Novel dinuclear and trinuclear palladium β-diiminate complexes containing amido–chloro double-bridges†

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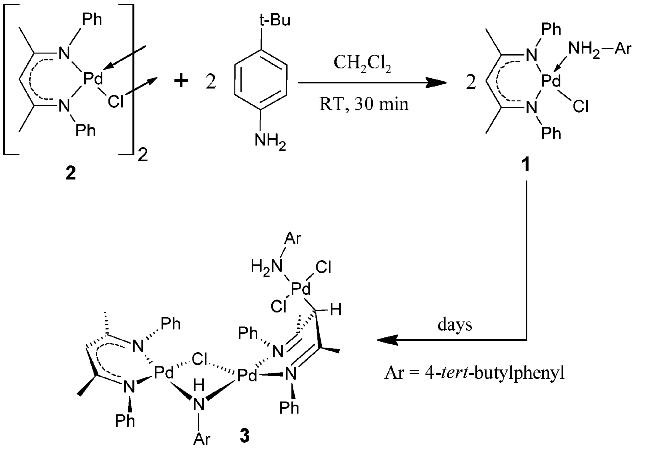
We report the formation of an unexpected trinuclear palladium β-diiminate complex from the decomposition of [Pd(Ph$_2$nacnac)(Cl)(4-H$_2$NC$_6$H$_4$-^{t}Bu)] (nacnac = β-diiminate derived from acetylacetone), the proposed reaction pathway, and the synthesis of the first dinuclear palladium complex with an amido–chloro double-bridge.

Despite the considerable development and interests in the chemistry of dinuclear palladium compounds, dinuclear Pd(II) complexes with amido or mixed amido–X bridges are scarce in the literature (X = halide or OH$^-$).[1] The previous work has concentrated on Pd$_2$(μ-OH)$_2$ bimetallic complexes in which the hydroxo bridge can be cleaved in the presence of an amine.[2–10] The coordinated amine can be deprotonated by one of the OH$^-$ groups, producing complexes with [Pd$_2$(μ-OH)(μ-NHR)] structural motifs. Ruiz *et al.* have used [{Pd(κ*C*,*N*-*ortho*-C$_6$H$_4$CH$_2$NMe$_2$)}$_2$(μ-OH)(μ-Br)] to prepare [{Pd(κ*C*,*N*-*ortho*-C$_6$H$_4$CH$_2$NMe$_2$)}$_2$(μ-Br)(μ-NHR)] (R = Ph, *p*-MeC$_6$H$_4$ and *p*-MeOC$_6$H$_4$), however without X-ray structural characterization.[11] A series of related dinuclear Pd(II) complexes with acetylacetonato (acac$^-$) ligands of general formula [{Pd(acac)}$_2$(μ-NHR)$_2$] (R = aryl) was reported in the early 1980s.[12]

The palladium–nacnac (nacnac = β-diiminate derived from acetylacetone) chemistry is still in its infancy compared to other metal–nacnacs.[13] Apart from our recent work,[14] only a few examples exist in the literature.[15–17] We have recently reported the synthesis and characterization of [Pd(Ph$_2$nacnac)(Cl)(4-H$_2$NC$_6$H$_4$-^{t}Bu)] **1** starting from the dimeric complex [Pd(Ph$_2$nacnac)(Cl)]$_2$ **2** and two equivalents of 4-*tert*-butylaniline (Scheme 1).[12]



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1

3

Scheme 1 Synthesis of **1** and formation of complex **3**.

Complex **1** was one in a series of new Pd–nacnac complexes of general formula [Pd(Ph$_2$nacanc)(Cl)(L)], where L = *N*-methyl-4,5-diphenylimidazole, CO, and 4-*tert*-butylaniline. Although **1** gave satisfactory elemental analysis, as well as ^{1}H and ^{13}C NMR and IR spectra in accordance to the proposed structure in Scheme 1, attempts‡ to obtain X-ray quality crystals of **1** produced an unexpected trimetallic palladium complex **3** (Scheme 1 and Fig. 1)§ along with small amount of a pale yellow material. The formation of **3** is a result of NH bond activation on the coordinated amine and takes place at room temperature without the need to exclude either oxygen or moisture.

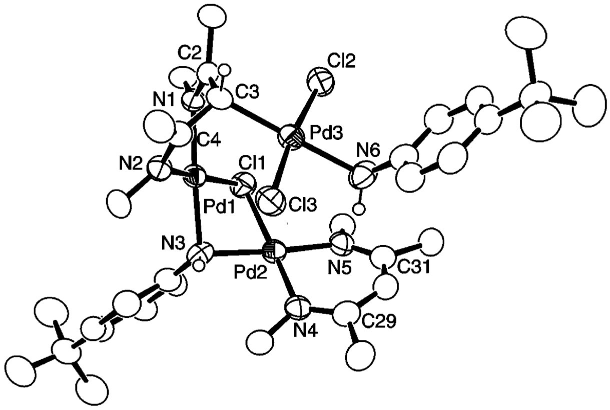

Fig. 1 The molecular structure of complex **3**. All hydrogen atoms (except for N*H*s) and phenyl carbon atoms (except for the *ipso* carbons) on (Ph$_2$nacnac)$^-$ are removed for clarity. Selected bond lengths (Å): Pd1–N3 2.087(5), Pd1–Cl1 2.3351(19), Pd2–N3 2.100(5), Pd2–Cl1 2.3941(18), Pd3–C3 2.119(6), N1–C2 1.288(7), N2–C4 1.297(7), N4–C29 1.337(8), N5–C31 1.327(8). Selected bond angles (°): Pd1–Cl1–Pd2 78.96(5), Pd1–N3–Pd2 91.81(19), N1–Pd1–N2 87.2(2), N4–Pd2–N5 90.8(2).

Complex **3** consists of two [Pd(Ph$_2$nacnac)]$^+$ moieties doubly bridged by an amide nitrogen atom and a chloride, with one of the two (Ph$_2$nacnac)$^-$ ligands bound to the third palladium through its β-carbon (C3 in Fig. 1). The two six-membered chelate rings have different conformations as a consequence of the additional Pd–C bond. The ring containing Pd1 has a boat conformation folding along N1 · · · N2 and C2 · · · C3 axes with a tetrahedral geometry around the β-C (C3), while the Pd2-containing ring has a half-chair conformation with Pd2 lying ~0.54 Å out of the plane defined by the ligand backbone. The corresponding bond lengths within the rings are different as well. For example, N1–C2 and N2–C4 bonds are similar to the N(sp^2)=C(sp^2) double bonds found

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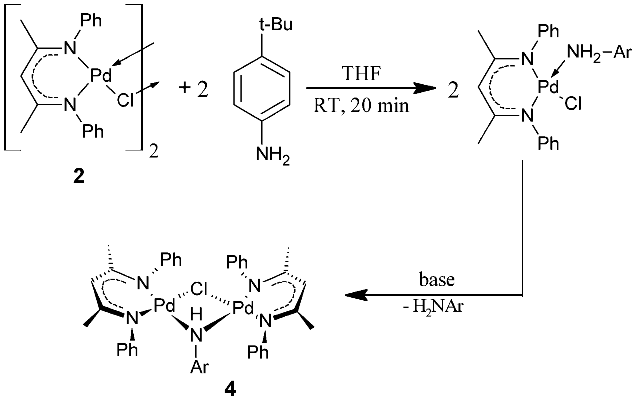
in κ*N*,*N'*-diimine palladium complexes[18–20] and shorter than N4–C29 and N5–C31 in the other ring. Besides the carbon donor atom, Pd3 is further coordinated by an aniline and two chloride ligands. A related complex in which $[Pd(CH_3CN)_3]^{2+}$ cation is coordinated to the β-C of $[(Ar'_2nacnac)Pd(CH_3CN)_2]^+$ (Ar' = 2,6-diisopropylphenyl) fragment has been reported previously.[15,16] The formation of complex **3** further indicates that the β-C of nacnac backbone retains sufficient nucleophilicity even in the charge-neutral Pd–nacnac complexes.

To understand the formation of **3**, we monitored the ^1H NMR of a freshly prepared sample of **1** in CD_2Cl_2 over a period of 14 days. During the course of the reaction a pale yellow precipitate of *trans*-$[PdCl_2(p\text{-}H_2NC_6H_4\text{-}^tBu)_2]$ **5** formed slowly.¶ The spectra show the formation of free $[Ph_2nacnac]H$ ligand identified by the distinct downfield shift at 12.71 ppm from the NH as well as the resonance at 4.88 ppm from H(β-C). Therefore, it appears that the amido bridge in **3** is a result of the deprotonation of the aniline ligand by $(Ph_2nacnac)^-$ and the $[Pd(H_2NAr)Cl_2]$ motif in complex **3** is a result of the nacnac-ligand loss from **1** due to the protonation. As such, the addition of a base to deprotonate the aniline should block this reaction pathway and prevent the loss of the nacnac ligand from **1** and in turn, the formation of **3**.

To test this hypothesis we treated 1 eq. of *in situ* generated **1** (from **2** and the aniline in 1 : 2 ratio) with 0.5 eq. of KO^tBu. As expected, the formation of **3** or $[Ph_2nacnac]H$ was not observed. Instead, the reaction produced complex **4** and free aniline (Scheme 2).* The use of two equivalents of the aniline with respect to **2** is crucial since using only one equivalent lowers the yield of **4** by about 50% indicating that the full conversion of **2** to **1** is required prior to the treatment with a base. When Et_3N instead of KO^tBu was used, the formation of **4** and free aniline were also observed. However, the reaction proceeded at a slower rate, similar to the decomposition timescale for **1** alone. In both cases neither free $[Ph_2nacnac]H$ in the solution nor **5** as precipitate was observed.



Scheme 2 Synthesis of complex **4** (Ar = $p\text{-}^tBu\text{-}C_6H_4$).

The ^1H NMR spectra of **4** are consistent with the proposed structure in Scheme 2. Thus, the methyl groups on the ligand backbone show two singlets at 1.43 and 1.57 ppm while the *tert*-butyl group gives a singlet at 1.22 ppm, integrated to six, six, and nine protons, respectively, against the resonance at 4.67 ppm from two H(β-C). These resonances are also observed in the NMR experiments monitoring the degradation of **1** in solution.

The structure of **4** has also been confirmed by X-ray crystallography (Fig. 2).†† The two $[Pd(Ph_2nacnac)]^+$ moieties are doubly bridged by an amido nitrogen atom and a chloride. The two six-membered chelate rings have similar half-chair conformations with the Pd(II) ions ~0.54 Å out of the planes defined by the remaining atoms in the rings. The metrical parameters of the bridge are similar to those found in **3**.

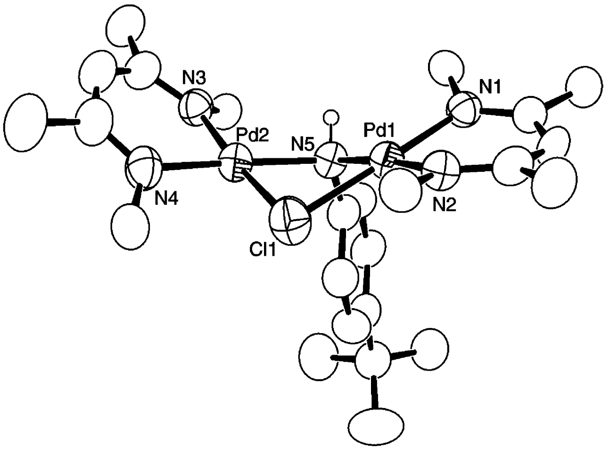
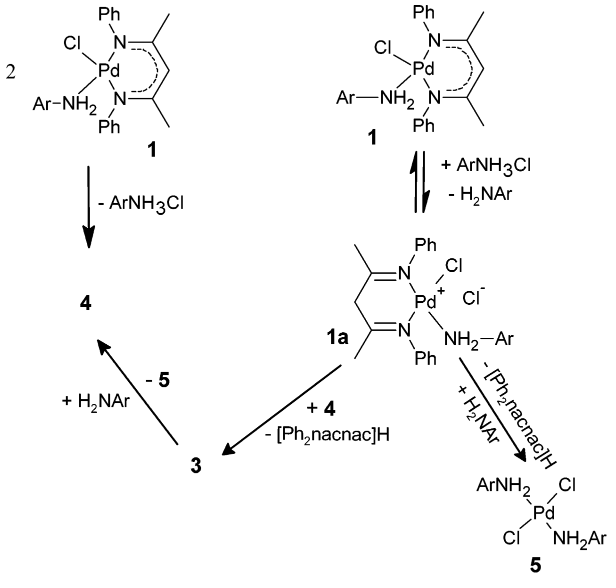


Fig. 2 The molecular structure of complex **4**. For clarity all the hydrogen atoms (except the amido hydrogen) are omitted and phenyl rings of $(Ph_2nacnac)^-$ backbone have been reduced to their *ipso* carbons. Selected bond lengths (Å): Pd1–N5 2.072(4), Pd2–N5 2.011(4), Pd1–Cl1 2.3241(17), Pd2–Cl1 2.3237(16). Selected bond angles (°): Pd1–N5–Pd2 97.67(17), Pd1–Cl1–Pd2 84.39(6).

The proposed reaction pathway for the formation of **3** on the basis of the above observations is shown in Scheme 3. The condensation of two molecules of **1** produces **4** and eliminates the aniline salt, $ArNH_3Cl$. In the absence of an exogenous base, the acidic $ArNH_3Cl$ protonates the nucleophilic β-carbon of the nacnac backbone in **1** to yield **1a** and the free aniline. The neutral β-diimine ligand in **1a** can then be displaced by either the free aniline to afford the insoluble **5**, or the nucleophilic β-C on the nacnac



Scheme 3 Proposed reaction pathways (Ar = $p\text{-}^tBu\text{-}C_6H_4$).

backbone of **4** to give **3**. The formation of **5** in this system is slow but irreversible because of the insolubility of **5**. It appears that **3** is only a metastable intermediate, trapped during the crystallization, while **4** and **5** are the thermodynamic products.

In conclusion, we have observed a facile NH activation in [Pd(Ph$_2$nacnac)(Cl)(4-H$_2$NC$_6$H$_4$-^{t}Bu)], producing an unusual trimetallic complex **3** containing a unique structural motif, [Pd$_2$(μ-Cl)(μ-HNR)], where the mixed amido–chloro double-bridge links the two [Pd(Ph$_2$nacnac)]$^+$ moieties. The formation of **3** has been rationalized through a series of experiments, during the course of which a convenient synthetic procedure for the novel amido–chloro doubly bridged bimetallic complex, **4**, has been developed. The reactivities of **4** and its analogues with other amines and their potential applications in catalysis are being investigated in our laboratory.

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Notes and references

‡ The crystals of **3**, as CH$_2$Cl$_2$ solvate, have been produced in ~40% yield by top-layering a concentrated CH$_2$Cl$_2$ solution of **1** with hexanes and further slow evaporation of the solvent after the layers mix for about 5 d. Unfortunately the bulk sample produced this way always contains trace amounts of **4** and **5**. Therefore, no satisfactory elemental analysis data were obtained. ^{1}H NMR (C$_6$D$_6$, 400 MHz, δ): 1.12 (s, 9H, CH$_3$, *tert*-Bu), 1.19 (s, 9H, CH$_3$, *tert*-Bu), 1.53 (s, 3H, CH$_3$, nacnac), 1.59 (s, 3H, CH$_3$, nacnac), 1.90 (s, 3H, CH$_3$, nacnac), 1.95 (s, 3H, CH$_3$, nacnac), 3.55 (br, 2H, NH), 4.53 (s, 1H, H(β-C), nacnac), 4.68 (s, 1H, H(β-C), nacnac), 6.01–6.05 (4H, m, aniline aromatic), 6.32–6.37 (4H, aniline aromatic), 6.65–7.91 (20H, Ph, nacnac).

§ Selected crystallographic data for complex **3**: The data were collected[22] on a Nonius Kappa-CCD diffractometer and processed with the DENZO-SMN package.[23] The structures were solved and refined with SHELXTL V6.10.[24] Empirical formula, C$_{54}$H$_{63}$Cl$_3$N$_6$Pd$_3$·CH$_2$Cl$_2$; FW 1306.58; triclinic, $P\bar{1}$; a = 11.9402(3) Å, b = 15.3099(7) Å, c = 15.5713(5) Å, α = 85.923(2)°, β = 78.728(3)°, γ = 88.962(2)°, V = 2784.49(17) Å^3, T = 150(2) K, Z = 2, D_c 1.370 g cm^{-3}; GOF on F^2, 1.040; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0634, wR_2 = 0.1592; R indices (for all data): R_1 = 0.1021, wR_2 = 0.1845.

¶ Complex **5**: ^{1}H NMR (400 MHz, dmso-d$_6$, δ): 1.19 (s, 9H, *tert*-Bu), 4.79 (br, s, 2H, H$_2$N), 6.48 (d, 2H, aniline aromatic, $^3J_{\text{H-H}}$ = 8.0 Hz), 7.02 (d, 2H, aniline aromatic, $^3J_{\text{H-H}}$ = 8.0 Hz). These data are in accordance with the spectrum obtained from a sample of **5** prepared according to the literature procedure for the synthesis of *trans*-[PdCl$_2$(H$_2$NAr)$_2$].[21]

* Synthesis of **4**: 4-*tert*-butylaniline (32 mg, 0.2 mmol) was added to a stirred solution of **2** (78 mg, 0.1 mmol) in THF (5.0 mL). The reaction changed colour from green to red within minutes. The reaction was left stirring for 20 min and solid KO^{t}Bu (11.5 mg, 0.1 mmol) was added. After 2.5 h the solution was filtered over a pad of Celite and solvent removed *in vacuo*. The red residue was re-dissolved in THF–hexanes (2.0 mL) and left in the freezer overnight. The red crystalline product was decanted and dried in vacuum to afford **4** (65 mg, 70%). Recrystallization from benzene–hexanes gives the analytically pure sample. X-Ray quality single crystals of **4** as benzene solvate were grown by slow evaporation of benzene–hexanes solution. ^{1}H NMR (C$_6$D$_6$, 400 MHz, δ): 1.22 (s, 9H, *tert*-Bu), 1.43 (s, 6H, CH$_3$), 1.57 (s, 6H, CH$_3$), 4.67 (s, 2H, H(β-C)), 6.36 (d, 2H, aniline, $^3J_{\text{H-H}}$ = 8.8 Hz), 6.60–6.62 (m, 4H, Ph), 6.69 (d, 2H, aniline, $^3J_{\text{H-H}}$ = 8.8 Hz), 6.86–6.95 (m, 12H, Ph), 7.06–7.09 (m, 4H, Ph). ^{13}C (C$_6$D$_6$, 100 MHz, δ): 24.17 (*C*H$_3$), 24.38 (*C*H$_3$), 31.90 (*C*H$_3$, *tert*-butyl), 98.03 (β-*C*, nacnac), 123.9, 124.9, 125.0, 125.2, 127.8, 128.1, 128.5, 129.4, 129.6 (phenyl and aniline rings), 149.9, 151.0, 151.7 (*ipso*-C on Ph and aniline rings), 157.1, 158.1 (*C*-N, nacnac backbone). Elemental analysis, calc. for C$_{50}$H$_{54}$N$_5$ClPd$_2$ (**4**·C$_6$H$_6$): C, 61.71; H, 5.59; N, 7.20%. Found: C, 62.16; H, 5.85; N, 6.96%.

†† Selected crystallographic data for complex **4**: The data were collected[22] on a Nonius Kappa-CCD diffractomter and processed with the DENZO-SMN package.[23] The structures were solved and refined with SHELXTL V6.10.[24] Empirical formula: C$_{44}$H$_{48}$ClN$_5$Pd$_2$·C$_6$H$_6$; FW 973.23; T 150(2) K; triclinic, $P\bar{1}$; a = 12.5418(4) Å, b = 13.5019(4) Å, c = 15.5413(5) Å, α = 106.2391(18)°, β = 105.9472(18)°, γ = 97.1865(16)°, V = 2370.66(13) Å^3, T = 150(2) K, Z = 2, D_c = 1.363 g cm^{-3}; GOF on F^2, 1.048; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0549, wR_2 = 0.1533; R indices (all data): R_1 = 0.0812, wR_2 = 0.1756.

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