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Synthesis and structures of new conformationally rigid 1-aza-1,3-dienes of the acenaphthene series

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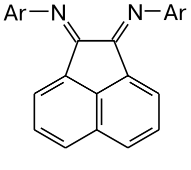
The Wittig reaction of 1-*tert*-butyliminoacenaphthen-2-one with benzylidenetriphenylphosphoranes produces new 1-aza-1,3-dienes of the acenaphthene series, which can bind butyllithium to the C=C bond of the enimine fragment C=C—C=N.

Key words: ketimines, imino ketones, enimines, phosphorus ylides, Wittig reaction, X-ray diffraction study, acenaphthenes.

Among a great variety of metal complexes, derivatives of aryl-substituted 1,3-dienes and 1,4-diaza-1,3-dienes (α,α-diimines) have attracted particular attention in the last few years. Transition metal complexes based on 1,3-dienes are widely used in organic synthesis and serve as polymerization catalysts.[1,2] In addition, these complexes can be involved in various highly selective carbometallation reactions, for example, with unsaturated hydrocarbons and reagents containing carbon—oxygen or carbon—nitrogen double bonds.[3]

Transition metal diimine complexes, in particular, complexes with acenaphthene-1,2-diimine (BIAN) derivatives, have attracted great interest in recent years. These complexes exhibit catalytic activity in the hydrogenation of alkynes,[4] the C—C bond formation,[5] the cycloisomerization,[6] and, particularly, the polymerization of various olefins[7] and acrylic monomers.[8]

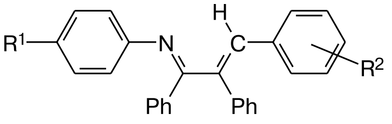


Ar-BIAN

In recent years, we have synthesized Group I, II, XIII, XIV, and XV metal complexes with the Ar-BIAN ligands (Ar is 2,6-diisopropylphenyl, 2,5-di-*tert*-butylphenyl, or 2-biphenyl).

Magnesium and aluminum complexes with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene show high reactivity with respect to various classes of organic compounds (ketones, nitriles, and halogen derivatives)[9] and exhibit catalytic activity in the ring-opening polymerization of lactides. Due to these facts, the synthesis and studies of metal complexes bases on 1,3-dienes and Ar-BIAN are promising lines of investigation in coordination chemistry.

1-Aza-1,3-dienes (enimines) occupy an intermediate position between 1,3-dienes and diimines. However, these compounds have received much less attention compared to dienes and diimines because their synthesis is more difficult.[10] Only a few such compounds are known. For example, the synthesis of enimines **A** and **B** was documented.[11]



A, B

A: R^1 = Me, R^2 = 4-Me, 4-OMe, 4-NMe$_2$
B: R^1 = OMe, R^2 = H, 4-Me, 3-Me

Data on complexes with 1-aza-1,3-dienes are scarce. Most of these complexes were synthesized by the exchange reactions of transition metal halides with magnesium or lithium salts of the corresponding enimines.[10,12] For example, the first homoleptic dinuclear titanium enimine complexes $[\{(2,6\text{-}Pr^i_2C_6H_3)N{=}CHCR{=}CHPh\}_2Ti]_2$ were synthesized by the reduction of two equivalents of 1-aza-1,3-diene $(2,6\text{-}Pr^i_2C_6H_3)N{=}CHCR{=}CHPh$ (R = H or Me) with two equivalents of magnesium in the presence of $TiCl_4(THF)_2$.[10]

It is interesting that the deprotonation of enimine ligands with bases can give Schrock-type carbene com-

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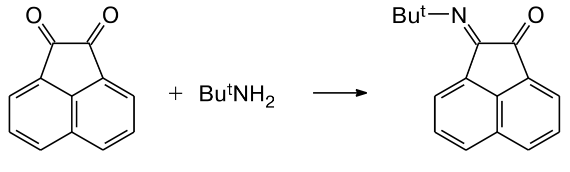
plexes. This characteristic feature distinguishes enimine ligands from BIAN ligands. For example, the deprotonation of titanium enimine complexes with methyllithium affords alkylidene complexes.[10] It should be noted that alkylidene complexes are often formed as intermediates that activate C—H and C—C bonds and play the key role in the olefin polymerization and metathesis.

Therefore, the chemistry of metal complexes with enimine ligands is poorly known and, consequently, is a promising field of investigation. In the present study, we synthesized two new enimines based on acenaphthene and investigated their structures and reactivity with respect to bases.

Results and Discussion

Synthesis and characterization of compounds 1—5. Imino ketone **1** was synthesized by the condensation of acenaphthenequinone with excess *tert*-butylamine in boiling toluene in the presence of concentrated formic acid for 24 h (Scheme 1).

Scheme 1



1

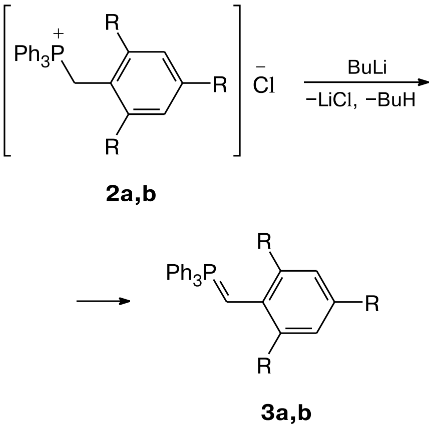
Reagents and conditions: toluene, HCOOH, Δ, 24 h.

To shift the equilibrium of the reaction toward the formation of product **1**, we used molecular sieves as water scavengers. It should be noted that, unlike the reactions with anilines, the reaction with excess *tert*-butylamine does not produce the corresponding diimine. Compound **1** was prepared in 43% yield and was identified by elemental analysis, IR spectroscopy, and ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of compound **1** in benzene shows a singlet for nine methyl protons of the *tert*-butyl group (δ 1.75) and signals for six nonequivalent aromatic protons of the naphthalene moiety of molecule **1**. The IR spectrum shows the presence of C=O (1718 cm^{-1}) and C=N (1626 cm^{-1}) groups in molecule **1**.

Phosphonium salts **2a** and **2b** were prepared by refluxing triphenylphosphine with benzyl chloride and 2,4,6-trimethylbenzyl chloride, respectively, in toluene for 24 h. Phosphorus ylides **3a** and **3b** were synthesized by the deprotonation of salts **2a** and **2b** with butyllithium in hexane (Scheme 2).

Scheme 2

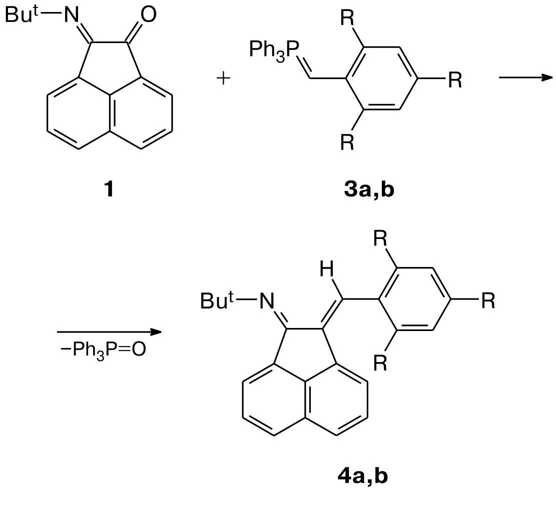


R = H (**a**), Me (**b**)

Ylides **3a,b** were isolated from hexane in yields higher than 90% as bright orange (**3a**) or red (**3b**) powders. Since these compounds are unstable in air, all operations associated with their synthesis and isolation were carried out *in vacuo*. In the present study, ylide **3b** was synthesized for the first time. This compound was characterized by elemental analysis, NMR spectroscopy, and IR spectroscopy. The crystal structure of compound **3b** was established by X-ray diffraction (Fig. 1, Tables 1 and 2). The IR spectra of ylides **3a,b** show stretching bands of the P=C bond at 973 (**3a**) and 978 cm^{-1} (**3b**). The ^{1}H NMR spectrum of compound **3b** in benzene has two singlets for the protons of the methyl groups in the *ortho* and *para* positions of the benzene ring. Due to the splitting from the phosphorus atom, the proton at the P=C double bond gives a doublet at δ 2.47.

Desired enimines **4a,b** were synthesized in 87 and 54% yields, respectively, by refluxing equimolar amounts of imino ketone **1** and phosphorus ylides **3a,b** in toluene for 3 h (Scheme 3). The IR spectra of compounds **4a,b**

Scheme 3

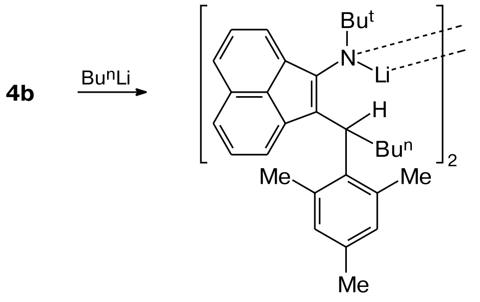


R = H (**a**), Me (**b**)

show an absorption band characteristic of the C=N double bond at 1608 (**4a**) or 1612 cm^{-1} (**4b**). The ^{1}H NMR spectra in benzene (for **4a**) and chloroform (for **4b**) unambiguously confirm the structures of enimines **4a,b**. The corresponding detailed assignments are given in the Experimental section. The structure of compound **4b** was confirmed by X-ray diffraction (Fig. 2, see Tables 1 and 2).

Since enimines can eliminate the hydrogen atom from the C=C double bond to form the carbon—metal bond, we examined the possibility of the deprotonation of compound **4b** with *n*-butyllithium. The reaction mixture turned blue-green, and a green finely crystalline precipitate along with red rhombic crystals were obtained immediately after mixing hexane solutions of Bu^{n}Li and **4b**. Both products have similar solubilities, due to which their quantitative separation was impossible. Several large red crystals were separated mechanically and studied by X-ray diffraction. This product was demonstrated to be dimeric lithium amide **5** that is formed as a result of the 1,4-addition of the organolithium compound to the conjugated enimine fragment C=C—C=N (Scheme 4).

Scheme 4



5

Interestingly, the dissolution of several individual red crystals in tetrahydrofuran gave rise to a blue solution.

The reactions with the use of other bases, such as potassium *tert*-butoxide and lithium diisopropylamide, did not give the desired deprotonation products of enimine **4b** as well. The reactions of these bases with compound **4b** afforded blue solutions. Unfortunately, we failed to isolate individual components from these solutions.

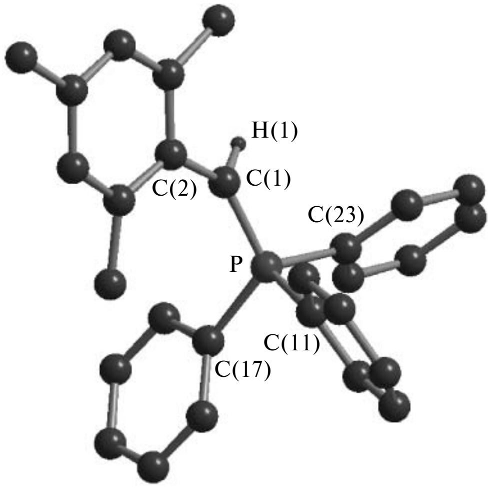


Fig. 1. Molecular structure of phosphorus ylide **3b**. The hydrogen atoms, except for the H(1) atom, are omitted.

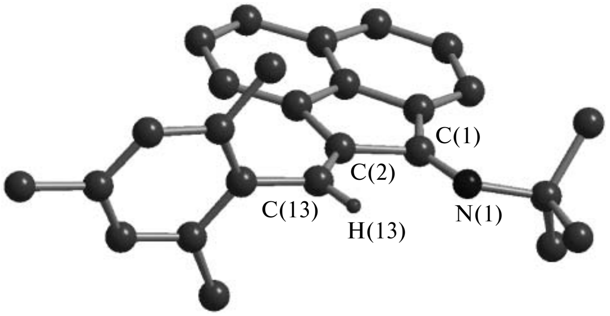


Fig. 2. Molecular structure of enimine **4b**. The hydrogen atoms, except for the H(13) atom, are omitted.

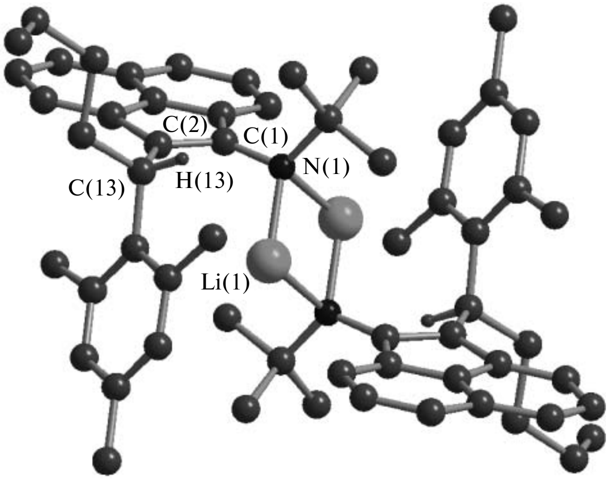


Fig. 3. Molecular structure of complex **5**. The hydrogen atoms, except for the H(13) atom, are omitted.

Molecular structures of compounds 3b, 4b, and 5. The structures of compounds **3b**, **4b**, and **5** were established by X-ray diffraction (Figs 1—3). Crystals of compounds **3b** and **4b** suitable for X-ray diffraction were grown from benzene and hexane, respectively. Selected bond lengths and bond angles in compounds **3b**, **4b**, and **5** are listed in Table 1. The crystallographic data and the X-ray data collection and refinement statistics are given in Table 2. The phosphorus atom in ylide **3b** has a distorted tetrahedral coordination (see Fig. 1), as evidenced by the bond angles at the phosphorus atom (approximately equal to 109°; see Table 1). The C(1)—P distance (1.688(2) Å) is noticeably shorter than the other P—C bonds (P—C(23), 1.816(2) Å; P—C(11), 1.816(2) Å; P—C(17), 1.834(2) Å),

Table 1. Selected bond lengths (d) and bond angles (ω) in molecules **3b**, **4b**, and **5**

Bond	d/Å	Angle	ω/deg
		3b	
P—C(1)	1.688(2)	C(1)—P—C(17)	117.5(1)
P—C(17)	1.834(2)	C(1)—P—C(11)	115.5(1)
P—C(11)	1.816(2)	C(1)—P—C(23)	106.9(1)
P—C(23)	1.816(2)	C(17)—P—C(11)	106.1(1)
C(1)—C(2)	1.457(3)	C(11)—P—C(23)	103.9(1)
		C(23)—P—C(17)	105.7(1)
		4b	
N(1)—C(1)	1.274(3)	N(1)—C(1)—C(2)	118.2(2)
C(2)—C(13)	1.330(3)	C(13)—C(2)—C(1)	123.5(2)
H(13)—C(13)	0.929(5)	H(13)—C(13)—C(2)	116.7(3)
C(1)—C(2)	1.518(3)		
		5	
C(2)—C(13)	1.527(6)	C(1)—C(2)—C(13)	121.8(4)
C(1)—C(2)	1.389(6)	C(1)—N(1)—Li(1)	110.9(3)
C(1)—N(1)	1.402(5)	C(2)—C(1)—N(1)	126.6(4)
Li(1)—N(1)	2.024(9)	H(13)—C(13)—C(2)	104.0(3)
H(13)—C(13)	1.00(1)		

which is indicative of the contribution of the ionic component to the binding and the presence of the positive charge on the phosphorus atom and the negative charge on the carbon atom.

In 1-aza-1,3-diene **4b** (see Fig. 2), the bond lengths in the conjugated enimine fragment C(13)=C(2)—C(1)=N(1) (C(13)—C(2), 1.330(3) Å; C(2)—C(1), 1.518(3) Å; C(1)—N(1), 1.274(3) Å) confirm the presence of the central C(2)—C(1) single bond and two C(13)=C(2) and C(1)=N(1) double bonds, which are similar in length to the corresponding bonds in the molecule of enimine PhCH=CH—CH=N(2,6-$\text{Pr}^{i}_{2}\text{C}_6\text{H}_3$) (1.351(5), 1.438(6), and 1.278(5) Å).[10a]

The conformational rigidity of the enimine is associated with the fact that the carbon atoms of the enimine system are involved in the fused hydrocarbon fragment (the acenaphthylene moiety). The C(13)—H(13) distance is 0.929(5) Å. However, due to the absence of steric crowding at the nitrogen atom, its lone electron pair is accessible to the complexation with metal cations, resulting in the formation of the dimeric structure of compound **5**.

The molecular structure of the complex, which was prepared by the addition of the butyllithium molecule to enimine **4b**, is shown in Fig. 3. According to the X-ray diffraction data, molecule **5** exists as a centrosymmetric dimer with two bridging lithium atoms bound to the

Table 2. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compounds **3b**, **4b**, and **5**

Parameter	**3b** · 1/2C_6H_6	**4b**	**5**
Molecular formula	$C_{31}H_{30}P$	$C_{26}H_{27}N$	$C_{60}H_{72}Li_2N_2$
Molecular weight	433.52	353.49	835.08
T/K	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$	$C2/c$
a/Å	12.156(5)	10.2075(4)	27.004(2)
b/Å	16.028(5)	9.0550(4)	8.6094(6)
c/Å	12.673(5)	22.7332(10)	24.225(2)
α/deg	90.000(5)	90.00	90.00
β/deg	91.939(5)	90.897(2)	119.098(5)
γ/deg	90.000(5)	90.00	90.00
V/Å^3	2467.7(16)	2100.95(15)	4921.3(7)
Z	4	4	4
d/g cm^{-3}	1.167	1.118	1.127
μ/mm^{-1}	0.127	0.064	0.063
F(000)	924	760	1808
Crystal dimensions/mm	0.60×0.42×0.35	0.26×0.36×0.48	0.28×0.36×0.48
Scan range, θ/deg	2.05—25.00	1.79—30.56	1.73—30.63
Indices h, k, l of measured reflections	$-14 \le h \le 9$	$-12 \le h \le 10$	$-30 \le h \le 30$
	$-19 \le k \le 18$	$-11 \le k \le 9$	$-8 \le k \le 9$
	$-15 \le l \le 15$	$-26 \le l \le 28$	$-27 \le l \le 27$
Number of observed reflections	15204	14035	13561
Number of independent reflections (R_{int})	4336 (0.1247)	4134 (0.0884)	3859 (0.1270)
Goodness-of-fit on F^2	1.012	0.975	1.074
R_1/wR_2 ($I > 2\sigma(I)$)	0.0510/0.1172	0.0620/0.1362	0.0825/0.2009
R_1/wR_2 (based on all reflections)	0.0845/0.1331	0.1419/0.1719	0.1220/0.2205
Residual electron density/e Å^3, $\rho_{\max}/\rho_{\min}$	0.338/−0.414	0.159/−0.227	0.322/−0.302

nitrogen atoms of the enimine fragment. The acenaphthylene planes are parallel to each other and are almost orthogonal to the planes of the phenyl substituents. The addition of the Bu^nLi molecule at 1,4 positions of the enimine fragment C(13)—C(2)—C(1)—N(1) leads to a change in the character of bonds in this fragment. Thus, the C(13)—C(2) and C(1)—N(1) distances (1.527(6) and 1.402(5) Å, respectively) are longer than the corresponding distances in the starting 1-aza-1,3-diene **4b** (1.3330(3) and 1.274(3) Å). On the contrary, the C(2)—C(1) bond in complex **5** (1.389(6) Å) is shorter than that in complex **4b** (1.518(3) Å). This confirms the electron density redistribution in the C(13)—C(2)—C(1)—N(1) fragment, resulting in the fact that the C(13)—C(2) and C(1)—N(1) bonds are single, whereas the C(2)—C(1) bond is double.

Experimental

Phosphorus ylides **3a,b** are sensitive to atmospheric moisture and oxygen. Hence, all operations associated with the synthesis, isolation, and identification of these compounds were carried out in evacuated Schlenk-type apparatus. Toluene, hexane, diethyl ether, and benzene were dried and stored over sodium benzophenone ketyl and condensed into a reaction vessel immediately before use. The IR spectra were recorded on a Specord-M80 spectrometer in Nujol mulls. The ^1H NMR spectra were measured on a Bruker DPX 200 spectrometer.

1-(*tert*-Butylimino)acenaphthen-2-one (1). *tert*-Butylamine (5.5 mL, 52 mmol) and 98% formic acid (1 mL) were added to a suspension of acenaphthenequinone (4.55 g, 25 mmol) in toluene (100 mL). The reaction mixture was refluxed for 24 h with continuous stirring with the use of a Soxhlet apparatus containing molecular sieves for absorption of water that was eliminated during the reaction. Then toluene was completely removed from the reaction mixture. The solid residue consisting of the product and unconsumed acenaphthenequinone was repeatedly extracted with hexane on a back-up filter. Compound **1** was isolated by crystallization from hexane as pale-yellow needle-like crystals (2.55 g, 43%), m.p. 136—138 °C (from hexane). Found (%): C, 81.01; H, 6.33. $C_{16}H_{15}NO$ (237.30 g mmol^{-1}). Calculated (%): C, 80.98; H, 6.37. IR (Nujol mulls), ν/cm^{-1}: 1718 (C=O); 1626 (C=N). ^1H NMR (200 MHz, C_6D_6, 20 °C), δ: 7.92 and 7.62 (both d, 1 H each, Ar, J = 7.3 Hz); 7.49 and 7.43 (both d, 1 H each, Ar, J = 8.1 Hz); 7.22 and 7.07 (both dd, 1 H each, Ar, J = 7.3 Hz, J = 8.1 Hz); 1.75 (s, 9 H, Bu^t).

Benzyltriphenylphosphonium chloride (2a). Benzyl chloride (10 mL, 90 mmol) was added to a solution of triphenylphosphine (10.52 g, 40 mmol) in toluene (125 mL). The reaction mixture was refluxed for 12 h with continuous stirring. The colorless precipitate that formed was separated, twice washed on a filter with toluene, and dried. The yield was 14.90 g (96%), m.p. 272—274 °C is consistent with the data published in the literature.[13]

(2,4,6-Trimethylbenzyl)triphenylphosphonium chloride (2b). The procedure for the synthesis and isolation is analogous to that used for **2a**. The yield was 95%, m.p. 228—230 °C is consistent with the data published in the literature.[14]

Benzylidenetriphenylphosphorane (3a). A hexane solution of *n*-butyllithium (4 mL of a 1.25 *M* solution, 5 mmol) was added to a suspension of phosphonium salt **2a** (1.73 g, 4 mmol) in hexane. The solution turned bright orange. Hexane was removed from the reaction mixture, and diethyl ether was added. This led to the formation of an orange precipitate of phosphorus ylide and colorless lithium chloride. Diethyl ether was removed, toluene (50 mL) was added by condensation, a colorless precipitate of lithium chloride was removed by filtration, and a solution of **3a** in toluene was obtained. The latter can be used for the *in situ* synthesis of **4a**. After the complete removal of the solvent, ylide **3a** was obtained as an orange powder. The yield was 1.52 g (97%). The ^1H NMR spectrum and m.p. 175—178 °C are completely identical to those published in the literature.[15]

(2,4,6-Trimethylbenzylidene)triphenylphosphorane (3b). The procedure for the synthesis and isolation is analogous to that used for **3a**. Phosphorus ylide **3b** was obtained as a red powder. The yield was 98%, m.p. 58—61 °C. Found (%): C, 85.30; H, 6.79. $C_{28}H_{27}P$ (394.49 g mmol^{-1}). Calculated (%): C, 85.27; H, 6.88. IR (Nujol mulls), ν/cm^{-1}: 978 (P=C). ^1H NMR (200 MHz, C_6D_6, 20 °C), δ: 7.82—7.68 and 7.08—6.88 (both m, 17 H, Ar); 2.47 (d, 1 H, =C—H, J = 7.7 Hz); 2.35 (s, 6 H, *o*-Me); 2.30 (s, 3 H, *p*-Me). The crystallization from benzene gave red rhombic crystals containing one benzene molecule per two molecules **3b** in the unit cell.

1-(*tert*-Butylimino)-2-(phenylmethylidene)acenaphthene (4a). A solution of imino ketone **1** (1.02 g, 4 mmol) in toluene (10 mL) was added to a solution of phosphorus ylide **3a** (1.52 g, 4 mmol) in toluene (15 mL) *in vacuo*. The reaction mixture was refluxed for 3 h. Then toluene was removed, and hexane was condensed into the mixture, which was accompanied by the formation of a colorless precipitate of triphenylphosphine oxide. The precipitate was separated by filtration. Hexane was removed from the filtrate, and isopropyl alcohol was added. The pale-yellow precipitate of enimine **4a** that formed was separated by filtration, twice washed on a filter with isopropyl alcohol, and dried. The yield was 1.17 g (87%), m.p. 108—110 °C, pale-yellow powder. Found (%): C, 88.52; H, 6.69. $C_{23}H_{21}N$ (311.42 g mol^{-1}). Calculated (%): C, 88.70; H, 6.80. IR (Nujol mulls), ν/cm^{-1}: 1608 (C=N). ^1H NMR (200 MHz, C_6D_6, 20 °C), δ: 8.45 (s, 1 H, =CH); 8.03 and 7.84 (both d, 1 H each, Ar of the naphthalene moiety, J = 7.3 Hz); 7.65—7.46 (m, 4 H, Ar of the naphthalene moiety); 7.44—7.10 (m, 5 H, $C_6\underline{H}_5$—CH=); 1.75 (s, 9 H, Bu^t).

1-(*tert*-Butylimino)-2-[(2,4,6-trimethylphenyl)methylidene]acenaphthene (4b). The procedure for the synthesis and isolation is analogous to that used for **4a**. Enimine **4b** was crystallized from hexane as pale-yellow rhombic crystals. The yield was 54%, m.p. 167—169 °C. Found (%): C, 87.99; H, 7.71. $C_{26}H_{27}N$ (353.49 g mol^{-1}). Calculated (%): C, 88.34; H, 7.70, N, 3.96. IR (Nujol mulls), ν/cm^{-1}: 1612 (C=N). ^1H NMR (200 MHz, $CDCl_3$, 20 °C), δ: 8.12 and 7.88 (both d, 1 H each, Ar of the naphthalene moiety, J = 7.3 Hz, J = 8.2 Hz); 7.80 (s, 1 H, =CH); 7.68—7.62 (m, 2 H, Ar of the naphthalene moiety); 7.40—7.30 (m, 1 H, Ar of the naphthalene moiety); 7.02 (s, 2 H, =CH—$C_6\underline{H}_2Me_3$); 6.82 (d, 1 H, Ar of the naphthalene moiety, J = 6.9 Hz); 2.42 (s, 3 H, *p*-$\underline{Me}C_6H_2$); 2.27 (s, 6 H, *o*-$\underline{Me}C_6H_2$); 1.73 (s, 9 H, Bu^t).

Dimer of lithium *N*-*tert*-butyl-*N*-{2-[1-(2,4,6-trimethylphenyl)pent-1-yl]acenaphthen-1-yl}amide (5). A solution of *n*-butyllithium in hexane (0.8 mL of a 1.25 *M* solution, 1 mmol) was added to a solution of compound **4b** (0.36 g, 1 mmol) in hexane (15 mL) *in vacuo*. The color of the solution changed from pale-yellow to blue-green, and a green finely crystalline precipitate containing inclusions of red rhombic crystals was obtained. Both products are similar in solubility, due to which their quantitative separation was impossible. Several large red crystals were separated mechanically and studied by X-ray diffraction.

X-ray diffraction study of compounds 3b, 4b, and 5. X-ray diffraction data sets were collected on a Siemens SMART CCD diffractometer (ω-φ-scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. Absorption corrections were applied using the SADABS program.[16] The structures were solved by direct methods with the use of the SHELXS97 program package[17] and refined by the full-matrix least-squares method on F^2 using the SHELXL97 program package.[18] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3).

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