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Anellated N-Heterocyclic Carbenes: 1,3-Dineopentylnaphtho[2,3-*d*]imidazol-2-ylidene: Synthesis, KOH Addition Product, Transition-Metal Complexes, and Anellation Effects

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Abstract: Two novel anellated N-heterocyclic carbenes (NHC), 1,3-dineopentylnaphtho[2,3-*d*]imidazol-2-ylidene, and 1,3-dineopentyl-2-ylidoimidazolo[4,5-*b*]pyridine were obtained by reduction of the respective thiones with potassium, the former also by deprotonation of the corresponding naphthimidazolium hexafluorophosphate by using excess KH in THF. The use of equimolar amounts of KH provided an unexpected formal addition product of this NHC with KOH. X-ray crystal structure analysis of the adduct provided evidence for a distorted tetrameric N-heterocyclic alkoxide, stabilized by two THF molecules. In C_6D_6 the compound undergoes disproportionation. Transition-metal complexes [(NHC)AgCl], [(NHC)Rh(cod)Cl], and (*E*)-[(NHC)$_2$PdCl$_2$] of the novel naphthimidazol-2-ylidene were synthesized. X-ray crystal structures and ^{1}H and ^{13}C NMR spectroscopic data provided detailed structural information. Comparing characteristic data with those of nonanellated and differently anellated NHCs or their complexes provides information on the influence of the extended anellation.

Keywords: anellation effects · carbenes · palladium · rhodium · silver

Introduction

Arduengo's first synthesis and isolation of stable imidazol-2-ylidene carbenes[1] triggered intensive research on the syntheses, structures, and chemical reactivity of N-heterocyclic diaminocarbenes.[2] This opened the way to a novel direct route to NHC transition-metal complexes and stimulated research on such complexes and their use in homogeneous catalysis.[3,4] In many transition-metal catalysts the air-sensitive phosphine donor ligands can be replaced by NHC ligands. Like phosphines, these stabilize low- and even zero-valent metals and are usually strong σ donors and weak π acceptors, as shown for linear bis(imidazol-2-ylidene) d^{10}-metal complexes by photoelectron spectroscopy[5] and quantum chemical calculations.[5,6] To extend the possibilities of ligand tuning and the scope of NHC-based catalysts, structural variations influencing the donor and acceptor strengths are desirable. One such variation is anellation by aromatic carbo- or heterocycles; this is currently gaining increasing interest.[7–14] Examples are NHCs **1**–**6**. The electron density

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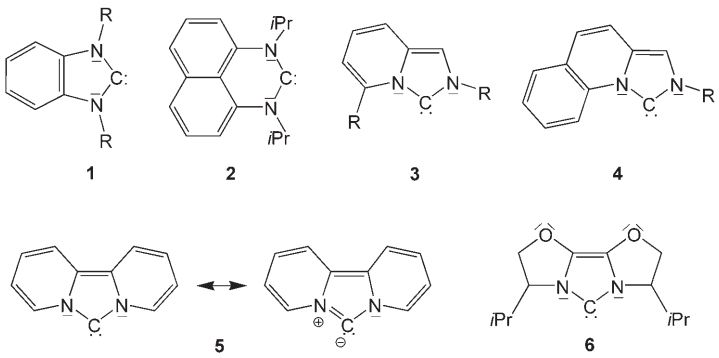
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author and contains figures for the packing of **13a**·H_2O, **14**·2THF·7C_6D_6, **15**, and **16**·CH_2Cl_2 in the crystal.



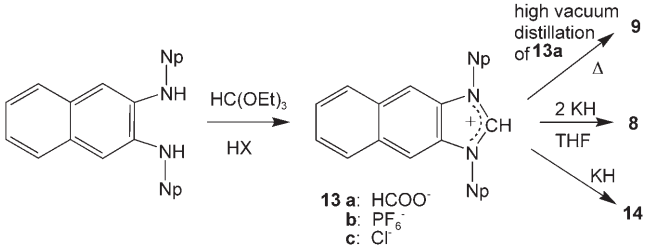
at C^2 varies with the π donor or acceptor properties of the anellated rings, depending on the interplay of the competition with C^2 for π density from the nitrogen lone electron pairs and σ–π-electron repulsion at C^2. Anellation destabilizes NHCs; this was shown by a quantum chemical study revealing easier reduction (less negative reduction potentials) of naphtho-, benzo-, and pyrido-anellated NHCs than of the nonanellated NHC, which is attributed to decreased loss of aromatic stabilization upon electron uptake.[15] Experimentally, this is established by the ready dimerization of nonbulky N-substituted benzimidazol-2-ylidenes[16,17] and the observation of the Wanzlik equilibrium for "frontier-sized" N-substituents,[17,18] while nonanellated imidazol-2-ylidenes are stable even with small substituents.[19] With N-neopentyl substituents, however, the benzimidazol-2-ylidene **1** is stable and even distillable,[7,8] similar to the homologous N-heterocyclic silylene (NHSi),[20] germylene (NHGe),[21] and stannylene (NHSn).[22] Even the related dineopentyl-substituted naphtho-anellated NHGe and NHSn are sufficiently stable to allow vacuum distillation,[23] and pyrido[*b*]-anellated NHSi, NHGe, and NHSn are stable at room temperature, though suffering from partial decomposition during high-vacuum distillation (NHSi > > NHGe > NHSn).[24] The unexpected high stability of these naphtho- and pyrido[*b*]-NHC homologues, along with the expected electron-withdrawing effect on C^2 and tunability of NHC ligands, prompted us to extend our investigations to related anellated N-heterocyclic carbenes.[25]

Results and Discussion

Synthesis of the anellated NHC: The novel anellated N-heterocyclic carbenes were prepared by two routes, the thione reduction[26] and the more widely used deprotonation of suitable precursors.[1,2] Dineopentyl-naphthimidazol-2-thione (**7**) reacts with equimolar amounts of solid potassium in THF at room temperature (16 h) with acceptable selectivity to give the naphthimidazol-2-ylidene **8** in good yield and purity. Only excess potassium or the use of the more reactive KC_8 causes partial reduction to **9** (Scheme 1). Comparative attempts to reduce dineopentyl benzimidazol-2-thione[7,8] and the pyrido[*b*]imidazol-2-thione **10** with solid potassium produced a very slow reaction for the former, which requires sodium potassium alloy or KC_8 to provide **1** (R = Np),[7,8] and less selective reduction of the latter, yielding a mixture of **11**, its reduction product **12**, and unconverted **10**.

The reduction of **7** and **10** was easier than the reduction of benzimidazol-2-thione and correlates with the easier formation of radical anions from naphthalene and pyridine than from benzene,[27] suggesting similar primary steps, while the formation of **12** in the presence of unconverted **10** accounts for a higher reactivity of the pyrido[*b*]- than of the naphtho-anellated NHC towards potassium.

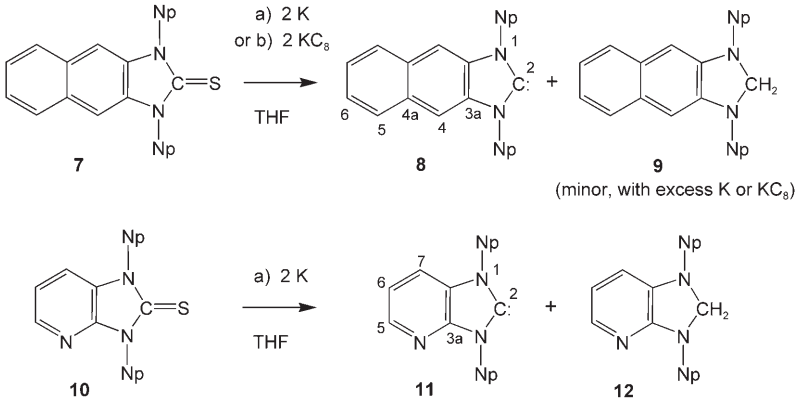
A widely applied, more convenient access to N-heterocyclic carbenes consists of the deprotonation of imidazolium precursors by suitable bases. Dineopentylnaphthimidazolium salts with formate, chloride, and hexafluorphosphate anions **13a–c** are obtained in excellent yields simply by heating *N,N′*-dineopentyl-2,3-diaminonaphthalene in triethyl orthoformate in the presence of a small excess of the corresponding acid or its ammonium salt (Scheme 2). The acidic proton



Scheme 2. Formation and reactions of *N,N′*-dineopentyl-naphthimidazolium salts **13**.

at C^2 appears at low field in the ^{1}H NMR spectrum (δ = 9.15–9.92 ppm) and undergoes slow H/D exchange in D_2O. Further evidence for the high C–H acidity is given by the crystal structure analysis of **13a**·H_2O (Figure 1, Table 1), presenting a C–H···O hydrogen bond to the formate anion with a very short H1···O22 distance of 2.036(16) Å (C···O 2.974(2) Å, < (CHO) 156.8(13)°). Normalization of the C–H bond length to 1.08 Å reduces this H···O distance further (cf. dineopentylbenzimidazolium salts[28]) to 1.96 Å, one of the shortest known C–H···O interactions.[29]

Attempts to remove the volatile, only moderately strong formic acid from **13a** by high vacuum distillation failed to give **8**. Instead, the reduction product **9** distilled in high yield.



Scheme 1. Reduction of **7** and **10** by solid potassium.

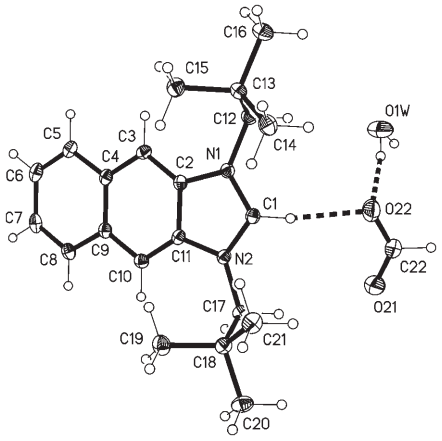


Figure 1. Molecular structure of the formula unit of **13a**·H_2O (ellipsoids with 30 % probability).

This behavior resembles the autoreduction reported recently for *N*,*N*′-dimethyl- and dibutylbenzimidazolium formate.[30]

Deprotonation to pure **8** was achieved by reaction of the hexafluorophosphate **13b** with two equivalents of KH in THF. The excess KH did not attack **8**. Reaction of **13b** with only equimolar amounts of KH in THF furnished **14** (Scheme 3), an unexpected and unusual addition product of **8** and KOH. The oxygen originates from traces of air rather than from KOH impurities in KH as reaction with excess KH gives only **8**. Formation of **14** along with **8** (57:43 mol %) was observed in reactions of **13b** or **13c** with one equivalent of KH in the presence of a small amount of KO*t*Bu. From single crystals, grown from the C_6D_6 solution of this mixture in the NMR tube, we were able to identify the nature of **14**. The high yield of the benzimidazol-2-ylidene **1** (R = Np) in the deprotonation of dineopentyl-benzimidazolium hexafluorophosphate, even with one equivalent

Table 1. Selected bond lengths [Å] and angles [°] of **14**·2THF·7C_6D_6, **13a**·H_2O, **15**, **16**·CH_2Cl_2 and (*E*)-**17**·CH_2Cl_2.

Assignment[a]	**13a**·H_2O[b]	**14**·2THF·7C_6D_6[c]	**15**	**16**·CH_2Cl_2[d]	(*E*)-**17**·CH_2Cl_2[e] (NHC-1, Cl-1)	(NHC-2, Cl-2)
C^2–metal or C^2–O	–	1.342(3)	2.079(3)	2.0206(16)	2.030(4)	2.080(4)
N^1–C^2/ C^2–N^3	1.3323(17), 1.3274(17)	1.497(3), 1.501(3)	1.351(3), 1.355(3)	1.364(2), 1.370(2)	1.364(6), 1.354(6)	1.359(6), 1.358(6)
N^1–C^5/ N^3–C^4	1.4058(17), 1.4043(16)	1.379(3), 1.387(3)	1.403(3), 1.401(3)	1.399(2), 1.403(2)	1.394(6), 1.409(5)	1.405(6), 1.408(6)
C^4–C^5	1.4082(18)	1.438(3)	1.404(4)	1.411(2)	1.415(6)	1.410(6)
N^1–CH_2/ N^3–CH_2'	1.4702(16) 1.4711(16)	1.456(3), 1.459(3)	1.464(3), 1.460(3)	1.461(2), 1.467(2)	1.475(6), 1.474(5)	1.466(6), 1.461(6)
metal–Cl	–	–	2.3178(7)	2.3779(4)	2.3047(13)	2.3267(13)
C^2-metal-Cl	–	–	176.56(7)	94.05(4)	86.40(13), 89.24(13)	93.67(13), 90.72(13)
C^2-Pd-$C^{2'}$	–	–	–	–	176.14(17)	
N^1-C^2-metal/ N^3-C^2-metal or N-C^2-O	–	NCO: 114.48(19), 114.96(18)	127.17(19), 125.09(19)	126.16(12), 127.40(12)	126.6(3), 126.1(3)	126.2(3), 125.3(3)
N^1-C^2-N^3	111.00(12)	98.00(17)	107.1(2)	106.11(13)	106.9(4)	106.9(4)
N^1-C^5-C^4/ N^3-C^4-C^5	106.01(11), 106.37(11)	106.9(2), 107.7(2)	105.7(2), 106.3(2)	106.00(14), 106.08(14)	106.3(4), 105.5(4)	105.8(4), 106.0(4)
C^2-N^1-C^5/ C^2-N^3-C^4	108.28(11), 108.25(11)	109.55(18), 108.66(18)	110.6(2), 110.2(2)	111.06(13), 110.64(13)	110.6(4), 110.6(4)	110.5(4), 110.3(4)
C^2-N^1-CH_2/ C^2-N^3-CH_2'	125.23(12), 125.34(11)	120.71(19), 117.92(18)	124.8(2), 125.1(2)	123.74(14), 123.60(13)	126.4(4), 125.5(4)	125.5(4), 126.5(4)
C^5-N^1-CH_2/ C^4-N^3-CH_2'	126.26(11), 126.26(11)	125.5(2), 123.14(19)	124.5(2), 124.6(2)	125.20(13), 125.04(14)	122.8(4), 123.9(4)	124.0(4), 123.2(4)

[a] Superscript assignment numbers refer to ring numbering (cf. Scheme 1); ring numbering: begin N^1 at N1, in the second NHC ligand of **17** at N3. [b] C–H···O hydrogen bonds see discussion; O_{water}–H1···O21 ($-x$, $2-y$, $-z$) with O–H 0.94(2), H···O 1.95(2) Å, angle 168(2)°; O_{water}–H2···O22 with O–H 0.94(2), H···O 1.90(2) Å, angle 173(2)°. [c] Contains 7C_6D_6; K1–O1 2.6907(17), K1–O1, K1–O1#1 2.6996 (17), K1–O1′#1 2.7054(17); O1-K1-O1#1 93.32(5), O1-K1-O1′#1 89.90(5), O1#1 K1-O1′#1 82.88(5); C1-O1-K1 108.94(13), C1-O1-K2 130.91(13). [d] Rh–C35 2.1055(17), Rh–C36 2.1278(16), Rh–C31 2.2018(17), Rh–C32 2.2387(17). [e] Refers to one of four independent molecules.

of KH in THF (78% after distillation),[28] suggests a higher disposition of **8** to addition reactions. The formation of dimers, which could be favored with small amounts of base (proton catalysis)[31] was not observed, indicating sufficient steric hindrance by the neopentyl substituents.

Structure and properties: The structure elucidation of **8** and **11** and their reduction products **9** and **12** is based on the conclusive full set of ^{1}H and ^{13}C NMR spectroscopic data. The most characteristic features in the NMR spectra of the novel N-heterocyclic carbenes **8** and **11** are the strong downfield shifts of the NCH_2 proton signals ($\Delta\delta_{8-9}(C_6D_6)=$ 1.43 ppm, $\Delta\delta_{11-12}$ ([D_8]THF) = 1.32, 1.17 ppm), attributable to the ring current effect, and the divalent ^{13}C nuclei (**8**: $\delta(C^2)=239.8$, **11**: $\delta(C^2)=234.7$, and **1**: (R = Np) $\delta(C^2)=$ 231.8 ppm[7,8]), arising from the interplay of π-charge density delocalization of the aromatic system into the π orbital of C^2 and repulsion by the lone electron pair. The strong downfield shift of C^2 compared to nonanellated imidazol-2-ylidenes is not regarded as lack of aromaticity (the magnitude of the ring current effect on $\delta(NCH_2)$ is similar), but as a consequence of the extension of the π system, which increases the polarizability and allows stronger π repulsion. An additional influence is the substitution of the β-C atoms by atoms of the anellated rings. The separation of the two effects is difficult. However, the comparison of **8** with the equally N-substituted **1** (R = Np, $\Delta\delta(C^2)=8.0$ ppm), possessing the same structural environment and nearly identical chemical shifts for the β position (C^{3a}) but with a more extended π system, provides evidence that the deshielding of C^2 is partly due to the shift of π density to the anellated rings. The influence of the more extended anellation in **8** is significantly stronger than the electron-withdrawing effect of the nitrogen atom in the pyridine-anellated **11** ($\Delta\delta=$ 2.9 ppm). Finally, it should be noted that the downfield shift of C^2 in the recently published naphtho-anellated pyrimidine-2-ylidene **2** with different architecture but comparable extension of the π system is very similar to that of **8**, even slightly stronger (**2**: $\delta(C^2)=241.7$ ppm).[10] The rather low anellation effect on the divalent carbon in the pyridine[*a*]- and quinoline[*a*]-anellated imidazol-2-ylidenes **3** and **4** ($\delta(C^2)=206.2$–208.7 ppm)[11] and even an upfield shift in the bis(pyridine[*a*])-anellated imidazol-2-ylidene **5** ($\delta(C^2)=$ 196.4 ppm)[12] with one and two bridgehead nitrogen atoms, respectively, can be attributed to a higher weight of polar resonance structures with negatively charged C^2 sites. The upfield shift of the oxazolidine-anellated NHC **6** ($\delta(C^2)=$ 195.8 ppm)[13] as compared to nonanellated aromatic NHC[1,2] reflects the influence of the +M substituents at the 4,5-position on the divalent carbon and marks this compound, like **5**, as an electron-rich NHC. Thus, anellation is a particularly suitable tool for tuning the electronic properties of N-heterocyclic carbenes.

Evidence for the structures of **9** and **12** is based on conclusive NMR spectroscopic data. Apart from the characteristic ^{1}H integral ratio and ^{13}C(DEPT) pattern of the NCH_2N ensemble, the strong shielding of C^4H and deshielding of the carbon nuclei adjacent to nitrogen, in particular the bridging carbon C^{3a}, should be mentioned. This reflects the repulsion of π electrons from C^{3a} to C^4H by the N lone pairs and can be expressed by a polar diimine resonance structure ($-CH{=}C_{bridge}{-}\mathit{N}R{-} \rightleftarrows -\mathit{CH}^{-}{-}C_{bridge}{=}\mathit{N}^{+}R-$). This effect is much smaller for **8** ($\Delta\delta_{9-8}=7.3$ (C^{3a}), −8.3, −5.3 ppm (C^4)) and thus indicates, indirectly, the lower electron density at nitrogen by π delocalization in the NHCs.

Compound **14** was identified by X-ray crystal structure analysis and proved to be a formal addition product of **8** and KOH. In the crystal (**14**·2 THF·7 C_6D_6), four naphthimidazolin-2-yl residues are bound at a $(KO)_4^{4-}$ cubane cluster, stabilized by two THF molecules (Figure 2), and displaying

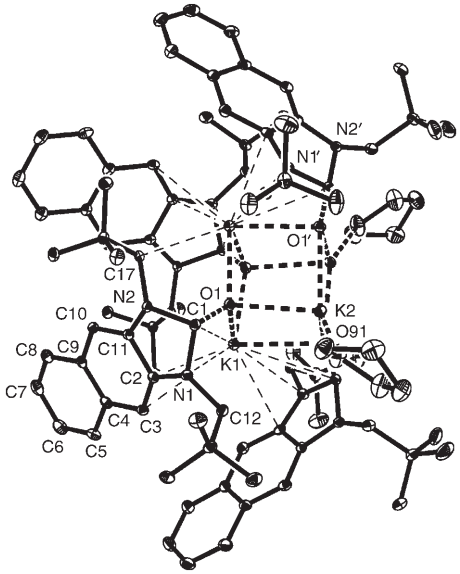
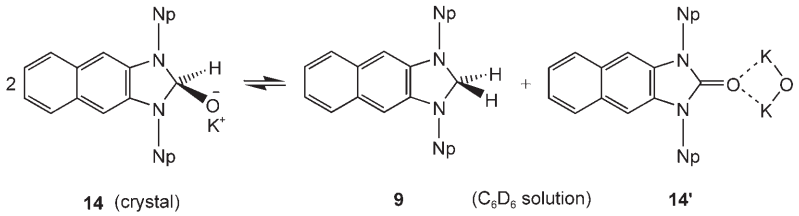


Figure 2. Molecular structure of **14**·2 THF·7 C_6D_6 in the crystal (C_6D_6 molecules and all H atoms are omitted for clarity. Ellipsoids with 30% probability).

crystallographic twofold symmetry. The two independent potassium atoms display quite different coordinations: K2 is simply coordinated by three cubane oxygens (K–O 2.63–2.66 Å) and a THF oxygen (K–O 2.77 Å), whereas K1 appears at first sight to be coordinated only by the three oxygens of the cubane unit (K–O 2.69–2.71 Å). Closer inspection reveals that the coordination of K1 is extended by contacts to various atoms of the imidazoline framework (to C1 3.37, C2 3.13, C3 3.45 Å within the asymmetric unit and to C17 3.32, N1′ 3.09, C1′ 3.32, C2′ 3.19, and C12′ 3.37 Å in the second half of the cubane generated by the twofold axis; these contacts are shown as thin dashed bonds in Figure 2). In both heterocyclic systems, the butyl groups are both directed away from the ring in the same direction, to the opposite side from the coordinating oxygen. There are also 3.5 molecules of C_6D_6 in the asymmetric unit, that is, seven per cubane (all solvent sites are well-ordered; despite the high solvent content, the crystals are reasonably stable and can be manipulated in air under the usual inert oil). This struc-

ture type is novel and distinct from all known structures of (anellated) imidazolium salts or complexes of N-heterocyclic carbenes. 2*H*-Imidazolium salts are planar; coordination to oxoanions XO_n^{m-} occurs via $(sp^2)C-H\cdots O_nX^{m-}$ hydrogen bonds,[2i] similar to those discussed above. The only structurally characterized imidazol-2-ylidene M^IOR complex (M^I = Li, R = mesityl) is also planar, built up from a N_2C-M^I substructure with bridging OR groups.[32] In **14**·2 THF·7 C_6D_6, however, the C1/C1′ atoms are displaced out of the ring plane by 0.42/0.35 Å towards O1 and are distorted tetrahedral (N1-C1-N2 98.00(17), O1-C1-N1 114.48(19), O1-C1-N2 114.96(18)°) with the fourth site occupied by the hydrogen (both these hydrogens were identified in difference syntheses). The fold angle between the N1/N2/C1 plane and the C1–O1 bond is $\Phi = 40°$. A description as a potassium salt of a distorted 2-hydroxynaphthimidazoline would fit best with this distorted tetrahedral coordination. The very long C1–N1/2 bonds (1.497(3), 1.501(3) Å) and the short C1–O bonds (1.342(3) Å) in **14**·2 THF·7 C_6D_6, which are considerably shorter than C–O single bonds in alcohols or alkoxides (MeOH: C–O 1.43 Å; MeOK: C–O 1.40 Å[33]) do not seem to agree well with a simple alcoholate model. However, even more extreme values (C–O 1.288, C–N 1.520, 1.527 Å) were observed in a distantly related complex of sodium.[34] Thus, the long C–N and short C–O bonds in **14**·2 THF·7 C_6D_6 may be seen as consequence of a marked shift of C1 from nitrogen towards oxygen, probably caused by a destabilizing electron repulsion within the cyclic orthoformate diamide, which restricts the existence of this structure to the crystalline state.

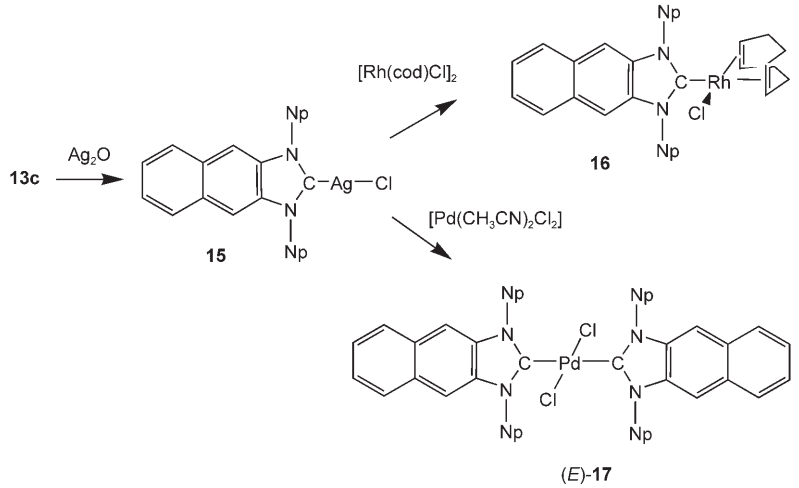
The solution ^1H and ^{13}C NMR spectra of **14** in C_6D_6, both before recrystallization and in solutions of single crystals, display the same two sets of ^1H and ^{13}C NMR data with equal intensity; the data of dihydronaphthimidazole **9** and those of a naphthimidazol-2-ylidene fragment with quaternary C^2, which are, however, different from the data of **8**. A salt of 2-hydroxy-naphthimidazoline can be excluded by the lack of the characteristic ^1H and ^{13}C resonances of the $N_2C(H)O$ group.[35] The aryl proton NMR spectra differ from data observed in *N*,*N*′-dialkyl naphthimidazoline-2-ones[36] or benzimidazoline-2-ones, but the more characteristic ^{13}C NMR spectroscopic data resemble those of benzimidazol-2-ones,[33] except that C^2 and C^{3a} appear at somewhat lower field ($\Delta\delta$ ca. 3.0 ppm). Thus, the spectra indicate disproportionation of **14** to an equimolar mixture of **9** and a complement **14′**, formally **8**·$(OK)_2$; this can be regarded as naphthimidazolin-2-one, which along with THF coordinates K_2O (Scheme 3).



Scheme 3. Disproportionation of **14** in solution (THF omitted).

Transition-metal complexes: Transition-metal complexes of benzimidazol-2-ylidene **1** have been obtained directly from suitable metal precursors and **1**,[7,8,37] while for less bulky N-substituted benzimidazol-2-ylidenes the ligands have been generated in situ from benzimidazolium salts,[38] from the dimers (tetraazafulvalenes),[18a,39] or by template synthesis.[40] Complexes of the above-mentioned anellated N-heterocyclic carbenes **2**, **3**, and **6** have been prepared directly from the carbene[10,11] or by deprotonation of suitable imidazolium salts.[11–13]

Transition-metal complexes of the novel naphtho-anellated ligand **8** were obtained more conveniently by the silver complex route[38b] than by free **8**. The silver chloride complex **15** (Scheme 4), soluble in CH_2Cl_2 and THF and somewhat light-sensitive, was prepared from **13c** and silver oxide in CH_2Cl_2. The silver is easily replaced by other transition metals. Solutions of **15** and $[\{Rh(cod)Cl\}_2]$ in CH_2Cl_2 react cleanly and in high yield to give **16**; **15** and (*E*)-$[Pd(CH_3CN)_2Cl_2]$ provide pure (*E*)-**17** in high yield, while the



Scheme 4. Transition-metal complexes **15**–**17** with **8** as the ligand.

reaction of **15** and [Pd(cod)Cl_2] is less selective and affords a mixture of (*Z*)-**17** and (*E*)-**17** in CH_2Cl_2. Crystals of **16** and **17** are stable to air and moisture for several days at room temperature. In solution, **17** decomposes on prolonged storage.

The novel NHC complexes with ligand **8** were characterized by solution NMR spectroscopy and by crystal structure analysis. The most characteristic proton signal of **15** is that of NCH_2, which is observed at $\delta(CD_2Cl_2)=4.35$ ppm and is significantly downfield from the respective signals of **8** ($\Delta\delta$ ca. 0.30 ppm), but is similar to those of the imidazolium salts **13** and suggests, as documented for nonanellated imidazolium salts,[41] a stronger ring current effect and aromaticity in the complexed than in the free N-heterocyclic carbene ligand. The ^{13}C NMR spectrum displays the signal of the divalent carbon nuclei centered at $\delta=197.5$ ppm as a double doublet with one-bond coupling constants $J(^{13}C,^{107,109}Ag)=$ 233, 269 Hz and thus clearly downfield from that of the analogous benzo-anellated complex (Np_2bimy–AgCl) at $\delta=$ 193.2 ppm, $J(^{13}C,^{107,109}Ag)=235$, 271 Hz)[28]. The splitting resembles that observed for dimesitylimidazol-2-ylidene–AgCl (Mes_2imy–AgCl) which also exists only as a monomer,[42] while dimers consisting of linear $(NHC)_2Ag^+$ cations and AgX_2^- anions (X = Cl, Br)[38b,43] or (NHC–Ag–μX)$_2$-bridging structures[43a] exhibit $^{13}C^2$ singlets due to partial dissociation and monomer–dimer equilibria in solution. Stable ionic $(NHC)_2Ag^+$ complexes show smaller $^{13}C,^{107,109}Ag$ coupling constants (180–190, 200–215 Hz).[38b,44] While the $^{13}C,^{107,109}Ag$ couplings in **15**, Np_2bimy–AgCl and Mes_2imy–AgCl are all similar, the coordination chemical shift $\Delta\delta$ ($\delta_{complex}-\delta_{ligand}$) of $^{13}C^2$ is influenced by the anellation. The shielding by complexation increases from Mes_2imy–AgCl via Np_2bimy–AgCl to **15** ($\Delta\delta=-34.7$, -38.6, -42.4 ppm). This may be attributed to the fall in π-density repulsion on complexation. The repulsion by the orthogonal electron lone pair at C^2 increases with the size of the π system and is particularly strong in **8**; thus the effect of coordination in **15** may be the largest one. An additional effect of back-donation in the C^2–Ag bonds seems possible. DFT calculations showed that π back-bonding interactions contribute approximately 20 or 15–30% to the overall orbital interaction energies, which are approximately 35% of the total bonding energy; this is supported by a comparison of the C^2–N bond lengths (1.345, 1.358, and 1.375 Å) of isostructural Mes_2imy–M complexes with I^+, Ag^+, and Pd^0 (incapable, capable, and very capable of π back-bonding, respectively).[6] For more detailed structural information, the crystal structure of **15** was studied (Figure 3). Complex **15** is planar with linear coordination of silver and shows no Ag···Ag interactions. The packing is determined by other contacts, a pairwise association of two molecules of **15** arranged at a distance of 3.58 Å (vertical distance between ligand ring planes) by means of a center of inversion, with intermolecular silver–carbon contacts Ag···C5 3.43, Ag···C6 3.11, Ag···C7 3.58 Å. The *tert*-butyl ends of the neopentyl groups are turned away from the parallel rings. The dimers are further associated via H···Cl contacts C3-H3···Cl (2.54 Å, 165°, operator $0.5-x$, $-0.5+y$, $0.5-z$) and C17–H17Ag···Cl (2.70 Å, 132°, operator $0.5+x$, $1.5-y$, $0.5+z$). The C^2–Ag and C^2–N bond lengths in **15** (Table 1) are similar to those reported for other NHC–Ag complexes[6,28,38b,42–44] and do not indicate any effect of anellation.

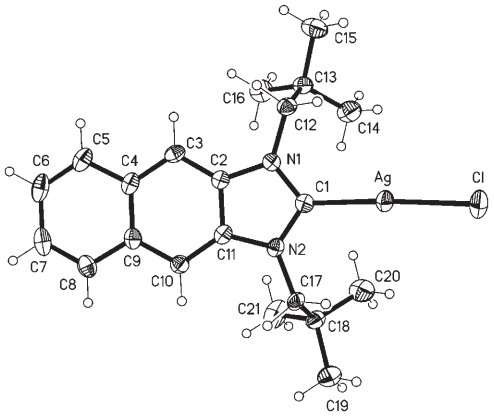


Figure 3. Molecular structure of **15** (ellipsoids with 50% probability).

Rhodium complex **16** also displays the NCH_2 protons downfield from those of the parent ligand ($\delta=4.43$ versus 4.06 ppm) and in the same range as those of the naphthimidazolium salts, but because of the anisotropic influence of the cod ligand, the second NCH_2 signal is shifted even further downfield to $\delta=5.49$ ppm. The divalent ^{13}C nuclei of **16** resonate at $\delta=208.1$ ppm as a doublet with $J(^{13}C,^{103}Rh)=$ 53 Hz, respectively. This is at considerably lower field than Rh(cod)Cl complexes of benzoanellated NHC ($\delta=$ 195–196 ppm)[16a,39b], but upfield from the C^2 resonances of the Rh(cod)Cl complexes of imidazolin-2-ylidene ligands ($\delta=$ 212–213 ppm)[45], of the naphthoanellated pyrimidin-2-ylidene type **2** ($\delta=213.3$ ppm)[10], and of the isoelectronic but more electron-withdrawing quinoxaline-anellated dineopentyl-imidazol-2-ylidene ($\delta=219.5$ ppm)[46]. The shielding by complexation ($\Delta\delta_{\mathbf{16-8}}=-31.7$ ppm) is markedly smaller than for the AgCl complex. A comparison with other anellated and nonanellated NHC–Rh(cod)Cl complexes indicates $\Delta\delta$ values in a small range (-28 to -33.5 ppm)[10,11,45,47] and without clear trends. Similarly, the one-bond coupling constants $^1J(^{13}C,^{103}Rh)$ vary only slightly (50–53 Hz). A small response to the anellation is observed, however, for the downfield C=C signals of the cod ligand. These downfield shifts increase slightly, but in a clear trend with increasing electron-withdrawal by anellation from non- (*c*Hex_2imy–Rh(cod)Cl, $\delta=97.5$ ppm)[47] via benzo- (Et_2bimy–Rh(cod)Cl, $\delta=99.7$ ppm)[39b] to naphtho- (**16**, $\delta=100.4$ ppm) and quinoxaline-anellated imidazol-2-ylidene–Rh(cod)Cl complexes ($\delta=102.5$ ppm).[46] Further information is provided by the crystal structure of **16**·CH_2Cl_2, depicted in Figure 4. Rhodium is coordinated in a slightly distorted square-planar fashion by the centers of the two C=C groups of cod, the chloride and the carbene with its ring plane oriented almost perpendicular (interplanar angle 89°) to the coordination plane. The C=C bond of cod in a *trans*-position to C^2 is significant-

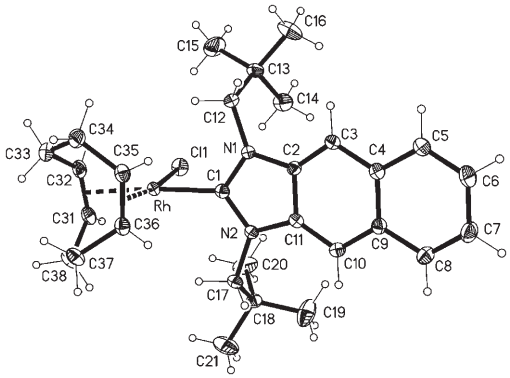


Figure 4. Molecular structure of **16**·CH_2Cl_2 (ellipsoids with 50% probability, solvent omitted).

ly shorter and displays longer Rh–C distances (C31–C32 1.376(3); C31–Rh 2.2018(17), C32–Rh 2.2387(17) Å) than the C=C bond *trans* to chloride (C35–C36 1.406(3); C35–Rh 2.1055(17), C36–Rh 2.1278(16) Å). This indicates a strong *trans*-influence of the anellated NHC ligand and considerably weaker coordinative bond of C=C *trans* to C^2 than *trans* to chloride. The only response to the anellation is a slight elongation of the distances between Rh and the two olefinic carbons *trans* to C^2 and of the double bond itself (*c*Hex_2imy–Rh(cod)Cl 2.175(3), 2.204(2), (C=C 1.353(7) Å *trans* to the carbene, 1.379(7) Å *trans* to chlorine;[47] Et_2bimy–Rh(cod)Cl 2.195(4), 2.228(4), 1.354(6)).[39b] The Rh–C^2 bond length of **16** is almost the same as in the latter carbene complexes and is not affected by the anellation. The molecules of **16**, as observed for **15**, are paired by a center of inversion; the rings C4–C9 and C2–C11 of the inverted molecule might be considered as "stacked", with an intercentroid distance of 3.74, vertical distance of 3.51, and a rather high lateral shift at 1.29 Å. The solvent molecule displays a short C–H···Cl contact to the coordinated chloride within the asymmetric unit, with H···Cl = 2.44 Å, angle = 158°.

The structure and *E* configuration (C1-Pd1-C31 176.14(17)°) of the palladium complex **17** (Figure 5), with

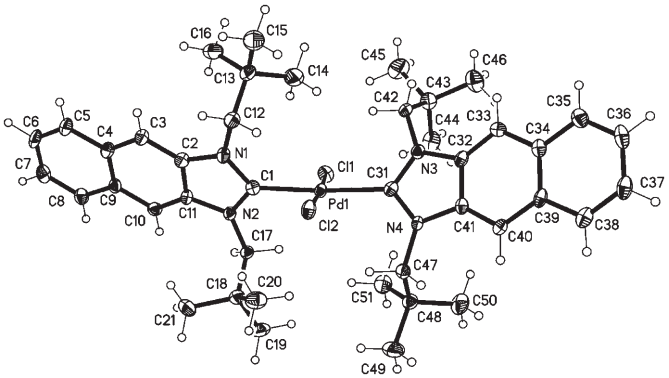


Figure 5. Molecular structure of one of the four independent complex molecules in **17**·CH_2Cl_2 (ellipsoids with 50% probability, solvent omitted).

the expected slightly distorted square-planar coordination sphere was confirmed by X-ray crystal structure analysis. The asymmetric unit contains four independent molecules of **17**, two with inversion symmetry, and three dichloromethane molecules. The angles between the two carbene ligands are 53, 43, 0, and 0° in the four molecules (the latter two by symmetry) and the interplanar angles between the carbene ligands and the coordination planes are 64/65, 62/79, 72, and 90°. The carbene ligands are bent slightly away from the direction of Pd–C, with the angles Pd-C-(midpoint of farthest bond) being 171/169, 176/160, 170, and 167°. For the first time, the butyl groups in one carbene ligand of each the first two molecules point to opposite sides of the ligand plane (pattern +−/++), but not in the third and fourth molecules (pattern ++/−−), which may account for the above-mentioned difference in the interplanar angles. The preference for the *E* configuration of the two NHC ligands, even in the synthesis from $[Pd(cod)Cl_2]$, may be imposed by the steric hindrance exerted by the neopentyl groups. The absence of bulky N-substituents favors the *Z* configuration of $[(NHC)_2PdX_2]$ complexes, shown for example, with dimethylimidazol-2-ylidene and iodide ligands.[48] The presence of two strong NHC donor ligands in the *trans*-position to each other distinguishes **17** from the LAgCl complex **15**, with a weak donor (Cl^-), and the LRh(cod)Cl push–pull complex **16**, with a π acceptor (C=C) ligand *trans* to the NHC ligand. Back-bonding (M→L) seems to be weak, as indicated by the slightly longer Pd–C bonds in **17** and *trans*-L_2PdI_2 with the donor-anellated NHC ligand **6** (2.030(4), 2.080(4); 2.035(3) Å)[13] in comparison to those in *cis*-L_2PdI_2 complexes with benzimidazol- and imidazol-2-ylidene complexes (1.983(5), 1.988(8); 1.990(3), 1.997(3) Å).[39a,48] In the NMR spectra of **17** the rather strong covalent Pd–C bonds in the *trans*-position cause a much stronger deshielding of the NCH_2 proton resonance than observed for the other complexes (**17**, **15**, **16**: $\delta(CD_2Cl_2) = 5.06$, 4.37, 4.43 ppm; **8**: $\delta(C_6D_6) = 4.06$ ppm) and this hints at an increased ring current effect and aromaticity as compared to free **8**. The strong upfield shift of the carbon resonance of $^{13}C^2$ by coordination, much larger in **17** than in **15** and **16** ($\Delta\delta = -51.2$, −42.4, −31.7 ppm), apart from core effects is also attributable to the covalent nature of the Pd–C bond which strongly reduces the repulsion of π electrons as compared to that in NHC ligands, markedly stronger in **17** ($\Delta\delta = -51.2$ ppm) than in the nonanellated *cis*-Me_2imyPdI_2 ($\Delta\delta = -47.0$ ppm).[48]

Conclusion

The synthesis of dineopentyl naphthimidazol-2-ylidene **8** was achieved by the thione reduction and by the imidazolium deprotonation route; the latter is more convenient. While use of small amounts of KH as deprotonation agents leads to preferred formation of a formal NHC–KOH addition product, the NHC is available in high yield by using excess KH in THF at room temperature. Anellation by the

more extended naphthalene π system destabilizes the NHC more than by the benzene π system, as is evident for example, from the thermal decomposition of the former but not of the latter in attempts at high vacuum distillation. The increased transfer of π density from the divalent carbon to the more extended anellated π system is displayed by the clear downfield shift of the $^{13}C^2$ resonance in the naphtho- as compared to the benzoanellated NHC, with nearly equal contributions of the σ skeleton on the carbon chemical shift. The lower stability of the pyrido[*b*]-anellated NHC, evident from the partial reduction of **11** by potassium during the synthesis from the respective thione, is caused more by kinetic reasons. The crystal structure of the NHC–KOH adduct shows a novel coordination mode of NHC towards bases of the type M^I-X-H, formation of a distorted N-heterocyclic alkoxide. The stability of this electron-rich orthoformate diamide is low and causes spontaneous disproportionation in solution. Transition-metal complexes with the extended anellated NHC are much more stable than the free ligands. The π density at C^2, very low in the free ligands due to strong polarization (σ-/π-electron repulsion), is strongly increased in transition-metal complexes with covalent metal−C bonds, indicated by the strong upfield ^{13}C NMR coordination shift.

Experimental Section

General remarks: All reactions were carried out in carefully dried, freshly distilled solvents. Reactions with air- or moisture-sensitive compounds were conducted under an argon atmosphere by using Schlenk techniques. *N,N′*-dineopentyl-2,3-diaminonaphthalene and -pyridine[23,24] were synthesized according to earlier reported procedures, other chemicals were purchased. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Shifts are referenced against TMS for ^1H and ^{13}C NMR spectra and H_3PO_4 (85%) for ^{31}P NMR spectra. Assignment numbers are given in Scheme 1. Coupling constants refer to *J*(H,H) unless stated otherwise. Assignments are based on CH-COSY NMR experiments, proton-coupled (**15**), and DEPT ^{13}C NMR spectra for selected compounds. Melting points (uncorrected) were determined by using a Sanyo Gallenkamp melting point apparatus; elemental analysis by using a CHNS-932 analyzer from LECO under standard conditions.

Thiones

1,3-Dineopentylnaphtho[2,3-*d*]imidazoline-2-thione (7): A solution of thiophosgene (3.0 mL, 39.1 mmol) in THF (20 mL) was added at −70 °C to a solution of *N,N′*-dineopentyl-2,3-diaminonaphthaline (10.0 g, 33.5 mmol) and triethylamine (10.0 mL, 72.1 mmol) in THF. The mixture was allowed to warm to room temperature and stirred overnight, the hydrochloride precipitate was separated, and the solvent was removed under vacuum. The pale-brown residue was determined to be NMR spectroscopically pure **7** (11.2 g, 98%). M.p. 169–171 °C (EtOH); ^1H NMR (C_6D_6): $\delta = 1.03$ (s, 18H; CMe_3), 4.15 (s, 4H; NCH_2), 7.23 (s, 2H; H^4), 7.32 (m, 2H; H^5), 7.73 ppm (m, 2H; H6); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 27.9$ (CMe_3), 34.2 (CMe_3), 53.8 (NCH_2), 104.7 (C^4), 123.4 (C^5), 126.5 (C^6), 128.9 (C^{4a}), 132.9 (C^{3a}), 176.8 ppm (C^2); IR (Nujol): $\tilde{\nu} = 1283$ st, 1212 st, 1194 st, 1150 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 340 (100) $[M]^+$, 307 (93), 283 (29) $[M-t\mathrm{Bu}]^+$, 251 (46), 237 (20), 228 (25), 213 (46), 43 (53); elemental analysis calcd (%) for $C_{21}H_{28}N_2S$ (340.53): C 74.07, H 8.29, N 8.23; found: C 73.73, H 8.15, N 8.12.

1,3-Dineopentyl-2-thioxo-imidazolino[4,5-*b*]pyridine (10): Thiophosgene (0.7 mL, 9.1 mmol) was added at −70 °C to a solution of *N,N′*-dineopentyl-2,3-diaminopyridine (2.25 g, 9.0 mmol) and triethylamine (2.5 mL, 18.0 mmol) in THF. The black mixture was allowed to warm to room temperature and stirred for 8 h. The hydrochloride was separated and washed with ether, the solvents were evaporated, and then the residue was distilled to give pale yellow oily **10** (0.81 g, 31%, b.p. 135 °C (0.01 Torr), which crystallized within few hours. Recrystallization from EtOH afforded colorless crystals. M.p. 90–91 °C; ^1H NMR (C_6D_6): $\delta =$ 0.90 (s, 9H; CMe_3), 1.53 (s, 9H; CMe_3), 3.93 (s, 2H; N^1CH_2), 4.45 (s, 2H; N^3CH_2), 6.50 (dd, $^3J = 5.0$, 7.9 Hz, 1H; H^6), 6.62 (dd, $^3J = 7.9$, $^4J = 1.5$ Hz, 1H; H^7), 8.05 ppm (dd, $^3J = 5.0$, $^4J = 1.5$ Hz, 1H; H^5); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 29.02$, 29.08 (CMe_3), 35.27, 35.54 (CMe_3), 53.80, 55.04 (NCH_2), 116.32 (C^6H), 117.71 (C^7H), 126.71 (C_q^{7a}), 142.34 (C^5H), 146.32 (C_q^{3a}), 174.72 ppm (C_q^2); IR (Nujol): $\tilde{\nu} = 1284$ st, 1251 m, 1197 st, 1177 st, 1152 cm^{-1} st; MS (EI, 70 eV): *m/z* (%): 291 (82) $[M]^+$, 258 (100) $[M-\mathrm{S}-\mathrm{H}]^+$, 234 (13) $[M-t\mathrm{Bu}]^+$, 220 (18), 202 (60) $[M-\mathrm{S}-t\mathrm{Bu}]^+$, 188 (55), 179 (33), 164 (40); elemental analysis calcd (%) for $C_{15}H_{25}N_3S$ (291.46): C 65.94, H 8.65, N 14.42; found: C 65.74, H 8.76, N 14.48.

NHCs by thione reduction: **1,3-Dineopentylnaphtho[2,3-*d*]imidazol-2-ylidene (8)**: A piece of potassium (200 mg, 5.1 mmol) cut in dry hexane was added to a solution of **7** (830 mg, 2.4 mmol) in THF (10 mL). After stirring for 16 h the potassium was consumed. The brown mixture was filtered, the solvent was removed under vacuum, and the residue was extracted with diethyl ether to give 500 mg of a pale-brownish solid **8** (purity = 90% based on ^1H NMR spectroscopic integration, corrected yield = 60%). Attempts at further purification by recrystallization with THF/hexane or toluene/hexane failed. An attempt at high vacuum sublimation caused decomposition. ^1H NMR (C_6D_6): $\delta = 1.02$ (s, 18H; CMe_3), 4.06 (s, 4H; NCH_2), 7.35 (m, 4H; H^5), 7.51 (s, 4H; H^4), 7.84 ppm (m, 4H; H^6); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 29.30$ (CMe_3), 34.67 (CMe_3), 59.59 (NCH_2), 107.32 (C^4H), 125.18 (C^5H), 129.01 (C^6H), 130.30 (C_q^{4a}), 137.21 (C_q^{3a}), 239.85 ppm (C_q^2); elemental analysis calcd (%) for $C_{21}H_{28}N_2$ (308.47): C 81.77, H 9.15, N 9.08; found: C 80.35 (incomplete combustion), H 9.38, N 8.86.

1,3-Dineopentylnaphtho[2,3-*d*]imidazol-2-ylidene (8) and 1,3-dineopentylnaphtho[2,3-*d*]imidazoline (9): A solution of **7** (219 mg, 0.64 mmol) in THF (10 mL) was added to a suspension of KC_8 (349 mg, 2.58 mmol) in THF at 0 °C. The mixture was stirred for 24 h at room temperature and filtered. THF was then evaporated, and C_6D_6 was added to the residue. The solution, separated from dark insoluble material, consisted of **8** and **9** (80 and 20%, respectively, based on the ^1H NMR spectroscopic integration of the NCH_2 signals). Removal of the solvent under vacuum afforded a colorless oil (172 mg). The ^1H and ^{13}C NMR data of **8** and **9** are consistent with those given above (**8**) and below (**9**), respectively.

1,3-Dineopentyl-2-ylido-imidazolo[4,5-*b*]pyridine (11) and 1,3-dineopentyl-imidazolino[4,5-*b*]pyridine (12): A piece of potassium (450 mg, 11.5 mmol) was added to a solution of **10** (1.30 g, 4.5 mmol) in THF (15 mL) at room temperature. The mixture was stirred for 16 h, filtered, and then washed with THF (2×5 mL). Removal of the solvent provided 0.8 g of a brown solid, which contained **11**, **12**, and **10** (ca. 40, 25, and 35%, respectively, based on the ^1H NMR integration of the NCH_2 signals). Attempts at further purification by recrystallization with THF/hexane or toluene/hexane caused partial decomposition, whereas an attempt at high vacuum sublimation caused complete decomposition.

*Compound **11***: ^1H NMR ([D_8]THF): $\delta = 1.00$ (s, 9H; CMe_3), 1.01 (s, 9H; CMe_3), 4.07 (s, 2H; N^1CH_2), 4.23 (s, 2H; N^3CH_2), 7.06 (dd, $^3J = 4.7$, 7.9 Hz, 1H; H^6), 7.74 (d, $^3J = 7.9$ Hz, 1H; H^7), 8.16 ppm (d, $^3J = 4.7$ Hz, 1H; H^5); $^{13}C\{^1H\}$ NMR ([D_8]THF): $\delta = 28.51$ (br, 2CMe_3), 33.93, 34.31 (CMe_3), 56.69 (N^1CH_2), 59.63 (N^3CH_2), 116.65, 118.16 (C^6H, C^7H), 128.24 (C_q^{7a}), 142.05 (C^5H), 149.18 (C_q^{3a}), 234.71 ppm (C_q^2).

*Compound **12***: ^1H NMR ([D_8]THF): $\delta = 0.97$ (br s, 18H; 2CMe_3), 2.77 (s, 2H; N^1CH_2), 3.06 (s, 2H; N^3CH_2), 4.89 (s, 2H; NCH_2N), 6.81 (t, $^3J \approx 5$ Hz, 1H; H^6), 6.25 (dd, $^3J \approx 5$, $^4J \approx 2$ Hz, 1H; H^7), 7.19 ppm (dd, $^3J \approx 4.5$, $^4J \approx 2$ Hz, 1H; H^5); $^{13}C\{^1H\}$ NMR ([D_8]THF): $\delta = 28.02$, 28.34 (CMe_3), 33.93, 34.38 (CMe_3), 59.17 (N^1CH_2), 63.86 (N^3CH_2), 80.02 (NCH_2N), 113.22, 107.04 (C^6H, C^7H), 136.19 (C^5H), 137.11 (C_q^{7a}), 156.03 ppm (C_q^{3a}).

Naphthimidazolium salts: **1,3-dineopentylnaphtho[2,3-*d*]imidazolium formate solvates (13a·4HCOOH, 13a·HCOOH, 13a·H_2O)**: Formic acid (64 μL, 85% in water, 1.42 mmol) was added to a solution of *N,N′*-dineopentyl-2,3-diaminonaphthalene (500 mg, 1.675 mmol) in triethyl orthoformate (15 mL), and the resulting solution was heated at 80°C for 15 h. After cooling to room temperature, hexane (10 mL) was overlayered. The crystals thus formed were separated. The crystal fraction used for elemental analysis is consistent with a composition **13a**·4HCOOH. The main portion was washed with hexane and dried in high vacuum to give crystals of **13a**·HCOOH (559 mg, 75%, m.p. 178–179°C). The composition of **13a**·HCOOH is in accordance with the ^{1}H NMR integration. Single crystals grown from the residual mother liquor proved to be **13a**·H_2O (selected bond lengths and angles Table 1, crystal data in Table 2). ^{1}H NMR (D_2O, THF): $\delta = 0.87$ (s, 18H; CMe_3), 4.14 (s, 4H; NCH_2), 7.42 (m, 2H; 5-H), 7.82 (m, 2H; H^6), 7.99 (s, 2H; H^4), 8.31 (s, 2H; $HCOO^-$), 9.34 ppm (s, 0.8H/0.2D; H^2); ^{13}C{^{1}H} NMR (D_2O): $\delta =$ 26.85 (CMe_3), 33.06 (CMe_3), 57.86 (NCH_2), 111.28 (C^4), 126.89 (C^5), 128.10 (C^6), 130.72, 130. 87 (C^{3a}, C^{4a}), 146.09 (C^2), 169.49 ppm (C=O); MS (EI, 70 eV, $T = 310$°C): *m/z* (%): 311 (16), 310 (85) $[M-2\,HCOOH]^+$, 308.8 (100) $[M-1]^+$, 253 (55), 195 (25), 183 (41), 182 (26), 181 (36), 169 (46), 168 (42); elemental analysis calcd (%) for **13a**·4HCOOH, $C_{26}H_{38}N_2O_{10}$ (538.60): C 57.98, H 7.11, N 5.20; found C 57.47, H 7.11, N 5.58.

1,3-Dineopentylnaphtho[2,3-*d*]imidazolium hexafluorophosphate (13b): *N,N′*-Dineopentyl-2,3-diaminonaphthalene (555 mg, 1.86 mmol), NH_4PF_6 (303 mg, 1.86 mmol), and triethyl orthoformate (10 mL) were heated to 130°C for 6 h in a rectification apparatus. Ethanol separates from the reaction mixture. After cooling to room temperature, a solid precipitated, which was washed with hexane (3×10 mL). Then the product was extracted with CH_3CN to give colorless crystals of **13b** (799 mg, 95%). M.p. >300°C; ^{1}H NMR ([D_6]DMSO): $\delta = 1.07$ (s, 18H; CMe_3), 4.48 (s, 4H; NCH_2), 7.66 (m, 2H; H^5), 8.19 (m, 2H; H^6), 8.75 (s, 2H; H^4), 9.92 ppm (s, 1H; H^2); ^{13}C{^{1}H} NMR ([D_6]DMSO): $\delta = 27.07$ (CMe_3), 33.24 (CMe_3), 56.99 (NCH_2), 111.87 (C^4), 126.55 (C^5), 128.18 (C^6), 130.84, 131.24 (C^{3a}, C^{4a}), 147.57 ppm (C^2); elemental analysis calcd (%) for $C_{21}H_{29}F_6N_2P$ (454.49): C 55.50, H 6.43, N 6.16; found: C 55.73, H 6.81, N 6.23.

1,3-Dineopentylnaphtho[2,3-*d*]imidazolium chloride (13c): Ethereal HCl (13.4 mL, 0.5 M, 6.70 mmol) was added to a solution of *N,N′*-dineopentyl-2,3-diaminonaphthalene (2.0 g, 6.70 mmol) in triethyl orthoformate (15 mL), and the resulting solution was heated at 90°C for 15 h. Hexane (10 mL) was then added at room temperature and the precipitate was separated and washed with hexane. Drying under vacuum provided NMR-spectroscopically pure off-white crystals of **13c** (2.2 g, 95%). M.p. >300°C; ^{1}H NMR (CD_3OD): $\delta = 1.15$ (s, 18H; CMe_3), 4.53 (s, 4H; NCH_2), 7.65 (m, 2H; H^5), 8.20 (m, 2H; H^6), 8.60 (s, 2H; H^4), 9.85 ppm (s, ca. 0.6H; H/D exchange; H^2); ^{13}C{^{1}H} NMR (CD_3OD): $\delta = 27.92$ (CMe_3), 34.58 (CMe_3), 58.94 (NCH_2), 112.87, (C^4), 128.07 (C^5), 129.46 (C^6), 132.66, 133.04 (C^{3a}, C^{4a}), 148.06 ppm (t, ^1J(C,D) = 33.8 Hz; C^2H and C^2D); MS (EI, 70 eV, $T = 290$°C): *m/z* (%): 310 (38) $[M-Cl]^+$, 309 (58)

Table 2. Crystal data and structure refinement of **13a**·H_2O and **14**·2THF·7C_6D_6.

	13a·H_2O	**14**·2THF·7C_6D_6
empirical formula	$C_{22}H_{32}N_2O_3$	$C_{134}H_{132}D_{42}K_4N_8O_6$
formula weight	372.50	2191.47
T [K]	133(2)	133(2)
λ [Å]	0.71073	0.71073
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2/n$
unit cell dimensions		
a [Å]	9.1498(12)	14.750(2)
b [Å]	9.4919(12)	15.781(2)
c [Å]	12.735(2)	26.583(4)
α [°]	93.696(4)	90
β [°]	108.849(4)	98.323(5)
γ [°]	90.496(6)	90
V [Å^3]	1044.1(3)	6122.8(15)
Z	2	2
ρ_{calcd} [Mg m^{-3}]	1.185	1.189
μ [mm^{-1}]	0.078	0.203
F(000)	404	2316
crystal size [mm^3]	0.23×0.22×0.16	0.30×0.25×0.22
θ range for data collection [°]	1.69–28.28	1.29–28.28
index ranges		
	$-12 \le h \le 11$	$-19 \le h \le 19$
	$-12 \le k \le 12$	$-21 \le k \le 20$
	$-16 \le l \le 16$	$-35 \le l \le 35$
reflections collected	10828	61771
independent reflections	5155 [$R_{int} = 0.0358$]	15206 [$R_{int} = 0.0860$]
completeness to θ	(28.25°) 99.3%	(28.25°) 100.0%
absorption correction	none	none
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	5155/1/256	15206/0/697
goodness-of-fit on F^2	1.022	1.054
final R indices [$I > 2\sigma(I)$]		
$R1$	0.0461	0.0663
$wR2$	0.1055	0.1402
R indices (all data)		
$R1$	0.0766	0.1193
$wR2$	0.1154	0.1556
absolute structure parameter	–	–
largest diff. peak and hole [e Å^{-3}]	0.282 and −0.202	0.610 and −0.355

$[M-1]^+$, 308 (26), 307 (20), 253 (32), 252 (41), 251 (19), 195 (60), 181 (47); elemental analysis calcd (%) for $C_{21}H_{29}N_2Cl$ (344.93): Cl 10.28; found: Cl 10.60. Carbon analyses were not satisfactory; however, conversion to analytically pure **13d** by treatment with $AgBF_4$ confirmed the composition.

1,3-Dineopentylnaphtho[2,3-*d*]imidazolium tetrafluoroborate (13d): $AgBF_4$ (280 mg, 1.438 mmol) was added to a solution of **13c** (496 mg, 1.438 mmol) in 15 mL CH_3CN. The suspension was stirred in the dark for 24 h at ambient temperature and filtered. The solvent was then removed under vacuum to give colorless crystals of **13d** (520 mg, 91%). M.p. 300°C; ^{1}H NMR (CD_3CN): $\delta=1.10$ (s, 18H; CMe_3), 4.39 (s, 4H; NCH_2), 7.65 (m, 2H; H^5), 8.16 (m, 2H; H^6), 8.46 (s, 2H; H^4), 9.15 ppm (s, ≈0.6H; H/D exchange; H^2); $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta=27.58$ (CMe_3), 34.23 (CMe_3), 58.70 (NCH_2), 112.49 (C^4), 127.93 (C^5), 129.17 (C^6), 132.41, 132.59 (C^{3a}, C^{4a}), 147.19 ppm (C^2H); MS (EI, 70 eV, $T=200$°C): *m*/*z* (%): 310 (24) $[M-BF_4]^+$, 309 (52) $[M-1]^+$, 308 (29), 252 (56), 195 (100), 183 (14), 182 (26), 168 (24); elemental analysis calcd (%) for $C_{21}H_{29}BF_4N_2$ (396.28): C 63.65, H 7.38, N 7.07; found: C 63.55, H 7.54, N 7.06.

Deprotonation experiments

High vacuum thermolysis of 13a·2HCOOH to 1,3-dineopentylnaphtho-[2,3-*d*]imidazoline (9): Thermolytic distillation of **13a**·2HCOOH (286 mg 0.65 mmol) at 170°C (bath)/10^{-5} bar afforded NMR-spectroscopically pure **9** (140 mg, 71%). ^{1}H NMR (C_6D_6): $\delta=0.88$ (s, 18H, CH_3), 2.63 (s, 4H, NCH_2), 4.60 (s, 2H, H^2), 6.60 (s, 2H, H^5), 7.28 (m, 2H, H^4), 7.68 ppm (m, 2H, H^4); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=27.98$ (CMe_3), 29.80 (CMe_3), 62.64 (NCH_2), 81.38 (C^2H_2), 99.05 (C^4H), 122.75 (C^5H), 126.00 (C^6H), 130.96 (C_q^{4a}), 144.57 ppm (C_q^{3a}); MS (%) for $C_{21}H_{30}N_2$ (310.48): MS (EI, 70 eV, $T=240$°C): *m*/*z* (%): 310 (11) $[M]^+$.

Deprotonation by KH or KH in the presence of catalytic amounts (5 mol%) of KO*t*Bu: A suspension of **13b** or **13c** in THF was added at −78°C to a suspension of 30% KH in mineral oil, washed beforehand with THF. The mixture was allowed to warm to room temperature and was then stirred overnight. After filtration the solvent was removed under vacuum, the residue was extracted with diethyl ether and the ether evaporated (separation from salts soluble in THF). The residue was extracted with C_6D_6. The ^{1}H and ^{13}C NMR spectra indicate formation of **8** and/or **14**. The ratios of **8** and **14** given below refer to the integration of the characteristic NCH_2 proton signals.

a) Compound **13b** (298 mg, 0.66 mmol) and KH (175 mg, 30%, 1.31 mmol) provided **8** (>95%); **14** was not detected.
b) Compound **13b** (415 mg, 0.91 mmol), KH (122 mg, 30%, 0.91 mmol), and KO*t*Bu (5 mg) provided a mixture of **8** and **14** (molar ratio 57:43%). Single crystals of **14**·2THF·7C_6D_6 (estimated ca. 50 mg) deposited from this solution. Separated single crystals, redissolved in C_6D_6, reveal two sets of signals with equal intensity, those of **9** and the complementary naphthimidazol-2-on M^I_2O complex **14′**.
c) Compound **13b** (1.03 g, 2.27 mmol) and KH (304 mg, 30%, 2.27 mmol) provided **14** (>90%); **8** was not detected.
d) Compound **13c** (210 mg, 0.61 mmol) and KH (270 mg, 30%, 2.02 mmol) provided a mixture of **8** and **14** (molar ratio 70:30%).

The ^{1}H and ^{13}C NMR spectroscopic data for **8** and **9** correspond to those given above.

*Compound **14′***: ^{1}H NMR (C_6D_6): $\delta=0.96$ (s, 18H; CH_3), 3.51 (s, 4H; NCH_2), 7.08 (s, 2H; H^4), 7.32 (m, 2H; H^5), 7.73 ppm (m, 2H; H^6); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=29.22$ (CMe_3), 35.41 (CMe_3), 53.57 (NCH_2), 104.86 (C^4H), 124.78 (C^5H), 128.13 (C^6H), 130.77 (C_q^{4a}), 133.34 (C_q^{3a}), 157.54 ppm (C_q^2); for crystal data of **14**·2THF·7C_6D_6 see Table 2; for selected bond lengths and angles see Table 1.

Transition-metal complexes

(1,3-Dineopentylnaphtho[2,3-*d*]imidazol-2-ylidene)silver chloride (15): Ag_2O (537 mg, 2.32 mmol) was added to a solution of **15c** (800 mg, 2.32 mmol) in CH_2Cl_2 (15 mL). The suspension was stirred for 24 h at ambient temperature and filtered. The solvent of the filtrate was partly removed under vacuum (to 5 mL), and hexane (10 mL) was added. The white precipitate was filtered and recrystallized from CH_2Cl_2 to give colorless crystals of **15** (900 mg, 86%). M.p. >300°C; ^{1}H NMR (CH-COSY, CD_2Cl_2): $\delta=1.16$ (s, 18H; CMe_3), 4.37 (s, 4H; NCH_2), 7.53 (m, 2H; H^5), 7.95 (s, 2H; H^4), 8.02 ppm (m, 2H; H^6); $^{13}C\{^1H\}$ NMR (CH-COSY, CD_2Cl_2): $\delta=29.27$ (CMe_3), 34.47 (CMe_3), 60.73 (NCH_2), 109.60 (C^4), 126.03 (C^5), 128.35 (C^6), 130.31 (C^{4a}), 134.63 (d, $^3J(^{13}C,^{107,109}Ag)\approx7.6$ Hz, C^{3a}), 197.53 ppm (2d, $^1J(^{13}C,^{107,109}Ag)=233.1$, 269.1 Hz, C^2); MS (EI, 70 eV, $T=345$°C): *m*/*z* (%): 452 (3), 450 (3) $[M]^+$, 418 (6), 416 (7), 417 (11), 415 (10) $[M-Cl]^+$, 308 (70) $[M-AgCl]^+$, 307 (47), 252 (100), 195 (94), 181 (57); elemental analysis calcd (%) for $C_{21}H_{28}N_2AgCl$ (451.77): C 55.83, H 6.25, N 6.20; found: C 52.34 (incomplete combustion), H 6.62, N 6.11; for crystal data of **15** see Table 3; for selected bond lengths and angles see Table 1.

(1,3-Dineopentylnaphtho[2,3-*d*]imidazol-2-ylidene)rhodium(1,5-cyclooctadiene) chloride (16): $[\{Rh(cod)Cl\}_2]$ (114.5 mg, 0.232 mmol) was added to a solution of silver complex **15** (210 mg, 0.465 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature in the dark to form a suspension, which after filtration gave a clear yellow solution. The solvent was partly removed, and the saturated solution stored overnight at −20°C to yield yellow single crystals of pure **16** (122 mg, 95%). ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta=1.28$ (s, 18H; CMe_3), 1.88–2.02 (m, 4H; CH_2), 2.44 (m, 4H; CH_2), 2.85 (brs, 2H; =CH), 4.43 (d, ^4J(H,Rh)= 13.8 Hz, 2H; NCH_2), 5.16 (brs, 2H, =CH), 5.49 (d, ^4J(H,Rh)=13.8 Hz, 2H; NCH_2), 7.47 (m, 2H; H^5), 7.77 (s, 2H; H^4), 7.94 ppm (m, 2H, H^6); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta=29.41$ (CH_2), 30.43 (satellite d, $J=19$ Hz, CMe_3), 33.30 (CH_2), 34.24 (CMe_3), 60.54 (NCH_2), 70.63 (d, J(Rh,C)= 13.6 Hz, =CH), 100.41 (d, J(Rh,C)=6.0 Hz, =CH), 107.83 (C^4H), 125.61 (C^5H), 128.34 (C^6H), 129.52 (C_q^{4a}), 136.31 (C_q^{3a}), 208.14 ppm (d, ^1J-(Rh,C)=52.8 Hz, C_q^2); MS (EI, 70 eV, $T=345$°C): *m*/*z* (%): 555 (1) $[M]^+$, 554 (1), 553 (3), 411 (27), 410 (100) $[M-cod-Cl]^+$, 408 (14), 405 (25), 403 (15), 394 (12), 390 (11), 51 (12); elemental analysis calcd (%) for $C_{29}H_{40}ClN_2Rh$ (555.01): C 62.76, H 7.26, N 5.05; found: C 61.28 (incomplete combustion), H 7.12, N 5.17; for crystal data of **16**·CH_2Cl_2 see Table 3, for selected bond lengths and angles see Table 1.

(*E*)-Bis-(1,3-dineopentylnaphtho[2,3-*d*]imidazol-2-ylidene)palladium chloride (17)

a) $[Pd(CH_3CN)_2Cl_2]$ (56.2 mg, 0.217 mmol) was added to a solution of the silver complex **15** (196 mg, 0.434 mmol) in CH_2Cl_2 (10 mL). Workup conducted as described for **16** produced yellow crystals of pure (*E*)-**17** (159 mg, 92%). ^{1}H NMR ($CDCl_3$, CD_2Cl_2): $\delta=1.34$ (s, 36H; CMe_3), 5.06 (brs, 8H; NCH_2), 7.47 (m, 4H; H^5), 7.89 (s, 4H; H^4), 7.95 ppm (m, 4H; H^6); $^{13}C\{^1H\}$ NMR ($CDCl_3$, CD_2Cl_2): $\delta=29.93$ (satellite d, $J=18.7$ Hz, CMe_3), 34.42 (CMe_3), 59.14 (NCH_2), 108.72 (C^4), 125.14 (C^5), 127.88 (C^6), 129.15 (C_q^{4a}), 135.09 (C_q^{3a}), 188.70 ppm (s, C^2); elemental analysis calcd (%) for $C_{42}H_{56}Cl_2N_4Pd$ (794.24): C 63.52, H 7.11, N 7.05; found: C 63.65, H 7.32, N 7.34.
b) $[Pd(cod)_2Cl_2]$ (45.2 mg, 0.158 mmol) was added to a solution of the silver complex **15** (127.2 mg, 0.282 mmol) in CH_2Cl_2 (10 mL). Workup conducted as above produced crystals, which were determined by NMR spectroscopy to be an *E*/*Z* mixture (95 mg, 76%). Single crystals grown by using CH_2Cl_2 overlayered with hexane at −20°C were (*E*)-**17**; for crystal data see Table 3, for selected bond lengths and angles see Table 1.

Crystal structure analysis

Data collection: Data were recorded at low temperature on a Bruker SMART 1000 CCD diffractometer using monochromated $Mo_{K\alpha}$ radiation, and where necessary corrected for absorption (program SADABS).

Structure refinement: The structures were refined anisotropically on F^2 by using the program SHELXL-97.[49] Hydrogen atoms were refined by using rigid methyl groups or a riding model.

Special details and exceptions: The following hydrogens were refined freely: **13a**·H_2O, water H (with distance restraints) and acidic CH; **16**, hydrogens at coordinated double bonds (with distance restraints). For the large structure **17** (1401 parameters), components of light atom *U* values were restrained by using the command DELU and methyl groups were refined by using a riding model starting from ideally staggered positions.

Table 3. Crystal data and structure refinement of **15**, **16**·CH_2Cl_2, and (*E*)-**17**·CH_2Cl_2.

	15	**16**·CH_2Cl_2	(*E*)-**17**·CH_2Cl_2
empirical formula	$C_{21}H_{28}AgClN_2$	$C_{30}H_{42}Cl_3N_2Rh$	$C_{43}H_{58}Cl_4N_4Pd$
formula weight	451.77	639.92	879.17
T [K]	133(2)	133(2)	133(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
unit cell dimensions			
a [Å]	10.2949(11)	11.7856(8)	15.3418(11)
b [Å]	16.7807(16)	17.6094(12)	16.2426(11)
c [Å]	12.5650(12)	14.3141(11)	31.233(2)
α [°]	90	90	85.905(4)
β [°]	103.561(4)	96.845(4)	82.543(4)
γ [°]	90	90	62.911(4)
V [Å^3]	2110.2(4)	2949.5(4)	6869.9(8)
Z	4	4	6
ρ_{calcd} [Mg m^{-3}]	1.422	1.441	1.275
μ [mm^{-1}]	1.087	0.873	0.673
F(000)	928	1328	2748
crystal size [mm^3]	0.16×0.14×0.04	0.40×0.25×0.12	0.30×0.23×0.09
θ range for data collection [°]	2.06–28.28	1.84–30.51	1.32–28.28
index ranges			
	$13 \le h \le 13$	$-16 \le h \le 16$	$-20 \le h \le 20$
	$-22 \le k \le 22$	$-25 \le k \le 25$	$-21 \le k \le 21$
	$-16 \le l \le 16$	$-20 \le l \le 20$	$-41 \le l \le 41$
reflections collected	29636	63538	140487
independent reflections	5231 [R_{int} = 0.0643]	9002 [R_{int} = 0.0370]	33999 [R_{int} = 0.0784]
completeness to θ	(28.25°) 100.0 %	(30.00°) 100.0 %	(28.25°) 99.7 %
absorption correction		semiempirical from equivalents	
max. and min. transmission	0.962 and 0.889	0.9025 and 0.7576	0.942 and 0.746
refinement method		full-matrix least-squares on F^2	
data/restraints/parameters	5231/0/232	9002/6/347	33999/387/1401
goodness-of-fit on F^2	0.890	1.082	1.051
final R indices [$I > 2\sigma(I)$]			
$R1$	0.0318	0.0275	0.0578
$wR2$	0.0563	0.0621	0.1487
R indices (all data)			
$R1$	0.0646	0.0420	0.1221
$wR2$	0.0625	0.0690	0.1800
largest diff. peak and hole [e Å^{-3}]	0.857 and −0.414	0.768 and −0.558	2.667 and −1.136

One dichloromethane molecule is disordered over two sites in the ratio 7/3.

For selected bond lengths and angles of **14**·2 THF·7 C_6D_6, **13a**·H_2O, **15**, **16**·CH_2Cl_2, and (*E*)-**17**·CH_2Cl_2 see Table 1. The crystallographic data of **13a**·H_2O and **14**·2 THF·7 C_6D_6 are listed in Table 2, those of **15**, **16**·CH_2Cl_2, and (*E*)-**17**·CH_2Cl_2 in Table 3.

CCDC-271541 (**14**), -271542 (**13a**·H_2O), -271544 (**15**), -271546 (**16**·CH_2Cl_2), and -271547 ((*E*)-**17**·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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