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Novel Intramolecular C_{Aryl}–S Bond Activation by an Electron Rich, Ring-Expanded-NHC-Rh centre: A Combined Experimental and DFT Study

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The reaction of (*o*-MeSPh)-*N*-functionalized tetrahydropyrimidinium salts with $KN(SiMe_3)_2$ and $[Rh(COD)Cl]_2$ in THF leads to the formation of a novel dimeric Rh^{III} bis-carbene complex. The reaction involves the unexpected cleavage/oxidative addition of the aryl-sulfur bond to give dimeric metallated Rh^{III} with bridging MeS< moieties. This unusual reaction is probably a consequence of the sterically imposing structure and strong donor capacity of ring-expanded *N*-heterocyclic carbenes (RE-NHCs). An X-ray structure of the $[(Ph,DIPP\text{-}NHC)Rh(Cl)(SMe)_2]$ product complex has been obtained, and DFT studies were undertaken to gain an insight into the reaction pathway.

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Introduction

Ring expanded-NHCs (RE-NHCs) offer markedly changed steric and electronic properties when compared with the more traditional 5-membered ring NHCs.[1–11] Several investigations into their structural properties, rich chemistry, and catalytic applications are now appearing.[1c,d,2,3,6–20] Key features of these large ring systems are their electronic properties, but more particularly their substantial steric demands. There is a marked increase in steric 'pressure' on the metal centre as the ring size increases from 5 through 6 to 7 for a set of related ligands and complexes,[5,6,7] leading to the interesting coordination chemistry and reactivity now noted for these systems. The large ring NHCs are highly effective in stabilizing novel complexes and they also promote unusual chemistry and catalytic performance;[11–19] for example, recent studies by Whittlesey and coworkers demonstrated that large ring NHCs can generate either metallated Ni^{II}, or novel Ni^{I} complexes depending on reaction conditions.[11]

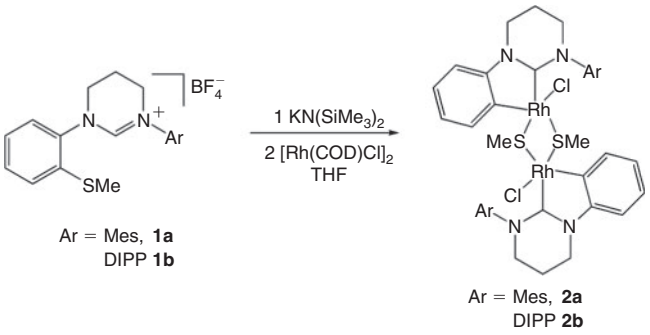
There is a substantial body of literature on C–S bond activation, largely related to dehydrodesulfurization of hydrocarbon feedstocks. An excellent review on the early literature was published in 1994.[21] More recent contributions report on a range of C–S activation processes (which include thiophenes, aliphatic thioethers etc. as the substrate).[22–30] To our knowledge there is only one report of aryl-S activation, which appears to be driven by chelation of the resulting product.[27] We report here a novel intramolecular aryl-S activation in which a SMe moiety is dissociated from the benzene ring of a methylthiophenyl-substituted RE-NHC, to form a SMe-bridged metallated-Rh dimer (Scheme 1). This also represents the first example of the use of a NHC as the 'spectator' ligand in a C–S activation process.

Results and Discussion

Preparation of Functionalized Tetrahydropyrimidinium Salts, and Reaction with a Rh^{I} Precursor

The salts **1a** and **b** were prepared in high yield via a stepwise process, as previously described for other unsymmetrically-substituted large ring heterocyclic salts.[13]

Reaction of the thioether-functionalized six-membered ring NHCs, **1a** or **1b**, with $[Rh(COD)Cl]_2$ led to aryl-S bond cleavage to give a Rh^{III} methylthio-bridged dimer, **2** (Scheme 1). It would appear that the reaction involves cleavage of the aryl-thioether by the electron rich Rh^{I}NHC centre, followed by coordination



Ar = Mes, **1a**
DIPP **1b**

Ar = Mes, **2a**
DIPP **2b**

Scheme 1. Synthesis of the Rh^{III} dimer.

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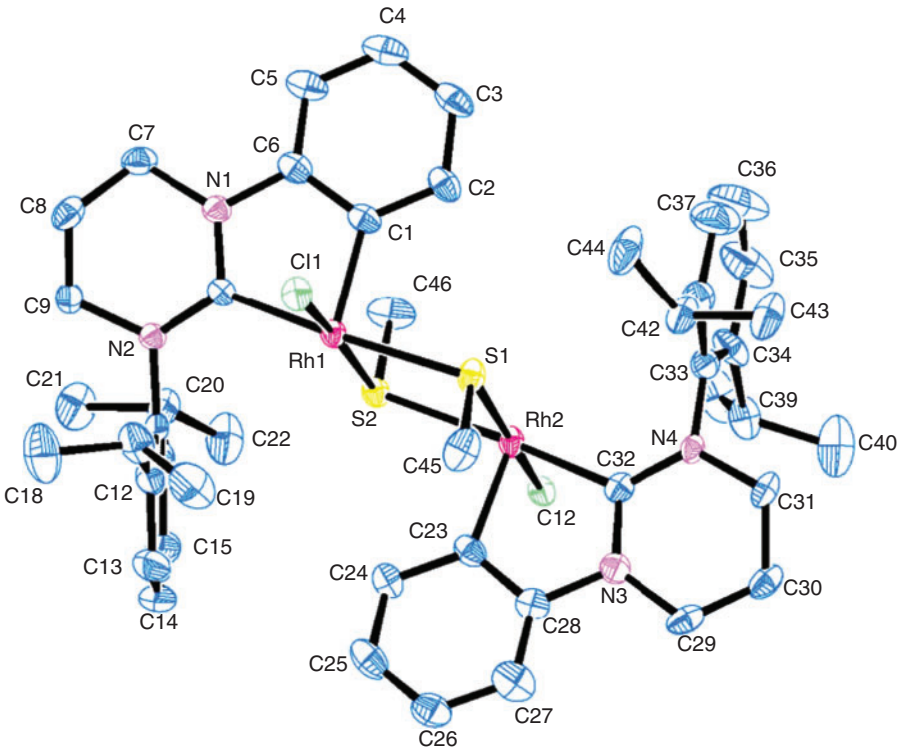


Fig. 1. Solid state molecular structure of complex **2b**. Hydrogen atoms have been omitted for clarity.

(metallation) of the resulting benzene ring and formation of the SMe-bridged Rh^{III} dimer.

The small C_{NHC}–N–Ar angle (a consequence of the very large N–C_{NHC}–N angle), which allows effective overlap with the C_{Ar}-sp^2 orbital, in combination with coordination of the strong σ-donor six-membered ring NHC (6-NHC), which generates an electron rich Rh^{I} centre, facilitates the rapid intramolecular attack on the MeS-phenyl moiety to form the *ortho*-metallated thio-bridged Rh^{III} dimer. Characterisation of these complexes was carried out by ^{1}H NMR, ^{13}C NMR and mass spectroscopy and in one case by X-ray analysis. The ^{13}C NMR signals for the carbene carbon appeared as a doublet at 202.3 ppm for complex **2a** and at 202.7 ppm for complex **2b**, indicating the formation of a Rh–C_{NHC} bond. The signals are within the range of Rh–C_{NHC} resonances observed for related NHC-Rh complexes. The ^{1}H NMR signals of *m*-CH_{Ar} are shifted downfield, and the hydrogen atoms in the SCH_3 group appeared as sharp singlets at 1.69 and 1.52 ppm for complex **2a** and **2b**, respectively.

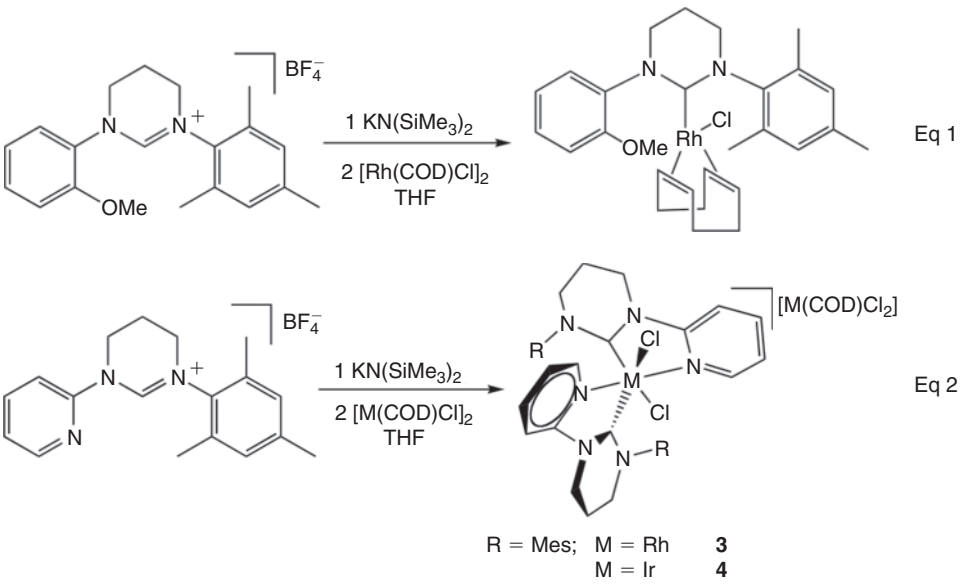
Crystals suitable for X-ray crystallography of complex **2b** were obtained by the diffusion of hexane into a saturated THF solution of the complex. The crystal structure of complex **2b** is shown in Fig. 1 and selected bond distances and angles are presented in Table 1. The structural arrangement of the complex shows that the molecular geometry around the rhodium cation is distorted square pyramidal with two coordination sites occupied by a bidentate aryl-carbene, a third coordination site is occupied by chloride (the two chloride atoms are in *trans* arrangement overall), and the remaining two sites are occupied by bridging SCH_3 groups.

The Rh–C_{NHC} bond lengths (1.996(7), 2.011(7) Å) are typical for Rh–C_{NHC} (σ-bond) complexes and imply a symmetric ligand coordination mode. The two Rh–C_{NHC} bond lengths are the same, within experimental error, and also very similar to the $C_{Ph}(sp^2)$–Rh bond lengths. The C_{NHC}–Rh–C_{Ph} bite-angles (C10–Rh1–C1) and (C32–Rh2–C23) are 80.4(3)° and 81.0(3)°. The tilt angles, θ, defined by the coordinated (Rh–Cl) atoms and the N–C_{NHC}–N plane are 79.38° and 86.85°.

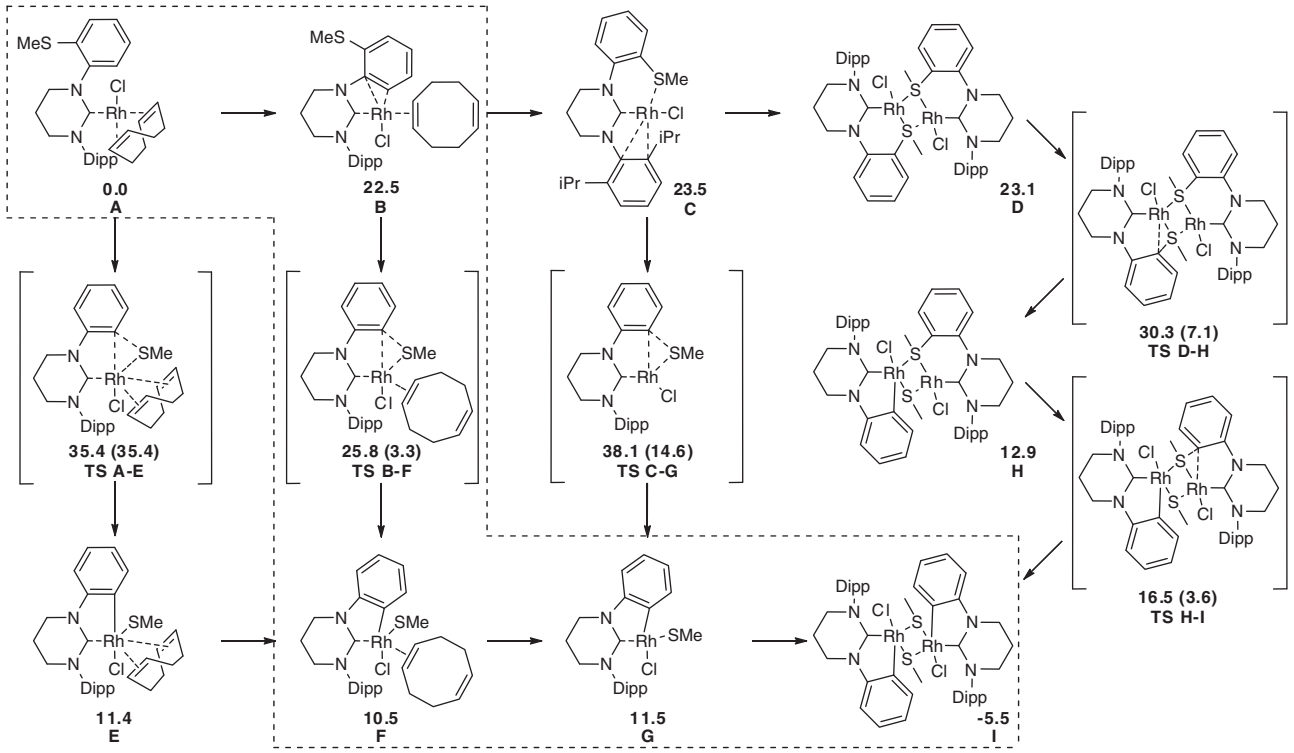
Table 1. Selected bond lengths (Å) and angles (°) for complex 2b

Lengths [Å]	Angles [°]
C10–Rh1 1.996(7)	N1–C10–N2 118.0(6)
C1–Rh1 1.971(7)	C10–N1–C6 114.4(6)
S1–Rh1 2.406(2)	C10–Rh1–C1 80.4(3)
S2–Rh1 2.4302(2)	C10–Rh1–Cl1 88.2(2)
Cl1–Rh1 2.362(2)	C1–Rh1–S1 96.2(2)
C10–N1 1.334(8)	Cl1–Rh1–S2 171.0(7)
C10–N2 1.345(8)	S1–Rh1–S2 82.6(6)
C32–Rh2 2.011(7)	N3–C32–N4 116.8(6)
C23–Rh2 1.970(7)	C32–N3–C23 114.7(7)
S1–Rh2 2.308(2)	C32–Rh2–C23 81.0(3)
S2–Rh2 2.417(2)	C32–Rh2–Cl2 92.6(2)
Cl2–Rh2 2.370(2)	C23–Rh2–S2 95.3(2)
C32–N3 1.358(9)	Cl2–Rh2–S1 171.1(7)
C32–N4 1.339(9)	S1–Rh2–S2 82.2(4)

The specific reaction noted in Scheme 1 appears unique for the *o*-SMe-aryl-substituted tetrahydropyrimid-2-ylidene ligands. No such reaction occurs with the *o*-OMe-substituted ligand, which reacts according to Eqn 1, Scheme 2.[13] However, the reaction of the pyridyl-functionalized salt (6-Py-Mes), with $KN(SiMe_2)_3$ and $[M(COD)Cl]_2$, (M = Rh or Ir), leads to the formation of bis(carbene) complexes $[M(6\text{-Py-Mes})_2Cl_2][M(COD)Cl_2]$, (M = Rh, **3** and Ir, **4**; Eqn 2, Scheme 2)[13] in which half the M^{I} in the complex $[M(COD)Cl]_2$ is oxidized to M^{III} to give the cation, $[M(6\text{-Py-Mes})_2Cl_2]^{+}$, and electrons are transferred to chloride ions, which then form the anionic M^{I} species $[M(COD)Cl_2]^{-}$.



Scheme 2. Reaction of *N*-functionalized tetrahydropyrimidinium salts with $KN(SiMe_3)_2$ and $[M(COD)Cl]_2$.



Scheme 3. Calculated possible reaction pathways leading to **2b** (I). Numbers are Gibbs free energies G_{vr} in kcal mol^{-1}. Numbers in brackets are relative free energies of transition states. The structures within the dashed lines represent the lowest energy reaction path.

The detailed mechanism for the process depicted in Scheme 1 is unclear. However, in broad terms, it is thought that in situ-generated NHC coordinates to the Rh^{I} to generate an extremely electron rich metal centre, which then undergoes rapid intramolecular oxidative addition of the MeS-phenyl moiety to form the *o*-metallated thio-bridged Rh^{III} dimer. It would appear that these RE-NHCs are extremely powerful electron donors with structural features that promote oxidation of the metal centre and metallation of the *N*-substituent. Oxidation of the metal centre was also noted for the pyridine-functionalized NHC in Scheme 2. To help better understand the process occurring, we have undertaken a computational study of the reaction depicted in Scheme 1.

Computational Studies: Rhodium Insertion into C–S Bond

DFT calculations were performed in order to gain better insight into the mechanism of the reaction. The various possible pathways that have been considered for the formation of **2b** are depicted in Scheme 3.

It was proposed that in situ-generated carbene reacts with $[Rh(COD)Cl]_2$ to give Rh^I complex **A**. This compound was chosen as the energy reference. We considered several possible Rh^I species. Complex **B** bears a COD ligand coordinated to rhodium with only one double bond. The rhodium atom coordination sphere is saturated by η^2-coordination of the 2-(MeS)-Ph- group. Its formation from **A** is endothermic by 22.5 kcal mol^{-1}.

The release of COD from **B** to give **C** is endothermic by 1.0 kcal mol^{-1}. In **C** the rhodium atom is σ-coordinated to SMe, Cl and the carbene carbon, and η^2-coordinated to the bulky Dipp group. The formation of a dimer **D** from a monomeric **C** leads to only 0.4 kcal mol^{-1} energy gain. In **D** two Rh^I atoms are bridged by SMe groups. All complexes **B**-**D** lie significantly higher in energy than the initial complex **A**.

For all complexes **A**-**D** insertion of the rhodium into the C–S bond was considered. For complexes **A**-**C** there is only one transition state leading to the Rh^{III} species, while for dimer **D** a two-step process with intermediate formation of mixed valence Rh^I/ Rh^{III} complex **H** was considered.

Transition state **TS A-E** corresponds to C–S bond activation in **A** to give the Rh^{III} complex **E**. The resulting complex lies 11.4 kcal mol^{-1} higher in energy than the starting complex **A**. In contrast to the transition from **A** to **B** (+22.5 kcal mol^{-1}) the loss of one coordination bond to the COD ligand in **E** yielding **F** is energetically favourable (−0.9 kcal mol^{-1}). The release of COD to give complex **G** is endothermic by only 1.0 kcal mol^{-1}. Dimerization of the complex **G** gives the final bimetallic complex **I**, which was observed experimentally.

Transition from **G** to **I** is characterized by a significant decrease in free energy (G_{vr}) of −17.0 kcal mol^{-1}. It is of interest to compare this with the formation of a Rh^I dimer **D**, for which ΔG_{vr} is only −0.4 kcal mol^{-1}. As a result, formation of the Rh^{III} dimer is a driving force for the total reaction. All intermediates **B**-**H** lie higher in energy than the starting complex **A**, and only complex **D** is lower in energy than **A**.

Insertion of rhodium into the C–S bond in **A**, without prior dissociation of COD, is associated with a high energy barrier of 35.4 kcal mol^{-1} (**TS A-E**). We suppose that this can be explained by high steric crowding of the rhodium coordination sphere by the COD and NHC ligands. For other Rh^I species, the energy barriers are significantly lower, from 14.6 kcal mol^{-1} for **TS C-G** down to only 3.3 kcal mol^{-1} for **TS B-F**.

Transition state **TS B-F** corresponds to the total energy barrier (25.8 kcal mol^{-1}) of the lowest energy reaction pathway: **A** → **B** → **TS B-F** → **F** → **G** → **I**. Notably, by far the major share of this energy is due to the loss of one coordination arm of the chelating COD ligand. Thus, if a less strongly bound ligand was chosen, the total energy barrier would be expected to be significantly reduced.

As a result, DFT modelling clearly shows that if the coordination sphere of the Rh^I complex is suitably preorganized, insertion of Rh^I into the C_{Ar}–S bond can readily proceed with a very low energy barrier. We expect that this observation can be utilized for the design of catalytic transformations of organosulfur compounds.

Computational Procedure

Computed structures are designated by letters, (e.g. **A**, **TS-AB**…) to differentiate them from the real complexes. Geometry optimization was carried out using the PBE generalized gradient functional.[31–33] Triple-ξ valence basis sets including TZ2P polarization functions [5,1,1,1,1/5,1,1,1,1/5,1,1,1] for Rh, [3,1,1/3,1,1/1,1] for Cl, S, N, C and [3,1,1/1] for H were used. The innermost electrons of Rh, Cl, S, N and C atoms were treated using ECP-SBKJC effective core potentials.[34–36] Vibrational frequencies were calculated for all stationary points either as minima ($i = 0$) or first order transition states ($i = 1$). Vibrational and rotational movements were considered in the estimation of the free energies $G_{vr} = G_{vib} + G_{rot}$. Translational movements were not taken into consideration since the reaction studied was carried out in solution, in which the translations are mostly suppressed. The IRC procedure was used for reliable identification of the transition states.[37] All calculations were performed using the PRIRODA program.[38,39]

Conclusions

It is now apparent from evidence presented here that these very basic (strong donor) and sterically highly demanding large-ring NHCs can lead to unique chemistry and the formation of unusual/unexpected structures. Here we have reported an unexpected C–S bond activation via oxidative addition of a C_{Aryl}–SMe bond to a Rh^I centre to give a novel a SMe-bridged Rh^{III} complex. The new complexes have been fully characterized, including an X-ray crystallographic structure. Importantly, DFT calculations indicate that the reaction follows a pathway in which the main energy barrier is the dissociation of the COD ligand. Based on these results and on previous studies by us and by others, it can be expected that this novel class of RE-NHC ligands will provide further unusual chemistry and new opportunities and applications.

Experimental Section

General Remarks: All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. $[Rh(COD)Cl]_2$, was synthesized according to literature methods. Solvents were dried using a Braun SPS system (hexane, CH_2Cl_2) or a Vacuum Atmospheres recirculating SPS system (THF). Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N_2 immediately before use, following standard literature methods. Air-sensitive compounds were stored and weighed in a glovebox. All other reagents were obtained commercially and used as received. ^{1}H and ^{13}C NMR spectra were obtained on Bruker Advance AMX 400, 500 or Jeol Eclipse 300 spectrometers, and referenced to tetramethylsilane ($\delta = 0$ ppm). Coupling constants J are expressed in Hz. HRMS were obtained on a Waters LCT Premier XE instrument and are reported as *m/z* (%).

Crystallographic Data

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC deposition number: 830919)

Data collection was carried out at 150K on a Bruker-Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems cooling apparatus and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined with SHELX-97.[40] All non-hydrogen atoms (except solvent and disordered Cl atoms) were refined anisotropically and the hydrogen atoms were inserted in idealized positions with U_{iso} set at 1.2 or 1.5 times the U_{eq} of the parent atom.

$C_{50}H_{68}Cl_2N_4Rh_2S_2$, $2(C_4H_8O)$, FW = 1154.03, t = 150(2) K, Monoclinic, C2/c, a = 43.1080(3) Å, b = 14.0820(4) Å, c = 18.2190(6) Å, β = 97.6640(10), V = 10961.0(5) Å^3, Z = 8, σ(cal) = 1.399 Mg/m^3, Crystal size = 0.10 × 0.10 × 0.06 mm^3, Total reflections = 28680, Independent reflections = 9317, R(int) = 0.0679, R_1 = 0.0735, wR_2 = 0.1485.

Preparation of Ethyl(2-methylthiophenyl)formamidate

2-(Methylmercapto)aniline (27.8 g, 0.20 mol), triethylorthoformate (50 mL; excess) and two drops of 2 M HCl were charged into a 200 mL flask. The flask was heated slowly using a heating mantle. At approximately 110°C, ethanol began to distil. When 95 % (22 mL) of the theoretical amount of ethanol had been collected, the flask was allowed to cool slowly. The excess of triethylorthoformate was removed by vacuum distillation at (60–80°C, 10 hPa). Upon further heating the final product, a pale yellow liquid distilled at (120–150°C). Yield 21 g (64 %). δ_H ($CDCl_3$, 400 MHz, 298K) 7.53 (s, 1H, NCH), 7.00 (d, 1H, *o*-CH), 6.95 (t, 1H, *m*-CH), 6.92 (t, 1H, *p*-CH), 6.64 (d, 2H, *m*-CH), 4.27 (m, 2H, OCH_2CH_3), 2.28 (s, 3H, SCH_3) 1.31 (t, 3H, OCH_2CH_3). δ_C ($CDCl_3$, 100 MHz, 298K) 155.4 (s, NCHN), 145.5 (s, Ar-C), 133.3 (s, Ar-C), 125.4 (s, Ar-CH), 125.2 (s, Ar-CH), 124.7 (s, Ar-CH), 119.6 (s, Ar-CH), 63.1 (s, OCH_2CH_3), 14.9 (s, SCH_3), 14.7 (s, OCH_2CH_3).

Preparation of N-*(2-methylthiophenyl)*-N′-*(2, 4, 6-trimethylphenyl) formamidine*

A 50-mL acid-free flask was charged with ethyl (2-methylthiophenyl)formamidate (5.85 g, 30.0 mmol) and 2,4,6-trimethylaniline (4.05 g, 30.0 mmol). The mixture solidified after stirring for 3 h at 50°C. The residue was recrystallized from toluene affording white crystals. Yield 7.3 g (86 %). δ_H ($CDCl_3$, 400 MHz, 298k) 7.68 (d, 1H, *o*-$CH_{o\text{-Mesph}}$), 7.58 (s, 1H, NCHN), 7.25 (t, 1H, *m*-$CH_{o\text{-Mesph}}$), 7.07 (t, 1H, *p*-$CH_{o\text{-Mesph}}$), 6.92 (d, 1H, *m*-$CH_{o\text{-Mesph}}$), 6.83 (s, 2H, *m*-CH_{Mes}), 2.33 (s, 3H, $SCH_{3\ o\text{-Mesph}}$), 2.18 (s, 3H, *p*-$CH_{3\ Mes}$), 2.04 (s, 6H, *o*-$CH_{3\ Mes}$). δ_C ($CDCl_3$, 100 MHz, 298k): δ 149.6 (s, NCHN), 133.8 (s, Ar-$C_{o\text{-Mesph}}$), 131.0 (s, Ar-C_{Mes}), 128.9 (s, Ar-C_{Mes}), 128.2 (s, Ar-C_{Mes}), 127.7 (s, Ar-$C_{o\text{-Mesph}}$), 125.3 (s, Ar-$CH_{o\text{-Mesph}}$), 123.1 (s, Ar-CH_{Mes}), 119.3 (s, Ar-$CH_{o\text{-Mesph}}$), 116.6(s, Ar-$CH_{o\text{-Mesph}}$), 114.6 (s, Ar-$CH_{o\text{-Mesph}}$), 18.6 (s, *p*-CH_3), 17.3 (s, *o*-CH_3), 14.2 (s, SCH_3).

Preparation of N-*(2-methylthiophenyl)* -N′-*(2,6-diisopropylphenyl) formamidine*

A 50-mL acid-free flask was charged with ethyl(2-methylthiophenyl) formamidate (5.85 g, 30.0 mmol) and 2,6-diisopropylaniline (5.32 g, 30.0 mmol). The mixture solidified after stirring for 3 h at 50°C. The residue was recrystallized from toluene affording white crystals. Yield 6.2 g (63 %). δ_H ($CDCl_3$, 400 MHz, 298 K) 7.93 (d, 1H, *o*-$CH_{o\text{-Mesph}}$), 7.71 (s, 1H, NCHN), 7.16 (t, 1H, *m*-$CH_{o\text{-Mesph}}$), 7.12 (t, 1H, *p*-CH_{Dipp}), 7.05 (d, 2H, *m*-CH_{Dipp}), 6.92 (t, 1H, *p*-$CH_{o\text{-Mesph}}$), 6.83 (d, 1H, *m*-$CH_{o\text{-Mesph}}$), 3.13 (sept., 2H, $CH(CH_3)_{2\ Dipp}$), 2.34 (s, 3H, $SCH_{3\ o\text{-Mesph}}$), 1.12 (d, 12H, $CH(CH_3)_{2\ Dipp}$). δ_C ($CDCl_3$, 100 MHz, 298k) 155.5 (s, NCHN), 142.6 (s, Ar-$C_{o\text{-Mesph}}$), 133.8 (s, Ar-C_{Dipp}), 132.8 (s, Ar-C_{Dipp}), 129.4 (s, Ar-$C_{o\text{-Mesph}}$), 125.5 (s, Ar-$CH_{o\text{-Mesph}}$), 124.7 (s, Ar-CH_{Dipp}), 123.9 (s, Ar-CH_{Dipp}), 119.6 (s, Ar-$CH_{o\text{-Mesph}}$), 118.9 (s, Ar-$CH_{o\text{-Mesph}}$), 114.2 (s, Ar-$CH_{o\text{-Mesph}}$, 28.4 (s, $CH(CH_3)_{2\ Dipp}$) 24.1 (s, $CH(CH_3)_2$), 18.5 (s, $CH(CH_3)_2$), 14.9 (s, SCH_3)).

*Preparation of 1-(2-methylthiophenyl)-3-(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydro-3*H-*[1,3]pyrimidinium bromide*

N-(2-methylthiophenyl)-*N′*-(2,4,6-trimethylphenyl)formamidine (2.84 g), K_2CO_3 (0.7 g, 5.0 mmol) and 2.03 mL of 1,3-dibromopropane (20.0 mmol) in 250 mL acetonitrile was heated under reflux for two weeks to yield 3.10 g (76 %) of white, crystalline material. δ_H ($CDCl_3$, 400 MHz, 298K) 8.06 (d, $^3J_{HH}$ 6.7, 1H, *o*-$CH_{o\text{-Mesph}}$), 7.55 (s, 1H, NCHN), 7.41 (t, $^3J_{HH}$ 6.2, 1H, *m*-$CH_{o\text{-Mesph}}$), 7.21 (t, $^3J_{HH}$ 6.2, 1H, *p*-$CH_{o\text{-Mesph}}$), 7.18 (d, $^3J_{HH}$ 6.7, 1H, *m*-$CH_{o\text{-Mesph}}$), 6.88 (s, 2H, *m*-CH_{Mes}), 4.29 (t, $^3J_{HH}$ 5.2, 2H, NCH_2), 4.05 (t, $^3J_{HH}$ 5.2, 2H, NCH_2), 2.61 (m, 2H, NCH_2CH_2), 2.49 (s, 3H, $SCH_{3\ o\text{-Mesph}}$), 2.37 (s, 6H, *o*-$CH_{3\ Mes}$), 2.23 (s, 3H, *p*-$CH_{3\ Mes}$). δ_C ($CDCl_3$, 100 MHz, 298K) 154.3 (s, NCHN), 140.3 (s, Ar-$C_{o\text{-Mesph}}$), 137.7 (s, Ar-C_{Mes}), 136.7 (s, Ar-C_{Mes}), 135.6 (s, Ar-C_{Mes}), 134.7 (s, Ar-$C_{o\text{-Mesph}}$), 131.1 (s, Ar-$CH_{o\text{-Mesph}}$), 129.9 (s, Ar-CH_{Mes}), 128.9 (s, Ar-$CH_{o\text{-Mesph}}$), 126.5 (s, Ar-$CH_{o\text{- Mesph}}$), 125.8 (s, Ar-$CH_{o\text{-Meoph}}$), 47.4 (s, NCH_2), 46.8 (s, NCH_2), 20.9 (s, NCH_2CH_2), 19.7 (s, *p*-$CH_{3\ Mes}$), 18.4 (s, *o*-$CH_{3\ Mes}$) 14.9 (s, $SCH_{3\ o\text{-Mesph}}$). *m/z* (ES) 325.1748, Calc. for $C_{23}H_{31}N_2O$: 325.1738. Anal. Calc. for $C_{20}H_{25}N_2OBr$: C 58.27, H 6.07, N 6.80. Found: C 58.09, H 6.07, N 6.99 %.

*Preparation of 1-(2-methylthiophenyl)-3-(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydro-3*H-*[1,3]pyrimidinium tetrafluoroborate 1a*

A solution of pyrimidinum bromide salt (2.42 g, 6.0 mmol) in 30 mL acetonitrile was mixed with a solution of sodium tetrafluoroborate (0.99 g, 9.0 mmol) in 30 mL distilled water. White crystals formed (2.15 g, 87 %). δ_H ($CDCl_3$, 400 MHz, 298K) 7.68 (d, $^3J_{HH}$ 6.5, 1H, *o*-$CH_{o\text{-Mesph}}$), 7.44 (s, 1H, NCHN), 7.38 (t, $^3J_{HH}$ 6.4, 1H, *m*-$CH_{o\text{-Mesph}}$), 7.21 (t, $^3J_{HH}$ 6.4, 1H, *p*-$CH_{o\text{-Mesph}}$), 7.18 (d, $^3J_{HH}$ 6.5, 1H, *m*-$CH_{o\text{-Mesph}}$), 6.86 (s, 2H, *m*-CH_{Mes}), 3.94 (t, $^3J_{HH}$ 5.4, 2H, NCH_2), 3.81 (t, $^3J_{HH}$ 5.4, 2H, NCH_2), 2.52 (m, 2H, NCH_2CH_2), 2.46 (s, 3H, $SCH_{3\ o\text{-Mesph}}$) 2.30 (s, 6H, o-$CH_{3\ Mes}$), 2.21 (s, 3H, p-$CH_{3\ Mes}$). δ_C ($CDCl_3$, 100 MHz, 298K) 154.1 (s, NCHN), 140.4 (s, Ar-$C_{o\text{-Mesph}}$), 137.8 (s, Ar-C_{Mes}), 136.7 (s, Ar-C_{Mes}), 135.7 (s, Ar-C_{Mes}), 134.8 (s, Ar-$C_{o\text{-Mesph}}$), 131.1 (s, Ar-$CH_{o\text{-Mesph}}$), 130.1 (s, Ar-CH_{Mes}), 128.3 (s, Ar-$CH_{o\text{-Mesph}}$), 126.7 (s, Ar-$CH_{o\text{-Mesph}}$), 125.9 (s, Ar-$CH_{o\text{-Mesph}}$), 46.8 (s, NCH_2), 46.4 (s, NCH_2), 20.9 (s, NCH_2CH_2), 19.4 (s, p-$CH_{3\ Mes}$), 17.7 (s, o-$CH_{3\ Mes}$) 14.9 (s, $SCH_{3\ o\text{-Mesph}}$).

*Preparation of 1-(2-methylthiophenyl)-3-(2,6-diisopropylphenyl)-3,4,5,6-tetrahydro-3*H-*[1,3]pyrimidinium bromide*

N-(2-methylthiophenyl)-*N′*-(2,6-diisopropylphenyl) formamidine (3.26 g), K_2CO_3 (0.7 g, 5 mmol) and 2.03 mL of 1,3-dibromopropane (20 mmol) in 250 mL acetonitrile was heated under reflux for three weeks to yield 3.25 g (72 %) of white, crystalline material. δ_H ($CDCl_3$, 400 MHz, 298 K) 7.88 (d, $^3J_{HH}$ 6.7, 1H, *o*-$CH_{o\text{- Meoph}}$), 7.56 (s, 1H, NCHN), 7.37 (t, $^3J_{HH}$ 6.8, 1H, *m*-$CH_{o\text{-Meoph}}$), 7.34 (t, $^3J_{HH}$ 7.8, 1H, *p*-CH_{Dipp}), 7.20 (d, $^3J_{HH}$ 7.8, 2H, *m*-CH_{Dipp}), 7.04 (t, $^3J_{HH}$ 6.8, 1H, *p*-$CH_{o\text{-Meoph}}$), 6.94 (d, $^3J_{HH}$ 6.7, 1H, *m*-$CH_{o\text{-Meoph}}$), 4.38 (t, $^3J_{HH}$ 5.5, 2H, NCH_2), 4.02 (t, $^3J_{HH}$ 5.5, 2H, NCH_2), 3.83 (s, 3H, $OCH_{3\ o\text{-Meoph}}$), 3.14 (sept., $^3J_{HH}$ 6.8, 2H, $CH(CH_3)_{2\ Dipp}$), 2.59 (m, 2H, NCH_2CH_2), 1.27 (d, $^3J_{HH}$ 6.8, 6H, $CH(CH_3)_{2\ Dipp}$), 1.17 (d, $^3J_{HH}$ 6.8, 6H, $CH(CH_3)_{2\ Dipp}$). δ_C ($CDCl_3$, 100 MHz, 298k) 154.3 (s, NCHN), 152.9 (s, Ar-$C_{o\text{-Meoph}}$), 149.3 (s, Ar-C_{Dipp}), 136.7 (s, Ar-C_{Dipp}), 131.6 (s, Ar-$C_{o\text{-Meoph}}$), 131.5 (s, Ar-$CH_{o\text{-Meoph}}$), 129.7 (s, Ar-CH_{Dipp}), 128.1 (s, Ar-CH_{Dipp}), 125.5

(s, Ar-$CH_{o\text{-Meoph}}$), 122.4 (s, Ar-$CH_{o\text{-Meoph}}$), 112.5 (s, Ar-$CH_{o\text{-Meoph}}$), 56.6 (s, OCH_3), 48.9 (s, NCH_2), 48.4 (s, NCH_2), 28.9 (s, $CH(CH_3)_2$), 25.1 (s, NCH_2CH_2), 24.8 (s, $CH(CH_3)_2$), 20.0 (s, $CH(CH_3)_2$). *m/z* (ES) 367.2216, Calc. for $C_{23}H_{31}N_2O$: 367.2208. Anal. Calc. for $C_{23}H_{31}N_2OBr$: C 60.81, H 6.83, N 6.17. Found: C 60.62, H 6.81, N 6.15 %.

Synthesis of complexes

*Synthesis of complex **2a***

$KNSi(Me_3)_2$ (82 mg, 0.41 mmol) and (6-*o*-MeSPh-Mes)BF_4 salt, **1a** (0.168 mg, 0.41 mmol) were placed in a Schlenk tube followed by the addition of THF (15 mL). The solution was stirred for 30 min and subsequently filtered into another Schlenk tube containing a THF solution (10 mL) of $[Rh(COD)Cl]_2$ (0.20 mmol). An immediate colour change was observed from light to dark yellow. After the reaction mixture was stirred at room temperature for 4 h, the volatiles were removed under reduced pressure. The yellow solid obtained was washed with hexane (2 × 10 mL) and dried. The yield was 0.114 g (60 %). δ_H (CD_2Cl_2, 500 MHz, 298 K) 7.56 (t, 1H, *m*-$CH_{o\text{-MeSPh}}$), 7.45 (d, 1H, *o*-$CH_{o\text{-MeSPh}}$), 7.34 (d, 1H, *m*-$CH_{o\text{-MeSPh}}$), 6.91 (t, 1H, *p*-$CH_{o\text{-MeSPh}}$), 6.84 (s, 1H, *m*-CH_{Mes}), 6.80 (s, 1H, *m*-CH_{Mes}), 3.83 (t, 2H, NCH_2), 3.72 (t, 2H, NCH_2), 2.38 (m, 2H, NCH_2CH_2), 2.25 (s, 3H, *o*-CH_3), 1.69 (s, 3H, SCH_3), 1.67 (s, 3H, *o*-CH_3), 1.61 (s, 3H, *p*-CH_3). δ_C (CD_2Cl_2, 100 MHz, 298 K) 202.3 (d, N*C*RhN), 149.8 (s, Ar-$C_{o\text{-MeSPh}}$), 148.0 (s, Ar-C_{Mes}), 140.3 (s, Ar-C_{Mes}), 140.1 (s, Ar-C_{Mes}), 137.3 (s, Ar-C_{Mes}), 136.4 (s, Ar-$C_{o\text{-MeSPh}}$), 132.9 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 123.4 (s, Ar-*C*H_{Mes}), 122.2 (s, Ar-*C*H_{Mes}), 121.9 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 120.6 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 108.3 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 45.4 (s, N*C*H_2), 44.2 (s, N*C*H_2), 20.5 (s, NCH_2CH_2), 19.2 (s, *p*-*C*H_3), 18.3 (s, *o*-*C*H_3), 17.7 (s, *o*-*C*H_3), 9.6 (s, S*C*H_3). *m/z* (HR-ES) 930.1425 $[M\text{-}Cl)]^+$, $C_{40}H_{48}N_4S_2Rh_2ClCH_3CN$ requires 930.1384. Anal. Calc. for $C_{40}H_{48}N_4S_2Rh_2Cl_2$: C 51.90, H 5.23, N 6.05. Found: C 52.67, H 5.84, N 6.24 %.

*Synthesis of complex **2b***

The same procedure as described for the synthesis of **2a** was employed using $KNSi(Me_3)_2$ (82 mg, 0.41 mmol), (6-*o*-MeSPh-Dipp).BF_4**1b** (0.187 mg, 0.41 mmol) and $[Rh(COD)Cl]_2$ (0.20 mmol). The reaction was stirred at RT for 2 h, the volatiles removed under reduced pressure and the yellow solid thus obtained was washed with hexane (2 × 10 mL) and dried. Crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution of the compound with hexane. Yield: 0.113 g (55 %). δ_H (CD_2Cl_2, 500 MHz, 298 K) 7.53 (t, 1H, *m*-$CH_{o\text{-MeSPh}}$), 7.40 (d, 1H, *o*-$CH_{o\text{-MeSPh}}$), 7.31 (d, 1H, *m*-$CH_{o\text{-MeSPh}}$), 6.89 (t, 1H, *p*-$CH_{o\text{-MeSPh}}$), 6.59 (t, 1H, *p*-CH_{Dipp}), 6.56 (d, 1H, *m*-CH_{Dipp}), 6.52 (d, 1H, *m*-CH_{Dipp}), 3.77 (t, 2H, NCH_2), 3.68 (t, 2H, NCH_2), 3.01 (m, 2H, C*H*$(CH_3)_{Dipp}$), 2.31 (m, 2H, NCH_2CH_2), 1.52 (s, 3H, S-*C*H_3), 1.45 (s, 3H, CH(*C*H_3)$_{Dipp}$), 1.28 (s, 3H, CH(*C*H_3)$_{Dipp}$), 1.22 (s, 3H, CH(*C*H_3)$_{Dipp}$), 1.08 (s, 3H, CH(*C*H_3)$_{Dipp}$).δ_C (CD_2Cl_2, 100 MHz, 298 K) 0.202.7 (d, N*C*RhN), 150.7 (s, Ar-$C_{o\text{-MeSPh}}$), 148.0 (s, Ar-C_{Dipp}), 140.6 (s, Ar-C_{Dipp}), 137.3 (s, Ar-$C_{o\text{-MeSPh}}$), 135.4 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 129.1 (s, Ar-*C*H_{Dipp}), 123.9 (s, Ar-*C*H_{Dipp}), 123.5 (1s, Ar-*C*H_{Dipp}), 122.2 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 121.9 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 109.5 (s, Ar-*C*$H_{o\text{-MeSPh}}$), 50.4 (s, N*C*H_2), 40.9 (s, N*C*H_2), 28.3 (s, *C*H$(CH_3)_{Dipp}$), 26.6 (s, *C*H$(CH_3)_{Dipp}$), 25.9 (s, NCH_2CH_2), 23.2 (s, *C*H_3), 22.9 (s, *C*H_3), 21.1 (s, *C*H_3), 19.6 (s, *C*H_3), 9.6 (s, S*C*H_3). *m/z* (HR-ES) 1014.3142 $[M\text{-}Cl]^+$, $C_{46}H_{60}N_4S_2Rh_2ClCH_3CN$ requires 1014.3138). Anal. Calc. for $C_{46}H_{60}N_4S_2Rh_2Cl_2.0.5CH_2Cl_2$: C 53.01, H 5.84, N 5.34. Found: C 52.65, H 5.84, N 6.31 %.

Accessory Publication

The Accessory Publication contains the CIF file and checkCIF file for complex **2b.** Computational data (Cartesian coordinates, energies of ground and transition states, and imaginary frequencies for transition states) are also included. The Accessory Publication is available on the Journal's website.

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