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Nickel(II), Palladium(II) and Rhodium(I) Complexes of New NHC-Thioether Ligands: Efficient Ketone Hydrosilylation Catalysis by a Cationic Rh Complex

Joffrey Wolf,[a] Agnès Labande,*[a] Jean-Claude Daran,[a] and Rinaldo Poli[a]

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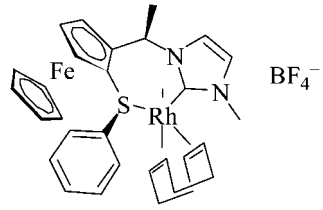
Five new, bifunctional imidazolium–thioether ligands of the general formula $RS(CH_2)_n(imidazolium)^+ArBr^-$ (n = 2 or 3, R = Et or *t*Bu, Ar = 2,4,6-trimethylphenyl or 2,6-diisopropylphenyl) have been synthesised in good overall yields by a general method and used as N-heterocyclic carbene precursors for complexation studies on various transition metals (Ni^{II}, Pd^{II} and Rh^{I}). Sulfur does not coordinate the nickel centre, whereas the two functional groups bind the palladium centre to form a dinuclear compound. Cationic rhodium(I) complexes have also been prepared and preliminary catalytic tests show that they have good activity for the hydrosilylation of ketones.

Introduction

N-Heterocyclic carbenes (NHC) have been thoroughly studied over the last 15 years.[1] Whereas the high strength of metal–NHC bonds has yielded new classes of robust catalysts,[2–4] the combination of NHCs and less strongly binding heteroatom donors has been investigated in order to combine robustness and activity in the corresponding complexes. Thus NHC–phosphane[5–10] and NHC-N donor[11,12] or NHC-O donor[13] ligands have been developed. Thioethers are soft donor ligands and have been successfully used in catalysis, mostly in combination with other donors such as phosphanes.[14] In combination with NHCs, they could provide potentially useful catalytic properties. A few NHC–thioether precursors have already been described, but they have mainly been used as bioactive compounds (antibacterials, fungicides)[15] or for heavy metal extraction from water.[16] Few carbene–thioether complexes have been isolated and characterised, respectively, by Seo et al. in 2003[9] and Ros et al. recently[17,18] (Figure 1). NHC–furan and NHC–thiophene ligands have also been described, but only the NHC moiety coordinates the metal centre.[19] We have recently described an efficient synthetic pathway for phosphane–imidazolium compounds, using 1-bromoalkyl-3-arylimidazolium bromides as key intermediates.[5,6] We have now extended this methodology to the synthesis of NHC–thioether precursors and report here the characterisation of these new ligands, as well as representative products of their complexation to various metals of interest in catalysis: nickel(II), palladium(II) and rhodium(I).



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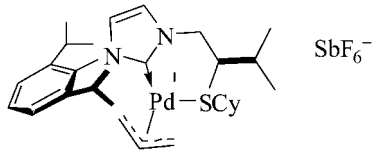

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Figure 1. NHC–thioether complexes described in the literature. (A) Seo et al.[9], (B) Ros et al.[17,18]

Results and Discussion

Ligand Syntheses

Compounds **5**–**7** were obtained from 1-(2-bromoethyl)-3-arylimidazolium bromides **1** and **2**, and compounds **8** and **9** from 1-(3-bromopropyl)-3-arylimidazolium bromides **3** and **4**, by nucleophilic substitution with lithium alkylthiolates (Scheme 1). An optimisation study has been carried out on the reaction of compound **1** with lithium *tert*-butyl

[a] Laboratoire de Chimie de Coordination, UPR CNRS 8241 (lié par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse),
205 route de Narbonne, 31077 Toulouse Cedex 4, France
Fax: +33-561553003
E-mail: agnes.labande@lcc-toulouse.fr
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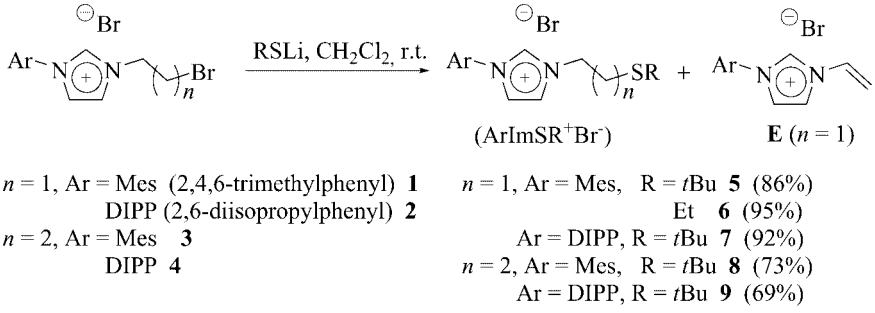


Scheme 1. Nucleophilic substitution on **1**–**4** bromides by lithium alkylthiolate reagents.

thiolate (Table 1). Alcohols and water are commonly used solvents for nucleophilic substitution reactions with thiolates,[20] whereas acetone and DMF are employed with phenolates.[21] Ethanol and DMF produced homogeneous mixtures with our substrates, contrary to acetone and dichloromethane. Our first attempt in ethanol at 60 °C, however, gave 62% of an elimination product, **E**, and only 7% of the expected compound. The temperature was lowered to 25 °C in order to improve the selectivity in favour of the substitution product: compound **5** was obtained in 14% yield, but again with 57% of elimination product (entry 1). A systematic study of the reaction conditions showed that the reaction is highly solvent-dependent, ethanol and acetone leading to substantial amounts of elimination product **E**, whereas dichloromethane and DMSO yield greater selectivity in favour of the substitution product but at slower rates. The conversion was also greatly improved when the reactions were carried out in more dilute media (entries 4 and 6). Under optimised reaction conditions (entry 6), **5** was obtained in very good yields (Scheme 1). These conditions were successfully applied to other substrates to afford thioethers **6**–**9** in good yields.

Table 1. Solvent and concentration screening for ligand **5** synthesis.[a]

Entry	Solvent	Solvent amount (mL)	**1**/**E**/**5**[b]
1	EtOH	2	29/57/14
2	Me_2CO	2	38/50/12
3	DMSO	2	85/00/15
4	DMSO	3	60/00/40
5	CH_2Cl_2	2	74/07/19
6	CH_2Cl_2	3	03/03/94
7	CH_2Cl_2	4	30/01/69

[a] **1** (0.5 mmol), *t*BuSLi (0.55 mmol), 17 h at room temperature. [b] Ratio determined by ethylene signal integration in ^{1}H NMR spectra of crude products.

The ^{1}H NMR signals of the acidic imidazolium protons are observed between 10.03 and 10.28 ppm for compounds **5**, **6** and **8**, and at δ = 9.87 ppm for compounds **7** and **9**, which denotes a greater shielding effect of the bulky DIPP compared to the mesityl group. Compounds **5** and **6** were analysed by single-crystal X-ray diffraction. The structures (Figure 2) show hydrogen bonds, as is typically observed for imidazolium bromides,[22] between the bromide anion and the C1 proton (Br1···H1–C1 2.637 Å for **5**, 2.624 Å for **6**).

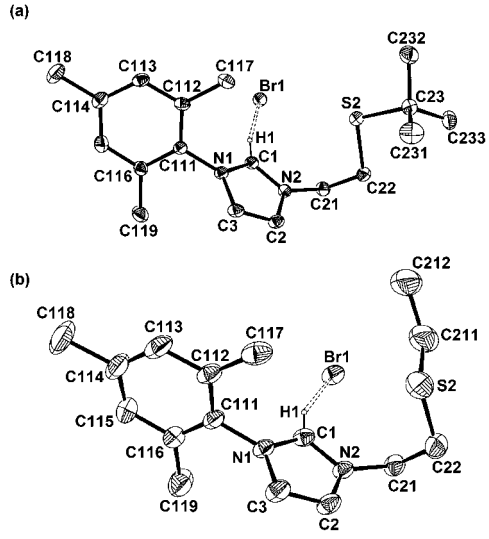
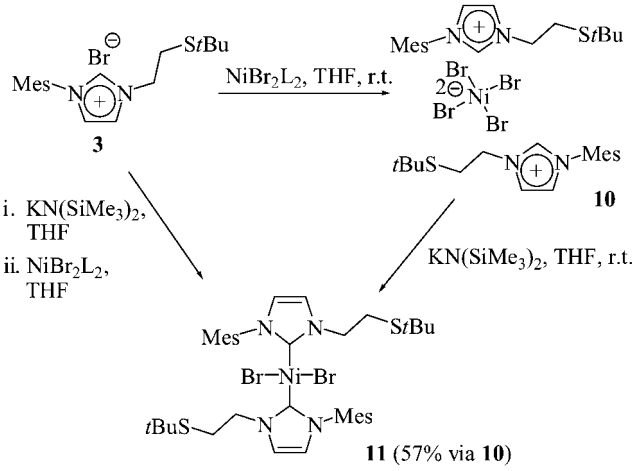


Figure 2. ORTEP views of **5** (a) and **6** (b). Ellipsoids are shown at the 30% probability level. All hydrogen atoms except H(1) and the solvent molecule (CH_2Cl_2) which co-crystallised with **5** are omitted for clarity.

Nickel Complexes

Preliminary complexation studies were carried out with the catalytically relevant metals nickel, palladium and rhodium. Our previous studies of the coordination of phosphane-imidazolium salts to Ni^{II} complexes of type NiX_2L_2 led to the isolation of zwitterionic compounds of the formula [$NiX_3(PPh_2ImAr)$], where ImAr is as defined in Scheme 1.[5,6] The analogous reaction of **5** with 1 equiv. of $NiBr_2$(DME) did not give the corresponding zwitterionic species with sulfur coordination. A $NiBr_4^{2-}$ species with two imidazolium/thioether counterions, **10**, was obtained instead (Scheme 2). Deprotonation of **10** with *t*BuOK led to the biscarbene complex **11**, with no sulfur coordination onto the nickel centre. The alternative strategy consisting of initial deprotonation of ligand **5** with a strong base, followed by reaction of the resulting free carbene with $NiBr_2$(DME), also led to the same product. The absence of sulfur coordination has two possible explanations: the bulkiness of the *tert*-butyl group prevents the coordination on the nickel, or the sulfur donor power is insufficient to compete with bromide for coordination. In order to con-

firm one of these hypotheses, we added 1 equiv. of **6**, which contains a less bulky ethyl substituent, to 1 equiv. of $NiBr_2(MeCN)_2$. During the treatment, unreacted nickel corresponding to half of the starting material was recovered. This result would be more in favour of the second hypothesis, although we have no further evidence to validate it.



Scheme 2. Nickel(II) complex synthesis.

The crystal structure of compound **11** has been resolved by X-ray analysis (Figure 3). As the nickel atom is located on an inversion centre, the geometry around it is perfectly square-planar. The imidazol-2-ylidene ring is planar [maximum deviation of 0.005(1) Å for atom N2] and is approximately perpendicular [angle of 75.06(5)°] to the coordination plane, thus limiting steric interactions. This was already observed for other previously described Ni^{II}–bis(NHC) complexes.[23] The mesityl ring forms an angle of 77.63(6)° with the NHC ring, and we can notice the existence of an interaction between a hydrogen from methyl C119 and Br1 (C119···Br1^{i} 2.75 Å). Selected bond lengths and angles are listed in Table 2.

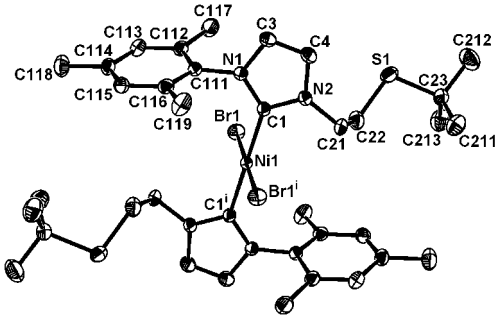


Figure 3. An ORTEP view of compound **11**. Ellipsoids are represented at the 50% probability level. Hydrogen atoms are omitted for clarity.

Although only one isomer is present in the crystal, analysis by ^1H and ^{13}C NMR revealed a mixture of two distinct isomers in solution in a ratio of 1:1.27. We believe that these

Table 2. Comparison of the main structural parameters of **11** and $NiBr_2$(1,3-dicyclohexylimidazol-2-ylidene)$_2$.

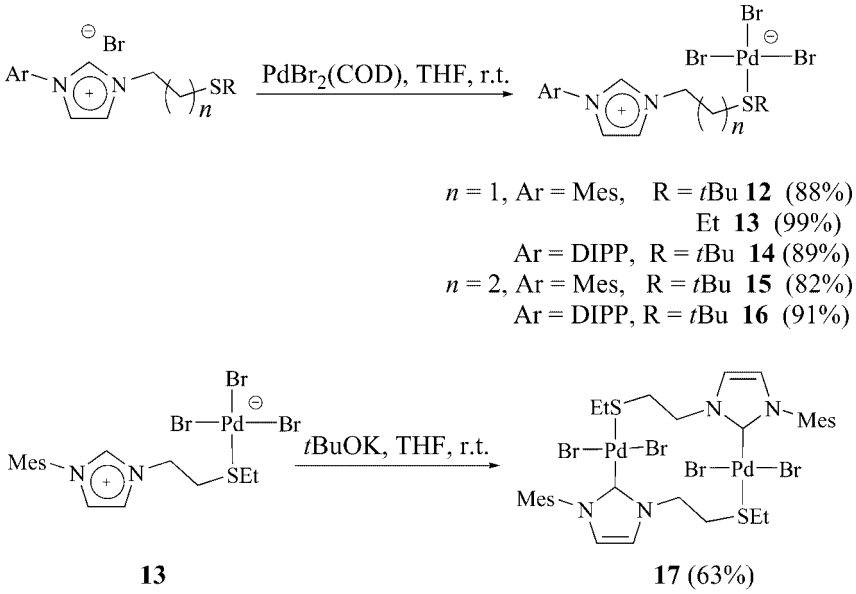
	11	$NiBr_2L_2$ [a]
Bond lengths [Å]		
Ni–Br	2.3113(5)	2.3113(4)
Ni–C1	1.9186(17)	1.908(3)
C1–N1	1.359(2)	1.353(4)
C1–N2	1.354(2)	1.347(4)
N2–C4	1.385(2)	1.394(5)
N1–C3	1.395(2)	1.390(5)
C3–C4	1.348(3)	1.333(5)
Bond angles [°]		
C1–Ni–C1i	180.00(9)	180.00
C1–Ni–Br1	89.48(5)	89.41(10)
C1–Ni–Br1i	90.52(5)	90.59(10)
Dihedral angles [°]		
N1–C1–Ni–Br1	74.43	
N2–C1–Ni–Br1i	75.41	
N1–C1–C1i–N2i	0.98	

[a] L = 1,3-dicyclohexylimidazol-2-ylidene.

are conformational isomers. In the crystalline compound, the aryl and thioether alkyl chains of the two imidazol-2-ylidene groups are mutually *anti* to afford a head-to-tail arrangement, which minimises steric interactions. Strong steric interactions between the N-substituents in a bis-NHC-Ni^{II} complex have been observed for $NiCl_2$[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]$_2$, resulting in a significant deviation from coplanarity for the two NHC rings.[24] For our compound, it is possible to envisage that the different N-substituents adopt a *syn* orientation in the second isomer and that there is a significant barrier for the 180° rotation that is required to interconvert them. Recent work by Gomes et al.[25] has shown that the energy barrier for a 180° rotation of a N-heterocyclic carbene along the C–Ni axis, in allyl Ni^{II} complexes, is 14–15 kcal mol^{-1} for NHCs bearing methyl substituents and becomes >18 kcal mol^{-1} with *tert*-butyl substituents. In our case, the imidazole-2-ylidene bears a bulky mesityl group on one side and a functionalised alkyl chain on the other side. Therefore it becomes possible to independently observe two conformational isomers.

Palladium Complexes

Contrary to the nickel system, addition of ligands **5**–**9** to $PdBr_2$(COD) led to the expected coordination of the sulfur and bromine atoms, leading to the zwitterionic complexes **12**–**16** in good yields (Scheme 3). A zwitterionic structure for these complexes, with a coordinated thioether function and a dangling imidazolium group, is suggested by the spectroscopic data. The typical signal of the acidic imidazolium proton is still present in the ^1H NMR spectra of all complexes and is situated between 9.00 and 9.61 ppm. Likewise, the elemental analyses of the complexes are in agreement with the calculated values. Subsequent deprotonation of **13** (Scheme 3) led to NHC complex **17**. The ^1H and ^{13}C NMR properties are consistent with the expected stoichiometry, as for the related phosphane-carbene complexes previously



Scheme 3. Synthesis of palladium(II) complexes.

described by Danopoulos et al.[7] and Lee et al.[26] The ^{13}C NMR signal of the carbene C atom is observed at δ = 155.75 ppm in the case of **17**, and respectively at δ = 157.2 and 162.4 ppm for the above-mentioned phosphane-carbene complexes. Moreover, the ^{1}H NMR spectrum of **17** only shows two protons for the imidazole cycle, appearing as doublets, and a 2D HMBC NMR experiment confirms the existence of a long-range coupling between these protons and the carbene C atom.

However, the X-ray structure (Figure 4) reveals that **17** is a dinuclear complex where each palladium centre displays a slightly distorted square-planar coordination environment. The two square-planar moieties are located face to face and the two NHC–thioether ligands span the metal centres in a relative *trans* arrangement. Pd–C and Pd–S bond lengths are comparable to the usual NHC–Pd^{II} and thioether–Pd^{II} bonds.[7,26,27] A similar arrangement is adopted by related NHC–oxazoline derivatives. Only three X-ray structures of Pd^{II} complexes possessing a chelating NHC–thioether ligand have been described:[17,18] in these cases, the sulfur atom is situated *cis* to the NHC moiety, with Pd–C and Pd–S distances of, respectively, 2.036–2.063 Å and 2.326–2.367 Å. Mass spectrometry analyses (FAB technique) confirm the existence of a dinuclear compound.

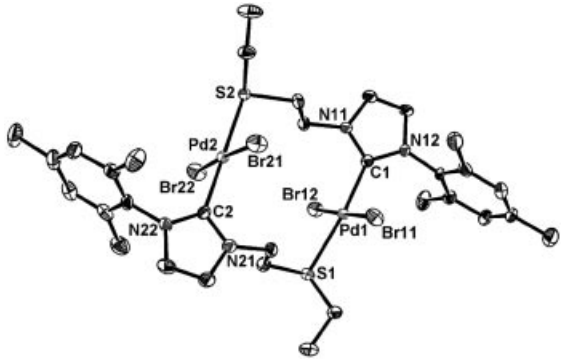
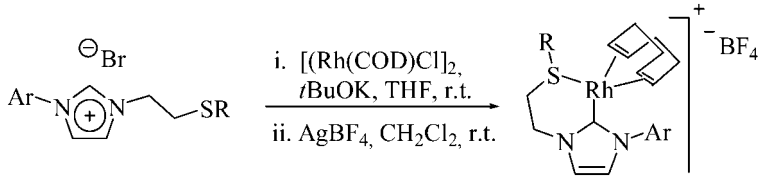


Figure 4. An ORTEP view of compound **17**. Ellipsoids are represented at the 30% probability level. Hydrogen atoms and a co-crystallised THF molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 1.990(4), Pd2–C2 1.983(4), Pd1–S1 2.3731(9), Pd2–S2 2.3622(9), Br21–Pd2–Br22 175.50(2), C1–Pd1–S1 173.10(12).

Rhodium Complexes

Addition of compounds **5**–**7** to $[Rh(COD)Cl]_2$ in the presence of a strong base (Scheme 4) led, after halide abstraction, to the formation of NHC derivatives **18**–**20**. The



R = *t*Bu, Ar = Mes **18** (81%)
Ar = DIPP **19** (79%)
R = Et, Ar = Mes **20** (76%)

Scheme 4. Synthesis of rhodium(I) complexes.

nature of these products, as salts of typical square-planar Rh^I complexes with *cis* chelating NHC–thioether ligands, is consistent with the spectroscopic characterisation. The ^{13}C NMR signals of the carbene C atoms appear around 173 ppm, which is the expected value for cationic NHC–Rh^I complexes.[10,18,28] The sulfur coordination on rhodium is suggested by the downfield shift (about 7 ppm) of the quaternary carbon on sulfur for complexes **18** and **19**, and of the S–CH_2CH_3 carbon signal (about 6 ppm) for complex **20**.[29]

The square-planar coordination environment in complexes **18**–**20** was confirmed by X-ray diffraction studies (Figure 5). Selected bond lengths and angles are listed in Table 3. The structures reveal slightly shorter Rh1–C1 bond lengths than in Seo's NHC–thioether complex. Rh1–S1 distances are within the same range, except compound **20**, for which we observe a shorter bond of 2.351(2) Å. The Rh1–C(COD) bonds *trans* to NHC are longer than the bonds *trans* to sulfur, which indicates a stronger *trans* influence of the NHC moiety. A boat-like conformation of the six-membered metallacycle is a common feature for all these structures. In the case of compound **20**, the deviation from the ideal 90° value of the C1–Rh1–S1 angle [82.5(2)°] could be because of a close contact between the methylene of the ethyl arm on sulfur (C311) and the COD ligand [intramolecular distances: C5–C311 3.45(1) Å and H5–H31A 2.36 Å; C6–C311 3.52(1) Å and H6–H31B 2.30 Å]. This value is consistent with the previously reported data for similar complexes.[10,18,30] This distortion cannot be observed in **18** and **19**, which have a bulky *tert*-butyl substituent on sulfur.

Table 3. Comparison of the main structural parameters of **18**–**20** and of the Rh^I complex described by Seo et al. (**A**).

	18	**19**	**20**	**A**[7]
Bond lengths [Å]				
Rh1–C1	2.032(4)	2.020(5)	2.042(7)	2.051(7)
Rh1–S1	2.4076(10)	2.3940(18)	2.351(2)	2.394(2)
Rh1–C11	2.145(4)	2.127(6)	2.149(6)	2.137(7)
Rh1–C12	2.175(4)	2.150(6)	2.148(8)	2.148(9)
Rh1–C15	2.199(4)	2.191(6)	2.175(6)	2.225(9)
Rh1–C16	2.222(4)	2.212(7)	2.228(8)	2.236(8)
C1–N1	1.351(5)	1.341(7)	1.360(9)	1.342(9)
C1–N2	1.366(5)	1.356(7)	1.365(9)	1.319(9)
S1–C5	1.827(4)	1.791(8)	1.806(9)	1.785(7)
S1–C6[a]	1.863(4)	1.848(9)	1.808(8)	1.802(7)
Bond angles [°]				
C1–Rh1–S1	88.93(11)	89.94(16)	82.5(2)	89.0(2)
N1–C–1–N2	104.0(3)	103.9(5)	104.1(6)	105.7(6)

[a] This carbon is labelled C111 for **19**.

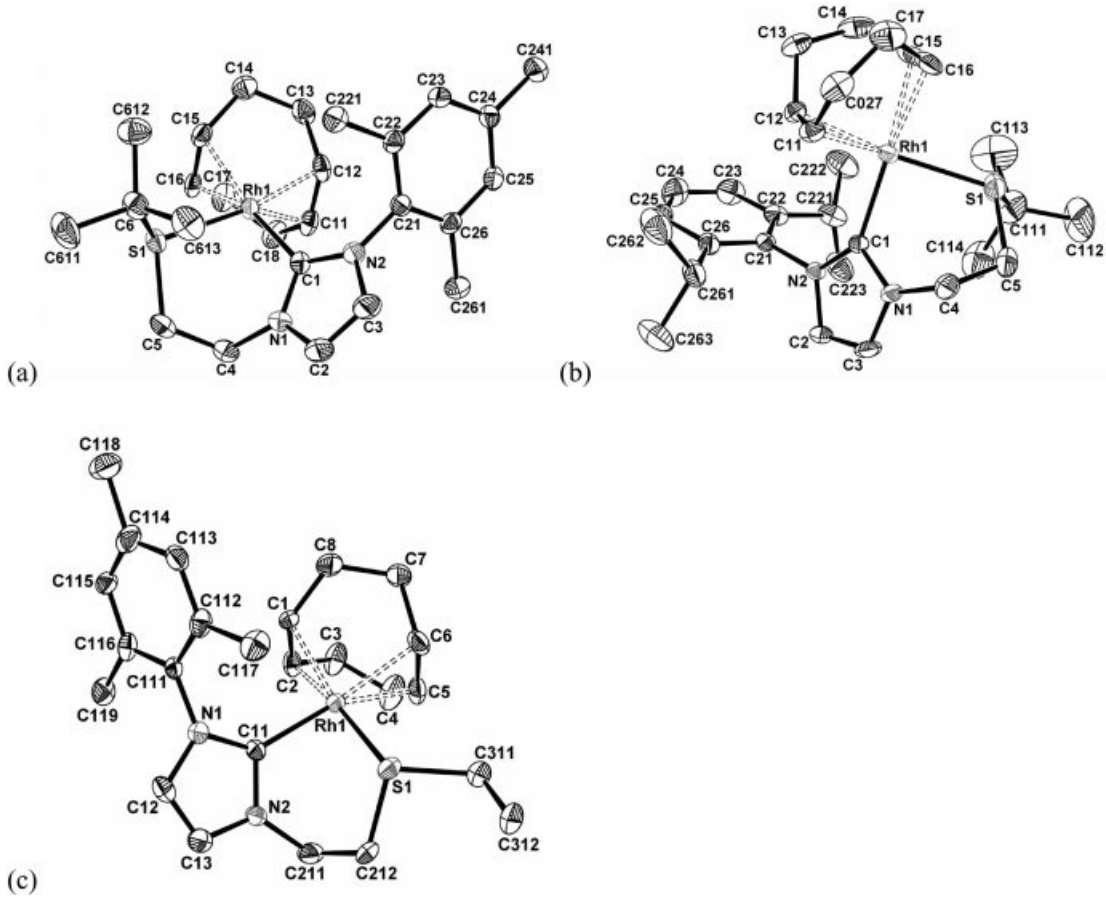


Figure 5. ORTEP views of the cations in complexes **18** (a), **19** (b) and **20** (c). Ellipsoids are represented at the 30% probability level. Hydrogen atoms, the counterion (BF_4) and a co-crystallised $CDCl_3$ molecule **18** are omitted for clarity.

Catalytic Hydrosilylation of Methyl Aryl Ketones

The catalysed hydrosilylation of ketones has attracted a lot of attention for many decades as it is an efficient synthetic alternative to the reduction of the carbonyl group by main group hydrides and catalytic hydrogenation.[31] Rhodium is the favoured catalytic metal for this process, even though other metals have been used. Neutral precatalysts derived from $RhCl(PPh_3)_3$,[32,33] $[RhCl(olefin)_2]_2$ [olefin = ethylene, cyclooctene; or $(olefin)_2$ = 1,5-cyclooctadiene, norbornadiene],[33–36] $RhH(PPh_3)_4$[37] or $RhCl_3L_3$[38] derivatives have most commonly been used to generate the active catalyst, but a few processes using cationic precursors have also been reported.[39,40] It has also been reported that the assistance of AgX (X = OSO_2CF_3, BF_4) is required in some cases to improve the catalytic activity,[38,41] presumably through transformation into a more active cationic species. The typical supporting ligands, including chiral versions for the enantioselective hydrosilylation of prochiral ketones, are based on P or N donors. Although several catalysts have shown outstanding activities,[36,41,42] the issue of catalyst stability and deactivation may hamper extension to large-scale production. As NHC ligands are likely to be solidly anchored to the metal centre, they may be expected to impart activity and stability to the catalytic system. Previous reports of ketone hydrosilylation using NHC ligands are limited.[12,43,44] For these reasons, we considered it of interest to test the catalytic activity of the cationic rhodium complexes **18**–**20**.

Preliminary catalytic tests have shown that these complexes are indeed active in the hydrosilylation of acetophenone and its derivatives (Tables 4 and 5, Scheme 5). The reactions were followed by TLC and the silylated intermediate was hydrolysed with MeOH before ^1H NMR analysis. The reactions were first carried out with 2 mol-% of **18**, in dichloromethane or THF. The yield of the expected alcohol reached 90% in dichloromethane in 17 h (Table 4, entry 1), whereas it was quantitative in THF (Table 4, entry 2). The catalyst loading was thus lowered to 1 mol-%. With a concentration of 1 M in acetophenone in THF, the yield reached 90% after 24 h. However, working in a more concentrated medium allowed us to get a total conversion of the substrate into the alcohol in only 4 h (entry 4). A similar result was obtained with complex **19** (Table 4, entries 5 and 6). Finally, complex **20** proved to be the most active, with a quantitative yield of alcohol in only 1 h at room temperature (Table 4, entry 7). The same trend was observed with 4-methoxyacetophenone (Table 5, entries 1–5): increasing the concentration allowed us to get a total conversion of the substrate into the desired alcohol in a reduced time, while **20** showed a better activity than **18** and **19**. Similar results were obtained with 4-fluoroacetophenone, bearing an electron-withdrawing substituent (Table 5, entries 6–8). The introduction of a methyl group *ortho* to the halide, however, slowed the reaction down. As an example, the reaction with **18** did not go to completion after 6 h, with only 78% conversion (Table 5, entry 9). Thus steric factors seem to have more influence than electronic factors on the issue of the reaction. Finally, no reaction occurred when other silanes (Et_3SiH, $MeEt_2SiH$ and $HSiCl_3$) were used with acetophenone.

Table 4. Hydrosilylation of acetophenone.[a]

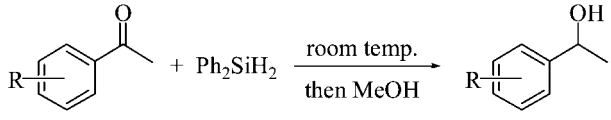
Entry	R	Catalyst (mol-%)	Solvent (concentration)	*t* (h)	Yield (%)[b]
1	H	**18** (2)	CH_2Cl_2 (1 M)	17	90
2	H	**18** (2)	THF (1 M)	17	99
3	H	**18** (1)	THF (1 M)	24	90
4	H	**18** (1)	THF (2 M)	4	99
5	H	**19** (1)	THF (1 M)	8	99
6	H	**19** (1)	THF (2 M)	4	99
7	H	**20** (1)	THF (2 M)	1	99

[a] Ketone (1 equiv.), diphenylsilane (1.1 equiv.), room temperature, then hydrolysis with MeOH. [b] Determined by integration of signals in ^1H NMR spectra of crude products.

Table 5. Hydrosilylation of acetophenone derivatives.[a]

Entry	R	Catalyst	Concentration	*t* (h)	Yield (%)[b]
1	4-OMe	**18**	1 M	24	80
2	4-OMe	**18**	2 M	3	98
3	4-OMe	**19**	1 M	6	99
4	4-OMe	**19**	2 M	2.5	99
5	4-OMe	**20**	2 M	2	99
6	4-F	**18**	2 M	4	96
7	4-F	**19**	2 M	4.5	99
8	4-F	**20**	2 M	2	99
9	2-Me	**18**	2 M	6	78[c]
10	2-Me	**19**	2 M	3.5	99
11	2-Me	**20**	2 M	3.5	99

[a] Ketone (1 equiv.), diphenylsilane (1.1 equiv.), room temperature, 1 mol-% catalyst, THF, then hydrolysis with MeOH. [b] Determined by integration of signals in ^1H NMR spectra of crude products. [c] The reaction was stopped before completion.



Scheme 5. Hydrosilylation of acetophenone and its derivatives with Rh^I complexes.

The activity of our complexes compares well with previously reported Rh^I systems bearing bifunctional NHC-oxazoline ligands. Thus, Bolm et al. obtain excellent yields of 1-phenylethanol with their system, using 2 mol-% of catalyst in THF at room temperature or at 0 °C.[44] Unfortunately there is no indication of reaction times, which does not allow a direct comparison with our results. On the other hand, César et al. report the hydrosilylation of acetophenone with diphenylsilane using 1 mol-% catalyst in dichloromethane at room temperature. In their case, the Rh^I complexes tested give from 70% to 93% yield in a maximum of 5 h.[12]

The higher catalytic activity observed at higher ketone concentration is in agreement with previous reports of a saturation effect: the reaction was found to be first order in ketone at low concentrations, but eventually became [ketone] independent at high concentrations.[35,40]

Conclusions

In conclusion, we have described a general and simple method for the preparation of new NHC–thioether precursors and explored their coordination chemistry. The coordination of sulfur on nickel was not observed, yielding complex **11** where the two ligands are monodentate through the NHC function and the thioether function is dangling. In the case of palladium(II), a dinuclear complex with *trans* carbene and sulfur coordination, **17**, was obtained. Rhodium(I) complexes with chelating carbene/thioether ligands were finally prepared in good yields. Preliminary catalytic studies have shown that these complexes are very active for the hydrosilylation of acetophenone and its derivatives. The asymmetric version of this reaction, as well as other catalytic reactions, is now under investigation, and the results will be published in due course.

Experimental Section

General Methods: Reactions involving air- or moisture-sensitive reagents and products were carried out under dry argon using Schlenk glassware and vacuum line techniques, and dry, purified solvents. All other steps were done without particular precautions. Elemental analyses were carried out by the Service d'Analyse du Laboratoire de Chimie de Coordination in Toulouse. ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data were recorded with a Bruker AV-500 spectrometer, operating at 500 MHz for ^{1}H and 125.8 MHz for ^{13}C and on a Bruker AV-200 spectrometer operating at 188 MHz for ^{19}F. The spectra were referenced internally using the signal from the residual protiosolvent (^{1}H), the signals of the solvent (^{13}C) or the signal of trifluoroacetic acid, 10% in C_6D_6 (^{19}F). Mass spectra (ESI) were obtained from acetonitrile or methanol solutions on a TSQ 7000 (Thermo Electron) and (FAB) from DMSO or DMF solutions on a Nermag R10-10 instrument. Electrospray high-resolution mass spectra were performed by the Service de spectroscopie de masse CESAMO de l'université de Bordeaux I. Chromatographic work was performed on silica gel 60 Å. $PdBr_2(COD)$,[45] 1-(2-bromoethyl)-3-(2,4,6-trimethylphenyl) imidazolium bromide **1**,[6] 1-(2-bromoethyl)-3-(2,6-diisopropylphenyl)imidazolium bromide **2**[6] and 1-(3-bromopropyl)-3-(2,4,6-trimethylphenyl)imidazolium bromide **3**[6] were prepared as described in the literature. Both lithium alkylthiolates were prepared by action of methyllithium on the corresponding thiols and used rapidly after their preparation. Other reagents were obtained from commercial sources and used as received.

1-[2-(*tert*-Butylthio)ethyl]-3-(2,4,6-trimethylphenyl)imidazolium Bromide (5): *t*BuSLi (170 mg, 1.77 mmol) was added to a solution of **1** (610 mg, 1.63 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for one day at room temperature. CH_2Cl_2 (20 mL) was added and the mixture was washed with water (10 + 5 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under vacuum to give a white, hygroscopic solid. Yield 535 mg (86%). Suitable X-ray colourless crystals were obtained by slow diffusion of diethyl ether in a CH_2Cl_2 solution. M.p. 88–92 °C. $C_{18}H_{27}BrN_2S$ (383.42): HRMS (ESI) *m*/*z*: calcd. 303.189496; found 303.190467. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 10.03 (t, ^4J = 1.6 Hz, 1 H, NC*H*N), 8.13 (t, $^{3,4}J$ = 1.5 Hz, 1 H, MesNC*H*=), 7.19 (t, $^{3,4}J$ = 1.6 Hz, 1 H, AlkN–C*H*=), 6.97 [s, 2 H, C*H* (Mes)], 4.89 (t, ^3J = 6.0 Hz, 2 H, NCH_2), 3.17 (t, ^3J = 6.1 Hz, 2 H, CH_2S*t*Bu), 2.31 (s, 3 H, *p*-CH_3), 2.06 (s, 6 H, *o*-CH_3), 1.27 (s, 9 H, S*t*Bu) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 141.26 [*p*-*C* (Mes)], 137.77 (N–*C*H–N), 134.31 [*o*-*C* (Mes)], 130.66 [N–*C* (Mes)], 129.81 [*C*H (Mes)], 124.13 (AlkN–*C*H=), 122.74 (MesN–*C*H=), 50.33 (N–*C*H_2), 43.33 [S*C*$(CH_3)_3$], 31.00 [SC(*C*$H_3)_3$], 29.32 (*C*H_2S), 21.11 [*p*-*C*H_3 (Mes)], 17.66 [*o*-*C*H_3 (Mes)] ppm. MS (ESI, positive mode): *m*/*z* (%) = 303.35 (100) [$C_{18}H_{27}N_2S^+$]. MS (ESI, negative mode): *m*/*z* (%) = 79 (100) [Br^-].

1-[2-(Ethylthio)ethyl]-3-(2,4,6-trimethylphenyl)imidazolium Bromide (6): EtSLi (246 mg, 3.61 mmol) was added to a solution of **1** (1.125 g, 3.01 mmol) in CH_2Cl_2 (18 mL). The mixture was stirred for one day at room temperature. CH_2Cl_2 (22 mL) was added and the mixture was washed with water (2 × 15 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under vacuum to give a white hygroscopic solid. Yield 1.07 g (95%). X-ray quality crystals were obtained by slow diffusion of diethyl ether in a CH_2Cl_2 solution. M.p. 117 °C. $C_{16}H_{23}BrN_2S$ (355.36): calcd. C 54.08, H 6.52, N 7.88; found C 53.96, H 6.51, N 8.00. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 10.08 (s, 1 H, NC*H*N), 8.26 (s, 1 H, MesNC*H*=), 7.16 (s, 1 H, AlkNC*H*=), 6.94 [s, 2 H, C*H* (Mes)], 4.90 (t, ^3J = 6.0 Hz, 2 H, NCH_2), 3.09 (t, ^3J = 6.1 Hz, 2 H, CH_2SEt), 2.62 (q, ^3J = 7.4 Hz, 2 H, SCH_2CH$_3$), 2.29 (s, 3 H, *p*-CH_3), 2.02 (s, 6 H, *o*-CH_3), 1.16 (t, ^3J = 7.4 Hz, 3 H, SCH$_2$CH_3) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 141.11 [*p*-C (Mes)], 137.97 (N*C*HN), 134.29 [*o*-C (Mes)], 130.67 [N*C* (Mes)], 129.73 [CH (Mes)], 123.98 (AlkN*C*H=), 122.93 (MesN*C*H=), 48.88 (N*C*H_2), 32.14 (*C*H_2SEt), 25.67 (S*C*H_2CH$_3$), 21.07 [*p*-*C*H_3 (Mes)], 17.61 [*o*-*C*H_3 (Mes)], 14.61 (SCH$_2$*C*H_3) ppm. MS (ESI, positive mode): *m*/*z* (%) = 275.15 (100) [$C_{16}H_{23}N_2S^+$]. MS (ESI, negative mode): *m*/*z* (%) = 79 (100) [Br^-].

1-[2-(*tert*-Butylthio)ethyl]-3-(2,6-diisopropylphenyl)imidazolium Bromide (7): *t*BuSLi (118 mg, 1.23 mmol) was added to a solution of **2** (410 mg, 0.99 mmol) in CH_2Cl_2 (6 mL). The mixture was stirred for one day at room temperature. CH_2Cl_2 (14 mL) was added and the mixture was washed with water (2 × 4 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under vacuum to give a pale yellow hygroscopic solid. Yield 387 mg (92%). M.p. 85–90 °C. $C_{21}H_{33}BrN_2S$ (425.48). HRMS (ESI) *m*/*z*: calcd. 345.236446; found 345.236823. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.87 (t, ^4J = 1.7 Hz, 1 H, NC*H*N), 8.38 (t, $^{3,4}J$ = 1.7 Hz, 1 H, AlkNC*H*=), 7.47 [t, ^3J = 7.8 Hz, 1 H, *p*-C*H* (DIPP)], 7.24 [d, ^3J = 7.8 Hz, 2 H, *m*-C*H* (DIPP)], 7.16 [t, $^{3,4}J$ = 1.7 Hz, 1 H, (DIPP)-NC*H*=], 4.91 (t, ^3J = 5.9 Hz, 2 H, NCH_2), 3.16 (t, ^3J = 5.9 Hz, 2 H, CH_2S*t*Bu), 2.28 [h, ^3J = 6.8, 6.9 Hz, 2 H, C*H*$(CH_3)_2$], 1.24 (s, 9 H, S*t*Bu), 1.15 [d, ^3J = 6.9 Hz, 6 H, CH(C$H_3)_2$], 1.09 [d, ^3J = 6.8 Hz, 6 H, CH(C$H_3)_2$] ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 145.42 [*o*-C (DIPP)], 137.94 (N*C*HN), 131.82 [*p*-CH (DIPP)], 130.07 [N*C* (DIPP)], 124.60 [*m*-CH (DIPP)], 124.27 (AlkN*C*H=), 123.84 [(DIPP)N*C*H=], 50.10 (N*C*H_2), 43.13 [S*C*$(CH_3)_3$], 30.99 [SC(*C*$H_3)_3$], 29.39 (*C*H_2S), 28.48 [*C*H$(CH_3)_2$], 24.40, 24.21 [CH(*C*$H_3)_2$] ppm. MS (ESI, positive mode): *m*/*z* (%) = 345.50 (100) [$C_{21}H_{33}N_2S^+$]. MS (ESI, negative mode): *m*/*z* (%) = 81 (100) [Br^-].

1-[3-(*tert*-Butylthio)propyl]-3-(2,4,6-trimethylphenyl)imidazolium Bromide (8): *t*BuSLi (130 mg, 1.35 mmol) was added to a solution of **3** (390 mg, 1.00 mmol) in CH_2Cl_2 (6 mL). The mixture was stirred for one day at room temperature. CH_2Cl_2 (14 mL) was added and the mixture was washed with water (2 × 10 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under vacuum to give a white, hygroscopic solid. Yield 290 mg (73%). M.p. 134–136 °C. $C_{19}H_{29}BrN_2S$ (397.42): HRMS (ESI) *m*/*z*: calcd. 317.205146; found 317.204589. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 10.28 (t, ^4J = 1.5 Hz, 1 H, NC*H*N), 7.93 (t, $^{3,4}J$ =

1.7 Hz, 1 H, NC*H*=), 7.24 (t, $^{3,4}J$ = 1.7 Hz, 1 H, =C*H*N), 6.98 [s, 2 H, C*H* (Mes)], 4.81 (t, ^{3}J = 6.9 Hz, 2 H, NCH_2), 2.63 (t, ^{3}J = 6.9 Hz, 2 H, CH_2S*t*Bu), 2.32 (q + s, ^{3}J = 6.9 Hz, 5 H, *p*-CH_3; NCH$_2$CH_2), 2.06 (s, 6 H, *o*-CH_3), 1.27 (s, 9 H, S*t*Bu) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 141.27 [s, *p*-C (Mes)], 137.99 (s, N*C*HN), 134.16 [s, *o*-C (Mes)], 130.67 [s, N*C* (Mes)], 129.86 [s, CH (Mes)], 123.42 (s, =*C*HN), 123.25 (s, =*C*H–N), 49.37 (s, NCH_2), 42.69 [s, S*C*(CH$_3$)$_3$], 30.83 [s, SC(*C*H$_3$)$_3$], 30.63 (s, NCH$_2$*C*H$_2$), 24.66 (s, *C*H$_2$S), 21.10 [s, *p*-*C*H$_3$ (Mes)], 17.71 [s, *o*-*C*H$_3$ (Mes)] ppm. MS (ESI, positive mode): *m*/*z* (%) = 317.4 (100) [$C_{19}H_{29}N_2S^+$]. MS (ESI, negative mode): *m*/*z* (%) = 81.0 (100) [Br^-].

1-[3-(*tert*-Butylthio)propyl]-3-(2,6-diisopropylphenyl)imidazolium Bromide (9): *t*BuSLi (130 mg, 1.35 mmol) was added to a solution of **4** (450 mg, 1.05 mmol) in CH_2Cl_2 (6 mL). The mixture was stirred for one day at room temperature. CH_2Cl_2 (14 mL) was added and the mixture was washed with water (2 × 15 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated under vacuum to give a pale yellow hygroscopic solid. Yield 318 mg (69%). M.p. 103–104 °C. $C_{22}H_{35}BrN_2S$ (439.50): HRMS (ESI) *m*/*z*: calcd. 359.252096; found 359.253029. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.87 (s, 1 H, NC*H*N), 8.14 (t, $^{3,4}J$ = 1.7 Hz, 1 H, AlkNC*H*=), 7.39 [t, ^{3}J = 7.8 Hz, 1 H, *p*-C*H* (DIPP)], 7.25 [d, ^{3}J = 7.9 Hz, 2 H, *m*-C*H* (DIPP)], 7.23 [t, $^{3,4}J$ = 1.7 Hz, 1 H, (DIPP) NC*H*=], 4.84 (t, ^{3}J = 6.8 Hz, 2 H, NCH_2), 2.61 (t, ^{3}J = 7.1 Hz, 2 H, CH_2S*t*Bu), 2.30 (q, ^{3}J = 6.9; 7.0 Hz, 2 H, NCH$_2$CH_2), 2.25 [h, ^{3}J = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 1.26 (s, 9 H, S*t*Bu), 1.17 [d, ^{3}J = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.10 [d, ^{3}J = 6.8 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 145.29 [s, *o*-*C* (DIPP)], 138.08 (s, N*C*HN), 131.85 [s, *p*-*C*H (DIPP)], 130.13 [s, N*C* (DIPP)], 124.63 [s, *m*-*C*H (DIPP)], 124.30 (s, AlkN*C*H=), 123.75 [s, (DIPP)N*C*H=], 49.43 (s, NCH_2), 42.61 [s, S*C*(CH$_3$)$_3$], 30.90 [s, SC(*C*H$_3$)], 30.82 (s, NCH$_2$*C*H$_2$), 28.67 [s, *C*H(CH$_3$)$_2$], 24.59 (s, *C*H$_2$S), 24.40, 24.19 [s, CH(*C*H$_3$)$_2$] ppm. MS (ESI, positive mode): *m*/*z* (%) = 359.4 (100) [$C_{22}H_{35}N_2S^+$]. MS (ESI, negative mode): *m*/*z* (%) = 80.8 (100) [Br^-].

Bis{1-[2-(*tert*-butylthio)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}nickel Dibromide (11): $NiBr_2(MeCN)_2$ (140 mg, 0.47 mmol) and **3** (383 mg, 1.00 mmol) were placed in a Schlenk tube and THF (15 mL) was added. After stirring for 5 min, a homogeneous blue-green solution was obtained. A freshly prepared KN(SiMe$_3$)$_2$ solution (5 mL, 0.2 M in THF) was added over 5 min during which the mixture colour became darker and changed to deep pink-red. The mixture was stirred at room temperature for 15 min and the solvent was removed under vacuum. The residue was washed with diethyl ether (20 mL) and filtered. The filtrate was concentrated (about 5 mL), precipitated in pentane (50 mL) and filtered. The solution was concentrated to give a pink-red solid. Yield 217 mg (57%). X-ray quality crystals were obtained by slow evaporation of a pentane solution. M.p. (dec.) 195–200 °C. $C_{36}H_{52}Br_2N_4NiS_2$ (823.47): calcd. C 52.51, H 6.37, N 6.80; found C 52.45, H 6.39, N 6.56. NMR shows signals for two isomers, 1.27:1 ratio. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.09 [s, 4 H, C*H* (Mes)], 6.97 (s, 2 H, AlkNC*H*=), 6.60 (s, 2 H, MesNC*H*=), 4.92 (s, 4 H, NCH_2), 3.18 (s, 4 H, CH_2S), 2.45 [s, 6 H, *p*-CH_3 (Mes)], 2.23 [s, 12 H, *o*-CH_3 (Mes)], 1.30 (s, 18 H, S*t*Bu). ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 169.74 (N*C*N), 138.41 [*p*-*C* (Mes)], 136.95 [*o*-*C* (Mes)], 136.03 [N*C* (Mes)], 129.03 [*C*H (Mes)], 122.66 (MesN*C*H=), 122.53 (AlkN*C*H=), 50.94 (NCH_2), 42.68 [S*C*(CH$_3$)$_3$], 31.05 [SC(*C*H$_3$)$_3$], 29.24 (*C*H$_2$S), 21.27 (*p*-*C*H$_3$), 19.99 (*o*-*C*H$_3$) ppm. Minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.01 (s, 2 H, AlkNC*H*=), 6.90 [s, 4 H, C*H* (Mes)], 6.53 (s, 2 H, MesNC*H*=), 5.37 (s, 4 H, NCH_2), 3.62 (s, 4 H, CH_2S), 2.54 [s, 6 H, *p*-CH_3 (Mes)], 1.94 [s, 12 H, *o*-CH_3 (Mes)], 1.42 (s, 18 H, S*t*Bu) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 169.34 (N*C*N), 137.51 [*p*-*C* (Mes)], 136.23 [*o*-*C* (Mes)], 135.56 [N*C* (Mes)], 129.09 [*C*H (Mes)], 123.21 (MesN*C*H=), 121.90 (AlkN*C*H=), 51.26 (NCH_2), 42.95 [S*C*(CH$_3$)$_3$], 31.21 [SC(*C*H$_3$)$_3$], 29.43 (*C*H$_2$S), 21.38 (*p*-*C*H$_3$), 19.47(*o*-*C*H$_3$) ppm. MS (DCI[NH_3]): *m*/*z* (%) = 743 (100) [$C_{36}H_{52}BrN_4S_2Ni^+$].

{1-[2-(*tert*-Butylthio)ethyl]-3-(2,4,6-trimethylphenyl)imidazolium}-palladium Tribromide (12): $PdBr_2$(COD) (146 mg, 0.39 mmol) was added to a solution of **5** (165 mg, 0.43 mmol) in THF (15 mL). The mixture was stirred for 1 h at room temperature and filtered. The orange solid obtained was washed with THF (15 mL), dichloromethane (10 mL) and dried in vacuo. Yield 223 mg (88%). M.p. (dec.) 245 °C. $C_{18}H_{27}Br_3N_2PdS$ (649.62): calcd. C 33.28, H 4.19, N 4.31; found C 33.26, H 4.35, N 4.98. ^{1}H NMR (500 MHz, [D$_6$]-DMSO, 25 °C): δ = 9.46 (s, 1 H, NC*H*N), 8.12 (s, 1 H, MesNC*H*=), 7.91 (s, 1 H, AlkNC*H*=), 7.14 [s, 2 H, C*H* (Mes)], 4.44 (s, 2 H, NCH_2), 3.12 (s, 2 H, CH_2S*t*Bu), 2.34 (s, 3 H, *p*-CH_3), 2.04 (s, 6 H, *o*-CH_3), 1.28 (s, 9 H, S*t*Bu) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]-DMSO, 25 °C): δ = 140.78 [*p*-*C* (Mes)], 138.18 (N*C*HN), 134.8 [*o*-*C* (Mes)], 131.57 [N*C* (Mes)], 129.73 [*C*H (Mes)], 124.34 (AlkN*C*H=), 123.68 (MesN*C*H=), 49.9 (NCH_2), 43.22 [S*C*(CH$_3$)$_3$], 31.22 [SC(*C*H$_3$)$_3$], 28.31 (S*C*H$_2$), 21.08 [*p*-*C*H$_3$ (Mes)], 17.38 [*o*-*C*H$_3$ (Mes)] ppm. MS (FAB, MNBA matrix): *m*/*z* (%) = 303 (100) [$C_{18}H_{27}N_2S^+$]; 489 (1) [$C_{18}H_{26}BrN_2SPd^+$]; 569 (1) [$C_{18}H_{27}Br_2N_2SPd^+$].

{1-[2-(Ethylthio)ethyl]-3-(2,4,6-trimethylpenyl)imidazolium}-palladium Tribromide (13): $PdBr_2$(COD) (170 mg, 0.44 mmol) was added to a suspension of **6** (145 mg, 0.4 mmol) in THF (2 × 10 mL). The mixture was stirred for 2 h at room temperature and filtered. The orange solid obtained was washed with THF (15 mL) and dried in vacuo. Yield 250 mg (99%). M.p. 177–179 °C. $C_{16}H_{23}Br_3N_2PdS$ (621.57): calcd. C 30.92, H 3.73, N 4.51; found C 30.58, H 3.57, N 4.56. ^{1}H NMR (500 MHz, [D$_6$]Me$_2$CO, 25 °C): δ = 9.00 (t, ^{4}J = 1.7 Hz, 1 H, NC*H*N), 7.84 (t, $^{3,4}J$ = 1.7 Hz, 1 H, MesNC*H*=C), 7.50 (t, $^{3,4}J$ = 1.8 Hz, 1 H, AlkNC*H*=C), 7.13 [s, 2 H, C*H* (Mes)], 4.88 (t, ^{3}J = 4.3 Hz, 2 H, NCH_2), 3.49 (t, ^{3}J = 4.3 Hz, 2 H, CH_2SEt), 3.00 (q, ^{3}J = 7.2 Hz, 2 H, SCH_2CH$_3$), 2.35 (s, 3 H, *p*-CH_3), 2.06 (s, 6 H, *o*-CH_3), 1.16 (t, ^{3}J = 7.3 Hz, 3 H, SCH$_2$CH_3) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]Me$_2$CO, 25 °C): δ = 141.30 [*p*-*C* (Mes)], 137.10 (N*C*HN), 134.86 [*o*-*C* (Mes)], 130.87 [N*C* (Mes)], 129.45 [*C*H (Mes)], 124.16 (AlkN*C*H=), 123.42 (MesN*C*H=), 47.94 (NCH_2), 36.11 (*C*H$_2$SEt), 32.26 (S*C*H$_2$CH$_3$), 20.17 [*p*-*C*H$_3$ (Mes)], 16.90 [*o*-*C*H$_3$ (Mes)], 12.63 (SCH$_2$*C*H$_3$) ppm. MS (FAB, MNBA matrix): *m*/*z* (%) = 275 (100) [$C_{16}H_{23}N_2S^+$]; 461 (1) [$C_{16}H_{22}BrN_2PdS^+$]; 543 (0.9) [$C_{16}H_{23}Br_2N_2PdS^+$].

{1-[2-(*tert*-Butylthio)ethyl]-3-(2,6-diisopropylphenyl)imidazolium}-palladium Tribromide (14): $PdBr_2$(COD) (374 mg, 1.00 mmol) was added to a solution of **7** (400 mg, 0.94 mmol) in THF (15 mL). The mixture was stirred for 2 h at room temperature and filtered. The orange solid obtained was washed with THF (2 × 15 mL), CH_2Cl_2 (15 mL) and dried in vacuo. Yield 579 mg (89%). M.p. 210–212 °C. $C_{21}H_{33}Br_3N_2PdS$ (691.70): calcd. C 36.47, H 4.81, N 4.05; found C 36.60, H 4.49, N 3.87. ^{1}H NMR (500 MHz, [D$_6$]-DMSO, 25 °C): δ = 9.59 (s, 1 H, NC*H*N), 8.16 [s, 1 H, (DIPP)-NC*H*=C], 8.10 (s, 1 H, AlkNC*H*=C), 7.64 [t, ^{3}J = 7.8 Hz, 1 H, *p*-C*H* (DIPP)], 7.47 [d, ^{3}J = 7.8 Hz, 2 H, *m*-C*H* (DIPP)], 4.47 (t, 2 H, NCH_2), 3.13 (t, 2 H, CH_2S*t*Bu), 2.51 [h, ^{3}J = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 1.28 (s, 9 H, S*t*Bu), 1.16 [d, ^{3}J = 6.9 Hz, 6 H, CH-(CH_3)$_2$], 1.14 [d, ^{3}J = 6.9 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 145.64 [*o*-*C* (DIPP)], 138.71 (N*C*HN), 131.98 [*p*-*C*H (DIPP)], 130.98 [N*C* (DIPP)], 125.69 [(DIPP)N*C*H=], 124.91 [*m*-*C*H (DIPP)], 123.60 (AlkN*C*H=), 49.84 (NCH_2), 43.07 [S*C*(CH$_3$)$_3$], 31.17 [SC(*C*H$_3$)$_3$], 28.48 (*C*H$_2$S), 28.40

[*C*H(CH$_3$)$_2$], 24.33, 24.30 [CH(*C*H$_3$)$_2$] ppm. MS (FAB, MNBA matrix): *m*/*z* (%) = 345 (100) [$C_{21}H_{33}N_2S^+$]; 611 (1) [$C_{21}H_{33}Br_2N_2SPd^+$].

{1-[3-(*tert*-Butylthio)propyl]-3-(2,4,6-trimethylphenyl)imidazolium}-palladium Tribromide (15): $PdBr_2$(COD) (141 mg, 0.38 mmol) was added to a solution of **8** (180 mg, 0.45 mmol) in THF (10 mL). The mixture was stirred for 2 h at room temperature and filtered. The orange solid obtained was washed with THF (2 × 10 mL) and dried in vacuo. Yield 206 mg (82%). M.p. 200–202 °C. $C_{19}H_{29}Br_3N_2PdS$ (663.65): calcd. C 34.39, H 4.40, N 4.22; found C 35.21, H 4.34, N 3.92. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 9.45 (s, 1 H, NC*H*N), 8.13 (s, 1 H, MesNC*H*=C), 7.95 (s, 1 H, AlkNC*H*=C), 7.16 [s, 2 H, C*H* (Mes)], 4.38 (s, ^3J = 6.7 Hz, 2 H, NCH_2), 2.55 (s, ^3J = 6.8 Hz, 2 H, CH_2S*t*Bu), 2.30 (s, 3 H, *p*-CH_3), 2.17 (t, ^3J = 7.0 Hz, 2 H, NCH$_2$CH_2), 2.04 (s, 6 H, *o*-CH_3), 1.27 (s, 9 H, S*t*Bu) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 140.74 [s, *p*-*C* (Mes)], 137.87 (s, N*C*HN), 134.76 [s, *o*-*C* (Mes)], 131.63 [s, N*C* (Mes)], 129.73 [s, *C*H (Mes)], 124.51 (s, AlkN*C*H=), 123.73 (s, MesN*C*H=), 49.35 (s, N*C*H$_2$), 42.64 [s, S*C*(CH$_3$)$_3$], 31.08 [s, SC(*C*H$_3$)$_3$], 29.96 (s, NCH$_2$*C*H$_2$), 24.81 (s, *C*H$_2$S), 21.09 [s, *p*-*C*H$_3$ (Mes)], 17.41 [s, *o*-*C*H$_3$ (Mes)] ppm. MS (FAB, MNBA matrix): *m*/*z* (%) = 317 (100) [$C_{19}H_{29}N_2S^+$]; 503 (1) [$C_{19}H_{28}BrN_2SPd^+$]; 583 (1) [$C_{19}H_{29}Br_2N_2SPd^+$].

{1-[3-(*tert*-Butylthio)propyl]-3-(2,6-diisopropylphenyl)imidazolium}-palladium Tribromide (16): $PdBr_2$(COD) (374 mg, 1.00 mmol) was added to a solution of **9** (505 mg, 1.15 mmol) in THF (20 mL). The mixture was stirred for 2 h at room temperature and filtered. The orange solid obtained was washed with THF (2 × 15 mL), CH_2Cl_2 (15 mL) and dried in vacuo. Yield 642 mg (91%). M.p. 184–186 °C. $C_{22}H_{35}Br_3N_2PdS$ (705.73): calcd. C 37.44, H 5.00, N 3.97; found C 37.79, H 4.79, N 3.99. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 20 °C): δ = 9.61 (s, 1 H, NC*H*N), 8.18 (s, 1 H, AlkNC*H*=), 8.12 [s, 1 H, (DIPP)NC*H*=], 7.63 [s, 1 H, *p*-C*H* (DIPP)], 7.46 [s, 2 H, *m*-C*H* (DIPP)], 4.42 (s, 2 H, NCH_2), 2.53 (s, 2 H, CH_2S*t*Bu), 2.28 [s, 2 H, C*H*(CH$_3$)$_2$], 2.17 (s, 2 H, NCH$_2$CH_2), 1.27 (s, 9 H, S*t*Bu), 1.14 [s, 12 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 20 °C): δ = 145.56 [s, *o*-*C* (DIPP)], 138.12 (s, N*C*HN), 130.96 [s, N*C* (DIPP)], 131.97 [s, *p*-*C*H (DIPP)], 125.73 [s, (DIPP)N*C*H=], 124.90 [s, *m*-*C*H (DIPP)], 124.00 (s, AlkN*C*H=), 49.52 (s, N*C*H$_2$), 42.58 [s, S*C*(CH$_3$)$_3$], 31.05 [s, SC(*C*H$_3$)$_3$], 29.92 (s, NCH$_2$*C*H$_2$), 28.53 [s, *C*H(CH$_3$)$_2$], 24.76 (s, *C*H$_2$S), 24.34, 24.27 [s, CH(*C*H$_3$)$_2$] ppm. MS (FAB, MNBA matrix): *m*/*z* (%) = 359 (100) [$C_{22}H_{35}N_2S^+$]; 545 (1) [$C_{22}H_{34}BrN_2SPd^+$]; 625 (1) [$C_{22}H_{35}Br_2N_2SPd^+$].

{1-[2-(Ethylthio)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}-palladium Dibromide Dimer (17): A solution of *t*BuOK (42 mg, 0.38 mmol) in THF (15 mL) was slowly added to a suspension of **13** (117 mg, 0.19 mmol) in THF (15 mL). The mixture was stirred for 2 h at room temperature and the solvent removed in vacuo. The resulting solid was dissolved in CH_2Cl_2 and filtered through Celite. The product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/acetone, 9:1). The product was crystallised by layer diffusion of diethyl ether into a THF solution to give yellow orange crystals. Yield 64 mg (63%). M.p. (dec.) 240 °C. $C_{32}H_{44}Br_4N_4Pd_2S_2$ (1081.3): calcd. C 35.54, H 4.10, N 5.18; found C 36.14, H 4.04, N 5.03. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 7.28 (d, ^3J = 1.9 Hz, 2 H, NC*H*=), 7.05 [s, 4 H, C*H* (Mes)], 6.96 (d, ^3J = 1.8 Hz, 2 H, MesNC*H*=), 4.60 (br. s, 4 H, CH_2N), 3.35 (br. s, 4 H, SCH_2CH$_3$), 2.75 (br. s, 4 H, CH_2SEt), 2.39 [s, 6 H, *p*-CH_3 (Mes)], 2.24 [s, 12 H, *o*-CH_3 (Mes)], 1.53 (t, ^3J = 7.3 Hz, 6 H, SCH$_2$CH_3) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2, 25 °C): δ = 155.75 (N*C*N), 139.28 [*p*-*C* (Mes)], 135.69 [N*C* (Mes)], 134.79 [*o*-*C* (Mes)], 129.09 [*C*H (Mes)], 125.09, 121.56 (N*C*H=), 51.67 (N*C*H$_2$), 35.81 (S*C*H$_2$CH$_3$), 32.62 (*C*H$_2$SEt), 20.88 [*p*-*C*H$_3$ (Mes)], 19.10 [*o*-*C*H$_3$ (Mes)], 14.00 (SCH$_2$*C*H$_3$) ppm. MS (FAB, MNBA matrix): *m*/*z* (%) = 245 (100) [$C_{14}H_{17}N_2S^+$]; 275 (47) [$C_{16}H_{23}N_2S^+$]; 461 (7) [$C_{16}H_{22}BrN_2SPd^+$]; 1001 (3) [$C_{32}H_{44}Br_3N_4S_2Pd_2^+$].

{1-[2-(*tert*-Butylthio)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene-1,4-cyclooctadienyl}rhodium(I) Tetrafluoroborate (18): [Rh(COD)Cl]$_2$ (77.2 mg, 0.16 mmol) was stirred for 15 min at room temperature with *t*BuOK (38.6 mg, 0.34 mmol) in THF (4 mL). The dark yellow solution was slowly added to a solution of **5** (120.0 mg, 0.31 mmol) in THF (4 mL). The mixture was stirred overnight at room temperature and the solvent was removed under vacuum. $AgBF_4$ (122.0 mg, 0.63 mmol) and CH_2Cl_2 (10 mL) were added to the residue and the reaction was stirred at room temperature for two additional hours. The mixture was filtered through Celite, concentrated under vacuum and purified by column chromatography on silica gel (eluent: CH_2Cl_2/Me_2CO, 17:3) to give a yellow-orange hygroscopic solid (152 mg, 81%). Suitable X-ray crystals were obtained by layer diffusion of pentane into a $CDCl_3$ solution. M.p. 99–101 °C. $C_{26}H_{38}BF_4N_2RhS$ (600.38): calcd. C 52.01, H 6.38, N 4.67; found C 51.67, H 5.86, N 4.54. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 80 °C): δ = 7.64 (d, ^3J = 1.8 Hz, 1 H, AlkNC*H*=), 7.34 (d, ^3J = 1.7 Hz, 1 H, MesNC*H*=), 7.13 [s, 2 H, C*H* (Mes)], 4.85 [s, 2 H, C*H* (COD)], 4.62 (t, ^3J = 5.3 Hz, 2 H, CH_2N), 3.90 [br. s, 2 H, C*H* (COD)], 2.97 (t, ^3J = 5.3 Hz, 2 H, CH_2S*t*Bu), 2.36 (s, 3 H, *p*-CH_3), 2.11–2.26 [m + s, 8 H, *o*-CH_3; CH_2 (COD)], 1.82–2.06 [br. m, 6 H, CH_2 (COD)], 1.25 (s, 9 H, S*t*Bu) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 80 °C): δ = 173.63 (d, $^1J_{Rh-C}$ = 49.8 Hz, N*C*N), 139.41 [*p*-*C* (Mes)], 135.88 [N*C* (Mes)], 135.37 [*o*-*C* (Mes)], 129.46 [*C*H (Mes)], 125.54 (MesN*C*H=), 123.10 (AlkN*C*H=), 96.86, 81.86 [*C*H (COD)], 51.11 [S*C*(CH$_3$)$_3$], 50.06 (N*C*H$_2$), 31.90, 29.38 [*C*H$_2$ (COD)], 30.01 [SC(*C*H$_3$)$_3$], 27.54 (S*C*H$_2$), 20.88 [*p*-*C*H$_3$ (Mes)], 19.11 [*o*-*C*H$_3$ (Mes)] ppm. ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ = –76.73 (s, BF_4) ppm. MS (ESI): *m*/*z* (%) = 513.3 (100) [$C_{26}H_{38}N_2RhS^+$].

{1-[2-(*tert*-Butylthio)ethyl]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene-1,4-cyclooctadienyl}rhodium(I) Tetrafluoroborate (19): Compound **19** was prepared using the same procedure as for **18**, from compound **7** (95.0 mg, 0.22 mmol), [Rh(COD)Cl]$_2$ (55.0 mg, 0.11 mmol), *t*BuOK (27.6 mg, 0.25 mmol) and $AgBF_4$ (87.0 mg, 0.45 mmol). After purification, the product was recovered as a yellow-orange solid (113 mg, 79%). Suitable X-ray crystals were obtained by slow evaporation of a saturated ether solution. M.p. (slow dec.) >150 °C. $C_{29}H_{44}BF_4N_2RhS$ (642.46): calcd. C 54.22, H 6.90, N 4.36; found C 54.46, H 6.64, N 4.48. ^{1}H NMR (500 MHz, [D$_6$]-DMSO, 80 °C): δ = 7.67 (s, 1 H, AlkNC*H*=), 7.57 [t, ^3J = 7.8 Hz, 1 H, *p*-C*H* (DIPP)], 7.43 [s, 1 H, (DIPP)NC*H*=], 7.41 [d, ^3J = 7.8 Hz, 2 H, *m*-C*H* (DIPP)], 4.87 [s, 2 H, C*H* (COD)], 4.68 (s, 2 H, CH_2N), 3.92 [br. s, 2 H, C*H* (COD)], 3.01 (s, 2 H, CH_2S*t*Bu), 2.5–2.6 [br. s, 2 H, C*H*(CH$_3$)$_2$], 2.14–2.24 [m, 2 H, CH_2 (COD)], 1.90–2.04 [m, 4 H, CH_2 (COD)], 1.80–1.90 [m, 2 H, CH_2 (COD)], 1.35 [d, ^3J = 4.1 Hz, 6 H, CH(CH_3)$_2$], 1.28 (s, 9 H, S*t*Bu), 1.08 [d, ^3J = 6.7 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (125.8 MHz, [D$_6$]-DMSO, 80 °C): δ = 173.02 (d, $^1J_{Rh-C}$ = 50 Hz, N*C*N), 146.04 [*o*-*C* (DIPP)], 135.06 [N*C* (DIPP)], 130.76 [*p*-*C*H (DIPP)], 127.06 [(DIPP)N*C*H=], 124.51 [*m*-*C*H (DIPP)], 122.84 (AlkN*C*H=), 96.71, 81.21 [*C*H (COD)], 50.95 [S*C*(CH$_3$)$_3$], 50.33 (N*C*H$_2$), 31.73, 29.36 [*C*H$_2$ (COD)], 30.00 [SC(*C*H$_3$)$_3$], 28.44 [*C*H(CH$_3$)$_2$], 27.74 (S*C*H$_2$), 25.62, 23.51 [*C*H(CH$_3$)$_2$] ppm. ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ = –76.83 (s, BF_4) ppm. MS (FAB, MNBA matrix): *m*/*z* (%) = 555 (100) [$C_{29}H_{44}N_2RhS^+$].

{1-[β-(Ethylthio)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene-1,4-cyclooctadienyl}rhodium(I) Tetrafluoroborate (20): Compound

20 was prepared using the same procedure as for **18**, from compound **6** (40.0 mg, 0.11 mmol), $[Rh(COD)Cl]_2$ (27.8 mg, 0.06 mmol), *t*BuOK (13.9 mg, 0.12 mmol) and $AgBF_4$ (48.0 mg, 0.25 mmol). After purification, the product was recovered as a yellow-orange solid (49 mg, 76%). M.p. (dec.) >70 °C. $C_{24}H_{34}BF_4N_2RhS$ (572.32): calcd. C 50.37, H 5.98, N 4.89; found C 48.89, H 5.59, N 4.57. HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{34}N_2RhS$ 485.1498; found 485.1512. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 80 °C): δ = 7.65 (d, ^3J = 1.8 Hz, 1 H, AlkNC*H*=), 7.34 (d, ^3J = 1.8 Hz, 1 H, MesNC*H*=), 7.12 [s, 2 H, C*H* (Mes)], 4.72 [s, 2 H, C*H* (COD)], 4.65 (t, ^3J = 5.3 Hz, 2 H, CH_2N), 3.97 [br. s, 2 H, C*H* (COD)], 2.93 (t, ^3J = 5.3 Hz, 2 H, CH_2SEt), 2.65 (q, ^3J = 7.3 Hz, 2 H, SCH_2CH$_3$), 2.36 (s, 3 H, *p*-CH_3), 2.07–2.23 [m + s, 8 H, *o*-CH_3; CH_2 (COD)], 1.86–2.05 [br. m, 6 H, CH_2 (COD)], 1.30 (t, ^3J = 7.3 Hz, 3 H, SCH$_2$CH_3) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]-DMSO, 80 °C): δ = 173.72 (d, $^1J_{Rh-C}$ = 50.3 Hz, N*C*N), 139.38 [*p*-*C* (Mes)], 135.85 [N*C* (Mes)], 135.28 [*o*-*C* (Mes)], 129.33 [*C*H (Mes)], 125.13 (MesN*C*H=), 122.99 (AlkN*C*H=), 94.36 [d, $^1J_{Rh-C}$ = 7.3 Hz, *C*H (COD)], 83.56 [br. s, *C*H (COD)], 51.88 (N*C*H$_2$), 32.00 (S*C*H$_2$CH$_3$), 31.91 (*C*H$_2$SEt), 31.78, 29.61 [*C*H$_2$ (COD)], 27.54 (S*C*H$_2$), 20.92 [*p*-*C*H$_3$ (Mes)], 18.45 [*o*-*C*H$_3$ (Mes)], 14.49 (SCH$_2$*C*H$_3$) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –76.08 (BF_4) ppm. MS (ESI): *m*/*z* (%) = 485.7 (100) [$C_{24}H_{34}N_2RhS^+$].

CCDC-631917 to -631922 and -637108 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of compounds **21** and **4**; crystallographic data for compounds **5**, **6**, **11**, **17**–**20**.

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