T-DCM	DCM	room temp.	13:5:2:0
2 ^[c]	2b [1.0]	T-DCM	DCM	room temp.	17:4:2:0
3 ^[c]	2 c [1.0]	T-DCM	DCM	room temp.	17:5:3:2
4	2a [1.0]	T-HYDRO	H_2O	room temp.	82:2:6:0
5	2b [1.0]	T-HYDRO	H_2O	room temp.	63:3:9:0
6	2c [1.0]	T-HYDRO	H_2O	room temp.	60:3:6:2
7	Rh ₂ (dpf) ₄ [1.0]	T-HYDRO	H_2O	room temp.	24:4:2:8
8	Rh ₂ (cap) ₄ [1.0]	T-HYDRO	H_2O	room temp.	76:3:6:0
9	2a [0.1]	T-HYDRO	H_2O	60	51:2:11:10
10	$Rh_2(cap)_4$ [0.1]	T-HYDRO	H_2O	60	36:20:0:0
11 ^[d]	2a [0.1]	T-HYDRO	H_2O	60	30:3:22:3
12 ^[e]	2a [1.0]	H_2O_2	H_2O	40	<5:0:0:0
13	none	T-HYDRO	H_2O	room temp.	_

[a] Reactions were performed with substrate (1.0 equiv.) and TBHP (4.0 equiv.) in air in a sealed tube for 20 h unless otherwise noted. T-DCM = TBHP in CH₂Cl₂, T-HYDRO = 70 wt.-% aqueous TBHP. [b] Yield determined by ¹H NMR analysis of the crude reaction mixture; see Supporting Information for details. [c] 50 mol-% NaHCO₃ and 5.0 equiv. of TBHP were used according to the conditions reported in ref.^[5] [d] Reaction was performed under argon. [e] 5.0 equiv. of 30% H_2O_2 were used.

Pages: 6



Dirhodium(II) Complexes of 2-(Sulfonylimino)pyrrolidine

Table 2. Rh₂(Msip)₄-catalyzed benzylic oxidation.

Entry	Substrate 3	Product(s) 4	Description	Yield ^[a] (Yield) ^[b] [%]
	<u> </u>	0	3a , 4a : $X = NO_2$	75 (25)
1	ſŢ`		3b , 4b : $X = CO_2Me$	50 ^[c]
	x	x	3c, 4c: X = OMe	76 ^[d] (75)
	\sim	0	3d. 4d : $n = 0$	76 (52)
2	, Vn		3e. 4e: $n = 1$	86
-	•	(¹ n	3f. 4f : $n = 2$	90
		• •		c 4[e] (41)
3	\bigwedge	ССССИ	3g, 4g: X = OMe	64 ⁽⁴¹⁾
5	x		3h , 4h : $X = Br$	41 ^[f]
		0		
		\sim		
4 ^[g]	\bigwedge	0	3i, 4i + 4i'	75 (83)
	\checkmark	\sim		
		- II		
	OAc	OAc		
e[h]			2: 4:	47[i] (40)
2.4	[]		3 j , 4 j	470 (48)
	\checkmark	Ö		
		0		
6 ^[j]			3k, 4k	95 (74)
	• •			
	$\sim \sim \sim$			
7			31, 41	97 (99)
	• 0 •	\sim		
		0		
- (b)	$\sim \sim \sim$	0		- 0-2
8 ^[n]		$\left(\begin{array}{c} \\ \end{array} \right) \left(\begin{array}{c} \\ \end{array} \right)$	3m, 4m + 4m' + 4m''	95 ^[K]
		\circ		
		$\left[\begin{array}{c} 1 \\ 1 \end{array} \right]$		
0	CI	٨Ť	2- 4-	27
9			511, 411	27
		~		
10			30 40	80
10	•		50,40	00
		0	3n . 4n : X = H	50 (70)
11	OMe		3a, 4a; X = OMe	$80^{[d,1]}$ (60)
	x		3r $4r$: X = NO ₂	$46^{[m]}(71)$
		^ · ·	51, 41.74 1102	40 (71)
12	ſ∼∩°₀	A.	35.45	50 ^[d]
		Ľ∕~^		
	~ ~	0		
13	[] î	o م	3t, 4t	59
	\checkmark	\checkmark		
		O ₂ tBu		
14 ^[h]			3u, 4u	86 ^[n]
	$\checkmark \checkmark$			

[a] Isolated yields for reactions in which Method A was carried out by using **2a** (1 mol-%), substrate (1.0 equiv.) and T-HYDRO[®] (70 wt.-% aqueous *tert*-butyl hydroperoxide, 4.0 equiv.) in H₂O (1.0 mL) at room temp. for 20 h. [b] Yields in parentheses were obtained when Method B was carried out by using **2a** (1 mol-%), substrate (1.0 equiv.), NaHCO₃ (50 mol-%) and TBHP-decane (5.0 equiv.) in DCE (1,2-dichloroethane) at 40 °C for 20 h. These are the same reaction conditions as in ref.^[5], except that the catalyst Rh₂(cap)₄ in ref.^[5] was replaced by **2a** here. [c] Methyl 4-(1-hydroxyethyl)benzoate was obtained in 6% yield. [d] 5 vol.-% methanol in water was used as solvent. [e] A small amount (<5%) of 4-methoxybenzaldehyde was observed. [f] 4-bromobenzaldehyde was obtained in 17% isolated yield. [g] Products *a*-tetralone (**4i**) and the dione **4i**' were obtained in a 1:1 ratio. [h] Substrates were dissolved in 0.4 mL of DCM. [i] Isolated as a mixture of C1/C4 isomers (9:1). [j] Reaction on a 1 g scale gave benzophenone (**4k**) in 92% yield. [k] The products anthraquinone (**4m**), anthrone (**4m**') and anthracene (**4m**') were obtained in a ratio of 6:2:1. [l] A small amount of 4-methoxybenzoic acid (<5%) was observed. [m] A small amount of *tert*-butyl 4-nitrobenzoate (<5%) was observed. [n] The reaction was performed at room temp. for 20 h and then at 60 °C for 5 h.

Date: 23-04-12 11:49:03

Pages: 6

SHORT COMMUNICATION

tions,whichgave85%totalyield(Entry 8).Rh₂(Msip)₄andRh₂-(cap)₄ performed similarly at 0.1 mol-% catalyst loading when catalyzing the oxidation of 1-ethyl-4-nitrobenzene at 60 °C, except that the product distributions differed to some extent (Entry 9 vs. Entry 10). The formation of ketone **4a**, benzyl alcohol **5a**, benzyl *tert*-butylperoxide **6a** and benzyl hydroperoxide **7a** were observed in different ratios when the reaction was conducted under different reaction conditions. Analogues of the above reaction products obtained during benzylic oxidation by using TBHP and CrO₃ as a catalyst were reported by Muzart.^[13] Finally, the experiments in Table 1 show that H₂O₂ is not a suitable oxidant for this transformation (Entry 12) and that no reaction occurs in the absence of dirhodium(II) catalyst (Entry 13).

With these preliminary results in hand (Table 1, Entry 4), the scope of catalytic benzylic oxidation was investigated by employing $Rh_2(Msip)_4$ (2a) as catalyst (Table 2). Oxidation of arylalkanes 3a-3j (Entries 1-5), including those containing primary benzylic positions (Entry 3), proceeded smoothly and produced the corresponding oxo derivatives in moderate to good yields. For diarylmethane derivatives 3k-3m, which are much more activated substrates, excellent yields were generally obtained (Entries 6-8). Preparation of benzophenone (4k) on a 1 g scale was achieved by using this protocol without obvious loss of yield (Entry 6: 92%) for a 1 g scale vs. 95% for a 50 mg scale). When substrates 3i and 3m, which possess two benzylic positions, were exposed to stronger reaction conditions (2 mol-% 2a, 8 equiv. T-HYDRO, room temp., 20 h), diones 4i' and 4m formed in 80% and 92% yield, respectively. This protocol was then expanded to the oxidation of benzyl chloride and methyl phenylacetate, leading to the formation of benzoic acid (3n) (Entry 9) and methyl oxo(phenyl)acetate (30) (Entry 10), respectively. Furthermore, acyclic and cyclic benzyl ethers **3p**-**3t** were oxidized to give the corresponding esters (Entries 11–13). Notably, in the case of 3s and 3t, ¹H NMR analysis of the reaction mixtures revealed 15-20% yields of the corresponding benzyl tert-butyl peroxides, which were generated by incorporation of tert-butyl peroxide into the substrates. In contrast, oxidation of N-tosyltetrahydroisoquinoline afforded peroxide 4u as the major product (86% yield) instead of the corresponding amide (Entry 14). We also subjected some substrates to anhydrous reaction conditions described in ref.^[5] using Rh₂(Msip)₄ as catalyst instead of $Rh_2(cap)_4$. We obtained yields comparable to those previously reported with Rh₂(cap)₄ (see yields in parentheses obtained with Method B, Table 2). Contrary to what was observed in most other reactions, the catalytic oxidation of benzyl methyl ether (**3p**) and methyl 4-nitrobenzyl ether (**3r**) gave higher yields when the reactions were performed in dichloroethane rather than in water (Entry 11; 4p and **4r**).^[6d,14]

The Rh₂(Msip)₄-catalyzed benzylic oxidation is most likely to involve the same dirhodium(5+) species that has been well documented in the Rh₂(cap)₄-catalyzed protocol.^[5,6] Consistent with the presence of a one-electron oxidized dirhodium core (Rh₂⁵⁺), addition of TBHP caused the Rh₂(Msip)₄ solution to change from light blue to pink red and a low-energy absorption peak to appear at 969 nm in the UV/Vis spectrum. Cyclic voltammetry measurements showed that $Rh_2(Msip)_4$ (**2a**) undergoes reversible one-electron oxidation at $E_{1/2} = 570$ mV vs. Ag/AgCl,^[15] which is much higher than the oxidation potential of $Rh_2(cap)_4$ ($E_{1/2} = 55$ mV vs. Ag/AgCl).^[6a] The higher oxidation potential of **2a** associated with its high catalytic efficiency suggests that an extreme propensity for one-electron oxidation is not a prerequisite for $Rh_2(Msip)_4$ in catalytic benzylic oxidation.

Conclusions

We have developed a new class of N,N-ligated dirhodium(II) tetraamidinates derived from 2-(sulfonylimino)pyrrolidines, and we have demonstrated their ability to catalyze benzylic oxidation. One of these complexes, (3,1)-Rh₂(Msip)₄, is highly efficient at promoting oxidation of a variety of benzylic derivatives by T-HYDRO[®] in water. This study describes the first successful catalytic application of neutral N,N-ligated dirhodium(II) complexes.

Experimental Section

General Procedure for the Synthesis of Dirhodium(II) Tetrakis[2-(sulfonylimino)pyrrolidines] [Rh₂(sip)₄ 2a–c]: Dirhodium(II) acetate (0.20 mmol), *N*-(pyrrolidinylidene)sulfonamide (2.4 mmol), and chlorobenzene (12 mL) were added to a 25 mL flask. The flask was fitted with a Soxhlet extraction apparatus contaning a thimble with 4.0 g oven-dried Na₂CO₃ and sand in a 3.5:1.5 ratio. The reaction mixture was incubated in an oil bath at 140 °C and refluxed under reduced pressure (140–210 Torr; water aspirator) for 32 h, and then cooled to room temperature and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography to give the desired product.

General Procedure for the Oxidation of 1-Ethyl-4-nitrobenzene with Dirhodium(II) Complexes: See Table 1. A mixture of 1-ethyl-4-nitrobenzene (0.30 mmol) and dirhodium(II) catalyst (1.0 mol-% or 0.1 mol-%) in the indicated solvent (1.0 mL) was stirred vigorously in a screw-cap vial (reactions at 60 °C were performed in a sealed tube). To the mixture was added 4.0 or 5.0 equiv. of TBHP-HY-DRO[®], TBHP-DCM or TBHP-decane in one portion through a syringe. The vial was tightly capped, and the reaction mixture was stirred at the indicated temperature for 20 h. Then the reaction mixture was extracted twice with ethyl acetate. The organic extracts were combined, dried with anhydrous MgSO₄, filtered and then concentrated under reduced pressure. The residues were used for crude ¹H NMR analysis.

General Procedure for the Rh₂(Msip)₄-Catalyzed Benzylic Oxidation in Water: See Table 2. The substrate (0.30 mmol) and catalyst 2a (1.0 mol-%) were stirred vigorously in water (1.0 mL) at room temperature in a screw-cap vial. To the reaction mixture was added 4.0 equiv. of TBHP (70 wt.-% in H₂O, 1.2 mmol) in one portion through a syringe. The vial was tightly capped, and the reaction mixture was stirred at room temperature for 20 h. Then the reaction mixture was extracted twice with ethyl acetate. The organic extracts were combined, dried with anhydrous MgSO₄, filtered, and then concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product.



Dirhodium(II) Complexes of 2-(Sulfonylimino)pyrrolidine

Supporting Information (see footnote on the first page of this article): Experimental details, characterization data and ¹H and ¹³C NMR spectra of all new compounds, as well as ¹H NMR spectra of the crude reaction mixtures (Table 1).

Acknowledgments

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SHORT COMMUNICATION



The synthesis of dirhodium(II) tetraamidinates derived from 2-(sulfonylimino)pyrrolidines and their use in the catalytic benzylic oxidation are described. A variety of benzylic derivatives, including strongly electron-deficient arylalkanes such as 1ethyl-4-nitrobenzene, can be readily oxidized by T-HYDRO® in the presence of 1.0 mol-% (3,1)-Rh₂(Msip)₄ in water under mild reaction conditions.

Dirhodium(II) Complexes

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Dirhodium(II) Complexes of 2-(Sulfonylimino)pyrrolidine: Synthesis and Application in Catalytic Benzylic Oxidation

Keywords: Rhodium / N ligands / Bridging ligands / Homogeneous catalysis / Benzylic oxidation