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Epimerization, diastereoselectivity and hemilability in dicationic chiral ruthenium complexes with bidentate (P^S) bisphosphine monosulfide ligands

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Abstract

The binding of heterobidentate P^S ligands introduces metal-centered chirality to the planar chiral parent complex $Ru(\eta^6:\eta^1\text{-}NMe_2C_6H_4C_6H_4PCy_2)Cl_2$. Observed diastereomeric ratios for the kinetic product vary dramatically depending upon ring size of the chelate formed with the P^S ligand. The complexes epimerize very slowly to thermodynamic product ratios that are substantially different from the kinetic product ratios.

Keywords: Chirality; Metal-centered chirality; Hemilabile

1. Introduction

The use of heterobidentate ligands in organometallic chemistry serves to impart steric and electronic asymmetry at a metal center. We recently reported work with heterobidentate P^N [1], P^O [2–6], and P^S [7–10] ligands, including successful applications in asymmetric catalysis [1,2,8–10]. The resulting metal complexes containing heterobidentate ligands can exhibit unique reactivity, and improved selectivity with respect to their C_2-symmetric counterparts, as a result of this asymmetry. An interesting feature of these ligands, notably the P^S and P^O variants, is the potential for diastereomeric equilibration *via* a hemilabile species, resulting from the dissociation of the S or O donor. In addition to allowing for chiral induction by the interconversion of isomers, such a hemilabile species can potentially serve the purpose of providing a catalytically active species owing to the generation of an open site for substrate binding [11–14].

As an extension of our earlier work [15–17], we wish to report the synthesis and dynamics of dicationic, planar chiral arene-tethered ruthenium complexes containing P^S chelates. These complexes are both planar chiral and chiral-at-metal, which allows for two diastereomeric forms that can interconvert *via* the aforementioned hemilabile species. Thus, a hemilabile intermediate can give rise to the epimerization of the chirality at the metal center, and this process is observable by NMR since it involves the interconversion of diastereomers. In addition, although the ability of arene-tethered ligands to control the metal chirality has been previously shown through the selective derivatization with monodentate ligands, the situation with chelates has not, to our knowledge, been addressed.

Our previous work has shown that the epimerization of metal chirality in mono- and dicationic ruthenium half-sandwich complexes is generally a relatively facile process, occurring with a half-life of minutes or hours [3–5,16]. However, one study has indicated that the situation with some dicationic variants may be quite different, as no metal epimerization was noted for complexes of the type $[Ru(\eta^6\text{-cymene})(\eta^2\text{-P^O})(amine)](SbF_6)_2$ [6]. This was attributed to the non-labile nature of the ligands, indeed, it is the

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16-electron species that gives rise to the epimerization. The present report details the preliminary studies on the non-rigid behavior of the title complexes, which will be relevant to the future development and application of this class of complex to asymmetric catalysis.

2. Results and discussion

The neutral arene-tethered species, $Ru(\eta^6{:}\eta^1\text{-}NMe_2C_6H_4C_6H_4PCy_2)Cl_2$ (**1**), is readily converted to the dicationic analogues $[Ru(\eta^6{:}\eta^1\text{-}NMe_2C_6H_4C_6H_4PCy_2)(P\text{–}S)](SbF_6)_2$ (**2**–**3**), with the addition of $AgSbF_6$ and the heterobidentate ligands $Ph_2PCH_2CH_2P(S)Ph_2$ (**L1**) and $Ph_2PCH_2P(S)Ph_2$ (**L2**) as shown in Fig. 1. The resulting dicationic complexes are obtainable in quantitative yields, and are extremely robust and stable complexes that are quite soluble in many common polar solvents (e.g. MeOH, MeCN, CH_2Cl_2, or acetone). They can be subjected to chromatography on silica gel, and left in untreated solutions for extended periods (>3 months) without observable decomposition. As the complexes are chiral-at-metal, two diastereomers are possible, depending on the *syn*/*anti* disposition of the ligands relative to the NMe_2 group (see Figs. 1 and 2). Using racemic **1**, the addition of **L1** or **L2** produces four stereoisomers, with the net result being a racemic pair of diastereomers. The mirror image relationship is indicated with the dotted line. We have noted previously that the planar chiral arene-tethered ligand can exert a strong influence on the metal chirality, owing to the directing effect of the dimethylamino group. That is, unfavorable steric interactions cause more bulky ligands to favor the *anti* binding site with respect to the NMe_2 group. This effect can be either kinetic or thermodynamic in nature.

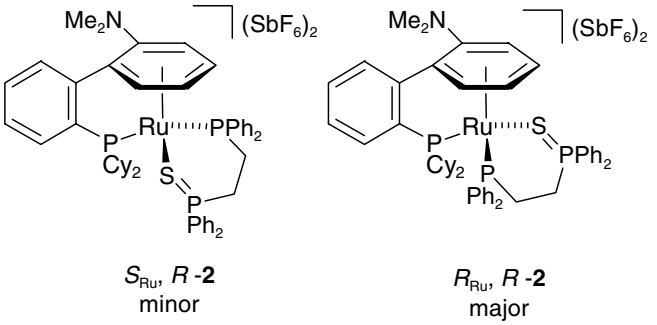


Fig. 2. The two diastereomers of **2** with (*R*) planar chirality.

The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** are an useful tool for determining their solution structure. For each of the compounds, there are three inequivalent phosphorus atoms (in each diastereomer) that are all coupled to one another; therefore, each of the phosphorus resonances is a doublet of doublets. Fig. 3 shows the $^{31}P\{^1H\}$ NMR spectra with the coupling constants ($J_{P\text{–}P}$) for the major isomer, which are also listed in Table 1 along with their respective assignments. Viewing the major isomer of **2**, the most upfield resonance, at 18.3 δ, corresponds to the directly coordinated phosphine (the P^{III}) in diphos(S). This phosphorus is coupled through the metal to the phosphorus nucleus of the arene-tethered ligand ($^2J_{P\text{–}P} =$

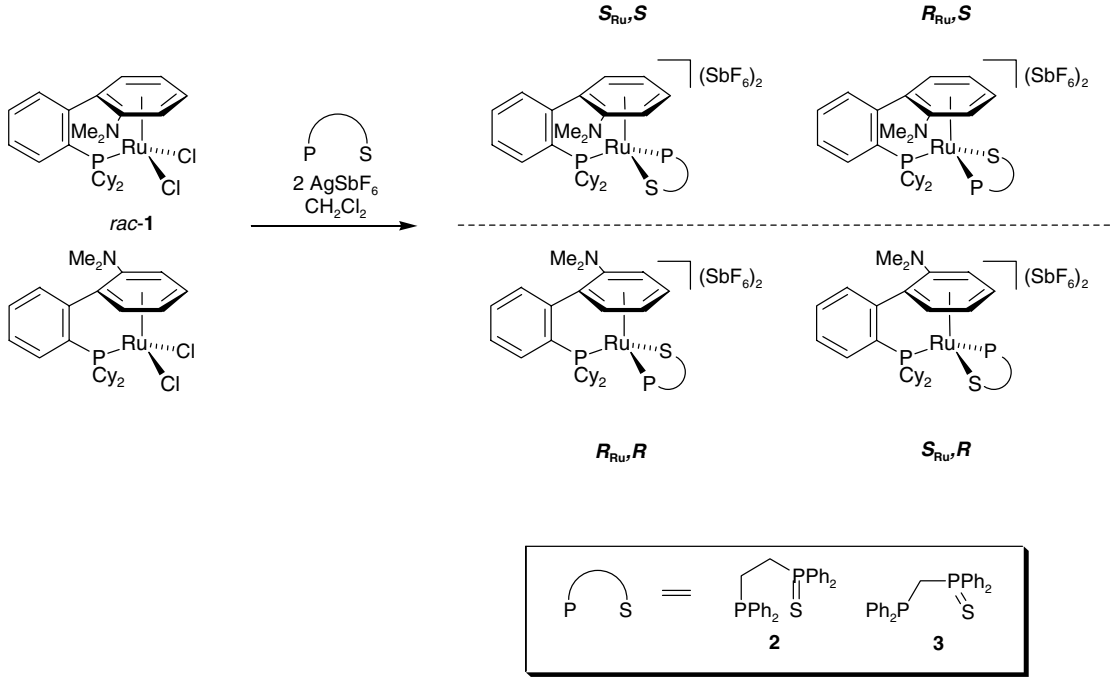


Fig. 1. Synthesis of dicationic P–S complexes. The chirality of metal center is assigned with the priority sequence being arene > S > PPh_2Alkyl > PCy_2Aryl. The planar chirality is assigned using the NMe_2-substituted carbon with the according to the Cahn–Ingold–Prelog rules, with the priority sequence being Ru > N > C-Aryl > C–H.

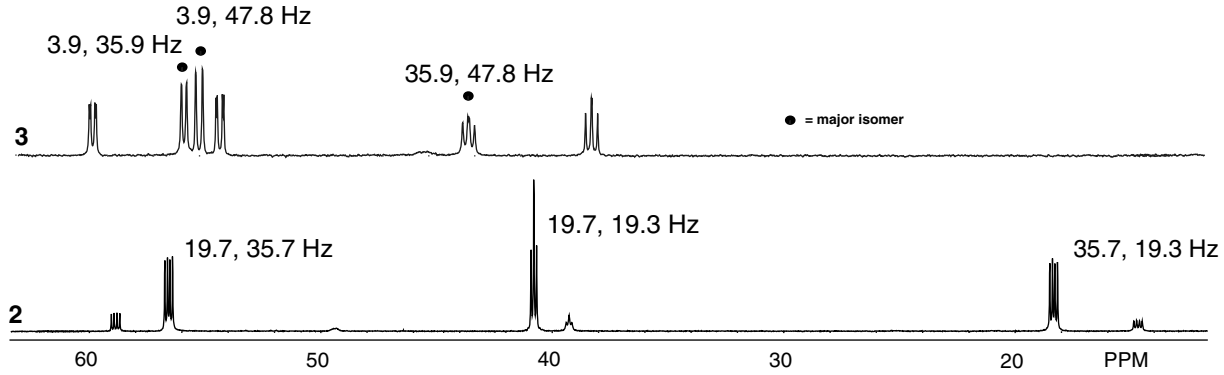
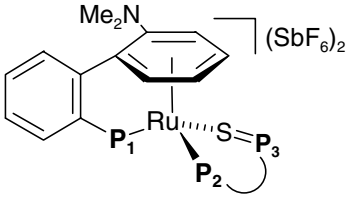


Fig. 3. The kinetic isomer mixtures for **2** and **3**. The $^{31}P\{^{1}H\}$ NMR of the kinetic products of **2** (bottom) and **3** (top) at 161.9 MHz in $(CD_3)_2CO$ at room temperature. The J_{P-P} are shown for only the major isomer in each case.

Table 1
J_{P-P} Constants for **2** and **3**



Complex	J_{P1-P2} (Hz)	J_{P1-P3} (Hz)	J_{P2-P3} (Hz)	J_{P2-P3} (Hz) free ligand [18]
2	35.7	19.7	19.3	49
3	35.9	3.9	47.8	79

35.7 Hz), as well as to the phosphine sulfide with $J_{P-P} = 19.7$ Hz. This latter coupling is decreased with respect to the free ligand (49 Hz) [18], which is the usual observation [18–22] and is indicative of a spin coupling contribution of opposite sign through the metal and thus indicates the coordination of the sulfur to the metal. Likewise, the phosphine of the arene-tethered ligand shows a coupling to the directly coordinated phosphine of diphos(S), but an additional smaller ^{3}J coupling of 19.7 Hz to the phosphorus atom (the P^{V}) bound to the sulfur is observed. The assignments were made on the basis that the most downfield resonance corresponds to the arene-tethered phosphine, and the large coupling of 35.7 Hz is the $^{2}J_{P-P}$ to

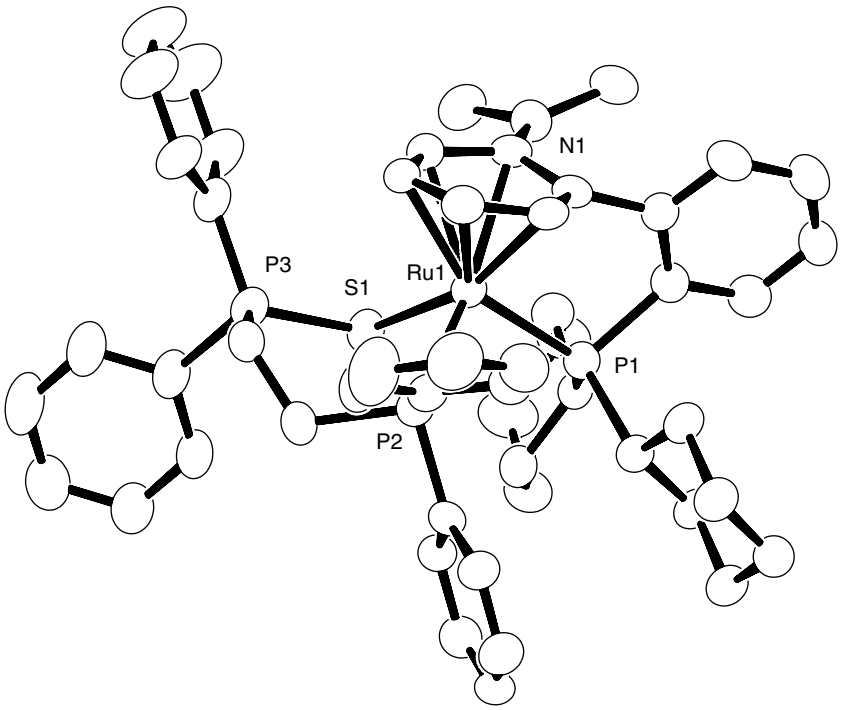


Fig. 4. ORTEP diagram of the cation of S_{Ru},*S*-2. Bond angles: S1–Ru1–P2, 86.42(5)°; P1–Ru1–P2, 99.74(6)°; S1–Ru1–P1, 90.81(5)°; Ru1–S1–P3, 105.35(7)°.

the P^{III} in the ligand. The $^{31}P\{^1H\}$ NMR of **3** shows similar coupling constants; a notable difference is that for this complex, the coupling of the arene-tethered phosphine to the phosphine sulfide is much smaller. Specifically, this coupling is only 3.9 Hz for the major isomer of **3** compared to 19.7 Hz in **2** (Fig. 2). This is perhaps due to the different bond angles, though we have been unable to quantify this as crystals of **3** that are suitable for X-ray analysis have not been forthcoming.

It is clear from the NMR spectra shown in Fig. 3 that **2** and **3** are produced with very different diastereoselectivities; while **2** forms as an 82:18 (64% de) mixture of isomers, the synthesis of **3** results in a 53:47 (6% de) ratio. Recrystallization of **2** yielded a racemic mixture of the major diastereomer. The stereochemistry of the major isomer of **2** was determined by X-ray analysis (Fig. 4), which shows the sulfide coordinated in the *syn* position relative to the NMe_2 group. This follows from previous observations, as the NMe_2 group has been shown to direct the larger ligand to the *anti* position, which in this case would be the P-donor.

Unfortunately, as crystals of **3** that were suitable for X-ray analysis were not available, we were unable to definitively assign the major isomer in **3**. The question arises, though, as to whether the isomeric mixtures are kinetically or thermodynamically controlled. The two diastereomers would most likely interconvert *via* a hemilabile intermediate (Fig. 5), created by the dissociation of the sulfide ligand. The observation of two isomers in the room temperature NMR spectra shows that, if such an exchange process were occurring, it must be slow on the NMR timescale. A fast exchange between the two isomers would result in an averaged spectrum where a single set of resonances would be present. Indeed, heating a solution of **2** in d_6-dmso to 95 °C in an NMR tube produced a spectrum that showed the same two isomers in a ratio of 52:48 (4% de, where the *syn* sulfide was still in excess). Even at the elevated temperature of 125 °C, no broadening is apparent in the NMR spectrum. Nevertheless, the interconversion is now fast enough to have reached an equilibrium ratio of isomers

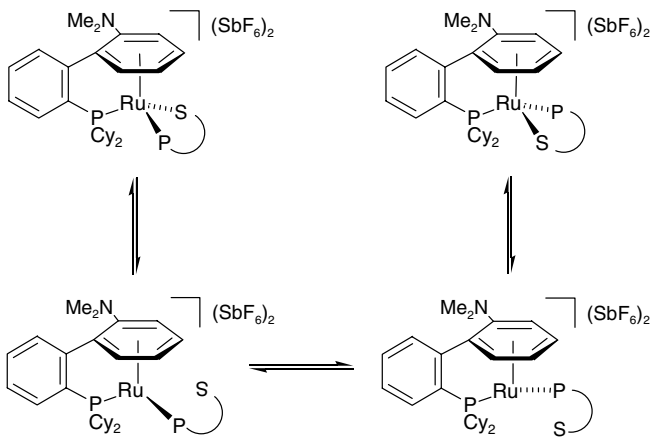


Fig. 5. Proposed interconversion *via* hemilabile species.

very quickly (less than 5 min) at 95 °C. Therefore, the ratio that is apparent upon the synthesis of **2** is the *kinetic* ratio of products. Allowing a d_6-dmso solution of the kinetic product of **2** at room temperature to stand over an extended period showed that the epimerization of the metal center occurred with a half-life of ~22 days, and this rate was approximately the same in acetone. In both solvents the final equilibrium ratio was 52:48 at room temperature. Therefore, although a strong kinetic preference exists which controls the metal-centered chirality in **2**, there is only a very small thermodynamic preference between the two diastereomers.

The kinetic preference is potentially useful in that the diastereomeric excess is maintained for extended periods in solution, as the epimerization of the metal-centered chirality is very slow. For **3**, a different effect was observed, as the 53:47 kinetic ratio of isomers was seen to equilibrate at 125 °C (in less than 5 min) to a ratio of 73:27 (46% de). In d_6-acetone at room temperature, the kinetic product equilibrated to 62:38 with a half-life of ~1.1 days. As with **2**, it was the same diastereomer that was preferred both kinetically and thermodynamically; however, while **2** exhibits a strong kinetic preference and almost no equilibrium preference, the trend is reversed for **3**. This is somewhat surprising, as the small difference of a single methylene linker between **L1** and **L2** have a comparatively large effect on the resulting complexes.

3. Conclusions

Bisphosphine monosulfides have been suggested as derivatives of bisphosphines that would effectively act as monodentate phosphines owing to the poor binding ability of the phosphine sulfide [23]. Although we have found a number of bidentate bisphosphine monosulfides analogues [7–10], one might anticipate that a dicationic intermediate could be a sufficiently hard acid that the Ru–S bond might be broken easily and that hemilability would be facile. This is clearly not the case. Thus the presence of the dicycloxylphenylphosphine and alkyldiphenylphospine donors provide sufficient electron density to provide a fairly soft Ru(II) that binds sulfur strongly. More specifically, the complexes **2** and **3** form as mixtures of two diastereomers, one in which the sulfide ligand binds *syn* with respect to the NMe_2 group, and the other with an *anti* bound sulfide. These two diastereomers, that probably equilibrate *via* a hemilabile 16 electron intermediate, interconvert very slowly. This process, the epimerization of the metal center, occurs with a half-life of 22 days in acetone at room temperature for **2**, and 1.1 days in acetone at room temperature for **3**. Since the hemilabile intermediate is the potential active Lewis acid catalyst, this process may be too slow in the case of **2** or **3** for these complexes to be very useful catalytically. The slow epimerization of these compounds reflects the strong bonding between the dicationic ruthenium center and the sulfide ligand. Nevertheless, the different diastereomeric

preferences and epimerization rates exhibited by the two complexes is surprisingly large considering that **L1** and **L2** only differ by a single methylene linker. We will continue to investigate similar complexes with various heterobidentate ligands having different bite angles, in order to better tune the lability and thermodynamic preferences, with the aim of utilizing these dicationic complexes in asymmetric catalysis.

4. Experimental

4.1. General methods

The manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. The THF and CH_2Cl_2 used for the syntheses of **L1**, **L2**, **2** and **3** were distilled over Na/benzophenone and CaH_2, respectively, under a nitrogen atmosphere. The complexes **2** and **3** were generally handled in untreated solvents subsequent to their preparation. 1,2-Bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)methane, sulfur, and silverhexafluoroantimonate were purchased from commericial sources and used directly. Complex **1** was prepared according to the previously reported procedure [15]. NMR spectra were recorded on a Bruker 400 MHz (operating at 162 MHz for ^{31}P and 100 MHz for ^{13}C). Chemical shifts are reported in ppm relative to TMS based upon the position of residual solvent peaks (^1H), or an H_3PO_4 external standard. Elemental analyses were performed by Atlantic Microlabs.

4.2. Synthesis of 1,2-bis(diphenylphosphino)ethane monosulfide (L1) and 1,2-bis(diphenylphosphino)methane monosulfide (L2)

A variation of a previously reported procedure was used [18]. A flame-dried flask was charged with the bisphosphine (2.5 mmol) and sulfur (1.75 mmol), and placed under a nitrogen atmosphere. THF (10 mL) was then added, and the solution was stirred for 18 h, at which point the solvent was removed under vacuum. The crude mixtures contained mixtures of the bisphosphines, the monosulfides, and the bissulfides. The respective monosulfides were isolated as white solids by column chromatography on silica gel eluting with 10% EtOAc in pentane. The yields (based on the bisphosphine) were 28% for **L1** and 36% for **L2**. Characterization data were in accord with that previously reported [18].

4.3. Synthesis of [Ru(η^6:η^1-$NMe_2C_6H_4C_6H_4PCy_2$)(**L1**)](SbF$_6$)$_2$ (**2**)

A flame-dried flask was charged with **1** (34 mg, 0.060 mmol), $AgSbF_6$ (42 mg, 0.12 mmol), and CH_2Cl_2 (5 mL) under a stream of nitrogen. **L1** (26 mg, 0.060 mmol) was then added, and the solution was stirred for 1 h, and then passed through a plug of silica gel. The product **2** was eluted with $(CH_3)_2CO$ as an 82:18 mixture of diastereomers; 75 mg (89%). Anal. Calc. for $C_{52}H_{60}F_{12}NP_3RuSSb_2$: C, 44.72; H, 4.33; N, 1.00. Found: C, 44.47; H, 4.48; N, 1.02%. Crystals were obtained by slow diffusion of Et_2O into a solution of the product in 2:1 CH_2Cl_2:MeOH.

4.3.1. Major isomer

^1H NMR (400 MHz, $(CD_3)_2CO$): 8.39–8.33 (2 H, m), 8.12–7.44 (22H, m), (CH_{arom}); 6.27 (1H, m, $CH_{\eta6\text{-arene}}$), 5.63 (1H, d, $J = 6.9$ Hz, $CH_{\eta6\text{-arene}}$), 5.53 (1H, dt, $J = 5.5$, 1.4 Hz, $CH_{\eta6\text{-arene}}$), 4.56 (td, $J = 5.5$, 2.6 Hz, $CH_{\eta6\text{-arene}}$), 4.01 (1H, m, $CH_{2ethylene}$), 3.64 (1H, m, $CH_{2ethylene}$), 3.21 (1H, m, $CH_{cyclohexyl}$), 3.19 (1H, m, $CH_{2ethylene}$), 2.95 (2H, m, $CH_{2ethylene}$ and $CH_{cyclohexyl}$), 2.734 (3H, s, $N(CH_3)_2$), 2.730 (3H, s, $N(CH_3)_2$), 2.20–0.60 (20H, m, $CH_{2cyclohexyl}$). $^{31}P\{^1H\}$ NMR (161.9 MHz, $(CD_3)_2CO$): 56.6 (dd, $J_{P-P} = 35.7$, 19.7 Hz), 40.8 (dd, $J_{P-P} = 19.7$, 19.3 Hz), 18.3 (dd, $J_{P-P} = 35.7$, 19.3 Hz).

4.3.2. Minor isomer

^1H NMR (400 MHz, $(CD_3)_2CO$): 8.45–8.40 (2H, m), 8.1–7.4 (22H, m, superimposed by major isomer), (CH_{arom}); 5.91 (1H, d, $J = 5.7$ Hz, $CH_{\eta6\text{-arene}}$), 5.84–5.73 (2H, m, $CH_{\eta6\text{-arene}}$), 4.65 (1H, br, $CH_{\eta6\text{-arene}}$), 4.00 (1H, m, $CH_{2ethylene}$, superimposed by major isomer), 3.65 (1H, m, $CH_{2ethylene}$, superimposed by major isomer); 3.20 (2H, m, $CH_{2ethylene}$ and $CH_{cyclohexyl}$, superimposed by major isomer), 3.00 (2H, m, $CH_{2ethylene}$ and $CH_{cyclohexyl}$, superimposed by major isomer), 2.22 (6H, $N(CH_3)_2$), 2.2–0.6 (20H, m, $CH_{2cyclohexyl}$, superimposed by major isomer). $^{31}P\{^1H\}$ NMR (161.9 MHz, $(CD_3)_2CO$): 58.9 (dd, $J_{P-P} = 39.5$, 19.8 Hz), 39.3 (br t, $J_{P-P} = 20$ Hz), 14.7 (dd, $J_{P-P} = 39.5$, 19.5 Hz).

4.4. Synthesis of [Ru(η^6:η^1-$NMe_2C_6H_4C_6H_4PCy_2$)(**L2**)](SbF$_6$)$_2$ (**3**)

This preparation was carried out analogously to **2** with **L2** in place of **L1**. The initial isomer ratio for **3** was 53:47. The yield was 91%. Crystals suitable for X-ray analysis were not obtained. Precipitation from CH_2Cl_2 and Et_2O occurred with the retention of CH_2Cl_2. Anal. Calc. for $C_{51}H_{58}F_{12}NP_3RuSSb_2 \cdot CH_2Cl_2$: C, 42.91; H, 4.15; N, 0.96. Found: C, 42.96; H, 4.16; N, 1.06%.

4.4.1. Major isomer

^1H NMR (400 MHz, $(CD_3)_2CO$): 8.22–8.12 (3H, m), 8.07–7.95 (3H, m), 7.90–7.25 (18H, m); (CH_{arom}); 6.31 (1H, d, $J = 7.0$ Hz, $CH_{\eta6\text{-arene}}$), 6.25 (1H, m, $CH_{\eta6\text{-arene}}$, superimposed by minor isomer), 5.80 (2H, m, $CH_{\eta6\text{-arene}}$), 5.21 (1H, ddd, $CH_{2methylene}$, superimposed by minor isomer), 4.82 (1H, dt, $^2J_{H-H} = 14.7$ Hz, $^2J_{P-H} = 10.4$ Hz, $CH_{2methylene}$), 3.194 (3H, s, $N(CH_3)_2$), 3.191 (3H, s, $N(CH_3)_2$), 2.99 (1H, m, $CH_{cyclohexyl}$), 2.70 (1H, m, $CH_{cyclohexyl}$), 2.15–0.40 (20H, m, $CH_{2cyclohexyl}$). $^{31}P\{^1H\}$ NMR (161.9 MHz, $(CD_3)_2CO$): 57.7 (dd, $J_{P-P} = 35.9$,

3.9 Hz), 56.1 (dd, $J_{P-P} = 47.8$, 3.9 Hz), 44.3 (dd, $J_{P-P} = 47.8$, 35.9 Hz).

4.4.2. Minor isomer

^{1}H NMR (400 MHz, $(CD_3)_2CO$): 8.22–8.12 (3H, m), 8.07–7.95 (3H, m), 7.90–7.25 (18H, m), (CH_{arom}); 6.45 (1H, dd, $J = 5.9$, 5.7 Hz, $CH_{\eta 6\text{-arene}}$), 6.26 (1H, d, $CH_{\eta 6\text{-arene}}$, superimposed by major isomer), 6.11 (1H, dd, $J = 5.9$, 6.1 Hz, $CH_{\eta 6\text{-arene}}$); 5.30 (1H, ddd, $^2J_{H-H} = 14.8$ Hz, $^2J_{P-H} = 11.8$ Hz, $^2J_{P-H} = 5.9$ Hz, $CH_{2methylene}$); 5.20 (1H, m, $CH_{\eta 6\text{-arene}}$, superimposed by major isomer), 5.11 (1H, dt, $^2J_{H-H} = 14.8$ Hz, $^2J_{P-H} = 8.3$ Hz, $CH_{2methylene}$), 2.70 (1H, m, $CH_{cyclohexyl}$, superimposed by major isomer), 2.59 (6H, s, $N(CH_3)_2$); 2.15–0.40 (21H, m, $CH_{2cyclohexyl}$). ^{31}P{^{1}H} NMR (161.9 MHz, $(CD_3)_2CO$): 60.6 (dd, $J_{P-P} = 39.4$, 9.7 Hz), 55.1 (dd, $J_{P-P} = 45.5$, 9.7 Hz), 38.9 (dd, $J_{P-P} = 45.5$, 39.4 Hz).

4.5. Structure determination and refinement

Crystals were obtained by slow diffusion of pentane into methylene chloride solution of **2**. Data were collected on a Nonius KappaCCD (Mo Kα radiation) diffractometer and were not specifically corrected for absorption other than the inherent corrections provided by Scalepack [24]. The structure was solved by direct methods (SIR92) [25] and refined on F for all reflections [26]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 2. A single diastereomer was obtained as a racemate upon recrystallization from methylene chloride/methanol/diethyl ether. The lattice contained methylene chloride solvate. The bond lengths are normal, but the dimethylamino group is planar rather than pyramidal owing to donation of the lone pair into the ring to balance the positive charge on the metal. The dimethyl amino group does, however, show a twist (32°) relative to the ring. Relevant distances and angles are Ru(1)–S(1), 2.421(1) Å; Ru(1)–P(1), 2.399(2) Å; Ru(1)–P(2), 2.391(2) Å; Ru(1)–S(1)–P(3), 105.36(7)°; P(1)–Ru(1)–P(2), 99.77(6)°; S(1)–Ru(1)–P(1), 90.80(5)°; S(1)–Ru(1)–P(2), 86.44(5)°.

Table 2
Crystallographic data for **2**

Compound	**2**
Color, shape	Red, block
Empirical formula	$C_{53}H_{62}Cl_2F_{12}NP_3RuSSb_2$
Formula weight	1481.52
Radiation (Å)	Mo Kα (monochr.) 0.71073
T (K)	173
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	
a (Å)	13.3078(7)
b (Å)	15.1479(8)
c (Å)	16.4674(9)
α (°)	77.768(4)
β (°)	72.761(3)
γ (°)	67.072(3)
V (Å^3)	2902.4(3)
Z	2
D_{calc} (g cm^{-3})	1.695
μ (cm^{-1}) (Mo Kα)	14.65
Crystal size (mm)	$0.08 \times 0.10 \times 0.10$
Reflections total, unique, used[a]	21689, 13446; 6614
R_{int}	0.046
Parameters, restraints	676, 0
R[a], wR[b], GOF	0.041, 0.041, 127
Residual density (e Å^{-3})	$-0.68 < 0.89$

[a] $R = \sum \| |F_o| - |F_c| \| / \sum |F_o|$, for all $I > 3\sigma(I)$.
[b] $wR = [\sum [w(|F_o| - |F_c|)^2] / \sum [w(F_o)^2]]^{1/2}$.

Acknowledgement

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Appendix A. Supplementary data

CCDC 619379 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge 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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