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Cationic complexes of dirhodium(II) with 1,8-naphthyridine: Catalysis of reactions involving silanes

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Abstract

The synthesis of cationic dirhodium(II) complexes by partial or total substitution of the acetate groups of $[Rh_2(OAc)_4]$ with different homoleptic neutral bidentate ligands has been attempted. The ligand 1,8-naphthyridine gave the best results: substitution of one as well as of all four acetate ligands is possible, giving rise to mono-, di- and tetra-cationic complexes. One of the resulting tetrasubstituted complexes has been structurally characterised and found to exhibit the expected lantern-shaped structure. All cationic complexes have been investigated as catalysts in different reactions involving silanes: promising results have been obtained, particularly in the silylformylation of alkynes.

Keywords: Rhodium; 1,8-naphthyridine; Hydrosilylation; Silylformylation; Silane alcoholysis

1. Introduction

Neutral dinuclear complexes of rhodium(II) are known to be catalytically active in a number of synthetically useful transformations [1]. The most popular reactions are metal-mediated decompositions of diazo derivatives, which upon formation of highly reactive metal carbene intermediates lead to cyclopropanations, insertions of the carbene moiety into C–H, C–C or heteroatom–H bonds, ylide formations or dipolar cycloaddition reactions; efficient asymmetric variants of many of these reactions have been developed as well [2,3]. Furthermore, neutral, electron poor dirhodium(II) complexes, such as dirhodium(II) perfluorocarboxylates do also efficiently catalyse many interesting reactions involving silanes, such as silane alcoholysis, hydrosilylations or silylformylations [4,5]. Despite the recognised fundamental importance of the electrophilicity of these complexes in determining their activity and selectivity in catalytic reactions, it is quite surprising that up to now no systematic study on the catalytic efficiency of related *cationic* complexes has been carried out.

We have an ongoing research program aimed at the preparation of different kinds of cationic dirhodium(II) complexes and at the evaluation of their catalytic performance in reactions involving diazocompounds or silanes. Complexes of this kind can be prepared starting from simple dirhodium(II) acetate upon partial or complete substitution of the acetate moieties with neutral ligands. Although cationic dirhodium(II) complexes in which the acetate ligands have been substituted by coordinated solvent molecules, most commonly acetonitrile, are quite well known [6], much less common are examples in which the acetate ligands have been substituted by *bidentate* neutral ligands [7,8].

We have recently reported on cationic dirhodium(II) complexes with oxothioether molecules which exhibit a

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rather unusual bidentate O–S coordination, in which each bidentate ligand occupies one equatorial and one axial site in the complex; preliminary tests indicate that such complexes are promising catalysts of both the silylformylation and the hydrosilylation of 1-hexyne with dimethylphenylsilane [9].

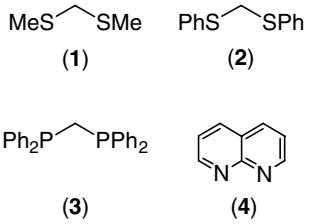
We wanted to extend such investigations to cationic complexes in which the lantern-shaped structure of the $[Rh_2(OAc)_4]$ precursor is preserved. Such complexes can be obtained by partial or total substitution of the acetate moieties with homoleptic rather than heteroleptic neutral bidentate ligands, as demonstrated in the literature by the successful application of ligands based on 1,8-naphthyridine [7,8]. Thus, in this contribution we wish to report on the development of an improved synthesis of cationic dirhodium(II) complexes with 1,8-naphthyridine and on the results of a systematic study on the catalytic activity of these complexes in different model reactions involving silanes, such as silylformylations, hydrosilylations and silane alcoholysis. Furthermore, preliminary results on our attempts to generalise this strategy for the synthesis of cationic dirhodium(II) complexes to other neutral bidentate ligands will be presented.

2. Results and discussion

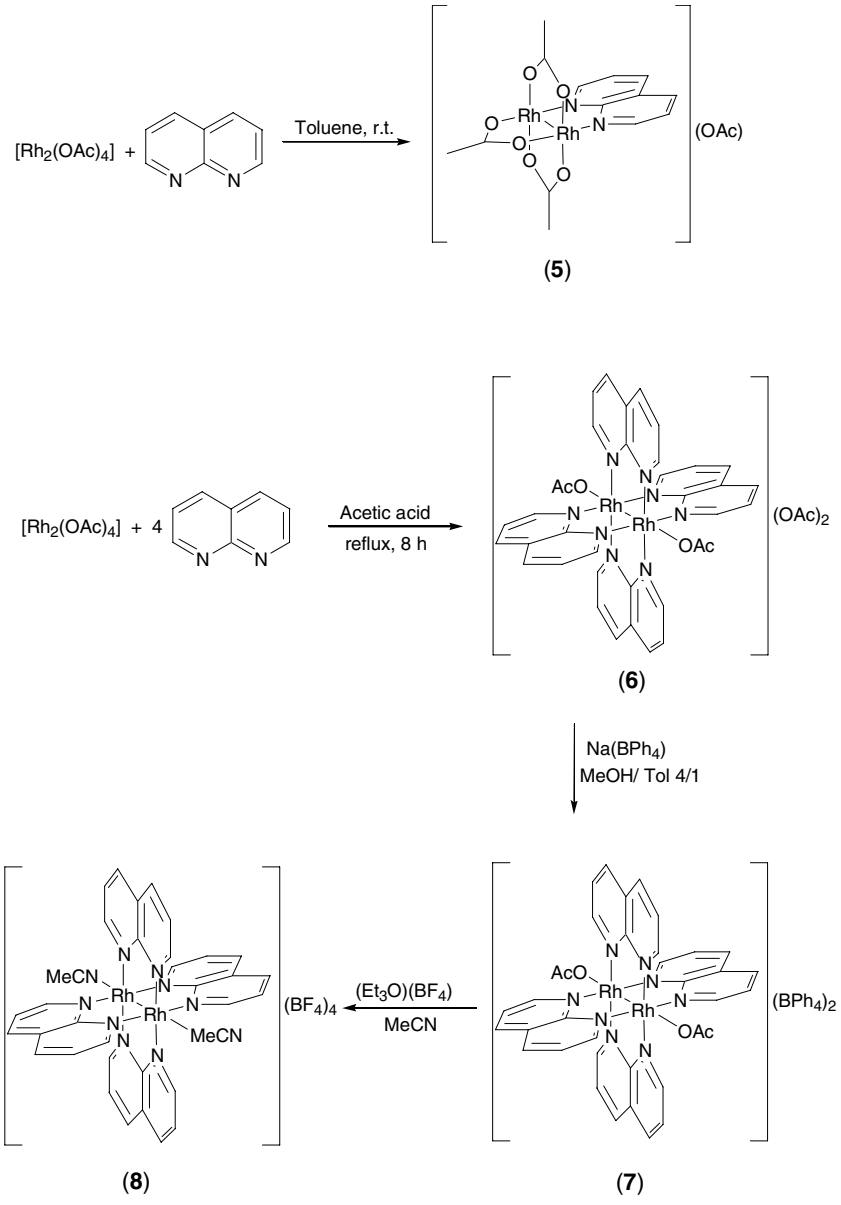
In the course of our study, we have investigated four different potential neutral bidentate ligands of N–N, P–P and S–S types, which are reported in Scheme 1.

The outcome of this investigation was that, in the case of P–P and S–S ligands, the bidentate ligands gave upon reaction with $Rh_2(OAc)_4$ in toluene at room temperature simple coordination to the free apical positions of the metal precursor, yielding poorly soluble coordination polymers. Upon forcing the reaction conditions by prolonged heating of the resulting products in acetic acid in order to labilise the acetate ligands and favour their substitution, the coordination polymer derived from (**1**) dissolved, yielding however a mixture of products of common stoichiometry $[Rh_2(MeSCH_2SMe)_2(OAc)_4]$, in which the ligand (**1**) probably occupies different coordination sites. In contrast, the coordination polymer derived from ligand (**2**) remained virtually insoluble, whereas in the case of the P–P ligand (**3**) the mononuclear rhodium(III) complex $[Rh(P–P)(OAc)_3]$ was formed, in accordance to previous observations by Cotton et al. with the same diphosphine ligand but using a different synthetic procedure [10]. The only exception to this general behaviour was observed with the 1,8-naphthyridine ligand (**4**). When $Rh_2(OAc)_4$ was reacted at room temperature with one or two equivalents of (**4**), no product derived from simple ligand addition was observed. Instead, a well-defined cationic complex was formed stemming from the neat substitution with a 1,8-naphthyridine ligand of one acetate ligand, which then acted as counterion (Scheme 2). Remarkably, no addition of a strong acid such as HCl, as reported, for example in Ref. [7], was necessary in order to allow the reaction to proceed. The structure of the complex was confirmed spectroscopically: the ^{1}H-NMR spectrum clearly reveals the presence of two kinds of bridging acetate ligands in a 2:1 ratio, as well as of an acetate counterion. Only the monosubstituted product (**5**) was formed, even in the presence of excess ligand. The substitution process could be pushed further by forcing the reaction conditions. Thus, by reacting $Rh_2(OAc)_4$ with four equivalents of (**4**) in acetic acid at reflux, complete substitution of the acetate ligands occurred, with formation of complex (**6**). The resulting complex was however only dicationic, in that two acetate ligands remained in the coordination sphere of the complex by occupying its apical positions, the other two acting as counterions, as confirmed by NMR analysis. Since the apical positions of dirhodium(II) complexes are usually their catalytically active sites, we expected their occupation by acetate ligands to have a negative effect on their reactivity. Therefore, we tried to remove the apical acetates by anion exchange with $NaBPh_4$. Such treatment only caused the substitution of the acetate counterions with two BPh_4^- anions, but left the coordinated acetates untouched, yielding complex (**7**). The apical acetates could finally be removed by treatment with Meerwein's salt triethyloxonium tetrafluoborate, which ethylated them yielding the tetracationic complex (**8**).

The structure of complex (**7**) · **10CH$_3$CN** was determined by X-ray diffraction methods. In the crystals, cations $[Rh_2(OAc)_2(Naft)_4]^{2+}$ (Naft = 1,8-naphthyridine), anions BPh_4^- and solvent molecules CH_3CN were found. An ORTEP view of the cation is shown in Fig. 1, together with the atomic labelling scheme. A selection of the most important bond distances and angles is listed in Table 1. The cationic complex is centrosymmetric with the inversion center on the midpoint of the Rh–Rh bond. The coordination of each Rh atom is essentially octahedral, with four nitrogen atoms of the four naphthyridine ligands lying on the equatorial plane, the acetate ion and the other Rh atom on the apical sites completing the octahedral coordination. The Rh–Rh bond distance of 2.448(1) Å falls within the expected range for dirhodium(II) complexes and is slightly longer than that reported for the complex $[Rh_2(OAc)_4(H_2O)_2]$ [11]; the four naphthyridine ligands bridge the Rh atoms through the N atoms with Rh–N bond lengths ranging from 2.050(3) to 2.077(3) Å, typical for $N_{(pyridil)}$–Rh coordination [12]. The acetate anions are bound to the Rh through an oxygen atom (Rh1–O1 bond length of 2.297(2) Å and O1–Rh1–Rh1′ bond angle of 173.94(5)°).



Scheme 1. Sketch of the employed bidentate ligands.



Scheme 2. Synthesis of the complexes.

In the crystals several CH_3CN solvent molecules are located in the voids left by the ions, forming with them an intricated network of weak Van der Waals interactions. A view of the crystal packing is reported in Fig. 2 (view along the crystallographic *a*-axis).

The catalytic activity of the various complexes was evaluated in a series of technologically relevant reactions involving silanes, such as the hydrosilylation of alkynes, the silylformylation of alkynes and the alcoholysis of silanes. The model reactions employed are reported in Scheme 3. In order to have some benchmark catalysts with which to critically evaluate the activity of the synthesised complexes, we involved in our study two additional catalysts, namely the parent dirhodium(II) acetate and the cationic complex $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$ bearing simple acetonitrile molecules as acetate substituents. Although this complex has long been known in the literature [6], it has to the best of our knowledge never been employed as catalyst before. The results of the various tests are reported in Table 2.

The hydrosilylation of 1-hexyne with dimethylphenylsilane was run at 90 °C in a solventless fashion using an excess of 1-hexyne as the solvent (catalyst/silane/hexyne ratio 1/1000/4000). The best results were obtained with the simple $Rh_2(OAc)_4$ precursor: (*Z*)-(1-dimethylphenylsilyl)-1-hexene was formed in 87% yield with 98% selectivity after 6 h, other products stemming mainly from the formal *cis*-addition of the silane to the triple bond. The cationic reference catalyst showed higher conversion but also poorer selectivity for the main reaction product. The less thermodynamically stable *Z*-product remained however largely predominant. This is in contrast with other reports

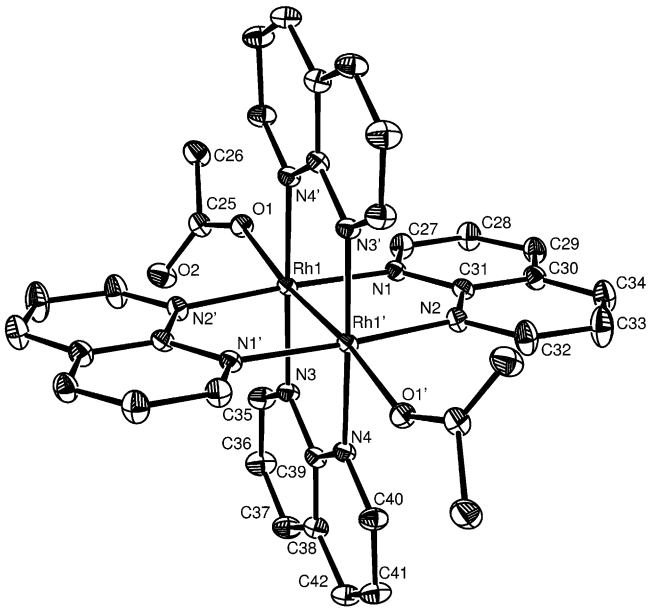


Fig. 1. View of the cation $[Rh_2(OAc)_2(Naft)_4]^{2+}$, with the atomic numbering scheme.

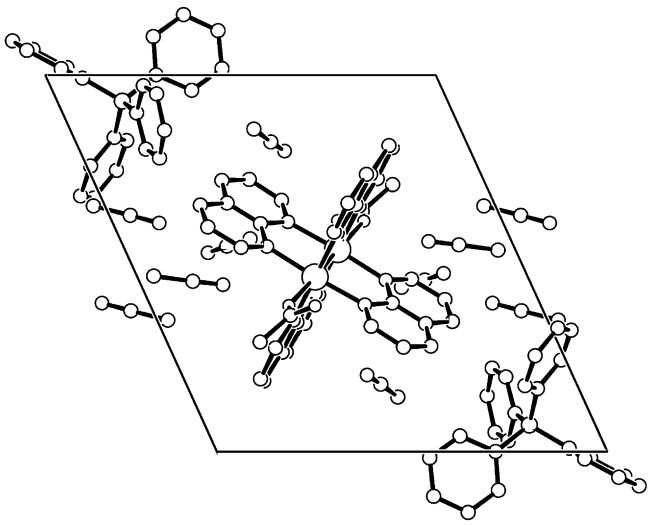


Fig. 2. Crystal packing of $[Rh_2(OAc)_2(Naft)_4](BPh_4)_2 \cdot 10CH_3CN$. View along the crystallographic *a*-axis.

from the literature where cationic rhodium-based catalysts were shown to exhibit a preference for *cis* hydrosilylation leading to the *E* isomer [13], but in accordance with results obtained with neutral, electron poor dirhodium(II) perfluorobutyrate [4b]. The performance of the naphthyridine complexes appeared to be much worse, both in terms of conversion and selectivity, although the *Z*-isomer remained predominant. Furthermore, two of the complexes turned out to be insoluble in the reaction mixture and were therefore not evaluated. Since also the performance of cationic dirhodium(II) complexes with oxothioethers was found to be inferior to that of simple $Rh_2(OAc)_4$ [8], it can be concluded that the presence of a positive charge on the dirhodium(II) catalyst does not appear to enhance its reactivity in this reaction [14]. We are currently attempting to find a rational explanation for the exceptional productivity observed with complex $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$.

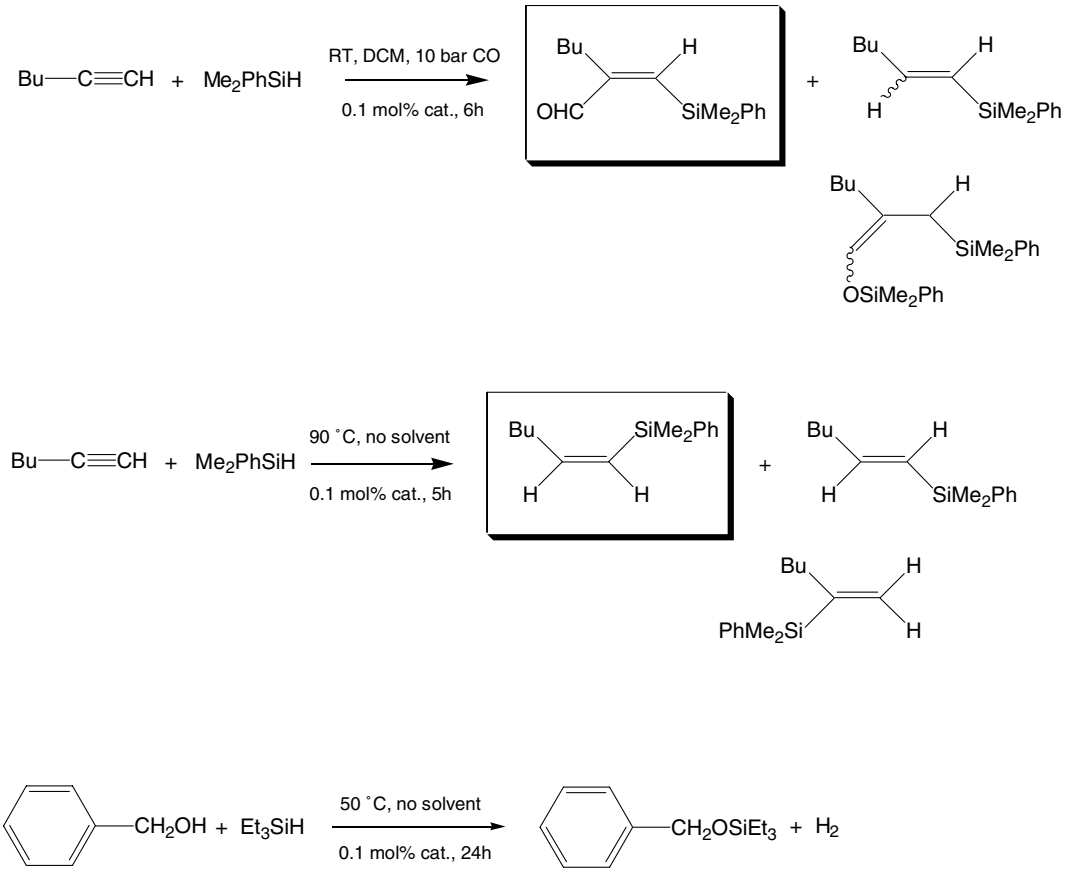
The silylformylation of 1-hexyne with dimethylphenylsilane could be performed in dichloromethane at a much lower temperature than the hydrosilylation reactions, namely at room temperature, under 10 atm of CO, using a 1/1000 catalyst/substrate ratio. In the case of this reaction the reactivity order of the various complexes changed quite radically. In fact, the parent $Rh_2(OAc)_4$ exhibited very poor productivity, whereas the cationic complexes were much more effective. Only the *Z* isomer of the silylformylated product was observed, which highlights the high regio- and stereoselectivity that can be obtained with these catalysts; other by-products stemmed almost exclusively from hydrosilylation of the triple bond, which is known to be the main competitive reaction. Particularly interesting was also the reactivity trend with the tetrasubstituted naphthyridine complexes. Whereas complexes (**6**) and (**7**) were almost inactive, complex (**8**) exhibited a comparable conversion (90% yield) and a higher selectivity (99%) than the cationic complex with acetonitrile ligands. These results highlight the importance of having free apical coordination sites in the complex catalyst. Compared with the previously reported cationic dirhodium(II) complexes with oxothioethers, we have obtained comparable conversions but much higher selectivities with the best catalysts presented in this work. Although not optimised, the catalytic performance of these complexes compares favourably with that of other rhodium-based catalysts such as dirhodium(II) perfluorobutyrate [4d,4e], $Rh_4(CO)_{12}$ [15,16] or solvated rhodium atoms [15]. Thus, it can be stated that the presence of a positive charge on the dirhodium(II) catalyst does significantly promote the silylformylation reaction.

Finally, the silane alcoholysis of triethylsilane with benzyl alcohol was run at 50 °C in a solventless fashion using a 1/1000 catalyst/substrate ratio. None of the employed catalysts was found to be very productive in this reaction. There is, however, a significant difference in the catalytic efficiency of the various complexes. In fact, whereas the

Table 1
Selected bond distances (Å) and angles (deg) in compound $[Rh_2(OAc)_2(Naft)_4](BPh_4)_2 \cdot 10CH_3CN$

Rh1–Rh1′	2.448(1)	Rh1–N4′	2.077(3)
Rh1–N3	2.050(3)	Rh1–O1	2.297(2)
Rh1–N2′	2.050(2)	O1–C25	1.269(3)
Rh1–N1	2.057(2)	O2–C25	1.245(3)
N3–Rh1–N2′	89.88(9)	N4′–Rh1–O1	87.03(9)
N3–Rh1–N1	88.16(9)	N3–Rh1–Rh1′	89.31(7)
N2′–Rh1–N4′	90.06(9)	N2′–Rh1–Rh1′	88.49(6)
N1–Rh1–N4′	91.73(9)	N1–Rh1–Rh1′	88.44(6)
N3–Rh1–O1	95.99(9)	N4′–Rh1–Rh1′	87.67(7)
N2′–Rh1–O1	94.45(8)	O1–Rh1–Rh1′	173.94(5)
N1–Rh1–O1	88.79(8)		

Symmetry transformations used to generate equivalent atoms: $-x+2$, $-y+1$, $-z+1$.



Scheme 3. Catalytic reactions investigated in the present work.

Table 2
Conversions and selectivities (in brackets) of the catalytic reactions with the various complexes

Catalyst	Hydrosilylation	Silylformylation	Silane alcoholysis
$Rh_2(OAc)_4$	87(98)	6(59)	10(100)
$[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$	100(90)	93(94)	25(100)
$[Rh_2(OAc)_3(Naft)](OAc)$ (**5**)	47(77)	73(93)	19(100)
$[Rh_2(OAc)_2(Naft)_4](OAc)_2$ (**6**)	31(84)	0	19(100)
$[Rh_2(OAc)_2(Naft)_4](BPh_4)_2$ (**7**)	n.s.[a]	7(64)	n.s.[a]
$[Rh_2(MeCN)_2(Naft)_4](BF_4)_4$ (**8**)	n.s.[a]	90(99)	3(100)

Reaction conditions: see Scheme 3.
[a] Catalyst not soluble.

$Rh_2(OAc)_4$ precursor reacted very slowly but did not apparently undergo decomposition in the course of the reaction, the cationic reference catalyst appeared to be extremely active, causing a sudden burst of dihydrogen production in the reaction mixture as soon as the silane was added; this catalyst, however, apparently deactivated very rapidly, thus finally giving an unsatisfactory yield. The naphthyridine complexes also exhibited poor performance, with the tetracationic complex (**8**) quite surprisingly being the worst catalyst in this reaction. A kinetic curve obtained with catalyst (**6**) and prolonged reaction times (Fig. 3) showed that the behaviour of such complexes is similar to the parent dirhodium acetate, in that the low yield is due to the intrinsically low catalyst activity and not to its rapid deactivation.

Thus, it would appear that cationic dirhodium(II) complexes are worse catalysts for this reaction than neutral, electron poor dirhodium(II) complexes, such as dirhodium perfluorocarboxylates. The latter catalysts were recently reported to reach almost complete conversion in model reactions under the same reaction conditions, even with a 1/10000 catalyst/substrate ratio [5b,5c]. However, very recent results from our group show that cationic dirhodium(II) complexes with oxothioether ligands exhibit even superior catalytic activities under similar reaction conditions (A. Biffis, M. Brichese, to be published). An explanation for such widely different results may be traced back to the different ligand set used. In fact, it is known that dirhodium(II) catalysts are able to coordinate both reaction partners of the silane alcoholysis reaction; however, coordi-

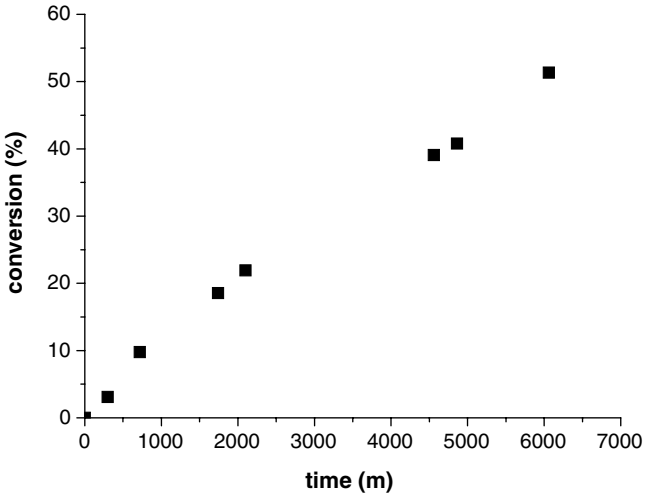


Fig. 3. Kinetic curve of triethylsilane alcoholysis with benzyl alcohol and catalyst (**6**).

nation of the silane leads to substrate activation and therefore to the catalytic event, whereas coordination of the alcohol leads to catalyst deactivation [4a]. Although the presence of a positive charge on the complex should increase its electrophilicity and favour silane activation, it may also lead to an increase in the ''hardness'' of the rhodium center, hence to the preferential coordination of oxygen donor ligands such as the alcohol. The choice of a proper ligand set should greatly help in modulating the character of the rhodium center, hence in promoting the catalytic activity.

In conclusion, we have shown that the presence of a positive charge on a dirhodium(II) complex affects its catalytic efficiency in a manner that strongly depends on the target reaction. In particular, cationic dirhodium(II) complexes with 1,8-naphthyridine ligands appear to be promising catalysts for the silylformylation of alkynes, whereas they are much less efficient in the hydrosilylation of alkynes. In the case of silane alcoholysis, the catalytic efficiency appears to have a stronger dependence on the particular ligand set used rather than on the complex charge. In order to rationalise all these experimental observation, a thorough mechanistic study of the underlying chemical processes is needed. We are currently engaged in designing target experiments which should clarify the role of the complex charge in these reactions, particularly in the case of the silylformylation reaction, for which the mechanism of action of dirhodium(II) catalysts is still quite obscure [4e].

3. Experimental section

3.1. General procedures

The reagents (Aldrich-Chemie) were high purity products and generally used as received. 1,8-Naphthyridine (Naft) was prepared following the method of Skraup [17]. The cationic complex $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$ was prepared according to the literature [6a]. Unless otherwise noted, solvents were dried before use and the reaction apparatus carefully deoxygenated; reactions were performed under argon and all operations were carried out under an inert atmosphere. The solution ^{1}H- and ^{13}C{^{1}H}-NMR spectra were acquired on Bruker Avance 300 MHz at room temperature. The chemical shifts were determined by reference to the residual solvent peaks, using tetramethylsilane as internal standard. The FTIR spectra were recorded on a Biorad FT S7 PC spectrophotometer at 2 cm^{-1} resolution in KBr disks.

3.2. Synthesis of the complexes

3.2.1. $[Rh_2(OAc)_3(Naft)](OAc)$ (**5**)

1,8-naphthyridine (70 mg, 0.54 mmol) was added to a suspension of $Rh_2(OAc)_4$ (200 mg, 0.45 mmol) in toluene (25 mL); the reaction mixture was stirred for 3 h at room temperature and then evaporated to small volume under reduced pressure. Treatment with diethyl ether gave a brown precipitate, which was filtered and dried under vacuum (70% yield). Anal. Calc. for $C_{16}H_{18}N_2O_8Rh_2$ ($M = 572.14$): C, 33.59; H, 3.17; N, 4.90. Found: C, 32.98; H, 3.16; N, 5.09%. ^{1}H NMR ($CDCl_3$): δ 1.81 (br, 3H, $CH_3CO_2^-$), 1.94 (s, 6H, $CH_3CO_2^-$), 2.60 (br, 3H, $CH_3CO_2^-$), 7.66 (m, 2H, Naft), 8.16 (m, 2H, Naft), 11.14 (m, 2H, Naft). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.8, 25.0 and 26.3 ($CH_3CO_2^-$), 125.1, 126.2, 140.4, 163.1 and 164.0 (Naft), 191.8 and 192.1 (CO_2^-). FT IR (KBr, cm^{-1}): 3054, 2853, 1559, 1412, 787 and 708.

3.2.2. $[Rh_2(OAc)_2(Naft)_4](OAc)_2$ (**6**)

1,8-naphthyridine (270 mg, 2.09 mmol) was added to a suspension of $Rh_2(OAc)_4$ (200 mg, 0.45 mmol) in acetic acid (30 mL); the reaction mixture was stirred for 8 h under reflux and then evaporated to small volume under reduce pressure; treatment with diethyl ether afforded an orange solid, which was filtered and dried under vacuum (61% yield). Anal. Calc. for $C_{40}H_{36}N_8O_8Rh_2 \cdot 4HOAc$ ($M = 1202.79$): C, 47.93; H, 4.35; N, 9.31. Found: C, 47.50; H, 4.24; N, 9.49. ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 9H, $CH_3CO_2^-$ and HOAc), 2.65 (s, 3H, $CH_3CO_2^-$), 7.78 (m, 4H, Naft), 8.67 (m, 4H, Naft), 9.20 (br, 2H, HOAc), 10.31 (m, 4H, Naft). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.9 and 27.4 ($CH_3CO_2^-$ and HOAc), 125.0, 126.1, 143.0, 159.7 and 161.3, 175.4 (CO_2^- and HOAc), 179.3 (CO_2^-). FT IR (KBr, cm^{-1}): 3420, 3059, 2851, 1711, 1582, 1373, 1325, 841 and 793.

3.2.3. $[Rh_2(OAc)_2(Naft)_4](BPh_4)_2$ (**7**)

A solution of excess $NaBPh_4$ in methanol (5 mL) was added dropwise and under vigorous stirring to a solution of complex (**6**) (200 mg, 0.17 mmol) in a mixture methanol/toluene 4/1 (10 mL); the yellow solid which precipitated was filtered, washed with methanol (2×5 mL) and dried under vacuum (71% yield). Anal. Calc. for $C_{84}H_{70}B_2N_8O_4Rh_2$ ($M = 1482.96$): C, 68.03; H, 4.76; N, 7.56. Found: C, 67.76; H, 4.89; N, 7.48. ^{1}H NMR

(CD_3CN): δ 2.60 (s, 3H, $CH_3CO_2^-$), 6.80, 6.96, 7.24 (m, 20H, BPh_4), 7.66 (m, 4H, Naft), 8.36 (m, 4H, Naft), 10.38 (m, 4H, Naft). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 27.4 ($CH_3CO_2^-$), 122.7 (Ph), 125.4 (Naft), 126.6 (Ph), 127.1 (Naft), 136.6 (Ph), 143.0 (Naft), 161.2 (Naft), 162.3 (Naft), 165.1 (Ph), 179.1 (CO_2^-). FT IR (KBr, cm^{-1}): 3053, 2985, 1578, 1371, 1515, 1324, 839, 789, 732 and 704.

3.2.4. *[Rh$_2$(MeCN)$_2$(Naft)$_4$](BF$_4$)$_4$ (**8**)*

(Et_3O)(BF_4) (1 M solution in CH_2Cl_2, 0.73 mL, 73.00 mmol) was added to a solution of complex (**7**) (180 mg, 12.1 mmol) in CH_3CN (15 mL). The reaction mixture was stirred for 24 h, then treated with diethyl ether (20 mL) to precipitate the product, as a green solid, which was filtered and dried under vacuum (88% yield). Anal. Calc. for $C_{36}H_{30}N_{10}B_4F_{16}Rh_2$ ($M = 1155.67$): C, 37.41; H, 2.61; N, 12.11. Found: C, 36.90; H, 2.51; N, 12.07. ^1H NMR (CD_3CN): δ 1.95 (s, 3H, CH_3CN), 7.82 (m, 4H, Naft), 8.58 (m, 4H, Naft), 9.66 (m, 4H, Naft). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 126.8 (Naft), 128.1 (Naft), 144.4 (Naft), 160.7 (Naft), 162.6 (Naft), acetonitrile signals not detected. FT IR (KBr, cm^{-1}): 3441, 2200, 1606, 1513, 1056, 839 and 788.

3.3. Catalytic tests

3.3.1. Silylformylations

The silylformylation reaction was performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. Me_2PhSiH, (0.31 mL, 2 mmol), 1-hexyne (0.23 mL, 2 mmol) and rhodium catalyst (0.002 mmol) were dissolved in dichloromethane (2 mL) under CO atmosphere in a Pyrex Schlenk tube. The obtained solution was introduced in the autoclave, previously placed under vacuum (0.1 mmHg), by a steel siphon. The reactor was pressurised with 10 atm CO and the mixture was stirred at room temperature for 6 h. After removal of excess CO (fume hood), the reaction mixture was diluted with pentane (10 mL), filtered on celite and concentrated under vacuum. The composition of the reaction mixture was determined by GLC, GC-MS and ^1H-NMR analysis [15].

3.3.2. Hydrosilylations

The hydrosilylation reaction was run in a Pyrex Carius tube fitted with a Corning Rotaflo tap. Me_2PhSiH (0.31 mL, 2 mmol) and 1-hexyne (0.92 mL, 8 mmol) were added, under argon atmosphere via syringe, to the rhodium catalyst (0.002 mmol). The suspension was stirred at 90 °C for 5 h and then subjected to GLC analysis to determine the conversion of the silane. The reaction mixture was filtered on celite and concentrated under vacuum in order to remove the excess alkyne. The isomeric composition of the reaction products was determined by ^1H-NMR analyses [18].

3.3.3. Silane alcoholysis

The silane alcoholysis reaction was run in a Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the rhodium catalyst (0.008 mmol), evacuated and filled with argon. 0.8 mL (7.89 mmol) benzyl alcohol were then added and the resulting solution was heated with stirring to 50 °C in a thermostated oil bath. After addition of 1.9 mL (11.81 mmol, 1.5 eq.) triethylsilane the solution was further stirred at 50 °C for 24 h. 0.1 mL samples were withdrawn after this period, diluted with 1 mL dichloromethane and analyzed by ^1H-NMR.

Table 3
Crystallographic data for the compound $[Rh_2(OAc)_2(Naft)_4](BPh_4)_2 \cdot 10CH_3CN$

Formula	C104 H100 B2 N18 O4 Rh2
Formula weight	1893.46
Crystal system	Triclinic
Space group	*P*-1
a (Å)	12.485(3)
b (Å)	14.119(5)
c (Å)	15.764(5)
α (°)	109.87(5)
β (°)	109.50(5)
γ (°)	97.83(3)
V (Å^3)	2363.8(13)
Z, D_{calcd} (g cm^{-3})	1, 1.33
F(000)	982
μ, cm^{-1}	33.18
Refl. collected	9248
Refl. unique	8891 ($R_{int} = 0.0241$)
Obs. Refl. [$I > 2\sigma(I)$]	8531
Parameters	591
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $wR_2 = 0.1110$
Final *R* indices all data	$R_1 = 0.0419$, $wR_2 = 0.1124$

$R_1 = \Sigma\|F_o\| - |F_c\|/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

3.4. X-ray structure determination of *[Rh$_2$(OAc)$_2$(Naft)$_4$](BPh$_4$)$_2$ · 10CH$_3$CN (**7**)*

Crystals of compound (**7**) suitable for X-ray analysis were grown by slow evaporation of a solution of the complex in CH_3CN. Data were collected on a Enraf Nonius CAD 4 single-crystal diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å). Because of the presence of several crystallisation solvent molecules, the crystals were unstable and decomposed rapidly in air at room temperature so the data were collected at 173 K, after coating the crystal with perfluoropolyether oil. Details for the X-ray data collection are collected in Table 3. The structure was solved by direct methods with SHELXS-97 and refined against F^2 with SHELXS-97 [19], with anisotropic thermal parameters for all non-hydrogen atoms. A correction for absorption was made (maximum and minimum value for the transmission coefficient was 1.000 and 0.636) [20]. Idealised geometries were assigned to the hydrogen atoms.

4. Supporting information available

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 294808 for compound (**7**). These data

can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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