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Multiple Coordination Geometries Supported by Methylene-Linked Guanidines

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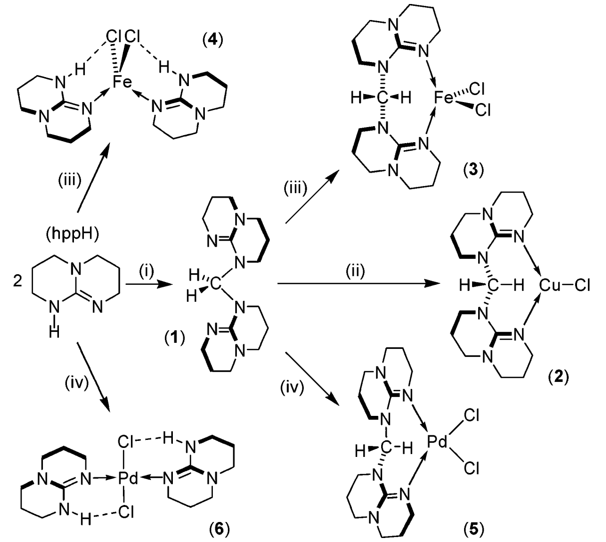
The methylene-linked bicyclic guanidine based on the 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) framework provides a versatile platform able to support trigonal-planar, tetrahedral, and square-planar metal centers.

As part of our study into the application of the neutral, bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH, Scheme 1) as a ligand in coordination chemistry,[1,2] we have previously reported that the copper(I) chloride complex $CuCl(hppH)_2$ is active for the radical polymerization of methyl methacrylate (MMA).[3] Under the conditions investigated, the polymerization did not proceed in a well-controlled fashion giving polymer molecular weights significantly greater than the calculated values for ideal behavior. On the basis of previous observations that monodentate ligands are inferior for the support of ATRP catalysts,[4] our research has been directed toward the development of novel classes of linked bis(guanidine) compounds,[5] where it is anticipated that chelation at the metal center will afford a more stable platform for the metal during the polymerization reaction.

Scheme 1. Coordination Geometries of Compounds Incorporating hppH and the Methylene-Linked Bis(guanidine), $H_2C\{hpp\}_2$[a]



[a] (i) 2 NaH, CH_2Cl_2, THF; (ii) CuCl, THF; (iii) $FeCl_2$, THF; (iv) $PdCl_2(COD)$, CH_2Cl_2.

Reports of bis(guanidine) compounds as neutral, chelating ligands have been published,[6] employing an ethyl-linker unit as the N_{imine}-substituent of each guanidine component.[7] A five-membered metallacycle forms upon chelation to a metal, and it is noted that copper(I) and copper(II) complexes containing the "NC_2NCu" structural motif have a propensity to form halobridged compounds of higher nuclearity.[8] In this contribution, we describe a novel class of methylene-bridged bis(guanidine) compounds where the linking group is present as the N_{amine}-substituent, affording eight-membered metallacycles. The versatility of this system is highlighted by the coordination at trigonal-planar, tetrahedral, and square-planar metal centers.

Deprotonation of hppH with NaH, performed in the presence of 0.5 equiv of CH_2Cl_2, affords the methylene-linked bis(guanidine) compound, $H_2C\{hpp\}_2$ (**1**), in a "one-pot" reaction (Scheme 1). Incorporation of a carbon substituent at the amidine N*H* position renders the six annular methylene units inequivalent by NMR spectroscopy in contrast to the silicon substituted analogue $Me_2Si\{hpp\}_2$ in which a fluxional process equates the two six-membered rings of each "hpp" unit.[5] The stoichiometric reaction between **1** and copper(I) chloride proceeds to afford $CuCl(H_2C\{hpp\}_2)$ (**2**). ^1H NMR spectroscopy indicated that

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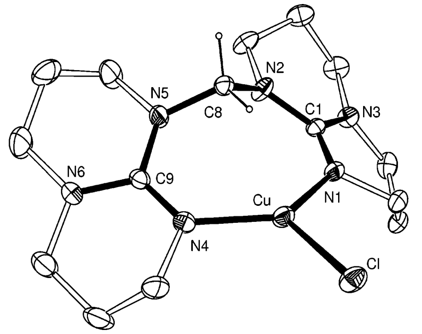

Figure 1. Molecular structure of **2** (thermal ellipsoids at 30%). Hydrogen atoms, excepting those of the bridgehead group, were omitted. Selected bond lengths (Å) and angles (deg): Cu−N(1) 1.956(4), Cu−N(4) 1.943(4), Cu−Cl 2.261(1), C(1)−N(1) 1.298(6), C(9)−N(4) 1.304(6), C(1)−N(2) 1.379(5), C(9)−N(5) 1.382(5), C(1)−N(3) 1.378(5), C(9)−N(6) 1.370(5). N(1)−Cu−N(4) 126.45(15), N(1)−Cu−Cl 113.03(11), N(4)−Cu−Cl 120.38(12).

asymmetry was maintained in the guanidine component of the ligand, with a low field singlet (δ 5.45) observed for the bridgehead methylene group. X-ray crystallography[9] confirms a monomeric, distorted trigonal-planar copper center at which **1** chelates through both imine nitrogen atoms (Figure 1). The N−Cu−N bite angle [126.45(15)°] differs by only 3.9° from the corresponding angle in the nonlinked bis-hppH analogue,[3] and the Cu−N distances [1.95 Å av] are essentially identical (within esd's), suggesting that nominal strain is imposed in the ligand on complexation. The C(8)-methylene group is positioned "above" the approximate N_2CuCl plane [max deviation 0.03 Å] in a "pseudoboat" conformation, creating an asymmetric metal environment in the solid-state with sufficient steric encumbrance to prevent dimerization via μ-Cl bridges. Compound **2** must, however, exhibit fluxionality in solution to afford a singlet for the bridgehead protons in the ^{1}H NMR spectrum, most likely interconverting via a low energy inversion of the medium-sized, eight-membered metallacycle.

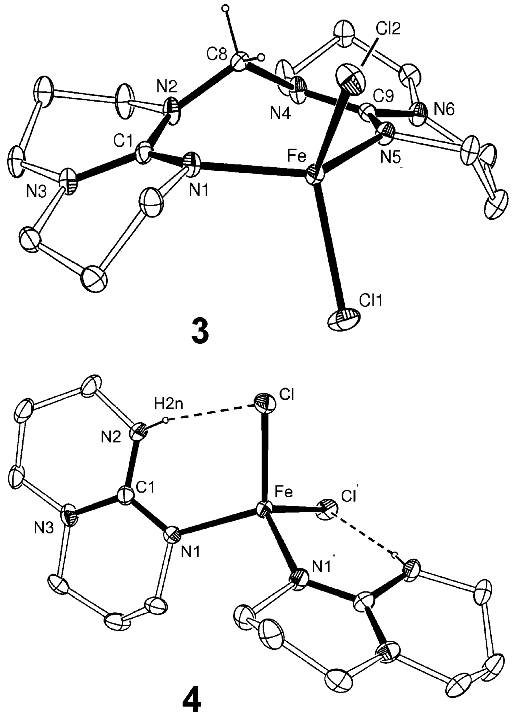

Figure 2. Molecular structures of **3** and **4** (thermal ellipsoids at 30%). Hydrogen atoms, excepting those of the bridgehead group (**3**) and guanidine N*H* (**4**), were omitted. Selected bond lengths (Å) and angles (deg): **3**, Fe−N(1) 2.016(2), Fe−N(5) 2.023(2), Fe−Cl(1) 2.3061(6), Fe−Cl(2) 2.3253(6), C(1)−N(1) 1.317(3), C(9)−N(5) 1.312(3), C(1)−N(2) 1.378(3), C(9)−N(4) 1.368(3), C(1)−N(3) 1.360(3), C(9)−N(6) 1.356(3); N(1)−Fe−N(5) 125.02(7), Cl(1)−Fe-Cl(2) 122.21(3); **4**, $(' -x + {}^{3}/_{2}, -y + {}^{1}/_{2}, z)$ Fe−N(1) 2.0395(14), Fe−Cl 2.3190(4), C(1)−N(1) 1.322(2), C(1)−N(2) 1.354(4), C(1)−N(3) 1.352(2), H(2n)⋯Cl 2.52; N(1)−Fe−N(1′) 107.52(9), N(1)−Fe−Cl 110.87(4), N(1)−Fe−Cl′ 107.94(5), Cl−Fe−Cl′ 111.63(3).

The ability of **1** to support tetrahedral coordination environments was investigated using iron(II) chloride, affording the paramagnetic complex $FeCl_2(H_2C\{hpp\}_2)$ (**3**). The nonlinked analogue, $FeCl_2(hppH)_2$ (**4**), was also prepared, and X-ray diffraction studies were performed for both compounds (Figure 2).[9]

The iron centers in both **3** and **4** exist in a monomeric, tetrahedral environment, with two "hpp" units coordinated via the N_{imine} atom, and two terminal chloride ligands. In **3**, the neutral bis(guanidine) again functions as a chelating, bidentate ligand, forming an eight-membered metallacycle. As noted in the trigonal-planar Cu(I) and Ag(I) complexes,[2,3] intramolecular hydrogen bonds [2.52 Å] are present in the tetrahedral complex **4**. The major structural difference in the geometry at iron in these two compounds is a much larger N−Fe−N angle in **3** [125.02(7)°] compared with **4** [107.52(9)°]. This value is comparable to that in trigonal-planar copper complex **2** and suggests that **1** is suited for the support of both trigonal-planar and tetrahedral metal geometries.

An additional feature often bestowed upon chelating ligands which form small and medium-sized metallacycles is an enforced *cis*-geometry at the metal center. This is particularly significant when considering square-planar complexes and has important consequences in many catalytic cycles involving carbon−carbon bond formation. $PdCl_2(COD)$ reacts with 1 equiv of **1**, or 2 equiv of hppH, via displacement

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(9) Crystal data for $C_{15}H_{26}ClCuN_6$ (**2**): $M = 389.41$, orthorhombic, *Aba*2 (No. 41), $a = 14.1579(10)$ Å, $b = 14.7107(9)$ Å, $c = 16.1177(7)$ Å, $V = 3356.9(3)$ Å^3, $T = 173(2)$ K, $Z = 8$, μ(Mo Kα) = 1.47 mm^{-1}, independent reflections = 2909 ($R_{int} = 0.079$), *R*1 [for 2281 reflections with $I > 2\sigma(I)$] = 0.039, *wR*2 (all data) = 0.086. Crystal data for $C_{15}H_{26}Cl_2FeN_6$ (**3**): $M = 417.17$, monoclinic, $P2_1$ (No. 4), $a = 9.4021(3)$ Å, $b = 8.2761(3)$ Å, $c = 12.2393(4)$ Å, $\beta = 108.886(2)°$, $V = 901.10(5)$ Å^3, $T = 173(2)$ K, $Z = 2$, μ(Mo Kα) = 1.14 mm^{-1}, independent reflections = 3903 ($R_{int} = 0.041$), *R*1 [for 3746 reflections with $I > 2\sigma(I)$] = 0.024, *wR*2 (all data) = 0.069. Crystal data for $C_{14}H_{26}Cl_2FeN_6$ (**4**): $M = 405.16$, orthorhombic, *Fdd*2 (No. 43), $a = 31.7631(7)$ Å, $b = 16.6091(4)$ Å, $c = 6.8574(1)$ Å, $V = 3617.67(13)$ Å^3, $T = 173(2)$ K, $Z = 8$, μ(Mo Kα) = 1.14 mm^{-1}, independent reflections = 1902 ($R_{int} = 0.037$), *R*1 [for 1839 reflections with $I > 2\sigma(I)$] = 0.020, *wR*2 (all data) = 0.050. Crystal data for $C_{15}H_{26}Cl_2N_6Pd$ (**5**): $M = 467.72$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 10.8148(2)$ Å, $b = 11.7393(2)$ Å, $c = 14.0895(3)$ Å, $V = 1788.78(6)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo Kα) = 1.35 mm^{-1}, independent reflections = 3136 ($R_{int} = 0.11$), *R*1 [for 3060 reflections with $I > 2\sigma(I)$] = 0.019, *wR*2 (all data) = 0.047. Crystal data for $C_{14}H_{26}Cl_2N_6Pd$ (**6a**): $M = 455.71$, monoclinic, $P2_1/c$ (No. 14), $a = 7.9773(2)$ Å, $b = 8.8734(3)$ Å, $c = 12.3324(3)$ Å, $\beta = 99.899(2)°$, $V = 859.96(4)$ Å^3, $T = 173(2)$ K, $Z = 2$, μ(Mo Kα) = 1.40 mm^{-1}, independent reflections = 1518 ($R_{int} = 0.035$), *R*1 [for 1391 reflections with $I > 2\sigma(I)$] = 0.021, *wR*2 (all data) = 0.053. Crystal data for $C_{14}H_{26}Cl_2N_6Pd$ (**6b**): $M = 455.71$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 9.3182(5)$ Å, $b = 12.1779(4)$ Å, $c = 15.3485(9)$ Å, $V = 1741.69(15)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo Kα) = 1.38 mm^{-1}, independent reflections = 2905 ($R_{int} = 0.039$), *R*1 [for 2794 reflections with $I > 2\sigma(I)$] = 0.025, *wR*2 (all data) = 0.064.

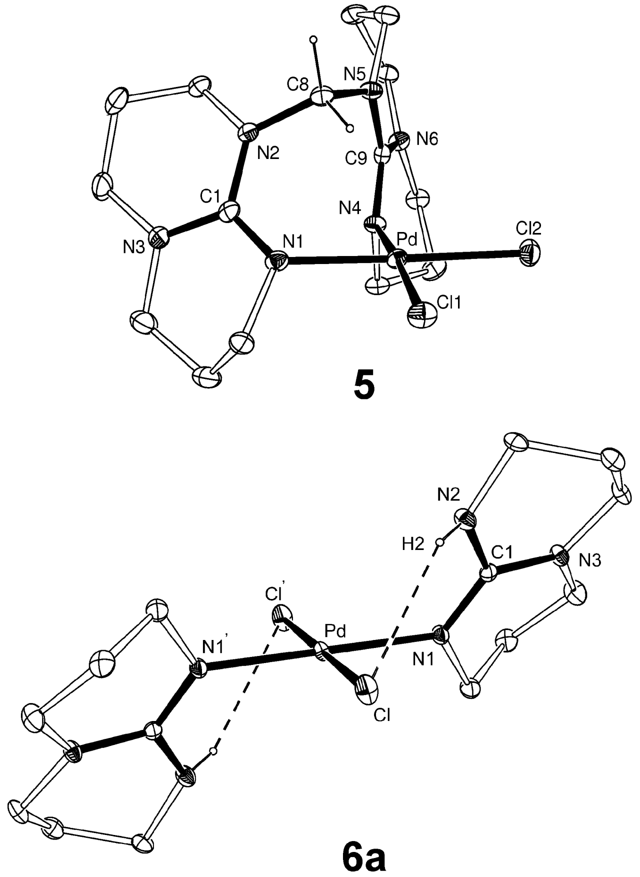

Figure 3. Molecular structures of **5** and **6a** (thermal ellipsoids at 30%). Hydrogen atoms, excepting those of the bridgehead group (**5**) and guanidine N*H* (**6a**), were omitted. Selected bond lengths (Å) and angles (deg): **5**, Pd−N(1) 2.037(2), Pd−N(4) 2.011(2), Pd−Cl(1) 2.3310(7), Pd−Cl(2) 2.3220(7), C(1)−N(1) 1.324(4), C(9)−N(4) 1.315(3), C(1)−N(2) 1.375(4), C(9)−N(5), 1.373(3), C(1)−N(3) 1.355(4), C(9)−N(6) 1.360(3), N(1)−Pd−N(4) 88.25(9), Cl(1)−Pd−Cl(2) 92.81(3), N(1)−Pd−Cl(1) 90.31(7), N(4)−Pd−Cl(2) 88.65(7); **6a**, (′ $-x+1$, $-y+1$, $-z+1$) Pd−N(1) 2.0292(19), Pd−Cl 2.3211(6), C(1)−N(1) 1.308(3), C(1)−N(2) 1.366(3), C(1)−N(3) 1.358(3), H(2)···Cl 2.62; N(1)−Pd−N(1′) 180.0, N(1)−Pd−Cl 91.42(6), N(1′)−Pd−Cl 88.58(6).

of the diene to afford $\mathrm{PdCl_2(H_2C\{hpp\}_2)}$ (**5**) and $\mathrm{PdCl_2(hppH)_2}$ (**6**), respectively. Key features of the ^{1}H NMR spectra indicate the formation of rigid solution-state structures for both compounds. In **5**, the bridgehead protons resonate as well separated doublets centered at δ 10.10 and 4.13, each showing large, two-bond coupling [14.9 Hz], while in **6**, no averaging of the annular methylene groups is observed. X-ray diffraction studies were performed on **5** and **6**[10] (Figure 3).[9]

Both compounds are monomeric in the solid-state with square-planar palladium centers containing only slight deviations in bond angle from ideal values [**5**, 88.25(9)−92.81(3)°; **6a**, 88.58(6)−91.42(6)°; **6b** 88.36(10)−91.84(9)°]. The *cis*-arrangement of the chlorides, present in the starting material, is enforced when the chelating bis(guanidine) is employed, while isomerization to the *trans*-structure is observed when using the monodentate ligand. The average Pd−N distances are experimentally indistinguishable in each case, despite the presence of intramolecular hydrogen-bonding interactions in **6a** [2.62 Å] and **6b** [2.66 Å av]. However, significant asymmetry is noted for the chelating ligand in **5**, where a significant "skew" is observed in the position of the bridgehead group.

In summary, we have synthesized a new class of methylene-linked guanidine compound and demonstrated its coordination potential at trigonal-planar, tetrahedral, and square-planar metal centers. X-ray crystallography shows the bite angle is relatively insensitive with respect to the geometry of the metal for trigonal-planar and tetrahedral metals and enforces a *cis*-geometry at square-planar palladium. Details of the application of selected complexes described in this contribution in catalytic processes (e.g., ATRP and C−C bond forming reactions) will be reported in due course.

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Supporting Information Available: Synthetic details for all compounds. X-ray structural data for **2**−**6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Layering a concentrated CH_2Cl_2 solution of $\mathrm{PdCl_2(hppH)_2}$ (**6**) with Et_2O resulted in the simultaneous formation of red prisms and needles. X-ray diffraction data were collected on representative crystals of each morphology, revealing monoclinic (**6a**) and orthorhombic (**6b**) space groups, respectively.