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Phosphaguanidines as Scaffolds for Multimetallic Complexes Containing Metal-Functionalized Phosphines

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Phospha(III)guanidines, $R_2PC\{NR'\}\{NHR'\}$, have been used to synthesize multimetallic compounds containing combinations of aluminum with platinum or copper, in which the main-group metal is N,N′-bound by an amidinate moiety, thereby generating a metal-functionalized phosphine that bonds to the transition metal through phosphorus.

Tandem catalysis offers significant advantages over the sequential performance of individual reactions, including circumventing the need for isolation and purification of intermediates (typically leading to loss of material) and reducing the time required to produce the final product.[1] The design of such systems remains a challenge, however, with important factors that need consideration including (i) compatibility of individual catalysts with all components of the reaction, (ii) assurance that neither of the individual catalytic cycles predominates, and (iii) control of the sequence of the reactivity.

The development of single molecular species that behave as tandem catalysts involves the incorporation of different metals in the same compound (or the same metal in different chemical environments), each of which is able to perform a separate chemical transformation. This, in turn, depends on the design of ligands that support metal fragments in distinct coordination environments, achieved using multifunctional ligands. Recent work has been presented by ourselves[2–6] and others[7] on the synthesis and coordination chemistry of phosphaguanidines, $R_2PC\{NR\}\{NHR'\}$. As a ligand precursor, the potential exists for metal bonding either through the amidine component (usually achieved through conversion to the corresponding amidinate anion) or with participation from the phosphine group. We report herein two systems in which the phosphaguanidine supports multiple metal fragments, including the first structurally characterized example of the κP,κN,N′ mode for a mixed Al/Cu system.

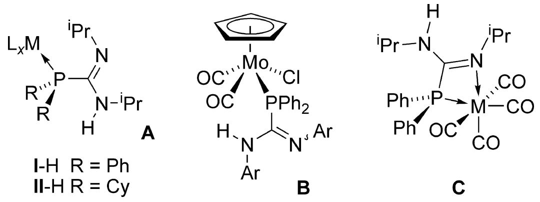

Figure 1.

Despite the obvious potential for neutral phospha(III)guanidines **I**-H and **II**-H to serve as κP-phosphine ligands at a metal center (**A**; Figure 1), this bonding mode has only been reported on the basis of spectroscopic data for cyclopentadienylmolybdenum complex **B**.[8] It should be noted that the reaction of **I**-H with $M(CO)_5(THF)$ in an attempt to generate P-bound phosphaguanidines led to elimination of a second 1 equiv of CO and additional contributions to the bonding through the N_{imine} atom (**C**).[3]

Previous work from our group has shown that the isolated aluminum phosphaguanidinate $Al(\mathbf{I})Me_2$ behaves as a metal-functionalized phosphine that will coordinate to platinum, affording the cis-square-planar complex $PtMe_2\{Al(\mathbf{I})Me_2\}_2$.[2] To develop a more general route to these “metal-functionalized phosphines”, the reaction with $PtMe_2(cod)$ was investigated *prior* to metal binding through the amidine component. Colorless crystals that analyzed as $PtMe_2(R_2PC\{N^iPr\}\{NH^iPr\})_2$ (**1**, R = Ph; **2**, R = Cy) were isolated in good yield upon crystallization from toluene. ^{31}P NMR data were consistent with a cis arrangement for the phosphines, with J_{PtP} values of 1800 and 1682 Hz for **1** and **2**, respectively. The ^{1}H NMR spectrum showed inequivalent

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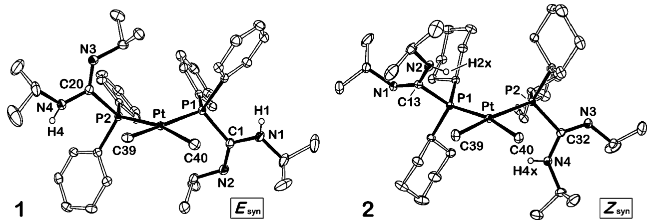

Figure 2. ORTEPs of **1** and **2**. Selected bond lengths (Å) and angles (deg). **1**: Pt−P1 2.293(1), Pt−P2 2.298(1), Pt−C39 2.109(4), Pt−C40 2.114(4), C1−N1 1.369(5), C1−N2 1.271(5), C20−N3 1.276(5), C20−N4 1.360(5); P1−Pt−P2 107.66(3), P1−Pt−C39 165.11(11), P1−Pt−C40 85.46(12), P2−Pt−C39 85.57(11), P2−Pt−C40 165.53(12), C39−Pt−C40 82.26(16). **2**: Pt−P1 2.3164(7), Pt−P2 2.3203(7), Pt−C39 2.101(3), Pt−C40 2.104(3), C13−N1 1.273(4), C13−N2 1.383(4), C32−N3 1.280(4), C32−N4 1.375(4); P1−Pt−P2 106.80(2), P1−Pt−C39 86.89(8), P1−Pt−C40 165.68(8), P2−Pt−C39 165.86(8), P2−Pt−C40 87.20(8), C39−Pt−C40 79.34(11).

isopropyl groups, suggesting that localized C–N single and C═N double bonds were retained within the amidine, as observed in the noncoordinated phosphaguanidines.[3]

Previous analysis of **I**-H and **II**-H has shown that the N*H* doublet is caused by coupling to the methine hydrogen of the N$_{amino}$ substituent, with no observable $^3J_{PH}$.[3,6] However, when the P,N-bonding mode is adopted, in which a Z_{anti} configuration of amidine substituents is enforced (**C**; Figure 1), the coupling to phosphorus is resolved and the N*H* proton resonates as a *pseudo*triplet.[3] The observed doublets in **1** and **2** at δ 4.46 and 5.39, respectively, are therefore consistent with a κP-bonding mode in which the N$_{imino}$ atom is not involved in bonding to the metal.

Crystallographic analysis[9] of **1** and **2** confirmed the cis-square-planar geometry at platinum, in which the amidine component of the phosphaguanidines is not contributing to the bonding, thereby remaining available for interaction with additional metal substrates (Figure 2). The P–Pt–P angles [**1**, 107.66(3) Å; **2**, 106.80(2) Å] are consistent with the phosphaguanidines being considered as a "bulky" phosphine-type ligand, being close in value to that found for the analogous bis(tricyclohexylphosphine) compound, PtMe$_2$(PCy$_3$)$_2$ [P–Pt–P = 108.60(5) Å].[10] The Pt–P bond lengths differ slightly between **1** (ave 2.296 Å) and **2** (ave 2.318 Å) but are consistent with other examples of *cis*-diphosphine-substituted platinum dimethyl compounds with related groups at phosphorus.[10,11]

The most notable structural difference between **1** and **2** is the relative position of the nitrogen substituents within the phosphaguanidine. Considering the −C{N^{i}Pr}{NH^{i}Pr} component, the *P*-diphenyl derivative adopts an E_{syn} configuration, while the corresponding *Z* isomer is observed in **2**. This difference is consistent with the lower barrier to isomerization about the C═N bond noted for noncoordinated **II**-H, in which both the E_{syn} and Z_{syn} isomers were observed in solution.[6] In both cases Δ_{CN} values[12] [**1**, 0.10 and 0.08 Å; **2**, 0.11 and 0.10 Å] are consistent with localized bonding.

Treatment of **1** with 2 equiv of AlMe$_3$ cleanly converts the amidine functional groups to the amidinate via protonolysis of one of the methyl ligands of aluminum. The product was identified spectroscopically as the previously reported trimetallic compound, PtMe$_2${Al(**I**)Me$_2$}$_2$ (**3**).[2] This alternative route demonstrates for the first time that a coordinated amidine can be deprotonated, extending the scope of this system to further development in the synthesis of multimetallic compounds.

Despite our best efforts, we were unable to isolate crystals of **3** suitable for X-ray analysis, and because we considered this an important technique for evaluating differences in bonding between **I**-H and Al(**I**)Me$_2$, an alternative system was examined. Copper(I) was selected as a suitable metal to replace the platinum because the coordination of phosphines is well-known and solution-state NMR data are readily available. The reaction between 2 equiv of **I**-H and CuBr afforded colorless crystals of CuBr(**I**-H)$_2$ (**4**) in reasonable yield. As for the platinum compounds, inequivalent isopropyl methyl groups and a doublet for the N*H* proton in the ^{1}H NMR spectrum suggested that bonding was through the P atom only, despite our previous studies in which we have shown that amidine and guanidine compounds readily coordinate to copper(I) centers through the N$_{imine}$ atom.[13]

The molecular structure of **4** (Figure 3) shows the expected distorted trigonal-planar geometry [Σ_{angles} = 359.92°] with both phosphaguanidines bonding as κP ligands. The largest angle is found between the two phosphaguanidine ligands [P–Cu–*P* = 127.59(2)°], although for this metal fragment, the value is significantly less than that in the corresponding bis(tricyclohexylphosphine) compound, CuBr(PCy$_3$)$_2$ [P–Cu–P = 135.6(1) Å],[14] being much closer to that in the bis(triphenylphosphine) analogue [P–Cu–P = 126.0(1) Å].[15] In addition, a significant difference is noted in the two P–Cu–Br angles [Δ_{PCuBr} = 8.82°], indicating a degree of coordinative

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(9) Crystallographic data. **1**: C$_{40}$H$_{56}$N$_4$P$_2$Pt·C$_7$H$_8$, M = 942.05, T = 173(2) K, monoclinic, space group $P2_1/c$ (No. 14), a = 13.3845(2) Å, b = 22.7704(3) Å, c = 15.5458(2) Å, β = 104.780(1)°, U = 4581.13(11) Å^3, Z = 4, D_c = 1.37 Mg m^{-3}, μ(Mo Kα) = 3.17 mm^{-1}, independent reflections = 7728 [R_{int} = 0.058], R1 [for 6438 reflections with $I > 2\sigma(I)$] = 0.030, wR2 (all data) = 0.063. **2**: C$_{40}$H$_{80}$N$_4$P$_2$Pt, M = 874.11, T = 173(2) K, monoclinic, space group $P2_1/c$ (No. 14), a = 11.8881(2) Å, b = 17.9465(3) Å, c = 21.0820(3) Å, β = 94.286(1)°, U = 4485.26(12) Å^3, Z = 4, D_c = 1.29 Mg m^{-3}, μ(Mo Kα) = 3.23 mm^{-1}, independent reflections = 8767 [R_{int} = 0.052], R1 [for 7609 reflections with $I > 2\sigma(I)$] = 0.023, wR2 (all data) = 0.053. **4**: C$_{38}$H$_{50}$BrCuN$_4$P$_2$, M = 768.21, T = 173(2) K, monoclinic, space group $P2_1/n$ (No. 14), a = 10.4275(1) Å, b = 17.1857(2) Å, c = 22.3749(3) Å, β = 97.210(1)°, U = 3977.96(8) Å^3, Z = 4, D_c = 1.28 Mg m^{-3}, μ(Mo Kα) = 1.66 mm^{-1}, independent reflections = 9060 [R_{int} = 0.054], R1 [for 7135 reflections with $I > 2\sigma(I)$] = 0.038, wR2 (all data) = 0.081. **5**: C$_{42}$H$_{60}$Al$_2$BrCuN$_4$P$_2$, M = 880.29, T = 173(2) K, monoclinic, space group $P2_1/n$ (No. 14), a = 14.0207(2) Å, b = 22.0117(3) Å, c = 16.2740(2) Å, β = 110.996(1)°, U = 4689.01(11) Å^3, Z = 4, D_c = 1.25 Mg m^{-3}, μ(Mo Kα) = 1.46 mm^{-1}, independent reflections = 8218 [R_{int} = 0.087], R1 [for 5932 reflections with $I > 2\sigma(I)$] = 0.049, wR2 (all data) = 0.103.

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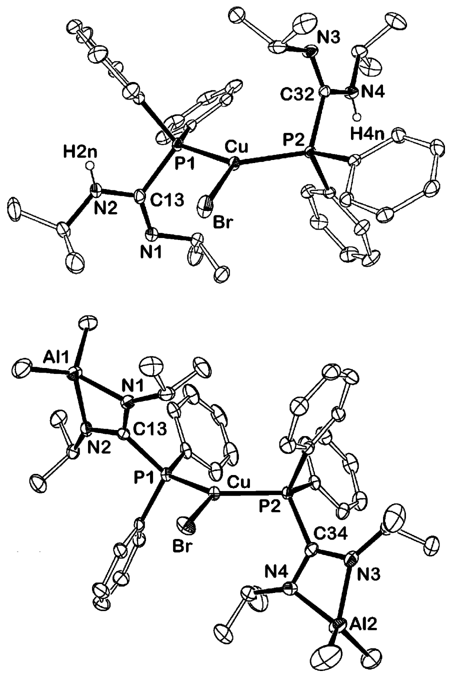

Figure 3. ORTEPs of CuBr(**I**-H)$_2$ (**4**) and CuBr{Al(**I**)Me$_2$}$_2$ (**5**). Selected bond lengths (Å) and angles (deg). **4**: Cu−P1 2.2401(6), Cu−P2 2.2223(6), Cu−Br 2.3434(3), P1−C13 1.881(2), C13−N1 1.278(3), C13−N2 1.369(3), P2−C32 1.874(2), C32−N3 1.271(3), C32−N4 1.365(3); P1−Cu−P2 127.59(2), P1−Cu−Br 111.756(18), P2−Cu−Br 120.574(19). **5**: Cu−P1 2.2246(10), Cu−P2 2.2379(10), Cu−Br 2.3646(6), P1−C13 1.865(3), C13−N1 1.331(5), C13−N2 1.333(4), N1−Al1 1.933(3), N2−Al1 1.952(3), P2−C34 1.869(4), C34−N3 1.328(4), C34−N4 1.326(5), N3−Al2 1.938(3), N4−Al2 1.925(3); P1−Cu−P2 130.45(4), P1−Cu−Br 117.24(3), P2−Cu−Br 112.22(3), N1−Al1−N2 68.47(13), N3−Al2−N4 68.74(13).

flexibility for these ligands as phosphines, depending on the orientation of the P substituents and the geometry of the metal fragment to which they are coordinated. The Cu–P distances are as expected,[15,16] and the amidine component is consistent with localized bonding [both Δ_{CN} values 0.09 Å] with an E_{syn} configuration.

Reaction of **4** with AlMe$_3$ (2 equiv) proceeds cleanly via alkane elimination to afford the corresponding trimetallic species CuBr{Al(**I**)Me$_2$}$_2$ (**5**). A slight shift in the ^{31}P NMR resonance was observed from δ –15.1 in **4** to δ –18.4 in **5**, and as expected for the N,N′-coordination of the amidinate to the aluminum center, the isopropyl groups are equivalent by NMR spectroscopy.

Crystals of **5** suitable for X-ray analysis were grown from toluene (Figure 3), revealing the first example in which the phosphaguanidinate anion serves as a bridge between different metal centers.[17] The Cu atom retains a trigonal-planar geometry in **5**, with a slight increase in the P–Cu–P angle consistent with a larger cone angle upon incorporation of the AlMe$_2$ groups, although it is noted that the Cu–P distances are not significantly perturbed. Viewing the molecule along the P···P vector in the P$_2$CuBr plane (Figure 4) shows that the relative position of the phosphorus substituents changes significantly from **4**, in which an almost perfectly staggered conformation is adopted, to **5**, in which the substituents are virtually eclipsed, maximizing the torsion between the AlMe$_2$ groups. The bonding within the amidinate portion of the ligand is as expected,[18] with a distorted tetrahedral geometry at aluminum and a small bite angle for the chelate [ave N–Al–N = 68.61°].

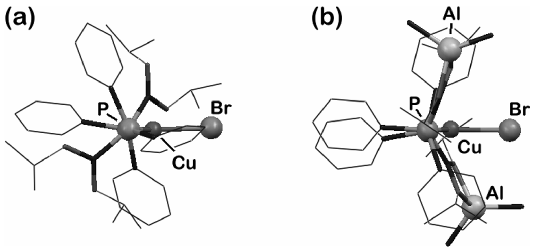

Figure 4. Schematic representations of (a) **4** and (b) **5**, viewed in the P$_2$CuBr plane through the P···P vector.

In summary, we have shown spectroscopically and structurally that the amidine group within κP-bonded phosphaguanidines does not interact with the metal in PtMe$_2$ and CuBr complexes and is therefore potentially available for interaction with additional metal fragments. This mode of reactivity has been confirmed by employing AlMe$_3$, which is known to cleanly convert the amidine to the corresponding amidinate via loss of methane and formation of the N,N′-chelate. Structural characterization of a trimetallic Al/Cu/Al complex confirms phosphaguanidinate as a bridge between the disparate metals, providing a general route to multimetallic complexes supported by this ligand framework. Further work investigating the effects that this association has on the chemical reactivity of the P- and N,N′-bonded metals, toward developing single molecules as tandem catalysts, is underway.

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Supporting Information Available: Experimental and full characterization data for **1**−**5** and X-ray data for **1**, **2**, **4**, and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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