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Syntheses, Structures, and Reactivities of Novel Palladium β-Diiminato−Acetate Complexes

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The reaction between (Ar_2nacnac)H (Ar = C_6H_5, ligand **a**; 2,6-(^{i}Pr)$_2C_6H_3$, ligand **b**) and [$Pd(OAc)_2$] produces red complexes [Pd(Ar_2nacnac)(OAc)] (**1a**: Ar = C_6H_5; **1b**: Ar = 2,6-(^{i}Pr)$_2C_6H_3$). Complex **1a** has a dimeric structure in the solid state with two bridging acetates, while a monomer−dimer equilibrium establishes in solution. Complex **1b** is monomeric in both the solid state and solution. Both are air- and moisture-stable compounds, unlike [Pd(Ph_2nacnac)$_2$] (**2**), which easily hydrolyzes in the presence of moisture to give [Pd(Phnacac)$_2$] (**3**) (Phnacac = {$CH_3C(NPh)CHC(O)CH_3$}$^-$). Compound **1a** reacts with metal acetates to produce heterotrimetallic complexes of a general formula [Pd(Ph_2nacnac)]$_2$-μ-[$M(OAc)_4$] (**4**, M = Cu; **5**, M = Zn). Treating **1a** with KOH in THF, or alternatively [Pd(Ph_2nacnac)Cl]$_2$ with KO^{t}Bu in wet THF, produces [Pd(Ph_2nacnac)(OH)]$_2$ (**6**).

Introduction

The β-diiminate ligands include a large variety of versatile bidentate, monoanionic N-donor ligands. Among these ligands, the ones derived from acetylacetone (acacH), nicknamed nacnac, have been a center of lively activities since the pioneering work done by Holm and Parks and by McGeachin.[1,2] The straightforward synthesis, broad tunability of both steric and electronic properties at the N donors, as well as the carbon backbone render the nacnac ligands popular in coordination chemistry.[3] They have been extensively used to stabilize metal centers of uncommon oxidation states and geometries. Some examples in main group chemistry include rare Mg(I),[4] Al(I),[5,6] Ge(I),[7] Ge(II),[6] and In(I).[8,9] Examples from transition metals include inverted sandwich complexes of V(I)[10] and Cr(I),[11] a Cr(II) hydride,[12] low-coordinate Ni(I) compounds,[13,14] and a Zn(I) dimer.[15] The transition metal nacnac chemistry has received a boost after the discoveries of highly active Zn-nacnac catalysts for the copolymerization of CO_2 and epoxides and the copolymerization of epoxides and cyclic anhydrides,[16−19] Fe-nacnac dinitrogen complexes,[20,21] and Cu-nacnac dioxygen complexes.[22−24]

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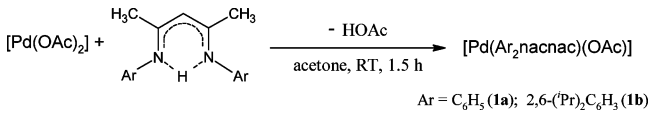
Scheme 1. Synthesis of Complex **1**



Despite the interest in transition metal nacnac complexes, relatively little work has been done with heavy transition metals. Among these, some interest has been paid to platinum[25−27] and iridium[28,29] complexes, all related to the C−H bond activation. The interest in Pd-nacnac chemistry stems directly from the Brookhart et al.'s work published in the mid-1990s. Brookhart and co-workers have developed a family of catalysts for olefin polymerization in which Pd is supported by α-diimine ligands.[30,31] These catalysts are particularly useful for the copolymerization of olefinic esters and nonpolar olefins for which the traditional early transition metal catalysts give unsatisfactory performance owing to their high oxophilicity. The *β*-diiminate analogues of these catalysts are yet to be developed and evaluated. Following previous reports on a series of well-studied Pd-nacnac complexes,[34−36] we have recently shown that [Pd(Ph$_2$-nacnac)Cl]$_2$ represents a versatile starting material for Pd-nacnac chemistry.[32,33] Herein, we report the syntheses, characterizations, and reactivities of novel [Pd(Ar$_2$-nacnac)(OAc)] (Ar = C_6H_5 or 2,6-(^{i}Pr)$_2C_6H_3$) complexes.

Results and Discussion

The addition of a [Ar$_2$nacnac]H (**a**: Ar = Ph; **b**: Ar = 2,6-^{i}Pr$_2C_6H_3$) solution to a Pd(OAc)$_2$ solution produces complexes **1a** and **1b** according to Scheme 1 in good yields (75−80%). Occasionally, and particularly in a high concentration regime (>0.01 M), a light pink precipitate forms within 15 min. While its formation lowers the yield, it does not change the identity of the final product. This pink material has extremely low solubility in common solvents, and its identity is still unknown.

The deep red complexes **1a** and **1b** are air- and moisture-stable. They have high solubility in common organic solvents (CH_2Cl_2, $CHCl_3$, acetone, THF, and CH_3CN). They dissolve well in nonpolar solvents (hexanes and ether), but their solubility in polar solvents (alcohols and water) is low.

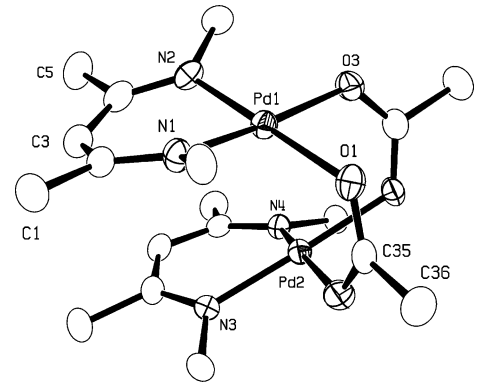


Figure 1. The molecular structure of **1a** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and phenyl rings (except for the ipso-carbons) are omitted for clarity. Selected bond lengths (Å): Pd1−N1, 1.989(3); Pd1−N2, 1.989(3); Pd1−O1, 2.062(2); Pd1−O3, 2.054(2); Pd2−N3, 1.994(3); Pd2−N4, 1.985(3); Pd2−O2, 2.054(2); Pd2−O4, 2.061(2); N1−C2, 1.325(4); N2−C4, 1.323(4); N3−C19, 1.328(4); N4−C21, 1.326(4). Selected bond angles (deg): N2−Pd1−N1, 90.25(11); N4−Pd2−N3, 91.55(11); O3−Pd1−O1, 87.74(9); O2−Pd2−O4, 88.39(9).

The molecular structure of **1a** is shown in Figure 1, while selected crystallographic data are presented in Table 1. The dimeric complex crystallized in the monoclinic space group $P2_1/n$. Two Pd(II) centers, bridged by two acetates, adopt the typical square-planar coordination geometry with two N and two O atoms taking the four coordination sites. The overall dimeric structure is similar to the structures of recently reported[37,38] cationic species [Pd(dmp)(OAc)]$^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline) and [Pd(bis-carbene)(OAc)]$^{2+}$ as well as the neutral compounds [Pd(Ph$_2$nacCl)(OAc)]$_2$ (Ph$_2$nacCl = {CH$_3$(PhN)C}$_2$CCl)[32] and palladacycle acetate dimer.[39]

Unlike **1a**, complex **1b** is a monomer (Figure 2) in the solid state. It crystallized in the monoclinic space group $P2_1/n$, with two independent molecules per asymmetric unit. Each square-planar Pd(II) center is chelated by a nacnac and an acetate ligand. The overall molecular geometry is similar to that of the previously reported [Pd(acac)(Ar$_2$nacnac)] (Ar = 2,6-^{i}Pr$_2C_6H_3$).[34]

In general, *β*-diiminato−acetate complexes are relatively scarce in the literature. Coates et al.'s work on [Zn(Ar$_2$nacnac)(OAc)]$_2$ (Ar = bulky aryl substituent) led to the development of highly active catalysts for the copolymerization of CO_2 and epoxides[16−18] and epoxides and cyclic anhydrides.[19] As confirmed by X-ray crystallographic analysis, these Zn complexes are all dimers in the solid state regardless of the steric bulk from the aryl substituents, likely because of the preferred tetrahedral geometry at the Zn(II) ion. The same has been observed for dimeric

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Table 1. Crystallographic Data for **1**−**6**

	1a	**1b**	**2**	**3**	**4**·2CH_2Cl_2	**5**·THF	**6**·2C_6H_6
formula	$C_{38}H_{40}N_4O_4Pd_2$	$C_{31}H_{44}N_2O_2Pd$	$C_{34}H_{34}N_4Pd$	$C_{22}H_{24}N_2O_2Pd$	$C_{44}H_{50}Cl_4CuN_4O_8Pd_2$	$C_{46}H_{54}N_4O_9Pd_2Zn$	$C_{46}H_{48}N_4O_2Pd_2$
fw	829.54	583.08	605.05	454.83	1181.02	1085.16	901.72
T (K)	150(2)	296(2)	150(2)	150(2)	150(2)	150(2)	150(2)
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$	$P\bar{1}$	$Pbcn$	$P2_1/c$
a (Å)	17.0440(5)	17.692(6)	10.8762(4)	16.9433(16)	8.4111(4)	28.9299(8)	13.7156(7)
b (Å)	11.5241(4)	16.787(6)	25.4132(9)	6.7425(7)	11.6681(3)	17.8215(5)	12.5422(7)
c (Å)	18.4938(4)	21.497(7)	15.3475(4)	18.0146(17)	13.2324(5)	17.8255(5)	11.6662(4)
α (deg)	90	90	90	90	84.756(2)	90	90
β (deg)	97.9268(18)	96.165(12)	97.4760(10)	108.697(3)	73.2241(18)	90	93.826(3)
γ (deg)	90	90	90	90	71.043(2)	90	90
V (Å^3)	3597.78(18)	6348(4)	4206.0(2)	1949.4(3)	1175.94(8)	9190.4(4)	2002.39(17)
Z	4	8	6	4	1	8	2
D_{calcd} (g·cm^{-3})	1.531	1.220	1.433	1.550	1.668	1.568	1.495
μ (mm^{-1})	1.044	0.611	0.692	0.971	1.487	1.350	0.941
no. of reflns collected	24340	46538	36941	5956	12361	43705	11836
no. of ind. reflns	8169	11094	9594	2222	5301	7951	3514
GOF on F^2	1.086	0.999	1.011	0.989	1.044	1.038	1.006
R [$I > 2\sigma(I)$]	$R_1 = 0.0392$ [a] $wR_2 = 0.0891$ [b]	$R_1 = 0.0535$ $wR_2 = 0.0943$	$R_1 = 0.0342$ $wR_2 = 0.0711$	$R_1 = 0.0262$ $wR_2 = 0.0642$	$R_1 = 0.0434$ $wR_2 = 0.0957$	$R_1 = 0.0511$ $wR_2 = 0.1152$	$R_1 = 0.0482$ $wR_2 = 0.1104$
R (all data)	$R_1 = 0.0650$ $wR_2 = 0.1017$	$R_1 = 0.1617$ $wR_2 = 0.1296$	$R_1 = 0.0578$ $wR_2 = 0.0796$	$R_1 = 0.0553$ $wR_2 = 0.0760$	$R_1 = 0.0622$ $wR_2 = 0.1080$	$R_1 = 0.0911$ $wR_2 = 0.1396$	$R_1 = 0.0835$ $wR_2 = 0.1309$

[a] $R_1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

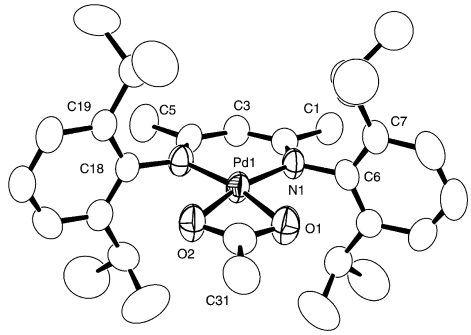
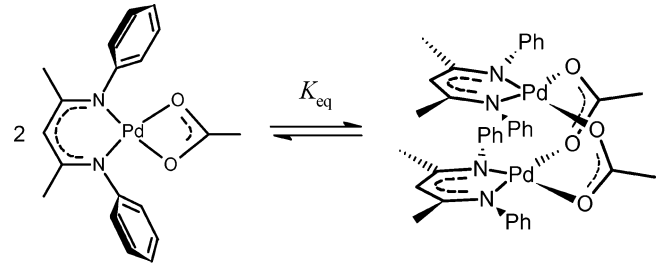


Figure 2. The molecular structure of complex **1b** with thermal ellipsoids drawn at 50% probability. All hydrogen atoms are omitted, and the disordered isopropyl groups are shown in only one orientation for clarity. Selected bond lengths (Å): Pd1−N1, 1.964(5); Pd1−N2, 1.971(5); Pd1−O1, 2.089(4); Pd1−O2, 2.118(4); N1−C2, 1.328(8); N2−C4, 1.309(9). Selected bond angles (deg): N1−Pd−N2, 92.1(2); O1−Pd1−O2, 61.94(16); N1−Pd1−O1, 102.43(17); N2−Pd1−O2, 103.58(19).

Scheme 2. Monomer/Dimer Equilibrium in a Solution of **1a**



monomer: κ^2-*O,O′*-OAc dimer: μ^2-$(OAc)_2$

$[Mn(Ar_2nacnac)(OAc)]_2$[40] and $[Mg(Ar_2nacnac)(OAc)]_2$ complexes (Ar = 2,6-(^{i}Pr)$_2$C$_6$H$_3$).[41] The only fully characterized monomeric nacnac-OAc complex other than **1b** is [Cu(Ar$_2$nacnac)(OAc)] (Ar = 2,4,6-Me$_2$C$_6$H$_2$).[42]

On the basis of ^{1}H and ^{13}C NMR spectra, **1a** is in equilibrium with, presumably, its monomer in solution (Scheme 2). The ratio of the two species is concentration-dependent, with higher concentrations favoring the dimeric form. Measurements of relative intensities of the resonances at 1.74 ppm (monomer) and 1.87 ppm (dimer) for nacnac CH_3 groups as a function of concentration (measured in the concentration range of 1.2∼6.5 × 10^{-5} M) provided the equilibrium constant of ∼4 mM^{-1} at 25 °C in CD_2Cl_2, indicating that the equilibrium lies on the dimer side. This is comparable to the value of 5 mM^{-1} for the related $[Pd(dmp)(OAc)]_2(OTf)_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline).[36] The formation of the dimer probably proceeds via a, so far unobserved, κ-*O*-OAc intermediate with acetate as a monodentate ligand and a vacant coordination site. The previously mentioned $[Zn(Ar_2nacnac)(OAc)]_2$ complexes also exist in a monomer−dimer equilibrium in their solutions with experimental evidence indicating involvement of a bimetallic complex in epoxide enchainment.[43]

On the other hand, no equilibrium has been observed for the monomeric complex **1b** in solution. Thus, the ^{1}H NMR spectrum shows two sets of resonances for diastereotopic isopropyl CH_3 groups at 1.24 and 1.44 ppm and singlets at 1.63 and 4.91 ppm for CH_3 and CH groups of the nacnac backbone. The acetate CH_3 group shows as a singlet at 1.48 ppm comparable to the resonance observed for the **1a** monomer (1.55 ppm). It is likely that the dimerization of **1b** is suppressed as a result of the steric effects of ^{i}Pr groups on phenyl rings in **1b**.

An alternative explanation for the observed equilibrium in a solution of **1a** could be ligand "scrambling". In this scenario, the **1a** dimer would be in equilibrium with $[Pd(Ph_2nacnac)_2]$ and $[Pd(OAc)_2]$ rather than with its monomer. To examine this possibility, we have prepared $[Pd(Ph_2nacnac)_2]$, complex **2** (Scheme 3). The ^{1}H NMR spectrum of **2** shows two singlets at 1.66 and 5.04 ppm from

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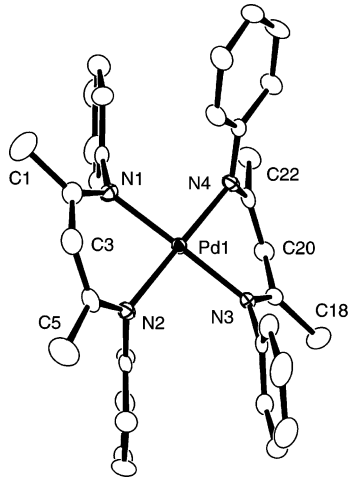
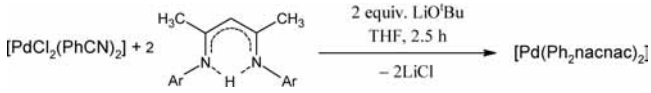


Figure 3. The molecular structure of complex **2** with thermal ellipsoids drawn at 50% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å): Pd1−N1, 2.020(2); Pd1−N2, 2.0294(19); Pd1−N3, 2.044(2); Pd1−N4, 2.0417(19); N1−C2, 1.316(3); N2−C4, 1.333(3); N3−C19, 1.311(3); N4−C21, 1.353(3). Selected bond angles (deg): N1−Pd1−N2, 86.77(8); N3−Pd1−N4, 86.35(8); N1−Pd1−N4, 93.74(8); N2−Pd1−N3, 93.13(8).

Scheme 3. Synthesis of Complex **2**



the CH_3 groups and H−C(β) on the ligand backbone, respectively. These resonances have not been observed in the NMR spectra of **1a**, and thus the ligand scrambling scenario can be ruled out. The X-ray structural analysis confirmed the structure of **2** as a bis-nacnac complex (Figure 3 and Table 1). Structurally, the closest relative of **2** is the previously reported complex [Pd(^{i}Pr$_2$nacnac)$_2$].[34] However, the other possible explanation for the solution behavior of **1a**, a higher-nuclearity species in equilibrium with the **1a** dimer, cannot be presently excluded.

Unlike complexes **1a** and **1b**, [Pd(Ph$_2$nacnac)$_2$] hydrolyzes easily in the presence of moisture. Thus, if the ether solution of **2** is left in air, within hours pale orange crystals of [Pd(Phnacac)$_2$] (**3**), (Phnacac = {CH$_3$C(O)CHC(NPh)CH$_3$}$^-$) start to form. Within a couple of days, the hydrolysis reaches ~60% yield. The hydrolysis of **2** produces **3** and free aniline simultaneously. The presence of aniline in the mother liquor has been confirmed by ^{1}H NMR spectroscopy. The structure of **3** has been confirmed by both NMR spectroscopy (^{1}H and ^{13}C) and single-crystal X-ray crystallography. Thus, the NMR spectra of **3** show resonances for two inequivalent CH_3 groups of the ligand backbone: 1.34 and 1.64 ppm in the ^{1}H and 23.76 and 24.19 ppm in the ^{13}C NMR spectra. The molecular structure of **3** is shown in Figure 4, and selected crystallographic data are given in Table 1. The compound crystallizes in the monoclinic space group *C*2/*c* with the palladium atom located on the center of inversion. The tendency of imine ligands to hydrolyze in the palladium coordination sphere has been well documented. The reactions took place with the aid of an acid[44−46] or water.[47−49]

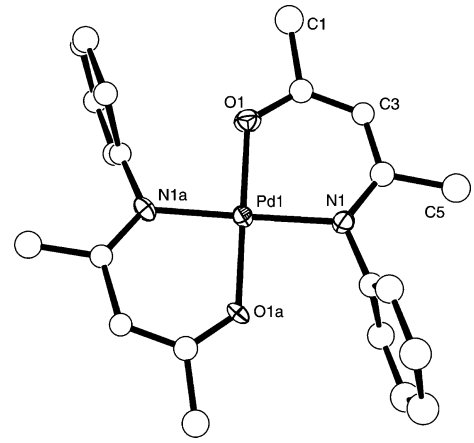
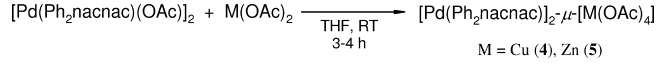


Figure 4. The molecular structure of **3**. All hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å): Pd1−O1, 1.996(9); Pd1−N1, 2.042(10); O1−C2, 1.294(15); N1−C4, 1.328(16). Selected bond angles (deg): O1−Pd1−N1, 91.4(4).

Scheme 4. Syntheses of Trimetallic Complexes **4** and **5**



However, to the best of our knowledge, this is the first example of partial hydrolysis of a nacnac ligand in a metal coordination sphere.

Complex **1a** reacts with metal acetates, M(OAc)$_2$ (M = Cu, Zn) to produce heterotrimetallic complexes of the general formula [Pd(Ph$_2$nacnac)]$_2$-μ-[M(OAc)$_4$] (M = Cu, **4**; M = Zn, **5**; Scheme 4). The reactions proceed smoothly at ambient temperature in THF, although the starting copper and zinc acetates are insoluble. Complexes **4** and **5** can be isolated in 80% and 70% yields, respectively.

A single-crystal X-ray diffraction analysis confirmed the structures for **4** and **5**. Their molecular structures are shown in Figures 5 and 6, respectively, while the crystallographic data have been summarized in Table 1. Complex **4** has an "S"-shaped structure with two [Pd(Ph$_2$nacnac)]$^+$ moieties bridged with a [Cu(OAc)$_4$]$^{2-}$ core. The Cu(II) center resides on a crystallographically imposed center of inversion. The Pd(II) and Cu(II) centers adopt the typical square-planar coordination geometry, with typical bond lengths and angles. In the case of complex **5**, significant distortion from an ideal tetrahedral geometry at the Zn(II) center occurs. The O−Zn−O angles range from ~89° (O2−Zn1−O4) to ~132° (O5−Zn1−O8). Judging from ^{1}H and ^{13}C NMR spectra, complex **5** does not retain its solid-state structure in solution since, along the resonances attributable to **5**, signals from other species have been observed, even in the case of analytically pure samples (E.A.). The other species present

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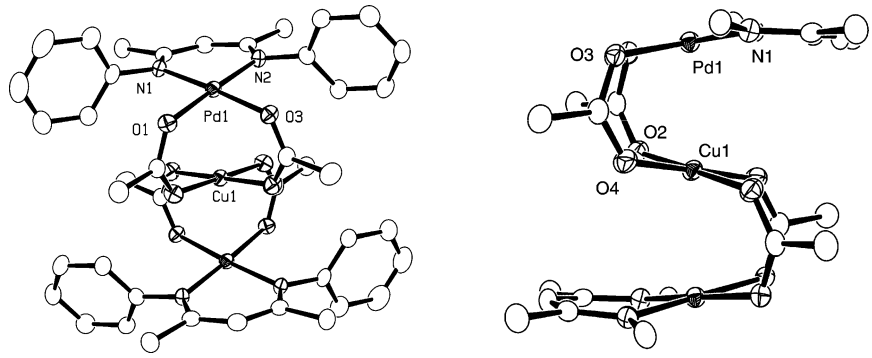


Figure 5. Two views of the molecular structure of complex **4** with thermal ellipsoids drawn at 50% probability. All hydrogen atoms are omitted, and the phenyl rings in the right view have been reduced to the ipso-carbons for clarity. Selected bond lengths (Å): Pd1−N1, 1.990(3); Pd1−N2, 1.989(3); Pd1−O1, 2.044(3); Pd1−O3, 2.053(3); N1−C2, 1.336(5); N2−C4, 1.326(5); Cu1−O4, 1.941(3); Cu1−O2, 1.966(3). Selected bond angles (deg): N1−Pd1−N2, 92.39(13); N1−Pd1−O1, 91.09(12); N2−Pd1−O3, 91.52(12); O1−Pd1−O3, 85.00(11); O2−Cu1−O4, 90.43(12).

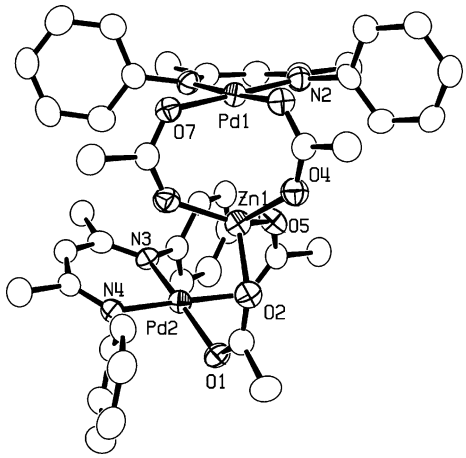
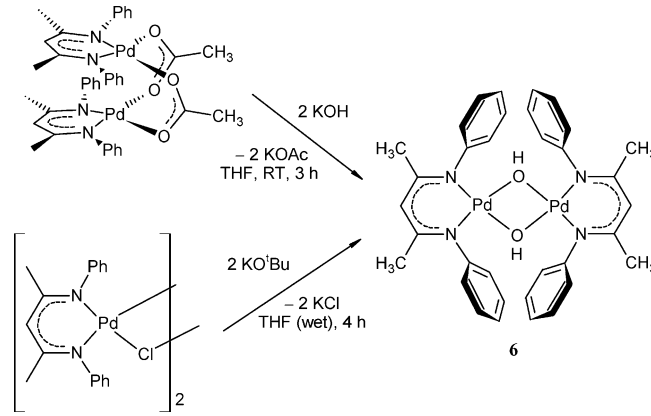


Figure 6. The molecular structure of complex **5** with thermal ellipsoids drawn at 50% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å): N1−Pd1, 1.996(4); N2−Pd1, 1.997(5); O7−Pd1, 2.049(4); O3−Pd1, 2.060(4); N4−Pd2, 1.995(4); N3−Pd2, 1.998(4); O1−Pd2, 2.041(4); O6−Pd2, 2.053(4); Zn1−O2, 1.980(4); Zn1−O4, 1.971(4); Zn1−O5, 1.941(4); Zn1−O8, 1.935(4). Selected bond angles (deg): N1−Pd1−N2, 92.7(2); O7−Pd1−O3, 85.92(15); N3−Pd2−N4, 93.00(19); O1−Pd2−O6, 86.06(15); O2−Zn1−O4, 88.94(17); O2−Zn1−O5, 111.44(17); O2−Zn1−O8, 104.53(16); O4−Zn1−O5, 101.15(17); O4−Zn1−O8, 110.51(18), O5−Zn1−O8, 131.93(17).

in the solution have not been identified yet but are probably lower nuclearity complexes.

Complexes **4** and **5** are related to several previously reported $[Pd(L_2)]$-μ-$[M(OAc)_4]$ complexes (L_2 = a bidentate or two monodentate ligands and M = Pd).[50−54] However, complexes **4** and **5** are the first rationally synthesized heterotrimetallic complexes in the family of $[Pd(L_2)]$-μ-$[M(OAc)_4]$ where M is a transition metal. Only recently, a related complex with a main group metal (M = Na) has been reported as well. The Na^+ center in this case, however, is also in close contact with two fluorine atoms from a neighboring BAr^F_4 (Ar^F = 3,5-$(CF_3)_2C_6H_3$) counterion (d_{Na-F} = ~2.5 Å) in the crystal lattice.[38]

Scheme 5. Syntheses of $[Pd(Ph_2nacnac)(OH)]_2$ (**6**)



When **1a** is treated with 2 equiv (considering **1a** as a dimer) of KOH in THF, the acetate ligands are easily replaced by two bridging hydroxo ligands to produce $[Pd(Ph_2nacnac)(OH)]_2$ (**6**). Alternatively, complex **6** can be prepared from $[Pd(Ph_2nacnac)Cl]_2$ and KO^{t}Bu in wet THF in a comparable yield (80% starting from **1a** vs 75% starting from $[Pd(Ph_2nacnac)Cl]_2$) (Scheme 5).

The structure of complex **6** has been confirmed by single-crystal X-ray diffraction analysis (Figure 7). It crystallizes from concentrated benzene solutions as a solvate, **6**·$2C_6H_6$, in the monoclinic space group $P2_1/c$. There is a crystallographically imposed center of inversion at the geometric center of each molecule of **6**. The palladium(II) center adopts a typical square-planar geometry with two N and two bridging O donor atoms occupying four coordination sites. Among a few crystallographically characterized $[M(nacnac)(OH)]_2$ complexes, **6** is most similar to the paramagnetic $[Cu(Ar_2nacnac)(OH)]_2$ (Ar = 2,6-dimethylphenyl) with two square-planar Cu(II) centers.[58] In the Ni(II) analogue $[Ni(Ar_2nacnacCF_3)(OH)]_2$ (Ar = 2,6-dimethylphenyl; nacnacCF_3 = nacnac derived from 1,1,1,5,5,5-hexafluopentane-2,4-dione), the square-planar geometry at the Ni(II) centers is tetrahedrally distorted.[59]

The hydroxyl protons of **6** give rise to a resonance at −5.24 ppm in the ^{1}H NMR spectrum, significantly more

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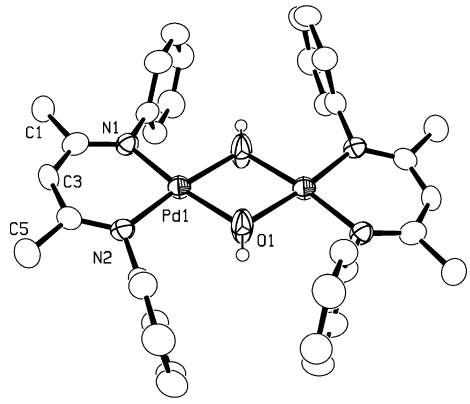

Figure 7. The molecular structure of complex **6**. All hydrogen atoms, except the hydroxyl hydrogen atoms, are omitted for clarity. Selected bond lengths (Å): Pd1−O1, 2.039(4); Pd1−N1, 1.984(4); N1−C2, 1.336(7); N2−C4, 1.337(7). Selected bond angles (deg): O1−Pd1−N2, 94.08(16); N1−Pd1−N2, 92.81(16).

upfield compared to the usual range of −0.25 to −3.5 ppm documented for both neutral and cationic $Pd_2(\mu\text{-}OH)_2$ species.[55−57] This upfield resonance can be explained by the shielding effect of phenyl rings on the Ph_2nacnac$^-$ backbone in whose pockets the OH groups lie. Tian et al. have observed similar shielding of acac methyl groups by aromatic rings on the nacnac ligand in [Pd(Ar$_2$nacnac)(acac)] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) compared to [Pd(^{i}Pr$_2$nacnac)(acac)].[34]

Unlike its chloro-bridged analogue [Pd(Ph$_2$nacnac)Cl]$_2$, the hydroxo-bridged dimer is a rather unreactive species. While [Pd(Ph$_2$nacnac)Cl]$_2$ reacts cleanly and rapidly with many monodentate, charge-neutral ligands,[32] complex **6** remains intact under forcing conditions. Thus, for example, no reaction has been observed between **6** and 2 equiv of *N*-methyl-4,5-diphenylimidazole at ambient temperature after 7 days or at elevated temperatures (∼50 °C) in C_6D_6 after several hours. The same low reactivity has been observed toward aniline and *p*-^{t}Bu-aniline. Both aniline and *p*-^{t}Bu-aniline readily react with [Pd(Ph$_2$nacnac)Cl]$_2$ and are known to react easily with μ-hydroxo Pd dimers to produce hydroxo-amido or bis-amido bridged Pd dimers.[55,60,61]

Our attempts to prepare [Pd(Ph$_2$nacnac)Cl]$_2$ from **1a** via OAc$^-$/Cl$^-$ exchange were unsatisfactory. Thus, the usual approaches for this transformation (e.g., treating **1a** with MCl (M = Li, Na) in water, acetone, or mixed solvent systems (water/acetone, water/MeOH, or water/EtOH)[62−65] did not produce the desired product. Rather **1a** was recovered along with unidentified species after 24∼42 h. Only small amount of [Pd(Ph$_2$nacnac)Cl]$_2$ was isolated (∼10% yield after recrystallization) by treating **1a** with NaCl in a CH_2Cl_2/water biphasic system in the presence of a phase-transfer catalyst ^{n}Bu$_4$NCl.

Summary

We have prepared and fully characterized two novel Pd-nacnac acetate complexes, **1a** and **1b**. These can be prepared in good yields from [Pd(OAc)$_2$] and the corresponding nacnacH ligands. The reactions do not require an external base, dry solvents, or low temperatures. The complexes are air- and moisture-stable solids. Complex **1a** is a dimer in the solid state, while in solution a monomer−dimer equilibrium is established. Complex **1b** exists as a monomer in the solid state and in solution, presumably because of the steric effect of the 2-propyl groups. Complex **1a**, similar to the previously reported [Pd(Ph$_2$nacnac)Cl]$_2$ dimer, is a suitable starting material for the preparation of Pd-nacnac complexes. Thus, it reacts with M(OAc)$_2$ to produce novel heterotrimetallic species of a general formula [Pd(Ph$_2$nacnac)]$_2$-μ-[M(OAc)$_4$] (M = Cu, Zn). The acetate ligands can be replaced with bridging hydroxyl groups to afford **6**. However, the substitution of acetates with chloride ligands produced dimeric [Pd(Ph$_2$nacnac)Cl]$_2$ in very low yield (∼10%). Unlike **1**, the bis-nacnac complex [Pd(Ph$_2$nacnac)]$_2$ (**2**) is prone to hydrolysis, and the partially hydrolyzed species [Pd(Phnacac)]$_2$ (**3**) can be isolated in good yield from a wet ether solution of **2**.

Experimental Section

General Methods and Materials. [Pd(OAc)$_2$], Cu(OAc)$_2$·H$_2$O (98%), Zn(OAc)$_2$·2H$_2$O, LiO^{t}Bu, and KO^{t}Bu were obtained from commercial sources and used without further purification. The ligands **a**[66] and **b**[35] and [PdCl$_2$(PhCN)$_2$][67] were prepared according to literature methods. The NMR spectra were recorded on a Varian 400 spectrometer working at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Both ^{1}H and ^{13}C spectra were recorded relative to the solvent residual signals but are reported relative to Me$_4$Si. Elemental analyses were performed at our department using a PE 2400 C/H/N/S analyzer.

X-Ray Crystallographic Analysis. Single crystals suitable for X-ray crystallographic analysis were obtained as described for each complex below. The single-crystal X-ray diffraction data for complexes **1a**, **4**, **5**, and **6** were collected at 150 K on a Bruker-Nonius Kappa-CCD diffractometer[68] with Mo Kα radiation (λ = 0.71073 Å). The data were processed with the DENZO-SMN package.[69] The diffraction data for complexes **1b**, **2**, and **3** were collected at the same temperature (except for **1b**, 296 K) on a Bruker Kappa-APEX II diffractometer. These data were processed using the Bruker Apex 2 software package.[70] All structures were solved

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by the direct methods and refined with SHELXTL V6.10.[71] All non-hydrogen atoms were refined anisotropically, except in the case of **3** (see below). The positions of hydrogen atoms were calculated with the riding model, and their contributions were included in the structure factor calculations. The crystallographic data are summarized in Table 1.

In the crystal structure of **1b**, the disordering observed for the isopropyl groups was successfully modeled. During the modeling process, a few C−C bond lengths were fixed with DFIX restraints. In the crystal structure of **3**, the whole molecule except for the Pd center is disordered over two positions, which has been modeled successfully. All hetero atoms in **3** were refined anisotropically, while carbon and hydrogen atoms were refined isotropically.

Synthesis of [Pd(Ph$_2$nacnac)(OAc)] (1a). A solution of Ph$_2$nacnacH (0.500 g, 2 mmol) in acetone (50 mL) was slowly added to a solution of [Pd(OAc)$_2$] (0.450 g, 2 mmol) in acetone (100 mL) with vigorous stirring. During the addition, the reaction mixture turns deep red. Occasionally, and especially if less solvent is used, a small amount of insoluble light pink material precipitates out, which can be removed by gravity filtration. After 1.5 h, the solvents were removed to dryness in vacuo, leaving a deep red solid product. Yield: 0.92 g (88.3%). Single crystals suitable for the X-ray analysis were obtained from the slow evaporation of a CHCl$_3$/hexanes (∼1:2 vol) solution over several days. ^{1}H NMR (CD$_2$Cl$_2$, monomer): δ 1.53 (s, 3H, CH$_3$ acetate), 1.74 (s, 6H, CH$_3$ nacnac backbone), 4.85 (s, 1H, CH nacnac backbone). ^{1}H NMR (CD$_2$Cl$_2$, dimer): δ 0.93 (s, 3H, CH$_3$ acetate), 1.88 (s, 6H, CH$_3$ nacnac backbone), 4.88 (s, 1H, CH nacnac backbone). The aromatic region of the ^{1}H NMR spectrum shows multiplets in the range of 7.11−7.31 ppm, for which the contributions from the monomer and dimer cannot be assigned clearly. ^{13}C NMR (CD$_2$Cl$_2$, monomer): δ 22.96 (CH$_3$ acetate), 23.53 (CH$_3$ nacnac backbone), 98.13 (CH nacnac backbone), 125.0, 128.20, 129.5 (phenyl), 150.2, 157.8 (*ipso*-C$_{Ph}$−N and C═N), 172.1 (CO, acetate). ^{13}C NMR (CD$_2$Cl$_2$, dimer): 20.58 (CH$_3$ acetate), 23.02 (CH$_3$ nacnac backbone), 100.5 (CH nacnac backbone), 125.5, 128.5, 128.7 (phenyl), 150.6, 157.8 (*ipso*-C$_{Ph}$−N and C═N), 182.4 (CO acetate). Anal. calcd for C$_{19}$H$_{20}$N$_2$O$_2$Pd: C, 55.02%; H, 4.86%; N, 6.75%. Found: C, 55.20%; H, 4.85%; N, 6.60%.

Synthesis of [Pd(DIPPh$_2$nacnac)(OAc)] (DIPPh = 2,6-(^{i}Pr)$_2$C$_6$H$_3$) (1b). This complex was prepared following the same procedure as described above for **1a**. The reaction between DIPPh$_2$nacnacH (0.420 g, 1 mmol) and [Pd(OAc)$_2$] (0.225 g, 1 mmol) gave 0.470 g (81%) of red product. Single crystals suitable for X-ray analysis were obtained by the slow evaporation of saturated Et$_2$O solution. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.21 (d, 12H, CH$_3$ ^{i}Pr, $^3J_{HH}$ = 6.8 Hz), 1.45 (s, 3H, CH$_3$ acetate), 1.59 (s, 6H, CH$_3$ nacnac backbone), 1.73 (d, 12 H, CH$_3$ ^{i}Pr, $^3J_{HH}$ = 6.8 Hz), 3.73 (sept, 1H, CH ^{i}Pr, $^3J_{HH}$ = 6.8 Hz), 4.84 (s, 1H, CH nacnac backbone), 7.09 (d, 4H, Ph, $^3J_{HH}$ = 7.6 Hz), 7.22 (t, 2H, Ph, $^3J_{HH}$ = 7.6 Hz). ^{13}C NMR (CD$_2$Cl$_2$): δ 22.44 (CH$_3$ nacnac backbone), 22.94 (CH$_3$ acetate), 23.77, 24.40 (CH$_3$ ^{i}Pr), 28.84 (CH, ^{i}Pr), 95.78 (CH nacnac backbone), 123.8, 127.3, 144.8 (phenyl), 142.6, 155.9 (*ipso*-C$_{Ph}$−N and C═N), 189.4 (C═O acetate). Anal. calcd for C$_{31}$H$_{44}$N$_2$O$_2$Pd: C, 63.85%; H, 7.61%; N, 4.80%. Found: C, 63.92%; H, 7.45%; N, 4.72%.

Synthesis of [Pd(Ph$_2$nacnac)$_2$] (2). A solution of [PdCl$_2$(PhCN)$_2$] (0.180 g, 0.5 mmol) in dry THF (4 mL) was added dropwise to a freshly prepared mixture of Ph$_2$nacnacH (0.250 g, 1 mmol) and LiO^{t}Bu (0.085 g, 1 mmol) in dry THF (12 mL). During the addition, the orange-red reaction mixture obtained a deep red color. After 2.5 h, the reaction mixture was filtered through a pad of Celite, and the filtrate was dried under vacuum. The red residue was extracted with dry pentane. The resulting solution was filtered over a pad of Celite, and solvents from the filtrate were then removed to yield 0.250 g (83%) of **2**. The crystals suitable for X-ray crystallographic analysis were obtained from slow evaporation of the pentane solution. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.66 (s, 12H, CH$_3$ nacnac backbone), 5.04 (s, 2H, CH nacnac backbone), 6.91−7.10 (m, 20H, Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 22.37 (CH$_3$ nacnac backbone), 108.8 (CH nacnac backbone), 122.9, 126.5, 127.7 (phenyl), 149.9, 160.5 (*ipso*-C$_{Ph}$−N and C═N nacnac). Anal. calcd for C$_{34}$H$_{34}$N$_4$Pd: C, 67.49%; H, 5.66; N, 9.26%. Found: C, 67.27%; H, 5.49%; N, 9.15%.

Hydrolysis of 2: Formation of Phnacac Complex 3. Approximately 80 mg of **2** was dissolved in 3 mL of regular (nondried) ether to produce a deep red solution. Pale orange crystals of **3** started to form within hours from the solution kept at ambient temperature in a sealed vial. After the solution was left overnight, the crystals were collected and washed with a small amount of cold ether to give crystalline **3** in ∼65% yield (0.045 g). The collected crystals were suitable for the X-ray crystallographic analysis. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.34 (s, 6H, CH$_3$), 1.64 (s, 6H, CH$_3$ nacac backbone), 4.84 (s, 2H, CH nacac backbone), 6.93 (dd, 4H, Ph, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.8 Hz), 7.14 (m, 2H, Ph), 7.26 (m, 4H, Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 23.76, 24.19 (CH$_3$ nacac backbone), 98.12 (CH nacac backbone), 125.1, 126.6, 128.3 (phenyl), 149.2, 163.4, 176.6 (*ipso*-C$_{Ph}$−N, C═N and C═O nacac). Anal. calcd for C$_{22}$H$_{24}$N$_2$O$_2$Pd: C, 58.09%; H, 5.32%, N, 6.16%. Found: C, 58.25%; H, 5.21%; N, 6.08%. The solvents were removed from the mother liquor, and the NMR spectrum of a viscous residue revealed the presence of aniline.

Synthesis of [Pd(Ph$_2$nacnac)]$_2$-μ-[Cu(OAc)$_4$] (4). To a solution of **1a** (0.045 g, 0.1 mmol) in 4 mL of THF was added solid Cu(OAc)$_2$·H$_2$O (0.01 g, 0.05 mmol) with stirring. Solid Cu(OAc)$_2$·H$_2$O gradually dissolved, and the reaction mixture turned to brown red. After 4 h, the solution was filtered through a small pad of Celite, and solvents of the filtrate were removed in vacuo. The brown residue was redissolved in DCM (∼2 mL), and this solution was top-layered with hexanes (∼2 mL). Brown crystals of **4**·2CH$_2$Cl$_2$ formed after several days. The crystals were collected and air-dried to give 0.047 g (79.5%) of **4**·2CH$_2$Cl$_2$. The crystals were suitable for the X-ray crystallographic analysis. Anal. calcd for C$_{44}$H$_{50}$Cl$_4$N$_4$O$_8$CuPd$_2$: C, 44.74%; H, 4.27%; N, 4.74%. Found: C, 44.60%; H, 4.23%; N, 4.99%.

Synthesis of [Pd(Ph$_2$nacnac)]$_2$-μ-[Zn(OAc)$_4$] (5). This complex was prepared as described for **4** but using Zn(OAc)$_2$·2H$_2$O (0.011 g, 0.05 mmol). The light red complex crystallized from a THF/hexanes mixture to give crystalline **5**. Yield: 0.035 g (70%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.28 (s, 12H, CH$_3$ acetate), 1.70 (s, 12H, CH$_3$ nacnac backbone), 4.99 (s, 2H, CH nacnac backbone), 7.10−7.30 (m, 20H, phenyl). ^{13}C NMR (CD$_2$Cl$_2$): δ 22.51 (CH$_3$ acetate), 24.42 (CH$_3$ nacnac backbone), 96.61 (CH, nacnac backbone), 125.7, 128.6, 129.1 (phenyl), 151.1, 156.9 (*ipso*-C$_{Ph}$−N and C═N), 181.2 (COO, acetate). Anal. calcd for C$_{42}$H$_{46}$N$_4$O$_8$Pd$_2$Zn: C, 49.81%; H, 4.54%; N, 5.56%. Found: C, 49.94%; H, 4.93%; N, 5.43%.

Synthesis of [Pd(Ph$_2$nacnac)(OH)]$_2$ (6). From 1a. Finely ground solid KOH (0.056 g, 1 mmol) was added in one portion to a solution of **1a** (0.410 g, 0.5 mmol calculated as a dimer) in 20 mL of THF with stirring. After 2.5 h of stirring, the reaction mixture was filtered through a small pad of Celite, and solvents were then removed in vacuo from the filtrate. The red residue was extracted with benzene, and the resulting solution was filtered through Celite

again. The red crystals of **6**·$2C_6H_6$ (suitable for X-ray crystallographic analysis) were deposited overnight. Yield: 0.362 g (80%).

From [Pd(Ph$_2$nacnac)Cl]$_2$. KO^{t}Bu (0.112 g, 1 mmol) was added to a solution of [Pd(Ph$_2$nacnac)Cl]$_2$ (0.390 g, 0.5 mmol) in THF (4 mL) followed by a drop of distilled water with stirring. The color of the reaction changed gradually from deep green to red. After 4 h, the reaction was filtered through Celite, and the solvent evaporated to dryness. The red residue was extracted with benzene and filtered through Celite. Slow evaporation of benzene from the filtrate produced red crystals of **6**·$2C_6H_6$. Yield: 0.340 g (75%).

^{1}H NMR (CD_2Cl_2): δ −5.24 (s, 2H, OH), 1.37 (s, 12H, CH_3), 4.53 (s, 2H, CH), 6.58 (m, 8H, Ph), 6.88 (m, 4H, Ph), 6.94 (m, 8H, Ph), 7.23 (s, 6H, C_6H_6). ^{13}C NMR (CD_2Cl_2): δ 23.38 (CH_3), 97.39 (CH), 126.0, 127.1, 129.2 (Ph), 149.9, 156.4 (*ipso*-C_{Ph}−N and C═N). Anal. calcd for $C_{34}H_{36}N_4O_2Pd_2$: C, 54.78%; H, 4.83%; N, 7.52%. Found: C, 54.56%; H, 4.95%; N, 7.41%.

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Supporting Information Available: ^{1}H NMR spectra of monomer/dimer equilibrium for complex **1a** at 25 °C and crystallographic data for **1**−**6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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