Electronic Supplementary Information

Mechanochemical C–H Bond Activation: Rapid and Regioselective Double Cyclopalladation Monitored by *in situ* Raman Spectroscopy

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EXPERIMENTAL DETAILS

General Methods. All chemicals were used as supplied. The ^{1}H NMR spectra were recorded at 25 °C in chloroform-*d* ($CDCl_3$) with spectrometers operating at 300 or 600 MHz. The atom numbering of azobenzenes used in the assignment of ^{1}H NMR resonances is given in Scheme S1. IR spectra were recorded in KBr pastilles and the selected data are collected in Table S1.

Crystal Structure Determination. Single crystals of **1A** and **1B** were grown from DMF and CH_2Cl_2/THF solutions, respectively. The X-ray measurements were performed on an Oxford Diffraction Xcalibur Nova R (microfocus Cu tube) and Oxford Xcalibur Sapphire3 (Mo tube) at room temperature, respectively. The program package CrysAlisPRO[1] was used for data reduction. The structures were solved using SHELXS97[2] and refined with SHELXL97.[3] Molecular geometry calculations were performed by PLATON[4] and molecular graphics were prepared using ORTEP-3[5] and CCDC-Mercury.[6] Crystallographic and refinement data for the structures reported in this paper are shown in Table S2. CCDC 1005635-1005636 contain the supplementary crystallographic data for this paper. They can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Raman Measurement of Mechanochemical Processes. For Raman collection, PD-LD LS2 laser source (784 nm) with optical fibber and Raman probe was coupled with Maya2000 Pro spectrometer (Oceanoptics). Probe was positioned straight under the transparent PMMA milling vessel. The vertical positioning of the Raman probe was adjusted using a precise movable stand such that the focus of the laser was 1-2 mm inside the vessel.

Synthesis:

All grinding experiments were performed at room temperature in a 14 mL PMMA jars using one 10 mm stainless steel grinding ball (4 g). A Retsch MM301 grinder mill operating at 30 Hz frequency was used for the synthesis. The complex **1A** was prepared by liquid-assisted grinding (4.5 h) of 123.61 mg of **1** and 121.28 mg of $Pd(OAc)_2$ in the presence of 25 μL of acetic acid. The green powder was obtained in 78% yield after purification with small amounts of water and THF. The complex **1A** was also prepared in a 39% yield by the solvent-based reaction according to the previously reported procedure.[7] The brown red powder of complex **1B** was obtained by the same mechanochemical procedure within 7.5 h in a 85% yield using 97.19 mg of **1A** and 97.57 mg of $Pd(OAc)_2$. The complexes **1A** and **1B** were also prepared by ion-and-liquid-assisted grinding reactions using 25 μL of acetic acid and 16.58 mg (**1A**) or 18. 70 mg (**1B**) of sodium acetate. The yields of complexes were similar to those obtained by LAG reactions.

IR SPECTROSCOPY

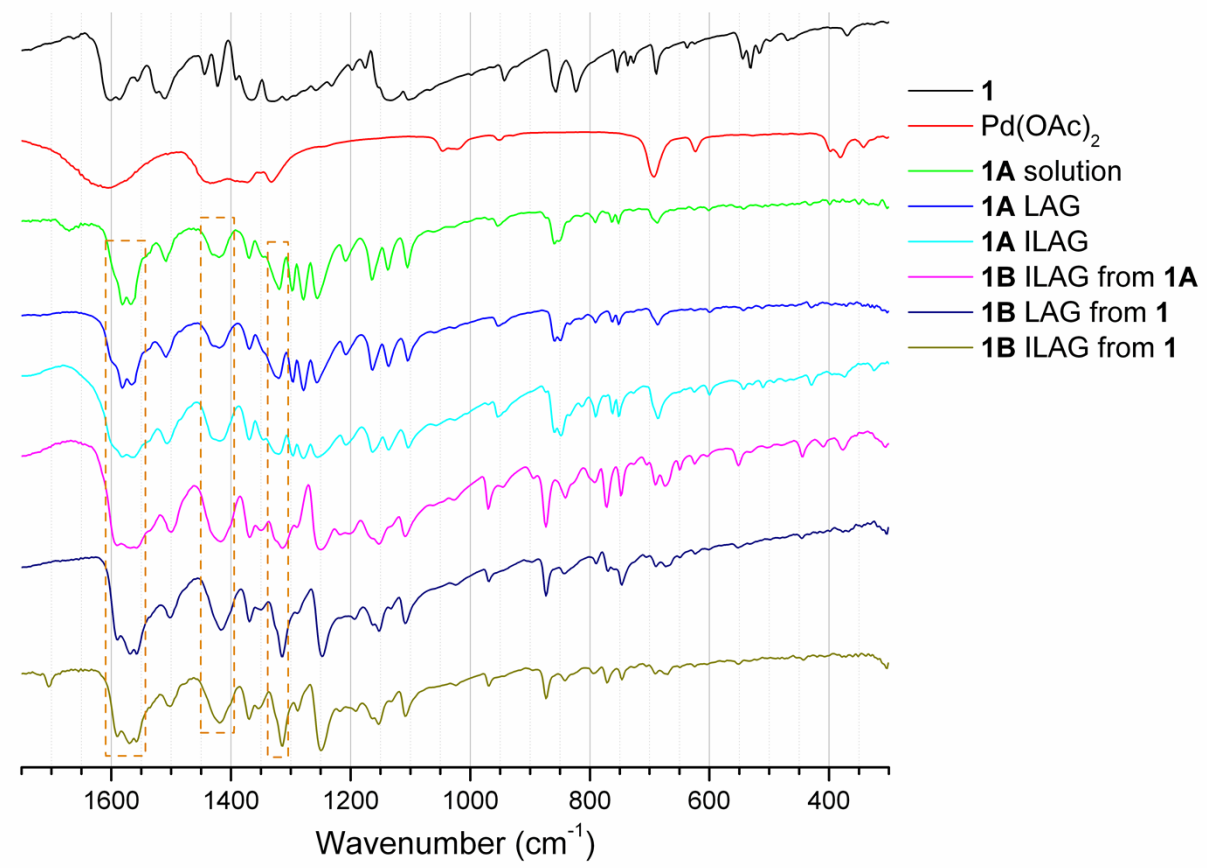


Figure S1. IR spectra (in KBr) of $Pd(OAc)_2$, azobenzene ligand **1**, **1A** from the solution synthesis and LAG and ILAG reaction products **1A** and **1B**.

Table S1
Selected IR data (in cm^{-1}) for **1**, $Pd(OAc)_2$ and cyclopalladated products **1A** and **1B**.

	$Pd(OAc)_2$	**1**	**1A**	**1B**
ν_{as}(COO),	1605 s br	1601 s	1601 sh	1591 s
ν(C=N)[a],		1587 s	1581 s	1569 s
ν(C=C)[a]			1567 s	1558 s
ν_{sym}(COO)	1430 s br	-	1431 m br	1417 s br
			1420 m br	
$\nu_{as}(NO_2)$	-	1524 s	1508 m	1502 m
		1508 s		
$\nu_{sym}(NO_2)$	-	1331 s br	1320 s	1314 s

[a] Not applicable to $Pd(OAc)_2$.

X-RAY CRYSTALLOGRAPHY

Table S2
Crystallographic data, collection and structure refinement details for 2(**1A**)·3DMF and **1B**·2THF.

Complex	2(**1A**)·3DMF	**1B**·2THF
Empirical formula	$C_{73}H_{85}N_{19}O_{19}Pd_4$	$C_{44}H_{52}N_8O_{14}Pd_4$
Formula wt. / g mol^{-1}	1958.20	1342.54
Crystal dimensions / mm	0.15 x 0.12 x 0.10	0.15 x 0.12 x 0.10
Color	Green	Purple
Solvent used for crystallization	DMF	CH_2Cl_2/THF
Space group	*Cc*	$P2_1/c$
a / Å	34.5770(4)	7.9571(3)
b / Å	16.50703(16)	23.6001(8)
c / Å	14.29901(15)	13.0293(5)
α / °	90	90
β / °	97.1631(10)	92.124(4)
γ / °	90	90
Z	4	2
V / Å^3	8097.66(15)	2445.07(16)
D_{calc} / g cm^{-3}	1.606	1.824
Diffractometer type	Oxford Xcalibur Nova	Oxford Xcalibur Sapphire3
Radiation	CuK_α	MoK_α
μ / mm^{-1}	7.730	1.521
Absorption correction	Multi-scans	-
T_{min}, T_{max}	0.462, 1.000	-
Θ range / °	2.97–75.87	4.30–27.00
Range of *h*, *k*, *l*	$43 \geq h \geq -43$ $20 \geq k \geq -18$ $16 \geq l \geq -17$	$10 \geq h \geq -8$ $32 \geq k \geq -22$ $16 \geq l \geq -12$
Reflections collected	20631	10294
Independent reflections	10405	3909
Observed reflections ($I \geq 2\sigma$)	10557	5247
R_{int}	0.0225	0.0283
R (F)	0.0274	0.0490
R_w (F^2)	0.0828	0.1222
Goodness of fit	1.102	1.101
No. of parameters	1055	316
F(000)	1264.0	1336.0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.501, –0.602	0.845, –0.558

Crystallographic data, collection and structure refinement details for 2(**1A**)·3DMF and **1B**·2THF are listed in Table S2, whereas the most important bond lengths are given in Table S3.

In general, both structures are *anti* isomers and confirm the mono- or dicyclopalladation of 4'-(*N,N*-dimethylamino)-4-nitroazobenzene (**1**). Each palladium atom is bonded in a slightly distorted square-planar geometry to four atoms: a carbon atom of the phenyl ring and the azo-nitrogen atom of the azobenzene ligand, and two oxygen atoms of two bridging acetate ligands mutually in *cis* position. The Pd–O bonds *trans* to carbon atoms are significantly longer than those *trans* to azo-nitrogen atoms in accordance with the higher *trans* influence of the aryl carbon as compared to the azo-nitrogen (Table S3).

Complex **1A** crystalizes from a DMF solution in a polar space group *Cc*. Two molecules of monocyclopalladated complex **1A** with opposite helicity and three DMF molecules are found in the asymmetric unit (Figure S2). The molecular structure corresponds to a dinuclear acetato-bridged complex in an *anti* open-book arrangement with nitro and dimethylamino groups lying one above the other. Distances between metal centers, *d*(Pd1a, Pd2a) = 2.8923(4) Å and *d*(Pd1b, Pd2b) = 2.8824(4) Å, are nonbonding and similar to the values reported for related complexes.[8]

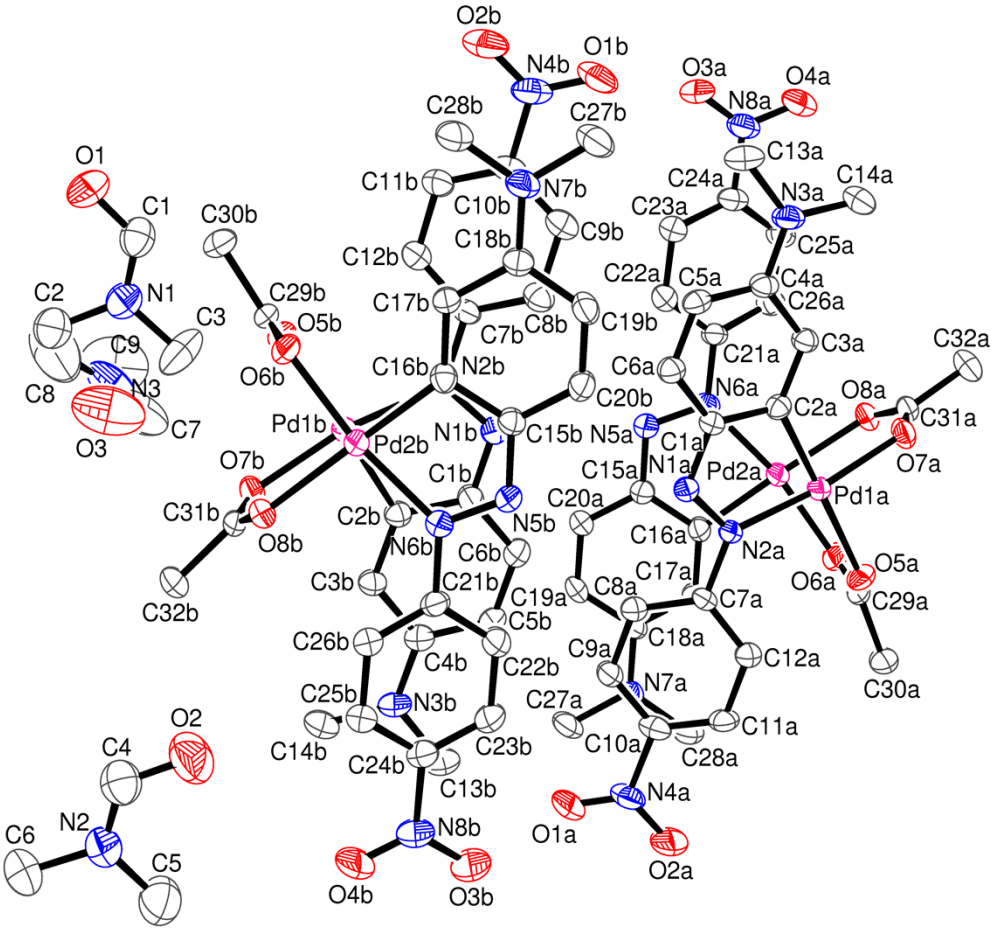


Figure S2. Molecular structure of 2(**1A**)·3DMF. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 30 % probability.

Symmetrically equivalent molecules of **1A** form chains along [010] direction through C–H···O–N interactions that connect dimethylamino groups with nitro groups of the neighbouring molecule. Symmetrically non-equivalent chains of **1A** are connected along the [100] direction by numerous C–H···O–N interactions of phenyl or dimethylamino groups with nitro groups on the „hydrophobic" side, and by C–H···O interactions of DMF methyl groups with nitro and phenyl C–H groups with DMF carbonyl oxygens (Figure S3). Two DMF molecules, through atoms O1 and O2, are connected to two symmetrically non-equivalent **1A** molecules, whereas the third DMF molecule with significantly larger displacement ellipsoids is only loosly bound by C–H···O3(DMF) interactions to methyl groups of two other DMF molecules (Figures S2 and S3). Furthermore, chains of symmetrically equivalent **1A** molecules are connected along the [001] direction by $\pi\cdots\pi$ interactions between phenyl and cyclopalladated rings.

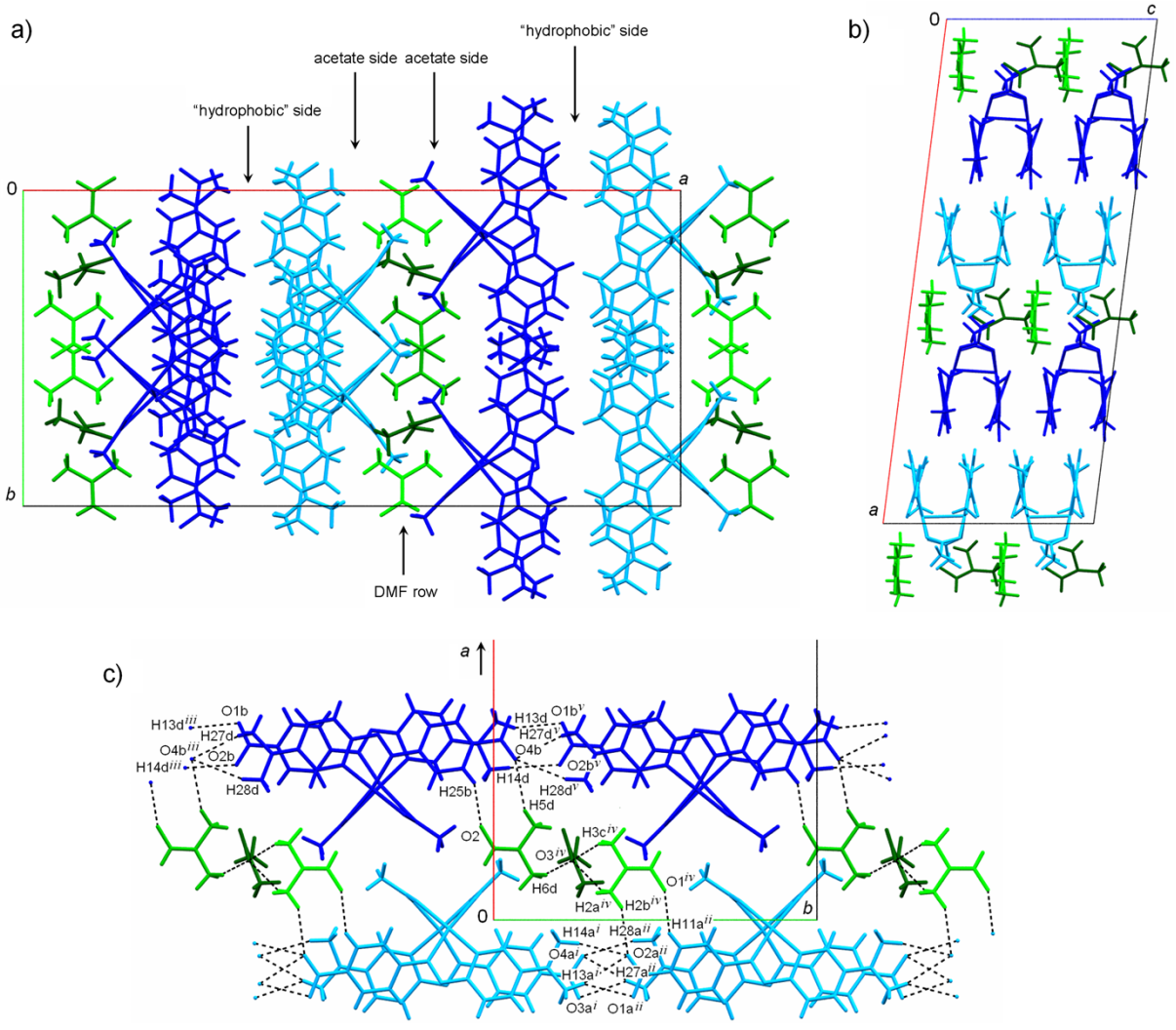


Figure S3. Packing of 2(**1A**)·3DMF. View on the packing along a) [001] and b) [010] direction; c) Details of DMF layer interactions with the acetate side of two symmetrically non-equivalent rows of **1A** viwed along [001] direction. Coloring is by symmetry equivalence. Symmetry operators are: *i* [-1/2+*x*, -1/2-*y*, -1/2+*z*], *ii* [-1/2+*x*, 1/2-*y*, -1/2+*z*], *iii* [*x*, -1+*y*, *z*], *iv* [*x*, -*y*, -1/2+*z*] and *v* [*x*, 1+*y*, *z*].

Complex **1B** was crystallized from CH_2Cl_2/THF as a THF disolvate (Figure S4). The molecular structure corresponds to a centrosymmetric tetranuclear acetato-bridged complex. It is a unique *anti* dimer (nitro and dimethylamino groups are on the same side of the molecule) with two dicyclopalladated azobenzene moieties forced by four *cis*-bonded acetate ligands to lie exactly above one another giving the molecule a center of symmetry.

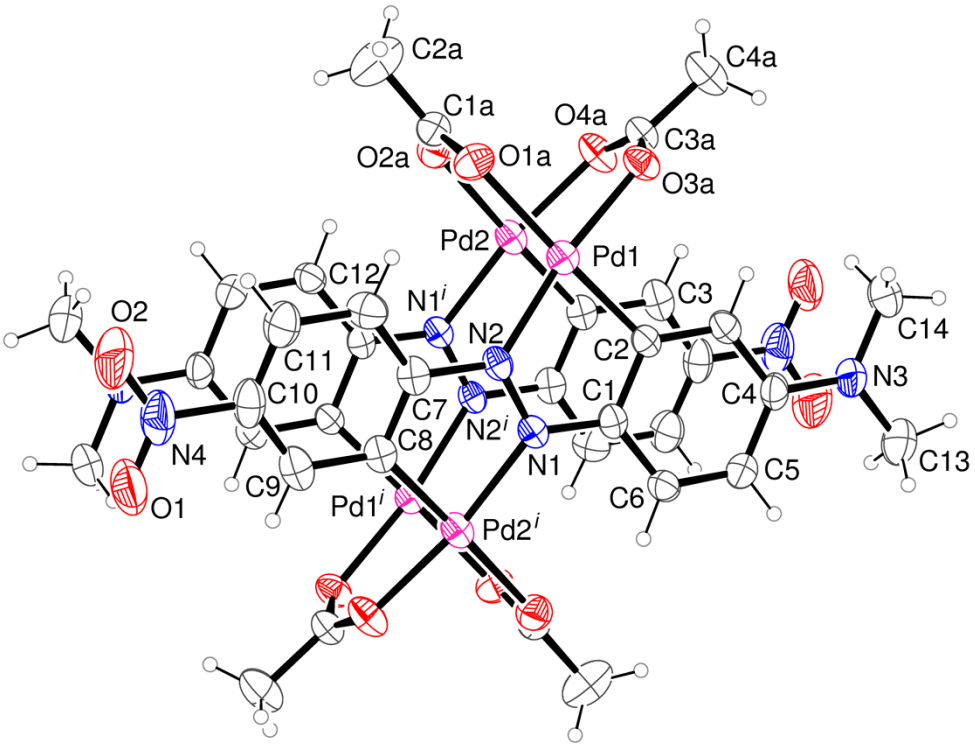
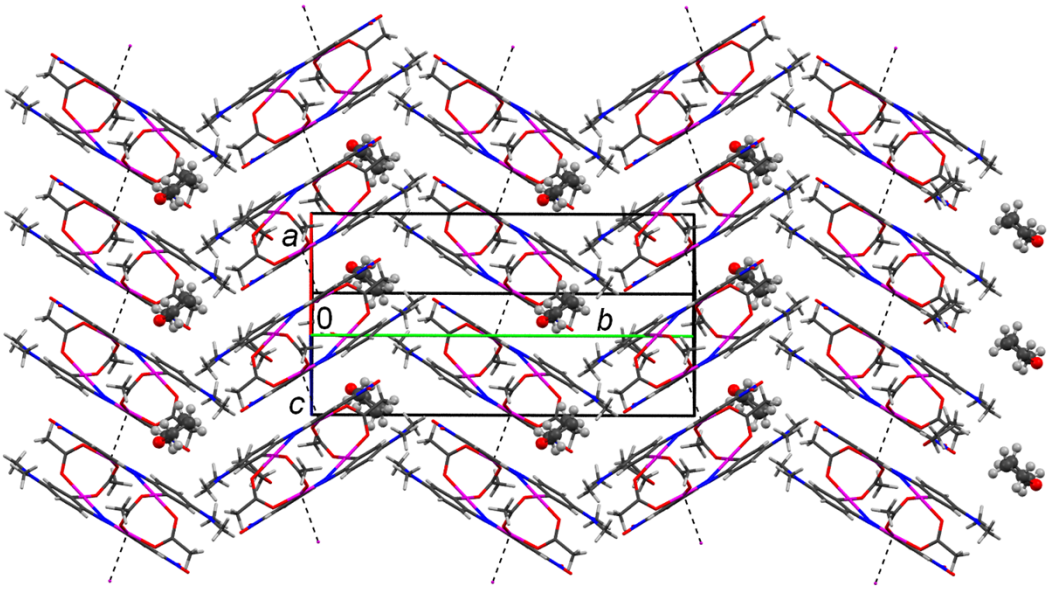
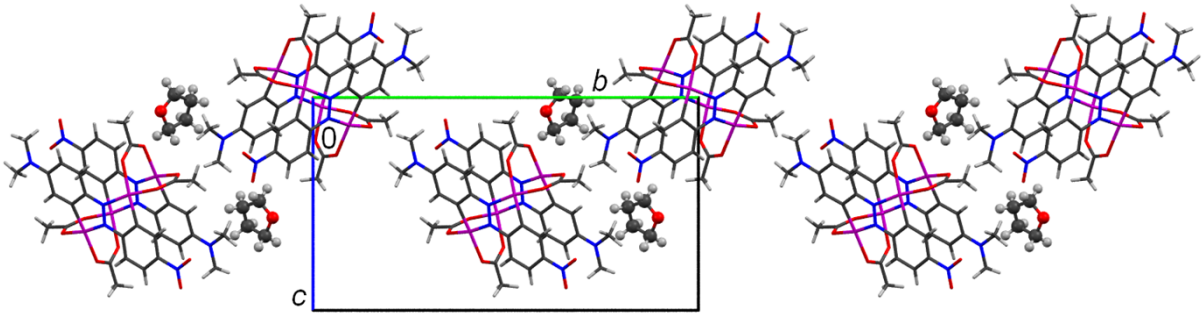


Figure S4. Molecular structure of **1B**. THF molecules are omitted for clarity. Displacement ellipsoids are drawn at 30 % probability. Hydrogen atoms are drawn as circles of arbitrary radii. Symmetry operator *i* [-*x*, 1-*y*, 1-*z*].

Centrosymmetric molecules of **1B** pack in infinite chains (Figure S5) in which two dicyclopalladated molecules are connected by Pd2···Pd2^i interactions (sym. op. *i* [1-*x*, 1-*y*, 1-*z*]) with the distances between the metal centers: *d*(Pd1, Pd2) = 2.8730(6) Å and *d*(Pd2, Pd2^i) = 3.1625(6) Å, *i.e.* shorter than a sum of two van der Waals radii of palladium atoms, indicating the interaction between the palladium atoms in two neighbouring molecules. These interactions form rows of dicyclopalladated molecules. Rows are connected by numerous weak C–H···O interactions of methyl and acetate groups. THF molecules are weakly bound in the crystal structure as they are not engaged in any interaction.



(a)



(b)

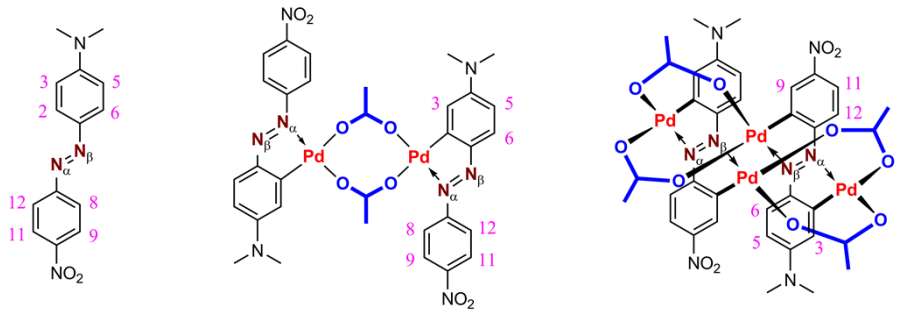
Figure S5. a) Packing of **1B**·2THF; b) view on the packing along the [100] direction. Interactions Pd2···Pd2^{i} are drawn as black stippled lines. THF molecules are drawn using the ball-and-stick style. Distances between the palladium atoms are *d*(Pd1, Pd2) = 2.8730(6) Å and *d*(Pd2, Pd2^{i}) = 3.1627(6) Å. Symmetry operator *i* [1-*x*, 1-*y*, 1-*z*].

Table S3
Selected bonds (Å) for 2(**1A**)·3DMF and **1B**·2THF. Sym. op. *i* [1-*x*, 1-*y*, 1-*z*] and *ii* [-*x*, 1-*y*, 1-*z*] for **1B**·2THF.

Bond	2(**1A**)·3DMF	Bond	2(**1A**)·3DMF
Pd1a–Pd2a	2.8923(4)	Pd1b–Pd2b	2.8824(4)
Pd1a–C2a	1.964(5)	Pd1b–C2b	1.960(5)
Pd1a–N2a	2.031(4)	Pd1b–N2b	2.039(4)
Pd1a–O5a	2.145(5)	Pd1b–O5b	2.158(4)
Pd1a–O7a	2.055(4)	Pd1b–O7b	2.045(4)
Pd2a–C16a	1.955(5)	Pd2b–C16b	1.961(5)
Pd2a–N6a	2.036(5)	Pd2b–N6b	2.041(5)
Pd2a–O6a	2.046(4)	Pd2b–O6b	2.052(4)
Pd2a–O8a	2.161(4)	Pd2b–O8b	2.155(4)
N1a–N2a	1.307(6)	N1b–N2b	1.305(6)
N1a–C1a	1.353(7)	N1b–C1b	1.344(7)
N2a–C7a	1.418(6)	N2b–C7b	1.420(7)
N3a–C4a	1.356(7)	N3b–C4b	1.353(7)
N4a–C10a	1.488(7)	N4b–C10b	1.459(7)
N5a–N6a	1.313(7)	N5b–N6b	1.312(6)
N5a–C15a	1.345(7)	N5b–C15b	1.355(7)
N6a–C21a	1.426(7)	N6b–C21b	1.424(7)
N7a–C18a	1.363(7)	N7b–C18b	1.344(7)
N8a–C24a	1.462(7)	N8b–C24b	1.476(9)

Bond	**1B**·2THF
Pd1–Pd2	2.8730(6)
Pd2–Pd2^{i}	3.1627(6)
Pd1–C2	1.947(5)
Pd1–N2	2.026(4)
Pd1–O1a	2.129(4)
Pd1–O3a	2.069(4)
Pd2–C8^{ii}	1.950(5)
Pd2–N1^{ii}	2.041(4)
Pd2–O2a	2.144(4)
Pd2–O4a	2.040(4)
N1–N2	1.311(6)
N1–C1	1.347(6)
N2–C7	1.406(6)
N3–C4	1.358(7)
N4–C10	1.470(11)

NMR SPECTROSCOPY



Scheme S1. Atom numbering of **1** and its complexes **1A** and **1B** used for ^{1}H NMR assignation.

Table S4
^{1}H NMR data (δ / ppm, J / Hz, $CDCl_3$) for ligand **1** and its complexes **1A** and **1B**.

1		**1A**		**1B**	
H-2,6	7.91 d (*J*=9.2)	H-3	5.61 d (*J*=2.4)	H-3	5.98 d (*J*=2.6)
H-3,5	6.76 d (*J*=9.2)	H-5	6.36 dd (*J*=9.0, 2.5)	H-5	6.03 dd (*J*=9.4, 2.5)
H-8,12	8.32 d (*J*=9.1)	H-6	7.55 (*J*=9.0)	H-6	7.61 d (*J*=8.9)
H-9,11	7.92 d (*J*=9.1)	H-8,12	7.49 d (*J*=9.0)	H-9	7.47 s
		H-9,11	7.92 d (*J*=9.0)	H-11	7.48 dd (*J*~10.0)
				H-12	7.73 d (*J*~9.6)

RAMAN MONITORING

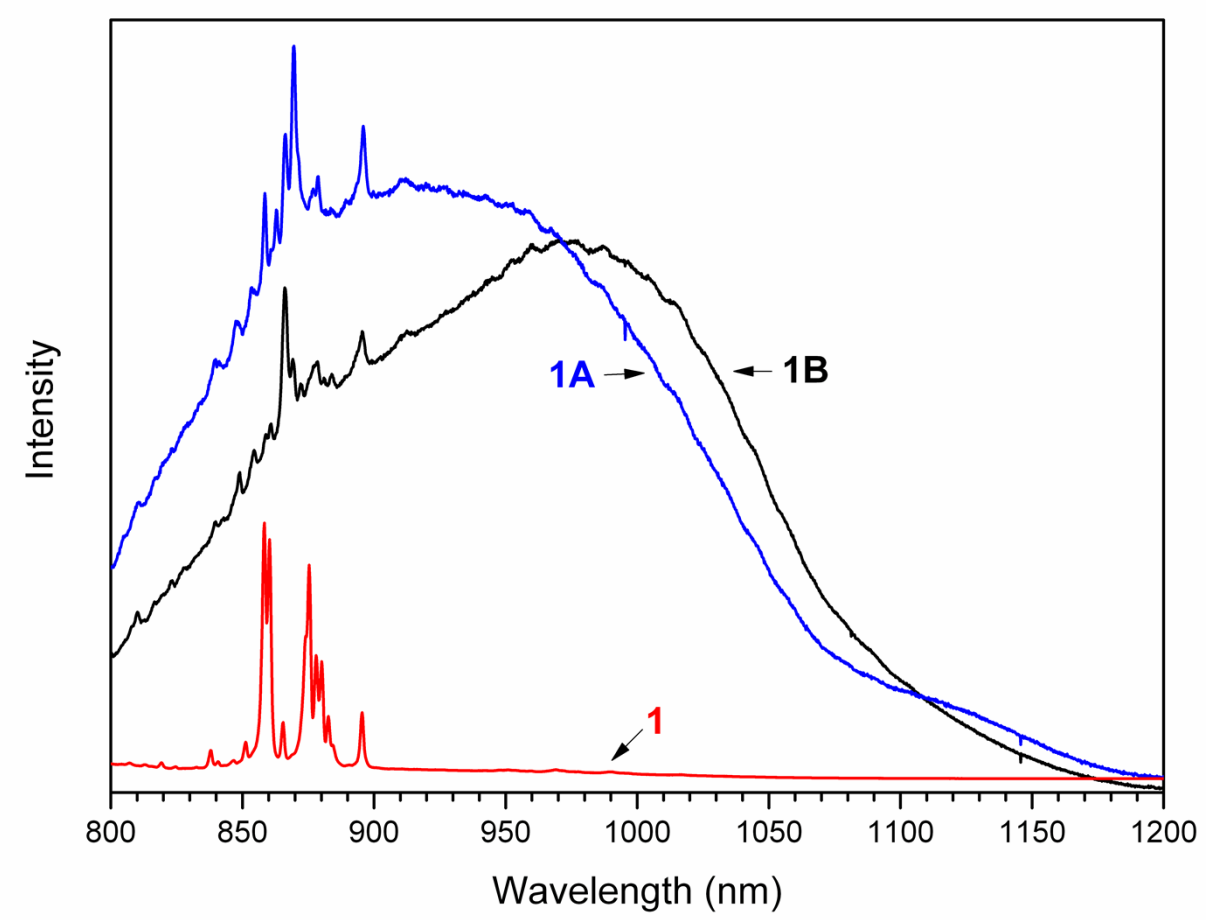


Figure S6. Raman spectra of **1**, **1A** and **1B** with shown luminescence bands. Excitation wavelength (λ_{exc}) was 784 nm.

COMPUTATIONAL DETAILS

Full geometry optimizations and vibrational calculations were performed using the B3LYP[9](ultrafine) method as implemented in Gaussian09 program.[10] The standard 6-311G** basis set was used for C, H, N and O atoms, whereas Pd atoms were modeled by the Stuttgart−Dresden (SDD) pseudopotential and the accompanying SDD basis set.[11]

Optimized geometries

Ligand 1 – C_s symmetry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.807697	2.892860	0.000000
2	6	0	-1.328932	0.966136	0.000000
3	6	0	-2.456319	0.122788	0.000000
4	6	0	-1.535970	2.353234	0.000000
5	6	0	-3.948612	2.052560	0.000000
6	6	0	-3.729823	0.646783	0.000000
7	6	0	1.752951	-2.498152	0.000000
8	6	0	1.529369	-1.114400	0.000000
9	6	0	3.043433	-3.006443	0.000000
10	6	0	2.625454	-0.233724	0.000000
11	6	0	4.110842	-2.113940	0.000000
12	6	0	3.916227	-0.731983	0.000000
13	1	0	-2.920073	3.967509	0.000000
14	1	0	-2.301571	-0.948088	0.000000
15	1	0	0.892907	-3.156043	0.000000
16	1	0	-0.665240	2.998420	0.000000
17	1	0	-4.571442	-0.031606	0.000000
18	1	0	3.239147	-4.069328	0.000000
19	1	0	2.437563	0.830869	0.000000
20	1	0	4.777525	-0.078588	0.000000
21	7	0	0.174457	-0.714084	0.000000
22	7	0	-0.001707	0.536102	0.000000
23	7	0	-5.217866	2.571788	0.000000
24	6	0	-5.420715	4.013075	0.000000
25	1	0	-4.983036	4.484344	0.887638
26	1	0	-4.983036	4.484344	-0.887638
27	1	0	-6.488443	4.223039	0.000000
28	6	0	-6.377056	1.690875	0.000000
29	1	0	-6.399544	1.048494	-0.887755
30	1	0	-6.399544	1.048494	0.887755
31	1	0	-7.282378	2.294665	0.000000
32	7	0	5.486444	-2.643317	0.000000
33	8	0	6.407564	-1.835280	0.000000
34	8	0	5.628684	-3.860308	0.000000

HF=-911.4633943
ZeroPoint=0.2651932
Thermal=0.2831887

Monocyclopalladated complex 1A – no symmetry constraints

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.437020	1.119465	-1.505703
2	46	0	0.437017	1.119707	1.505528
3	8	0	-1.668000	2.677720	-0.881763
4	8	0	1.667990	2.677869	0.881335
5	8	0	1.232094	2.511170	-1.328348
6	8	0	-1.232111	2.511369	1.327947
7	7	0	0.518465	-0.616812	-2.141177
8	7	0	-0.518459	-0.616464	2.141289
9	6	0	-2.515918	-2.375282	-2.496674
10	1	0	-2.179245	-3.357410	-2.808007
11	7	0	-0.236879	-1.635566	-2.367242
12	6	0	2.398154	-2.153997	-1.805215
13	1	0	1.698145	-2.950968	-1.599304
14	6	0	-3.853483	-2.106497	-2.347557
15	1	0	-4.574246	-2.887193	-2.540182
16	7	0	0.236885	-1.635178	2.367524
17	6	0	1.905099	-0.879901	-2.136560
18	7	0	-5.619236	-0.541963	-1.787337
19	6	0	-3.311679	0.200637	-1.696436
20	1	0	-3.615422	1.190933	-1.391398
21	6	0	-2.398140	-2.153696	1.805527
22	1	0	-1.698128	-2.950690	1.599722
23	6	0	-6.070007	0.794054	-1.403745
24	1	0	-7.156840	0.805595	-1.379474
25	1	0	-5.730587	1.547244	-2.121005
26	1	0	-5.709256	1.069229	-0.408329
27	6	0	-2.797506	0.163415	2.419921
28	1	0	-2.409277	1.137492	2.679896
29	6	0	2.797509	0.163033	-2.419923
30	1	0	2.409277	1.137074	-2.680030
31	8	0	6.454964	-2.611706	-1.382975
32	6	0	2.515926	-2.374868	2.497079
33	1	0	2.179256	-3.356945	2.808575
34	6	0	-1.970726	-0.068232	-1.830172
35	7	0	5.619240	-0.541662	1.787423
36	6	0	4.163537	-0.048388	-2.324201
37	1	0	4.870276	0.743712	-2.527797
38	6	0	4.293002	-0.807573	1.942155
39	6	0	3.853491	-2.106106	2.347912
40	1	0	4.574256	-2.886769	2.540663
41	8	0	6.806028	-0.522223	-1.848706
42	6	0	-1.555647	-1.372701	-2.241216
43	6	0	1.785129	3.037213	-0.330891
44	6	0	-6.621861	-1.587956	-1.983770
45	1	0	-7.607481	-1.169744	-1.794758
46	1	0	-6.474569	-2.417719	-1.286332
47	1	0	-6.602546	-1.973602	-3.008340
48	6	0	4.631574	-1.302915	-1.939363
49	6	0	3.760764	-2.365941	-1.702656
50	1	0	4.160810	-3.327119	-1.413030
51	6	0	-1.905092	-0.879554	2.136702
52	6	0	-4.292998	-0.807897	-1.942017
53	6	0	-3.760749	-2.365660	1.702993
54	1	0	-4.160791	-3.326877	1.413495
55	6	0	3.311681	0.200919	1.696409

56	1	0	3.615420	1.191165	1.391202
57	6	0	-4.631563	-1.302605	1.939557
58	6	0	1.970729	-0.067930	1.830195
59	6	0	-1.785149	3.037251	0.330407
60	6	0	1.555654	-1.372331	2.241457
61	6	0	6.070007	0.794287	1.403591
62	1	0	7.156840	0.805824	1.379305
63	1	0	5.730595	1.547604	2.120722
64	1	0	5.709246	1.069287	0.408129
65	6	0	-4.163532	-0.048024	2.324225
66	1	0	-4.870275	0.744101	2.527711
67	6	0	2.694343	4.224136	-0.593028
68	1	0	3.447420	3.950176	-1.335134
69	1	0	3.174864	4.563808	0.322556
70	1	0	2.100533	5.035830	-1.019669
71	6	0	6.621866	-1.587624	1.984019
72	1	0	7.607487	-1.169439	1.794952
73	1	0	6.474578	-2.417494	1.286705
74	1	0	6.602545	-1.973116	3.008646
75	6	0	-2.694395	4.224190	0.592359
76	1	0	-2.100658	5.035894	1.019078
77	1	0	-3.447595	3.950248	1.334349
78	1	0	-3.174776	4.563828	-0.323311
79	8	0	-6.454949	-2.611481	1.383355
80	7	0	-6.067112	-1.494107	1.716472
81	8	0	-6.806019	-0.521932	1.848783
82	7	0	6.067123	-1.494380	-1.716254

HF=-2534.8174189
ZeroPoint=0.6162013
Thermal=0.6662483

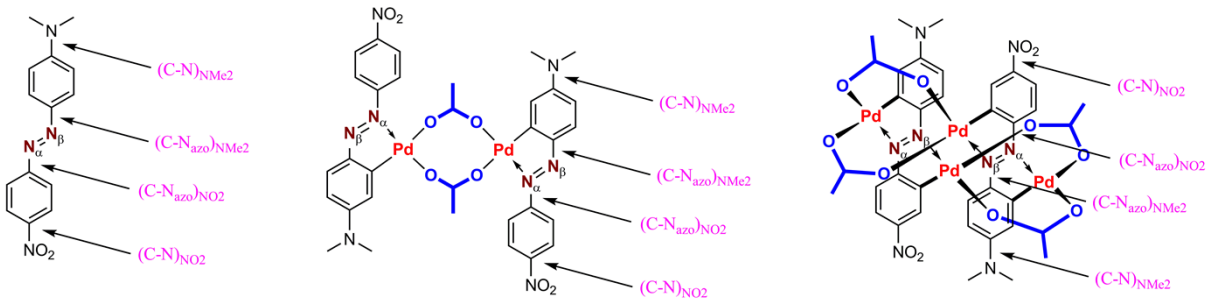
Dicyclopalladated complex 1B – C_i symmetry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.186748	-3.018293	1.066785
2	8	0	-3.017064	-3.086381	-1.191629
3	6	0	-3.557108	-3.379057	-0.086863
4	6	0	-4.808130	-4.230820	-0.165944
5	1	0	-4.664581	-5.029651	-0.893844
6	1	0	-5.635786	-3.608661	-0.518130
7	1	0	-5.057238	-4.641535	0.810634
8	7	0	-0.283298	0.668689	1.882131
9	7	0	0.062143	-0.595802	1.924073
10	6	0	-1.626857	0.887569	1.870181
11	7	0	-5.771526	1.374735	1.797682
12	6	0	2.265852	0.340188	1.900599
13	6	0	-2.475329	-0.256879	1.774204
14	6	0	1.436048	-0.799158	2.017645
15	6	0	-3.837682	-0.092386	1.771514
16	1	0	-4.463554	-0.966056	1.669806
17	6	0	-2.188671	2.180336	1.971404
18	1	0	-1.538019	3.041376	2.041394
19	6	0	1.973486	-2.077341	2.233664
20	1	0	1.315301	-2.928589	2.336112
21	6	0	3.639375	0.173824	1.952576

22	1	0	4.309048	1.014547	1.850117
23	6	0	-4.423265	1.207738	1.846403
24	6	0	-3.550967	2.335055	1.958123
25	1	0	-3.960217	3.331813	2.028257
26	6	0	3.349264	-2.234370	2.267129
27	1	0	3.801705	-3.206185	2.401280
28	7	0	5.614371	-1.297797	2.012211
29	6	0	4.161982	-1.112403	2.104298
30	6	0	-6.353768	2.711692	1.679929
31	1	0	-7.437443	2.622094	1.677693
32	1	0	-6.051824	3.198950	0.746926
33	1	0	-6.067692	3.343537	2.524639
34	8	0	6.320158	-0.297793	1.892128
35	6	0	-6.667055	0.230110	1.628538
36	1	0	-7.687295	0.553883	1.824594
37	1	0	-6.422711	-0.559932	2.340118
38	1	0	-6.622466	-0.171069	0.609875
39	8	0	6.053414	-2.445574	2.026373
40	46	0	-1.275743	-1.993225	-1.517609
41	46	0	-1.470046	-1.923858	1.514323
42	8	0	-0.369799	-3.764760	1.210432
43	8	0	-0.199537	-3.812808	-1.038631
44	6	0	-0.042565	-4.303313	0.115601
45	6	0	0.644854	-5.654273	0.197013
46	1	0	0.317070	-6.196837	1.083010
47	1	0	1.724341	-5.491377	0.277100
48	1	0	0.453985	-6.235427	-0.704510
49	8	0	3.186748	3.018293	-1.066785
50	8	0	3.017064	3.086381	1.191629
51	6	0	3.557108	3.379057	0.086863
52	6	0	4.808130	4.230820	0.165944
53	1	0	4.664581	5.029651	0.893844
54	1	0	5.635786	3.608661	0.518130
55	1	0	5.057238	4.641535	-0.810634
56	7	0	0.283298	-0.668689	-1.882131
57	7	0	-0.062143	0.595802	-1.924073
58	6	0	1.626857	-0.887569	-1.870181
59	7	0	5.771526	-1.374735	-1.797682
60	6	0	-2.265852	-0.340188	-1.900599
61	6	0	2.475329	0.256879	-1.774204
62	6	0	-1.436048	0.799158	-2.017645
63	6	0	3.837682	0.092386	-1.771514
64	1	0	4.463554	0.966056	-1.669806
65	6	0	2.188671	-2.180336	-1.971404
66	1	0	1.538019	-3.041376	-2.041394
67	6	0	-1.973486	2.077341	-2.233664
68	1	0	-1.315301	2.928589	-2.336112
69	6	0	-3.639375	-0.173824	-1.952576
70	1	0	-4.309048	-1.014547	-1.850117
71	6	0	4.423265	-1.207738	-1.846403
72	6	0	3.550967	-2.335055	-1.958123
73	1	0	3.960217	-3.331813	-2.028257
74	6	0	-3.349264	2.234370	-2.267129
75	1	0	-3.801705	3.206185	-2.401280
76	7	0	-5.614371	1.297797	-2.012211
77	6	0	-4.161982	1.112403	-2.104298
78	6	0	6.353768	-2.711692	-1.679929
79	1	0	7.437443	-2.622094	-1.677693
80	1	0	6.051824	-3.198950	-0.746926
81	1	0	6.067692	-3.343537	-2.524639
82	8	0	-6.320158	0.297793	-1.892128

83	6	0	6.667055	-0.230110	-1.628538
84	1	0	7.687295	-0.553883	-1.824594
85	1	0	6.422711	0.559932	-2.340118
86	1	0	6.622466	0.171069	-0.609875
87	8	0	-6.053414	2.445574	-2.026373
88	46	0	1.275743	1.993225	1.517609
89	46	0	1.470046	1.923858	-1.514323
90	8	0	0.369799	3.764760	-1.210432
91	8	0	0.199537	3.812808	1.038631
92	6	0	0.042565	4.303313	-0.115601
93	6	0	-0.644854	5.654273	-0.197013
94	1	0	-0.317070	6.196837	-1.083010
95	1	0	-1.724341	5.491377	-0.277100
96	1	0	-0.453985	6.235427	0.704510

HF=-3246.6837057
ZeroPoint=0.7010537
Thermal=0.7629919



Scheme S2. Bond denotation for Raman assignation.

Table S5

Experimental (d_{exp}) and calculated (d_{calc}) bond lengths (in Å) for **1**, **1A** and **1B**.

	1		**1A**		**1B**	
	d_{exp}[a]	d_{calc}	d_{exp}[b]	d_{calc}	d_{exp}[b]	d_{calc}
d(N=N)	1.258(6), 1.271(15)	1.262	1.305(6)-1.313(7)	1.288	1.311(6)	1.312
d(C–N_{azo})$_{NMe2}$	1.400(5), 1.412(14)	1.395	1.344(7)-1.355(7)	1.351	1.347(6)	1.361
d(C–N_{azo})$_{NO2}$	1.422(6), 1.422(13)	1.413	1.418(6)-1.426(7)	1.411	1.406(6)	1.392

[a] Data collected at 150(2) K.[12]
[b] Data collected at 298(2) K.

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