Electronic Supporting Information

Formation of a Dimeric Tungsten (I) Complex via C-H activation

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NMR spectra

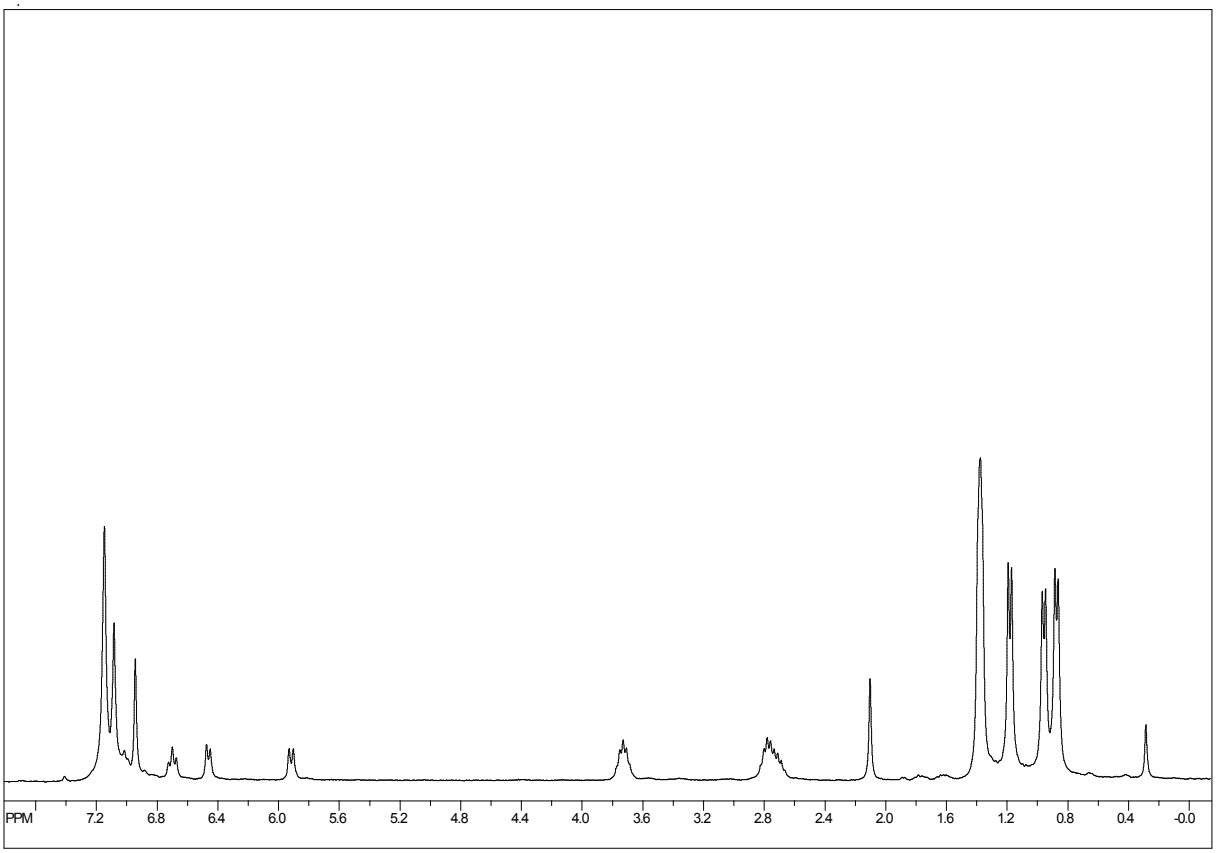

Figure S1. ^{1}H NMR spectrum of **2**.

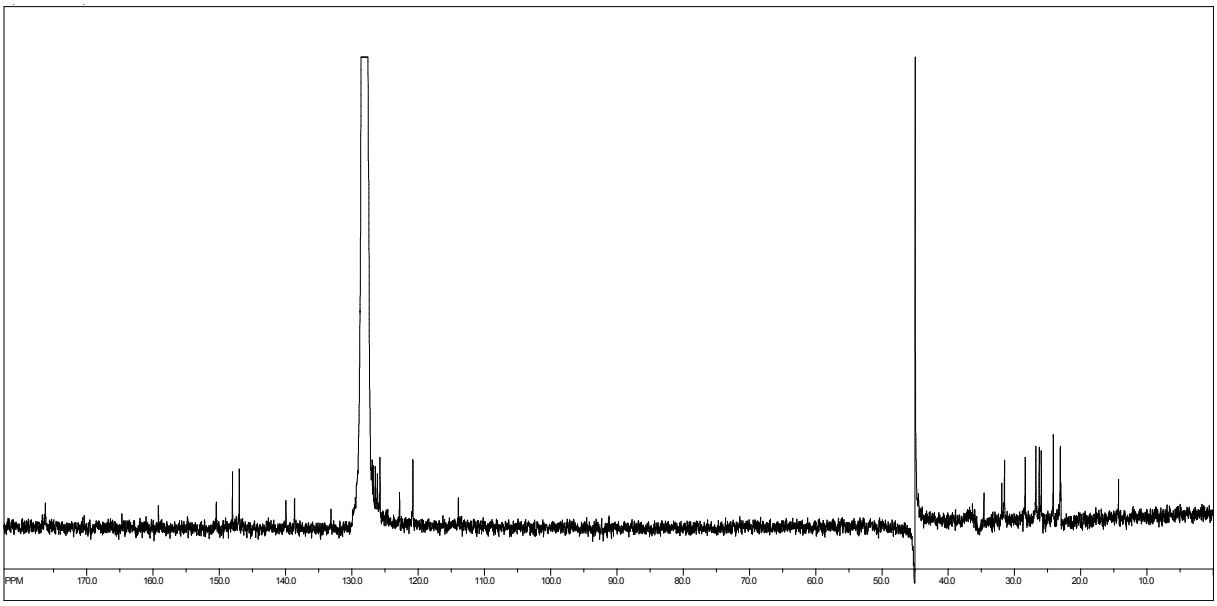

Figure S2. ^{13}C NMR spectrum of **2** (peak at 45 ppm is a spike).

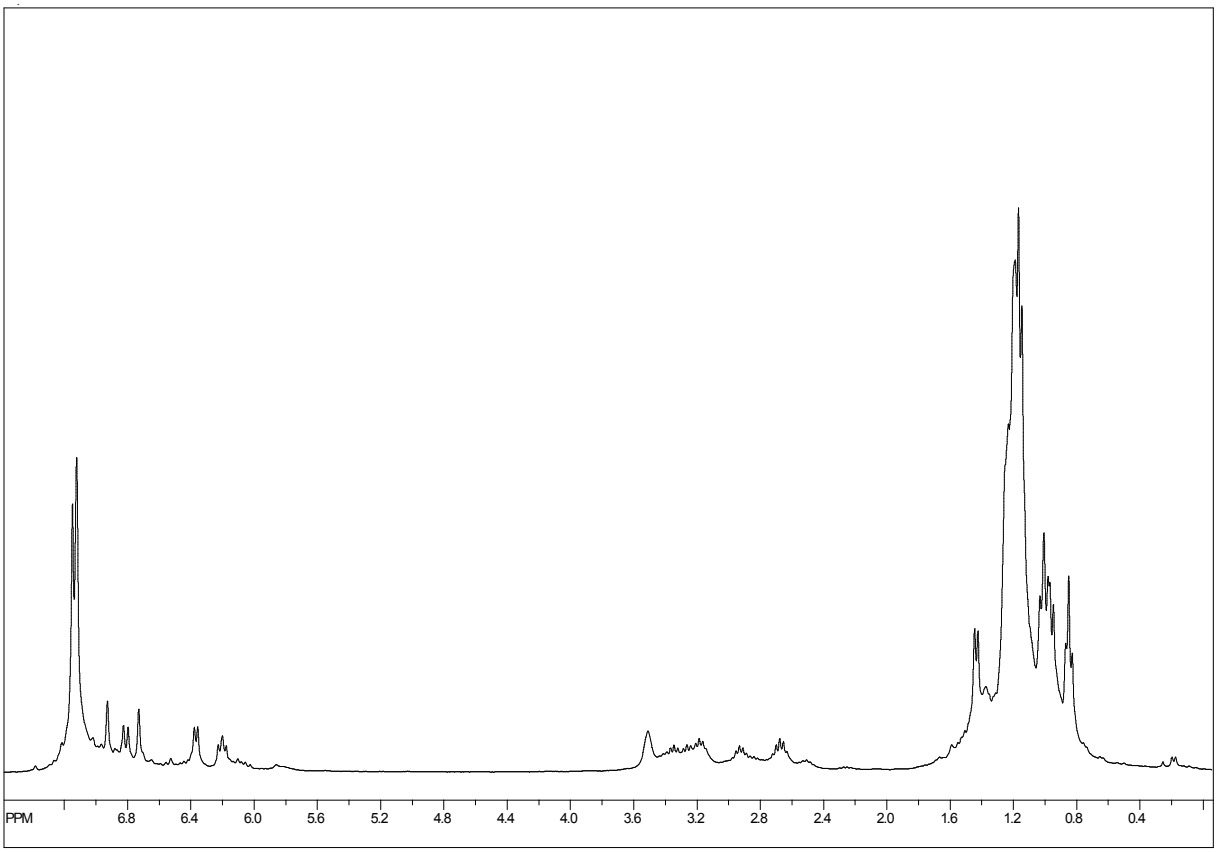

Figure S3. ^{1}H NMR spectrum of **3**.

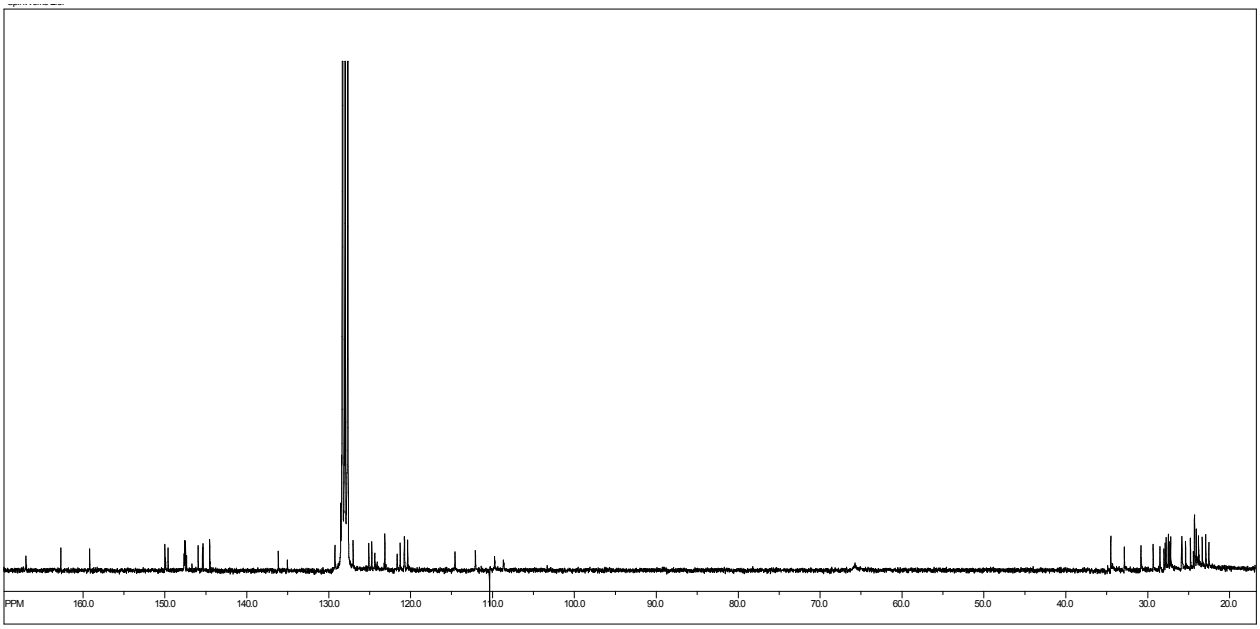

Figure S4. ^{13}C NMR spectrum of **3**.

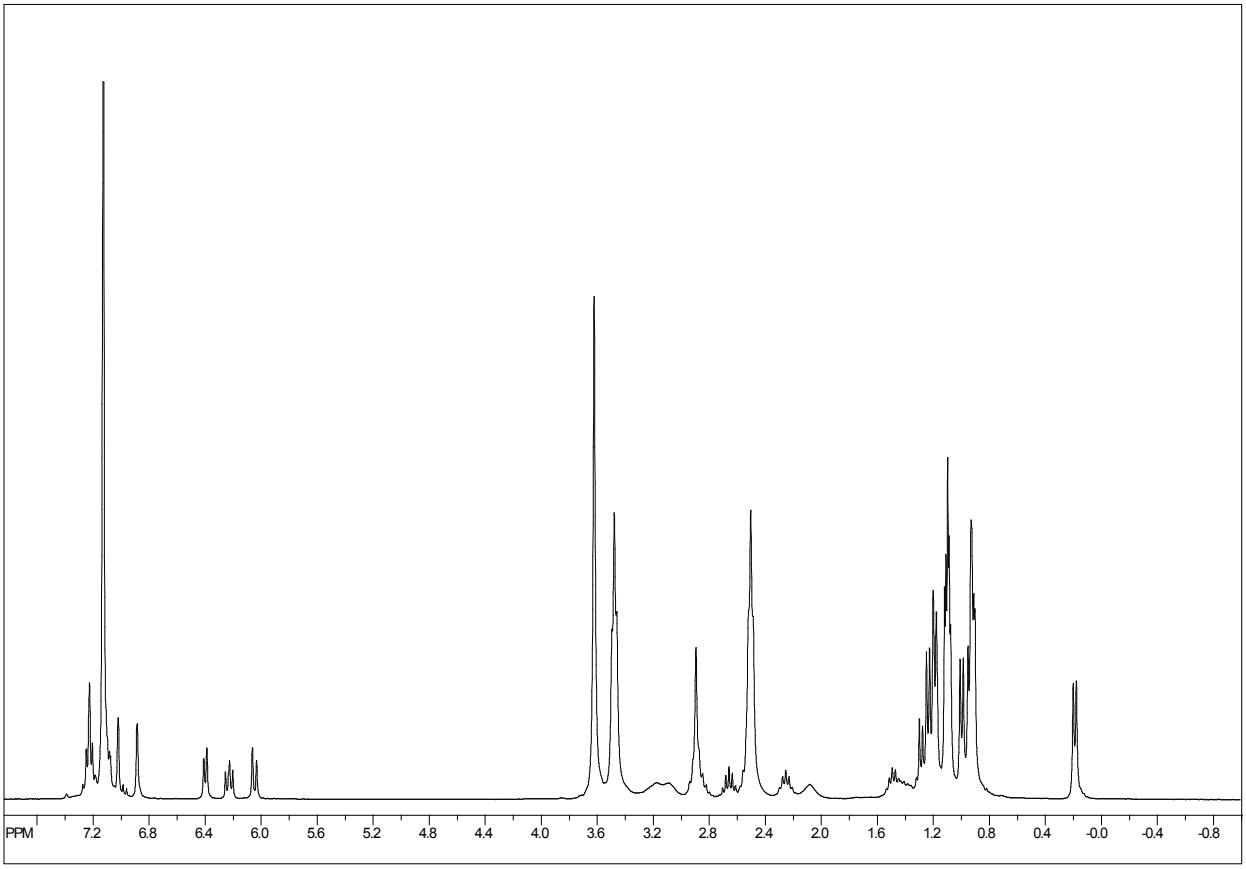

Figure S5. ^{1}H NMR spectrum of **4**.

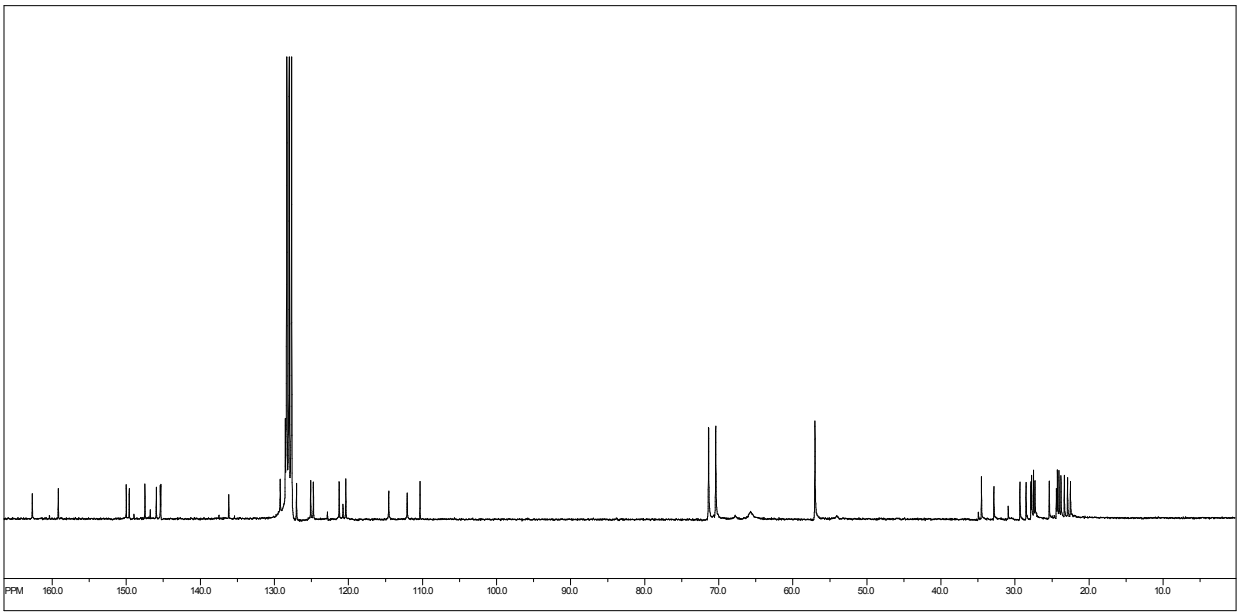

Figure S6. ^{13}C NMR spectrum of **4**.

Computational methods

Density functional theory (DFT) calculations were performed with the *TURBOMOLE*[1] program package. The RI-DFT method[2] applying the BP86 functional[3] with the m5 grid and *Grimme`s*[4] dispersion correction (DFT-D3) was used for all calculations. The geometry was optimized applying the triple zeta basis set def2-TZVP[5] for all atoms and the def2-ecp effective core potential for W[6].

Table S1: Comparison of calculated geometries of **3** and **4** and results of X-Ray diffraction.

Compound	W(1)-W(2) [Å]	W(1)-N(1) [Å]	W(2)-N(2) [Å]	W(1)-C(8) [Å]	W(2)-H [Å]
3 (calculated)	2.198	2.136	2.101	-	-
3 (X-ray)	2.207	2.104	2.081	-	-
4 (calculated)	2.234	2.110	2.137	2.217	1.734
4 (X-ray)	2.228	2.175	2.087	2.314	-

Table 2: Energies (in E_h).of the LUMO and first six HOMOs of **3** and **4**.

Orbital	Energy (**3**)	Energy (**4**)
LUMO	0.133679	0.148171
HOMO	0.104161	0.103682
HOMO-1	0.073048	0.063816
HOMO-2	0.043558	0.007508
HOMO-3	0.013376	0.001554
HOMO-4	0.009525	-0.008771
HOMO-5	-0.002148	-0.011761

DFT geometry of 3

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W	21.3952030	7.9039230	26.5265415
N	23.6770250	9.3284728	25.0078368
N	21.4298116	8.8120012	24.6322490
C	18.9698576	8.7750413	24.4342968
C	20.4216236	9.1127779	22.4320987
H	19.5079182	9.1090868	21.8281218
C	21.6564184	9.5106587	21.8832796
C	22.7579735	9.6327630	22.7500716
C	20.3170956	8.8357689	23.7910128
C	25.9922620	9.6706257	24.2533493
C	16.2649050	8.8663432	25.3164855
C	14.8120344	8.9461015	25.7656860
H	14.7220092	9.8376328	26.4158062
C	19.3037003	11.2157071	25.1605379
H	20.3096606	10.9727767	24.7922305
C	18.1368076	7.6304133	24.3249506
C	24.7680923	10.1864449	24.7467843
C	26.5881152	8.0028174	22.4292469
H	27.6241749	8.3690688	22.2890530
H	26.5771801	6.9280603	22.1629817
H	25.9371913	8.5383922	21.7140899
C	18.4440649	9.9614470	25.0192881
C	26.0987378	8.2003196	23.8740913
H	25.0811410	7.7843175	23.9462551
C	24.6468794	11.5702222	25.0510865
C	16.8029235	7.7049062	24.7564613
H	16.1732798	6.8131651	24.6658051
C	18.7682874	12.3650241	24.2885008
H	18.7048843	12.0535650	23.2296863
H	19.4413068	13.2423382	24.3476074
H	17.7592166	12.6876095	24.6109220
C	27.0971871	10.5282243	24.1408469
H	28.0553929	10.1281594	23.7891003
C	18.1730736	5.8901576	22.4699954
H	17.0723005	5.7647880	22.4879996
H	18.6184089	4.9303874	22.1397443
H	18.4154971	6.6604787	21.7155893

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H	16.7117901	10.9025777	25.8877834
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C	23.3248660	12.1398358	25.5581697
H	22.5788483	11.3337048	25.5066735
C	13.8670622	9.1579989	24.5655816
H	14.1529594	10.0602669	23.9950755
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H	13.9243227	8.2958078	23.8743572
C	25.7737659	12.3925893	24.9185155
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H	28.0114305	7.8069671	24.8822624
C	22.8172429	13.2920024	24.6760039
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H	21.8226760	13.6313701	25.0230507
H	23.4977539	14.1660514	24.6991391
C	18.7062329	6.2989427	23.8532081
H	19.7975371	6.4355690	23.7561296
C	19.4700029	11.6362407	26.6295374
H	20.1412914	12.5129108	26.7041492
H	19.9301464	10.8083280	27.2010437
H	18.5027020	11.9060699	27.0963615
C	18.4818436	5.1933919	24.9006505
H	18.8775912	5.5022882	25.8849935
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C	14.3671451	7.7313997	26.5996643
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H	22.4437128	12.9487106	27.3871921
H	23.6390619	11.6511173	27.6546239
H	24.1958979	13.3034360	27.2153596
H	21.7453045	9.7738390	20.8236648
H	23.7296834	9.9749411	22.3835052
W	23.4960252	8.4093946	26.9279486
N	21.2143977	6.9851237	28.4467629
N	23.4617904	7.5009233	28.8220875
C	25.9214293	7.5372341	29.0186604
C	24.4706199	7.1981700	31.0216971
H	25.3845511	7.2009881	31.6253373
C	23.2357511	6.8006649	31.5707362
C	22.1338526	6.6797783	30.7042506
C	24.5747051	7.4761662	29.6630236
C	18.8991807	6.6449755	29.2020586
C	28.6233947	7.4488552	28.1273689
C	30.0739390	7.3697317	27.6705487
H	30.1562962	6.4891592	27.0046343
C	25.5875565	5.0962931	28.2930335
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DFT geometry of 4

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N	8.0269841	2.4754344	11.0660887
C	8.3300786	1.6336194	9.9860781
C	9.1099584	0.4934568	10.1780668
C	9.6625991	0.1881607	11.4488970
C	9.4734409	1.1140684	12.4836225
C	8.7257836	2.2689633	12.2573707
N	7.7358672	2.0090519	8.7812543
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H	5.5078697	2.3309817	11.1229955

Refrences:

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