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Copper-Induced Ammonia N-H Functionalization

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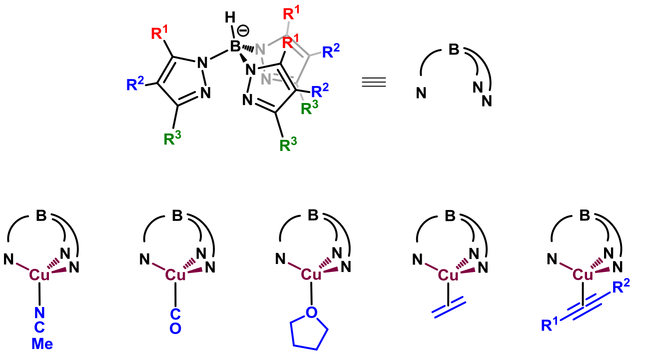
The activation of ammonia has been achieved with the aid of the $Tp^{Ms}Cu$ core (Tp^{Ms} = hydrotris(3-mesytil-pyrazolyl)borate) Complexes of general composition $Tp^{Ms}Cu(amine)$ (**1**-4) including the ammonia adduct $Tp^{Ms}Cu(NH_3)$ (**1**) have been synthesized and fully spectroscopic- and structurally characterized. Coordinated ammonia in **1** has been reacted with Ph_3CPF_6 yielding $Tp^{Ms}Cu(NH_2CPh_3)$ (**5**) as the result of N-H cleavage and N-C bond formation. In a parallel manner the catalytic functionalization of ammonia with ethyl diazoacetate leading to glycinate derivatives has been developed with $Tp^{Ms}Cu(THF)$ as the catalyst, in the first example of this transformation with a copper-based system.

Introduction

The activation of the N-H bonds of ammonia yet constitutes a challenge for current chemistry, particularly in the context of metal-catalysed (hydro)amination reactions.[1] Ammonia can coordinate a number of transition metals, and subsequent reactivity may lead to amido, imido (nitrene) and even nitrido complexes, that could serve as intermediates in catalytic cycles.[2,3] During the last decade a family of tetracoordinate complexes bearing the Tp^xCu moiety (Tp^x = hydrotrispyrazolylborate ligand) and a fourth donor ligand such as CH_3CN,[4] CO,[5] PR_3[6] alkene[7] or alkyne[8] has been developed (Scheme 1). The use of Tp^{Ms} [hydrotris(3-mesitylpyrazolyl)borate] provided interesting features to those complexes due to the interaction between the aryl rings with olefin/alkyne ligands. Interestingly, we found that in spite of the large number of Tp^xCuL complexes reported to date, the ammonia derivative remained yet undescribed. With this idea in mind, we started this work that has led to the synthesis and structural characterization of $Tp^{Ms}Cu(NH_3)$, as well as a series of related $Tp^{Ms}Cu(NR_3)$ for comparative purposes. The availability of the ammonia adduct has allowed the study of the reactivity of the N-H bonds, from which we have observed N-H bond cleavage and subsequent N-C bond formation in a process that provides a net NH_3 functionalization. Additionally, in a parallel manner, the catalytic functionalization of ammonia upon insertion of $CHCO_2Et$ carbene units (from ethyl diazoacetate, N_2CHCO_2Et, EDA) has been achieved employing $Tp^{Ms}Cu(THF)$ as the catalyst. The latter has only been described to date with iron-based catalysts, [9] the current work constituting, to the best of our knowledge, the first example of a copper-catalysed ammonia functionalization with this strategy, since previous examples with this metal being were described only with substituted amines.[10].

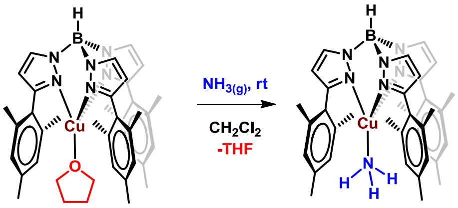


Scheme 1. Previously described Tp^xCuL complexes.

Results and Discussion

Synthesis and characterization of $Tp^{Ms}Cu(NH_3)$ (1).

The ammonia adduct $Tp^{Ms}Cu(NH_3)$ (**1**) has been synthesized using $Tp^{Ms}Cu(THF)$ as the starting material, following a procedure already described for other olefin or alkyne Tp^x-copper adducts in our group (eqn (1)).[7,8] Ammonia gas was bubbled through a colourless solution of $Tp^{Ms}Cu(THF)$ in dichloromethane for 15-20 min, and the solution was then stored in the freezer at -30 ºC from which colourless crystalline material was collected in 95% isolated yield after three successive crops. The formulation of this compound as $Tp^{Ms}Cu(NH_3)$ (**1**) came straightforwardly from its spectroscopic and analytical data. For instance, the ^1H NMR spectrum



(1)

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showed the typical resonances of the coordinated Tp^{Ms} ligand with one signal for each independent nucleus of the pyrazolyl moiety, as the result of a local C_{3v} symmetry that makes the

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three pyrazolyl rings equivalents. In addition, a broad singlet located at δ 0.59 ppm that integrated for 3H has been assigned to coordinated NH_3. The IR spectrum displayed a broad absorption at 3374 cm^{-1} attributable to ν(N-H) typical for the first row transition metal ammonia complexes.[11]

Interestingly, attempts to isolate other $Tp^xCu(NH_3)$ complexes using Tp^x ligands (Tp^x = Tp* or Tp^{Br3}) different from Tp^{Ms} have failed. It seems that the steric protection provided by the mesytil substitutent is crucial for the stability of the ammonia adduct.

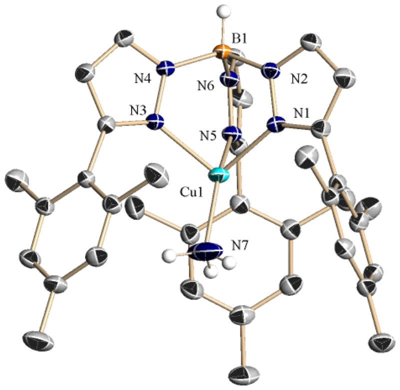
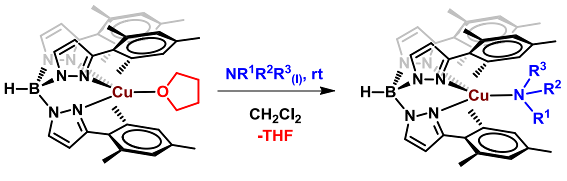


Figure 1. ORTEP view of the molecule of complex $Tp^{Ms}Cu(NH_3)$ (**1**) (Hydrogen atoms of the pyrazolyl groups have been omitted for clarity)

Figure 1 shows the structure of the molecules of **1** as the result of X-ray diffraction studies. The complex is mononuclear, with the Tp^{Ms} ligand coordinated in a κ³-*N,N,N* fashion and the NH_3 moiety bonded to the copper centre occupying the fourth coordination site of a slightly distorted tetrahedron formed by the four N donors. Additional comments on distances and angles are provided in the next section.



$R^1 = R^2 = H$; R^3 = Et, **2**
R^1 = H; $R^2 = R^3$ = Et, **3**
$R^1 = R^2 = H$; R^3 = Bn, **4**

Scheme 2. Synthesis of the $Tp^{Ms}Cu(amine)$ adducts **2-4**.

Synthesis and characterization of complexes $Tp^{Ms}Cu(NR_3)$ (2-5).

For the sake of comparison with the ammonia adduct **1** we have prepared a series of amine adduct of general composition $Tp^{Ms}Cu(NR_3)$ (Scheme 2) upon ligand exchange from $Tp^{Ms}Cu(THF)$ at room temperature. Crystalline materials were collected in 60-80% yield upon direct cooling of the reaction mixtures (see Experimental Section). These new copper-amine adducts are stable under vacuum in the solid state and even under air for short periods of time. Their spectroscopic and analytical data were in agreement with their formulation as the amine adduct of the $Tp^{Ms}Cu$ moiety.

X-ray studies carried out with complexes **2**-**4** have shown in all cases a distorted tetrahedral geometry around the copper centre. Figure 2 shows the ORTEP view of the molecules of **4** as a representative example (see ESI for those of complexes **2** and **3**). Table 1 contains a list of selected bond distances and angles for complexes **1**-**4**. The Cu(1)-N(pyr) (N1, N3 or N5) averaged 2.073 Å in **1**, 2.08 Å in **2**, 2.11 Å in **3** and 2.073 Å in **4**. These values are slightly shorter than those found in the olefin adducts $Tp^{Ms}Cu(olefin)$ (2.15-2.21 Å)[7] or in the alkyne adducts $Tp^{Ms}Cu(alkyne)$ (2.10 Å).[8] This is probably the result of the exclusive sigma donation of the amine ligand to the metal centre in contrast with the back-bonding capabilities of both olefin and alkyne ligands. The Cu-N(amine) distance also deserves some comment. The Cu(1)-N(7) distance in **7** of 1.960(2) Å is similar to those previously found in $CuCl(NH_3)(olefin)$ (1.987Å)[12a] or $Cu(L)(NH_3)$ (1.973 Å, L = bidentate ligand).[12b] Such distance slightly increases when moving from **1** to **4**, probably accounting for the augment of the steric volume of the amine ligand.

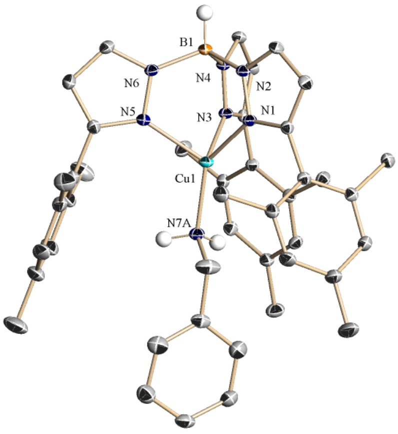
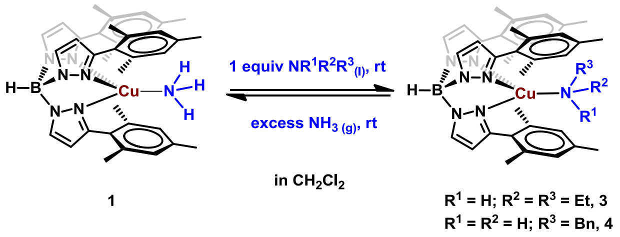


Figure 2. ORTEP view of the molecule of complex $Tp^{Ms}Cu(NH_2CH_2Ph)$ (**4**) (Hydrogen atoms of the pyrazolyl groups have been omitted for clarity)

Table 1. List of selected bond distances [Å] and angles [°] for copper compounds **1-4**.

	1	**2**	**3**	**4**
Cu-N(7)	1.960(2)	1.985(9)	2.006(5)	2.011(4)
Cu-N(1)	2.0841(14)	2.082(2)	2.1309(17)	2.0959(13)
Cu-N(3)	2.0882(16)	2.082(2)	2.090(4)	2.0884(13)
Cu-N(5)	2.0538(15)	2.082(2)	2.1309(17)	2.0505(14)
N(1)-Cu-N(7)	126.90(12)	140.0(4)	108.84(15)	135.00(12)
N(3)-Cu-N(7)	115.93(9)	115.0(4)	129.87(16)	121.19(13)
N(5)-Cu-N(7)	132.22(11)	118.9(7)	132.96(15)	118.85(13)

The relative reactivity of the above complexes toward amine exchange has been studied (Scheme 3). Thus, when complex **1** was reacted with one equiv of either diethyl or benzylamine, complete conversion into **3** or **4** was respectively observed whereas bubbling of ammonia through the solutions of **3**-**4** returned **1** in solution. From these results it seems reasonable proposing that the substituted amine provides more stable adducts albeit the difference in energy is not large given the possibility of reversion with excess of ammonia.



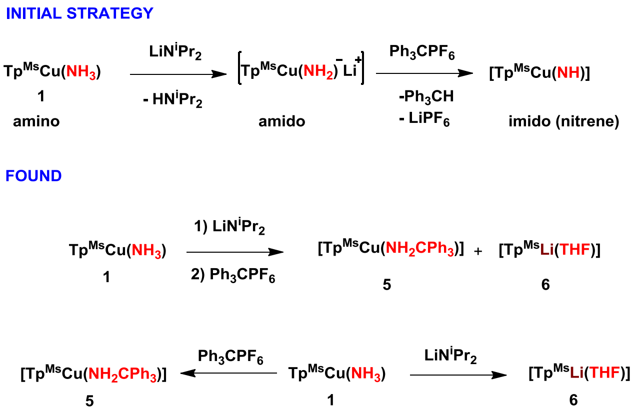
Scheme 3. Amine exchange in complexes **1**-**4**

Ammonia N-H functionalization.

N-H cleavage and N-C bond formation. On the basis of the availability of the ammonia complex **1**, we have studied its reactivity toward hydrogen abstraction, with the aim of the consecutive formal proton and hydride abstraction and final nitrene formation (Scheme 4).[2,3] We planned the use of lithium diisopropylamide (LDA) and a triphenylmethyl salt (Ph_3CPF_6) as respective proton and hydride scavengers. The one-pot reaction, either at low or room temperature, led to a somewhat dirty reaction mixture from which we have isolated two products: $Tp^{Ms}Cu(NH_2CPh_3)$ (**5**) and $Tp^{Ms}Li(THF)$ (**6**). Separate experiments carried out with **1** and LDA and Ph_3CPF_6, respectively, have afforded compounds **6** and **5**, respectively (Scheme 4).

The formation of complex **5** from **1** and Ph_3CPF_6 escapes from the common role of hydride scavenger. Formally, the Ph_3C group replaces one of the H atoms of ammonia, HPF_6 being likely formed for reaction balance. Complex **5** was isolated in 16 % yield from that reaction mixture as colourless crystals, some of them suitable for an X-ray diffraction studies. Figure 3 shows the ORTEP view where the formation of triphenylmethylamine is demonstrated. Moreover, this compound has been independently prepared upon reacting $Tp^{Ms}Cu(THF)$ and commercial NH_2CPh_3 following the aforementioned procedure described for compounds **2**-**4** (see ESI). Spectroscopic, analytical and even structural data for both samples were identical.

The solid-state structure of **5** (Figure 3) has shown some interesting features. A similar, distorted tetrahedral geometry is observed around the copper centre for **1**-**5**. However, in the case of **5** the values of the Cu-N(pyr) distances are somewhat larger: 2.340 Å for Cu(1)-N(1) and 2.301 Å Cu(1)-N(2), the third one yet resembling the values found for **1**-**4** (See Scheme 5). In good agreement with this, two sets of resonances for the mesytil pyrazolyl units are observed in the NMR with relative ratio 2:1. In addition, a weak NOE effect has been detected between the NH_2 hydrogen nuclei and the aromatic resonances. These data support the proposal of a certain interaction of the NH_2 hydrogens with the π-system of the mesytil rings. This would preclude the rotation of the Cu-N(amine) bond, decreasing the symmetry of the molecule. To shed light on this idea, the related complex $Tp^{Ms}Cu(NH_2CHPh_2)$ (**7**) bearing diphenylmethylamine has been prepared and fully characterized, including X-ray studies (see ESI for full details). The absence of the third phenyl group in **7** decreases the steric pressure around the metal centre to such extend that the Cu-N(pyr) distances found are very similar to those already commented for complexes **1**-**4** (Scheme 5).



Scheme 4. Top: the targeted transformation. Bottom: the observed transformations. Leading to complexes **5** and **6**.

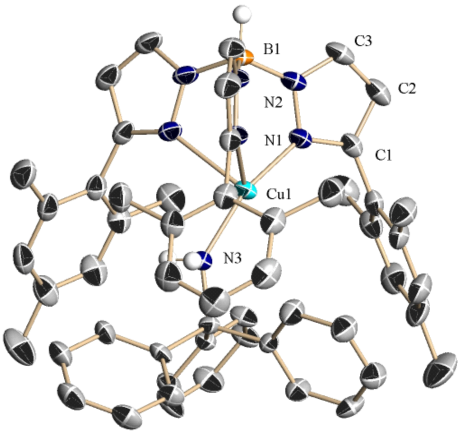
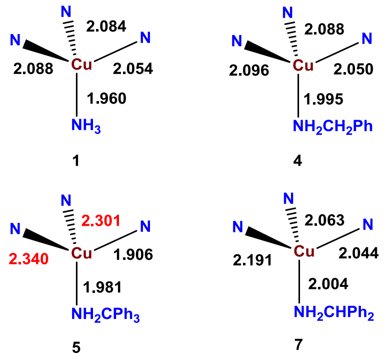


Figure 3. Structure of $Tp^{Ms}Cu(NH_2(CPh_3))$ **5** (Hydrogen atoms of the pyrazolyl groups have been omitted for clarity)

Complex $Tp^{Ms}Li(THF)$ (**6**) has been isolated as colourless crystals, from which NMR data showed the typical pattern of the coordinated Tp^{Ms} ligand as well as coordinated tetrahydrofuran. The observation of a slight difference in the chemical shifts and the lack of good elemental analysis prompted us to determine its X-ray structure from which the presence of lithium, and not copper, bonded to the ligands was assessed. The loss of copper could be related with the highly reductant power of LDA, albeit we have not been able to isolate any copper species from the reaction mixture. We believe that this finding is of interest for the researchers in the field of tryspyrazolylborate-containing transition metal complexes, since this simple "transmetallation" is not expected

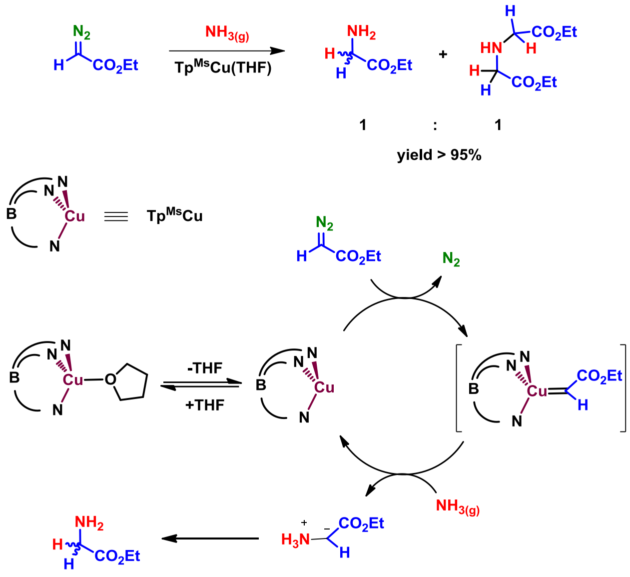


Scheme 5. Comparison of bond distances (Å) around the copper centre for several complexes $Tp^{Ms}Cu(amine)$,

Ammonia N-H functionalization by carbene insertion.

Last decade we reported on the catalytic insertion of carbene $CHCO_2Et$ units (from ethyl diazoacetate) into N-H bonds of several amines in good yields with several Tp^xCuL complexes as the catalyst.[10] In spite of the interest of this reactions, that lead to aminoacid formation, its application to ammonia as the substrate is reduced to the work by Gross and co-worker with an iron-based catalyst.[9] On the basis of this, we have now studied the catalytic potential of the complex $Tp^{Ms}Cu(THF)$ toward the reaction of ethyl diazoacetate and ammonia. The reaction was performed upon dissolving the catalyst in dichloromethane followed by saturation of the solution with ammonia gas. After 10 min of bubbling, EDA was slowly added with the aid of a syringe pump for 1h. After that time, the reaction mixture was stirred for additional 72h and the reaction was investigated by GCMS. A mixture of the two products derived from the formal insertion of one or two carbene groups into the N-H bonds of ammonia in relative ratio of 50:50 (Scheme 6) was observed, with an overall yield of >95% (EDA-based). These results brings copper into line with iron for the direct transformation of ammonia into glycine ester.

Gross and co-worker reported[13] on the mechanism of the iron-based reaction to occur with *no formation of iron-carbene intermediates*, at variance of many other metal-diazoacetate transformations. This is at variance with our $Tp^{Ms}Cu$-based system, for which the copper-carbene intermediates have already been detected and spectroscopically characterized.[14] From this $Tp^{Ms}Cu{=}C(H)CO_2Et$ species, it is very likely that a N-ylide is formed, since a related transformation with esters and similar catalysts have revealed such behaviour.[15] A final 1,2-shift from the ylide to the formal insertion product would account for the formation of the aminoacid derivative.



Scheme 6 Top: Formation of glycine derivatives from ammonia. Bottom: plausible reaction pathway.

Conclusions

We have prepared and fully characterized the ammonia complex $Tp^{Ms}Cu(NH_3)$ (**1**), that completes a series of Tp^xCuL complexes (L = MeCN, CO, olefin, alkyne), a a series of related $Tp^{Ms}Cu(amine)$ complexes. The N-H bond of coordinated ammonia has been replaced with the bulkier Ph_3C group upon reaction with Ph_3CPF_6, yielding $Tp^{Ms}Cu(NH_2CPh_3)$ in a rare example in which the trytil cation does not formally acts as hydride scavenger. The reaction of **1** with a strong base such as LDA induced the decomposition of **1** toward $Tp^{Ms}Li(THF)$, an unexpected case of transmetallation reaction. In addition to the above stoichiometric N-H functionalization, the first copper-catalyzed activation of ammonia N-H bonds has been achieved with $Tp^{Ms}Cu(THF)$ as the catalyst for the reaction with ethyl diazoacetate, leading to glycine derivatives.

Experimental

General Methods. All procedures were performed in a glovebox under an inert atmosphere of dinitrogen or using standard Schlenk techniques. All substrates were purchased from Sigma-Aldrich and used without further purification. Solvents were dried and degassed before use. The Tp$^{\mathrm{Ms}}$Cu(THF)^{4a} complex was prepared according to literature methods. NMR spectra were recorded on Agilent 400 MR or Agilent 500 DD2, ^{1}H and ^{13}C NMR shifts are reported relative to tetramethylsilane. FT-IR spectra were collected on a Nicolet IR200 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400.

Synthesis of Tp$^{\mathrm{Ms}}$Cu(NH$_3$) (1). The complex Tp$^{\mathrm{Ms}}$Cu(THF) (0.22g, 0.31 mmol) was dissolved in dichloromethane (20 mL) and NH$_3$ was bubbled through the solution at room temperature for 10 min. The solution was cooled at -30ºC leading to the isolation of colourless crystalline material in 95% yield after successive crops. Anal. Calcd for $C_{36}H_{43}BCuN_7\bullet CH_2Cl_2$: C, 60,62; H, 6.19; N, 13.37. Found: C, 60.24; H, 6.21; N, 13.17. IR(KBr): ν(B-H), 2434 cm^{-1}; ν(N-H), 3375 cm^{-1} (br). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 0.59 (s, 3H, NH_3), 1.92 (s, 18H, C$H_{3\mathrm{mesityl}}$), 2.25 (s, 9H, C$H_{3\mathrm{mesityl}}$), 6.03 (d, 3H, J = 2 Hz, CH $_{\mathrm{pyrazol}}$), 6.81 (s, 6H, CH_{mesityl}) 7.77 (d, 3H, J = 2 Hz, CH_{pyrazol}). ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 20.1 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.7 $C\mathrm{H}_{3\mathrm{mesityl}}$), 103.8 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 127.5($C\mathrm{H}_{\mathrm{mesityl}}$), 132.1 ($C\mathrm{q}_{\mathrm{mesityl}}$), 133.8 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 136.8 ($C\mathrm{q}_{\mathrm{mesityl}}$), 137.5 ($C\mathrm{q}_{\mathrm{mesityl}}$), 149.3 ($C\mathrm{q}_{\mathrm{pyrazol}}$).

General synthetic protocol for complexes Tp$^{\mathrm{Ms}}$Cu[amines] (2-5 and 7). To a solution of complex Tp$^{\mathrm{Ms}}$Cu(THF) (0.08 g, 0.114 mmol) in dichloromethane (15 mL) 4 equiv of the corresponding amine were added (0.34 mmol). After 5 min of stirring the solvent was concentrated and the solution cooled at -30ºC from which colourless crystals of **2**-**5** were collected in 60-80% yield. The complex **7** was prepared in the same way but adding only one equivalent of amine. The crystalisation was performedand in pentane (5-10 mL) to obtain yellow crystals. 43 % Yield.

Tp$^{\mathrm{Ms}}$Cu(ethylamine) (2). Anal. Calcd for $C_{38}H_{47}BCuN_7\bullet\frac{1}{2}CH_2Cl_2$: C, 64.34; H, 6.73; N, 13.64. Found: C, 64.50; H, 6.75; N, 13.33. IR(KBr): ν(B-H), 2422 cm^{-1}; ν(N-H), 3313, 3267 cm^{-1} (br) ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 0.12 (br s, 3H, C$H_{3\mathrm{amine}}$), 0.85 (br s, 2 H, NH_2), 1.37 (br s, 2H, C$H_{2\mathrm{amine}}$) , 1.89 (s, 18H, C$H_{3\mathrm{mesityl}}$), 2.21 (s, 9H, C$H_{3\mathrm{mesityl}}$), 6.00 (d, 3H, J = 2 Hz, CH_{pyrazol}), 6.78 (s, 6H, CH_{mesityl}) 7.74 (d, 3H, J = 2 Hz, CH_{pyrazol}). ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 16.8 ($C\mathrm{H}_{3\mathrm{amine}}$), 20.2 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.6 ($C\mathrm{H}_{3\mathrm{mesityl}}$), δ 39.5 ($C\mathrm{H}_{2\mathrm{amine}}$), 101.6 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 127.4 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 132.2 ($C\mathrm{q}_{\mathrm{mesityl}}$), 133.8 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 136.8 ($C\mathrm{q}_{\mathrm{mesityl}}$), 137.5 ($C\mathrm{q}_{\mathrm{mesityl}}$), 149.4 ($C\mathrm{q}_{\mathrm{pyrazol}}$).

Tp$^{\mathrm{Ms}}$Cu(diethylamine) (3). Anal. Calcd for $C_{40}H_{51}CuN_7$: C, 68.22; H 7.30; N, 13.92. Found: C, 68.03; H, 7.63; N, 13.76. IR(KBr): ν(B-H), 2445 cm^{-1}; ν(N-H), 3249, 3264 cm^{-1}. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.24 (t, 6H, C$H_{3\mathrm{amine}}$), 1.28 (s, 1H, NH_{amine}), 1.58 (m, 2H, C$H_{2\mathrm{amine}}$), 1.78 (m, 2H, C$H_{2\mathrm{amine}}$), 2.06 (s, 9H, C$H_{3\mathrm{mesityl}}$), 2.08 (s, 18H, C$H_{3\mathrm{mesityl}}$), 5.97 (d, 3H, J = 2 Hz, CH_{pyrazol}), 6.71 (s, 6H, CH_{mesityl}) 7.77 (d, 3H, J = 2 Hz, CH_{pyrazol}). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ 12.6 ($C\mathrm{H}_{3\mathrm{amine}}$), 20.6 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.7 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 42.9 ($C\mathrm{H}_{2\mathrm{amine}}$), 104.0 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 127.6 ($C\mathrm{H}_{\mathrm{mesityl}}$), 133.0 ($C\mathrm{q}_{\mathrm{mesityl}}$), 134.9($C\mathrm{H}_{\mathrm{pyrazol}}$), 136.6 ($C\mathrm{q}_{\mathrm{mesityl}}$), 137.8 ($C\mathrm{q}_{\mathrm{mesityl}}$), 150.1 ($C\mathrm{q}_{\mathrm{pyrazol}}$).

Tp$^{\mathrm{Ms}}$Cu(benzylamine) (4). Anal. Calcd for $C_{43}H_{49}BCuN_7\bullet\frac{1}{3}CH_2Cl_2$: C, 67.92; H, 6.53; N, 12.80. Found: C, 68.36; H, 6.47; N, 12.94. IR(KBr): ν(B-H), 2421 cm^{-1}, ν(N-H), 3321, 3271 cm^{-1}.^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 1.24 (t, 2H, N$H_{2\mathrm{amine}}$), 1.96 (s, 18H, C$H_{3\mathrm{mesityl}}$), 2.15 (s, 9H, C$H_{3\mathrm{mesityl}}$), 2.39 (t, 2H, C$H_{2\mathrm{amine}}$), 6.06 (d, 3H, J = 2 Hz, CH_{pyrazol}), 6.50 (d, 2H, J = 6.9 Hz, C$H_{\mathrm{arom\ amine}}$), 6.79 (s, 6H, CH_{mesityl}), 7.23 (m, 3H,C$H_{\mathrm{arom\ amine}}$), 7.79 (d, 3H, J = 2 Hz, CH_{pyrazol}).^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 20.2 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.6 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 48.8 ($C\mathrm{H}_{2\mathrm{amine}}$), 103.6 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 126.2 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 126.9 ($C_{\mathrm{qarom\ amine}}$), 127.5 ($C\mathrm{H}_{\mathrm{mesityl}}$), 128.3 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 132.3($C_{\mathrm{qmesityl}}$), 133.9 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 136.9 ($C_{\mathrm{qmesityl}}$), 137.6 ($C_{\mathrm{qmesityl}}$), 141.4 ($C_{\mathrm{q\ arom\ amine}}$), 149.3 ($C_{\mathrm{qpyrazol}}$).

Tp$^{\mathrm{Ms}}$Cu(Triphenylmethylamine) (5). Anal. Calcd for $C_{55}H_{57}CuN_7$: C 74.19; H, 6.45; N, 11.01. Found: C, 74.36; H, 6.45; N, 11.05. IR(KBr): ν(B-H), 2255 cm^{-1}; ν(N-H), 3305, 3255 cm^{-1}. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 1.80 (s, 6H, C$H_{3\mathrm{mesityl}}$), 1.81 (s, 12H, C$H_{3\mathrm{mesityl}}$), 1.93 (s, 6H, C$H_{3\mathrm{mesityl}}$), 2.30 (s, 3H, C$H_{3\mathrm{mesityl}}$), 3.26 (s, 2H, NH_2), 5.98 (d, 2H, J = 2 Hz, CH_{pyrazol}), 6.02 (d, 4H, J = 7.6 Hz, C$H_{\mathrm{arom\ amine}}$), 6.08 (d, 1H, J = 2 Hz, CH_{pyrazol}), 6.32 (s, 4H, CH_{mesityl}), 6.75 (s, 2H, CH_{mesityl}), 7.07 (t, 4H, J = 7.6 Hz, C$H_{\mathrm{arom\ amine}}$), 7.26 (m, 7 H, C$H_{\mathrm{arom\ amine}}$), 7.78 (d, 2H, J = 2 Hz, CH_{pyrazol}), 7.82 (d, 1H, J = 2 Hz, CH_{pyrazol}).^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 20.0 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.4 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.6 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.9 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 103.9 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 106.1 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 126.5 ($C_{\mathrm{q}}$), 126.8 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 127.4 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 127.8 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 127.8 ($C\mathrm{H}_{\mathrm{mesityl}}$), 128.0 ($C\mathrm{H}_{\mathrm{mesityl}}$), 128.0 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 128.3 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 130.2 ($C$q), 131.7 ($C$q), 134.9 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 135.9 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 136.8 ($C$q), 137.2 ($C$q),137.3 ($C$q), 145.8 ($C$q), 148.84 ($C$q), 150.4 ($C$q), 152.5 ($C$q).

Tp$^{\mathrm{Ms}}$Cu(Diphenylmethylamine) (7). Anal. Calcd for $C_{49}H_{53}BCuN_7$: C, 72.27; H, 6.57; N, 12.04. Found: C,71.92; H, 6.842; N, 11.99. IR(KBr): ν(B-H), 2434 cm^{-1}; ν(N-H), 3262, 3311 cm^{-1} (br). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 1.91 (s, 18H, C$H_{3\mathrm{mesityl}}$), 2.09 (s, 9H, C$H_{3\mathrm{mesityl}}$), 3.76 (br, 1H, CH_{amine}), 6.04 (d, 3H, J = 2 Hz, CH_{pyrazol}), 6.50 (br, 4H, C$H_{\mathrm{arom\ amine}}$), 6.56 (s, 6H, CH_{mesityl}), 7.20 (m, 6H,C$H_{\mathrm{arom\ amine}}$), 7.80 (d, 3H, J = 2 Hz, CH_{pyrazol}).^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 20.3 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.8 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 61.4 ($C\mathrm{H}_{\mathrm{amine}}$), 104.0 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 126.2 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 126.8 ($C\mathrm{q}_{\mathrm{arom\ amine}}$), 127.9 ($C\mathrm{H}_{\mathrm{mesityl}}$), 128.1 ($C\mathrm{H}_{\mathrm{arom\ amine}}$), 131.9($C\mathrm{q}_{\mathrm{mesityl}}$), 134.3 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 136.9 ($C\mathrm{q}_{\mathrm{mesityl}}$), 137.1 ($C\mathrm{q}_{\mathrm{mesityl}}$), 143.9 ($C\mathrm{q}_{\mathrm{arom\ amine}}$), 149.9 ($C\mathrm{q}_{\mathrm{pyrazol}}$).

Isolation of Tp$^{\mathrm{Ms}}$Li(THF) (6). This complex was isolated from the reaction of complex **1** (0.1 mmol) and LDA (0.1 mL of a 2 M solution in THF) or BuLi (0.08 mL of a 2,5 M solution in Hexane). The first method complex **1** was dissolved in dicloromethane (10 mL) and cooled to -50 ° C .Next was added LDA. The reaction was stirred for 30 min. After was filtered and concentrated and cooled at -30ºC. White-Brown crystals were obtained that correspond to compound (**6**) Yields 32%. the second method to solution of 1 in (15 mL) of tetrahydrofurane was added 100 µL of BuLi .The reaction followed the same previous procedure to give white crystals. Yield 36%

Anal. Calcd for $C_{40}H_{48}BLiN_6O$: C 74.3 , H 7.48, N 13.00. Found: C 74.55, H 7.55, N 13.27. 1H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.22 (s, 4H, C$H_{2\mathrm{thf}}$), 1.85 (s, 18H, C$H_{3\mathrm{mesityl}}$), 2.20 (s, 9H, C$H_{3\mathrm{mesityl}}$), 2.69 (s, 4H, C$H_{2\mathrm{thf}}$), 5.97 (d, 3H, J = 2 Hz, CH_{pyrazol}), 6.77 (s, 6H, CH_{mesityl}) 7.78 (d, 3H, J = 2 Hz, CH_{pyrazol}). 13C{1H} NMR (125 MHz, CD$_2$Cl$_2$): δ 20.1 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 20.6 ($C\mathrm{H}_{3\mathrm{mesityl}}$), 24.9 ($C\mathrm{H}_{2\mathrm{thf}}$), 66.9 ($C$H2thf), 103.9 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 127.3($C\mathrm{H}_{\mathrm{mesityl}}$), 132.2 ($C\mathrm{q}_{\mathrm{mesityl}}$), 134.8 ($C\mathrm{H}_{\mathrm{pyrazol}}$), 136.7 ($C\mathrm{q}_{\mathrm{mesityl}}$), 137.5 ($C\mathrm{q}_{\mathrm{mesityl}}$), 150.7 ($C\mathrm{q}_{\mathrm{pyrazol}}$).

X-ray structure determination. The structures of complexes **1**-**7** have been determined and deposited in the CCDC with the following codes: **1**, CCDC-1443209; **2**, CCDC-1443210; **3**, CCDC-

1443211; **4**, CCDC-1443212; **5**, CCDC-1443213; **6**, CCDC-1443214 and **7**, CCDC-1443215. See ESI for full details on their determination.

Amine Exchange Reactions. A solution of Tp^{Ms}Cu(NH$_3$) (**1**) in 0.6mL of deuterated solvent dichloromethane was placed in a NMR tube and one equiv of the corresponding amine was added. NMR analysis showed the formation of **3** or **4** in a few minutes. Complex **1** was restored upon bubbling ammonia gas through the solution for several minutes.

Carbene transfer reaction from ethyl diazoacetate (EDA) to ammonia. A solution of Tp^{Ms}Cu(THF) (0.08 mmol) in dichloromethane 20 mL was saturated with ammonia upon gentle bubbling for 15 min. Then the NH_3 supply was disconnected and a solution of EDA (1.6 mmol in 5 mL of dichloromethane) was slowly added for 1 h. After an overall 72 h time of stirring, the mixture was taken to dryness and the residue was investigated by NMR spectroscopy that show the exclusive formation of ethyl glycinate ester $NH_2CH_2CO_2Et$ and the bis-functionalized product $NH(CH_2CO_2Et)_2$ in ca. equimolar amounts (yields established by GCMS). No carbene dimers nor unreacted EDA was observed after that time.

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References

1 (a) L. B Huang, M. Arndt, K. Goosen, H. Heydt and L. J. Goosen, *Chem. Rev.* 2015, **115**, 2596. (b) J. Kim, H. J. Kim and S. Chang, *Eur. J. Org. Chem.* 2013, 3201. (c) J. L. Klinkenberg and J. F. Hartwig, *Angew. Chem. Int. Ed.* 2011, **50**, 86.

2 K. R. Powell, P. J. Pérez, L. Luan, S. G. Feng, P. S. White, M. Brookhart and J. L. Templeton, *Organometallics*, 1994, **13**, 1851.

3 E. D. Blue, A. Davis, D. Conner, T. B. Gunnoe, P. D. Boyle and P. S. White, *J. Am. Chem. Soc.*, 2003, **125**, 9435.

4 (a) J. L. Schneider, S. M. Carrier, C. E. Ruggiero, Jr. V. G Young and W. B. Tolman, *J. Am. Chem. Soc.*, 1998, **120**, 11408. (b) E. Despagnet-Ayoub, K. Jacob, L. Vendier, M. Etienne, E. Alvarez, A. Caballero, M. M. Díaz-Requejo and P. J. Pérez, *Organometallics* 2008, **27**, 4779.

5 (a) M. R. Churchill, B. G. DeBoer, F. J. Rotella, O. Abu.Salah and M. I. Bruce, *Inorg. Chem.*, 1975, **14**, 2051. (b) H. V. R. Dias and X. Wang, *Dalton Trans.,* **2005**, 2985.

6 H. V. R. Dias, W. Jin , H.-J. Kim and H.-L. Lu, *Inorg. Chem.* 1996, **35**, 2317.

7 C. Martín, J. M. Muñoz-Molina, A. Locati, E. Alvarez, F. Maseras, T.R. Belderrain and P. J. Pérez, *Organometallics*, 2010, **29**, 3481.

8 C. Martín, M. Sierra, E. Álvarez, T. R. Belderrain and P. J. Pérez, *Dalton Trans.*, 2012, **41**, 5319.

9 I. Aviv and Z. Gross, *Chem. Commun.*, 2006, 4477.

10 See for example: M. E. Morilla, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *Chem. Commun.,* 2002, 2998 and references cited therein.

11 K. Nakamoto*, Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 5ª ed, John Wiley & Sons: Hoboken, New Jersey, 2009.

12 (a) G. Groger, F. Olbrich, P. Schulte and U. Behrens, *J. Organomet. Chem.*, 1998, **557**, 251. (b) J. B. Tommasino, F. N. R. Renaud, D. Luneau and G. Pilet, *Polyhedron*, 2011, **30**, 1663.

13 I. Aviv and Z. Gross, *Chem. Eur. J.*, 2008, **14**, 3995-4005.

14 A. Pereira, Y. Champouret, C. Martín, E. Álvarez, M. Etienne, T. R. Belderraín, and P. J. Pérez, *Chem. Eur. J*. 2015, **21**, 9769.

15 R. Gava, M. A. Fuentes, M. Besora, T. R. Belderrain, K. Jacob, F. Maseras, M. Etienne, A. Caballero and P. J. Pérez, *ChemCatChem* 2014, **6**, 2206.