The Al(I) bisimidinate Al(DDP) as a metalloid NHC type ligand for Pd(0) complexes and clusters

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Two clusters with a Pd_2 core and Al(DDP) (DDP = 2-((2, 6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)-2-pentene) as a bridging ligand have been synthesized and characterized by single crystal structural analysis; the results suggest a strong similarity of the coordination properties of NHC's and the group 13 analogue Al(DDP).

Clusters of the type $[M_a(ECp^*)_b]$ (M = Pd, Pt; E = Al, Ga, In) represent an interesting family of intermetallic molecular compounds.[1] The coordination properties of the ligands ECp* go beyond their isolobal CO or phosphine analogues, not only by stabilizing unprecedented cluster structures and compositions but also by creating very electron rich and thus unusually reactive transition metal centers. In fact, unexpected C–H, Si–H and even C–C bond activations were observed at $[Ni(AlCp^*)_3]$,[2] $[Fe(AlCp^*)_n]$[3] and $[RhCp^*(CH_3)_2(GaCp^*)]$.[4] Aiming at a study of the reactive unsaturated intermediates of such bond activation reactions, we recently started to investigate the coordination chemistry of the sterically highly demanding group 13 bisimidinate Ga(DDP).[5,6] This metalloid ligand is isolobal to NHC's and, as expected for metalloid ligands, exhibits strong Lewis-acidic properties when coordinated to a transition metal center. Additionally it is able to kinetically stabilize reactive unsaturated species by its high steric demand. Thus, the Ga centers in the complexes $[(PPh_3)_2Rh\{GaCl(DDP)\}]$ and $[Au\{Ga(DDP)\}_2]^+$ were found to be very electrophilic, despite the fact that they are coordinated to the quite electron rich centers Rh(I) and Au(I), respectively.[7] Here we now wish to report on our first results using Roesky's lighter analogue Al(DDP)[8] as ligand. The very vivid and rich reactivity patterns of Al(DDP) towards small molecules has been recently reviewed.[9]

Reaction of $[Pd_2(dvds)_3]$ with one equivalent of Al(DDP) in hexane at room temperature immediately leads to a yellow solution. On removal of the solvent, yellow needles of the dimeric compound $[\{Pd(dvds)\}_2\{\mu^2\text{-Al(DDP)}\}]$ (**1**) can be isolated (Scheme 1). The ^1H NMR spectrum of **1** shows one broad signal for the $SiMe_2$ groups at room temperature, indicating a fluctional process intermolecularly exchanging dvds ligands. Indeed, at −60 °C, this broad signal splits into six distinct, yet partially overlapping singlets.† On reaction of $[Pd_2(dvds)_3]$ with an excess of Al(DDP), the monomeric compound [(dvds)Pd{Al(DDP)}] (**2**) is obtained, as shown by NMR spectroscopy and single crystal structure analysis, which will be reported elsewhere.

The molecular structure of **1** (Fig. 1) consists of two {(dvds)Pd}-moieties bridged by one Al(DDP) ligand.‡ The Pd–Pd distance of 2.859 Å is similar to the one in $Pd_3(GaCp^*)_8$ (2.843 Å), but significantly longer than in $Pd_2(GaCp^*)_5$ (2.609 Å).[1] The Al(DDP) ligand is almost symmetrically located between the two Pd centers, exhibiting Pd–Al bond distances of 2.424 (Pd1–Al) and 2.442 Å (Pd2–Al), respectively. The two planes each formed by the olefinic carbon atoms of one dvds ligand and one Pd center are almost exactly perpendicular to each other, therefore forcing the Al(DDP)-ring slightly out of plane. The C–C bond lengths of 1.40 and 1.42 Å point to a rather high degree of π-backbonding, comparable to the monomeric NHC complex (NHC)Pd(dvds) (NHC = $(MesN)_2C_3H_2$).[10] It should be noted, that the C–C bond lengths in the monomeric complex {Al(DDP)}Pd(dvds) are within the same range (*ca.* 1.41 Å). Thus, Al(DDP) should be considered not only isolobal to NHC's but also as a similarly strong σ-donor ligand. The dvds ligands in **1** can be readily replaced by reaction with excess of GaCp* in hexane at room temperature, giving

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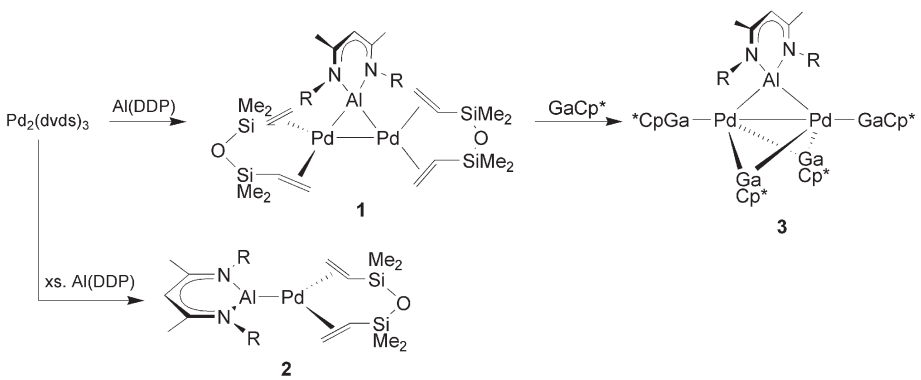

Scheme 1 R = $C_6H_3(^iPr)_2$.

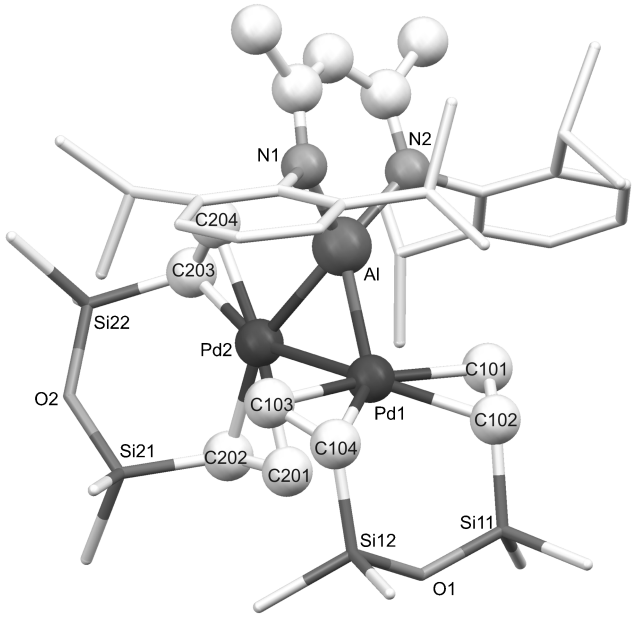

Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Pd1–Pd2 2.8589(7), Pd1–Al 2.4234(18), Pd2–Al 2.4419(18), C101–C102 1.401(9), C103–C104 1.401(9), C201–C202 1.420(9), C203–C204 1.420(9), Pd1–Al–Pd2 71.97(5), N1–Al–N2 94.0(2).

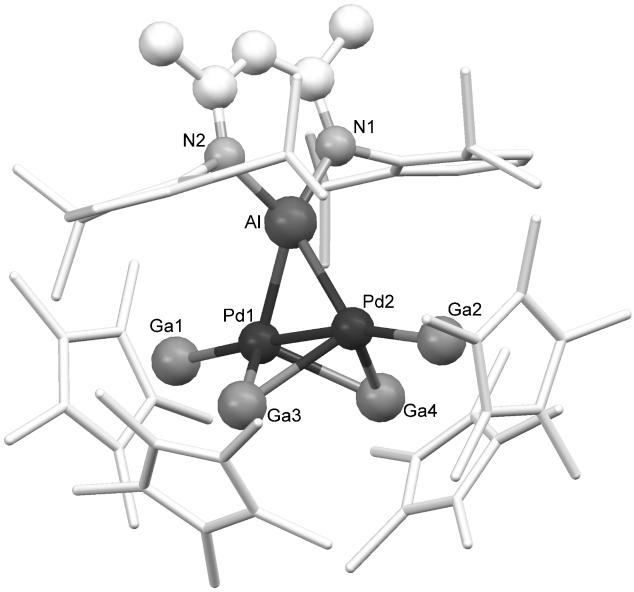

Fig. 2 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Pd1–Pd2 2.5824(15), Pd1–Al 2.456(3), Pd1–Ga1 2.3765(17), Pd1–Ga3 2.4960(17), Pd1–Ga4 2.4956(15), Pd2–Ga2 2.4172(17), Pd2–Ga3 2.539(2), Pd2–Ga4 2.5204(15), Pd2–Al 2.559(3), Al–N1 1.956(8), Al–N2 1.939(8), Ga1–Pd1–Pd2 177.29(5), Pd1–Pd2–Ga2 168.70(5), N1–Al–N2 92.3(4).

the dimeric cluster compound $[Pd_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_2\{\mu^2\text{-}Al(DDP)\}]$ (**3**) (Scheme 1). **3** is the first example of a heterobimetallic cluster exhibiting a sterically encumbered E(DDP) ligand in a bridging position, confirming once more the strong preference of Al(I) for a bridging coordination mode.

Complex **3** crystallizes in the monoclinic space group $P2_1/n$.‡ The molecular structure (Fig. 2) consists of a central Pd_2 unit with a significantly shorter Pd–Pd distance (2.582 Å) compared to **1** or the homoleptic compound $[Pd_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (2.609 Å). The Pd_2 unit of **3** is surrounded by two terminal and two bridging GaCp* as well as one bridging Al(DDP) ligand, leading to a distorted, dipalladium-centered trigonal-bipyramidal structure. As pointed out above, the Al(DDP) ligand is located in a bridging position. This fact is consistent with ligand exchange reactions in $M_2(GaCp^*)_5$ (M = Pd, Pt) giving $[Pt_2(GaCp^*)_2(\mu^2\text{-}AlCp^*)_3]$ and $[Pd_2(AlCp^*)_2(\mu^2\text{-}AlCp^*)_3]$, respectively.[1] The terminal Pd–Ga bond lengths in **3** (2.376 and 2.418 Å) are slightly longer than in $Pd_2(GaCp^*)_5$ (2.358 and 2.367 Å) or the monomeric compound $Pd(GaCp^*)_4$ (2.366 Å), but comparable to the ones in $Pd_3(GaCp^*)_8$ (2.399 and 2.418 Å). The bridging Pd–Ga bonds are distinctly longer (2.496 and 2.520 Å) than the terminal bonds, but are similar to the ones in $Pd_2(GaCp^*)_5$ (2.494 and 2.502 Å). The Ga2–Pd2–Pd1 unit is almost linear, whereas the Pd2–Pd1–Ga1 angle is significantly distorted (168.7°), possibly an effect of the unsymmetric orientation of the Al(DDP) ligand.

In contrast to the related compound $Pd_2(GaCp^*)_5$, the ^1H NMR spectrum of **3** at room temperature shows two sets of signals for the bridging and the terminal GaCp* moieties (δ = 1.96 ppm and 1.97 ppm, 30H each).† However, on heating the solution to 60 °C, only one signal for the Cp* moieties can be observed, pointing to a fast exchange of the bridging and the terminal GaCp* ligands on the NMR timescale. At −80 °C in toluene-d_8 a splitting of the GaCp* signals is found giving 4 distinguishable resonances (1.92, 1.94, 1.98 and 2.02 ppm), suggesting an unsymmetric solution structure similar to the molecular structure observed in the solid state.

Our results show, that Al(DDP) exhibits strong σ-donor abilities towards transition metal centers similar to NHC's promising a rich coordination chemistry. Although Al(DDP) and Ga(DDP) may certainly be viewed as exotic congeners to NHC's, the chemistry of the latter however, having developed rapidly over the last decade, is a strong motivation to further elucidate the limits of highly electron donating isolobal systems, with the group 13 title species certainly representing an interesting example.

Notes and references

† *Spectroscopic data* for **1**: δ_H (298 K, 250.1 MHz, C_6D_6) 7.20–7.00 [m, 6H, Ar], 5.01 [s, 1H, γ-C], 3.25 [bs, 6H, C_2H_3], 3.07 [sept, 4H, ^{i}Pr], 2.96 [sept, 4H, ^{i}Pr], 2.75 [bs, 6H, C_2H_3], 1.45 [s, 6H, C*Me*], 1.26 [d, 6H, ^{i}Pr-*Me*], 1.12 [d, 6H, ^{i}Pr-*Me*], 1.06 [d, 6H, ^{i}Pr-*Me*], 0.9 [d, 6H, ^{i}Pr-*Me*], 0.29 (bs, 24H, Si*Me*]; δ_C (298 K, 62.9 MHz, C_6D_6) 172.7 [CN], 146.9 [Ar], 146.5 [Ar], 145.2 [Ar], 142.3 [Ar], 134.6 [Ar], 127.9 [Ar], 127.2 [Ar], 104.7 [γ-C]; 31.9 [C_2H_3], 31.2 [*C*Me], 29.1 [C_2H_3], 27.2 [CH*Me*$_2$], 27.0 [CH*Me*$_2$], 26.7 [CH*Me*$_2$], 26.6 [CH*Me*$_2$], 3.2 [br, Si*Me*]. Elemental anal. calc. for $C_{45}H_{77}AlN_2O_2Pd_2Si_4$, C, 52.46; H, 7.53; N, 2.72. Found: C, 52.48; H, 7.60; N, 2.63.

Spectroscopic data for **3**: δ_H (298 K, 250.1 MHz, C_7D_8) 7.15–6.95 [m, 6H, Ar], 4.93 [s, 1H, γ-C], 3.39 [sept, 8H, ^{i}Pr], 1.97 [s, 30H, GaCp*], 1.96 [s, 30H, GaCp*], 1.37 [d, 6H, ^{i}Pr-*Me*], 1.35 [s, 6H, C*Me*], 1.14 [d, 6H, ^{i}Pr-*Me*]; δ_C (298 K, 62.9 MHz, C_7D_8) 166.6 [CN], 144.8 [Ar], 143.6 [Ar], 143.2 [Ar], 137.7 [Ar], 113.5 [γ-C], 113.3 [br, ring atoms GaCp*], 29.05 [C*Me*], 28.9 [C*Me*], 25.2 [CH*Me*$_2$], 24.8 [CH*Me*$_2$], 24.5 [CH*Me*$_2$], 24.2 [CH*Me*$_2$], 11.5 [Cp**Me*], 10.8 [Cp**Me*]. Elemental anal. calc. for $C_{69}H_{101}AlGa_4N_2Pd_2$: C, 56.10; H, 6.89; N, 1.90. Found C, 55.87; H, 6.65; N, 1.75

‡ *Crystallographic data* for **1** (greenish-yellow, 0.3 × 0.15 × 0.1 mm): $C_{45}H_{77}AlN_2O_2Pd_2Si_4$, M = 1030.23, monoclinic, a = 21.1864(18), b = 13.2927(9), c = 21.8095(17) Å, β = 112.833(8)°, V = 5618.2(8) Å^3, T = 97(2) K, space group $P2_1/c$, Z = 4, μ(Mo-Kα, λ = 0.71073 Å) = 0.773 mm^{-1}, 43443 reflections measured, 9913 unique (R_{int} = 0.0556) which were used in all calculations. One disordered hexane molecule is present in the asymmetric unit and could not be refined. The final w$R2(F^2)$ was 0.1470 (all data);

measurements: Oxford Excalibur 2; programs used: SHELXS-97 and SHELXL-97. CCDC 294432.

Crystallographic data for **3**·C_6D_6 (red, 0.35 × 0.20 × 0.20 mm) $C_{75}H_{107}AlGa_4N_2Pd_2$, M = 1555.29, monoclinic, a = 23.511(14), b = 13.358(3), c = 25.139(8) Å, β = 112.74(4)°, V = 7281(5) Å^3, T = 100(2) K, space group $P2_1/n$, Z = 4, μ(Mo-Kα, λ = 0.71073 Å) = 1.995 mm^{-1}, 68115 reflections measured, 16792 unique (R_{int} = 0.1255) which were used in all calculations. The final w$R2$(F^2) was 0.1562 (all data); measurements: Oxford Excalibur 2; programs used: SHELXS-97 and SHELXL-97. CCDC 294433. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518065a

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