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Synthesis of transition metal complexes bearing bis-NHC ligands bridged by a thioether group
Síntesis de complejos de metales de transición soportados por ligandos bis-NHC puenteados por un grupo tioéter

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Abstract

The present work describes the synthesis of two novel bis-imidazolium salts (**1** and **2**) featuring a bridging thioether moiety prepared by the reaction of 1,4-bis{[2-(bromomethyl)phenyl]thio}butane with mesitylimidazole and methylimidazole under refluxing conditions. The new salts are air and moisture stable and they are highly soluble in polar solvents. Characterization of salts **1** and **2** was carried out through nuclear magnetic resonance of ^{1}H and ^{13}C nuclei and in case of salt **1**, its structure was determined via x-Ray diffraction studies. Salts **1** and **2** were treated with excess of hexamethyldisilazane (KHMDS) and two equivalents of $AuCl(SMe)_2$ or one equivalent of $[Pd(allyl)Cl]_2$ providing the respective bis-carbenic gold(I) **3** and palladium(II) **4-5** complexes in excellent yields. The new metallic complexes were characterized via ^{1}H and ^{13}C-NMR spectroscopy. The palladium complexes **4-5**, were preliminary tested as catalyst in the synthesis of biphenyl via a Suzuki cross-coupling process.

Keywords: Synthesis, N-heterociclic carbenes, Gold(I), Palladium(II), Tioether.

Resumen

En el presente trabajo se describe la síntesis de dos nuevas sales de bis-imidaziolio puenteadas a través de un grupo tioéter (**1** y **2**), las cuales fueron preparadas mediante la reacción de 1,4-bis{[2-(bromometil)fenil]tio}butano con mesitileno- y metil-imidazol bajo condiciones de reflujo. Las nuevas sales son estables a humedad y aire y son solubles en disolventes polares. en La caracterización de las sales **1** y **2** se llevó a cabo mediante técnicas de espectroscopía de resonancia magnética nuclear de ^{1}H y ^{13}C y en el caso de la sal **1**, su estructura fue determinada mediante difracción de rayos X. Las sales **1** y **2** fueron tratadas con exceso de hexametildisilazano (KHMDS) y dos equivalentes de $AuCl(SMe_2)$ o un equivalente de $[Pd(C_2H_5)Cl]_2$ para obtener los respectivos complejos bis-carbénicos de oro(I) **3** y paladio(II) **4-5** en excelentes rendimientos. Los nuevos complejos metálicos **3-5** fueron caracterizados mediante técnicas de RMN de ^{1}H y ^{13}C. Los complejos de paladio **4** y **5**, fueron utilizados como catalizadores en la síntesis de bifenilo mediante acoplamiento cruzado de Suzuki.

Palabras Clave: Síntesis, Carbenos N-heterocíclicos, Oro(I), Paladio(II), Tioéter.

1. Introduction

Ever since their isolation a little more than two decades ago, cyclic diamino carbenes, also referred to as N-heterocyclic carbenes (NHCs), have gained a privileged status among ancillary ligands for transition metals (Crudeen *et al*., 2004). Their strong sigma-donor properties often result in robust metal-carbon bonding which produces highly stable metal complexes with applications in several fields including catalysis, materials, medicine, among others (Diez-Gonzalez *et al*., 2009).

The steric and electronic properties of NHCs can be readily adjusted via modification of their structural features including the aryl or aliphatic *N*-substituents at the central imidazolium ring or by the NHC backbone functionalization with electron-donor or electron-withdrawing groups (Kühl *et al*., 2007). The functionalization of NHCs with donor-groups provides the opportunity of generating potential multidentate ligands which in due course can increase the stability of the resulting

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complexes via ligand chelation (Normand *et al.*, 2008). Nowadays, a myriad of bidentated chelating, tripodal and pincer-type NHCs have been reported in the literature and explored as catalyst in a series of organic transformations including formation of new C-C, C-N, C-Si and C-O bonds (John *et al.*, 2010).

As NHCs form strong M-C bonds, the presence of extra donor centers that form weaker bonds with the metal centers offers the possibility of generating hemilabile systems. The hemilability concept has gained importance in the catalysis area as such type of ligands display the capability of delivering free coordination sites which can either be employed for organic substrate activation or stabilization of the active catalytic species (Braunstein *et al.*, 2001).

A large amount of chelating NHC ligands found in the literature usually feature donor atoms such N, O, and P while, the analogue sulfur derivatives are less explored (Bierensteil *et al.*, 2011). With the ability of the sulfur center to be present in +2 and +6 oxidation states, NHC ligands can integrate thioether, thiolate, sulfonate, thiophene and sulfoxide groups, generating interesting platforms with hemilability potential (Huynh *et al.*, 2006).

We report herein the synthesis and characterization of two novel bis-imidazolium salts (**1** and **2**) featuring a bridging thioether moiety and their use as precursors for preparation of bis-carbenic gold(I) **3** and palladium(II) **4** and **5** complexes obtained in excellent yields.

2. Materials and methods

2.1. General methods

Commercially available reagents and solvents were used as received. All manipulations related to the synthesis of metal complexes were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. NMR spectra were obtained with a Bruker Ascend (400 MHz) spectrometer. X-Ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELX 2014 (Sheldrick, 2014) and refined by full matrix least squares against F^2 (Van der Sluis *et al*., 1990). All non-hydrogen atoms were refined anisotropically. The position of the hydrogen atoms was kept fixed with common isotropic display parameters.

*2.2. Synthesis of imidazolium salts **1** and **2***

To a pressure tube equipped with a magnetic bar were added 1,4-bis{[2-(bromomethyl)phenyl]thio}butane (1 equiv), 1-mesitylimidazole or 1-methylimidazole (3 equiv) and 5 mL of dry toluene. The reaction mixture was refluxed at 110 °C for 24 h. The reaction was allowed to reach room temperature and diethyl ether (20 mL) was added to the reaction mixture. The precipitated formed was filtered, washed with petroleum ether (2 x 20 mL) and dried under vacuum. Recrystallization by diethyl ether diffusion into a concentrated MeCN solution of the crude material allowed the isolation of the pure imidazolium salts **1** and **2**.

Bis-1,3-imidazolium salt **1**: White powder, 80% yield, soluble in DCM and $CHCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.24 (s, 2H, NC*H*N), 7.70 (dd, J_{ort} = 7.58 Hz, J_{met} = 1.34 Hz, 2H, CH_{ar}), 7.59 (t, J = 1.84 Hz, 2H, CH_{im}), 7.40 (dd, J_{ort} = 7.88 Hz, J_{met} = 1.40 Hz, 2H, CH_{ar}), 7.35 (td, J_{ort} = 7.62 Hz, J_{met} = 1.51 Hz, 2H, CH_{ar}), 7.25 (td, J_{ort} = 7.46 Hz, J_{met} = 1.98 Hz, 2H, CH_{ar}), 7.25 (t, J = 1.96 Hz, 2H, CH_{im}), 6.94 (s, 4H, CH_{ar}), 5.60 (s, 4H, NCH_2), 2.95 (t, J = 6.60 Hz, 4H, SCH_2), 2.28 (s, 6H, CH_3), 2.03 (s, 12H, CH_3), 1.75 (q, J = 3.42 Hz, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 141.21, 138.00, 136.54, 134.33, 133.60, 131.52, 131.22, 130.75, 130.49, 129.85, 127.67, 123.66, 122.90, 52.09, 34.36, 28.01, 21.13, 17.80.

Bis-1,3-imidazolium salt **2**: White powder, 84% yield, partially soluble in DCM and $CHCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 10.47 (s, 2H, NC*H*N), 7.60 (dd, J_{ort} = 7.58 Hz, J_{met} = 1.58 Hz, 2H, CH_{ar}), 7.45 (t, J = 1.84 Hz, 2H, CH_{im}), 7.40 (td, J_{ort} = 7.98 Hz, J_{met} = 1.67 Hz, 2H, CH_{ar}), 7.36 (td, J_{ort} = 7.52 Hz, J_{met} = 1.59 Hz, 2H, CH_{ar}), 7.29 (dd, J_{ort} = 7.46 Hz, J_{met} = 1.72 Hz, 2H, CH_{ar}), 7.27 (t, J = 1.90 Hz, 2H, CH_{im}), 5.71 (s, 4H, NCH_2), 4.10 (s, 6H, NCH_3), 2.95 (t, J = 6.66 Hz, 4H, SCH_2), 1.75 (q, J = 3.36 Hz, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm): 138.10, 136.70, 133.39, 131.30, 131.28, 130.63, 127.77, 123.55, 121.99, 51.81, 37.04, 34.56, 27.92

2.3. Synthesis of gold(I) complexes

In a Schlenk flask, in the absence of light and under inert N_2 atmosphere, the appropriate imidazolium salt (1.0 equiv), potassium hexamethyldisilazane (1.4 equiv), and chloro(dimethylsulfide)gold(I) (2.0 equiv) were combined and dissolved in 5 mL of dry tetrahydrofuran at -78 °C. The resulting mixture was stirred for 24 h. The final violet suspension was dried under vacuum and extracted with dichloromethane (5 mL). After cannula filtration and removal of the solvent, the crude material was purified via chromatography column using a mixture of dicloromethane/ethanol (95:5).

Dinuclear gold(I) complex **3**: Yellowish white powder, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.45 (dd, J_{ort} = 7.91 Hz, J_{met} = 1.34 Hz, 2H, CH_{ar}), 7.35 (td, J_{ort} = 7.52 Hz, J_{met} = 1.87 Hz, 2H, CH_{ar}), 7.29 (dd, J_{ort} = 7.70 Hz, J_{met} = 1.96 Hz, 2H, CH_{ar}), 7.24 (dd, J_{ort} = 7.52 Hz, J_{met} = 1.41 Hz, 2H, CH_{ar}), 7.07 (d, J = 1.95 Hz, 2H, CH_{im}), 6.95 (s, 4H, CH_{ar}), 6.84 (d, J = 1.95 Hz, 2H, CH_{im}), 5.62 (s, 4H, NCH_2), 2.99 (t, J = 6.91 Hz, 4H, SCH_2), 2.32 (s, 6H, CH_3), 2.03 (s, 12H, CH_3), 1.84 (q, J = 3.45 Hz, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 176.33, 139.72, 136.23, 135.19, 134.89, 134.85, 130.66, 129.65, 129.58, 129.52, 127.13, 122.44, 120.75, 53.08, 34.16, 28.17, 21.25, 18.02. The analogue dinuclear gold(I) complex supported by the 1-methylimidazolium salt **2** was unstable and could not be isolated and characterized.

2.4. Synthesis of allyl palladium(II) complexes

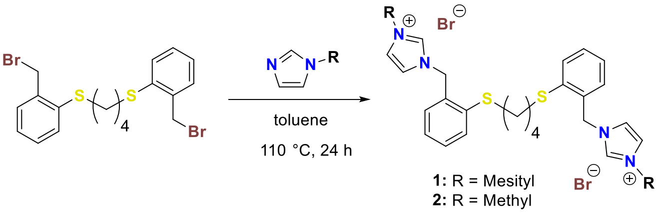
In a Schlenk flask, under inert N_2 atmosphere, the appropriate imidazolium salt (1.0 equiv), potassium hexamethyldisilazane (1.4 equiv), and bis(η^3-allyl)di(μ-chloro)dipaladium(II) (1 equiv) were combined and dissolved in 5 mL of dry tetrahydrofuran at -78 °C. The resulting mixture was stirred for 24 h. The final yellow solution was dried under reduced pressure and extracted with dichloromethane (5 mL) and filtered through a cannula. The solvent volume was reduced to 2 mL and hexane (10 mL) was added to induce precipitation of the product. The solid was filtered and washed with hexanes (2 x 5 mL) to provide pure products as pale yellow solids.

Dinuclear palladium(II) complex **4**: Yellow powder, 91 % yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ(ppm): 7.27 (d, J = 7.70 Hz, 2H, CH_{ar}), 7.17 (t, J = 7.52 Hz, 2H, CH_{ar}), 7.16 (d, J = 7.46 Hz, 2H, CH_{ar}), 7.07 (t, J = 7.46 Hz, 2H, CH_{ar}), 6.85 (s, 2H, CH_{im}), 6.82 (s, 2H, CH_{im}), 5.40 (s, 2H, NCH_2), 5.38 (s, 2H, NCH_2), 5.08 (m, 2H, J = 13.20 Hz, CH_{allyl}), 4.12 (d, 2H, J = 8.07 Hz, CH_{allyl}), 3.70 (s, 6H, NCH_3), 3.32 (s, 2H, CH_{allyl}), 3.02 (d, 2H, J = 13.70 Hz, CH_{allyl}), 2.83 (t, J = 6.60 Hz, 4H, SCH_2), 2.13 (s, 2H, CH_{allyl}), 1.66 (m, J = 6.60 Hz, 4H, CH_2). ^{13}C NMR (101 MHz, CDCl$_3$) δ(ppm): 180.27, 136.45, 135.19, 129.90, 128.86, 126.70, 122.27, 121.95, 114.76, 71.70, 52.61, 51.09, 38.45, 34.06, 28.03.

Dinuclear palladium(II) complex **5**: Yellow powder, 93% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ(ppm): 7.45 (d, J = 7.58 Hz, 2H, CH_{ar}), 7.39 (d, J = 7.82 Hz, 2H, CH_{ar}), 7.28 (t, J = 7.58 Hz, 2H, CH_{ar}), 7.19 (t, J = 7.46 Hz, 2H, CH_{ar}), 7.09 (s, 2H, CH_{im}), 6.92 (s, 2H, CH_{ar}), 6.90 (s, 2H, CH_{ar}), 6.88 (s, 2H, CH_{im}), 5.74 (s, 2H, NCH_2), 5.71 (s, 2H, NCH_2), 4.77 (sept, J = 6.66 Hz, 2H, CH_{allyl}), 4.03 (d, J = 7.33 Hz, 2H, CH_{allyl}), 3.18 (d, J = 7.97 Hz, 2H, CH_{allyl}), 2.94 (t, J = 6.66 Hz, 4H, SCH_2), 2.83 (d, J = 13.45 Hz, 2H, CH_{allyl}), 2.30 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 1.77 (q, J = 9.05 Hz, 4H, CH_2), 1.71 (d, J = 11.62 Hz, 2H, CH_{allyl}). ^{13}C NMR (100 MHz, CDCl$_3$) δ(ppm): 182.07, 138.91, 136.98, 136.48, 135.79, 135.40, 130.66, 130.22, 129.16, 128.94, 126.76, 122.39, 122.30, 114.49, 71.39, 53.37, 51.92, 34.36, 28.26, 21.20, 18.75, 18.38.

3. Results and discussion

The construction of the bis-imidazolium salts **1** and **2** was carried out according to Scheme 1. The treatment of 1,4-bis{[2-(bromomethyl)phenyl]thio}butane with a slight excess of mesityl- or methyl imidazole under refluxing conditions using dry toluene, resulted in the formation of brown suspensions. After work-up and purification by means of recrystallization, the respective bis-imidazolium salts **1** and **2** were obtained in good yields as white solids.



Scheme 1. Synthesis of imidazolium salts **1** and **2**.

The identification of the imidazolium salts **1** and **2** was conveniently assessed by ^{1}H and ^{13}C-NMR spectroscopy. For both cationic salts, the NMR spectra show equivalent signals consistent with highly symmetric structural patterns. Formation of the imidazolium salts **1** and **2** was easily monitored by the presence of the characteristic singlet in ^{1}H-NMR due to the acidic imidazolium protons in the region of δ = 10.24-10.47 ppm (Figure 1) and the peaks at δ = 141.21-138.10 ppm in ^{13}C-NMR belonging to the imidazolium C-2 atom. The representative peaks of the imidazolium backbone CH groups (7.45-7.47 ppm) and the single peak (6.96 ppm) corresponding to aromatic CH-groups of the mesityl fragment in salt **1** are consistent with the successful construction of the cationic compounds.

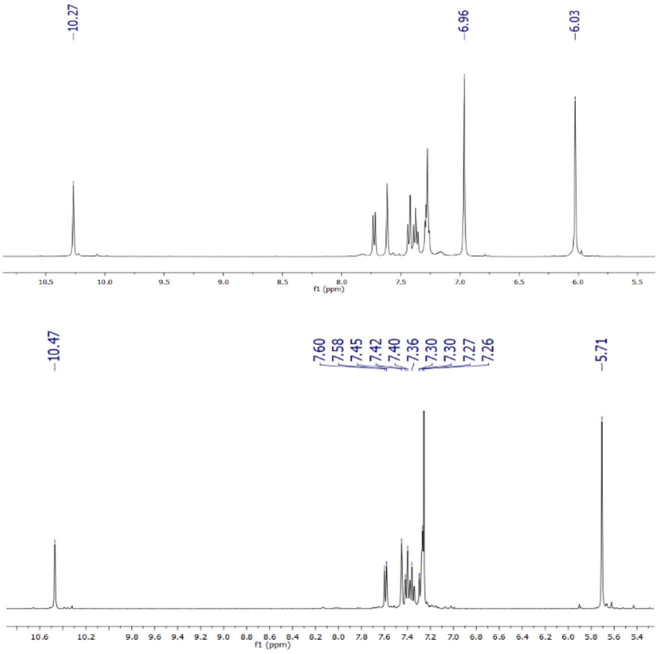


Figure 1. ^{1}H-NMR (100 MHz, CDCl$_3$) spectrum section of bis-imidazolium salts **1** (top) and **2** (bottom).

Unambiguous characterization of salt **2** was achieved by X-ray diffraction studies with the molecular structure depicted in Figure 2.

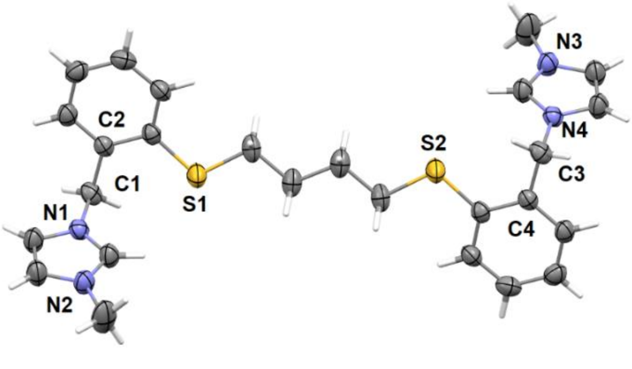
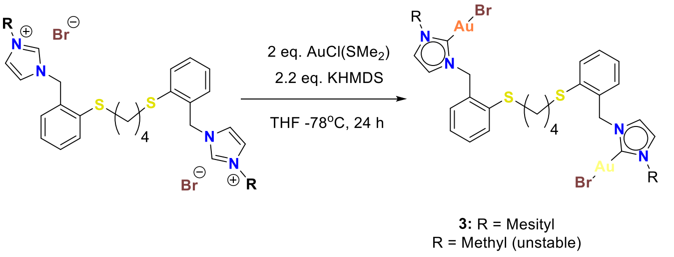


Figure 2. Molecular structure of salt **2**. Ellipsoids shown at 40% of probability. Counterions and crystallization solvents omitted for clarity.

Imidazolium salt **1** crystallizes in the monoclinic P_21/c space group. The C-C and C-N bond distances and C-C-N angles observed in the crystal structure of **2** are similar to other cationic analogues (Crabtree, 2013). The imidazolium fragment is almost perpendicular to the aryl fragment with N1-C1-C2 and N4-C3-C4 angles close to 111(7)°.

A comparison of the sigma-donation of the new imidazolium salts **1** and **2**, using the already available $^{1}J_{CH}$ coupling constants from ^{1}H NMR spectra was obtained (Meng *et al.*, 2019). The coupling values for **1** (219.42 Hz) and **2** (221.35 Hz) fall between the normal range as reported in analogue classical NHC ligands (208-223 Hz).

To initially explore the coordination capabilities of the new bis-imidazolium salts **1** and **2**, we tested their reactivity with potassium hexamethyldisilazane (KHMDS) in the presence of AuCl(SMe$_2$) under strict absence of light (Scheme 2).



Scheme 2. Synthesis of dinuclear gold(I) complexes.

After work-up and purification, complex **3** was obtained in good yields as a white solid (89%), however the analogue complex supported by the NHC with a N-methyl substituent was unstable and could not be isolated. Complex **3** is highly soluble in chlorinated solvents, THF and acetonitrile, and is air and moisture stable. The formation of gold complex **3** was primarily confirmed by ^{1}H and ^{13}C NMR spectroscopy showing the disappearance of the acidic CH peak of the former imidazolium salt and as expected, presenting a new NHC-Au peak located at 176.3 ppm (Figure 3).

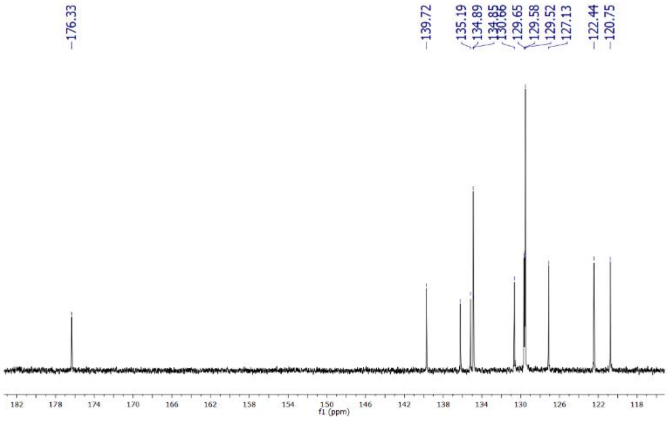
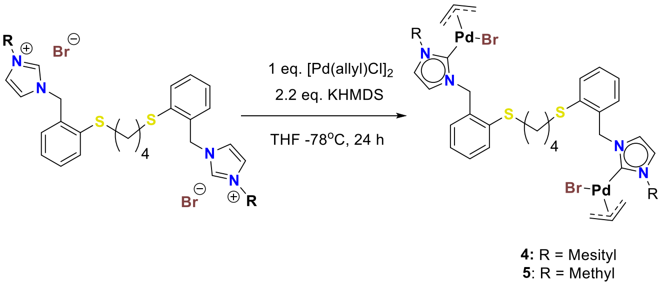


Figure 3. ^{13}C-NMR (100 MHz, CDCl$_3$) spectrum section of gold complex **3**.

Motivated by the successful preparation of the gold complexes, we followed a similar strategy for the preparation of palladium(II) carbene derivatives. Thus, the treatment of bis-imidazolium salts **1** and **2** with excess of KHMDS (2.2 equiv) and one equivalent of the dimeric [Pd(allyl)Cl]$_2$ in THF at -78°C (Scheme 3), resulted in the formation of the respective complexes **4** and **5** in excellent yields (91-93%).



Scheme 3. Synthesis of palladium(II) complexes **4** and **5**.

The formation of palladium complexes **4** and **5**, was confirmed in ^{1}H-NMR spectroscopy by the lack of the acidic CH imidazolium proton and the presence of five new peaks in the aliphatic area corresponding to the allyl moiety coordinated to the palladium center. Particularly revealing is the multiplet signal located between 4.77-5.08 ppm, belonging to the central CH group of the allyl fragments. All the signals of the ligand backbone are symmetrical showing a single set of peaks in each bimetallic complex. Additionally, ^{13}C-NMR spectroscopy shows the presence of new NHC-Pd peaks located at 182.07 and 180.27 ppm for complexes **4** and **5**, respectively (Figure 4).

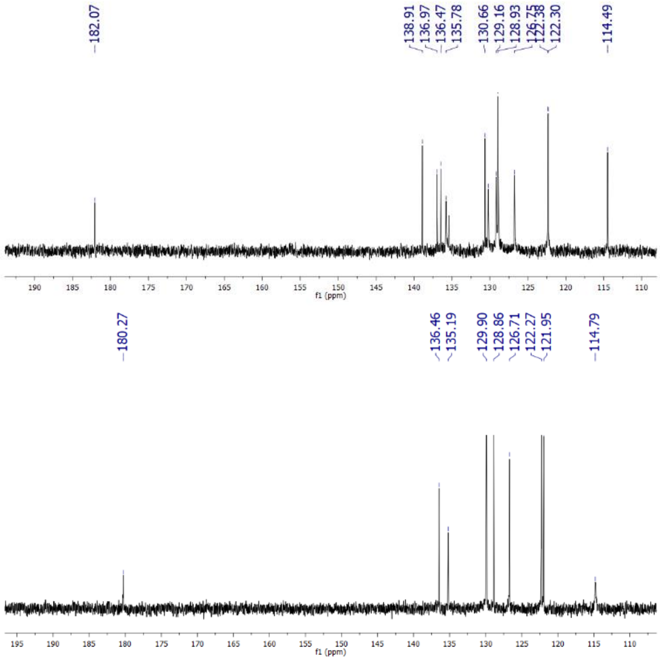
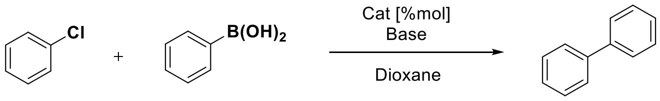


Figure 4. ^{13}C-NMR (100 MHz, CDCl$_3$) spectrum section of palladium complexes **4** (top) and **5** (bottom).

Cross coupling reactions represent one of the most important classes of catalytic carbon-carbon bond forming reactions. The most widely used catalysts in this field are based on transition metal complexes from groups 8-10 and those containing palladium are particularly efficient in a variety of processes (Selander *et al.*, 2011). Recently, efforts have been focused on the design and preparation of palladium complexes bearing NHC ligands as they have demonstrated good catalytic performances and thermal stabilities compared to classical phosphine or amine-based complexes (Gonzalez-Sebastian *et al.*, 2019).

The biphenyl motif is highly important in organic synthesis as is often present in natural products and fine chemicals. Typically, aryl bromides or iodides are employed in the Suzuki coupling with boronic acids to render biphenyl products in the presence of metal catalysts. However, the use of "unreactive" aryl chlorides as coupling partners in this process is in constant development (Liu, *et al*., 2019). With this in mind, we decided to preliminary test the catalytic applicability of the bimetallic complexes **4** and **5** in the formation of biphenyl. Thus, chlorobenzene and phenylboronic acid were chosen as model substrates to optimize the reaction conditions of the palladium precatalysts **4** and **5**. Initial reaction conditions involved the charge of 1 mol% of the catalyst, 1.5 equiv of sodium tert-butoxide as base, dry dioxane as solvent at 80ºC. According to Table 1 (entries 1 and 2), the conversion to the corresponding bipenyl reached a maximum of 59% when using complex **4** as precatalyst in 2 h of reaction.

Table 1. Optimization of the preparation of byphenyl via Suzuki coupling using complexes **4** and **5.**



Entry	Cat	Cat mol%	Temp (°C)	Base	Time (h)	Conv [%][a]
1	**4**	1	80	NaO^tBu	2	59
2	**5**	1	80	NaO^tBu	2	46
3	**4**	1	80	NaO^tBu	4	83
4	**5**	1	80	NaO^tBu	4	64
5	**4**	3	80	NaO^tBu	2	79
6	**5**	3	80	NaO^tBu	2	76
7	**4**	2	80	NaO^tBu	4	96
8	**4**	3	80	NaO^tBu	4	99
9	**4**	3	65	NaO^tBu	4	68
10	**4**	3	80	K_2CO_3	4	48

Reaction conditions: chlorobenzene (0.10 mmol), phenylboronic acid (0.12 mmol), base (0.15 mmol), dioxane (2 mL). [a]Isolated yields.

Increasing the reaction time (4 h), results in the increase of yield up to 83% with complex **4**. However, the optimal results (99% yield) are obtained when the addition of complex **4** is increased to 3 mol% at 80ºC for 4 h (as depicted in entry 8). Interestingly, as observed in entries 9 and 10, the reaction performance is strongly dependent on temperature and the base employed.

4. Conclusions

In conclusion, we have prepared two novel bis-imidazolium salts (**1** and **2**) featuring a bridging thioether moiety through the treatment of 1,4-bis{[2-(bromomethyl)phenyl]thio}butane with methylimidazole and mesitylimidazole. Their subsequent deprotonation with a strong base such as KHMDS in presence of $AuCl(SMe)_2$ or $[Pd(allyl)Cl]_2$, resulted in the facile synthesis of the respective gold (**3**) and palladium (**4** and **5**) complexes in one step. The imidazolium salts and the corresponding carbene-metal complexes were characterized by ^1H and ^{13}C NMR spectroscopy and in the case of salt **1** via single crystal X-ray diffraction.

Preliminary catalytic testing of the palladium complexes in Suzuki cross-coupling, showed a better performance when using complex **4**. This result may be related to the enhanced thermal stability of **4** provided by the more sterically protected mesitylimidazole fragment compared to complex **5**, which contains a smaller methylimidazole moiety. This proposal is also consistent with the failure in the isolation of the gold complex supported by the carbene derived from the methylimidazolium salt **2**.

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