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Pyrazole-Derived Remote Dicarbenes: Versatile Ligands for Di- and Tetranuclear Complexes

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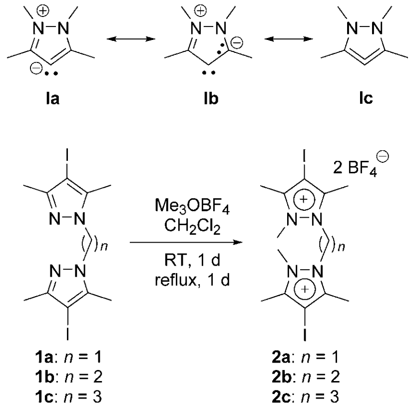
The spectacular success of N-heterocyclic carbenes (NHCs) as a new class of ligands in organometallic chemistry and their application to catalytic systems has been primarily attributed to their strong electron-donating nature.[1] The extension to yet stronger donors has recently lead to the design of non-conventional NHCs[2] including remote NHCs (*r*NHCs),[3] cyclic (alkyl)aminocarbenes (CAACs)[4] and "carbodicarbenes" (CDCs), which can also be regarded as zerovalent carbon complexes.[5] In relation to this development, we have recently introduced complexes of pyrazole-based *remote* and *abnormal* NHCs, which are isomeric to imidazolin-2-ylidenes and thus were termed pyrazolin-4-ylidenes.[6] However, their true nature is currently still under debate, and as depicted in Scheme 1, these ligands can be represented by a zwitterion (**Ia**),[7] an abnormal *r*NHC (**Ib**)[6,8] or a neutral cyclic bent allene (**Ic**).[9,10]



Scheme 1. Selected resonance structures of "pyrazolin-4-ylidenes" (**Ia–c**) and synthesis of di(pyrazolium) salts **2a–c**.

Although more detailed investigations are required to reveal their true identity, there is no doubt that they form a new class of strongly donating ligands (**L**) as shown by an even lower CO stretching frequency in [RhCl(**L**)(CO)$_2$] compared to those in classical NHCs or phosphine analogues.[9a] Owing to the substantial carbenoid ligand character in their metal complexes we will refer to them as abnormal *r*NHCs in this work.[6,8] The coordination chemistry of such abnormal *r*NHCs is poorly understood and only monodentate examples have been reported. Bi- or multidentate ligands of this type capable of constructing macrocyclic entities through metal-directed self-assembly, an area of great interest,[11] remain unknown. Among such architectures, molecular squares built from four metal-containing corners linked by four spacers have been widely studied.[12] Commonly-used spacers contain nitrogen donor groups, whereas spacers utilizing carbon donors are very rare. Only recently, Bielawski reported linear di- or polynuclear complexes incorporating Janus-type NHCs as spacers.[13] Employing these spacers, a Ni rectangle with 4,4′-bipyridine as a second linker was reported by Hahn.[14] Herein, we report on the coordination chemistry of unprecedented remote and abnormal dicarbenes and their use as a new class of organometallic spacers for the formation of di- and tetranuclear Pd^{II} complexes.

The suitable ligand precursors with bridges of different lengths (**2a–c**) were obtained through alkylation of 4,4′-diiododipyrazoles[15] **1a–c** with Me$_3$OBF$_4$ as white solids in moderate to high yields of 86%, 93% and 62%, respectively (Scheme 1). The topology of **2a–c** ensures the exclusive formation of di- or polynuclear complexes and prevents chelation of the resulting dicarbenes.

Dipyrazolium salt **2c** was reacted with a pre-mixed solution of [Pd$_2$(dba)$_3$]/PPh$_3$ (1:4 ratio, dba = dibenzylideneacetone) in CH$_2$Cl$_2$ (Scheme 2) in an attempt to synthesize a dinuclear Pd^{II}–dicarbene complex. Owing to the long propylene chain, the two pyrazolium moieties are not likely to interfere with each other to a significant extent, and oxidative addition is expected to proceed in a similar manner as that

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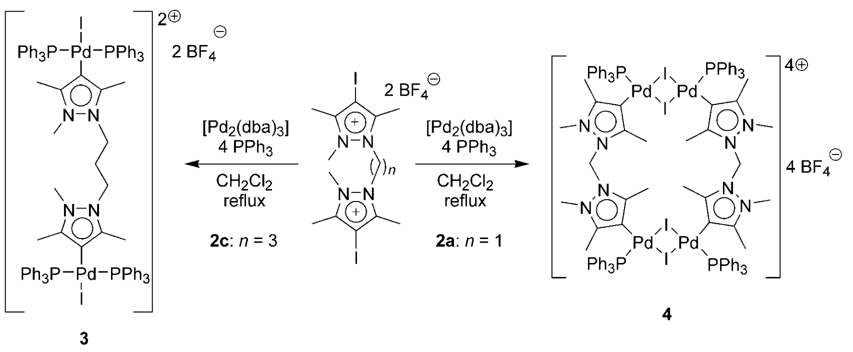

Scheme 2. Synthesis of dinuclear and tetranuclear Pd^{II}–di-*r*NHC complexes **3** and **4**.

for mono-pyrazolium salts. On the other hand, the insolubility of **2c** in CH_2Cl_2 as a result of its high charge and the difficulty of conducting two oxidative additions on a single molecule demanded a prolonged reaction time of $\approx$18 h (overnight) after which the first dinuclear di-*r*NHC complex **3** was obtained as yellow crystals (36% yield).

Its ESI MS spectrum corroborates the formation of a dinuclear complex by an isotopic envelope centered at $m/z = 888$, owing to the dicationic $[M-2\,BF_4]^{2+}$ fragment. In addition, its ^1H NMR spectrum shows upfield shifts for all signals of the bridging di-*r*NHC ligand compared to those of its ligand precursor (**2c**). The NCH_2 and CH_2 protons of the propylene bridge resonate as a triplet at $\delta = 3.76$ ppm and a quintet at $\delta = 1.53$ ppm, which indicates free rotation of the propylene bridge even in close proximity of the bulky PPh_3 ligands on each Pd center. The ^{13}C signal for the carbon donor atom appears at $\delta = 128.7$ ppm as a triplet with a coupling constant of $^2J(C,P) = 7.3$ Hz, suggesting a *trans* arrangement of the two PPh_3 ligands at each Pd center. Correspondingly, only one singlet was observed at $\delta = 22.7$ ppm in the ^{31}P NMR spectrum.

The identity of complex **3** was unambiguously confirmed by X-ray diffraction analysis on single crystals obtained by slow evaporation of a CH_2Cl_2/hexane solution.[16] The molecular structure depicted in Figure 1 shows the expected *trans* configuration, as found in solution by NMR spectroscopy. The two Pd^{II} centers are linked by the propylene-bridged di-*r*NHC ligand with each adopting a square-planar geometry. The two cyclic carbene planes are oriented almost perpendicular to the respective $PdICP_2$ coordination plane with dihedral angles of 85.02 and 81.85° to relieve steric congestion. The Pd–C bond lengths of 2.011(9) and 2.013(8) Å are also comparable to those observed for mononuclear analogues[6b,c] and standard Pd^{II}–NHC complexes.

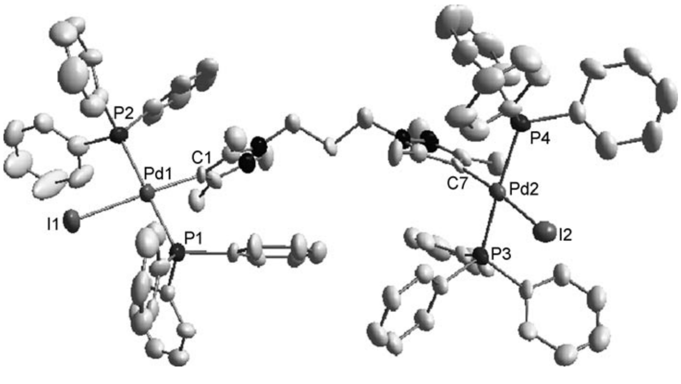

Figure 1. Molecular structure of the dinuclear cation of $\mathbf{3}\cdot 2\,CH_2Cl_2$ showing 50% probability ellipsoids; BF_4^- ions, hydrogen atoms and solvent molecules are omitted for clarity.

Double oxidative addition of **2a** to $[Pd_2(dba)_3]/PPh_3$ was more difficult, owing to steric interferences arising from the short methylene-bridge, which was also found to prevent complex-formation analogous to **3**. Instead, an interesting tetranuclear complex **4** was isolated as a yellow crystalline material. Its structure was confirmed by X-ray diffraction analysis on single crystals of the toluene solvate $\mathbf{4}\cdot 2\,C_6H_5CH_3$ obtained from a concentrated CH_3CN/toluene solution (Figure 2).[16] Compound **4** consists of a tetranuclear cation balanced by BF_4^- counter-anions. The four Pd^{II} centers and the bridging iodo ligands form two rhombuses, which are linked by two di-*r*NHC ligands to form a rectangular macrocyclic structure with dimensions of 7.051 × 8.338 Å. Notably, the corners of this rectangle are not formed by the Pd atoms, but by the CH_2-spacer of the dicarbene and the bridging anions I2/I2A. The latter are found to be partially replaced by Cl captured from the reaction media CH_2Cl_2 with occupancy ratio of 70:30 (I:Cl).[17] In Figure 2 only iodido ligands are shown for clarity. The two cyclic carbene planes in one ligand are almost perpendicular

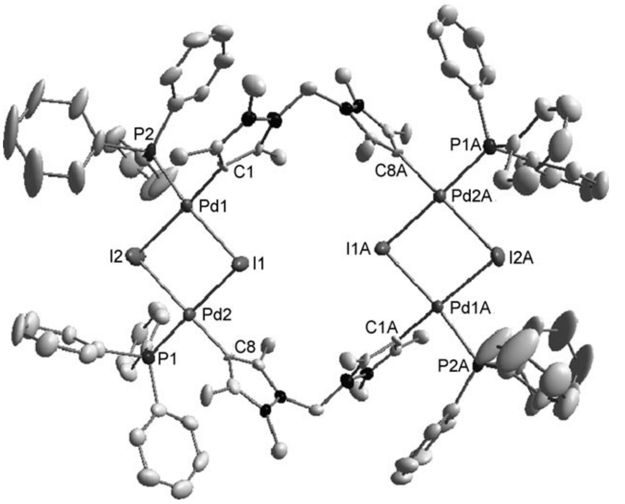

Figure 2. Molecular structure of the tetranuclear cation of $\mathbf{4}\cdot 2\,C_6H_5CH_3$ showing 50% probability ellipsoids; BF_4^- ions, hydrogen atoms and solvent molecules are omitted for clarity.

to each other with an angle of 88.37°. They are also almost perpendicular to their respective coordination planes with dihedral angles of 87.74 and 81.74°, respectively. In addition, the two coordination planes are perfectly parallel to each other. The Pd–C bonds of 1.976(7) and 1.970(7) Å are slightly shorter than those in dinuclear **3** in line with a more Lewis acidic metal center in complex **4**.

The structure of **4** is retained in CH_2Cl_2 as evidenced by its ESI MS spectra, which shows isotopic patterns corresponding to tetranuclear cations with different bridging halido ligands (I^- vs Cl^-) plus one or two BF_4^- anions. Owing to insufficient solubility of **4** in CD_2Cl_2, NMR analysis was performed in CD_3CN. The ^1H NMR spectrum shows singlets at $\delta = 3.33$ and 3.24 ppm, indicating two inequivalent N-Me groups attributed to two unsymmetrical cyclic carbenes linked by the methylene bridge (Figure 2). The methylene protons are diastereotopic, but their resonances accidentally overlap to give a broad pseudo-doublet at $\delta \approx 6.12$ ppm, suggesting restricted rotation around the N–CH_2 bond.

Finally, the oxidative addition of **2b** to $[Pd_2(dba)_3]/PPh_3$ was attempted. However, this reaction gave rise to an intractable product mixture from which no Pd–*r*NHC complexes were isolated. This outcome is probably owed to the intermediate length of the ethylene spacer, which may neither favor the formation of dinuclear nor tetranuclear complexes. Attempts to selectively synthesize such complexes containing the ethylene-bridged di-*r*NHC ligand by stoichiometry control were also conducted to no avail.

In summary, we have reported the first complexes of pyrazole-derived di-*r*NHC ligands. Remote changes in the ligand topology four bonds away from the carbon donor have substantial influences on the nuclearity of the resulting complexes. The oxidative addition of **2c** to Pd^0/PPh_3 afforded the dinuclear complex **3**, whereas precursor **2a** gave rise to the tetranuclear rectangle **4** with two bridging di-*r*NHC ligands. Importantly, we have demonstrated that novel dipyrazolin-4-ylidenes are versatile building-blocks for di- or tetranuclear architectures and further work to extend these coordination motifs to polynuclear assemblies is underway in our laboratories.

Acknowledgements

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[16] Selected crystallographic data for **3** and **4** are given in the Supporting Information. CCDC-752859 (**3**) and 752860 (**4**) 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/data_request/cif.

[17] Efforts to avoid the iodido–chlorido scrambling by changing to nonchlorinated solvents such as CH_3CN, THF and toluene led to the formation of either Pd black (in CH_3CN) or intractable mixtures (in THF and toluene). Attempts to change the chloro atoms in **4** by salt metathesis with NaI in CH_3CN were also met with no success. Finally, the oxidative addition of 4,4′-dichloro-2,2′,3,3′,5,5′-hexamethyl-1,1′-methylenedipyrazolium bis(tetrafluoroborate) with $[Pd_2(dba)_3]/PPh_3$ *ceteris paribus* also proved unsuccessful, owing to the stronger C–Cl bond as evidenced by the full recovery of the precursor salt.

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