Synthesis, Characterization, and Reactivity of a Versatile Dinuclear Palladium β-Diiminate Complex

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The reaction of (Ph_2nacnac)H (Ph_2nacnac = $[CH(C(CH_3)NPh)_2]^-$) with $[PdCl_2(C_6H_5CN)_2]$ in the presence of a base (KO^{t}Bu) yields $[Pd(Ph_2nacnac)Cl]_2$ (**1**) as an air- and moisture-stable solid. The dimeric structure in **1** has been confirmed by X-ray crystallographic analysis. This complex has proven to be a useful starting material for the rich and novel Pd-nacnac chemistry. Thus, treatment of **1** with neutral monodentate ligands *N*-methyl-4,5-diphenylimidazole (**L1**), 4-*tert*-butylaniline (**L2**), and CO results in the scission of the chloride bridge and the formation of mononuclear Pd species [Pd(Ph_2nacnac)Cl(**L1**)] (**2**), [Pd(Ph_2nacnac)Cl(**L2**)] (**3**), and [Pd(Ph_2nacnac)Cl(CO)] (**4**), respectively. The reaction of **1** with an oxidant $PhI(OAc)_2$ produces a novel homobimetallic complex $[\{Pd(Ph_2nacCl)\}_2(\mu\text{-}OAc)_2]$ (**5**) (Ph_2nacCl = $[ClC(C(CH_3)NPh)_2]^-$), resulting from the oxidation of coordinated nacnac ligand rather than the Pd(II) metal center. In the presence of 6 equiv of CuCl complex **1** reacts with 4 equiv of **L1** to afford a novel heteromultinuclear complex $\{[Pd(Ph_2nacnac)(\mathbf{L1})_2]_2(\mu\text{-}Cu_6Cl_8)\}$ (**6**).

Introduction

The β-diiminate ligands (**I**, Scheme 1) have gained particular attention in coordination chemistry.[1] Much of this interest stems from the fact that their steric and electronic properties can be easily tuned by choosing the appropriate substituents on the nitrogen donor atoms. The most developed subgroup of this ligand class contains the β-diiminates derived from acetylacetone. These have been popularly nicknamed nacnac (**III**) to reflect the similarity with their isoelectronic parent acetylacetonate (acac, **II**) ligand.

To date the nacnac complexes of many main group elements, most transition metals, and several lanthanides and actinides have been reported. This high popularity of nacnac ligands is in part due to the ability of carefully designed ligands to stabilize unusual oxidation states and geometries. Thus $(ArNC(CH_3)CHC(CH_3)NAr)^-$ (Ar = 2,6-diisopropylphenyl) has recently been used to isolate crystalline rare Al(I),[2] Ge(I),[3] and Cr(I)[4] complexes. The same ligand enabled isolation and characterization of three-coordinate Fe(II),[5,6] Cu(II),[7,8] and Zn(II)[9,10] species as well as the coordinatively and electronically unsaturated five-coordinate Pt(IV) species $[Pt(Ar_2nacnac)Me_3]$.[11] Most of the nacnac coordination chemistry reported to date is concentrated on the first row transition metals. This trend is mostly due to the discovery of the highly active Zn-nacnac catalysts for the copolymerization of CO_2 and epoxides[12,13] and more recently for epoxides and cyclic anhydrides,[14] Cu-nacnac dioxygen complexes,[15–18] and models of the type 1 copper protein active site[7,19] as well as Fe-nacnac dinitrogen[20,21] and sulfido[22] complexes. Also recently a unique Cr(II) phenyl hydride supported by nacnac ligand $[\{(Ar_2nacnac)Cr\}_2(\mu\text{-}Ph)(\mu\text{-}H)\}]$[23] and $[(Ar_2nacnac)Zn-Zn(Ar_2nacnac)]$ complex containing the Zn^I-Zn^I bond[24] have been reported.

However, while the first row transition metal nacnac chemistry is well developed, the second and third row counterpart is

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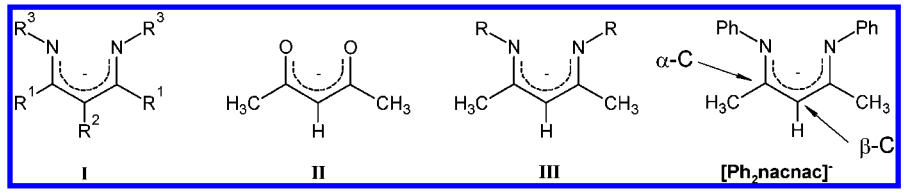
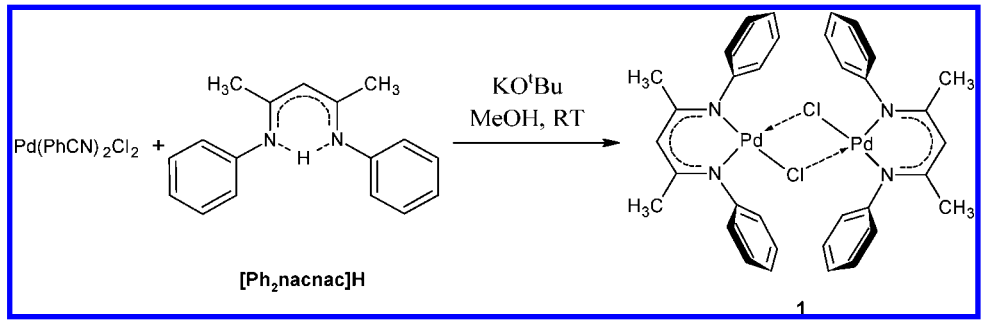
Scheme 1



Scheme 2. Synthesis of [Pd(Ph$_2$nacnac)Cl]$_2$ (1)



lagging behind. This is particularly true for late transition metals. Good examples of this case are Group 10 metals. The nickel nacnac chemistry is one of the earliest in this field[25,26] and includes catalysts for olefin polymerization[27,28] and unusual low coordinate Ni(I) complexes.[5,29–32] For the heavier Group 10 metals the situation is different. For platinum, apart from the above-mentioned [Pt(Ar$_2$nacnac)Me$_3$] (Ar = 2,6-diisopropylphenyl) complex and its noted relevance to the C−H bond activation, the only recent examples of Pt-nacnac monomethyl species have been reported as the responsible species for the dehydrogenation of ethers and alkanes.[33] Palladium nacnac chemistry is also limited to a small number of well-characterized species. These include the fully characterized complexes [Pd(^{i}Pr$_2$nacnac)$_2$],[34] [Pd(η^3-C$_3$H$_5$)(^{i}Pr$_2$nacnac)],[34] the unstable complex [Pd(acac)(Ar$_2$nacnac)] (Ar = 2,6-diisopropylphenyl) that isomerizes into [Pd(acac)(κ^2-C,N-Ar$_2$nacnac)],[34] [Pd(Ar$_2$-nacnac)ClMe],[36] and the dinuclear complex [(CH$_3$CN)$_3$-Pd-{μ-CH(C(Me)NAr)$_2$}Pd(CH$_3$CN)$_2$](BF$_4$)$_3$.[34,35] Compound [Pd{CH(C(Ph)NSiMe$_3$)$_2$}$_2$] has also been briefly mentioned in a review.[1] The underdeveloped Pd-nacnac chemistry could be attributed at least in part to the lack of a good starting material that would allow the entry to participate in more advanced coordination chemistry.

Herein we report the synthesis, full characterization, and reactivities of a versatile Pd-nacnac compound, [Pd(Ph$_2$-nacnac)Cl]$_2$ (**1**) (Ph$_2$nacnac = [CH(C(CH$_3$)NPh)$_2$]$^-$). Complex **1** is easily obtainable, air- and moisture-stable, and can easily be transformed into novel Pd-nacnac species. To avoid confusion with numbering schemes in crystal structures, the middle carbon of the nacnac backbone will be called the β-carbon (β-C) for the purposes of general discussion (Scheme 1).

Results and Discussion

Synthesis and Structure of [Pd(Ph$_2$nacnac)Cl]$_2$ (1). The reaction of Ph$_2$nacnacH, KO^{t}Bu, and Pd(PhCN)$_2$Cl$_2$ at a 1:1:1 molar ratio in methanol produces [Pd(Ph$_2$nacnac)Cl]$_2$ (**1**) as a green precipitate in 65% yield (Scheme 2).

Other palladium compounds, such as Pd(MeCN)$_2$Cl$_2$ and PdCl$_2$, can also be used as starting materials. The use of methanol as a solvent is particularly convenient since all the starting materials are soluble in it while the product is not. The synthesis of **1** can also be performed with acetone and triethylamine in the place of methanol and KO^{t}Bu, respectively. However, the yield is usually ∼50%, presumably due to the instability of acetone under basic condition.

Complex **1** is an air- and moisture-stable compound and is soluble in most common, nonpolar organic solvents (CHCl$_3$, CH$_2$Cl$_2$, toluene, benzene, etc.) but sparingly soluble to insoluble in alcohols, acetone, and water. It appears to be stable in the solution since no decomposition was observed visually or spectroscopically (NMR and IR) over several days. Tian et al. attempted to synthesize similar compounds by treating (cod)$_2$PdCl$_2$ with Li(^{i}Pr$_2$nacnac) at low temperature, but obtained [Pd(^{i}Pr$_2$nacnac)$_2$] along with Pd black instead.[34]

The molecular structure of **1** is shown in Figure 1, while the selected crystallographic data are presented in Table 1. The dimeric complex **1** crystallized in the monoclinic space group $P2_1/n$ with a crystallographically imposed inversion center in the middle. The Pd(II) center adopts a typical square-planar coordination geometry, with two N and two bridging Cl atoms occupying the four coordination sites and displaying typical bond lengths and angles. The six-membered chelate ring adopts a boat conformation, folding along N1···N2 and C2···C3 axes. The dihedral angle between the planes defined by N1, Pd, N2 and C2, C3, C4 is ∼27°.

The ^{1}H and ^{13}C NMR spectra are consistent with the symmetrical structure found in the solid state. Thus the methyl groups of Ph$_2$nacnac backbone appear as a sharp singlet at 1.56 ppm in ^{1}H NMR and 23.56 ppm in ^{13}C NMR. The aromatic region of ^{1}H NMR consists of three sets of multiplets with the integration ratio of 1:2:2. UV–vis absorption measurements at

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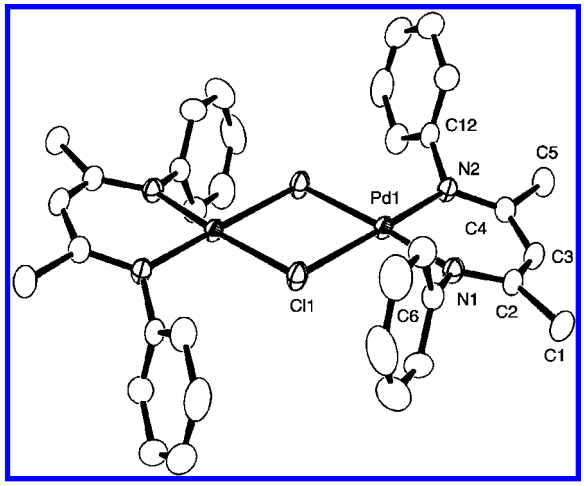

Figure 1. The molecular structure of $[Pd(Ph_2nacnac)Cl]_2$ (**1**) with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd1−N1 = 2.001(3), Pd1−N2 = 2.003(3), Pd1−Cl1 = 2.342(1), Pd1−Cl1A = 2.356(1), N1−*C*2 = 1.330(5), N2−C4 = 1.332(4). Selected angles (deg): N1−Pd1−N2 = 91.4(1), N1−Pd1−Cl1 = 93.24(9), Cl1−Pd1−Cl1A = 81.25(4).

different concentrations suggest that **1** does not dissociate in a CH_2Cl_2 solution.

Reactions of 1 with Monodentate Neutral Ligands. Complex **1** has proven to be an excellent starting material for the entry to the novel Pd-nacnac chemistry. It exhibits reactivity at both the Pd center (breaking the chloro-bridge) and the coordinated Ph_2nacnac ligand. The reactions involving the bridge cleavage are outlined in Scheme 3.

The addition of a stoichiometric amount of *N*-methyl-4,5-diphenylimidazole (**L1**) to a solution of **1** in CH_2Cl_2 within minutes produces a red solution from which [Pd(Ph_2-nacnac)Cl(**L1**)] (**2**) can be isolated. The ^{1}H and ^{13}C NMR spectra support the structure shown in Scheme 3. Due to the introduction of **L1**, the two methyl groups of the nacnac backbone of **2** are inequivalent, which display in the ^{1}H NMR spectrum as two sharp singlets at 1.55 and 1.69 ppm, indicating a lower symmetry of complex **2** compared to **1**. The same groups resonate at 23.86 and 24.33 ppm in the ^{13}C NMR spectrum.

The single-crystal X-ray diffraction analysis of **2** confirmed the proposed structure. The molecular structure of complex **2** is shown in Figure 2 while the selected structural data are summarized in Table 1. Complex **2** crystallized in the monoclinic space group *C*2/*c*. The geometry at the Pd center is square planar with three N and one Cl donor atoms occupying the four coordination sites. The six-membered chelate ring, unlike in **1**, is now almost planar with the dihedral angle between the Pd, N1, N2 and C2, C3, C4 planes of ∼3.5°. The imidazole ring of **L1** and one of the nacnac phenyl rings are facing each other probably due to the steric effects and the weak $\pi-\pi$ stacking interactions between the two rings. The chlorine atom is in close contact with the hydrogen atom on the imidazole ring of an adjacent molecule with the Cl···H distances of ∼2.77 Å (Figure 3), leading to the formation of molecule pairs in the crystal lattice of **2**.

The reaction of **1** with 4-*tert*-butylaniline (**L2**) similarly produces a red complex [Pd(Ph_2nacnac)Cl(**L2**)], **3** (Scheme 3). On the basis of ^{1}H and ^{13}C NMR spectra it is expected that **3** has a similar structure to that of **2**. Thus, the methyl groups of the Ph_2nacnac ligand give two sharp singlets at 1.70 and 1.71 ppm in ^{1}H NMR along with a singlet for the *tert*-butyl group at 1.29 ppm. Similarly the two methyl groups of the nacnac backbone resonate at 23.86 and 24.39 ppm, respectively, in the ^{13}C NMR spectrum. A broad singlet at 3.82 ppm in the ^{1}H NMR spectrum integrating to two protons is assigned to the $-NH_2$ group. The IR spectrum exhibits two sharp, medium-intensity bands at 3211 and 3304 cm^{-1} for the symmetric and asymmetric NH_2 stretches, respectively.

Bubbling CO through a solution of **1** produces a red complex [Pd(Ph_2nacnac)Cl(CO)] (**4**). The complex is stable only under CO atmosphere. If CO gas is removed it slowly loses CO and forms the characteristic green solution of **1** (as confirmed by ^{1}H and ^{13}C NMR and IR). In the ^{1}H NMR spectrum of **4** all characteristic resonances are shifted downfield compared to those of **1**, probably due to the electron-withdrawing effect of the new CO ligand. Thus two signlets for $-CH_3$ groups appear at 1.79 and 1.84 ppm while H(βC) appears at 4.98 ppm (4.66 ppm in **1**). A similar trend is visible in the ^{13}C NMR spectrum in which the coordinated CO appears at 168.7 ppm, at a significantly higher field than the free CO (184 ppm). The IR spectrum of a freshly prepared solution of **4** in either CCl_4 or toluene exhibits a sharp band at 2130 cm^{-1} assigned to the CO stretch, shifted by only 13 cm^{-1} compared to free CO (2143 cm^{-1}). The small shift indicates that the Pd−CO bond involves mostly the σ-donation with a relatively small contribution from π-backbonding. This places the CO ligand in compound **4** at the borderline between classical (ν(CO) > 2143 cm^{-1}) and nonclassical carbonyls (ν(CO) < 2143 cm^{-1}).[37]

Addition of pentane saturated with CO to a concentrated solution of **4** in toluene followed by cooling the resulting pale red solution to −30 °C under 1 atm of CO produces single crystals of **4** suitable for X-ray crystallographic analysis. Interestingly, when wet crystals of **4** were left standing in air, single crystals of **1** of high quality were obtained as confirmed by X-ray crystallography.

Compound **4** crystallized in the triclinic space group $P\bar{1}$. There are two independent molecules of **4** in the asymmetric unit (Figure 4). The two molecules are held together by intermolecular interactions between a chloride ligand in one molecule and a carbonyl carbon in the other. The Cl1···C36 and Cl2···C18 contact distances are 3.359(7) and 3.192(7) Å, respectively, and both are less than the sum of the van der Waals radii. This type of intermolecular interaction is relatively scarce in the literature. The notable example is the neutral complex $[Pd(CO)_2(SO_3F)_2]$ that shows several C(CO)···O(SO_3F) interactions.[38] Similarly, in the crystal lattice of Au(CO)Cl each carbon atom interacts with four Cl ligands of neighboring molecules.[39] The steric bulk of phenyl rings in the structure of **4** probably prevents the formation of a more extensive network. The C'O bond lengths (C18−O1 = 1.107(8) Å and C36−O2 = 1.109(8) Å) are similar in the two molecules found in the asymmetric unit. Both C≡O bonds appear to be somewhat shorter than the C≡O bond in free CO (1.12822 Å).[37]

Reaction of 1 with PhI(OAc)$_2$. Both Pt(IV) and Pd(IV) species have been proposed as the responsible intermediates for the catalytic functionalization of C−H bonds. Prompted by the successful isolation of the five-coordinate Pt(IV)-nacnac compound by Goldberg and co-workers,[11] we attempted to oxidize complex **1** to a Pd(IV) species using iodobenzene−diacetate that has been used successfully in the catalytic systems to

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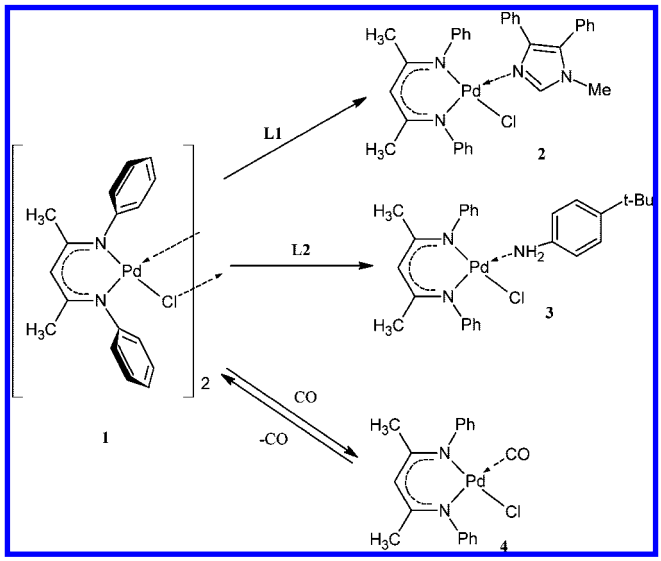
Table 1. Crystallographic Data for 1, 2, 4, 5, and 6

	1	2	4	5	6·C_6H_6
formula	C_{34} $H_{34}N_4Cl_2Pd_2$	$C_{33}H_{31}N_4ClPd$	$C_{18}H_{17}N_2OClPd$	$C_{38}H_{38}N_4O_4Cl_2Pd_2$	$C_{104}H_{96}N_{12}Cl_8Cu_6Pd_2$
FW	782.36	625.47	419.19	898.45	2391.57
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
space group	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	7.4968(2)	29.4540(10)	9.3629(5)	17.8544(4)	12.6173(3)
b (Å)	9.9044(4)	14.3066(6)	10.1302(6)	11.2625(2)	19.6119(8)
c (Å)	21.6197(2)	15.0385(5)	20.1619(12)	18.3314(4)	20.1906(8)
α (deg)	90	90	97.107(4)	90	86.249(1)
β (deg)	97.241(2)	112.939(5)	93.707(3)	90.086(1)	85.637(2)
γ (deg)	90	90	114.448(3)	90	87.367(2)
V (Å^3)	1592.59(9)	5835.9(4)	1713.21(17)	3686.17(13)	4966.8(2)
Z	2	8	4	4	2
D_c (g·cm^{-3})	1.632	1.424	1.625	1.620	1.599
μ (mm^{-1})	1.327	0.756	1.244	1.167	1.881
θ range (deg)	3.01 to 27.51	2.94 to 27.57	2.96 to 25.0	2.91 to 27.50	3.00 to 27.58
no. of refln collected	9521	18427	12874	28397	49342
no. of indept refln	3594	6678	5691	8399	22458
no. of parameters	190	355	417	457	1205
GOF on F^2	1.065	1.022	1.076	1.038	1.003
R [$I > 2\sigma(I)$]	$R_1 = 0.0427$	$R_1 = 0.0458$	$R_1 = 0.0681$	$R_1 = 0.0413$	$R_1 = 0.0620$
	$wR_2 = 0.1077$	$wR_2 = 0.1107$	$wR_2 = 0.1776$	$wR_2 = 0.0832$	$wR_2 = 0.1378$
R (all data)	$R_1 = 0.0520$	$R_1 = 0.0669$	$R_1 = 0.0813$	$R_1 = 0.0733$	$R_1 = 0.1262$
	$wR_2 = 0.1155$	$wR_2 = 0.1243$	$wR_2 = 0.1906$	$wR_2 = 0.0961$	$wR_2 = 0.1676$

Scheme 3. Reactivity of [Pd(Ph$_2$nacnac)Cl]$_2$ (1)



oxidize Pd(II) to Pd(IV).[40–44] Oxidations with PhI(OAc)$_2$ usually produce two acetate anions. We reason that the two acetate anions could serve as ligands to saturate the coordination sphere of Pd(IV) with or without a coordinating solvent.

However, the reaction of compound **1** and PhI(OAc)$_2$ did not allow the access to Pd(IV) species. Instead, a homobimetallic complex [(Ph$_2$nacCl)Pd]$_2$(μ-OAc)$_2$ (**5**) was produced, which contains a novel nacnac ligand ClC(C(CH$_3$)NPh)$_2$ (Ph$_2$nacCl) coordinated to Pd(II) centers (Scheme 4). The reaction is fast and completed within minutes monitored by NMR spectroscopy.

The ^{1}H NMR spectrum of **5** lacks the characteristic resonance of the proton on the β-carbon usually found at about 4.7 ppm. The methyl groups of the nacnac backbone show a sharp singlet at 2.15 ppm, a significant downfield shift compared to those of the complexes described in the previous sections and consistent with the presence of an electron-withdrawing group on the nacnac backbone. A similar trend is observed in the ^{13}C NMR spectrum. Thus, the β-carbon shows a signal at 105.1 ppm, downfield shifted by ~10 ppm compared with those of compounds **1**−**4**. The IR absorption bands at 1568 (asym) and 1430 (sym) cm^{-1} are consistent with the presence of bridging acetates. The similar ligand [ClC(C(Me)NAr$_2$]$^-$ (Ar = 2,6-diisopropylphenyl) has been reported previously.[8]

The proposed structure of **5** in Scheme 4 was confirmed by X-ray crystallography (Figure 5). The new Ph$_2$nacCl ligand coordinates to the Pd(II) center in a bidentate fashion, producing a six-membered chelate ring in a boat conformation folding along the N1···N2 and C2···C4 and N3···N4 and C19···C21 axes. The dihedral angles between the N−Pd−N and nacnac C−C−C planes are significantly different between the two six-

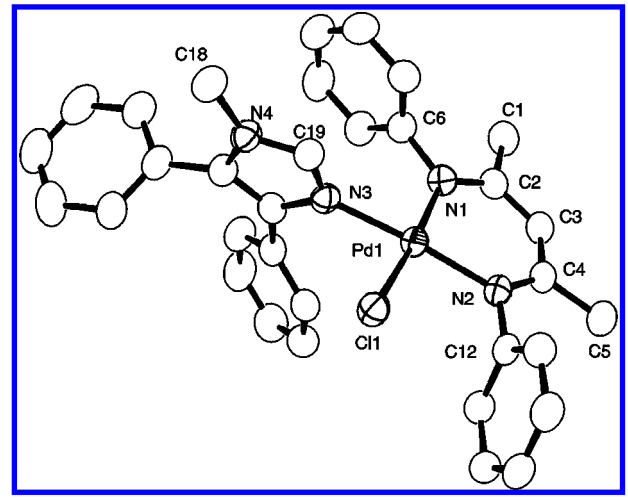


Figure 2. The molecular structure of [Pd(Ph$_2$nacnac)Cl(**L1**)] (**2**) with hydrogen atoms omitted for clarity. The thermal ellipsoids are plotted at 50% probability. Selected bond lengths (Å): Pd1−Cl1 = 2.3419(9), Pd1−N1 = 2.019(3), Pd1−N2 = 2.008(3), Pd1−N3 = 2.049(3), N1−C2 = 1.330(4), N2−C4 = 1.322(4). Selected angles (deg): N1−Pd1−N2 = 91.2(1), N1−Pd1−N3 = 91.9 (1), N2−Pd1−Cl1 = 93.82(8), N3−Pd1−Cl1 = 83.15(8).

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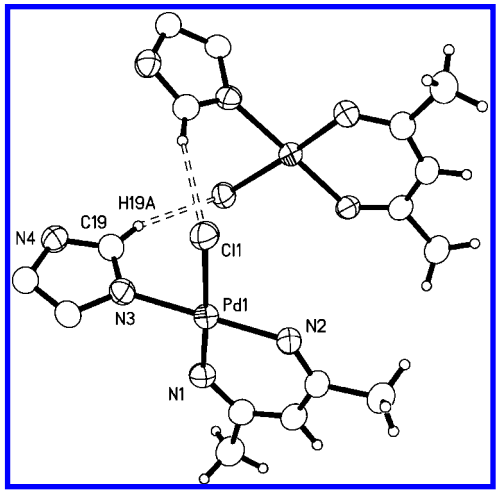


Figure 3. A diagram showing the Pd−Cl···H−C interactions (Cl···H = ∼2.77 Å) in the crystal lattice of **2**, with thermal ellipsoids at 50% probability. The methyl group of **L1** and all phenyl groups are omitted for clarity.

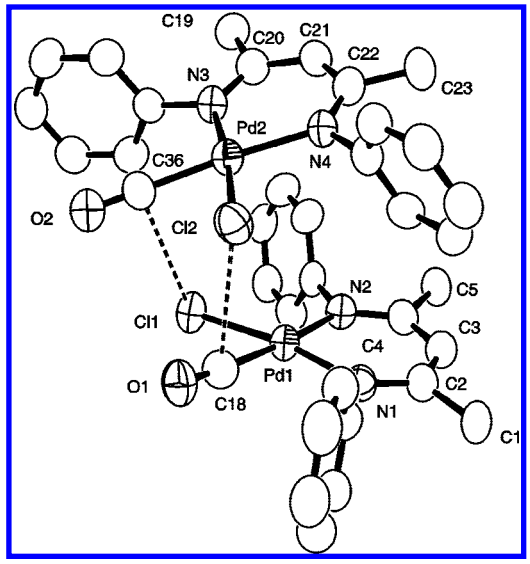
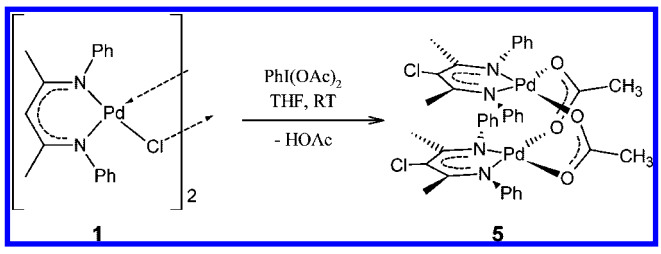


Figure 4. The molecular structures of two independent molecules of [Pd(Ph$_2$nacnac)Cl(CO)] (4) as found in the asymmetric unit (all hydrogen atoms are omitted for clarity, ellipsoids at 50% probability). Selected bond lengths (Å): Pd1−C18 = 1.950(8), Pd1−N1 = 2.016(5), Pd1−N2 = 2.018(6), Pd1−Cl1 = 2.335(2), C18−O1 = 1.107(8), Pd2−C36 = 1.928(7), Pd2−N3 = 2.020(6), Pd(2)−N4 = 2.013(5), Pd2−Cl2 = 2.323(2), C36−O2 = 1.109(8). Selected angles (deg): C18−Pd1−N1 = 93.1(3), N1−Pd1−N2 = 91.6(2), N2−Pd1−Cl1 = 95.0(2), Cl1−Pd1−C18 = 80.5(2), C36−Pd2−N3 = 94.2(3), N3−Pd2−N4 = 92.3(2), N4−Pd2−Cl2 = 93.5(2), Cl2−Pd2−C36 = 79.9(2).

Scheme 4



membered chelate rings in **5**. The dihedral angle between the N1−Pd1−N2 and C2−C3−C4 planes (54.8°) is significantly larger than that between the N3−Pd2−N4 and C19−C20−C21 planes (31.3°). The reason for this difference probably lies in the crystal packing effects. The two six-membered chelate rings are in a staggered conformation with the twist angle of 28.3°. Two acetate ligands bridge over two of the [Pd(Ph$_2$nacCl)]$^+$ motifs producing a dimeric species.

Coordination Chemistry of the *β*-Carbon of the Nacnac Ligand. Reaction between **1** and 4 equiv of **L1** in the presence of 6 equiv of CuCl produces a novel complex **6** (Scheme 5).

The structure of **6** has been confirmed by X-ray crystallography. The complex cocrystallized with benzene in the triclinic space group $P\bar{1}$. The unit cell contains two different molecules **6A** and **6B** (Figure 6). Both **6A** and **6B** have crystallographically imposed inversion center symmetry. Each molecule contains a unique $[Cu_6Cl_8]^{2-}$ cluster attached to the nacnac β-carbon atoms of two [Pd(Ph$_2$nacnac)(**L1**)$_2$]$^+$ fragments through two Cu−C bonds. The geometry around the nacnac β-C can be best described as distorted trigonal pyramidal (the hydrogen atom on β-C was located from the difference Fourier map) with the β-C of the nacnac ligand at the center of the trigonal base and the Cu atom at the top of the pyramid. Within the trigonal base, the sum of the bond angles around the β-C is ∼352° in **6A** and ∼350° in **6B**. Coordination of the β-carbon of Pd-nacnac species has been reported previously in a dinuclear complex [(CH$_3$CN)$_3$Pd-{μ-CH(C(Me)NAr)$_2$}Pd(CH$_3$CN)$_2$]-(BF$_4$)$_3$, in which the geometry around the β-C can be described as a distorted tetrahedron.[35]

The structures of the [Pd(Ph$_2$nacnac)(**L1**)$_2$]$^+$ fragments do not differ significantly in **6A** and **6B**. The structure of such a fragment in molecule **6A** is shown in Figure 7. It consists of a square-planar Pd(II) center coordinated by four nitrogen donor atoms from a bidentate Ph$_2$nacnac ligand and two *N*-methyl-4,5-diphenylimidazole ligands (**L1**). The six-membered chelate ring is once again in a boat conformation with a dihedral angle between N1, Pd1, N2 and C2, C3, C4 planes of 47.5°. The two **L1** ligands are "antiparallel" with their methyl groups pointing in opposite directions. The dinuclear complex [(CH$_3$CN)$_3$Pd-{μ-CH(C(Me)NAr)$_2$}Pd(CH$_3$CN)$_2$](BF$_4$)$_3$ reported by Feldman[35] has been described as two localized C═N double bonds (1.274(5) Å and 1.294(5) Å) and two C−C single bonds (1.477(6) Å and 1.469(6) Å) and an sp^3 hybridized β-C atom within the six-membered chelate ring. However, the bond lengths in the nacnac backbone of complex **6** (N1−C2 = 1.309(6) Å, N2−C4 = 1.310(6) Å, C2−C3 = 1.424(8) Å, C3−C4 = 1.408(8) Å) suggest a certain level of delocalization over the two N, two α-C, and two β-C atoms.

The $[Cu_6Cl_8]^{2-}$ clusters in **6A** and **6B** are both centrosymmetric. The $[Cu_6Cl_8]^{2-}$ cluster in **6A** (Figure 8, left) can be viewed as two six-membered Cu_3Cl_3 rings in a chair conformation doubly linked together by two μ_2-Cl ions. Each Cu(I) ion is three-coordinate with an almost perfect trigonal-planar geometry (average sum of angles around Cu: 357.5°). Each chloride ion is two-coordinate with a bent local geometry. The cluster in molecule **6B** (Figure 8, right) can be viewed as a 12-membered Cu_6Cl_6 ring capped by two μ_4 chlorides (Cl7 and its symmetry related counterpart). Each of the remaining chlorides is two-coordinate with a bent local geometry. The Cu5 center is bound to three chloride ions with pseudo-T-shaped coordination geometry. The Cu6 center is tetrahedrally coordinated by four chloride ions, while the tetrahedral Cu4 center is bound to three chloride ions and one C donor from the nacnac ligand. The two $[Cu_6Cl_8]^{2-}$ clusters are, to the best of our knowledge, the first of this kind that have been structurally characterized.

The Cu−C bonds (Cu1−C3 = 2.123(7) Å and Cu4−C52 = 2.197(6) Å) in complex **6** are significantly longer than a typical

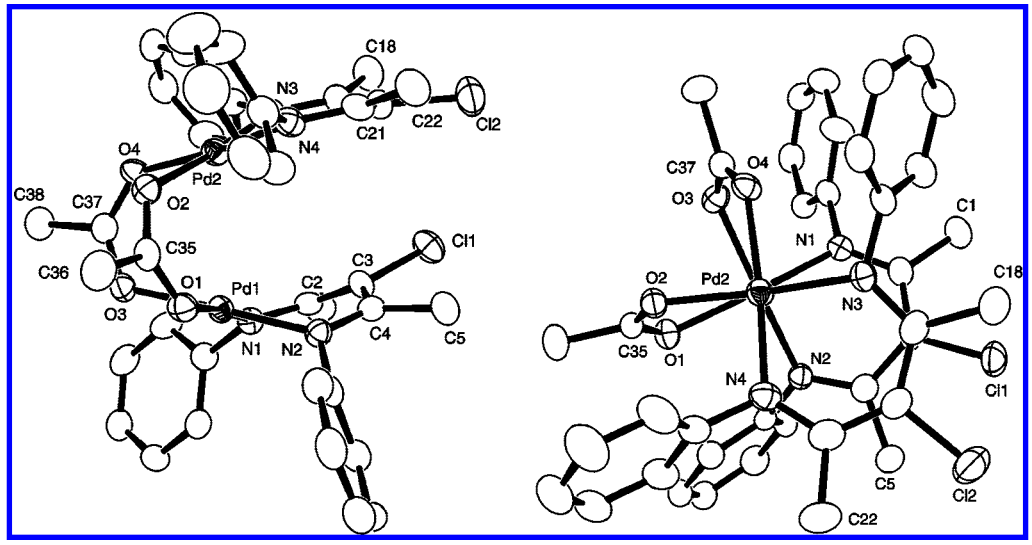
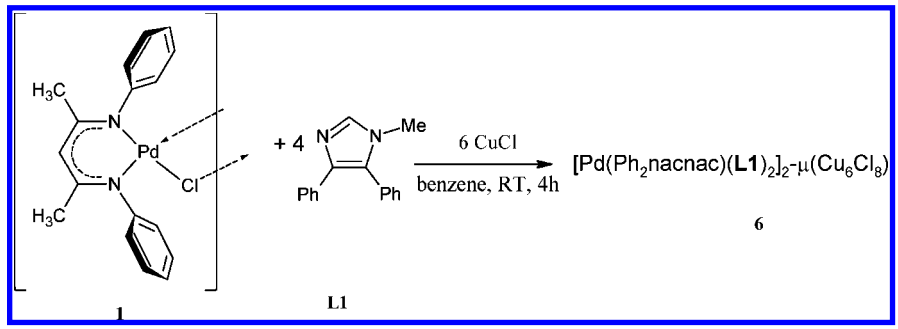


Figure 5. The molecular structure of complex **5** with thermal ellipsoids at 50% probability (left: side view; right: view along the Pd1−Pd2 axis with Pd2 on top). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd1−N1 = 1.989(3), Pd1−N2 = 1.979(3), Pd1−O1 = 2.050(2), Pd1−O3 = 2.049(2), Pd2−N3 = 1.983(3), Pd2−N4 = 1.995(3), Pd2−O2 = 2.042(2), Pd2−O4 = 2.049(2). Selected angles (deg): N1−Pd1−N2 = 87.4(1), N1−Pd1−O3 = 90.8(1), N2−Pd1−O1 = 93.6(1), O1−Pd1−O3 = 88.1(1), N3−Pd2−N4 = 90.7(1), N4−Pd2−O2 = 91.1(1), N3−Pd2−O4 = 92.0(1), O2−Pd2−O4 = 85.7(1).

Scheme 5



Cu−C bond (∼1.9 Å),[46] indicating weak interactions between the $[Cu_6Cl_8]^{2-}$ cluster and the β-C of the nacnac backbone. The metal–carbon bond in complex **6** could be interpreted as weak, π-type interactions rather than a typical σ bond as found in $[(CH_3CN)_3Pd\text{-}\{\mu\text{-}CH(C(Me)NAr)_2\}Pd(CH_3CN)_2](BF_4)_3$. Although **6A** and **6B** found in the crystal lattice show different structural features, the solution NMR spectra show only one set of sharp ^1H and ^{13}C signals for the $[Pd(Ph_2nacnac)(\mathbf{L1})_2]^+$ motif, possibly due to the dissociation of the $[Cu_6Cl_8]^{2-}$ clusters or a fast equilibrium between **6A** and **6B** in solution. Because of the net +1 charge on the $[Pd(Ph_2nacnac)(\mathbf{L1})_2]^+$ fragment, the proton on the β-C displays a signal at 5.21 ppm, downfield shifted compared to all compounds in the above sections. The proton on the imidazole ring of the **L1** ligand is situated in the shielding region of two phenyl rings in a sandwich manner. Thus, it resonates at 5.53 ppm, upfield shifted by 1.73 ppm compared to that in compound **2**.

The Cu−βC bond has been reported in $[Li(Et_2O)(Ar_2nacnac)]_2\text{-}\mu_2(Cu_2I_2)$ (Ar = 2,6-diisopropylphenyl).[45] It is worth pointing out that complex **6** is the first one in which the β-C carbon from a positively charged fragment exhibits a nucleophilic character toward a negatively charged species $[Cu_6Cl_8]^{2-}$.

The conformations of six-membered Pd-Ph_2nacnac rings warrant a short mention. Whether the ring will adopt a boat or planar structure seems dependent on the nature of other ligands around the Pd(II) center. In complexes **2** and **4** the rings are almost planar, while in **1**, **5**, and **6** the rings are in a boat conformation. The terminal chloride ligand in **2** and **4** might play a role due to its π-donating capability. The chloride ligands in **1** are in bridging mode and thus their π-donating capability is reduced. However, it is hard to make a clearer picture because palladium nacnac complexes remain scarce in the literature.

Conclusions

We have prepared and fully characterized a novel Pd-nacnac complex $[Pd(Ph_2nacnac)Cl]_2$(**1**), which is air- and moisture-stable in the solid state and in solution. It can serve as a very versatile and useful starting material for rich and novel Pd-nacnac chemistry. Complex **1** shows several places of reactivity which can be targeted separately or in combination: cleavage of the Cl bridge, full substitution of chloride ligands, and reactivity on the coordinated Ph_2nacnac ligand. Thus, the chloride bridge can easily be broken with monodentate, neutral ligands such as amines (in **3**), imines (in **2**), and CO (in **4**) to produce the mononuclear Pd-nacnac species. The reactions complete within minutes at ambient conditions. The reaction of **1** with $PhI(OAc)_2$ produces a homobimetallic complex $[Pd(Ph_2nacCl)_2(\mu\text{-}OAc)_2]$ (**5**), a product of the oxidation of

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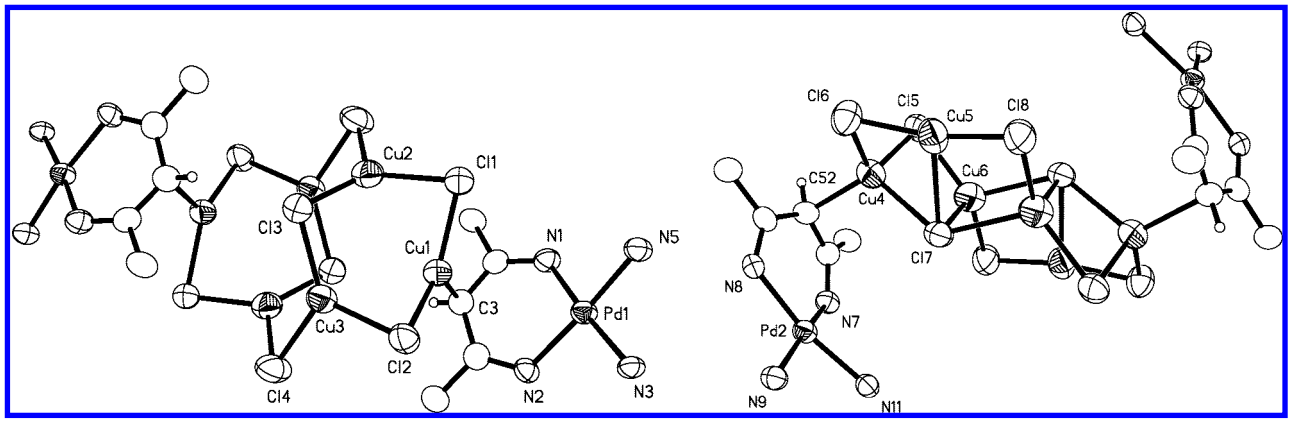

Figure 6. Two independent molecules of $[Pd(Ph_2nacnac)(\mathbf{L1})_2]_2$-$\mu$-$(Cu_6Cl_8)$ (**6**) and their partial numbering scheme: molecule **6A** (left) and molecule **6B** (right). Phenyl groups and protons of the methyl groups of the nacnac ligands and all carbon and hydrogen atoms of **L1** are omitted for clarity; the thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Cu1−C3 = 2.123(7), Cu4−C52 = 2.197(6).

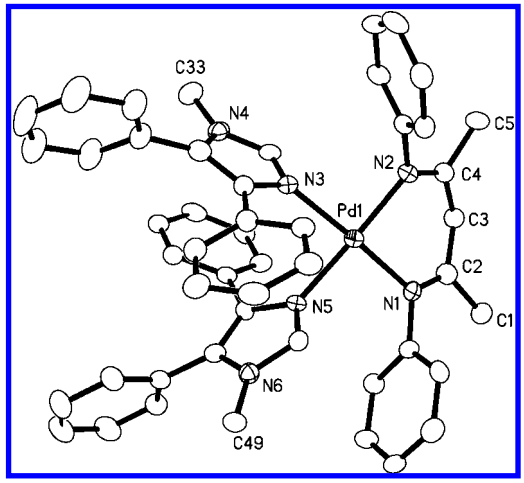

Figure 7. The structure of $[Pd(Ph_2nacnac)(\mathbf{L1})_2]^+$ fragment from molecule **6A** with thermal ellipsoids at 30% probability and the partial labeling scheme. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd1−N1=2.029(4), Pd1−N2 = 2.016(4), Pd1−N3 = 2.051(4), Pd1−N5 = 2.050(4), N1−C2 = 1.309(6), N2−C4 = 1.310(6), C2−C3 = 1.424(8), C3−C4 = 1.408(8). Selected angles (deg): N2−Pd1−N1 = 90.00(17), N1−Pd1−N5 = 93.45(16), N2−Pd1−N3 = 91.84(17), N5−Pd1−N3 = 85.15(16).

coordinated nacnac along with the replacement of the bridging chloride ligands. The β-carbon of the nacnac backbone shows significant nucleophilicity as can be seen from the formation of complex **6** in which two different, overall negatively charged $[Cu_6Cl_8]^{2-}$ clusters bind to $[Pd(Ph_2nacnac)(\mathbf{L1})_2]^+$ fragments. These fragments are in turn products of complete substitution of the chloride ligands from the starting complex **1**.

The X-ray crystal structures of complexes **1**, **2**, **4**, **5**, and **6** have been determined. Each complex contains a typical square-planar Pd(II) center. The six-membered Pd-Ph_2nacnac ring adopts either boat (in **1**, **5**, and **6**) or planar conformation (in **2** and **4**). The reason for this difference is unclear at the moment.

Further reactivity including the possible catalytic activity of **1** and its derivatives and a mechanistic study on various reactions of **1** are currently under investigation in our group.

Experimental Section

General. Unless otherwise stated, all preparations and manipulations were performed in air. All solvents used were of reagent grade. $Pd(PhCN)_2Cl_2$[47] and Ph_2nacnacH[48] were prepared according to the literature procedures. 4-*tert*-Butylaniline (99%) was purchased from Alfa Aesar. Copper(I) chloride (99%), triethylamine (reagent grade), and $PhI(OAc)_2$ (98%) were obtained from Aldrich Chemical Co. *N*-Methyl-4,5-diphenylimidazole (**L1**) was prepared from commercially available reagent grade 4,5-diphenylimidazole (Aldrich) and NaH/MeI in dry THF. CD_2Cl_2 and C_6D_6 were purchased from Cambridge Isotope Laboratories, Inc. CO gas was supplied by BOC Canada.

NMR spectra were recorded on Varian 400 or a Mercury 400 instruments both working at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Both ^{1}H and ^{13}C NMR spectra were referenced relative to the solvent's residual signals but are reported relative to Me_4Si. IR spectra were measured on a Perkin-Elmer SpectrumOne instrument, using KBr plates. UV–vis spectra were recorded on a Perkin-Elmer UV–vis/NIR Lambda 900 spectrometer, using a 1 cm cuvette. Elemental analyses were performed at our Chemistry Department with a PE 2400 C/H/N/S analyzer.

X-ray Crystallographic Analysis. Single crystals suitable for X-ray crystallographic analysis of **1**, **2**, **4**, **5**, and **6** were obtained as described for each complex below. The single-crystal X-ray diffraction data were collected at 150 K on a Nonius Kappa-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The data were processed with the Denso-SMN package.[49] The structures were solved and refined with SHELXTL V6.10.[50] All non-hydrogen atoms were refined anisotropically. The positions for hydrogen atoms were either calculated or directly located from a difference Fourier map and their contributions were included in the structure factor calculations. The crystallographic data are summarized in Table 1.

Synthesis of $[Pd(Ph_2nacnac)Cl]_2$ (1). A clear, yellow solution of $[Ph_2$nacnac$]H$ (50 mg, 0.2 mmol) and KO^{t}Bu (22 mg, 0.2 mmol) in methanol (2 mL) was added dropwise to a stirred solution of $Pd(C_6H_5CN)_2Cl_2$ (76 mg, 0.2 mmol) in methanol (4 mL). A red precipitate formed halfway through the addition. The mixture was stirred overnight (~20 h) and the precipitate changed color from red to brown and finally to green. The precipitated product was filtered off and washed with a small amount of methanol. The crude material was dissolved in a minimum amount of toluene. Pentanes were added to the green solution (about 20 times the volume of used toluene) and the solution was placed in the freezer (−30 °C)

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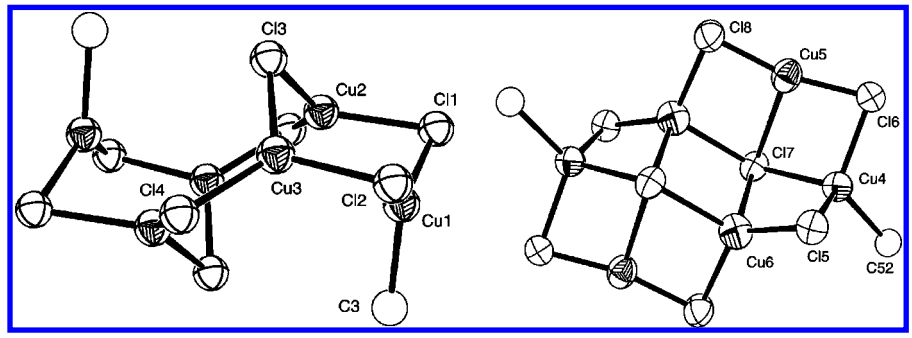

Figure 8. The structures of two Cu−Cl clusters: from molecule **6A** (left) and from molecule **6B** (right). The $[Pd(Ph_2nacnac)(\mathbf{L1})_2]^+$ fragments have been reduced to a connecting β-C atom.

overnight. The clear, colorless liquid was decanted leaving dark green needle crystals that were dried in air to give **1** in 65% yield (51 mg). The crystals obtained were suitable for X-ray crystallographic analysis. ^{1}H NMR (CD_2Cl_2) δ 1.56 (s, 6H, CH_3), 4.66 (s, 1H, CH), 6.74–6.76 (m, 4 H, Ph), 7.00–7.04 (m, 2H, Ph), 7.08–7.13 (m, 4H, Ph). ^{13}C NMR (CD_2Cl_2) δ 23.56 (*C*H_3), 96.38 (*C*H), 125.9, 127.8, 128.5 (phenyl), 150.7 (*C*$_{Ph}$-N), 156.6 (*C*═N). IR (Nujol, cm^{-1}): 1560 ($\nu_{C=N}$). UV–vis (CH_2Cl_2) 582 nm; 400 ± 3 L·mol^{-1}·cm^{-1}. Anal. Calcd for $C_{34}H_{34}Cl_2N_4Pd_2$: C, 52.19; H, 4.38; N, 7.16. Found: C, 52.54; H, 4.54; N, 7.21.

Synthesis of [Pd(Ph$_2$nacnac)Cl(L1)] (2). A solution of *N*-methyl-4,5-diphenylimidazole (**L1**; 23 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was added to a dark green solution of **1** (39 mg, 0.05 mmol) in CH_2Cl_2 (2 mL). The solution turned red within minutes. The reaction was stirred for 30 min and the solvent was removed in vacuo to leave a red residue. The crude product was dissolved in a minimum amount of ether, filtered through a pad of Celite. Addition of hexanes precipitated **2** as a red powder, which was filtered, washed with a small amount of hexanes, and vaccuum-dried. Yield 87% (55 mg). The crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of hexanes into a concentrated solution of **2** in THF. ^{1}H NMR (CD_2Cl_2) δ 1.55 (s, 3H, CH_3 nacnac), 1.69 (s, 3H, CH_3 nacnac), 3.20 (s, 3H, C*H*$_3$−N imidazole), 4.70 (s, 1H, CH nacnac), 6.91–6.63 (m, 2H, Ph), 7.00–7.16 (m, 8H, Ph), 7.26 (s, 1H, N−C*H*−N imidazole), 7.29–7.39 (m, 8H, Ph), 7.97–8.00 (m, 2H, Ph). ^{13}C NMR (CD_2Cl_2) δ 23.86 (*C*H_3 nacnac), 24.33 (*C*H_3 nacnac), 33.47 (N−*C*H_3 imidazole), 97.09 (*C*H nacnac), 124.5, 124.8, 127.3, 127.9, 128.0, 128.1, 128.4, 129.0, 129.3, 129.4, 129.8, 130.6, 130.9, 132.6 (phenyl), 137.0, 139.0 (*C*═C, imidazole), 139.0 (N*C*N, imidazole), 151.6, 153.3, 157.2, 158.2 (*ipso*-*C*$_{Ph}$—N and *C*═N). IR (Nujol, cm^{-1}) 1557 ($\nu_{C=N}$). Anal. Calcd for $C_{33}H_{31}ClN_4Pd$: C, 63.37; H, 5.00; N, 8.96. Found: C, 62.96; H, 5.09; N, 8.74.

Synthesis of [Pd(Ph$_2$nacnac)Cl(L2)] (3). A solution of 4-*tert*-butylaniline (**L2**, 14 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was added to a green solution of **1** (39 mg, 0.05 mmol) in CH_2Cl_2 (2 mL). The solution turned red within minutes. Stirring was continued for 20 min and the solvents were removed in vacuo leaving a red solid residue. The crude product was washed with hexanes and vaccuum-dried to yield 48 mg (90%) of complex **3**. ^{1}H NMR (CD_2Cl_2) δ 1.29 (s, 9H, (CH_3)C−), 1.70 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 3.82 (s, br, 2H, NH_2), 4.81 (s, 1H, CH), 6.95–7.00 (m, 2H, phenyl), 7.03–7.07 (m, 4H, Ph), 7.10–7.23 (m, 4H, Ph), 7.25–7.31 (m, 4H, Ph). ^{13}C NMR (CD_2Cl_2) δ 23.86 (*C*H_3), 24.39 (*C*H_3), 31.60 (*C*H_3, *tert*-butyl), 97.59 (*C*H nacnac), 124.2, 125.0, 125.9, 126.3, 126,5, 127.7, 127.8, 128.0, 128.1, 129.8 (Ph), 137.0, 149.7, 150.4, 153.4, 157.1, 158.6 (*ipso*-*C*$_{Ph}$—N and *C*═N). IR (Nujol, cm^{-1}) 3211, 3304 (ν_{NH}). Anal. Calcd for $C_{27}H_{32}ClN_3Pd$: C, 60.01; H, 5.97; N, 7.78. Found: C, 60.42; H, 6.14; N, 7.71.

Synthesis of [Pd(Ph$_2$nacnac)Cl(CO)] (4). The red solutions of complex **4** can generally be prepared by bubbling CO through a solution of **1** for 15–20 min. To obtain the NMR spectra, CO was bubbled through a green solution of **1** (28 mg) in CD_2Cl_2 in a J. Young NMR tube. After 15 min the tube was closed and the collected spectra confirmed a full conversion of **1**. For the IR measurements, CO was bubbled through a solution of **1** in either CCl_4 or toluene for 20 min. The crystals suitable for X-ray crystallographic analysis were obtained by adding pentane saturated with CO to a solution of **4** in toluene in a vial under a blanket of CO. The pale red solution was then cooled in the freezer (−30 °C) to produce the crystalline **4** within a few hours. ^{1}H NMR (CD_2Cl_2) δ 1.79 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 4.98 (s, 1H, CH), 6.95–6.98 (m, 2H, phenyl), 7.16–7.20 (m, 1H, phenyl), 7.23–7.40 (m, 7H, phenyl). ^{13}C NMR (CD_2Cl_2) δ 22.50 (*C*H_3), 25.09 (*C*H_3), 96.64 (*C*H), 125.8, 127.2, 128.0, 128.4, 129.7 (phenyl C), 150.9, 157.8, 159.7, 160.3 (*C*═N and *ipso*-*C*$_{Ph}$—N), 168.7 (*C*O). IR (CCl_4 solution, cm^{-1}) 2130 (ν_{CO}), 1593 ($\nu_{C=N}$), ($PhCH_3$ solution, cm^{-1}) 2130 (ν_{CO}). The instability of **2** did not allow for elemental analysis.

Oxidation of 1: Synthesis of [Pd(Ph$_2$nacCl)]$_2$-(μ-OAc)$_2$ (5). Iodobenzene diacetate (16 mg, 0.05 mmol) in THF (1 mL) was added dropwise to a solution of **1** (19 mg, 0.025 mmol) in THF (0.3 mL). The resulting solution was stirred overnight. Hexanes (4 mL) were added to the red solution producing a small amount of brown solid, which was removed by filtration through a pad of Celite. The filtrate was placed in the freezer (−30 °C). The solvent was decanted from the precipitated product, which was dried in air to give **5** in 75% yield. The crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of hexanes into a concentrated solution of **5** in THF. ^{1}H NMR (CD_2Cl_2) δ 0.96 (s, 6H, C*H*$_3$COO), 2.15 (s, 12H, CH_3 nacnac), 7.15–7.17 (m, 8H, aromatic), 7.19–7.23 (m, 4H, aromatic), 7.30–7.34 (m, 8H, aromatic). ^{13}C NMR (CD_2Cl_2) δ 22.36, 23.30 (nacnac and OAc CH_3), 105.1 (*C*Cl), 125.7, 127.9, 128.7 (aromatic), 149.8, 157.3 (*ipso*-*C*$_{Ph}$—N and *C*═N), 182.2 (O*C*O acetate). IR (Nujol, cm^{-1}) 1568, 1430 (ν_{OAc}). Anal. Calcd for $C_{38}H_{38}Cl_2N_4O_4Pd_2$: C, 50.80; H, 4.26; N, 6.24. Found: C, 50.79; H, 4.14; N, 6.18.

Synthesis of [Pd(Ph$_2$nacnac)(L1)$_2$]$_2$-μ-(Cu$_6$Cl$_8$) (6). *N*-Methyl-4,5-diphenylimidazole (**L1**, 46 mg, 0.2 mmol) was added to a stirred green solution of **1** (39 mg, 0.05 mmol) in dry C_6H_6 (4 mL) in an N_2-filled glovebox. Within minutes the color of the reaction mixture changed to red. After 30 min of stirring, CuCl (30 mg, 3mmol) was added and stirring was continued for 4 h. The slightly cloudy red solution was filtered through a small pad of Celite. Slow evaporation of the solvent from the filtrate gave large red crystals of **6**·C_6H_6 in 45% yield. ^{1}H NMR (CD_2Cl_2) δ 1.99 (s, 12H, nacnac-C*H*$_3$), 2.93 (s, 12H, **L1**-C*H*$_3$), 5.21 (s, 2H, β-C*H*), 5.53 (s, 4H, imidazole-C*H*), 6.99–7.04 (m, 8H, aromatic), 7.05–7.14 (m, 12H, aromatic), 7.19 (t, broad, J = 7.4 Hz, 12H, aromatic), 7.38–7.50 (m, 14H, aromatic), 7.54–7.62 (m, 12H, aromatic), 7.80–7.88 (m, 8H, aromatic). ^{13}C NMR (CD_2Cl_2) δ 24.49, 33.70, 98.55, 125.71, 127.44, 128.20, 128.44, 128.68, 128.75, 128.84, 128.97, 129.64, 129.86, 129.93, 130.86, 132.88,

136.36, 139.47, 151.35, 159.34. Anal. Calcd for $C_{98}H_{90}N_{12}Cl_8Cu_6Pd_2 \cdot C_6H_6$: C, 52.22; H, 4.05; N, 7.03. Found: C, 52.35; H, 3.99, N, 6.93.

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Supporting Information Available: Crystallographic data for **1**, **2**, **4**, **5**, and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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