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Pyrazole-Bridged NHC Ligands and Their Dimetallic (Allyl)palladium Complexes

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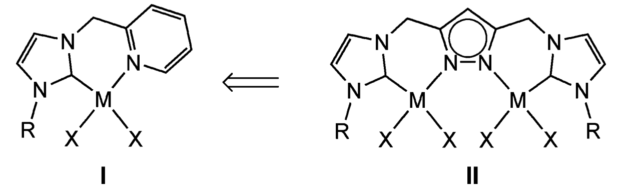
A set of compartmental pyrazole-based ligands with appended NHC donors has been synthesized and isolated as $[H_4L]Cl_3$ and $[H_3L](PF_6)_2$ salts. Dinuclear (allyl)palladium complexes of these ligands are conveniently accessible via the in situ prepared silver species. Three complexes $[(allyl)_2Pd_2L]PF_6$ and one derivative $[(methallyl)_2Pd_2L]PF_6$ have been characterized crystallographically, which revealed that the metal ions are positioned in close proximity [d(Pd···Pd) = 3.97–4.05 Å], with two possible mutual orientations of the (meth)allyl ligands within the dimetallic pocket. NMR spectroscopy shows slow interconversion of these isomers (k = 0.05–0.4 s^{-1}), where the (meth)allyl ligands are detached *trans* to the carbene during this η^3-η^1-η^3 dynamic process.

Introduction

N-Heterocyclic carbenes (NHC) have become one of the most popular ligand classes for transition metals.[1–3] The original and most commonly used NHCs usually bear two identical bulky hydrocarbon groups at the nitrogen atoms of the imidazole ring, and the required symmetric imidazolium salts that serve as precursors for such NHCs are conveniently accessible by standard preparation procedures.[4] Over the last years manifold variations have been introduced into this chemistry, like substitutions at the backbone of the imidazole or NHCs having different groups in the periphery,[5–7] including linkers to connect several NHCs within one ligand molecule and/or side arms containing additional heteroatoms as potential donor atoms in pincer complexes.[8,9] Carbenes bearing appended N-heterocycles such as pyridine (e.g., type **I** in Scheme 1) [10,11] have attracted particular attention and have shown promising potential in catalytic applications.[12]

A further elaboration is the combination of carbenes with chelating moieties that can act as a bridging unit between two metal ions, giving rise to highly preorganized dimetallic arrangements where the two metal ions are held in close proximity. We and others have recently developed bis(NHC) ligands with a potentially bridging pyridazine moiety,[13,14] and we now report some related systems based on a central pyrazolate core (type **II**, Scheme 1). Pyrazolates with chelating side arms in the 3- and 5-positions of the heterocycle have proven successful for generating manifold dimetallic complexes,[15–19] with valuable applications in bioinorganic modelling and catalysis.[20–22] The targeted pyrazolate/NHC hybrid compounds **II** can formally be described as dinuclear versions of the established type **I** complexes, where the proximate metal ions in **II** might cooperate during substrate turnover. We describe here a convenient and versatile synthetic access to the required compartmental ligand systems, and the structural and NMR spectroscopic characterization of their dinuclear (allyl)palladium complexes. Parallel to and independent of our investigation, a first example of such a pyrazolate/NHC ligand (R = Me) together with its Ag^I and Au^I complexes has recently been reported by Zhou and Chen,[23] and even more recently the molecular structures of Ni and Rh complexes (R = $C_6H_3Me_2$-2,6) have been communicated.[24]



Scheme 1.

Results and Discussion

Synthesis of the pyrazole/imidazolium ligand precursors is possible by a straightforward approach (Scheme 2).[25] Starting from 3,5-bis(chloromethyl)-1-(tetrahydropyran-2-

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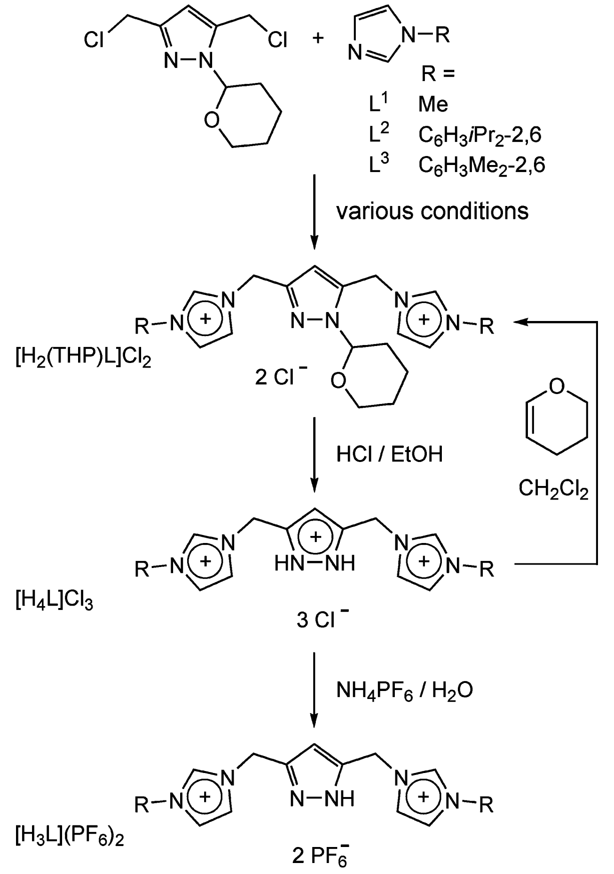
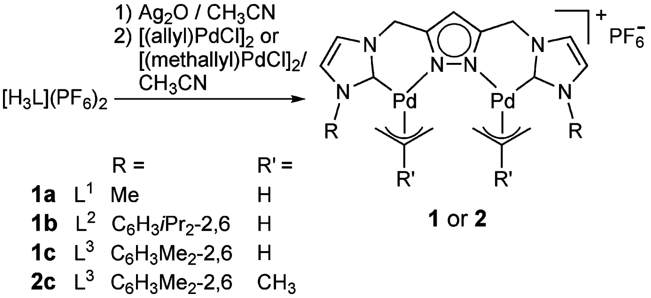
yl)pyrazole[26] and various *N*-substituted imidazoles, ligand precursors $[H_2(THP)L]Cl_2$ and $[H_4L]Cl_3$ can be prepared. Reaction conditions have to be set carefully in order to obtain the THP-protected compound, since trace amounts of acid may remove the THP group, and hence a base such as Na_2CO_3 should be added to the reaction mixture. Reaction temperature is another crucial parameter, as the THP protecting group can be cleaved off at elevated temperatures (approx. 160 °C). These issues become irrelevant, however, when $[H_4L]Cl_3$ is the desired product, and acidification of the crude product with ethanolic HCl yields the hydrochloride salt directly (if necessary, this can again be converted into the THP-protected compound). Ion exchange with NH_4PF_6 finally affords $[H_3L](PF_6)_2$. Yields of all steps are usually good, making this an efficient synthetic method (see Supporting Information for experimental and analytical data). Problems reported by others when using the non-protected pyrazole starting material were not encountered here,[23] and in our hands addition of NaI[24] to achieve the initial substitution reaction was not necessary. Compounds $[H_2(THP)L]Cl_2$, $[H_4L]Cl_3$, and $[H_3L](PF_6)_2$ derived from three different *N*-substituted imidazoles (R = Me, $C_6H_3i Pr_2$-2,6, $C_6H_3Me_2$-2,6) were prepared and fully characterized, and crystals suitable for X-ray diffraction could be grown for $[H_2L^2]Cl_2$, $[H_2L^2](PF_6)_2$ and $[H_2L^3](PF_6)_2$ from ethanol/hexanes or acetonitrile/diethyl ether. Molecular structures and crystallographic data are provided as Supporting Information (Figures S1–S3). Rather close contacts are found between the imidazolium-C^2–H protons and the counteranions in all cases. While these interactions can be regarded as hydrogen bonding in the case of $[H_2L^2]Cl_2$, the situation is less clear for $[H_2L^2](PF_6)_2$ and $[H_2L^3](PF_6)_2$, since both PF_6^- are disordered, and no direct C–H···F interaction to a single fluorine atom is discernible. A similar situation was observed for the PF_6^- salts of related pyridazine/NHC hybrid compounds.[13a]

Deprotonation of any ligand precursor $[H_3L](PF_6)_2$ by KHMDS (potassium hexamethyldisilazane) and addition of a suitable metal precursor complex is a potentially useful access to yield the desired dimetallic products. However, in our hands an alternative procedure proved to be advantageous. Dissolution of $[H_3L](PF_6)_2$ in acetonitrile and addition of Ag_2O gave the corresponding silver complexes. One such complex has previously been identified as a tetranuclear cluster in the case of $[H_3L^1](PF_6)_2$ (R = Me).[23] MS data for the corresponding silver complexes of ligands L^2 and L^3 show prominent peaks with *m*/*z* values characteristic for $[(Ag_4L_2)(PF_6)]^+$, indicating the formation of silver clusters similar to that of L^1. Transmetallation of the silver complexes with $[(allyl)PdCl]_2$ or $[(methallyl)PdCl]_2$ then cleanly gave the targeted dimetallic complexes **1** and **2** (Scheme 3).

Crystallisation of **1a**–**c** and **2c** was achieved by diffusion of diethyl ether into acetonitrile solutions, and crystals of all four compounds were studied by X-ray diffraction. Molecular structures of **1a** and **1b** are provided in Figures S4 and S5 (see Supporting Information), those of **1c** and **2c** are shown in Figures 1 and 2.



Scheme 2. Synthesis of ligand precursors.



Scheme 3. Synthesis of palladium complexes **1** and **2**.

The Pd1···Pd2 distances for **1a**–**c** and **2c** lie in the range 3.97–4.05 Å, which is shorter than in the related (cod)Rh complex of L^3 [*d*(Rh1···Rh2) = 4.21 Å].[24] Inspection of the metric parameters of all four complexes reveals that their dimetallic nature and the pyrazolato bridge do not cause any significant differences compared to related mononuclear compounds: a CSD (Cambridge Structural Database) search for the (allyl)Pd–$C^{carbene}$ fragment ($C^{carbene}$ = part of an NHC) gave 24 hits. In most cases an additional chlorine atom is bound to Pd. The Pd–$C^{carbene}$ distances of 2.03–2.04 Å observed in **1a**–**c** and **2c** agree well with the mean Pd–$C^{carbene}$ distance of 2.04 Å of those 24 compounds found in the database, as do the Pd–C^{allyl} bond lengths (range for **1a**–**c** and **2c**: 2.03–2.19 Å; CSD: 2.03–2.28 Å). Deprotonation of the imidazolium-C^2–H and co-

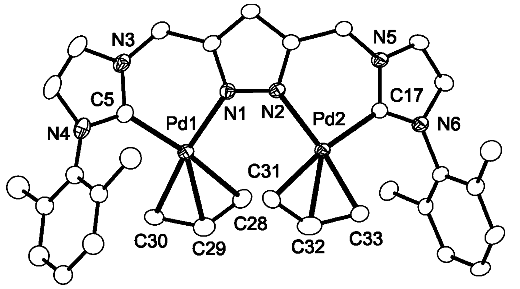


Figure 1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **1c**. For the sake of clarity all hydrogen atoms, disorder, the solvent molecule, and PF_6^- have been omitted. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.075(4), Pd1–C5 2.036(5), Pd1–C28 2.183(5), Pd1–C29 2.129(7), Pd1–C30 2.119(5), Pd2–N2 2.087(4), Pd2–C17 2.035(5), Pd2–C31 2.190(6), Pd2–C32 2.132(7), Pd2–C33 2.113(6), Pd1···Pd2 3.9711(5), C28–C29 1.341(10), C29–C30 1.401(10), C31–C32 1.351(9), C32–C33 1.396(10), N3–C5 1.353(7), N4–C5 1.340(8), N5–C17 1.350(7), N6–C17 1.357(6); N1–Pd1–C5 86.6(2), N1–Pd1–C28 102.2(2), N1–Pd1–C29 133.7(2), N1–Pd1–C30 170.0(2), C5–Pd1–C28 169.4(2), C5–Pd1–C29 137.6(3), C5–Pd1–C30 102.7(2), N2–Pd2–C17 86.24(19), N2–Pd2–C31 103.2(2), N2–Pd2–C32 134.9(3), N2–Pd2–C33 171.3(2), C17–Pd2–C31 169.5(2), C17–Pd2–C32 136.5(3), C17–Pd2–C33 101.9(2), C28–C29–C30 123.1(7), C31–C32–C33 123.6(7), N3–C5–N4 104.3(5), N5–C17–N6 104.3(4).

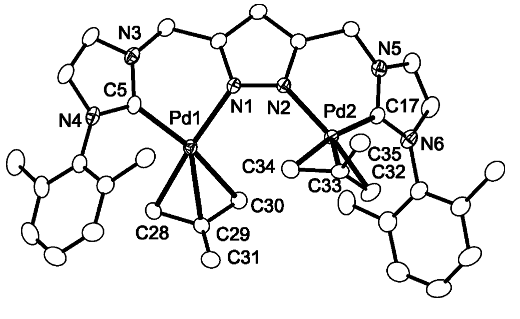
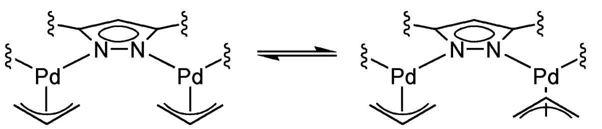


Figure 2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **2c**. Only one of the two crystallographically independent molecules is shown. For the sake of clarity all hydrogen atoms, the solvent molecule, and PF_6^- have been omitted. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.079(3), Pd1–C5 2.026(3), Pd1–C28 2.108(4), Pd1–C29 2.183(4), Pd1–C30 2.182(4), Pd2–N2 2.075(3), Pd2–C17 2.031(3), Pd2–C32 2.102(4), Pd2–C33 2.164(3), Pd2–C34 2.179(4), Pd1···Pd2 3.9929(4), C28–C29 1.419(5), C29–C30 1.396(5), C32–C33 1.407(5), C33–C34 1.394(5), N3–C5 1.350(5), N4–C5 1.359(5), N5–C17 1.361(4), N6–C17 1.352(4); N1–Pd1–C5 86.99(13), N1–Pd1–C28 166.99(13), N1–Pd1–C29 136.76(12), N1–Pd1–C30 102.93(13), C5–Pd1–C28 101.11(15), C5–Pd1–C29 135.21(15), C5–Pd1–C30 167.53(15), N2–Pd2–C17 86.07(12), N2–Pd2–C32 171.01(14), N2–Pd2–C33 134.02(11), N2–Pd2–C34 103.08(13), C17–Pd2–C32 102.85(15), C17–Pd2–C33 135.05(14), C17–Pd2–C34 170.72(14), C28–C29–C30 116.6(4), C32–C33–C34 117.5(4), N3–C5–N4 104.4(3), N5–C17–N6 103.9(3).

ordination to Pd decreases the N–C–N angle by approximately 5°. The resulting N–C–N angle is around 104°, which again is in very good agreement with those of other Pd–NHC compounds (mean value 104.9°). Due to the chelate effect, the bite angle $N^{pyrazolate}$–Pd–$C^{carbene}$ is smaller than 90°. The allyl ligands in the dimetallic complexes **1a** and **1b** are disordered over two positions, the disorder involving all atoms in **1a** but only the central carbon atoms in **1b**, whereas no disorder of the methallyl ligand is found in **2c**. In accordance with that observation, inspection of the structures of **1c** and **2c** shows that two different mutual orientations of the allyl groups are possible in these dimetallic frameworks (Scheme 4).



Scheme 4.

In order to probe whether these two forms equilibrate in solution, all complexes were investigated in detail by NMR spectroscopy. Room-temperature ^1H and ^{13}C NMR spectra of **1a–c** and **2c** in acetonitrile reveal that indeed in all cases two distinct but symmetric isomeric states are assumed (hereafter referred to as "**A**" and "**B**" for the major and minor states, respectively). For example, each of **1aA** and **1aB** displays a single ^1H resonance for the *N*-methyl group, one characteristic AB pattern for the bridging CH_2 groups, and five resonances for the two allyl ligands. **1aA** and **1aB** are nearly equally populated (^1H integral ratios of about 1:0.9) over a large temperature range (–35 to 45 °C).

A ^1H-EXSY spectrum of **1a** shows that **1aA** and **1aB** slowly ($k = 0.4\ s^{-1}$) interconvert by rotation of a single allyl ligand (Figure 3). Allyl resonances could be assigned from intra-allyl NOE correlations (gray peaks in Figure 3) and an NOE correlation between $H^{cis,syn}$ and the *N*-Me group; the assignment is in accordance with literature data.[27] This type of allyl rotation is known to proceed via an η^1 binding mode where the second coordination site may be temporarily occupied by a solvent molecule.[27] Due to the pronounced *trans* effect of the NHC donor, the CH_2 group *trans* to the carbene is weakened and more labile than the CH_2 group *cis* to the carbene (i.e., *trans* to the pyrazolate). In the case of **1a**, it therefore is the latter that remains attached to the Pd center in the η^1 intermediate, thereby exchanging these two protons. A similar exchange is observed in acetonitrile for **1c** ($k = 0.2\ s^{-1}$), and, with more skewed (2:1) populations, for **1b** ($k_{AB} = 0.1\ s^{-1}$, $k_{BA} = 0.2\ s^{-1}$) and **2c** ($k_{AB} = 0.05\ s^{-1}$, $k_{BA} = 0.1\ s^{-1}$). Decreased rates and disturbed populations are likely due to increased steric hindrance of the bulkier imidazole *N*-substituents and methallyl ligands, respectively. In chloroform, exchange between **2cA** and **2cB** is at least one order of magnitude slower, which is in accordance with the proposed involvement of the solvent in the interconversion.

When a single crystal of **2c** was dissolved in acetonitrile at –35 °C, a ^1H NMR spectrum of almost pure **2cA** with very little **2cB** was obtained, which slowly re-equilibrated towards the 2:1 ratio within 1 h. The **A** subspectrum can thus be assigned to the complex in which the two (meth)allyl ligands are oriented approximately parallel, as seen in

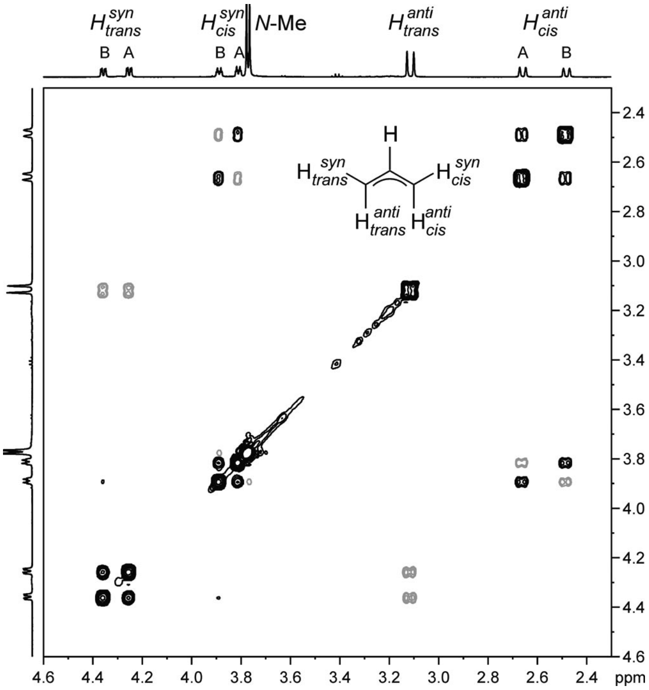


Figure 3. Part of the ^{1}H-EXSY spectrum of **1a** in CD_3CN. Exchange correlations are shown in black, NOE correlations are shown in gray. The spectrum was acquired at 25°C with 384×512 data points in a total of 2.5 h by using a 500 MHz spectrometer with a mixing time of 500 ms.

the crystal structure of **2c**. The pyrazolato/NHC ligand itself seems to be dynamic in solution, as can be deduced from several broad peaks at –35 °C that merge and become sharp due to an "average" plane of symmetry at room temperature (see Figure S6). A single η^3-η^1-η^3 isomerization changes the relative orientation of the two allyl ligands, and thus replaces the local mirror symmetry by an apparent C_2 axis (Scheme 4).

Conclusions

A straightforward procedure has been developed for the synthesis of compartmental pyrazolato/NHC hybrid ligands with side-arm substituents of different size, and several pyrazolato-bridged dimetallic palladium complexes could be conveniently obtained via the in situ prepared silver complexes. These highly preorganized dinucleating ligand scaffolds position the two (allyl)palladium fragments in close proximity, which appears to be a favourable situation for cooperative effects in metal-mediated substrate transformations. Two features appear to be particularly attractive in this regard: bulky aryl substituents at the periphery (such as in L^2 and L^3) shield the dimetallic active site and create a true binding pocket, and the pronounced *trans* effect of the strong σ-donor NHC ligands labilizes those coordination sites that are directed towards the centre between the two metal ions. NMR spectroscopy confirms that the allyl ligands are detached *trans* to the carbene during their rotation in a η^3-η^1-η^3 process, which leads to slow interconversion (k = 0.05–0.4 s^{-1}) of different isomers. We are currently exploring the reactivity and anticipated catalytic applications of these novel complexes.

Experimental Section

General Procedure for the Synthesis of Pd Complexes: A mixture of $[H_3L](PF_6)_2$ (1.0 equiv.) and Ag_2O (2.5 equiv.) in CH_3CN was stirred under exclusion of light at room temp. for 24 h. Activated charcoal was added, and the mixture was filtered through Celite®. The solvent was removed from the filtrate, and the crude product was dried under vacuum. This product was used without further purification, it was dissolved in acetonitrile, and a solution of $[(allyl)PdCl]_2$ or $[(methallyl)PdCl]_2$ in CH_3CN was added (2.0 equiv.). This mixture was again stirred under exclusion of light at room temp. for 24 h and then filtered using activated charcoal and Celite®. Most of the solvent was evaporated from the filtrate, the remaining concentrated solution was poured into diethyl ether, and the precipitate that formed was collected by filtration and dried under vacuum, to yield **1a**–**c** and **2c**. Crystalline material could be obtained at room temp. by diffusion of diethyl ether into acetonitrile solutions of the corresponding complexes. Experimental details for the syntheses of all ligand precursors (9 compounds) as well as analytical data for palladium complexes **1a**–**c** and **2c** are given as Supporting Information. CCDC-667625, -667626, -667627, -667628, -667629, -667630, and -667631 contain the supplementary crystallographic data for $[H_3L^2]Cl_2$, $[H_3L^2](PF_6)_2$, $[H_3L^3](PF_6)_2$, **1a**, **1b**, **1c**, and **2c**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Supporting Information (see footnote on the first page of this article): Preparatory, analytical and crystallographic data.

Acknowledgments

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