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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.

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Abstract:

Five new, bifunctional imidazolium-thioether ligands of general formula $\text{RS}(\text{CH}_2)_n\text{Im}^+\text{Ar BF}_4^-$ ($n = 2$ or 3 , $\text{R} = \text{Et}$ or $t\text{-Bu}$, $\text{Ar} = 2,4,6\text{-trimethylphenyl}$ or $2,6\text{-diisopropylphenyl}$) 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],[3],[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-phosphine^[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 phosphines.^[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] Only few examples of carbene-thioether complexes were 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 phosphine-imidazolium compounds, using 1-bromoalkyl-3-aryl-imidazolium 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).

<Figure 1>

Results and Discussion

(a) Ligand syntheses

Compounds **5-7** were obtained from 1-(β -bromoethyl)-3-aryl imidazolium bromides **1** and **2**, and compounds **8** and **9** from 1-(γ -bromo-n-propyl)-3-aryl imidazolium 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 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.

<Scheme 1 and Table 1>

The ¹H NMR signals of the acidic imidazolium protons are observed between 10.03 and 10.28 ppm for compounds **5**, **6** and **8**, and at 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 analyzed 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>

(b) Nickel complexes

Preliminary complexation studies were carried out with the catalytically relevant metals nickel, palladium and rhodium. Our previous studies of the coordination of phosphine-imidazolium salts to Ni(II) complexes of type NiX_2L_2 led to the isolation of zwitterionic compounds of formula $[\text{NiX}_3(\text{PPh}_2\text{ImAr})]$, where ImAr is as defined in Scheme 1.^[5,6] The analogous reaction of **5** with one equivalent of $\text{NiBr}_2(\text{DME})$ 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 alternatively strategy consisting of initial deprotonation of ligand **5** with a strong base, followed by reaction of the resulting free carbene with $\text{NiBr}_2(\text{DME})$, 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 confirm one of these hypotheses, we added one equivalent of **6**, which contains a less bulky ethyl substituent, to one equivalent of $\text{NiBr}_2(\text{MeCN})_2$. 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>

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...Br1ⁱ = 2.75 Å). Selected bond distances and angles are listed in Table 2.

<Figure 3 and Table 2>

Although only one isomer is present in the crystal, analysis by ¹H and ¹³C NMR revealed a mixture of two distinct isomers in solution in a ratio of 1:1.27. We believe that these are conformational isomers. In the crystalline compound, the aryl and thioether alkyl chain 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 NiCl₂(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.

(c) Palladium complexes

Contrary to the nickel system, addition of ligands **5-9** to PdBr₂(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 ¹³C NMR properties are consistent with the expected stoichiometry, as for the related phosphine-carbene complexes previously described by Danopoulos^[7] and Lee.^[26] The ¹³C NMR signal of the carbenic carbon is observed at 155.75 ppm in the case of **17**, and respectively at 157.2 and 162.4 ppm for the abovementioned phosphine-carbene complexes. Moreover, the ¹H 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 carbenic carbon.

<Scheme 3>

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 centers in a relative *trans* arrangement. Pd-C and Pd-S bond lengths are comparable to 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 in *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>

(d) Rhodium complexes

Addition of compounds **5-7** to $[\text{Rh}(\text{COD})\text{Cl}]_2$ in the presence of a strong base (Scheme 4) led, after halide abstraction, to the formation of NHC derivatives **18-20**. The 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 carbenic carbons 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 (ca. 7 ppm) of the quaternary carbon on sulfur for complexes **18** and **19**, and of the $\text{S}-\text{CH}_2\text{CH}_3$ carbon signal (ca. 6 ppm) for complex **20**.^[29]

<Scheme 4>

The square planar coordination environment in complexes **18** to **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 $\text{Rh1}-\text{C1}$ bond lengths than in Seo's NHC-thioether complex. $\text{Rh1}-\text{S1}$ distances are within the same range, except compound **20**, for which we observe a shorter bond of 2.351(2) Å. The $\text{Rh1}-\text{C}(\text{COD})$ 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 6-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 $\text{C1}-\text{Rh1}-\text{S1}$ angle [82.5(2)°] could find an explanation in the existence of a close contact between the methylene of the ethyl arm on sulfur (C311) and the COD ligand [intramolecular distances: $\text{C5}-\text{C311} = 3.45(1)$ Å and $\text{H5}-\text{H31A} = 2.36$ Å; $\text{C6}-\text{C311} =$

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.

<Figure 5 and Table 3>

(e) Catalytic hydrosilylation of methyl aryl ketones

The catalyzed hydrosilylation of ketones has attracted a lot of attention for many decades since 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 pre-catalysts derived from $\text{RhCl}(\text{PPh}_3)_3$,^[32,33] $[\text{RhCl}(\text{olefin})_2]_2$ (olefin = ethylene, cyclooctene; or (olefin)₂ = 1,5-cyclooctadiene, norbornadiene),^[33-36] $\text{RhH}(\text{PPh}_3)_4$ ^[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 ($\text{X} = \text{OSO}_2\text{CF}_3, \text{BF}_4$) is required in some cases to improve the catalytic activity,^[38,41] presumably via 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. Since NHC ligands are likely to be solidly anchored to the metal center, 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 interesting to test the catalytic activity of the cationic rhodium complexes **18** to **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 1M in acetophenone in THF, the yield reached 90% after 24h. However, working in a more concentrated medium allowed us to get a total conversion of the substrate into the alcohol in only 4h (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 1h 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 6h, 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.

<Scheme 5 and Table 4>

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 5h.^[12]

The higher catalytic activity observed at higher ketone concentration agrees with previous reports of a saturation effect: the reaction was found 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 via 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, are 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 a dry argon atmosphere using Schlenk glassware and vacuum line techniques, and dry, purified solvents. All others steps were done without particular precautions. Elemental analyses were carried out by the “Service d’Analyse du Laboratoire de Chimie de Coordination” in Toulouse. ¹H and ¹³C{¹H} NMR data were recorded on a Bruker AV-500 spectrometer, operating

respectively at 500 MHz for ^1H 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 (^1H), 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. $\text{PdBr}_2(\text{COD})$,^[45] 1-(β -bromoethyl)-3-(2,4,6-trimethylphenyl) imidazolium bromide **1**,^[6] 1-(β -bromoethyl)-3-(2,6-diisopropylphenyl) imidazolium bromide **2**^[6] and 1-(γ -bromo-*n*-propyl)-3-(2,4,6-trimethylphenyl) imidazolium bromide **3**^[6] were prepared as described in the literature. Both lithium alkylthiolates were prepared by action of methyl lithium on the corresponding thiols and used rapidly after their preparation. Other reagents were obtained from commercial sources and used as received.

1-(β -(*tert*-butylthio)-ethyl)-3-(2,4,6-trimethylphenyl) imidazolium bromide, 5. *t*-BuSLi (19 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 colorless crystals were obtained by slow diffusion of diethyl ether in a CH_2Cl_2 solution. Mp 88-92°C. $\text{C}_{18}\text{H}_{27}\text{BrN}_2\text{S}$ (383.42): HRMS (ESI) *m/z*: calcd: 303.189496, found: 303.190467. ^1H NMR (500 MHz, CDCl_3 , 25°C): δ = 10.03 (t, 4J = 1.6 Hz, 1H, NCHN), 8.13 (t, $^{3,4}J$ = 1.5 Hz, 1H, MesNCH=), 7.19 (t, $^{3,4}J$ = 1.6 Hz, 1H, AlkN-CH=), 6.97 (s, 2H, CH (Mes)), 4.89 (t, 3J = 6.0 Hz, 2H, NCH₂), 3.17 (t, 3J = 6.1 Hz, 2H, CH₂*St*-Bu), 2.31 (s, 3H, *p*-CH₃), 2.06 (s, 6H, *o*-CH₃), 1.27 (s, 9H, *St*-Bu). ^{13}C NMR (125.8 MHz, CDCl_3 , 25°C): δ = 141.26 (*p*-C (Mes)), 137.77 (N-CH-N), 134.31 (*o*-C (Mes)), 130.66 (N-C (Mes)), 129.81 (CH (Mes)), 124.13 (AlkN-CH=), 122.74 (MesN-CH=), 50.33 (N-CH₂), 43.33 (SC(CH₃)₃), 31.00 (SC(CH₃)₃), 29.32 (CH₂S), 21.11 (*p*-CH₃ (Mes)), 17.66 (*o*-CH₃

(Mes)). 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-(β -(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 x 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. Mp 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%. 1H NMR (500 MHz, $CDCl_3$, 25°C): δ = 10.08 (s, 1H, NCHN), 8.26 (s, 1H, MesNCH=), 7.16 (s, 1H, AlkNCH=), 6.94 (s, 2H, CH (Mes)), 4.90 (t, 3J = 6.0 Hz, 2H, NCH₂), 3.09 (t, 3J = 6.1 Hz, 2H, CH₂SEt), 2.62 (q, 3J = 7.4 Hz, 2H, SCH₂CH₃), 2.29 (s, 3H, *p*-CH₃), 2.02 (s, 6H, *o*-CH₃), 1.16 (t, 3J = 7.4 Hz, 3H, SCH₂CH₃). ^{13}C NMR (125.8 MHz, $CDCl_3$, 25°C): δ = 141.11 (*p*-C (Mes)), 137.97 (NCHN), 134.29 (*o*-C (Mes)), 130.67 (NC (Mes)), 129.73 (CH (Mes)), 123.98 (AlkNCH=), 122.93 (MesNCH=), 48.88 (NCH₂), 32.14 (CH₂SEt), 25.67 (SCH₂CH₃), 21.07 (*p*-CH₃ (Mes)), 17.61 (*o*-CH₃ (Mes)), 14.61 (SCH₂CH₃). 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-(β -(*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 x 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%). Mp 85-90°C. $C_{21}H_{33}BrN_2S$ (425.48); HRMS (ESI) m/z : calcd: 345.236446, found: 345.236823. 1H NMR (500 MHz, $CDCl_3$, 25°C): δ = 9.87 (t, 4J = 1.7 Hz, 1H, NCHN), 8.38 (t, $^{3,4}J$ = 1.7 Hz, 1H, AlkNCH=), 7.47 (t, 3J = 7.8 Hz, 1H, *p*-CH (DIPP)), 7.24 (d, 3J = 7.8 Hz, 2H, *m*-CH (DIPP)), 7.16 (t, $^{3,4}J$ = 1.7 Hz, 1H, (DIPP)NCH=), 4.91 (t, 3J = 5.9 Hz, 2H, NCH₂), 3.16 (t, 3J = 5.9 Hz, 2H, CH₂St-Bu), 2.28

(h, $^3J = 6.8; 6.9$ Hz, 2H, $CH(CH_3)_2$), 1.24 (s, 9H, *St*-Bu), 1.15 (d, $^3J = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.09 (d, $^3J = 6.8$ Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$, 25°C): $\delta = 145.42$ (*o*-C (DIPP)), 137.94 (NCHN), 131.82 (*p*-CH (DIPP)), 130.07 (NC (DIPP)), 124.60 (*m*-CH (DIPP)), 124.27 (AlkNCH=), 123.84 ((DIPP)NCH=), 50.10 (NCH₂), 43.13 (SC(CH₃)₃), 30.99 (SC(CH₃)₃), 29.39 (CH₂S), 28.48 ($CH(CH_3)_2$), 24.40, 24.21 ($CH(CH_3)_2$). 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-(γ -(*tert*-butylthio)-*n*-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 x 10 mL). The organic phase was dried (MgSO₄), filtered and concentrated under vacuum to give a white, hygroscopic solid. Yield: 290 mg (73%). Mp 134-136°C. $C_{19}H_{29}N_2SBr$ (397.42): HRMS (ESI) m/z : calcd: 317.205146, found: 317.204589. 1H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 10.28$ (t, $^4J = 1.5$ Hz, 1H, NCHN), 7.93 (t, $^3, ^4J = 1.7$ Hz, 1H, NCH=), 7.24 (t, $^3, ^4J = 1.7$ Hz, 1H, =CHN), 6.98 (s, 2H, CH (Mes)), 4.81 (t, $^3J = 6.9$ Hz, 2H, NCH₂), 2.63 (t, $^3J = 6.9$ Hz, 2H, CH_2St -Bu), 2.32 (q + s, $^3J = 6.9$ Hz, 5H, *p*-CH₃ ; NCH₂CH₂), 2.06 (s, 6H, *o*-CH₃), 1.27 (s, 9H, *St*-Bu). ^{13}C NMR (125.8 MHz, $CDCl_3$, 25°C): $\delta = 141.27$ (s, *p*-C (Mes)), 137.99 (s, NCHN), 134.16 (s, *o*-C (Mes)), 130.67 (s, NC (Mes)), 129.86 (s, CH (Mes)), 123.42 (s, =CHN), 123.25 (s, =CH-N), 49.37 (s, NCH₂), 42.69 (s, SC(CH₃)₃), 30.83 (s, SC(CH₃)₃), 30.63 (s, NCH₂CH₂), 24.66 (s, CH₂S), 21.10 (s, *p*-CH₃ (Mes)), 17.71 (s, *o*-CH₃ (Mes)). 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-(γ -(*tert*-butylthio)-*n*-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 x 15 mL). The organic phase was dried (MgSO₄), filtered and concentrated under vacuum to give a pale yellow hygroscopic solid. Yield: 318 mg (69%). Mp 103-104°C. $C_{22}H_{35}BrN_2S$ (439.50): HRMS (ESI) m/z : calcd: 359.252096, found: 359.253029. 1H NMR (500

MHz, CDCl₃, 25°C): δ = 9.87 (s, 1H, NCHN), 8.14 (t, ³J = 1.7Hz, 1H, AlkNCH=), 7.39 (t, ³J = 7.8Hz, 1H, *p*-CH (DIPP)), 7.25 (d, ³J = 7.9Hz, 2H, *m*-CH (DIPP)), 7.23 (t, ³J = 1.7Hz, 1H, (DIPP)NCH=), 4.84 (t, ³J = 6.8Hz, 2H, NCH₂), 2.61 (t, ³J = 7.1Hz, 2H, CH₂St-Bu), 2.30 (q, ³J = 6.9; 7.0Hz, 2H, NCH₂CH₂), 2.25 (h, ³J = 6.9Hz, 2H, CH(CH₃)₂), 1.26 (s, 9H, St-Bu), 1.17 (d, ³J = 6.8Hz, 6H, CH(CH₃)₂), 1.10 (d, ³J = 6.8Hz, 6H, CH(CH₃)₂). ¹³C NMR (125.8 MHz, CDCl₃, 25°C): δ = 145.29 (s, *o*-C (DIPP)), 138.08 (s, NCHN), 131.85 (s, *p*-CH (DIPP)), 130.13 (s, NC (DIPP)), 124.63 (s, *m*-CH (DIPP)), 124.30 (s, AlkNCH=), 123.75 (s, (DIPP)NCH=), 49.43 (s, NCH₂), 42.61 (s, SC(CH₃)₃), 30.90 (s, SC(CH₃)₃), 30.82 (s, NCH₂CH₂), 28.67 (s, CH(CH₃)₂), 24.59 (s, CH₂S), 24.40; 24.19 (s, CH(CH₃)₂). MS (ESI, positive mode): *m/z* (%) = 359.4, (100) [C₂₂H₃₅N₂S⁺]; MS (ESI, negative mode): *m/z* (%) = 80.8, (100) [Br⁻].

Complexes preparation

Bis-[1-(β -(*tert*-butylthio)-ethyl)-3-(2,4,6-trimethylphenyl) imidazol-2-ylidene] nickel dibromide, 11. NiBr₂(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 homogenous blue-green solution was obtained. A freshly prepared KN(SiMe₃)₂ solution (5 mL, 0.2M 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 (*ca.* 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. Mp 195-200°C, dec. C₃₆H₅₂Br₂N₄S₂Ni (823.47) Calcd: C 52.51, H 6.37, N 6.80%; found: C 52.45, H 6.39, N 6.56%. In NMR, two isomers can be observed with a 1.27:1 ratio. Major isomer: ¹H NMR (500 MHz, CDCl₃, 25°C): δ = 7.09 (s, 4H, CH (Mes)), 6.97 (s, 2H, AlkNCH=), 6.60 (s, 2H, MesNCH=), 4.92 (s, 4H, NCH₂), 3.18 (s, 4H, CH₂S), 2.45 (s, 6H, *p*-CH₃ (Mes)), 2.23 (s, 12H, *o*-CH₃ (Mes)), 1.30 (s, 18H, St-Bu). ¹³C NMR (125.8 MHz, CDCl₃, 25°C): δ = 169.74 (NCN), 138.41 (*p*-C (Mes)), 136.95 (*o*-C (Mes)), 136.03 (NC (Mes)), 129.03 (CH (Mes)), 122.66

(MesNCH=), 122.53 (AlkNCH=), 50.94 (NCH₂), 42.68 (SC(CH₃)₃), 31.05 (SC(CH₃)₃), 29.24 (CH₂S), 21.27 (*p*-CH₃), 19.99 (*o*-CH₃). Minor isomer: ¹H NMR (500 MHz, CDCl₃, 25°C): δ = 7.01 (s, 2H, AlkNCH=), 6.90 (s, 4H, CH (Mes)), 6.53 (s, 2H, MesNCH=), 5.37 (s, 4H, NCH₂), 3.62 (s, 4H, CH₂S), 2.54 (s, 6H, *p*-CH₃ (Mes)), 1.94 (s, 12H, *o*-CH₃ (Mes)), 1.42 (s, 18H, *St*-Bu). ¹³C NMR (125.8 MHz, CDCl₃, 25°C): δ = 169.34 (NCN), 137.51 (*p*-C (Mes)), 136.23 (*o*-C (Mes)), 135.56 (NC (Mes)), 129.09 (CH (Mes)), 123.21 (Mes-NCH=), 121.90 (Alk-NCH=), 51.26 (NCH₂), 42.95 (SC(CH₃)₃), 31.21 (SC(CH₃)₃), 29.43 (CH₂S), 21.38 (*p*-CH₃), 19.47(*o*-CH₃). MS (DCI[NH₃]): *m/z* (%) = 743, (100) [C₃₆H₅₂BrN₄S₂Ni⁺].

1-(β-(*tert*-butylthio)ethyl)-3-(2,4,6-trimethylphenyl) imidazolium palladium tribromide, 12.

PdBr₂(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 hour 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%). Mp 245°C dec. C₁₈H₂₇Br₃N₂SPd (649.62) Calcd: C 33.28, H 4.19, N 4.31%; found: C 33.26, H 4.35, N 4.98%. ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ = 9.46 (s, 1H, NCHN), 8.12 (s, 1H, MesNCH=), 7.91 (s, 1H, AlkNCH=), 7.14 (s, 2H, CH (Mes)), 4.44 (s, 2H, NCH₂), 3.12 (s, 2H, CH₂*St*-Bu), 2.34 (s, 3H, *p*-CH₃), 2.04 (s, 6H, *o*-CH₃), 1.28 (s, 9H, *St*-Bu). ¹³C NMR (125.8 MHz, DMSO-*d*₆, 25°C): δ = 140.78 (*p*-C (Mes)), 138.18 (NCHN), 134.8 (*o*-C (Mes)), 131.57 (NC (Mes)), 129.73 (CH (Mes)), 124.34 (AlkNCH=), 123.68 (MesNCH=), 49.9 (NCH₂), 43.22 (SC(CH₃)₃), 31.22 (SC(CH₃)₃), 28.31 (SCH₂), 21.08 (*p*-CH₃ (Mes)), 17.38 (*o*-CH₃ (Mes)). MS (FAB, MNBA matrix): *m/z* (%) = 303, (100) [C₁₈H₂₇N₂S⁺]; 489, (1) [C₁₈H₂₆BrN₂SPd⁺]; 569, (1) [C₁₈H₂₇Br₂N₂SPd⁺].

1-(β-(ethylthio)ethyl)-3-(2,4,6-trimethylphenyl)imidazolium palladium tribromide, 13.

PdBr₂(COD) (170 mg, 0.44 mmol) was added to a suspension of **6** (145 mg, 0.4 mmol) in THF (2 x 10 mL). The mixture was stirred for 2 hours at room temperature and filtered. The orange solid obtained was washed with THF (15 mL) and dried in vacuo. Yield: 250 mg (99%). Mp 177-179°C. C₁₆H₂₃Br₃N₂SPd (621.57) Calcd: C 30.92, H 3.73, N 4.51%; found: C 30.58, H 3.57, N 4.56%. ¹H

NMR (500 MHz, Me₂CO-*d*₆, 25°C): δ = 9.00 (t, ⁴*J* = 1.7 Hz, 1H, NCHN), 7.84 (t, ^{3,4}*J* = 1.7 Hz, 1H, MesNCH=C), 7.50 (t, ^{3,4}*J* = 1.8 Hz, 1H, AlkNCH=C), 7.13 (s, 2H, CH (Mes)), 4.88 (t, ³*J* = 4.3 Hz, 2H, NCH₂), 3.49 (t, ³*J* = 4.3 Hz, 2H, CH₂SEt), 3.00 (q, ³*J* = 7.2 Hz, 2H, SCH₂CH₃), 2.35 (s, 3H, *p*-CH₃), 2.06 (s, 6H, *o*-CH₃), 1.16 (t, ³*J* = 7.3 Hz, 3H, SCH₂CH₃). ¹³C NMR (125.8 MHz, Me₂CO-*d*₆, 25°C): δ = 141.30 (*p*-C (Mes)), 137.10 (NCHN), 134.86 (*o*-C (Mes)), 130.87 (NC (Mes)), 129.45 (CH (Mes)), 124.16 (AlkNCH=), 123.42 (MesNCH=), 47.94 (NCH₂), 36.11 (CH₂SEt), 32.26 (SCH₂CH₃), 20.17 (*p*-CH₃ (Mes)), 16.90 (*o*-CH₃ (Mes)), 12.63 (SCH₂CH₃). MS (FAB, MNBA matrix): *m/z* (%) = 275, (100) [C₁₆H₂₃N₂S⁺]; 461, (1) [C₁₆H₂₂BrN₂PdS⁺]; 543, (0.9) [C₁₆H₂₃Br₂N₂PdS⁺].

1-(β-(*tert*-butylthio)ethyl)-3-(2,6-diisopropylphenyl) imidazolium palladium tribromide, 14.

PdBr₂(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 hours at room temperature and filtered. The orange solid obtained was washed with THF (2 x 15 mL), CH₂Cl₂ (15 mL) and dried in vacuo. Yield: 579 mg (89%). Mp 210-212°C. C₂₁H₃₃Br₃N₂SPd (691.70) Calcd: C 36.47, H 4.81, N 4.05%; found: C 36.60, H 4.49, N 3.87%. ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ = 9.59 (s, 1H, NCHN), 8.16 (s, 1H, (DIPP)NCH=C), 8.10 (s, 1H, AlkNCH=C), 7.64 (t, ³*J* = 7.8 Hz, 1H, *p*-CH (DIPP)), 7.47 (d, ³*J* = 7.8 Hz, 2H, *m*-CH (DIPP)), 4.47 (t, 2H, NCH₂), 3.13 (t, 2H, CH₂St-Bu), 2.51 (h, ³*J* = 6.8 Hz, 2H, CH(CH₃)₂), 1.28 (s, 9H, St-Bu), 1.16 (d, ³*J* = 6.9 Hz, 6H, CH(CH₃)₂), 1.14 (d, ³*J* = 6.9 Hz, 6H, CH(CH₃)₂). ¹³C NMR (125.8 MHz, DMSO-*d*₆, 25°C): δ = 145.64 (*o*-C (DIPP)), 138.71 (NCHN), 131.98 (*p*-CH (DIPP)), 130.98 (NC (DIPP)), 125.69 ((DIPP)NCH=), 124.91 (*m*-CH (DIPP)), 123.60 (AlkNCH=), 49.84 (NCH₂), 43.07 (SC(CH₃)₃), 31.17 (SC(CH₃)₃), 28.48 (CH₂S), 28.40 (CH(CH₃)₂), 24.33, 24.30 (CH(CH₃)₂). MS (FAB, MNBA matrix): *m/z* (%) = 345, (100) [C₂₁H₃₃N₂S⁺]; 611, (1) [C₂₁H₃₃Br₂N₂SPd⁺].

1-(γ-(*tert*-butylthio)-*n*-propyl)-3-(2,4,6-trimethylphenyl) imidazolium palladium tribromide, 15.

PdBr₂(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 hours at room temperature and filtered. The orange solid

obtained was washed with THF (2 x 10 mL), and dried in vacuo. Yield: 206 mg (82%). Mp 200-202°C. C₁₉H₂₉Br₃N₂SPd (663.65) Calc: C 34.39, H 4.40, N 4.22 %; found: C 35.21, H 4.34, N 3.92, %. ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ = 9.45 (s, 1H, NCHN), 8.13 (s, 1H, MesNCH=C), 7.95 (s, 1H, AlkNCH=C), 7.16 (s, 2H, CH (Mes)), 4.38 (s, ³J = 6.7Hz, 2H, NCH₂), 2.55 (s, ³J = 6.8Hz, 2H, CH₂St-Bu), 2.30 (s, 3H, *p*-CH₃), 2.17 (t, ³J = 7.0Hz, 2H, NCH₂CH₂), 2.04 (s, 6H, *o*-CH₃), 1.27 (s, 9H, St-Bu). ¹³C NMR (125.8 MHz, DMSO-*d*₆, 25°C): δ = 140.74 (s, *p*-C (Mes)), 137.87 (s, NCHN), 134.76 (s, *o*-C (Mes)), 131.63 (s, NC (Mes)), 129.73 (s, CH (Mes)), 124.51 (s, AlkNCH=), 123.73 (s, MesNCH=), 49.35 (s, NCH₂), 42.64 (s, SC(CH₃)₃), 31.08 (s, SC(CH₃)₃), 29.96 (s, NCH₂CH₂), 24.81 (s, CH₂S), 21.09 (s, *p*-CH₃ (Mes)), 17.41 (s, *o*-CH₃ (Mes)). MS (FAB, MNBA matrix): m/z (%) = 317, (100) [C₁₉H₂₉N₂S⁺]; 503, (1) [C₁₉H₂₈BrN₂SPd⁺]; 583, (1) [C₁₉H₂₉Br₂N₂SPd⁺].

1-(γ-(*tert*-butylthio)-*n*-propyl)-3-(2,6-diisopropylphenyl) imidazolium palladium tribromide, 16. PdBr₂(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 hours at room temperature and filtered. The orange solid obtained was washed with THF (2 x 15 mL), CH₂Cl₂ (15 mL) and dried in vacuo. Yield: 642 mg (91%). Mp 184-186°C. C₂₂H₃₅Br₃N₂SPd (705.73) Calc: C 37.44, H 5.00, N 3.97%; found: C 37.79, H 4.79, N 3.99%. ¹H NMR (500 MHz, DMSO-*d*₆, 20°C): δ = 9.61 (s, 1H, NCHN), 8.18 (s, 1H, AlkNCH=), 8.12 (s, 1H, (DIPP)NCH=), 7.63 (s, 1H, *p*-CH (DIPP)), 7.46 (s, 2H, *m*-CH (DIPP)), 4.42 (s, 2H, NCH₂), 2.53 (s, 2H, CH₂St-Bu), 2.28 (s, 2H, CH(CH₃)₂), 2.17 (s, 2H, NCH₂CH₂), 1.27 (s, 9H, St-Bu), 1.14 (s, 12H, CH(CH₃)₂). ¹³C NMR (125.8 MHz, DMSO-*d*₆, 20°C): δ = 145.56 (s, *o*-C (DIPP)), 138.12 (s, NCHN), 130.96 (s, NC (DIPP)), 131.97 (s, *p*-CH (DIPP)), 125.73 (s, (DIPP)NCH=), 124.90 (s, *m*-CH (DIPP)), 124.00 (s, AlkNCH=), 49.52 (s, NCH₂), 42.58 (s, SC(CH₃)₃), 31.05 (s, SC(CH₃)₃), 29.92 (s, NCH₂CH₂), 28.53 (s, CH(CH₃)₂), 24.76 (s, CH₂S), 24.34; 24.27 (s, CH(CH₃)₂). MS (FAB, MNBA matrix): m/z (%) = 359, (100) [C₂₂H₃₅N₂S⁺]; 545, (1) [C₂₂H₃₄BrN₂SPd⁺]; 625, (1) [C₂₂H₃₅Br₂N₂SPd⁺].

1-(β -(ethylthio)ethyl)-3-(2,4,6-trimethylphenyl)imidazo-2-ylidene palladium dibromide dimer, 17. To a suspension of **13** (117 mg, 0.19 mmol) in THF (15 mL) was slowly added a solution of *t*-BuOK (42 mg, 0.38 mmol) in THF (15 mL). The mixture was stirred for 2 hours at room temperature and the solvent removed in vacuo. The resulting solid was dissolved in CH₂Cl₂ and filtered on Celite. The product was purified by column chromatography on silica gel (eluent: CH₂Cl₂: acetone 9:1). The product was crystallised by layers diffusion of diethyl ether into a THF solution to give yellow orange crystals. Yield: 64 mg (63%). Mp 240°C, dec. C₃₂H₄₄Br₄N₄S₂Pd₂ (1081.3) Calcd: C 35.54, H 4.10, N 5.18%; found: C 36.14, H 4.04, N 5.03%. ¹H NMR (500 MHz, CD₂Cl₂, 25°C): δ = 7.28 (d, ³J = 1.9 Hz, 2H, NCH=), 7.05 (s, 4H, CH (Mes)), 6.96 (d, ³J = 1.8 Hz, 2H, MesNCH=), 4.60 (br s, 4H, CH₂N), 3.35 (br s, 4H, SCH₂CH₃), 2.75 (br s, 4H, CH₂SEt), 2.39 (s, 6H, *p*-CH₃ (Mes)), 2.24 (s, 12H, *o*-CH₃ (Mes)), 1.53 (t, ³J = 7.3 Hz, 6H, SCH₂CH₃). ¹³C NMR (125.8 MHz, CD₂Cl₂, 25°C): δ = 155.75 (NCN), 139.28 (*p*-C (Mes)), 135.69 (NC (Mes)), 134.79 (*o*-C (Mes)), 129.09 (CH (Mes)), 125.09, 121.56 (NCH=), 51.67 (NCH₂), 35.81 (SCH₂CH₃), 32.62 (CH₂SEt), 20.88 (*p*-CH₃ (Mes)), 19.10 (*o*-CH₃ (Mes)), 14.00 (SCH₂CH₃). MS (FAB, MNBA matrix): m/z (%) = 245, (100) [C₁₄H₁₇N₂S⁺]; 275, (47) [C₁₆H₂₃N₂S⁺]; 461, (7) [C₁₆H₂₂BrN₂SPd⁺]; 1001, (3) [C₃₂H₄₄Br₃N₄S₂Pd₂⁺].

1-(β -(*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, 0.143 mmol) in THF (4 mL). The mixture was stirred overnight at room temperature and the solvent was removed under vacuum. AgBF₄ (122.0 mg, 0.63 mmol) and CH₂Cl₂ (10 mL) were added to the residue and the reaction was stirred at room temperature for two additional hours. The mixture was filtered on Celite, concentrated under vacuum and purified by column chromatography on silica gel (eluent: CH₂Cl₂:Me₂CO 17:3) to give a yellow-orange hygroscopic solid (152 mg, 81%). Suitable X-ray crystals were obtained by layers diffusion of pentane into a CDCl₃ solution. Mp 99-101°C. C₂₆H₃₈BF₄N₂RhS (600.38) Calcd: C

52.01, H 6.38, N 4.67%; found: C 51.67, H 5.86, N 4.54%. ^1H NMR (500 MHz, DMSO- d_6 , 80°C) : δ = 7.64 (d, 3J = 1.8 Hz, 1H, AlkNCH=), 7.34 (d, 3J = 1.7 Hz, 1H, MesNCH=), 7.13 (s, 2H, CH (Mes)), 4.85 (s, 2H, CH (COD)), 4.62 (t, 3J = 5.3 Hz, 2H, CH₂N), 3.90 (br s, 2H, CH (COD)), 2.97 (t, 3J = 5.3 Hz, 2H, CH₂St-Bu), 2.36 (s, 3H, *p*-CH₃), 2.11-2.26 (m + s, 8H, *o*-CH₃; CH₂ (COD)), 1.82-2.06 (br m, 6H, CH₂ (COD)), 1.25 (s, 9H, St-Bu). ^{13}C NMR (125.8 MHz, DMSO- d_6 , 80°C) : δ = 173.63 (d, $^1J_{\text{Rh-C}}$ = 49.8 Hz, NCN), 139.41 (*p*-C (Mes)), 135.88 (NC (Mes)), 135.37 (*o*-C (Mes)), 129.46 (CH (Mes)), 125.54 (MesNCH=), 123.10 (AlkNCH=), 96.86, 81.86 (CH (COD)), 51.11 (SC(CH₃)₃), 50.06 (NCH₂), 31.90, 29.38 (CH₂ (COD)), 30.01 (SC(CH₃)₃), 27.54 (SCH₂), 20.88 (*p*-CH₃ (Mes)), 19.11 (*o*-CH₃ (Mes)). ^{19}F NMR (188 MHz, CDCl₃, 25°C) : δ = -76.73 (s, BF₄). MS (ESI): *m/z* (%) = 513.3, (100) [C₂₆H₃₈N₂RhS⁺].

1-(β -(*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 AgBF₄ (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. Mp: slow decomposition after 150°C. C₂₉H₄₄BF₄N₂RhS (642.46) Calcd: C 54.22, H 6.90, N 4.36%; found: C 54.46, H 6.64, N 4.48%. ^1H NMR (500 MHz, DMSO- d_6 , 80°C) : δ = 7.67 (s, 1H, AlkNCH=), 7.57 (t, 3J = 7.8 Hz, 1H, *p*-CH (DIPP)), 7.43 (s, 1H, (DIPP)NCH=), 7.41 (d, 3J = 7.8 Hz, 2H, *m*-CH (DIPP)), 4.87 (s, 2H, CH (COD)), 4.68 (s, 2H, CH₂N), 3.92 (br s, 2H, CH (COD)), 3.01 (s, 2H, CH₂St-Bu), 2.5-2.6 (br s, 2H, CH(CH₃)₂), 2.14-2.24 (m, 2H, CH₂ (COD)), 1.90-2.04 (m, 4H, CH₂ (COD)), 1.80-1.90 (m, 2H, CH₂ (COD)), 1.35 (d, 3J = 4.1 Hz, 6H, CH(CH₃)₂), 1.28 (s, 9H, St-Bu), 1.08 (d, 3J = 6.7 Hz, 6H, CH(CH₃)₂). ^{13}C NMR (125.8 MHz, DMSO- d_6 , 80°C) : δ = 173.02 (d, $^1J_{\text{Rh-C}}$ = 50 Hz, NCN), 146.04 (*o*-C (DIPP)), 135.06 (NC (DIPP)), 130.76 (*p*-CH (DIPP)), 127.06 ((DIPP)NCH=), 124.51 (*m*-CH (DIPP)), 122.84 (AlkNCH=), 96.71, 81.21 (CH (COD)), 50.95 (SC(CH₃)₃), 50.33 (NCH₂), 31.73, 29.36 (CH₂ (COD)), 30.00 (SC(CH₃)₃), 28.44 (CH(CH₃)₂), 27.74 (SCH₂), 25.62, 23.51 (CH(CH₃)₂). ^{19}F NMR (188 MHz,

CDCl₃, 25°C) : δ = -76.83 (s, BF₄). MS (FAB, MNBA matrix): m/z (%) = 555, (100) [C₂₉H₄₄N₂RhS⁺].

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 AgBF₄ (48.0 mg, 0.25 mmol).. After purification, the product was recovered as a yellow-orange solid (49 mg, 76%). Mp: >70°C dec. C₂₄H₃₄BF₄N₂RhS (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 C₂₄H₃₄N₂RhS: 485.1498, found : 485.1512. ¹H NMR (500 MHz, DMSO-*d*₆, 80°C) : δ = 7.65 (d, ³*J* = 1.8 Hz, 1H, AlkNCH=), 7.34 (d, ³*J* = 1.8Hz, 1 H, MesNCH=), 7.12 (s, 2H, CH (Mes)), 4.72 (s, 2H, CH (COD)), 4.65 (t, ³*J* = 5.3 Hz, 2H, CH₂N), 3.97 (br s, 2H, CH (COD)), 2.93 (t, ³*J* = 5.3 Hz, 2H, CH₂SEt), 2.65 (q, ³*J* = 7.3 Hz, 2H, SCH₂CH₃), 2.36 (s, 3H, *p*-CH₃), 2.07-2.23 (m + s, 8H, *o*-CH₃; CH₂ (COD)), 1.86-2.05 (br m, 6H, CH₂ (COD)), 1.30 (t, ³*J* = 7.3 Hz, 3H, SCH₂CH₃). ¹³C NMR (125.8 MHz, DMSO-*d*₆, 80°C) : δ = 173.72 (d, ¹*J*_{Rh-C} = 50.3 Hz, NCN), 139.38 (*p*-C (Mes)), 135.85 (NC (Mes)), 135.28 (*o*-C (Mes)), 129.33 (CH (Mes)), 125.13 (MesNCH=), 122.99 (AlkNCH=), 94.36 (d, ¹*J*_{Rh-C} = 7.3 Hz, CH (COD)), 83.56 (br s, CH (COD)), 51.88 (NCH₂), 32.00 (SCH₂CH₃), 31.91 (CH₂SEt), 31.78; 29.61 (CH₂ (COD)), 27.54 (SCH₂), 20.92 (*p*-CH₃ (Mes)), 18.45 (*o*-CH₃ (Mes)) , 14.49 (SCH₂CH₃). ¹⁹F NMR (188MHz, CDCl₃) : δ = -76.08 (BF₄). MS (ESI): m/z (%) = 485.7, (100) [C₂₄H₃₄N₂RhS⁺].

Crystallographic Data

CCDC 631917-631922 and CCDC 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.

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Tables

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 ₂ CO	2	38 /50/ 12
3	DMSO	2	85 /00/ 15
4	DMSO	3	60 /00/ 40
5	CH ₂ Cl ₂	2	74 /07/ 19
6	CH ₂ Cl ₂	3	03 /03/ 94
7	CH ₂ Cl 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 signals integration in ¹H NMR spectra of crude products.

Table 2. Comparison of the main structural parameters of **11** and NiBr₂(1,3-bis(cyclohexyl)imidazol-2-ylidene)₂.

	11	NiBr ₂ L ₂ ^a
Bond distances (Å)		
Ni-Br	2.3113(5)	2.3113(4)
Ni-C(1)	1.9186(17)	1.908(3)
C(1)-N(1)	1.359(2)	1.353(4)
C(1)-N(2)	1.354(2)	1.347(4)
N(2)-C(4)	1.385(2)	1.394(5)
N(1)-C(3)	1.395(2)	1.390(5)
C(3)-C(4)	1.348(3)	1.333(5)
Bond angles (°)		
C(1)-Ni-C(1i)	180.00(9)	180.00
C(1)-Ni-Br(1)	89.48(5)	89.41(10)
C(1)-Ni-Br(1i)	90.52(5)	90.59(10)
Dihedral angles (°)		
N(1)-C(1)-Ni-Br(1)	74.43	
N(2)-C(1)-Ni-Br(1i)	75.41	
N(1)-C(1)-C(1i)-N(2i)	0.98	

a) L = 1,3-bis(cyclohexyl)imidazol-2-ylidene.

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 distances (Å)				
Rh(1)-C(1)	2.032(4)	2.020(5)	2.042(7)	2.051(7)
Rh(1)-S(1)	2.4076(10)	2.3940(18)	2.351(2)	2.394(2)
Rh(1)-C(11)	2.145(4)	2.127(6)	2.149(6)	2.137(7)
Rh(1)-C(12)	2.175(4)	2.150(6)	2.148(8)	2.148(9)
Rh(1)-C(15)	2.199(4)	2.191(6)	2.175(6)	2.225(9)
Rh(1)-C(16)	2.222(4)	2.212(7)	2.228(8)	2.236(8)
C(1)-N(1)	1.351(5)	1.341(7)	1.360(9)	1.342(9)
C(1)-N(2)	1.366(5)	1.356(7)	1.365(9)	1.319(9)
S(1)-C(5)	1.827(4)	1.791(8)	1.806(9)	1.785(7)
S(1)-C(6) ^a	1.863(4)	1.848(9)	1.808(8)	1.802(7)
Bond angles (°)				
C(1)-Rh(1)-S(1)	88.93(11)	89.94(16)	82.5(2)	89.0(2)
N(1)-C(1)-N(2)	104.0(3)	103.9(5)	104.1(6)	105.7(6)

a: this carbon is labeled C(111) for **19**

Table 4. Hydrosilylation of acetophenone.^a

Entry	R	Catalyst (mol%)	Solvent (concentration)	t (h)	Yield (%) ^b
1	H	18 (2)	CH ₂ Cl ₂ (1M)	17	90
2	H	18 (2)	THF (1M)	17	99
3	H	18 (1)	THF (1M)	24	90
4	H	18 (1)	THF (2M)	4	99
5	H	19 (1)	THF (1M)	8	99
6	H	19 (1)	THF (2M)	4	99
7	H	20 (1)	THF (2M)	1	99

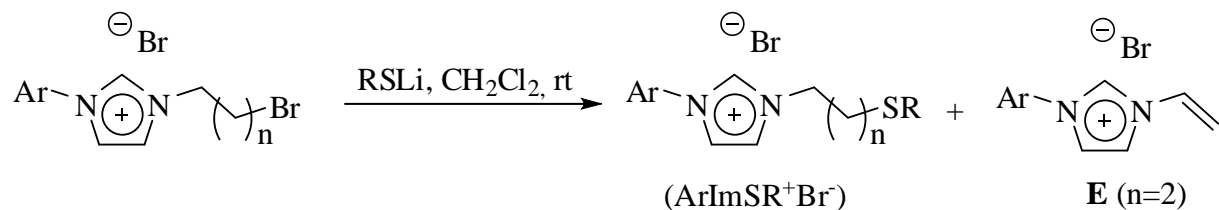
a) Ketone (1 eq.), diphenylsilane (1.1 eq.), room temperature, then hydrolysis with MeOH. b) Determined by integration of signals in ¹H NMR spectra of crude products.

Table 5. Hydrosilylation of acetophenone derivatives.^a

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

a) Ketone (1 eq.), diphenylsilane (1.1 eq.), 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.

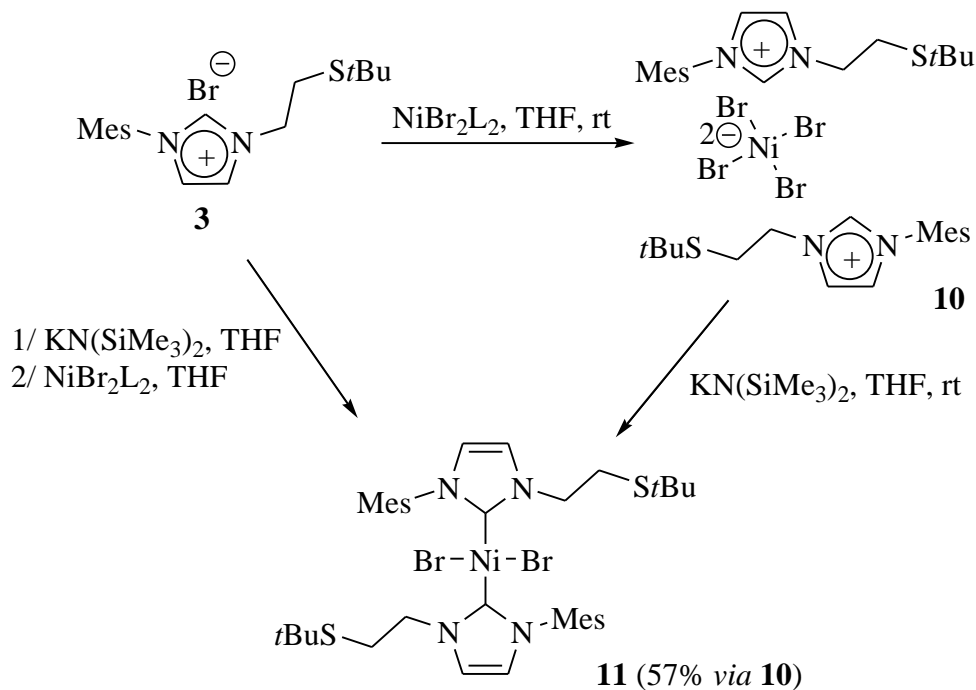
Schemes and figures



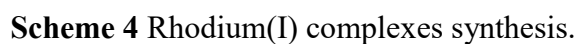
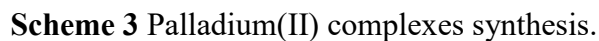
n=2, Ar = Mes (2,4,6-trimethylphenyl) **1**
DIPP (2,6-diisopropylphenyl) **2**
n=3, Ar = Mes **3**
DIPP **4**

n=2, Ar = Mes, R = *t*Bu **5** (86%)
Et **6** (95%)
Ar = DIPP, R = *t*Bu **7** (92%)
n=3, Ar = Mes, R = *t*Bu **8** (73%)
Ar = DIPP, R = *t*Bu **9** (69%)

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



Scheme 2 Nickel(II) complex synthesis.



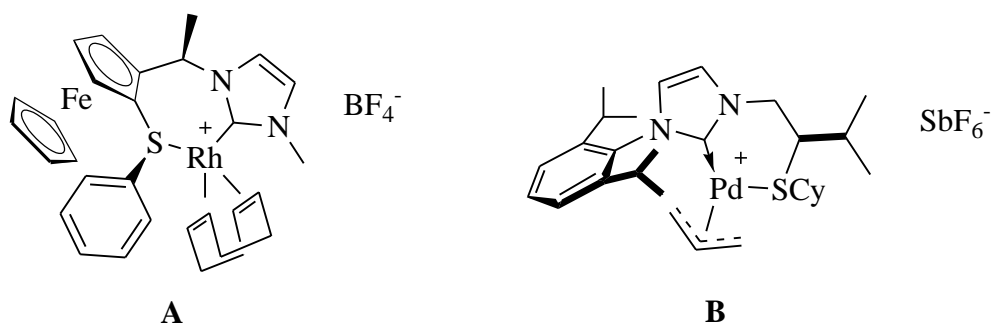


Figure 1 NHC-thioether complexes described in the literature. (a) Seo *et al.* (**A**), (b) Ros *et al.* (**B**).

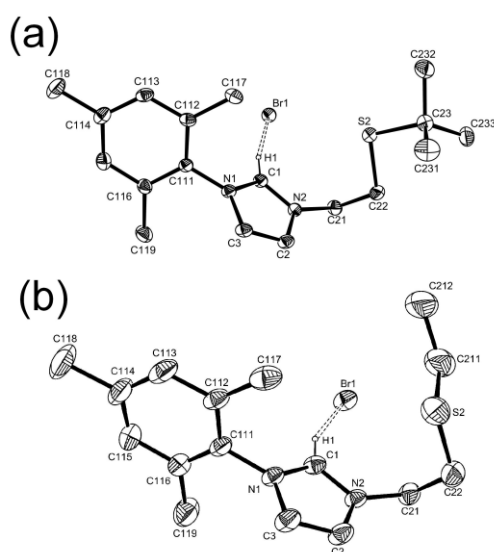


Figure 2 ORTEP views of **5** (a) and **6** (b). Ellipsoids are shown at the 30% probability level. All hydrogen atoms excepted H(1) and the solvent molecule which co-crystallized with **5** are omitted for clarity.

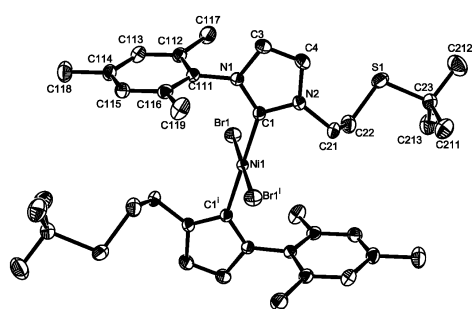


Figure 3 An ORTEP view of compound **11**. Ellipsoids are represented at the 50% probability level. Hydrogens are omitted for clarity.

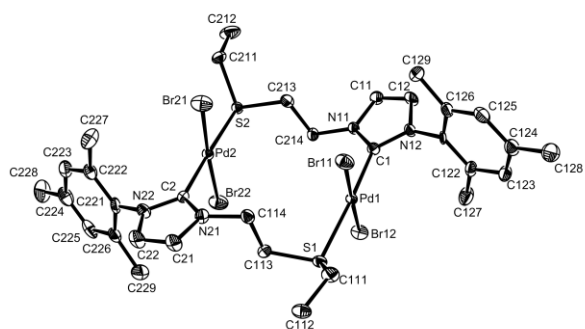
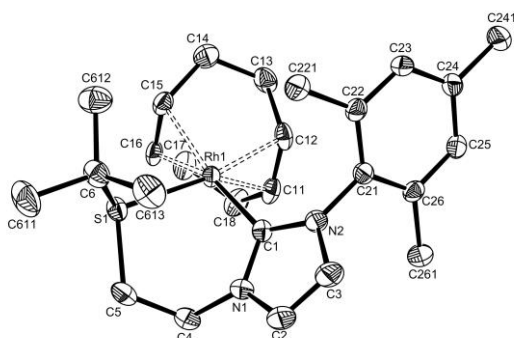
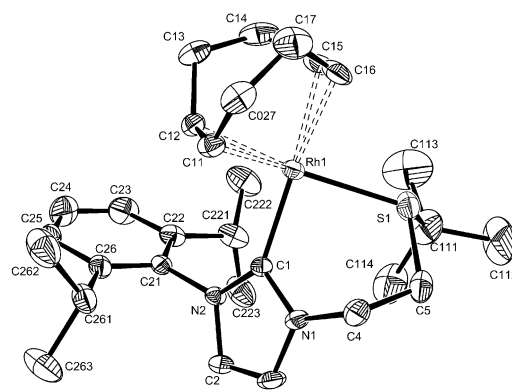


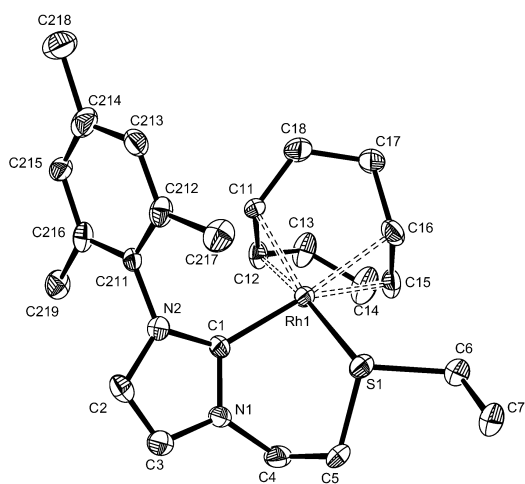
Figure 4 An ORTEP view of compound **17**. Ellipsoids are represented at the 30% probability level. Hydrogen atoms and co-crystallized THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-C(1), 1.990(4); Pd(2)-C(2), 1.983(4); Pd(1)-S(1), 2.3731(9); Pd(2)-S(2), 2.3622(9); Br(21)-Pd(2)-Br(22), 175.50(2); C(1)-Pd(1)-S(1), 173.10(12).



(a)



(b)



(c)

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 counter ion (BF_4) and a co-crystallized CDCl_3 molecule (**18**) are omitted for clarity.

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Graphical abstract

A series of new, bifunctional imidazolium-thioether ligands have been synthesised using a general method and used as N-heterocyclic carbene precursors for complexation studies on various transition metals (Ni(II), Pd(II) and Rh(I)). Rh(I) complexes showed a good activity for the hydrosilylation of ketones.

Keywords: N-heterocyclic carbenes / S ligands / Nickel / Palladium / Rhodium

