Articles

(*β*-Diketiminato)palladium Complexes

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Reaction of $Pd(acac)_2$ with 1 equiv of the lithium *β*-diketiminate Li($^iPr_2$-nacnac) ($^iPr_2$-nacnac = CH{C(Me)N^{i}Pr}$_2$) affords the dark red mixed-ligand complex (acac)Pd($^iPr_2$-nacnac) (**1**), while with 2 equiv of Li($^iPr_2$-nacnac) the light red homoleptic Pd($^iPr_2$-nacnac)$_2$ (**2**) is formed. A similar reaction of $Pd(acac)_2$ with the more bulky (THF)Li(Ar_2-nacnac) (Ar_2-nacnac = CH{C(Me)N(C_6H_3-2,6-$^iPr_2$)}$_2$) proceeds only to the stage of the mixed-ligand complex. While below 0 °C red (acac)Pd(κ^2N,N-Ar_2-nacnac) (**4**) is isolated as the kinetically controlled product, which is stable in the solid state, this complex isomerizes in solution at ambient temperature to yield the lighter red and chiral (acac)Pd(κ^2C,N-Ar_2-nacnac) (**5**), displaying a novel nacnac bonding mode. The reaction of $[Pd(MeCN)_4](BF_4)_2$ and that of the Pd(I) complex $[Pd_2(MeCN)_6](BF_4)_2$ with (THF)Li(Ar_2-nacnac) gives [(κ^2N,N-Ar_2-nacnac)Pd$(MeCN)_2$]-(BF_4) (**6**). The κ^2N,N-Ar_2-nacnac ligand in **6** is sufficiently nucleophilic to displace acetonitrile from $[Pd(MeCN)_4](BF_4)_2$ and produce the pure dinuclear [$(MeCN)_3$Pd{μ-CH(C(Me)N$Ar)_2$}Pd$(MeCN)_2$]$(BF_4)_3$ (**A**), previously accessible only in a mixture. From the reactions of {(η^3-C_3H_5)Pd(μ-Cl)}$_2$ with Li($^iPr_2$-nacnac) and (THF)Li(Ar_2-nacnac) the mixed-ligand complexes (η^3-C_3H_5)Pd($^iPr_2$-nacnac) (**3a**) and (η^3-C_3H_5)Pd(κ^2N,N-Ar_2-nacnac) (**3b**) have been obtained. Reaction of (cod)PdMeCl with (THF)Li(Ar_2-nacnac) affords (Ar_2-nacnac)PdMe(MeCN) (**7**). An anisotropic effect of the Ar_2-nacnac ligand in the ^{1}H NMR spectra of **3b** and **4** can be noted. The structures of **2**, **3a**, **4**, and **5** have been determined by X-ray crystallography.

Introduction

(*β*-Diketiminato)metal complexes have attracted much attention in recent years. Original interest focused on the study of the classical coordination chemistry of homoleptic M(II) (M = Co, Ni, Cu) complexes,[1] but soon it emerged that *β*-diketiminate ligands are rather versatile with respect to possible substituents and bonding modes.[2] A major development came with the implementation[3a] of the twofold *N*-2,6-diisopropylphenyl-substituted pentane-2,4-diiminate ligand HC{C(Me)NAr}$_2^-$ (Ar = C_6H_3-2,6-$^iPr_2$), which due to the particular electronic properties of the Schiff base donor N atoms and the large bulk of the aryl substituents turned out to be especially suited to impose unusual properties on its metal complexes. Pentane-2,4-diiminate ligands with relatively bulky *N*-alkyl substituents such as isopropyl and *tert*-butyl have also become accessible.[4] The catchy acronym R_2-nacnac[5] for the substituted pentane-2,4-diiminates has been coined to account for the fact that the ligands represent nitrogen derivatives of acac. Recent studies have revealed the ability of *β*-diketiminate ligands to stabilize metals in unusual oxidation states such as Al(I),[6] Ga(I),[7] Sc(I),[8] Ni(I),[9] and Ni(III)[9c] and to invoke unusual coordination numbers such as three-coordinate M(II) (M = Fe, Co, Ni)[9a,10] and five-coordinate Pt(IV).[11]

In view of these unusual properties and the fact that the *β*-diketiminate ligand is monoanionic and bidentate like the *π*-allyl ligand, we were intrigued to study what effect replacing the *π*-allyl group by the *β*-diketiminate ligand would have on our Pd−*π*-allyl chemistry.[12] Although *β*-diketiminate complexes

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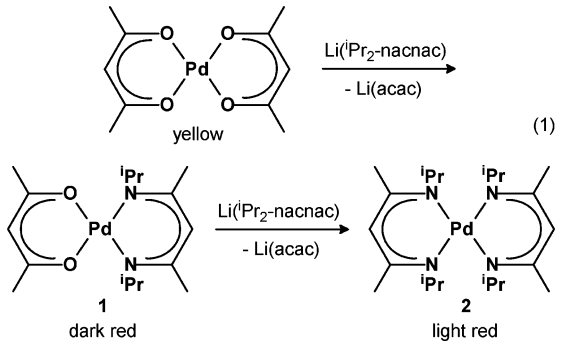
with nickel have been widely investigated,[1,9,13] relatively little is known about palladium. The reaction of $[Pd(MeCN)_4](BF_4)_2$ with Ar_2-nacnacH affords the dinuclear tricationic $[(MeCN)_3Pd\{\mu\text{-}CH(C(Me)NAr)_2\}Pd(MeCN)_2](BF_4)_3$ (**A**; Ar = C_6H_3-2,6-$^iPr_2$) as an impure product.[3a] (cod)$PdCl_2$ reacts with $LiCH(C(Ph)NSiMe_3)_2$ to give the centrosymmetric square-planar $Pd\{CH(C(Ph)NSiMe_3)_2\}_2$ (**B**), mentioned in a review.[2] The reaction of (cod)PdMeCl with Tl(Ar_2-nacnac) and a salicylaldimine gives (Ar_2-nacnac)PdMe(κ^1N-PhCH═NCH_2Ph) (**C**) in quantitative yield.[14] Furthermore, addition of a β-diimine to $PdCl_2$ yields the adduct $\{Me_2C(C(Me)NC_6H_4\text{-}2\text{-}^iPr)_2\}PdCl_2$,[15a] and oxidative addition of methallyloxyphosphonium salts to Pd(0) in the presence of various neutral β-iminoamines results in the formation of cationic β-diimine complexes $[(\eta^3\text{-}C_3H_4Me)Pd\{CH_2(C(Me)NAr')_2\}]Y$ (Y = PF_6, BArF).[15b]

We now wish to report our findings on the reactions of various Pd(I) and Pd(II) starting complexes with Li($^iPr_2$-nacnac) and Li(Ar_2-nacnac), which afford Pd($^iPr_2$-nacnac)$_2$ (**2**), (η^3-C_3H_5)Pd($^iPr_2$-nacnac) (**3a**), (acac)Pd(κ^2N,N-Ar_2-nacnac) (**4**), and its isomer (acac)Pd(κ^2C,N-Ar_2-nacnac) (**5**) as structurally characterized products.

Results and Discussion

Pd(II)−^{i}Pr$_2$-nacnac Complexes 1−3a. Reacting $Pd(acac)_2$ with 2 equiv of Li($^iPr_2$-nacnac) in diethyl ether by heating the mixture from −78 °C to ambient temperature affords a red solution, from which light red crystals of the homoleptic complex **2** separate in 73% yield. When only 1 equiv of Li($^iPr_2$-nacnac) is used, the dark red mixed-ligand intermediate **1** can be isolated in 28% yield, but some **2** is also formed. The synthesis of **2** from $Pd(acac)_2$ is thus likely to pass through **1** as an intermediate (eq 1). Complex **1** does not form by ligand



metathesis between $Pd(acac)_2$ and **2**. Complexes **1** and **2** dissolve well in pentane and other solvents.

Complexes **1** and **2** have been characterized by their DSC, MS, and NMR spectra and additionally, in the case of **2**, by single-crystal X-ray crystallography. Solid **1** is thermally stable to about 120 °C and **2** to 153 °C (DSC), at which temperatures melting occurs with decomposition. In the EI mass spectra of both complexes the molecular ions are observed as intense peaks (**1**, *m*/*e* 386, 53%; **2**, *m*/*e* 468, 33%). While fragmentation of $\mathbf{1}^+$ is initiated by cleavage of a methyl group (*m*/*e* 371, 48%) to eventually give the unassigned *m*/*e* 165 as the base ion, $\mathbf{2}^+$ fragments by eliminating $^iPr_2$-nacnac − H to afford the base ion $[(^iPr_2\text{-nacnac})PdH]^+$ (*m*/*e* 288).

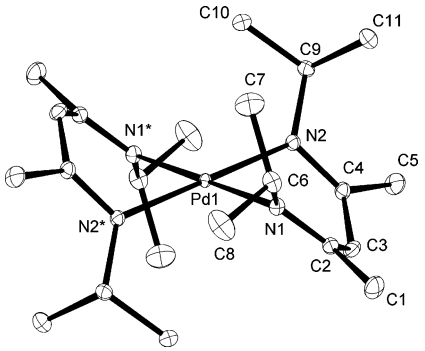


Figure 1. Molecular structure of Pd($^iPr_2$-nacnac)$_2$ (**2**). Selected bond distances (Å), bond angles (deg), and interplanar angles (deg): Pd1−N1 = 2.045(1), Pd1−N2 = 2.042(1), N1−C2 = 1.321(2), N2−C4 = 1.331(2), C2−C3 = 1.412(2), C3−C4 = 1.408(2); N1−Pd1−N2 = 82.85(5); Pd1,N1,N2/N1,N2,C2,C4 = 49(1), N1,N2,-C2,C4/C2,C3,C4 = 23(1), Pd1,N1,N2/N1,N2,C6,C9 = 103(1).

The ^{1}H and ^{13}C NMR spectra (Table 1) of **1** show enantiotopic isopropyl methyl groups in agreement with an apparent C_{2v} symmetry, indicating either a planar or a flexible envelope structure of the Pd($^iPr_2$-nacnac) chelate. In contrast, for **2** the isopropyl methyl groups are diastereotopic, as expected for a rigid envelope conformation of the Pd($^iPr_2$-nacnac) chelate rings, giving rise to C_{2h} symmetry of the complex in solution. Both complexes furnish the characteristic resonances for the central CH groups of the acac and $^iPr_2$-nacnac ligands (**1**, δ(H) 5.27 and 4.33; **2**, 4.77).

The molecular structure of **2** has been determined by X-ray crystallography, and details of the structure refinement are given in Table 2. Complex **2** crystallizes with two independent molecules in the elementary cell. The structure of one molecule is depicted in Figure 1; a similar structure was outlined for complex **B**. The Pd(II) center in **2** is coordinated in an exact plane by the four N atoms of the two $^iPr_2$-nacnac ligands, and the geometry of the N atoms is trigonal planar, in accord with sp^2 hybridization (sum of the three angles at nitrogen is 359°). The ^{i}Pr substituents at N are bent to the same side out of the coordination plane and away from Pd (plane angle Pd1,N1,-N2/N1,N2,C6,C9 = 103°), presumably as a consequence of their bulk, and the N1−Pd1−N2 angle at 82.85(5)° is smaller than the ideal 90° (cf. **3a** and **4**), so that the six-membered Pd(nacnac) chelate rings adopt a pronounced boat conformation with folds along N1···N2 and C2···C4 and interplanar angles Pd1,N1,-N2/N1,N2,C2,C4 of 49° and N1,N2,C2,C4/C2,C3,C4 of 23°. Apart from the inversion center the two independent molecules exhibit no additional symmetry and adopt almost identical conformations, despite different crystal environments (root-mean-square deviation 0.04 Å), indicating that the 12 methyl groups have little flexibility and are close-packed, completely shielding the core of the complex.

In an attempt to synthesize $\{(^iPr_2\text{-nacnac})Pd(\mu\text{-Cl})\}_2$, the $^iPr_2$-nacnac analogue of $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-Cl})\}_2$, we reacted (cod)$PdCl_2$ with 1 equiv of Li($^iPr_2$-nacnac), but instead of the expected product we isolated small amounts of **2**. The reaction of (cod)$PdCl_2$ with 2 equiv of Li($^iPr_2$-nacnac) similarly gave **2** in low yield (30%). Both reactions were carried out in diethyl ether by starting at −78 °C, and some palladium black was

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Table 1. ^{1}H and ^{13}C NMR Data of Complexes 1−7 and of Reference Compounds in CD_2Cl_2 at 25 °C[a]

^{1}H NMR Data

	δ(H)							
	acac		nacnac		^{i}Pr			
	CH	Me	CH	Me	CH	Me	phenyl	other
^{i}Pr$_2$-nacnacH			4.38	1.89	3.67	1.19		11.36 (NH)
Li(^{i}Pr$_2$-nacnac)			4.60	1.73	3.65	1.09, 1.08		
(THF)Li(Ar$_2$-nacnac)			4.59	1.66	3.09	1.20, 1.02	7.06, 6.95	
Pd(acac)$_2$	5.42	2.01						
(acac)Pd(^{i}Pr$_2$-nacnac) (**1**)	5.27	1.98	4.33	1.87	3.31	1.48		
Pd(^{i}Pr$_2$-nacnac)$_2$ (**2**)			4.77	1.89	3.15	1.22, 1.07		
(acac)Pd(κ^2*N*,*N*-Ar$_2$-nacnac) (**4**)	4.92	1.13	4.86	1.68	3.39	1.23, 1.20	7.13, 7.04	
(acac)Pd(κ^2*C*,*N*-Ar$_2$-nacnac) (**5**)	5.22	1.78, 1.75	2.65	1.93, 1.83	3.66, 3.46, 3.26, 2.82	1.37, 1.29, 1.24, 1.19, 1.17, 1.15, 1.12, 1.09	7.27, 7.16 deg, 7.08 deg, 6.99	
[(Ar$_2$-nacnac)Pd(MeCN)$_2$](BF$_4$) (**6**)			5.11	1.76	3.25	1.49, 1.25	7.26, 7.17	1.72 (MeCN)
[(MeCN)$_3$Pd{μ-CH(C(Me)NAr)$_2$}-Pd(MeCN)$_2$](BF$_4$)$_3$ (**A**)			6.17	2.30	3.61, 3.00	1.59, 1.55, 1.40, 1.24	7.47, 7.36, 7.31	3.04, 2.42, 2.34, 1.86 (MeCN)
(Ar$_2$-nacnac)PdMe(MeCN) (**7**)			4.71	1.62, 1.59	3.40, 3.36	1.36, 1.27, 1.20, 1.17	7.15−7.00 (4 signals expctd)	1.48 (MeCN), −0.47 (PdMe)
	allyl		nacnac		^{i}Pr			
	CH	CH$_2$	CH	Me	CH	Me	phenyl	
(η^3-C$_3$H$_5$)Pd(^{i}Pr$_2$-nacnac) (**3a**)[b]	4.75	3.53 (syn), 2.26 (anti)	4.47	1.96	3.61	1.26, 1.15		
(η^3-C$_3$H$_5$)Pd(Ar$_2$-nacnac) (**3b**)	5.24	2.16 (anti), 1.76 (syn)	4.79	1.67	3.49, 3.19	1.28, 1.20, 1.19, 1.16	7.12−7.00 (3 signals expctd)	

^{13}C NMR Data

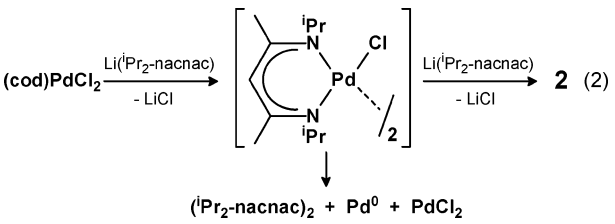
	δ(C)									
	acac			nacnac			^{i}Pr			
	C=O	CH	Me	C=N	CH	Me	CH	Me	phenyl	other
^{i}Pr$_2$-nacnacH				158.2	94.0	18.9	47.2	25.0		
Li(^{i}Pr$_2$-nacnac)				163.3	64.7	14.3	51.0	23.5, 23.5		
(THF)Li(Ar$_2$-nacnac)				163.3	68.0	25.2	28.0	24.2, 23.4	149.1, 140.9, 123.1, 122.7	
Pd(acac)$_2$	187.3	101.4	25.3							
1	185.5	99.2	19.8	156.7	99.2	25.5	52.3	24.7		
2				161.2	106.5	26.9	50.6	23.5, 19.7		
4	186.0	99.6	24.4	157.1	94.5	24.2	28.3	24.0, 23.8	145.0, 144.0, 125.7, 122.9	
5	188.0, 174.8	99.9	22.6, 21.7	210.0, 195.2	10.8	28.8, 28.6	28.4, 28.4, 27.6, 27.0	24.0, 23.9, 23.8, 23.7, 23.5, 23.1, 23.0, 22.9	148.9, 141.7, 141.0, 137.5, 137.2, 136.6, 127.6, 124.1, 123.5, 123.0, 122.7, 122.5	
6				157.7	96.0	23.0	28.5	23.8, 23.7	148.0, 143.4, 128.2, 124.0	120.1, 1.9 (MeCN)
A				182.7	36.0	25.9	30.1, 29.6	24.3, 24.3, 24.2, 24.2	145.3, 141.4, 140.4, 130.6, 126.0, 125.2	4.9, 4.4, 3.1, 2.8 (*Me*CN)
7				158.8, 158.4	93.6	25.8, 23.8	28.1, 27.9	24.2 deg, 24.0, 23.5	149.7, 149.4, 142.2 deg, 124.6, 124.4, 123.2, 123.1	118.0, 2.2 (MeCN), 0.9 (PdMe)
	allyl			nacnac			^{i}Pr			
	CH	CH$_2$		C=N	CH	Me	CH	Me	phenyl	
3a[b]	108.3	52.1		157.2	96.2	24.3	51.2	24.0, 20.0		
3b	115.4	61.1		159.1	94.1	22.8	28.3, 27.9	24.4, 24.0, 23.8, 23.4	154.3, 140.7, 139.5, 124.4, 123.5, 123.3	

[a] deg = degenerate. [b] Solvent C_6D_6.

Table 2. Crystal Data for Pd(^{i}Pr$_2$-nacnac)$_2$ (2), (η^3-C$_3$H$_5$)Pd(^{i}Pr$_2$-nacnac) (3a), (acac)Pd(κ^2*N*,*N*-Ar$_2$-nacnac) (4), and (acac)Pd(κ^2*C*,*N*-Ar$_2$-nacnac) (5)

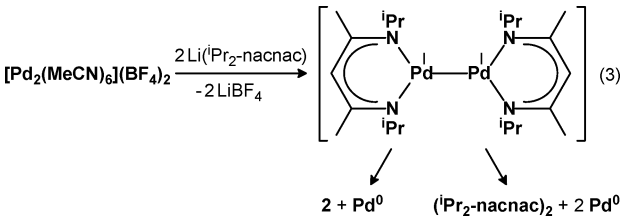
	2	3a	4	5
empirical formula	$C_{22}H_{42}N_4Pd$	$C_{14}H_{26}N_2Pd$	$C_{34}H_{48}N_2O_2Pd$	$C_{34}H_{48}N_2O_2Pd$
color	orange-red	yellow	orange	yellow
formula wt	469.00	328.77	623.14	623.14
temp (K)	100	100	100	100
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
unit cell dimens				
a (Å)	8.1121(2)	9.0662(3)	35.0185(5)	18.0221(5)
b (Å)	9.6711(3)	17.4148(7)	10.6251(1)	10.6425(2)
c (Å)	16.6998(4)	9.6064(4)	20.5768(3)	17.2769(4)
α (deg)	78.659(1)	90.0	90.0	90.0
β (deg)	82.887(1)	101.143(2)	121.351(1)	107.205(1)
γ (deg)	65.204(1)	90.0	90.0	90.0
V (Å^3)	1164.88(5)	1488.1(1)	6538.29(15)	3165.43(13)
Z	2	4	8	4
V/*Z* (Å^3)	582.4	372.0	817.3	791.4
calcd density (Mg m^{-3})	1.337	1.467	1.266	1.308
abs coeff (mm^{-1})	0.810	1.230	0.598	0.617
F(000) (e)	496	680	2624	1312
cryst size (mm^3)	0.19 × 0.18 × 0.12	0.06 × 0.06 × 0.05	0.20 × 0.14 × 0.08	0.130 × 0.090 × 0.024
θ range for data collecn (deg)	3.14−31.48	3.06−31.57	3.24−31.48	3.45−31.52
index ranges	$-11 \le h \le 11$ $-14 \le k \le 14$ $-24 \le l \le 24$	$-13 \le h \le 13$ $-25 \le k \le 25$ $-14 \le l \le 14$	$-51 \le h \le 51$ $-15 \le k \le 15$ $-30 \le l \le 29$	$-26 \le h \le 26$ $-14 \le k \le 15$ $-25 \le l \le 25$
no. of rflns collected	26 528	13 710	89 328	49 431
no. of indep rflns	7540 (R_{int} = 0.0352)	4709 (R_{int} = 0.1158)	10 856 (R_{int} = 0.0507)	10 524 (R_{int} = 0.0577)
no. of rflns with $I > 2\sigma(I)$	7091	3991	9510	7985
completeness (%)	97.6 (θ = 31.48°)	94.4 (θ = 31.57°)	99.8 (θ = 31.48°)	99.7 (θ = 31.52°)
abs cor	semiempirical from equivalents	Gaussian	semiempirical from equivalents	semiempirical from equivalents
max/min transmissn	1.00/0.75	0.955/0.902	1.00/0.94	1.00/0.86
full-matrix least squares	F^2	F^2	F^2	F^2
no. of data/restraints/params	7540/0/247	4709/0/155	10 856/0/356	10 524/0/375
goodness of fit on F^2	1.115	1.067	1.080	1.045
final *R* indices ($I > 2\sigma(I)$)				
R1	0.0285	0.0691	0.0302	0.0394
wR2	0.0759	0.2031	0.0714	0.0799
R indices (all data)				
R1	0.0300	0.0876	0.0379	0.0649
wR2	0.0769	0.2454	0.0748	0.0880
largest diff peak/hole (e Å^{-3})	0.783/−0.808	3.21/−2.21 (1.1/0.69 Å from Pd1)	0.511/−0.986	0.501/−0.729

formed, even at about −50 °C. Workup of the reaction mixtures led to isolation of an elusive colorless compound which has been tentatively assigned as the neutral ligand dimer (^{i}Pr$_2$-nacnac)$_2$. It seems likely that the intermediate {(^{i}Pr$_2$-nacnac)-Pd(μ-Cl)}$_2$ is not stable and reacts partly with further Li(^{i}Pr$_2$-nacnac) to give **2**, while the rest decomposes with reduction of palladium and oxidation of the ligand (eq 2). The formation of



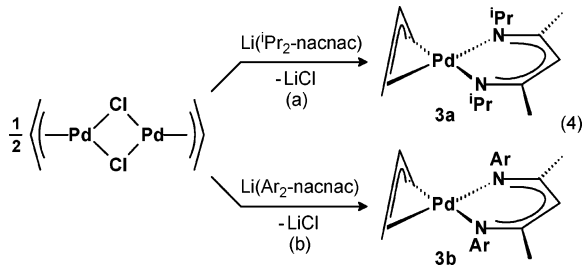
(^{i}Pr$_2$-nacnac)$_2$ appears analogous to that of (Ar$_2$-nacnac)$_2$ (Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$), which was obtained when Ar$_2$-nacnacH was treated with $AgPF_6$ in the presence of triethylamine.[16]

We also attempted to synthesize the dimeric Pd(I) complex {(^{i}Pr$_2$-nacnac)Pd}$_2$, a pendent to the various Ni(I) complexes, by reacting [Pd$_2$(MeCN)$_6$](BF$_4$)$_2$ with 2 equiv of Li(^{i}Pr$_2$-nacnac) in diethyl ether, but at around −50 °C some palladium black precipitated, as observed previously with (cod)PdCl$_2$, and complex **2** was isolated from the solution in about 30% of the theoretical yield. The formation of these products can be conceived as a disproportion reaction of Pd(I) into Pd(0) and Pd(II) passing via a hypothetical dimer (eq 3). Workup of the mother liquor also gave some ligand dimer (^{i}Pr$_2$-nacnac)$_2$.



Warming a mixture of {(η^3-C$_3$H$_5$)Pd(μ-Cl)$_2$}$_2$ with Li(^{i}Pr$_2$-nacnac) in diethyl ether from −78 to 0 °C leads to isolation of the light yellow mixed-ligand complex **3a** (eq 4a). The solid compound (mp 153 °C dec, DSC) is stable at ambient temperature for a short period but is best stored cold. Whereas **3a** decomposes quickly in THF and CH_2Cl_2, even at low temperatures, it is more stable in diethyl ether and, in particular, in benzene. In the EI mass spectrum (55 °C) the molecular ion of **3a** appears with high intensity (44%). M$^+$ fragments by cleavage of an isopropyl substituent, whereas, quite unexpectedly, the

(16) Shimokawa, C.; Itoh, S. *Inorg. Chem.* **2005**, *44*, 3010.

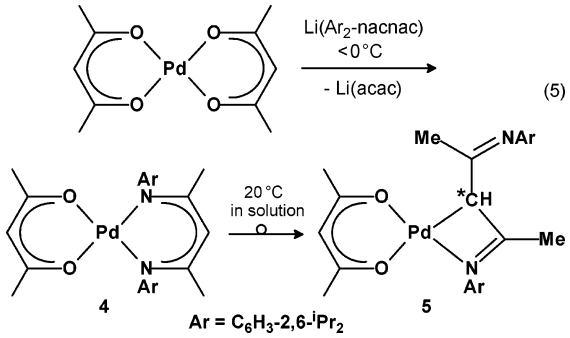


allyl group remains attached. In the ambient-temperature ^{1}H and ^{13}C NMR spectra of **3a** in C_6D_6 both the allyl and the ^{i}Pr$_2$-nacnac resonances are sharply resolved with diastereotopic methyl groups at the isopropyl substituents, indicating structural rigidity of the π-allyl group.

In the crystal structure of **3a** (Table 2 and Figure 2) the Pd(II) center is coordinated in a square-planar fashion by the β-diketiminate and the π-allyl ligand, with the meso carbon of the latter tilted away from the Pd center in the usual manner (plane angle C12,C13,C14/C12,C14,Pd1 = 109°). As for **2**, the geometry of the sp^2 N atoms in **3a** is trigonal planar (the sum of the angles at N is 359°). The six-membered Pd(nacnac) chelate ring also displays a boat conformation, but with plane angles Pd1,N1,N2/N1,N2,C2,C4 of 30° and N1,N2,C2,C4/C2,C3,C4 of 16° it is less folded than in **2** (angles of 49 and 23°, respectively), and the N1−Pd1−N2 angle at 88.9° is close to the expected 90°. This is presumably a consequence of the reduced steric repulsion in **3a**, since the ^{i}Pr substituents attached to N are bent toward the Pd atom (plane angle Pd1,N1,N2/N1,N2,C6,C9 of 72°) instead of away as in the case of **2** (103°).

Pd(II)−Ar$_2$-nacnac Complexes 3b−7. The reaction of $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)_2\}_2$ with (THF)Li(Ar$_2$-nacnac) affords yellow crystals of **3b** (eq 4b). As for **3a**, in the EI mass spectrum of the neutral **3b** the molecular ion is observed with high intensity. It breaks down by elimination of the allyl ligand (unlike **3a**, which cleaves off an ^{i}Pr substituent) to give [(Ar$_2$-nacnac)Pd]$^+$ (*m*/*e* 523) as the base ion. The ^{1}H and ^{13}C NMR spectra of **3b** (Table 1) are in agreement with C_S symmetry of the complex. The occurrence of 15 ^{13}C signals for the Ar$_2$-nacnac ligand confirms the rigid coordination of the ligands at Pd and the nonrotating nature of the *N*-C$_6$H$_3$-2,6-^{i}Pr$_2$ substituents, with their phenyl ring planes orientated perpendicular to the coordination plane. In the ^{1}H NMR spectrum the allyl syn protons (δ(H) 1.76) unexpectedly resonate upfield from the anti protons (δ(H) 2.16), which is attributed to an anisotropic effect of the nacnac phenyl rings.

Warming a mixture of Pd(acac)$_2$ and (THF)Li(Ar$_2$-nacnac) (Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$) in pentane from −78 to 0 °C results in the formation of the red mixed-ligand complex **4** (an analogue of **1**) as the kinetically controlled product (eq 5). No Pd(Ar$_2$-nacnac)$_2$ is formed (as a possible analogue of **2**), even when an excess of (THF)Li(Ar$_2$-nacnac) is used.



Isolated **4** is stable at ambient temperature. The melting point of **4** determined by DSC is 227 °C, and no phase change is indicated below this temperature. In the EI mass spectrum (120 °C) the molecular ion (*m*/*e* 622) is observed as the base ion. It fragments by cleaving off acetylacetonate to afford the intense [Pd(Ar$_2$-nacnac)]$^+$ (*m*/*e* 523, 40%).

The molecular structure of **4** is shown in Figure 3. The complex consists of almost planar (acac)Pd (rms deviation 0.029 Å) and Pd(κ^2*N*,*N*-Ar$_2$-nacnac) units (rms deviation 0.028 Å), which are tilted by 7° to each other at the formally square planar Pd(II) center. While the O1−Pd1−O2 angle of the (acac)Pd chelate at 90.51(5)° is normal, the N1−Pd1−N2 angle of the Pd(κ^2*N*,*N*-Ar$_2$-nacnac) chelate at 92.61(5)° is much larger than the corresponding angle in **2** (83°) and slightly larger than that in **3a** (89°). The ipso C atoms of the phenyl rings also lie in the Pd(κ^2*N*,*N*-Ar$_2$-nacnac) plane (the sum of the angles at trigonal-planar N is 360°), with the planes of the phenyl rings approximately lying perpendicular to this (plane angles of 84 and 90°).

The solution ^{1}H and ^{13}C NMR spectra of **4** (Table 1) are consistent with point symmetry C_{2v}, which is almost that found for the molecule in the crystal (but less so for its environment). Thus, for the Ar$_2$-nacnac ligand there are 4 phenyl ring ^{13}C resonances, and the 4 isopropyl groups are equivalent, but as they have diastereotopic Me groups, a total of 10 ^{13}C resonances occur for this ligand. Due to diastereotopy of the Me groups a

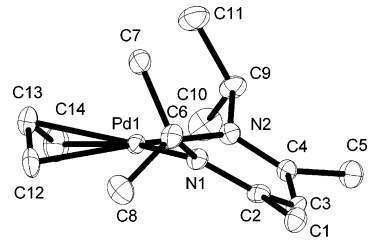


Figure 2. Molecular structure of (η^3-C$_3$H$_5$)Pd(^{i}Pr$_2$-nacnac) (**3a**). Selected bond distances (Å), bond angles (deg), and interplanar angles (deg): Pd1−N1 = 2.088(4), Pd1−N2 = 2.088(4), N1−C2 = 1.323(6), N2−C4 = 1.322(6), C2−C3 = 1.406(5), C3−C4 = 1.415(6), Pd1−C12 = 2.147(5), Pd1−C14 = 2.170(6); N1−Pd1−N2 = 88.9(1); Pd1,N1,N2/N1,N2,C2,C4 = 30(1), N1,N2,C2,C4/C2,C3,C4 = 16(2), Pd1,N1,N2/N1,N2,C6,C9 = 72.

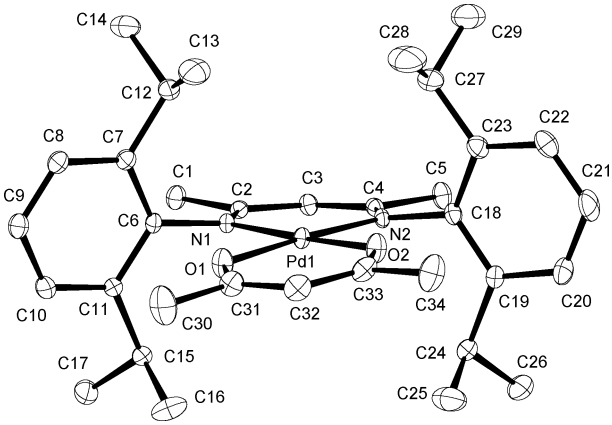


Figure 3. Molecular structure of (acac)Pd(κ^2*N*,*N*-Ar$_2$-nacnac) (**4**). Details of the structure refinement are given in Table 2. Selected bond distances (Å), bond angles (deg), and interplanar angles (deg): Pd1−N1 = 1.993(1), Pd1−N2 = 1.992(1), N1−C2 = 1.326(2), N2−C4 = 1.328(2), C2−C3 = 1.403(2), C3−C4 = 1.398(2), Pd1−O1 = 2.020(1), Pd1−O2 = 2.009(1); O1−Pd1−O2 = 90.51(5), N1−Pd1−N2 = 92.61(5); Pd1,N1,N2,C2,C3,C4/Pd1,O1,O2,C31,C32,C33 = 7(1).

possible rotation of the phenyl substituents about the N−C bond can be excluded. The acac Me groups of **4** give rise to an ^{1}H NMR high-field signal at δ(H) 1.13 (cf. Pd(acac)$_2$ and **1**: δ(H) $\approx$ 2.0), which is also attributed to an anisotropic effect of the adjacent phenyl rings.

When a solution of **4** in pentane or diethyl ether is kept at ambient temperature for 2 h, the complex isomerizes into the thermodynamically more stable **5**. Complex 5 is also obtained directly from Pd(acac)$_2$ and (THF)Li(Ar$_2$-nacnac) by performing the reaction of eq 5 at 20 °C. The crystals of **5** are red like those of **4**, but slightly lighter. Both isomers show very similar melting points (**5**; 229 °C, DSC) and give rise to practically the same EI mass spectra.

In the solution ^{1}H and ^{13}C NMR spectra of **5** all carbon atoms of the acac ligand (5 signals) and Ar$_2$-nacnac ligand (29 signals) are inequivalent, so that the spectra must be attributed to an asymmetric structure with nonrotating C$_6$H$_3$-2,6-^{i}Pr$_2$ substitutents. The central methine group of the nacnac ligand furnishes the resonances δ(H) 2.65 and δ(C) 10.8, which are shifted substantially upfield compared with **4** (δ(H) 4.86 and δ(C) 94.5) and which are in agreement with its carbanionic character. The coordination of this ligand in **5** is reminiscent of that of the κ^1*C*-acac ligand in (κ^2*O*,*O*-acac)Pd(PPh$_3$)(κ^1*C*-acac) (**D**; δ(H) 3.54).[17a,b] Since one of the imine groups is additionally coordinated to Pd, the isomerization of **4** to **5** results in the formation of a chiral center at the coordinated C atom. The spectra rule out a possible exchange of the coordinated and noncoordinated C(Me)═NAr imine moieties.

The results of the X-ray crystal structure analysis of **5** are shown in Figure 4. The Pd ion is coordinated in a square-planar fashion by anionic acac and κ^2*C*,*N*-nacnac ligands. The latter represents a formal azaallyl ligand,[18] in which the electrons are localized in an enyl structure and which coordinates to Pd(II) via the methine carbon and one imine nitrogen atom through σ-type bonds (and not a σ and a π bond), forming an almost planar four-membered chelate ring (plane angle Pd,N1,C3/N1,C2,C3 = 8°). Within the ring the N1−Pd1−C3 angle at 66.5(1)° is the smallest, while the other three angles range from 88.9 to 106.6°. While the Pd1−C3 length at 2.057(2) Å lies in the typical range for Pd−C single bonds (2.00−2.11 Å), it is shorter than in the closely related **D** (2.11 Å)[17a] and derivatives (2.07−2.11 Å).[17c−g] The Pd1−N1 bond at 2.015(2) Å is only slightly longer than in **4** (1.99 Å, mean). For the κ^2*C*,*N*-Ar$_2$-nacnac backbone in **5** the N1−C2 and N2−C4 bonds have the same short bond length of 1.281(3) Å (**4**, 1.33 Å, mean), as expected for an imine, whereas C2−C3 at 1.500(3) Å inside the ring and C3−C4 at 1.478(3) Å outside the ring are in agreement with C(sp^2)−C(sp^3) single bonds (both bonds are significantly longer than in **4**: 1.40 Å, mean). It is worth noting that the Pd1−O1 bond (2.084(2) Å), located trans to Pd1−C3, is significantly longer than Pd1−O2 (2.013(2) Å), located trans to Pd1−N1. The κ^2*C*,*N*-Ar$_2$-nacnac coordination is thus best explained by a strong coordination of the central carbanionic C3

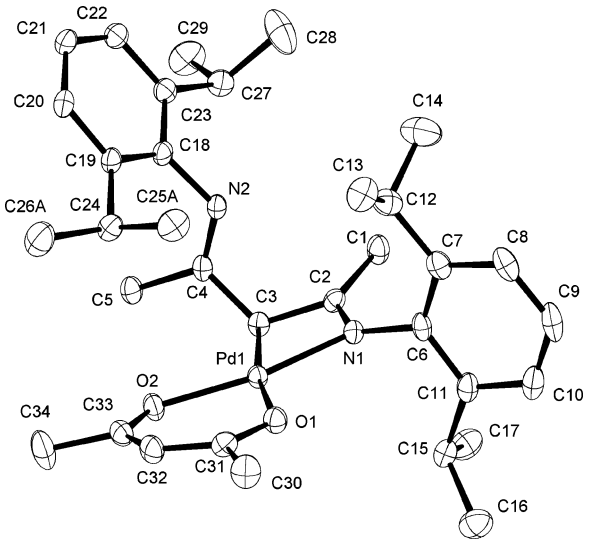
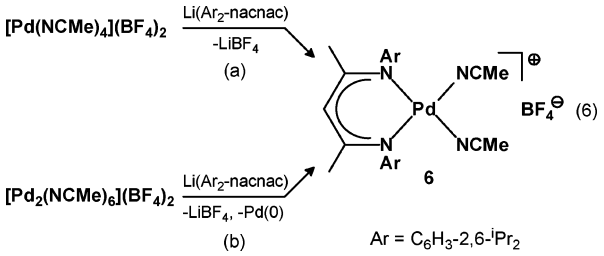


Figure 4. Molecular structure of (acac)Pd(κ^2*C*,*N*-Ar$_2$-nacnac) (**5**). Details of the structure refinement are given in Table 2. Selected bond distances (Å) and angles (deg): Pd1−N1 = 2.015(2), Pd1−C3 = 2.057(2), N1−C2 = 1.281(3), N2−C4 = 1.281(3), C2−C3 = 1.500(3), C3−C4 = 1.478(3), Pd1−O1 = 2.084(2), Pd1−O2 = 2.013(1); O1−Pd1−O2 = 92.64(6), N1−Pd1−C3 = 66.5(1), Pd1−C3−C2 = 88.9(1), C3−C2−N1 = 106.6(2), C2−N1−Pd1 = 97.4(1); Pd1,N1,C3/N1,C2,C3 = 8(2), Pd1,N1,C3/Pd1,O1,O2 = 3(1), Pd1,O1,O2/O1,O2,C31,C32,C33 = 8(2).

at the Pd center in the form of a Pd−C single bond and relatively weak coordination of one imine nitrogen atom to complete the fourfold coordination around the Pd(II) center, with the formation of the four-membered chelate ring. This coordination mode of a nacnac ligand appears to be new, and only two other reports of crystal structures of azaallyl-type (didehydrometallaazetane-type) complexes, one of them involving palladium, are currently listed in the Cambridge Structural Database.[19]

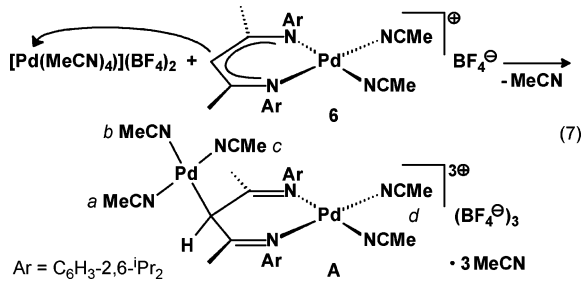
Treating [Pd(MeCN)$_4$](BF$_4$)$_2$ with 1 equiv or an excess of (THF)Li(Ar$_2$-nacnac) in diethyl ether affords the red mixed-ligand complex **6** (eq 6a) and, again, no Pd(Ar$_2$-nacnac)$_2$.



Complex **6** is likewise formed when the Pd(I) complex [Pd$_2$(MeCN)$_6$](BF$_4$)$_2$ is reacted with (THF)Li(Ar$_2$-nacnac) at −78 °C (eq 6b); the reaction also affords Pd black and some ligand dimer (Ar$_2$-nacnac)$_2$.[16] Reaction 6a is remarkable, since it was reported that equal amounts of [Pd(MeCN)$_4$](BF$_4$)$_2$ and Ar$_2$-nacnacH react to give dinuclear **A** (characterized by X-ray) and [Ar$_2$-nacnacH$_2$]BF$_4$, half of the Ar$_2$-nacnacH thereby functioning as a base to neutralize HBF$_4$.[3a] While complex **6** has been inaccessible in that study and **A** has only been isolated as a mixture, we found that **6** prepared by us can be combined with 1 equiv of [Pd(MeCN)$_4$](BF$_4$)$_2$ in acetonitrile to afford the dinuclear **A** in a pure state (eq 7). Obviously, the central methine group of the κ^2*N*,*N*-Ar$_2$-nacnac ligand in **6** has retained sufficient nucleophilicity so that it is able to displace one acetonitrile ligand in [Pd(MeCN)$_4$](BF$_4$)$_2$ and undergo a bridging coordination to another Pd(II) center. The electron distribution of the

(17) (a) Baba, S.; Ogura, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn* **1974**, *47*, 665. Horike, M.; Kai, Y.; Yasuoka, N.; Kasai, N. *J. Organomet. Chem.* **1974**, *72*, 441. (b) Werner, H.; Kraus, H.-J. *Chem. Ber.* **1980**, *113*, 1072. (c) Siedle, A. R.; Pignolet, L. H. *Inorg. Chem.* **1981**, *20*, 1849. (d) Kurokawa, T.; Miki, K.; Tanaka, N.; Kasai, N. *Bull. Chem. Soc. Jpn*. **1982**, *55*, 45. (e) Xu, C.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N.; Rheingold, A. L.; Yap, G. *Inorg. Chem.* **1995**, *34*, 4767. (f) Cheng, J.-K.; Li, Z.-J.; Chen, Y.-B.; Qin, Y.-Y.; Kang, Y.; Wen, Y.-H.; Yao, Y.-G. *Chin. J. Struct. Chem.* **2003**, *22*, 43. (g) Navarro, O.; Marion, N.; Stevens, E. D.; Scott, N. M.; Gonzalez, J.; Amoroso, D.; Bell, A.; Nolan, S. P. *Tetrahedron* **2005**, *61*, 9716.

(18) For a Pd−thiaallyl complex, see: Tamaru, Y.; Kagotani, M.; Yoshida, Z. *J. Org. Chem.* **1979**, *44*, 2816. Miki, K.; Tanaka, N.; Kasai, N. *J. Organomet. Chem.* **1981**, *208*, 407.

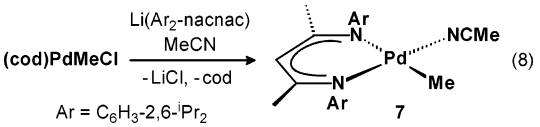


κ^2N,N-nacnac−dienyl system thereby becomes localized in a 2,4-diimin-3-yl structure. While **A** crystallizes from MeCN with three molecules of solute MeCN, it is depleted from the solute MeCN by drying at ambient temperature under vacuum.

The ESIpos mass spectrum of the ionic **6** affords the cascade of ions $[(Ar_2\text{-nacnac})Pd(MeCN)_2]^+$, $[(Ar_2\text{-nacnac})Pd(MeCN)]^+$, and $[(Ar_2\text{-nacnac})Pd]^+$, with the last as the base ion. The spectrum of **A** is very similar to that of **6**. In the ^{13}C NMR spectrum of **6** in CD_2Cl_2 (Table 1) only 10 ^{13}C signals are found for the Ar_2-nacnac ligand, corresponding to C_{2v} symmetry and a planar or fluttering Pd(Ar_2-nacnac) ring having nonrotating C_6H_3-2,6-^{i}Pr$_2$ substituents (as in the case of **4**). The central methine group of the nacnac ligand in **6** (CD_2Cl_2) gives rise to signals at δ(H) 5.11 and δ(C) 96.0 (in CD_3CN: δ(H) 5.25 and δ(C) 96.5).

Having the pure dinuclear **A** in our hands, we reinvestigated its NMR spectra (Table 1). It should be recalled that **A** displays an approximate C_s-symmetrical structure with the $(MeCN)_3Pd$ moiety lying in the symmetry plane.[3a] Thus, there are four different types of MeCN ligands a−d. In fact, for **A**, which has been depleted under vacuum from the solute MeCN, in CD_2Cl_2 solution at ambient temperature three separate MeCN signals a−c at δ(H) 3.04, 2.42, and 2.34 (each 3 H) and δ(C) 4.9, 4.4, and 3.1 are found for the $(MeCN)_3Pd$ moiety and further sharp signals d at δ(H) 1.86 (6 H) and δ(C) 2.8 for the two equivalent MeCN ligands of the diimine−Pd moiety. When the spectrum of **A** containing three MeCN solute molecules is observed, the signals c (originally at δ(H) 2.34 and δ(C) 3.1) are coalesced with the solute signals, and with an increasing concentration of MeCN the signals b and a also coalesce. Eventually, with a larger amount of MeCN only the signal of the free MeCN in rapid exchange with all MeCN ligands a−d is found. The spectra show that (a) the $(MeCN)_3Pd$ moiety with three inequivalent MeCN ligands is nonrotating in solution, (b) each of the three MeCN ligands has an individual rate of exchange with free MeCN, and (c) the exchange rates of ligands a−c are markedly higher than that of d. Feldman et al.[3a] have given ^1H NMR data for the impure **A** in neat CD_3CN. Here, due to the exchange of all acetonitrile ligands with the solvent, merely one signal for uncoordinated MeCN is observed. In addition to C_s symmetry, the ambient-temperature ^1H and ^{13}C spectra of **A** in CD_2Cl_2 and CD_3CN evidence nonrotating C_6H_3-2,6-^{i}Pr$_2$ substituents of the 2,4-diimin-3-yl ligand. The PdCH group of **A** in CD_2Cl_2 furnishes resonances at δ(H) 6.17 and δ(C) 36.0 (CD_3CN: δ(H) 5.45 and δ(C) 37.5), of which, as compared to the corresponding nacnac methine resonances in **6**, the ^{13}C resonance is shifted upfield as expected for an sp^3-C−Pd moiety, but for the ^1H resonance an unexpected deshielding is noted (cf. PdCH of **5**: δ(H) 2.65 and δ(C) 10.8), which is explained by anisotropy exerted here by the 2,4-diimin-3-yl ligand.

While the reaction of (cod)$PdCl_2$ with (THF)Li(Ar_2-nacnac) in pentane or diethyl ether did not yield a defined product (in particular, no Pd(Ar_2-nacnac)$_2$), the reaction of (cod)PdMeCl with (THF)Li(Ar_2-nacnac) in acetonitrile afforded the PdMe complex **7** (eq 8), which represents a parent complex of **C** (see the Introduction).



Complex **7** has C_s symmetry due to its square-planar structure. The "halves" of the Ar_2-nacnac ligand are inequivalent with the planes of the N-C_6H_3-2,6-^{i}Pr$_2$ substituents perpendicular to the coordinate plane, so that a total of 19 ^{13}C signals results for this ligand. The MeCN and PdMe resonances are inconspicuous (Table 1). The exchange of the MeCN ligand with free MeCN is relatively slow and does not affect the symmetry of the complex.

Finally, it is worth emphasizing that, with the exception of the MeCN-ligated complexes, all other isolated Pd−nacnac complexes have only a limited stability in solution at ambient temperature, so that over the course of several hours some Pd black is precipitated. Clearly, the ease with which these complexes undergo degradation with reduction of Pd(II) to Pd(0) poses a major obstacle to a substantial expansion of Pd−nacnac chemistry.

Conclusions

We have reported the synthesis and properties of a series of Pd(II)−nacnac complexes **1**−**7**, containing the ^{i}Pr$_2$-nacnac and Ar_2-nacnac (Ar = C_6H_3-2,6-^{i}Pr$_2$) ligands. While the isolated complexes are quite stable at ambient temperature, the MeCN-free complexes slowly decompose in solution with the formation of elementary palladium, presumably due to an internal redox reaction between Pd(II) and the nacnac ligand. Particularly interesting aspects of this work are (i) the unprecedented isomerization of a κ^2N,N-nacnac ligand into a κ^2C,N-nacnac ligand (**4** → **5**) with the creation of a chiral center, (ii) the high nucleophilicity of the methine carbon in the κ^2N,N-nacnac ligand in **6**, undergoing coordination to another Pd(II) center, and (iii) the anisotropic effect of the C_6H_3-2,6-^{i}Pr$_2$ substituents in the ^1H NMR spectra of **3b** and **4**.

Experimental Section

All manipulations were carried out under argon with Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$. Li(^{i}Pr$_2$-nacnac) was synthesized in a modified literature procedure,[1c,4a] so that a new protocol is given below. (THF)Li(Ar_2-nacnac),[20] $[Pd(MeCN)_4](BF_4)_2$,[21a] $[Pd_2(MeCN)_6](BF_4)_2$,[21b] (cod)$PdCl_2$,[22] (cod)PdMeCl,[23] and $\{(\eta^3\text{-}C_3H_5)PdCl\}_2$[24] were prepared as published. $Pd(acac)_2$ (Aldrich; 99% pure) was commercially available. Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. EI mass spectra were recorded at 70 eV and refer to ^{106}Pd. For the ESI mass spectra an ESQ3000 instrument was used.

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^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra at 75.5 MHz (both relative to TMS) on Bruker AMX-300 and DPX-300 instruments. If not given otherwise, the NMR data of the products are listed in Table 1. DSC spectra at a 5 K min^{-1} heating rate were recorded with the Mettler-Toledo TA8000 thermal analysis system having a DSC820 measuring module.

MeC(N^{i}Pr)CH═C(OH)Me. An equimolar mixture of acetylacetone (100.1 g, 1.00 mol) and isopropylamine (59.1 g, 1.00 mol) in 400 mL of CH_2Cl_2 was kept at ambient temperature for 2 days, whereupon a thin water layer was formed. The organic phase was separated and dried over Na_2SO_4. The product was distilled under vacuum to give a colorless liquid (bp 64 °C at 0.01 mmHg): yield 105 g (74%); $C_8H_{15}NO$ (141.2). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.16 (d, 6H, NCH*Me*$_2$), 1.88 (s, 3H, N═CMe), 1.90 (s, 3H, OCMe), 3.70 (sept, 1H, NCH), 4.86 (s, 1H, ═CH−), 10.75 (s, 1H, OH).

^{i}Pr$_2$-nacnacH. MeC(N^{i}Pr)CH═C(OH)Me (28.24 g, 200 mmol) dissolved in 150 mL of CH_2Cl_2 was treated with 200 mL of a 1 M solution of triethyloxonium tetrafluoroborate (200 mmol) in CH_2Cl_2 at 0 °C. The mixture was stirred at ambient temperature for 30 min, and 2 equiv of isopropyl amine (23.64 g, 400 mmol) in 100 mL of CH_2Cl_2 was added. (Excess ^{i}PrNH$_2$ seems necessary because of the formation of some ^{i}PrNH$_3$BF$_4$.) After 1 h the volatiles were removed under vacuum and the remaining dark brown solid was dissolved in a mixture of 300 mL of water, KOH (11.22 g, 200 mmol), and 200 mL of pentane. The water phase was washed twice with 100 mL of pentane, and the combined organic phase was dried over Na_2SO_4. Vacuum distillation gave a colorless liquid (bp 84 °C at 0.01 mmHg): yield 29.0 g (80%); $C_{11}H_{22}N_2$ (182.3).

Li(^{i}Pr$_2$-nacnac). ^{i}Pr$_2$-nacnacH (9.11 g, 50 mmol) dissolved in 150 mL of pentane was mixed with 20 mL of a 2.5 M solution of ^{t}BuLi (50 mmol) in pentane at −78 °C. The reaction mixture was slowly warmed to ambient temperature and kept overnight. The precipitated colorless Li(^{i}Pr$_2$-nacnac) was separated from the mother liquor, washed with pentane, and dried under vacuum: yield 7.5 g (80%); $C_{11}H_{21}LiN_2$ (188.2).

(acac)Pd(^{i}Pr$_2$-nacnac) (1). A suspension of Pd(acac)$_2$ (304 mg, 1.00 mmol) in 15 mL of diethyl ether was stirred with a solution of Li(^{i}Pr$_2$-nacnac) (188 mg, 1.00 mmol) also in 15 mL of diethyl ether, thereby slowly warming the mixture from −78 to 0 °C (4 h). Insoluble materials were removed by filtration, and the clear red filtrate was concentrated to a volume of about 5 mL. Cooling to −40 °C gave red crystals: yield 110 mg (28%). EI-MS (85 °C): *m*/*e* (%) 386 ([M]$^+$, 53), 371 ([M − CH$_3$]$^+$, 48), 165 (100). ESIpos-MS (CH_2Cl_2): *m*/*e* (%) 387 ([M + H]$^+$, 100). Anal. Calcd for $C_{16}H_{28}N_2O_2Pd$ (386.8): C, 49.68; H, 7.30; N, 7.24; Pd, 27.51. Found: C, 49.54; H, 7.18; N, 7.16; Pd, 27.42.

Pd(^{i}Pr$_2$-nacnac)$_2$ (2). A suspension of Pd(acac)$_2$ (304 mg, 1.00 mmol) in 15 mL of diethyl ether was combined with a solution of Li(^{i}Pr$_2$-nacnac) (376 mg, 2.00 mmol) in 10 mL of ether at −78 °C. The stirred reaction mixture was warmed to ambient temperature overnight. Insoluble materials were removed by filtration, and the clear red filtrate was concentrated to a volume of about 5 mL. Slow cooling of the solution to −40 °C gave light red crystals, which were freed from the mother liquor by means of a capillary, washed with a small volume of cold pentane, and dried under vacuum (25 °C): yield 340 mg (73%); mp 153 °C dec (DSC). EI-MS (75 °C): *m*/*e* (%) 468 ([M]$^+$, 33), 288 ([(^{i}Pr$_2$-nacnac)PdH]$^+$, 100). Anal. Calcd for $C_{22}H_{42}N_4Pd$ (469.0): C, 56.34; H, 9.03; N, 11.95; Pd, 22.69. Found: C, 56.15; H, 8.86; N, 11.87; Pd, 22.58.

(η^3-C$_3$H$_5$)Pd(^{i}Pr$_2$-nacnac) (3a). A suspension of {(η^3-C$_3$H$_5$)Pd(μ-Cl)}$_2$ (364 mg, 1.00 mmol) in 20 mL of pentane was combined with a solution of Li(^{i}Pr$_2$-nacnac) (376 mg, 2.00 mmol) in 15 mL of pentane at −78 °C. The stirred mixture was slowly warmed to 0 °C, and the precipitated LiCl was removed by filtration. After the solution was concentrated under vacuum to a volume of 10 mL, it was slowly cooled to −40 °C to obtain yellow crystals: yield 410 mg (62%); mp 95 °C dec (DSC). Crystals suitable for X-ray analysis were recrystallized from diethyl ether. EI-MS (55 °C): *m*/*e* (%) 328 ([M]$^+$, 44), 285 ([M − ^{i}Pr]$^+$, 41), 165 (100). Anal. Calcd for $C_{14}H_{26}N_2Pd$ (328.8): C, 51.14; H, 7.97; N, 8.52; Pd, 32.37. Found: C, 51.03; H, 8.04; N, 8.46; Pd, 32.54.

(η^3-C$_3$H$_5$)Pd(Ar$_2$-nacnac) (3b). Synthesis was as for **3a**, but {(η^3-C$_3$H$_5$)Pd(μ-Cl)}$_2$ (364 mg, 1.00 mmol) was reacted with (THF)Li(Ar$_2$-nacnac) (993 mg, 2.00 mmol): yellow crystals; yield 800 mg (71%); mp 170 °C dec (DSC). EI-MS (120 °C): *m*/*e* (%) 564 ([M]$^+$, 74), 523 ([Pd(Ar$_2$-nacnac)]$^+$, 100). Anal. Calcd for $C_{32}H_{46}N_2Pd$ (565.2): C, 68.01; H, 8.20; N, 4.96; Pd, 18.83. Found: C, 68.17; H, 8.15; N, 4.82; Pd, 18.69.

(acac)Pd(κ^2*N*,*N*-Ar$_2$-nacnac) (4). A suspension of Pd(acac)$_2$ (304 mg, 1.00 mmol) in 15 mL of pentane was combined with a solution of (THF)Li(Ar$_2$-nacnac) (496 mg, 1.00 mmol) in 15 mL of pentane at −78 °C. The stirred reaction mixture was slowly warmed to 0 °C, at which temperature it was kept for 7 h. Insoluble materials were removed by filtration, and the clear orange filtrate was concentrated under vacuum (0 °C) to a volume of 8 mL. Slow cooling of the solution to −40 °C gave red crystals, which were freed from the mother liquor and dried under vacuum (0 °C): yield 410 mg (66%); mp 227 °C (DSC). EI-MS (120 °C): *m*/*e* (%) 622 ([M]$^+$, 100), 523 ([Pd(Ar$_2$-nacnac)]$^+$, 40). ESIpos-MS (CH_2Cl_2): *m*/*e* (%) 622 ([M]$^+$, 100). Anal. Calcd for $C_{34}H_{48}N_2O_2Pd$ (623.2): C, 65.53; H, 7.76; N, 4.50; Pd, 17.08. Found: C, 64.56; H, 7.77; N, 4.45; Pd, 17.06.

(acac)Pd(κ^2*C*,*N*-Ar$_2$-nacnac) (5). Synthesis and workup were as for **4**, but the reaction mixture was stirred at ambient temperature overnight: red crystals; yield 330 mg (53%); mp 229 °C (DSC). EI-MS (135 °C): *m*/*e* (%) 622 ([M]$^+$, 100), 523 ([Pd(Ar$_2$-nacnac)]$^+$, 64). ESIpos-MS (CH_2Cl_2): *m*/*e* (%) 623 ([M + H]$^+$, 100), 418 ([Ar$_2$-nacnacH]$^+$, 96). Anal. Calcd for $C_{34}H_{48}N_2O_2Pd$ (623.2): C, 65.53; H, 7.76; N, 4.50; Pd, 17.08. Found: C, 64.58; H, 7.78; N, 4.43; Pd, 17.06.

[(Ar$_2$-nacnac)Pd(MeCN)$_2$](BF$_4$) (6). Route a. A solution of [Pd(MeCN)$_4$](BF$_4$)$_2$ (444 mg, 1.00 mmol) in 15 mL of acetonitrile was combined with a solution of (THF)Li(Ar$_2$-nacnac) (496 mg, 1.00 mmol) in an equal volume of acetonitrile at −40 °C. The mixture was stirrred while the temperature was raised to ambient. The resulting burgundy red solution was filtered and concentrated to about 10 mL. Cooling the solution to −40 °C afforded dark red crystals, which were isolated and dried under vacuum (20 °C): yield 510 mg (74%).

Route b. Synthesis was as for route a, but with [Pd$_2$(MeCN)$_6$](BF$_4$)$_2$ (632 mg, 1.00 mmol) as the starting material. After separation of some Pd black by filtration, the concentrated solution was cooled to −40 °C to afford dark red crystals: yield 510 mg (37% referenced to Pd). ESIpos-MS (CH_2Cl_2): *m*/*e* (%) 605 ([(Ar$_2$-nacnac)Pd(MeCN)$_2$]$^+$, 20), 564 ([(Ar$_2$-nacnac)Pd(MeCN)]$^+$, 15), 523 ([Pd(Ar$_2$-nacnac)]$^+$, 100). Anal. Calcd for $C_{33}H_{47}BF_4N_4Pd$ (693.0): C, 57.20; H, 6.84; N, 8.08; B, 1.56; Pd, 15.36. Found: C, 57.08; H, 6.74; N, 7.97; Pd, 15.46. For recording the NMR spectra, the complex was recrystallized from CH_2Cl_2 to eliminate traces of adherent MeCN.

(Ar$_2$-nacnac)PdMe(MeCN) (7). Solutions of (cod)PdMeCl (265 mg, 1.00 mmol) and (THF)Li(Ar$_2$-nacnac) (496 mg, 1.00 mmol), each in 10 mL of acetonitrile, were combined at −20 °C. While the mixture was stirred, the temperature was increased to ambient. The mixture was filtered to remove the precipitated LiCl and concentrated under vacuum to a volume of 10 mL. Cooling the solution to −40 °C afforded brown crystals: yield 440 mg (76%). Anal. Calcd for $C_{32}H_{47}N_3Pd$ (580.2): C, 66.25; H, 8.17; N, 7.24; Pd, 18.34. Found: C, 66.18; H, 8.20; N, 7.20; Pd, 18.27.

[(MeCN)$_3$Pd{μ-CH(C(Me)NAr)$_2$}Pd(MeCN)$_2$](BF$_4$)$_3$ (A). Complexes **6** (693 mg, 1.00 mmol) and [Pd(MeCN)$_4$](BF$_4$)$_2$ (444 mg, 1.00 mmol) were dissolved in 15 mL of acetonitrile at ambient temperature. Cooling the solution to −40 °C gave large yellow

crystals, which contained three molecules of solute MeCN. Drying under vacuum at ambient temperature depleted the product from the solute MeCN: yield 750 mg (68%). Anal. Calcd for $C_{39}H_{56}B_3F_{12}N_7Pd_2$ (1096.2): C, 42.73; H, 5.15; N, 8.49; Pd, 19.42. Found: C, 42.47; H, 5.22; N, 9.01; Pd, 19.40.

Supporting Information Available: CIF files, giving X-ray crystallographic data for **2**, **3a**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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