Rhodium complexes with diimines derived from glyoxal: crystal structure of [Rh(SnCl₃)(NBD)(GCH)] (NBD = norbornadiene; GCH = glyoxal bis(cyclohexylimine)

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Abstract

[{Rh(L₂)Cl}₂] (L₂ ≡ COD, or norbornadiene (NBD)) react with α-diimines (LL) derived from glyoxal, irrespective of the stoichiometric ratios employed, to give [Rh₂(L₂)Cl₂(LL)] when L₂ ≡ COD or [Rh(Cl)(L₂)(LL)] when L₂ = NBD. Solutions of COD compounds contain dinuclear [{Rh(COD)(Cl)}₂(μ-LL)] species with bridging LL groups and ionic [Rh(COD)(LL)]⁺[Rh-(COD)Cl₂]⁻ species, in temperature-dependent ratios. The NBD compounds are pentacoordinated in the solid state and undergo rearrangements in solution. When the reactions are performed in the presence of SnCl₂, pentacoordinated [Rh(SnCl₃)-(diolefin)(LL)] are obtained, which in solution undergo SnCl₃⁻ dissociation. The molecular structure of [Rh(SnCl₃)(NBD)(GCH)] (GCH = glyoxalbis(cyclohexylimine)) has been determined by an X-ray diffraction study. It is best described as distorted square pyramidal with the equatorial positions occupied by the diolefin and the diimine respectively, and the SnCl₃ fragment in the apical position.

1. Introduction

α-Diimines (RN: C(R')C(R'): NR(LL)) have a versatile coordination chemistry [1]. In their reactions with [{RhL₂Cl}₂] (L₂ = COD or norbornadiene (NBD); L ≡ CO) they give different types of product, depending on the stoichiometric ratios employed and/or the nature of LL or L₂. With Rh:LL = 2:1, both dinuclear [{Rh(L₂)(Cl)}₂(μ-LL)] [2–4] and ionic [Rh(L₂)(LL)]⁺-[Rh(L₂)Cl₂]⁻ [4–9] have been described. With diazadienes, the existence of both forms in equilibrium in solution has been reported [2,4,5]. When Rh:LL = 1:1 pentacoordinated [6–8,10] and tetracoordinated cationic [5,6,11] or neutral [12,13] species have been obtained. α-Diimine-type bioxazoline ligands afford dinuclear [(LL)Rh(μ-Cl)₂Rh(CO)₂] compounds containing chlorine bridges and a terminal LL group [14].

[{Rh(diolefin)Cl}₂]–chiral phenanthroline systems promote asymmetric transfer hydrogenation of ketones using alcohols as a hydrogen source [15] and Rh–diazadiene compounds catalyse regioselective and stereoselective homogeneous hydrosilation reactions [13,16]. Recently, we have reported the reactions of [{RhL₂Cl}₂] with α-diimines derived from biacetyl and their reactions with SnCl₂ [17], on account of the catalytic potential of transition metal complexes containing covalently bonded tin compounds in organic transformations [18]. We report now the reactions of [{RhL₂Cl}₂] (L₂ ≡ COD or NBD) with α-diimines (RN: C(H)C(H): NR(LL)) derived from glyoxal compounds such as glyoxalbis-(cyclohexylimine) (GCH), glyoxalbis(4-dimethylaminoanil) (GAA) and glyoxalbis(4-hydroxy-anil) (GHA), which give different products, depending mainly on the nature of L₂, and their reactions with SnCl₂. The solution behaviour of the isolated compounds and the crystal structure of [Rh(SnCl₃)(NBD)(GCH)] are also discussed.

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2. Results and discussion

[{Rh(diolefin)Cl}$_2$] reacts with α-diimines derived from the glyoxal compounds GCH, GAA or GHA, irrespective of the stoichiometric ratios (1 : 1 or 1 : 2), to afford different types of compound depending on the diolefin in the starting dimer.

When diolefin $\equiv$ COD, complexes formulated as [Rh$_2$(COD)$_2$Cl$_2$(LL)] are obtained, whose analytical, conductivity and IR data are collected in Table 1. The IR spectra show the expected ligand bands. The conductivity values in acetone, corresponding to non-electrolytes for LL $\equiv$ GAA and GHA, suggest dinuclear structures with bridging LL ligands [Rh$_2$(COD)$_2$Cl$_2$(μ-LL)], whereas when LL = GCH the rather high conductivity value indicates a degree of ionic dissociation as in [Rh(COD)(LL)]$^+$[Rh(COD)Cl$_2$]$^-$. In methanol solution the three compounds behave as 1 : 1 electrolytes, corresponding to the ionic formulation.

The ^{1}H NMR spectra of these complexes in CDCl$_3$ indicate equilibrium between each form, shifted to the dinuclear compound at low temperatures (Table 2). [{Rh$_2$(COD)$_2$Cl$_2$}(GAA)] at room temperature shows two resonances due to the imine protons, at 10.15 and 8.58 ppm respectively. The low field resonance indicates σ-N, σ-N' bridging of the diimine [2,4,5], while the higher field resonance corresponds to a σ, σ'-N, N' chelate bonding in a cationic species. Different signals for the N substituents and the olefinic protons in both compounds are also observed. On cooling, the intensity of the signals due to the ionic compound decreases and by −40°C only the resonances due to [Rh$_2$(COD)$_2$-Cl$_2$](μ-GAA) are observed. [{Rh$_2$(COD)$_2$Cl$_2$}(GCH)]

behaves similarly but shows a greater tendency to the ionic form, consistent with the conductivity data. At room temperature, equilibrium is reached much more rapidly, the imine proton resonances are broad, and the olefinic protons show a strong signal at 4.17 ppm together with some other broad and weak resonances. On cooling, signals of the dinuclear and the ionic compounds are observed and by −60°C [{Rh$_2$(COD)$_2$-Cl$_2$}(μ-GCH)] is the main species although a small amount of the ionic compound is still observed. Comparison of these results with those obtained for diimines derived from biacetyl [17] confirms the higher tendency of unsubstituted RN=C(H)C(H)=NR to behave as σ-N, σ-N' bridges [4]. When comparing these results and those reported previously with R $\equiv$ isopropyl [2] or C$_6$H$_4$OMe-4 [5] we observe that the tendency to dinuclear formation in solution is highest for the compound containing GAA. After mixing equimolar amounts of [{Rh$_2$(COD)$_2$Cl$_2$}(LL)] and LL, the ^{1}H NMR spectra obtained at room temperature show the presence of starting material and uncombined LL only, although on lowering the temperature a higher proportion of the cationic species [Rh(COD)(LL)]$^+$ is observed. These cationic species can be obtained easily by reaction of [{Rh(COD)Cl}$_2$] and LL (1 : 2 stoichiometric ratio) followed by addition of bulky anions (Table 1). These compounds behave as 1 : 1 electrolytes in acetone or methanol solution. Their ^{1}H NMR spectra show the imino hydrogen resonance at a slightly lower field than the uncombined LL and only one signal for the olefinic protons (Table 2). The spectra remain unaltered on cooling to −60°C. All these data indicate mononuclear cationic species.

Table 1
Analytical and physical data for the complexes

Compound	Anal. Found (Calc.) (%)			Λ_M (Ω^{-1} cm^2 mol^{-1})	ν(C=N) (cm^{-1})	ν(M–Cl) (cm^{-1})
	C	H	N			
[Rh$_2$(COD)$_2$Cl$_2$(GCH)]	49.93(50.51)	6.52(6.78)	3.94(3.93)	53 [a]; 97 [b]	1600(m)	301(w)
[Rh$_2$(COD)$_2$Cl$_2$(GAA)]	51.88(51.86)	5.87(5.89)	7.18(7.11)	12 [a]; 63 [b]	1594(s)	324(w)
[Rh$_2$(COD)$_2$Cl$_2$(GHA)]	47.55(49.14)	4.66(4.95)	3.83(3.82)	9 [a]; 60 [b]	1600(s)	350(w)
[Rh(COD)(GCH)][PF$_6$]	43.86(45.89)	6.21(6.30)	4.54(4.86)	91 [a]; 70 [b]	1618(w)	–
[Rh(COD)(GAA)][PF$_6$]	47.34(48.01)	5.25(5.27)	8.52(8.61)	71 [a]; 54 [b]	1591(s)	–
[Rh(Cl)(NBD)(GCH)]	55.87(55.94)	6.64(7.15)	5.68(6.21)	12 [a]; 20 [b]	1640(w)	318(w)
[Rh(Cl)(NBD)(GAA)]	55.65(57.21)	5.56(5.76)	10.34(10.67)	16 [a]; 30 [b]	1596(s)	323(w)
[Rh(Cl)(NBD)(GHA)]	52.49(53.58)	4.55(4.28)	5.50(5.95)	15 [a]; 73 [b]	1605(s)	317(m)
[Rh(NBD)(GCH)][PF$_6$]	44.36(45.01)	6.19(5.76)	4.75(5.00)	113 [a]; 63 [b]	1640(w)	–
[Rh(NBD)(GAA)][PF$_6$]	47.55(47.33)	4.22(4.77)	8.37(8.83)	111 [a]; 87 [b]	1598(w)	–
[Rh(NBD)(GHA)][BF$_4$]	48.04(48.31)	3.84(3.86)	5.22(5.73)	90 [a]; 23 [b]	1605(s)	–
[Rh(SnCl$_3$)(COD)(GCH)]	39.64(40.25)	4.98(5.53)	4.39(4.27)	58 [a]; 96 [b]	1633(m)	300(m); 284(m)
[Rh(SnCl$_3$)(NBD)(GCH)]	38.89(39.38)	4.67(5.04)	4.13(4.37)	30 [a]; 90 [b]	1647(w)	306(m); 293(m)
[Rh(SnCl$_3$)(COD)(GAA)]	42.65(42.75)	4.70(4.69)	7.43(7.67)	31 [a]; 50 [b]	1602(s)	305(m), 291(m)
[Rh(SnCl$_3$)(NBD)(GAA)]	42.79(42.03)	4.18(4.23)	7.59(7.84)	10 [a]; 57 [b]	1597(s, broad)	296(m), 280(m)
[Rh(SnCl$_3$)(COD)(GHA)]	40.27(39.07)	3.41(3.58)	3.70(4.14)	21 [a]; 47 [b]	1591(m)	313(m)
[Rh(SnCl$_3$)(NBD)(GHA)]	38.13(38.20)	3.01(3.05)	3.91(4.24)	12 [a]; 100 [b]	1587(m)	307(s), 295(m)

[a] Conductivity measurements were carried out in approximately 2.5 × 10^{-4} in acetone solutions.

[b] Conductivity measurements were carried out in approximately 2.5 × 10^{-4} methanol solutions.

When diolefin ≡ NBD, only complexes formulated as pentacoordinate [Rh(Cl)(NBD)(LL)] are obtained (Table 1). These compounds are non-conducting in acetone, although the conductivity is enhanced in methanol solution. The ^{1}H NMR spectra (Table 2) show only one resonance for the imino hydrogen, at a slightly lower field compared with the uncombined LL, one resonance for the olefinic protons, and one resonance for the methyne protons of the norbornadiene. These spectra remain unaltered on cooling to −60°C, indicating equilibration of these protons which could be a ligand dissociation process. Although chlorine dissociation cannot be excluded, opening of the chelate ring seems most likely in this case. When recording the ^{1}H NMR spectra of [{Rh(NBD)Cl}$_2$]:LL = 1:1 mixtures in CDCl$_3$ (Fig. 1) the olefinic region appears broad and unresolved, indicating an interchange of NBD between the pentacoordinated [Rh(Cl)(NBD)(LL)] and the starting material [{Rh(NBD)Cl}$_2$]. On cooling, the rate of exchange is reduced and signals corresponding to both compounds are observed, together with low intensity resonances that can be ascribed to a dinuclear compound [{Rh(NBD)Cl}$_2$(μ-LL)].

This could be responsible for the NBD interchange, by opening the chelate ring. After adding bulky anions A$^-$ to the solutions of these pentacoordinated compounds, cationic [Rh(NBD)(LL)]$^+$A compounds can be obtained (Tables 1 and 2).

Reaction of [{Rh(diolefin)Cl}$_2$]:LL = 1:2 mixtures with SnCl$_2$ leads to pentacoordinated [Rh(SnCl$_3$)(diolefin)(LL)] (Table 1). Their IR spectra show bands due to LL coordinated through the imine nitrogens and ν(Sn–Cl), indicative that the SnCl$_3^-$ group is bonded to rhodium [19]. Some of the conductivity values in acetone solution are rather high for non-electrolytes and suggest a certain degree of ionic dissociation, enhanced in methanol solution. This process is confirmed by variable-temperature NMR measurements of the GCH and GAA compounds (Table 2). The GHA compounds are very slightly soluble in common organic solvents and no spectra could be obtained at low temperatures. The chemical shifts for the imino hydrogen resonance in these complexes indicates σ, σ'-N, N' chelate bonding. At room temperature the ^{1}H NMR spectra show only one resonance for all olefinic protons and only one resonance for the methyne pro-

Table 2
Selected NMR data

Compound	Temperature (°C)	(solvent)	δ (ppm), ^{1}H NMR					δ [a] (ppm), ^{119}Sn NMR
			H–C=N	C$_6$H$_4$	CH$_3$	HC=	HC<	
[Rh$_2$(COD)$_2$Cl$_2$(GAA)]	20	(CDCl$_3$)	10.15 [b] 8.58 [c](br)	(8.16(d); 6.76(d)) [b] (7.72(br); 6.76(br)) [c]	[3.09] [b] [3.04] [c]	(4.73; 4.18; 3.60; 3.50) [b] 4.18 [c,d]		
	−40	(CDCl$_3$)	10.17 [b]	(8.25(d); 6.76(d)) [b]	[3.12] [b]	(4.76; 4.65; 4.17; 3.50; 3.43) [b]		
[Rh$_2$(COD)$_2$Cl$_2$(GCH)]	20	(CDCl$_3$)	9.71(br) [b] 8.57(br) [c]			(4.64(br); 3.58(br)) [b] 4.17 [c,d]		
	−60	(CDCl$_3$)	9.70 [b]			(4.60; 4.56; 4.16; 4.10; 3.93; 3.69; 3.48) [b]		
			8.6 [c](weak)			(4.25) [c](weak); (4.16) [d]		
[Rh(COD)(GAA)][PF$_6$]	20	(CDCl$_3$)	8.33(s)	7.34(d); 6.70(d)	3.04	4.09		
[Rh(COD)(GCH)][PF$_6$]	20	(CDCl$_3$)	8.13(s)			4.34(s)		
[Rh(Cl)(NBD)(GAA)]	20	(CDCl$_3$)	8.12(s)	7.39(d); 6.63(d)	2.97(s)	3.47	3.47	
[Rh(Cl)(NBD)(GCH)]	20	(CDCl$_3$)	8.15(s)			3.73	3.68	
[Rh(Cl)(NBD)(GHA)]	20	(CD$_3$OD)	8.24(s)	7.31(d); 6.80(d)		3.41	3.47	
[Rh(NBD)(GAA)][PF$_6$]	20	(CDCl$_3$)	7.62(s)	7.20(d); 6.47(d)	2.95(s)	3.59	3.59	
[Rh(NBD)(GCH)][PF$_6$]	20	(CDCl$_3$)	8.13(s)			3.71	3.68	
[Rh(SnCl$_3$)(COD)(GCH)]	20	(CD$_2$Cl$_2$)	8.08(s)			4.30		214
	−70	(CD$_2$Cl$_2$)	8.07(s)			4.63; 3.80		229 (J = 447 Hz)
[Rh(SnCl$_3$)(NBD)(GCH)]	20	(CDCl$_3$)	7.94(d)			3.77	3.64	223
	−60	(CDCl$_3$)	8.03(s)			3.95; 3.67	3.89; 3.51	226 (J = 691 Hz)
[Rh(SnCl$_3$)(NBD)(GAA)]	20	(CD$_2$Cl$_2$)	8.08(d)	7.17(d); 6.78(d)	3.10(s)	3.60	3.60	
	−80	(CD$_2$Cl$_2$)	7.83(s)	7.04(d); 6.65(d)	2.98(s)	3.57; 3.41	3.57; 3.26	
[Rh(SnCl$_3$)(COD)(GHA)]	20	(acetone-d_6)	8.36(s)	7.30(d); 6.93(d)		4.00		
[Rh(SnCl$_3$)(NBD)(GHA)]	20	(acetone-d_6)	8.36(s)	7.20(d); 6.92(d)		3.51	3.51	

[a] From acetone : acetone-d_6 : 1 : 1.
[b] [Rh$_2$(COD)$_2$Cl$_2$(μ-LL)].
[c] [Rh(COD)(LL)]$^+$.
[d] [Rh(COD)Cl$_2$]$^-$.

tons of norbornadiene. On cooling, these signals disappear and split into two signals, each thus giving two resonances for the olefinic protons of 1,5-cyclooctadiene or norbornadiene and also two resonances for the methyne protons of norbornadiene, but the signals due to the imino protons remain sharp. The ^{119}Sn NMR spectra of [Rh(SnCl$_3$)(diolefin)(GCH)] in acetone solution at room temperature (Table 2) show only broad singlets, at lower fields relative to SnMe$_4$, indicating SnCl$_3^-$ groups. On cooling, these singlets resolve into doublets owing to the coordination of SnCl$_3^-$ to rhodium and the values of chemical shifts and coupling constants are similar to those of analogous compounds containing diimines derived from biacetyl [17]. As expected, ^1J(Rh–Sn) is higher for the compound containing NBD [20].

The crystal structure of [Rh(SnCl$_3$)(NBD)(GCH)] was determined. Final atomic parameters are listed in Table 3. The crystal contains discrete well-separated molecules per asymmetric unit. Table 4 contains selected bond distances and angles. Fig. 2 shows an ORTEP view of the molecule with the numbering schemes. The coordination around the rhodium atom is best described as distorted square pyramidal with the equatorial positions occupied by C(1122) and C(4455) (C(1122) and C(4455) being the centres of the C(1)=C(2) and C(4)=C(5) bonds respectively) and by the nitrogen atoms of the diimine with the SnCl$_3$ in the axial position. The best least-squares plane for N(1)N(2)-

Table 3
Atomic coordinates for [Rh(SnCl$_3$)(NBD)(GCH)]

Atom	x	y	z	U_{eq} (Å^2)
Rh	0.52011(10)	−0.10344(10)	0.63859(4)	326(3)
Sn	0.29276(9)	0.05114(9)	0.64220(4)	419(3)
Cl(1)	0.10212(40)	−0.02792(43)	0.69158(16)	702(15)
Cl(2)	0.31741(46)	0.27765(40)	0.67721(19)	773(17)
Cl(3)	0.15359(48)	0.11776(55)	0.56861(18)	902(19)
N(1)	0.5271(10)	−0.1448(11)	0.7126(3)	414(36)
N(2)	0.3999(11)	−0.2860(10)	0.6422(4)	440(37)
C(1)	0.7355(13)	−0.0234(15)	0.6395(5)	504(49)
C(2)	0.6364(14)	0.0850(14)	0.6316(5)	494(47)
C(3)	0.6153(14)	0.1000(16)	0.5755(5)	565(51)
C(4)	0.5373(15)	−0.0344(16)	0.5633(5)	543(51)
C(5)	0.6354(15)	−0.1391(17)	0.5719(5)	586(57)
C(6)	0.7745(14)	−0.0716(16)	0.5876(5)	545(51)
C(7)	0.7675(15)	0.0638(19)	0.5590(6)	707(62)
C(8)	0.4554(15)	−0.2518(14)	0.7264(6)	534(51)
C(9)	0.3844(14)	−0.3270(13)	0.6870(5)	463(46)
C(10)	0.5953(13)	−0.0570(14)	0.7520(4)	408(41)
C(11)	0.7045(19)	−0.1348(19)	0.7844(7)	923(77)
C(12)	0.7792(21)	−0.0437(20)	0.8237(8)	1112(88)
C(13)	0.6769(24)	0.0316(20)	0.8532(7)	970(85)
C(14)	0.5693(19)	0.1076(19)	0.8212(7)	806(72)
C(15)	0.4916(17)	0.0162(17)	0.7826(5)	663(61)
C(16)	0.3207(15)	−0.3669(15)	0.6034(5)	563(53)
C(17)	0.4096(17)	−0.4603(17)	0.5754(6)	670(61)
C(18)	0.3289(22)	−0.5386(20)	0.5351(7)	917(80)
C(19)	0.2314(27)	−0.4542(28)	0.5045(7)	1273(11)
C(20)	0.1393(19)	−0.3605(20)	0.5325(7)	875(76)
C(21)	0.2212(19)	−0.2796(19)	0.5721(6)	812(71)

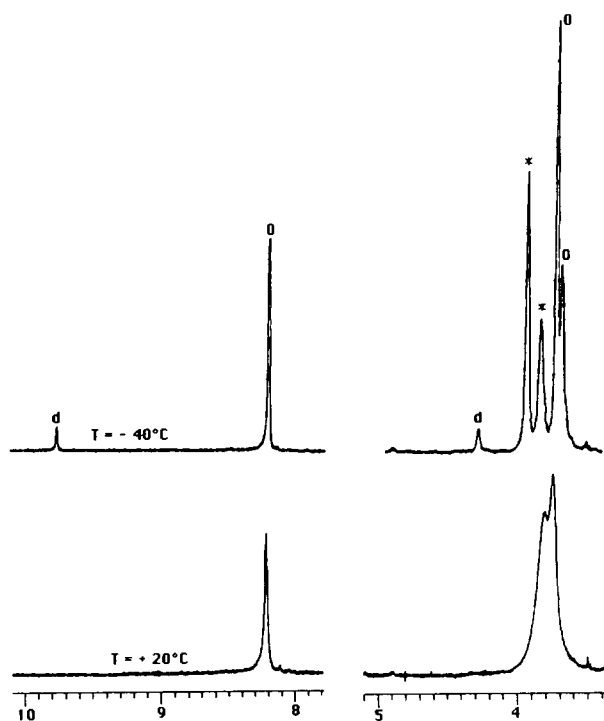Thermal parameters as $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i a_j \times 10^4$.

Fig. 1. Variable-temperature ^{1}H NMR spectra of [{Rh(NBD)Cl}$_2$]:
GCH = 1:1 mixtures in CDCl$_3$: *, [{Rh(NBD)Cl}$_2$]; 0, [Rh(Cl)-(NBD)(GCH)]; d, [{Rh$_2$(NBD)$_2$Cl$_2$}(μ-GCH)].

C(1122)C(4455) shows a maximum deviation of 0.02(1) Å for C(1122) with the Rh atom at 0.325(1) Å above this plane. This plane forms dihedral angles of 85.2(3)° with the N(2)C(1122)RhSn plane, 171.4(4)° with the N(1)C(8)C(9)N(2) plane and 99.4(5)° with the C(1)C(2)-C(4)C(5) plane. The Rh–C(1122) and Rh–C(4455) distances of 2.03(1) and 2.05(1) Å respectively are equal within experimental error, confirming equivalent positions. This compound contains asymmetric Rh–N distances (Rh–N(1), 2.03(1) Å; Rh–N(2), 2.10(1) Å), as has also been observed in other pentacoordinated compounds containing diimines [21]. This asymmetry may be due to a slight difference in the disposition of the cyclohexyl groups. Both of them adopt the expected chair conformation with C(13) only 0.03(2) Å above the N(1)N(2)C(1122)C(4455) plane, while C(19) lies 0.16(3) Å above this plane and closer to the rhodium atom. The angles and bond lengths involving the SnCl$_3^-$ fragment are as expected [22].

3. Experimental details

The preparation of the metal complexes was carried out at room temperature under dinitrogen by standard

Table 4

Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for [Rh(SnCl₃)(NBD)(GCH)]

Bond distances

Rh–Sn	2.610(1)	C(3)–C(7)	1.56(2)
Rh–N(1)	2.03(1)	C(4)–C(5)	1.38(2)
Rh–N(2)	2.10(1)	C(5)–C(6)	1.50(2)
Rh–C(1)	2.16(1)	C(6)–C(7)	1.52(2)
Rh–C(2)	2.14(1)	C(8)–C(9)	1.42(2)
Rh–C(4)	2.15(1)	C(10)–C(11)	1.51(2)
Rh–C(5)	2.18(1)	C(10)–C(15)	1.49(2)
Sn–Cl(1)	2.41(4)	C(11)–C(12)	1.52(3)
Sn–Cl(2)	2.39(4)	C(12)–C(13)	1.47(3)
Sn–Cl(3)	2.40(5)	C(13)–C(14)	1.49(3)
N(1)–C(8)	1.30(2)	C(14)–C(15)	1.52(2)
N(1)–C(10)	1.48(2)	C(16)–C(17)	1.47(2)
N(2)–C(9)	1.29(2)	C(16)–C(21)	1.49(2)
N(2)–C(16)	1.47(2)	C(17)–C(18)	1.45(3)
C(1)–C(2)	1.41(2)	C(18)–C(19)	1.50(2)
C(1)–C(6)	1.54(2)	C(19)–C(20)	1.49(3)
C(2)–C(3)	1.52(2)	C(20)–C(21)	1.50(3)
C(3)–C(4)	1.52(2)		
Rh–C(1122)	2.03(1)		
Rh–C(4455)	2.05(1)		

Bond angles

C(4)–Rh–C(5)	37.1(5)	N(1)–Rh–N(2)	77.1(4)
C(2)–Rh–C(5)	77.4(5)	Sn–Rh–C(5)	124.5(4)
C(2)–Rh–C(4)	65.6(5)	Sn–Rh–C(4)	87.9(4)
C(1)–Rh–C(5)	63.8(5)	Sn–Rh–C(2)	86.4(4)
C(1)–Rh–C(4)	77.3(5)	Sn–Rh–C(1)	124.1(4)
C(1)–Rh–C(2)	38.3(5)	Sn–Rh–N(2)	92.1(3)
N(2)–Rh–C(5)	101.4(5)	Sn–Rh–N(1)	93.3(3)
N(2)–Rh–C(4)	111.9(5)	Rh–Sn–Cl(3)	122.1(1)
N(2)–Rh–C(2)	177.2(5)	Rh–Sn–Cl(2)	118.6(1)
N(2)–Rh–C(1)	143.5(5)	Rh–Sn–Cl(1)	118.2(1)
N(1)–Rh–C(5)	142.2(5)	Cl(2)–Sn–Cl(3)	96.7(2)
N(1)–Rh–C(4)	170.9(5)	Cl(1)–Sn–Cl(3)	99.0(2)
N(1)–Rh–C(2)	105.4(5)	Cl(1)–Sn–Cl(2)	97.5(2)
N(1)–Rh–C(1)	94.7(4)		

Schlenk techniques. [{Rh(COD)Cl}₂] [23], [{Rh(NBD)-Cl}₂] [24] and α-diimines [25] were prepared as previously reported.
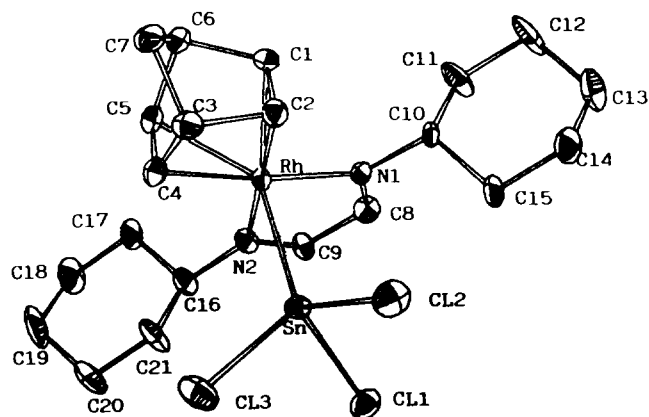
Fig. 2. View of [Rh(SnCl₃)(C₇H₈)(C₁₄N₂H₂₄)] showing the numbering scheme.

Microanalysis was carried out with a Perkin–Elmer 240C microanalyser. Conductivities were measured in acetone or methanol solution with a Metrohm E 518 conductimeter. IR spectra were recorded with a Perkin–Elmer 598 spectrophotometer in the range 4000–200 cm⁻¹ or with a Nicolet Fourier transform IR 740 instrument in the range 4000–50 cm⁻¹ using Nujol mulls between polyethylene sheets or KBr pellets. NMR spectra were recorded with an XL-300 Varian spectrometer, ¹H (tetramethylsilane internal standard) spectra were measured from CDCl₃, CD₃OD, CD₂Cl₂ or acetone-d^6 solutions at variable temperature in 5 mm tubes. ¹¹⁹Sn (SnMe₄ external standard) spectra were measured from acetone : acetone-d_6 = 1 : 1 solutions at variable temperature in 10 mm tubes.

3.1. Preparation of [Rh₂(COD)₂Cl₂(LL)]

To a CH₂Cl₂ solution (LL ≡ GCH or GAA) or MeOH suspension (LL ≡ GHA) of [{Rh(COD)Cl}₂] (0.06 mmol) was added an equimolar amount (0.06 mmol) of the corresponding LL upon which solutions or a suspension (LL ≡ GHA) were obtained. Addition of hexane gave precipitates that were filtered off, washed with reaction solvent and vacuum dried (yield, 54–64%).

3.2. Preparation of [Rh(Cl)(NBD)(LL)]

To a CH₂Cl₂ solution (LL ≡ GCH or GAA) or acetone suspension (LL ≡ GHA) of [Rh(NBD)Cl]₂ (0.06 mmol) was added 2 equivalents (0.12 mmol) of the corresponding LL upon which dark solutions or a suspension (LL ≡ GHA) were formed. Addition of hexane gave dark precipitates. The compounds obtained were filtered off, washed with reaction solvent and vacuum dried (yield, 43–69%).

3.3. Preparation of [Rh(SnCl₃)(diolefin)(LL)] (LL ≡ GCH or GAA)

To a CH₂Cl₂ solution of [{Rh(diolefin)Cl}₂] (0.06 mmol) was added 2 equivalents (0.12 mmol) of the corresponding LL. Addition of a methanol solution of SnCl₂ (0.12 mmol) led, after removal of CH₂Cl₂, to the precipitation of dark compounds. The solids obtained were filtered off, washed with MeOH and vacuum dried (yield, 65–88%).

3.4. Preparation of [Rh(SnCl₃)(COD)(GHA)]

To a CH₂Cl₂ solution of [{Rh(COD)Cl}₂] (0.06 mmol) was added 2 equivalents of GHA and SnCl₂ (0.12 mmol) in methanol. Removal of CH₂Cl₂ led to a dark solid that was filtered off, washed with MeOH and vacuum dried (yield, 59%).

3.5. Preparation of [Rh(SnCl₃)(NBD)(GHA)]

To a CH_2Cl_2 solution of [{Rh(NBD)Cl}$_2$] (0.06 mmol) was added 2 equivalents of GHA and $SnCl_2$ (0.12 mmol) in methanol. Removal of CH_2Cl_2 and MeOH gave a brown residue that was recrystallized from CH_2Cl_2–hexane (yield, 90%).

3.6. Preparation of [Rh(diolefin)(LL)][PF₆] (LL ≡ GCH or GAA)

To a CH_2Cl_2 solution of [{Rh(diolefin)Cl}$_2$] (0.06 mmol) was added 2 equivalents of the corresponding LL and of NH_4PF_6 (0.12 mmol). After filtration of the NH_4Cl formed an addition of hexane to the clear solution thus obtained, dark solids precipitated. These were filtered off, washed with hexane and vacuum dried (yield, 43–82%).

3.7. Preparation of [Rh(NBD)(GHA)]BF₄

To an acetone solution of [{Rh(NBD)Cl}$_2$] (0.06 mmol) was added 2 equivalents of $AgBF_4$ (0.12 mmol). After 30 min the AgCl formed was filtered off and the filtrate dropped into an acetone solution containing GHA (0.12 mmol). Addition of hexane gave a brown precipitate that was filtered off, washed with hexane and vacuum dried (yield, 80%).

Table 5
Crystal and refinement data for [Rh(SnCl₃)(NBD)(GCH)]

Formula	$RhSnCl_3N_2C_{21}H_{32}$
M_r	640.45
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.383(3)
b (Å)	9.669(2)
c (Å)	26.967(5)
β (°)	93.24(2)
V (Å^3)	2443(1)
Z	4
$F(000)$	1272
ρ_{calc} (g cm^{-3})	1.74
Temperature (K)	294
μ (cm^{-1})	20.3
Crystal dimensions (mm)	0.2×0.15×0.15
Diffractometer	Enraf–Nonius CAD4
Radiation	Graphitemonochromated
	Mo Kα (λ = 0.71069 Å)
Scan technique	$\Omega/2\theta$
θ (°)	$1 < \theta < 25$
Data collected	(−11,0,0) to (11,11,32)
Number of unique data	4566
Number of unique data (I) ≥ 2σ(I)	2678
Standard reflections	3/64 reflections
R_{int} (%)	2.7
R_F (%)	4.9
R_{wF} (%)	5.9
Average shift/error	0.063

3.8. Crystal structure determination

Crystal data and details of the procedure are given in Table 5. The crystals are deep-blue prisms. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Rh, Sn, P and Cl were taken from the *International Tables for X-Ray Crystallography* [26]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [27] was applied at the end of the isotropic refinement. The maximum and minimum absorption correction factors were 1.398 and 0.721 respectively.

Final mixed refinement employed fixed isotropic factors and coordinates for H atoms led to $R = 4.9$. The final difference synthesis show no significant electron density. No trend in ΔF versus F_o or (sin θ)/λ was observed. Most of the calculations were carried out with the X-RAY 80 system [28].

4. Supplementary material

Thermal parameters, hydrogen parameters and structural factors can be obtained from the authors on request, and have been deposited at the Cambridge Crystallographic Data Centre.

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