Cyclopalladation of 1,1′-Azonaphthalene (= Di(naphthalen-1-yl)diazene): Isolation and Characterization of Two Isomeric Complexes

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The cyclopalladation of 1,1′-azonaphthalene (= di(naphthalen-1-yl)diazene; **2**) with bis(hexafluoroacetylacetonato)palladium(II) (**3**; [Pd(hfa)$_2$]) yields the *ortho*-palladated complex (1,1,1,5,5,5-hexafluoropentane-2,4-dionato-κ^2O,O')[1-(naphthalen-1-ylazo-κN^2)naphthalen-2-yl-κC^2]palladium(II) (**4**) as well as the *peri*-palladated complex (1,1,1,5,5,5-hexafluoropentane-2,4-dionato-κ^2O,O')[8-(naphthalen-1-ylazo-κN^2)naphthalen-1-yl-κC^1]-palladium(II) (**5**); their structures were corroborated by X-ray analyses. The formation of the novel *peri*-metallated product **5** containing a six-membered palladacycle strongly depends upon the reaction conditions.

Introduction. – The cyclometallation reaction – albeit described for the first time some 25 years ago [1][2] – still has an enormous potential as a synthetic tool when employed for the *ortho*-functionalization of suitable arenes [3–8]. Only recently, cyclopalladated complexes were described that catalyze the *Heck* olefination [9] or aryl-coupling reactions [10] in homogeneous solution with high turnover numbers. Other cyclopalladated complexes exhibit some promising liquid-crystalline [11–13] or photochemical and electrochemical [14–16] properties. The cyclometallation principle can also be applied effectively to the laboratory-scale syntheses of dyestuff molecules and dyestuff precursors [17].

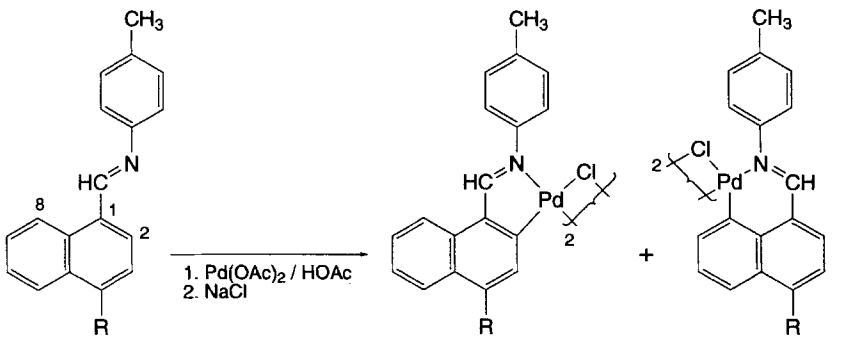
Whereas the papers on investigations of the C–H activation at phenylic *ortho*-positions are copious, far less has been reported on the cyclometallation of naphthalene moieties so far [6][18–28], despite the fact that the naphthalene ring is more reactive towards electrophilic cyclometallating agents. Furthermore, naphthalenes with donor-bearing substituents at C(1) offer both the *ortho*- and the *peri*-position for the cyclometallation.

To make 1-substituted naphthalenes like naphthalen-1-amine (**1**) amenable to cyclopalladation, they have to be converted into suitable donor-bearing cyclometallands, as, *e.g.*, the corresponding 1,1′-azonaphthalene (= di(naphthalen-1-yl)diazene; **2**). Transforming the original naphthalen-1-amine (**1**) into the symmetrical 1,1′-azonaphthalene (**2**) has several advantages: this cyclometalland is providing a donor atom for each of the two naphthalene moieties, and the desired functional groups can be introduced into both rings by two separate metallation/cleavage sequences. Finally, the bis-*ortho*-substituted azonaphthalene would yield two identical *ortho*-functionalized naphthalen-1-amines upon complete reduction of the azo bridge.

The cyclopalladation of the unsubstituted 1,1′-azonaphthalene (**2**) is expected to occur at the C(2) center *ortho* to the azo bridge, as was shown earlier for various 1-(phenylazo)naphthalenes [26][27]. There, the naphthalene *peri*-position (C(8)) was only

accessible to cyclopalladation after all the *ortho*-positions had been blocked by methyl groups [25][26]. Also, if the donor atom is directly attached to the naphthalene C(1), the only possibility to form a five-membered metallacycle is the metallation at position C(8) [1][18][19]. Furthermore, indirect cyclometallation methods (as *e.g.*, transmetallations [29] or ligand-exchange reactions [30]) provide a way to *peri*-metallated naphthalene moieties [31–34]. For the *Schiff* bases with the structural formula shown in *Scheme 1*, however, the cyclopalladation with palladium acetate in AcOH always yields a mixture of *ortho*- and *peri*-palladated complexes, the regioselectivity being dependent on the reaction temperature [21]: For the cyclometalland with R = H, increasing the reaction temperature favors the formation of the *peri*-palladated product, whereas the contrary holds true for the *Schiff* base with R = MeO (*Scheme 1*).

Scheme 1. *Effect of Temperature on the Regioselectivity of the Cyclopalladation of Aromatic* Schiff *Bases* [21]



R = H	25°	80%	20%
	80°	60%	40%
R = MeO	25°	40%	60%
	80°	50%	50%

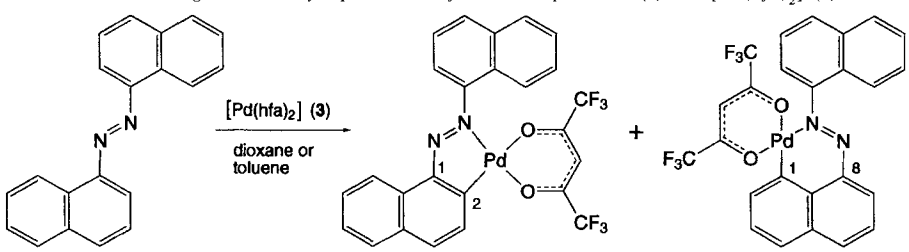
Results and Discussion. – Because the classical azo coupling reaction cannot be applied to unactivated naphthalenes [35], the cyclometalland 1,1′-azonaphthalene (**2**) was synthesized by diazotization of naphthalen-1-amine (**1**) and subsequent treatment of the diazonium solution with sodium acetate and sodium sulfite [36]. Although the yield (59%) was moderate, this method is still preferable to, *e.g.*, the reduction of 1-nitronaphthalene [37][38] which usually yields even lower amounts of the symmetrical coupling product.

The organometallic reagent bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-κ^2O,O')-palladium(II) ([Pd(hfa)$_2$]; **3**) was prepared by simply adding Na_2PdCl_4 to a solution of [Na(hfa)][39].

For the cyclopalladation reaction, the cyclometalland **2** was reacted with **3** in either toluene or dioxane. This afforded a mixture of the two isomeric complexes **4** and **5** (*Scheme 2*), the isomer ratio depending upon the solvent and the reaction temperature (*Table 1*). The cyclopalladation in *toluene* required high reaction temperatures: whereas at room temperature only traces of the isomeric complexes **4** and **5** could be detected, the

reaction run for 18 h in boiling toluene afforded the *ortho*-metallated complex **4** in 59% yield, besides 25% of *peri*-complex **5** (*Table 1, Entry 1*). The formation of the cyclopalladated complexes **4** and **5** was monitored in an experiment run with equimolar amounts of cyclometalland **2** and the palladating species $[Pd(hfa)_2]$ (**3**) in perdeuterated toluene ((D_8)toluene) at 100° (*Table 1, Entry 2*). Samples were taken at distinct time intervals and analyzed with the aid of ^{1}H-NMR spectroscopy (*Table 2*). During the first 20 h of the reaction at 100°, predominantly *peri*-complex **5** was formed, but after 90 h, the distribution amounted to 57.4% of *ortho*-complex **4** and only 42.6% of *peri*-complex **5**. From

Scheme 2. *Regioselective Cyclopalladation of 1,1'-Azonaphthalene* (**2**) *with* $[Pd(hfa)_2]$ (**3**)



2 **4** **5**

Table 1. *Regioselectivity of the Cyclopalladation of* **2** *with* $[Pd(hfa)_2]$ (**3**): *Formation of* ortho-*Complex* **4** vs. peri-*Complex* **5**

Entry	Reaction conditions			Yield (isolated)%		
	solvent	*T*	*t*	total	**4**	**5**
1	toluene	reflux	18 h	84	59	25
2	(D_8)toluene	100°	93 h	[a])	48	36
		reflux	+ 43 h	84[b])	84	0
3	dioxane	room temp.	25 d	[a])	6	12
		100°	+ 1 d	97	37	60
4	dioxane	reflux	31 h	99	39	60

[a]) Yield determined by ^{1}H-NMR spectroscopy. [b]) Yield not significant because of samples taken for ^{1}H-NMR spectroscopy.

Table 2. *Cyclopallation of* **2** *with* $[Pd(hfa)_2]$ (**3**) *in* (D_8)*Toluene at 100°: Composition of the Reaction Mixture, Monitored by* ^{1}*H-NMR Spectroscopy*

Reaction time/h	0.5	1.5	3	5.5	19	29	90	136[a])
$[Pd(hfa)_2]$ (**3**)/%	90.1	80.1	66.7	53.0	19.4	8.5	0.0	0.0
ortho-Complex **4**/%	4.4	8.3	14.0	19.7	38.1	48.8	57.4	100.0
peri-Complex **5**/%	5.5	11.6	19.3	29.3	42.5	42.7	42.6	0.0

[a]) After 93 h, the reaction temperature was raised from 100 to 130°.

this solution, after heating under reflux for two days, exclusively the *ortho*-complex **4** was isolated in 84% yield (*Table 1, Entry 2*). This leads to the assumption that under the prevailing reaction conditions, the kinetically favored *peri*-palladated product **5** was converted into the thermodynamically controlled *ortho*-palladated complex **4**, a hypothesis that could be verified by boiling a solution of the isolated *peri*-complex **5** in toluene, which led to the almost quantitative formation of *ortho*-complex **4**.

On the contrary, the reaction carried out in *dioxane* always afforded a mixture of the two isomeric complexes **4** and **5**. Even at reflux temperature, both **4** and **5** were obtained (*Table 1, Entry 4*). Stirring the mixture at room temperature for 25 days gave only a low conversion and a product distribution of 2:1 in favor of *peri*-complex **5** (*Table 1, Entry 3*). Heating this mixture to 100° for one day afforded 97% of the same 2:1 mixture. The same result was obtained after a reaction time of 31 h at reflux temperature (*Table 1, Entry 4*).

Efforts to separate the mixture of the two isomeric complexes **4** and **5** by recrystallization were rather unsatisfying. Indeed, in spite of the formation of different types of crystals for **4** and **5**, their solubility in all the solvents tested is comparable. The mixture **4**/**5** could finally be separated by means of column chromatography on aluminium oxide. With toluene/MeOH, *peri*-complex **5** was eluted first and quantitatively, whereas *ortho*-complex **4** showed a greater affinity to the stationary phase so that part of it remained on the column and could not be eluted, not even with pure MeOH. Nevertheless, both **4** and **5** could be isolated analytically pure by this procedure.

The structures of the complexes **4** and **5** then were unequivocally established with the aid of NMR-spectroscopic and X-ray crystal-structure analyses.

The ^{1}H-NMR spectrum of the *ortho*-palladated complex **4** shows the *AB* spin-coupling pattern expected for the protons H–C(3) and H–C(4) at 7.68 and 7.86 ppm, respectively, with a typical coupling constant of 8.5 Hz. At 6.10 ppm, a *s* is observed for the methine proton of the hfa moiety. The ^{13}C-NMR spectrum of the *ortho*-complex **4** shows seven quaternary signals, two of which appear at considerably lower field compared to the signals of the free cyclometalland **2**. These two low-field resonances could be assigned to C(2) (161.8 ppm) and C(1) (158.5 ppm). This means that the signal of the metallated center C(2) is shifted by *ca.* 50 ppm towards lower field compared to C(2) of the cyclometalland **2**, which is in agreement with results described earlier [40–43]. The ^{19}F-NMR spectrum exhibits two *s* for the two nonequivalent CF_3 groups.

The ^{1}H-NMR spectrum of the *peri*-palladated complex **5** exhibits three *ABM* spin-coupling patterns of which the two adjacent ones could be assigned with the aid of two-dimensional NMR spectra (^{1}H,^{13}C heteronuclear multiple bond correlation spectroscopy, HMBC). Compared to complex **4**, the hfa proton of complex **5** is slightly shielded, its *s* being located at 5.89 ppm. In the ^{13}C-NMR spectrum, each of the seven quaternary aromatic C-atoms can be detected, albeit a complete assignment has not been possible yet. But even with the signals unassigned, it can be seen that the palladation of the *peri*-position C(1) of **5** has a much smaller deshielding influence on this center compared to the *ortho*-palladation at C(2) of **4** because of the absence of ^{13}C-NMR signals for **5** at such a low field strength. In the ^{19}F-NMR spectrum, the two different CF_3 groups give rise to two *s* at almost the same chemical shifts as the respective CF_3 groups of the *ortho*-palladated complex **4**.

Recrystallization of complex **4** from hexane afforded triclinic red needles of the space group $P\bar{1}$ and allowed the determination of its crystal structure (*Fig. 1*), which displays the following features: the F-atoms F(35) *pseudo-trans* to the coordinating N-atom N(21) are disordered, showing a remarkable degree of mobility within the crystal lattice. The Pd–O(31) bond *trans* to the Pd–C bond is longer by 0.08 Å compared to the one *trans* to Pd–N, which can be attributed to the stronger *trans*-influence [44] of the carbanion compared to the azo N-donor. The lengths of the Pd–C and the Pd–N bonds (1.94 *vs.*

2.03 Å, resp.) are comparable to those of an analogous azobenzene complex [45]. The endocyclic (referring to the diazapalladacycle) (C(11)–N(11) bond is significantly shorter than the exocyclic C(21)–N(21) bond (1.38 *vs.* 1.42 Å) and the N=N bond is slightly longer than that in azobenzene [46].

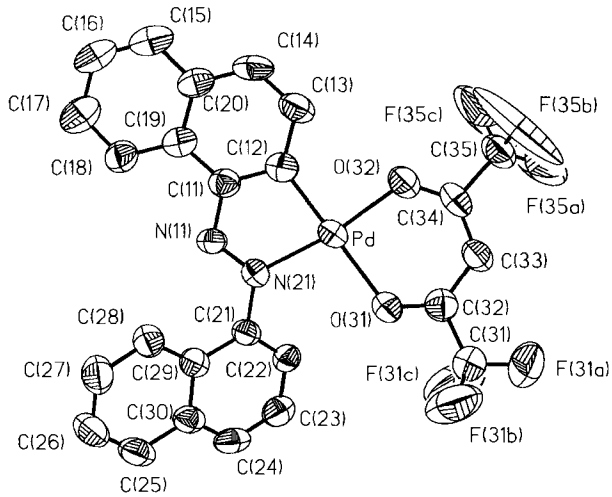


Fig. 1. *Molecular structure of* **4** *showing 50% probability displacement ellipsoids.* H-Atoms are omitted for clarity. Arbitrary numbering.

The diazapalladacycle of the *ortho*-metallation product **4** is a rather distorted pentagon with the bond angles around the square-planar coordination geometry of the Pd-center deviating significantly from 90° (*Table 3*). Furthermore, it is almost coplanar with both the metallated naphthalene ring and the co-ligand hfa. The non-metallated naphthalene moiety, however, is free to twist out of the plane of the rest of the molecule by an angle of 141°.

Table 3. *Selected Structural Data for Complexes* **4** *and* **5**. For numbering, see *Figs. 1* and *2*.

	ortho-Complex **4**		*peri*-Complex **5**	
Bond lengths/Å	Pd–N(21)	2.031(5)	Pd–N(21)	1.971(5)
	Pd–C(12)	1.940(7)	Pd–C(18)	1.961(6)
	Pd–O(31)	2.108(5)	Pd–O(31)	2.138(5)
	Pd–O(32)	2.031(5)	Pd–O(32)	2.059(5)
	C(11)–N(11)	1.375(8)	C(11)–N(11)	1.385(9)
	C(21)–N(21)	1.424(8)	C(21)–N(21)	1.450(8)
	N(11)–N(21)	1.273(7)	N(11)–N(21)	1.258(7)
Bond angles/°	N(21)–Pd–C(12)	78.9(3)	N(21)–Pd–C(18)	90.1(2)
	N(21)–Pd–O(31)	100.1(2)	N(21)–Pd–O(31)	92.5(2)
	O(31)–Pd–O(32)	89.1(2)	O(31)–Pd–O(32)	86.5(2)
	O(12)–Pd–O(32)	92.0(2)	C(18)–Pd–O(32)	91.2(2)

Slow evaporation of the solvent from a solution of **5** in hexane afforded *peri*-complex **5** as monoclinic orange prisms of the space group $P2_1/c$ and allowed the establishment of its crystal structure (*Fig. 2*). The square-planar coordination sphere around the Pd-center of the *peri*-palladated complex **5** shows coordination angles that are closer to the ideal value of 90° than in the *ortho*-palladated complex **4** (*Table 3*). The six-membered diazapalladacycle has a rather distorted hexagonal geometry with all angles wider than 120° except for the 'bite' angle at the Pd-center, which indicates clearly the geometrical constraints exerted by the Pd-atom. As already observed for *ortho*-complex **4**, the stronger *trans*-influence [44] of the carbanion donor compared to the azo N-donor lengthens the bond *trans* to the Pd–C by 0.08 Å compared to the one *trans* to the Pd–N bond. The lengths of the Pd–C bonds of *ortho*-complex **4** and *peri*-complex **5** are almost the same (1.94 *vs.* 1.96 Å), whereas the lengths of the Pd–N bonds differ significantly (2.03 *vs.* 1.97 Å), obviously for geometrical constraints (*Table 3*). The endocyclic C(11)–N(11) bond is significantly shorter than the exocyclic C(21)–N(21) bond (1.39 *vs.* 1.45 Å), *i.e.*, this difference in bond lengths is more pronounced for the *peri*-complex **5** compared to the *ortho*-complex **4**.

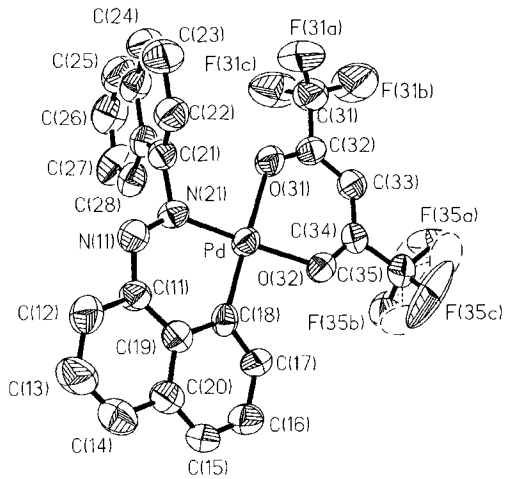


Fig. 2. *Molecular structure of* **5** *showing 50% probability displacement ellipsoids.* H-Atoms are omitted for clarity. Arbitrary numbering.

For steric reasons, the azonaphthalene moiety can no longer be planar within complex **5**, the non-metallated naphthalene ring turning out of the plane formed by the cyclopalladated fragment by an angle of 104°. In contrast to *ortho*-complex **4**, the metallacycle with the hfa co-ligand is not planar in the *peri*-complex **5**, the Pd-hfa fragment protruding from the plane represented by the metallated naphthalene unit by an angle of 17°, which is believed to be caused by electronic repulsions between H–C(17) and O(32).

In view of the fact that cyclopalladation reactions involving N-donors as cyclometallands usually lead to five-membered palladacycles [47][48], it is quite unusual that here the metallating species [Pd(hfa)$_2$] (**3**) activates the *peri* C–H bond forming a six-membered palladacyle with coordination of the Pd-center to the more distant azo N-atom

N(21). This is obviously the first example of a *peri*-palladated naphthalene derivative with a *six-membered* metallacycle described so far, where there is also a choice for the formation of a five-membered ring. If the commonly used $[Pd(OAc)_2]$ is employed for the cyclometallation, the 1,1′-azonaphthalene (**2**) is palladated exclusively at the *ortho*-position at 60° in AcOH and in the presence of NaOAc (89% yield); the same reaction in $CHCl_3$ at 45–50° also leads to the *ortho*-palladated complex, but in only 73% yield [49]. These results with $[Pd(OAc)_2]$ as metallating species are consistent with the cyclometallations of some 1-(phenylazo)naphthalenes described earlier [26][27].

Conclusions. – This surprising *peri*-palladation of 1,1′-azonaphthalene (**2**) when $[Pd(hfa)_2]$ (**3**) is employed as the cyclometallating agent might lead to a somewhat revised view of the cyclometallation mechanism with electrophilic metal species: In this special case, the better accessability and higher reactivity of the *peri*-position for both steric and electronic reasons (the *peri*-H-atom is more easily removed than the *ortho*-H-atom [50][51]) strongly favors the formation of the kinetically controlled product **5** containing a six-membered metallacycle, which in the course of the reaction is transformed to the thermodynamically favored *ortho*-palladated complex **4** with a five-membered palladacycle. This proves –further to the experiment where the *peri*-complex **5** was converted completely into the *ortho*-complex **4** under the reaction conditions (as described above) – that the formation of the Pd–C bond can be regarded as a reversible process. More investigations must still be done to elucidate the intrinsic mechanism of the more than 30-years old [52] cyclometallation reaction with Pd^{II} and Pt^{II}. After all, the employment of $[Pd(hfa)_2]$ (**3**) for the cyclopalladation in polar solvents like dioxane will open the unique opportunity to synthesize *peri*-palladated complexes which could be cleaved by suitable reagents [17] to yield *peri*-functionalized naphthalene derivatives with potential use in the syntheses of dyestuff molecules and precursors.

We thank Mr. *F. Bangerter* for his outstanding work on the NMR spectrometers and him and Dr. *P. Skrabal* for helpful discussions.

Experimental Part

General. All commercially available chemicals employed were reagent grade and used without further purification, unless otherwise stated. Na_2PdCl_4 was purchased from *Métaux Précieux SA Métalor*. Reactions with organometallic reagents were carried out in either dioxane (*J. T. Baker B. V. Baker Analyzed*® reagent) or toluene (*Fluka, puriss.*) which were used without further purification. M.p.: *Electrothermal IA 9100* capillary apparatus: uncorrected. IR Spectra: *Perkin-Elmer-783* IR spectrometer; region 4000–400 cm^{-1} in KBr matrix for org. compounds; region 4000–200 cm^{-1} in CsBr matrix for organometallic compounds. ^1H- and ^{13}C-NMR Spectra: *Bruker-AMX-400*, *Bruker-AMX-500*, *Bruker-AM300-WB*, or *Bruker-AC200-P* spectrometer; δ in ppm with $SiMe_4$ as internal standard, coupling constants J in Hz. ^{19}F-NMR Spectra: *Bruker-AC200-P* spectrometer; δ in ppm relative to $CFCl_3$ as external standard. FAB Mass spectra: *ZAB2-SEQ* spectrometer; *m/z* (% rel. to intensity of base peak (= 100%)). Elemental analyses were performed at the Laboratory of Organic Chemistry, ETHZ.

Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-κ²O,O′)palladium(II) (**3**) [39]. At r.t., 1,1,1,5,5,5-hexafluoropentane-2,4-dione (3.0 ml, 21.5 mmol) was slowly added to 1M NaOH (22 ml) and stirred for 10 min. Na_2PdCl_4 (3.15 g, 10.7 mmol) was then added in two portions, and the mixture was stirred vigorously for 3 h. The residue was filtered off, washed with H_2O, and extracted with CH_2Cl_2 (100 ml). The org. phase was dried (Na_2SO_4) and evaporated to yield a yellow solid which was sublimated at 50°/high vacuum: **3** (3.73 g, 67%). M.p. 98–99°. IR: 3140*w*, 1730*w*, 1660*s*, 1630*m*, 1600*s*, 1530*s* (br.), 1435*s*, 1340*m*, 1260*s*, 1230–1100*s*, 1070*w*, 1020*w*, 940*w*, 815*m*, 790*m*, 750*w*, 730*w*, 720*m*, 690*w*, 660*m*, 600*w*, 570*m*, 540*w*, 520*w*, 430*w*, 340*w*, 300*w*, 250*w*. ^1H-NMR ($CDCl_3$, 200 MHz): 7.26 (*sept.*, ^4J(HF) = 0.4, CH). ^{13}C-NMR ($CDCl_3$, 76 MHz): 93.9 (*s*, CH); 114.7 (*q*, ^1J(CF) = 284, CF_3); 176.2 (*q*, ^2J(CF) = 37, C=O). ^{19}F-NMR ($CDCl_3$, 188 MHz): 73.3 (*s*, CF_3).

Di(naphthalen-1-yl)diazene (**2**) [36]. To a vigorously stirred suspension of naphthalen-1-amine (**1**; 9.50 g, 66.3 mmol) in H_2O (200 ml) and conc. HCl soln. (9 ml) at 5°, a precooled soln. of conc. H_2SO_4 (7.5 ml) in H_2O (100 ml) was added, followed by the dropwise addition of a precooled soln. of $NaNO_2$ (4.75 g, 68.8 mmol) in H_2O (35 ml). After 10 min stirring in an ice bath, a precooled soln. of NaOAc (24.0 g, 293 mmol) in H_2O (100 ml) was added keeping the temp. of the mixture below 4°. At pH 4, a precooled soln. of Na_2SO_3 (10.0 g, 79.3 mmol) in H_2O (80 ml) was added carefully, the evolving N_2 producing a thick orange foam. After the addition of the sulfite soln., the mixture was stirred 2 h at r.t. and then filtered and the residue washed with H_2O. Recrystallization from EtOH yielded 5.47 g (59%) of **2**. Orange solid. M.p. 184–186°. IR: 3080*w*, 3040*w*, 1585*w*, 1565*w*, 1500*m*, 1390*m*, 1370*w*, 1340*m*, 1210*m*, 1150*w*, 1140*w*, 1080*w*, 1040*w*, 1010*m*, 970*w*, 950*w*, 910*w*, 865*w*, 800*s*, 780*s*, 740*w*, 710*w*, 650*w*, 590*m*, 570*w*, 550*w*, 480*w*, 465*w*, 430*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 7.57–7.63 (*m*, 2 H, H–C(6)); 7.61 (*dd*, J_o = 7.8, 7.9, 2 H, H–C(3)); 7.65–7.70 (*m*, 2 H, H–C(7)); 7.94 (*dd*, J_o = 8.2, J_m = 1.2, 2 H, H–C(5)); 7.98 (*dd*, J_o = 7.6, J_m = 1.2, 2 H, H–C(2)); 8.02 (*d*, J_o = 8.0, 2 H, H–C(4)); 9.04–9.06 (*m*, 2 H, H–C(8)). ^{13}C-NMR ($CDCl_3$, 76 MHz): 112.3 (C(2)); 123.6 (C(8)); 125.7 (C(3)); 126.5 (C(6)); 127.0 (C(7)); 128.0 (C(5)); 131.4 (C(4)); 131.5 (C(9)); 134.4 (C(10)); 148.3 (C(1)).

(1,1,1,5,5,5-Hexafluoropentane-2,4-dionato-κ²O,O′)[1-(naphthalen-1-ylazo-κN²)naphthalen-2-yl-κC²]-palladium(II) (**4**) *and (1,1,1,5,5,5-Hexafluoropentane-2,4-dionato-κ²O,O′)[8-(naphthalen-1-ylazo-κN²)naphthalen-1-yl-κC¹]palladium(II)* (**5**). *General Procedure*: A soln. of **2** (141.2 mg, 0.50 mmol) and **3** (260.3 mg, 0.50 mmol) in solvent (10 ml) was stirred for several hours at mostly elevated temp. (see *Table 1*). The mixture was evaporated, the residue dissolved in CH_2Cl_2, and the soln. filtered over *Celite*. The isomers **4** and **5** were separated by column chromatography (aluminium oxide, act. III, toluene/MeOH 20:1).

Complex **4**: IR (CsBr): 3050*w*, 1670*m*, 1630*s*, 1590*w*, 1570*m*, 1550*m*, 1525*m*, 1510*m*, 1500*m*, 1470*s*, 1430*w*, 1390*w*, 1370*w*, 1330*m*, 1260*s*, 1210*s*, 1200*s*, 1150*s*, 1100*m*, 1070*w*, 1020*w*, 970*w*, 950*w*, 880*w*, 850*w*, 820*m*, 790*m*, 770*m*, 765*m*, 745*m*, 680*m*, 660*w*, 650*w*, 590*w*, 580*w*, 560*w*, 540*w*, 530*w*, 490*w*, 430*w*, 390*w*, 350*w*, 300*w*. ^{1}H-NMR ($CDCl_3$, 500 MHz): 6.10 (*s*, H–C(hfa)); 7.51–7.58 (*m*, 4 H); 7.60 (*dd*, J_o = 8.2, 7.5, H–C(3′)); 7.68 (*d*, J_o = 8.6, H–C(3)); 7.78 (*dd*, J_o = 7.4, J_m = 1.1, H–C(2′)); 7.86 (*d*, J_o = 8.5, H–C(4)); 7.90 (*d*, J_o = 8.2, H–C(4′)); 7.95–7.97 (*m*, 1 H); 8.01–8.02 (*m*, 1 H); 8.46–8.48 (*m*, H–C(8) or H–C(8′)); 8.63–8.65 (*m*, H–C(8) or H–C(8′)). ^{13}C-NMR ($CDCl_3$, 126 MHz): 91.3 (H–*C*(hfa)); 117.2 (*q*, ^1J(CF) = 286, CF_3); 117.7 (*q*, ^1J(CF) = 284, CF_3); 122.2; 123.2; 123.6; 124.6; 126.1; 126.8; 126.9 (C(9′)); 127.3; 128.3; 128.8; 128.9; 129.2; 131.1 (C(4′)); 131.5 (C(9)); 132.7 (C(10)); 133.9 (C(4)); 134.1 (C(10′)); 147.2 (C(1′)); 158.5 (C(1)); 161.8 (C(2)); 175.1 (*q*, ^2J(CF) = 35, C=O); 176.3 (*q*, ^2J(CF) = 35, C=O). ^{19}F-NMR ($CDCl_3$, 188 MHz): −76.3 (*s*, CF_3); −75.0 (*s*, CF_3). FAB-MS (*I* > 10%): 599 (10), 598 (18), 597 (19), 596 (31), 595 (23), 594 (37, M^+), 593 (25), 391 (22), 390 (14), 389 (41), 388 (16), 387 (50), 386 (36), 385 (20), 371 (13), 308 (13), 307 (49), 295 (10), 293 (11), 292 (10), 290 (10), 289 (28), 283 (22), 282 (42), 281 (100), 280 (15), 279 (17), 269 (12), 268 (16), 267 (28), 266 (14), 255 (10), 254 (18), 253 (41), 252 (56), 239 (14), 215 (11), 202 (10). Anal. calc. for $C_{25}H_{14}F_6N_2O_2Pd$ (594.79): C 50.48, H 2.37, F 19.16, N 4.71, O 5.38; found: C 50.55, H 2.20, F 19.39, N 4.77, O 5.57.

Crystal-Structure Analysis of **4**[1]: $C_{25}H_{14}F_6N_2O_2Pd$; formula weight 594.8; red needle 0.03 × 0.08 × 0.9 mm, triclinic, space group $P\bar{1}$, a = 7.534(4) Å, b = 13.362(7) Å, c = 22.751(11) Å, α = 88.64(2)°, β = 89.07(3)°, γ = 79.33(2)°, V = 2250(2) Å³, Z = 4, $\rho_{calc.}$ = 1.753 g/cm³, μ = 7.360 mm⁻¹, F(000) = 1172. Collection of data was performed on a *Picker-Stoe* diffractometer (highly oriented graphite crystal monochromatized CuK_α radiation, λ = 1.54178 Å). Number of reflections collected 4631 (ω scan, 3.0 < 2θ < 100.0°, *T* 293 K), independent reflections 4631, observed reflections 3906, min./max. transmission 0.489/0.803. Solution and refinement: *Siemens* SHELXTL PLUS (VMS), *Patterson* methods, refinement method full-matrix least squares, quantity minimized $\sum\omega(F_o - F_c)^2$, absolute structure N/A, weighting scheme $w^{-1} = s^2(F_o^2) + (0.1000P)^2 + 0.0000P$ where $P = (F_o^2 + 2F_c^2)/3$, number of parameters refined 650; final *R* indices (obs. data): *R* 4.44%, R_w 13.83%; *R* indices (all data): *R* 5.15%, R_w 14.48%.

Complex **5**: IR (CsBr): 3060*w*, 1670*m*, 1640*s*, 1590*w*, 1550*m*, 1520*m*, 1480*s*, 1440*m*, 1420*s*, 1390*m*, 1380*m*, 1360*m*, 1345*m*, 1250*s*, 1210*s*, 1200*s*, 1150*s*, 1100*s*, 1050*w*, 1020*w*, 980*w*, 970*w*, 945*w*, 895*w*, 860*w*, 825*m*, 800*s*, 785*m*, 770*s*, 755*m*, 740*w*, 680*m*, 660*w*, 640*w*, 600*w*, 590*w*, 570*w*, 530*w*, 520*w*, 480*w*, 420*w*, 350*w*, 335*w*, 300*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 5.89 (*s*, H–C(hfa)); 7.51–7.58 (*m*, 4 H); 7.61 (*dd*, J_o = 7.7, 7.7, H–C(3) or H–C(6)); 7.75 (*dd*, J_o = 7.5, 7.4, H–C(3) or H–C(6)); 7.85 (*d*, J_o = 7.6, H–C(4) or H–C(5)); 7.93–7.99 (*m*, 2 H); 8.21

[1]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/79. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK. (fax + 44-(0)1223-336033 or e-mail teched@chemcrys.cam.ac.uk).

(*dd*, J_o = 7.6, J_m = 0.9, H–C(2) or H–C(7)); 8.25–8.27 (*m*, H–C(8')); 8.32 (*dd*, J_o = 8.1, J_m = 1.2, H–C(4) or H–C(5)); 8.54 (*dd*, J_o = 7.4, J_m = 1.4, H–C(2) or H–C(7)). ^{13}C-NMR ($CDCl_3$, 126 MHz): 90.4 (H–*C*(hfa)); 113.5 (C(9)); 116.8 (*q*, ^1J(CF) = 287, CF_3); 117.6 (*q*, ^1J(CF) = 285, CF_3); 119.6; 122.2; 124.6; 125.4 (C(3) or C(6)); 126.6 (2C, C(3) or C(6)); 127.0; 127.6 (C(4) or C(5)); 128.0 (C(9')); 128.3; 129.5; 132.7 (C(10)); 133.2 (C(1) or C(8)); 133.8 (C(10')); 134.2 (C(2) or C(7)); 139.7 (C(2) or C(7)); 140.3 (C(4) or C(5)); 149.8 (C(1')); 149.9 (C(1) or C(8)); 175.0 (*q*, ^2J(CF) = 35, C=O); 176.3 (*q*, ^2J(CF) = 35, C=O). ^{19}F-NMR ($CDCl_3$, 188 MHz): –76.9 (*s*, CF_3); –75.3 (*s*, CF_3). FAB-MS (I > 10%): 599 (22), 598 (39), 597 (46), 596 (74), 595 (54), 594 (100, M^+), 593 (71), 592 (30), 544 (12), 543 (11), 542 (22), 541 (16), 540 (27), 539 (20), 538 (13), 524 (12), 391 (31), 390 (19), 389 (63), 388 (23), 387 (75), 386 (56), 385 (30), 282 (21), 281 (55), 280 (11), 279 (11). Anal. calc. for $C_{25}H_{14}F_6N_2O_2Pd$ (594.79): C 50.48, H 2.37, F 19.16, N 4.71; found: C 50.65, H 2.52, F 19.19, N 4.62.

Crystal-Structure Analysis of **5**[1]): $C_{25}H_{14}F_6N_2O_2Pd$, formula weight 594.8; orange prism 0.12 × 0.16 × 0.5 mm, monoclinic, space group $P2_1/c$, a = 8.727(8) Å, b = 13.35(2) Å, c = 19.76(2) Å, β = 96.53(7)°, V = 2288(4) Å^3, Z = 4, $\rho_{calc.}$ = 1.727 g/cm^3, μ = 0.886 mm^{-1}, F(000) = 1176. Collection of data was performed on an *Picker-Stoe* diffractometer (highly oriented graphite crystal monochromatized MoK_α radiation, λ = 0.71073 Å). Number of reflections collected 2257 (ω scan, 3.0 < 2θ < 40.0°, T 293 K), independent reflections 2129, observed reflections 1649, min./max. transmission 0.870/0.910. Solution and refinement: *Siemens* SHELXTL PLUS (VMS), *Patterson* methods, refinement method full-matrix least squares, quantity minimized $\sum w(F_o - F_c)^2$, absolute structure N/A, weighting scheme $w^{-1} = s^2(F_o^2) + (0.0761P)^2 + 0.0000P$ where $P = (F_o^2 + 2F_c^2)/3$, number of parameters refined 355; final R indices (obs. data): R 4.08%, R_w 9.65%; R indices (all data): R 5.58%, R_w 10.53%.

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