Electronic Supporting Information

The Doubly-Bonded Ditungsten Anion [W₂Cp₂(μ-PPh₂)(NO)₂]⁻: An Entry to the Chemistry of Unsaturated Nitrosyl Complexes.

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General Procedures and Starting Materials. All manipulations and reactions were carried out under an argon (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use.¹ Complex $[W_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_4]$ was prepared as described previously,² and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338-343 K. Filtrations were carried out through diatomaceous earth unless otherwise stated. Chromatographic separations were carried out using jacketed columns refrigerated by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 70-290 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach activity IV. IR stretching frequencies of CO and NO ligands were measured in solution (using CaF₂ windows), are referred to as v(XO) (X = C, N) and are given in wave numbers (cm⁻¹). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (1 H), 100.63 (13 C{ 1 H}), and 121.50 MHz (³¹P{¹H}), at 298 K in CD₂Cl₂ solution unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (¹H, ¹³C) or external 85% aqueous H_3PO_4 solutions (³¹P). Coupling constants (*J*) are given in Hertz.

Preparation of $[W_2Cp_2(\mu-I)(\mu-PPh_2)(CO)_2]$ (1). Neat HBF₄·OEt₂ (90 µL, 0.656 mmol) was added to a solution of complex $[W_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_4]$ (0.350 g, 0.440 mmol) in dichloromethane (20 mL), and the mixture was stirred at room temperature for 5 min to give a black solution which was filtered. The filtrate was concentrated under vacuum to ca. 4 mL and then petroleum ether (10 mL) was added, which caused precipitation of a black solid which was separated from the solution, washed with diethyl ether (4 x 10 mL) and dried under vacuum to give essentially pure $[W_2Cp_2(\mu -$ PPh₂)(CO)₄]BF₄ as a dark brown powder. This solid was then dissolved in 1,2dichloroethane (20 mL) and stirred at room temperature with solid NaI (1.50 g, 10 mmol) for 30 min, then refluxed for 70 min to give a black solution which was filtered using a canula. Removal of the solvent from the filtrate and washing of the residue with petroleum ether (2 x 10 mL) gave compound 1 as a black, air-sensitive powder (0.343 g, 90%). Anal. Calcd for C₂₄H₂₀IO₂PW₂: C, 33.29; H, 2.33. Found: C, 33.57; H, 2.29. ν(CO)(CH₂Cl₂): 1885 (w, sh), 1842 (vs). ¹H NMR: δ 7.90-7.00 (m, 10H, Ph), 5.35 (s, 10H, Cp). ³¹P{¹H} NMR. δ 75.8 (s, J_{PW} = 317). ¹³C{¹H} NMR: δ 231.2 (d, J_{PC} = 6, J_{CW} = 201, WCO), 148.5 [d, J_{CP} = 49, C¹(Ph)], 132.2 [d, J_{CP} = 10, C²(Ph)], 128.6 [d, J_{CP} = 2, $C^{4}(Ph)$], 128.3 [d, $J_{CP} = 11$, $C^{3}(Ph)$], 88.6 (s, Cp).

Preparation of $[W_2Cp_2(\mu-I)(\mu-PPh_2)(NO)_2]$ (2). Nitric oxide (5% in N₂) was gently bubbled for 7 min through a solution of compound 1 (0.343 g, 0.396 mmol) in tetrahydrofuran (20 mL) at 233 K to give an orange solution. Solvent was then removed

under vacuum, and the residue was dissolved in toluene (20 mL) and then refluxed for 30 min to give a yellow-orange solution. After removal of solvent from this solution, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed at 288 K. Elution with dichloromethane/petroleum ether (2/1) gave a yellow-orange fraction yielding, after removal of solvents, compound **2** as a yellow-orange solid (0.250 g, 84%). Anal. Calcd for $C_{22}H_{20}IN_2O_2PW_2$: C, 30.37; H, 2.32; N, 3.22. Found: C, 30.47; H, 2.26; N, 3.19. v(NO)(CH₂Cl₂): 1583 (w, sh), 1561 (vs). ¹H NMR: δ 7.55-7.33 (m, 10H, Ph), 5.40 (d, $J_{HP} = 1$, 10H, Cp). ³¹P{¹H} NMR: δ 147.5 (s, $J_{PW} = 364$).

Preparation of Acetonitrile Solutions of Na[W₂Cp₂(μ-PPh₂)(NO)₂] (3). Sodium amalgam (1 mL of a 0.5% alloy, excess) was added to a suspension of compound **2** (0.250 g, 0.287 mmol) in acetonitrile (20 mL), and the mixture was vigorously stirred at room temperature for 10 min to give a brown solution containing compound **3** as the major species. This solution was separated from the excess amalgam using a canula and was thus ready for further use. The ³¹P{¹H} NMR spectrum of this solution showed no resonances other than that of **3**. v(NO)(MeCN): 1463 (vs). ³¹P{¹H} NMR (MeCN): δ 207.8 (s, *J*_{PW} = 360).

Preparation of [W₂Cp₂(μ-H)(μ-PPh₂)(NO)₂] (4). Solid (NH₄)PF₆ (0.108 g, 0.663 mmol) was added to an acetonitrile solution of compound **3**, prepared as described above, and the mixture was stirred at room temperature for 10 min to give a red solution. After removal of the solvent under vacuum, the residue was dissolved in toluene to give a purple solution which was filtered. Removal of solvent from the filtrate yielded essentially pure compound **4** as a red-brown solid (0.142 g, 66% based on **2**). Further purification of **4** can be achieved upon chromatographic workup on alumina at 253 K using dichloromethane/petroleum ether mixtures. The crystals used in the X-ray diffraction study were grown by the slow diffusion of layers of toluene and petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for C₂₂H₂₁N₂O₂PW₂: C, 35.51; H, 2.84; N, 3.76. Found: C, 35.15; H, 2.45; N, 3.42. ν(NO)(CH₂Cl₂): 1580 (w, sh), 1552 (vs). ¹H NMR: δ 7.80-7.10 (m, 10H, Ph), 5.63 (s, 10H, Cp), -10.79 (s, *J*_{HW} = 145, 1H, μ-H). ³¹P{¹H} NMR: δ 212.8 (s, *J*_{PW} = 375).

Preparation of $[W_2Cp_2H(\mu-PPh_2)(CO)(NO)_2]$ (5). Carbon monoxide was gently bubbled for 1 min through a stirred solution of compound 4 (0.025 g, 0.034 mmol) in dichloromethane (10 mL) at room temperature, and stirring was continued for a further 5 min to yield a yellow-orange solution. After removal of solvent from this solution, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed at 288 K. Elution with dichloromethane/petroleum ether (1/1) gave a yellow-orange fraction yielding, after removal of solvents, compound **5** as a yelloworange solid (0.012 g, 46%). Anal. Calcd for C₂₃H₂₁N₂O₃PW₂: C, 35.78; H, 2.74; N, 3.63. Found: C, 36.15; H, 2.83; N, 3.44. v(CO)(CH₂Cl₂): 1925 (s); v(NO)(CH₂Cl₂): 1634 (m), 1590 (vs). ¹H NMR: δ 7.90-6.60 (m, 10H, Ph), 5.50, 5.44 (2s, 2 x 5H, Cp), -1.09 (d, $J_{HP} = 9$, $J_{HW} = 104$, 1H, W–H). ³¹P{¹H} NMR: δ 118.2 (s, $J_{PW} = 304$, 299).

Preparation of [AuW_2Cp_2(\mu-PPh_2)(NO)_2\{P(p-tol)_3\}] (6). Solid $[AuCl\{P(p-tol)_3\}]$ (0.031 g, 0.058 mmol) was added to an acetonitrile solution of compound 3, prepared from 2 (0.050 g, 0.057 mmol) as described above, and the mixture was stirred at 273 K for 15 min to give a green solution. After removal of solvent from this solution, the residue was extracted with dichloromethane/petroleum ether (1/3) and the extracts were chromatographed at 253 K. Elution with dichloromethane/petroleum ether (2/1) gave a green fraction yielding, after removal of solvents, compound 6 as a green solid (0.028 g, 40% based on 2). The crystals used in the X-ray diffraction study were grown by the slow diffusion of layers of toluene and petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for C44H43N2Cl2AuO2P2W2 (6·CH2Cl2): C, 39.75; H, 3.26; N, 2.11. Found: C, 39.37; H, 3.05; N, 1.79. ν(NO)(CH₂Cl₂): 1535 (w, sh), 1513 (vs). ¹H NMR: δ 7.62-7.20 (m, 22H, Ph and *p*-tol), 5.55 (s, 10H, Cp), 2.40 (s, 9H, Me). ${}^{31}P{}^{1}H{}$ NMR: δ 219.2 (d, $J_{PP} = 6$, ${}^{1}J_{PW} = 316, \mu$ -P), 80.9 (d, $J_{PP} = 6, {}^{2}J_{PW} = 87, Au$ -P).

Preparation of Acetonitrile Solutions of Na[W₂Cp₂(μ-PPh₂)(μ-S)(NO)₂] (7). Solid sulfur (0.0025 g, 0.010 mmol) was added to an acetonitrile solution of compound **3**, prepared from **2** (0.040 g, 0.046 mmol) as described above, and the mixture was stirred at room temperature for 5 min to give a brown solution containing compound **7** as the major species, ready for further use. v(NO)(MeCN): 1485 (vs). ³¹P{¹H} NMR (MeCN): δ 119.5 (s, *J*_{PW} = 362).

Preparation of [W₂Cp₂(μ-PPh₂)(μ-SMe)(NO)₂] (8). Neat Me₂SO₄ (5 μL, 0.053 mmol) was added to an acetonitrile solution of compound **7**, prepared as described above, and the mixture was stirred at room temperature for 5 min to give a brown greenish solution. After removal of solvent from this solution, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed at 253 K. Elution with dichloromethane/petroleum ether (2/1) gave a yellow fraction yielding, after removal of solvents, compound **8** as a yellow solid (0.016 g, 44% based on **2**). Anal. Calcd for C₂₃H₂₃N₂O₂PSW₂: C, 34.96; H, 2.93; N, 3.55; S, 4.05. Found: C, 34.90; H, 3.01; N, 3.54; S, 3.53. v(NO)(CH₂Cl₂): 1575 (w, sh), 1554 (vs). ¹H NMR: δ 7.65-7.25 (m, 10H, Ph), 5.42, 5.36 (2s, 2 x 5H, Cp), 2.50 (s, 3H, Me). ³¹P{¹H} NMR: δ 125.6 (s, *J*_{PW} = 365).

X-Ray Structure Determination of Compounds 4 and 6. X-ray intensity data for these compounds were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated MoK_{α} radiation at 100 K. The software APEX³ was used for collecting frames with ω/ϕ scans measurement method. For compound 6, the Bruker SAINT software was used for data reduction,⁴ and a multi-scan absorption correction was applied with SADABS.⁵ Using the program suite WINGX,⁶ the structure was solved by Patterson interpretation and phase expansion using SHELXL2014,⁷ and refined with full-matrix least squares on F^2 using SHELXL2014. Positional parameters and anisotropic temperature factors for all non-H atoms were refined anisotropically and all hydrogen atoms were geometrically placed and refined using a riding model. This complex was found to crystallize with a dichloromethane molecule disordered over two sites, satisfactorily refined with 0.5 occupancies. The strongest residual peaks for $\mathbf{6}$ after convergence (3.66-1.33 eA^{-3}), were located close the heavier atoms [Au(1), W(1), W(2)] and Cl(3)]. For compound 4, pseudo-merohedral twinning was found to occur in the crystal. The experimental data were treated as two domain twinned data, with fractional contribution of each domain 0.610(2)/0.390(2) and both domains related by a binary axis placed along the *a* axis. The program Cell Now⁸ was used to determine the twin law, the cell dimensions and orientation matrixes, and a multi-scan absorption correction was applied with TWINABS.⁹ The structure was solved as described for **6** except for the bridging hydride. The latter atom could not be located in the final difference map, therefore possible positions were investigated by a potential energy minima search using the program HYDEX.¹⁰ One minimum was found between W(1) and W(2) at approximately 1.85 Å from both tungsten atoms, in agreement with the DFT-computed structure, so this was assigned to the hydride ligand and refined riding on both metal atoms. Further crystallographic data for these compounds are collected in Table S1.

Computational Details. All DFT calculations were carried out using the GAUSSIAN03 package,¹¹ in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional,¹² and the Lee–Yang–Parr correlation functional.¹³ Effective core potentials and their associated double- ζ LANL2DZ basis set were used for the W atoms.¹⁴ The light elements (P, O, N, C and H) were described with the 6-31G* basis.¹⁵ Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of compound **4**. Frequency analyses were performed for all the stationary points to ensure that a minimum structure with no imaginary frequencies was achieved. For interpretation purposes, natural population analysis (NPA) charges were derived from the natural bond order (NBO) analysis of the data.¹⁶ Molecular orbitals and vibrational modes were visualized using

the MOLEKEL program.¹⁷ The topological analysis of ρ was carried out with the *Xaim* routine.¹⁸

	4	6.CH ₂ Cl ₂
mol formula	$C_{22}H_{21}N_2O_2PW_2$	$C_{44}H_{43}AuC_{12}N_2 \\ O_2P_2W_2$
mol wt	744.08	1329.30
cryst syst	monoclinic	monoclinic
space group	$P 2_1/n$	<i>C</i> 2/c
radiation (λ , Å)	0.71073	0.71073
<i>a</i> , Å	10.2924(7)	26.4510(17)
<i>b</i> , Å	16.6964(10)	11.1889(8)
<i>c</i> , Å	12.2534(7)	33.062(2)
α , deg	90	90
β , deg	90.101(2)	111.422(4)
γ, deg	90	90
$V, Å^3$	2105.7(2)	9108.9(11)
Z	4	8
calcd density, g cm ⁻³	2.347	1.939
$absorp coeff, mm^{-1}$	11.014	8.476
temperature, K	100.0(1)	100.0(1)
θ range (deg)	1.22 to 28.35	1.32 to 26.37
index ranges (h, k, l)	-13, 13; -22, 21; -16, 16	-32, 32; -13, 13; -41, 41
no. of reflns	24129	66036
no. of indep reflns (R_{int})	5241 (0.0521)	9294 (0.0772)
refines with $I > 2\sigma(I)$	3553	6277
R indexes [data with $I > 2\sigma(I)$] ^a	$R_1 = 0.0452$ w $R_2 = 0.0964^{\ b}$	$R_1 = 0.0565$ w $R_2 = 0.1190^c$
R indexes (all data) ^{<i>a</i>}	$R_1 = 0.0895$ w $R_2 = 0.12^{b}$	$R_1 = 0.1007$ w $R_2 = 0.1355^c$
GOF	1.027	1.058
restraints/params	326 / 263	0 / 526
$\Delta \rho(\max., \min.),$ eÅ ⁻³	3.844, - 2.536	3.662, -1.759

Table S1. Crystal Data for New Compounds

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. wR = [\Sigma w(|F_{o}|^{2} - |F_{c}|^{2}) / \Sigma w|F_{o}|^{2}]^{1/2}. w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP] \text{ where } P = (F_{o}^{2} + 2F_{c}^{2})/3. {}^{b}a = 0.0420, b = 35.9346. {}^{c}a = 0.0478, b = 282.03.$

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Optimized Structures of Anions 3 and 3B, and Hydride 4.

Table S2. DFT-Optimized Geometries for 3, 3B and 4 (distances in Å, angles in deg.)

	3	3B	4
W26-W27	2.580	2.601	2.724
W26-P	2.439	2.445	2.429
W27–P	2.439	2.444	2.429
W26-N21	1.782	1.993	1.791
W26-N22	_	2.003	_
W27-N21	_	2.003	_
W27-N22	1.782	1.994	1.791
W26-H28	_	_	1.863
W27-H28	_	_	1.864
N21-O23	1.231	1.259	1.208
N22–O24	1.231	1.259	1.208
W26-P-W27	63.9	64.3	68.2
W26-H28-W27	_	_	93.9
W26-W27-N22	97.0		100.1
W27-W26-N21	97.0		99.9
W26-N21-W27	_	81.2	_
W26-N22-W27	_	81.2	_
N21-W26-W27-N22	-171.7	-155.3	-175.9

Table S3: Molecular orbitals of 3

OM Energy (eV) Assignment

LUMO 114

1.96

 $\pi^*{}_{MM}$

HOMO 113

-0.96

 $\pi *_{MM} + \pi_{M\text{-}NO}$



MO 112

-1.21

 π/σ_{MM}

Contributions (%): W(26) 37, W(27) 37, P 5, NO's 5, Other 16



Contributions (%): W(26) 25, W(27) 25, P 1, NO's 39, Other 9

Table S4: Molecula	ar orbitals of 4
OM	
Energy (eV)	
Assignment	
LUMO 114	AT I
-2.04	
$\pi^*{}_{MM}$	TIT FOR
	Contributions (%): W(26) 35, W(27) 35, P 8, NO's 3, H28 0, Other 17
HOMO 113 -4.87 π* _{MM} + π _{M-NO}	
	Contributions (%):W(26) 17, W(27) 17, P 0, NO's 58, H28 0, Other 7
MO 112 -5.34	
O _{MM}	

Contributions (%):W(26) 30, W(27) 30, P 3, NO's 20, H28 0, Other 17



 $\pi_{MM} + \pi_{M\text{-}NO}$

Contributions (%):W(26) 18, W(27) 18, P 9, NO's 18, H28 0, Other 36



Table S5: Cartesian	coordinates for	the optimized	structure of 3

Syı	mbol	Х	Y	Z			
С	-1.54	6619	90	3.6612	250	1.75	78370
Η	-2.28	3304	80	3.0045	570	2.19	97000
С	0.31	6781	0	-0.9752	840	2.36	07530
Η	-0.56	5852	00	-0.994	1540	1.7	405420
С	1.65	3477	0	-0.8630	970	1.89	14680
Η	1.94	0597	0	-0.7335	5270	0.85	62230
С	2.51	3307	0	-0.8556	270	3.02	86130
Η	3.59	0647	0	-0.7528	3650	3.00	55690
С	1.71	3911	0	-0.9916	600	4.19	69420
Η	2.07	1000	0	-1.0061	.090	5.21	90470
С	0.34′	7633	0	-1.0573	000	3.78	68300
Η	-0.50)8944	40	-1.160	9950	4.4	409460
С	-1.31	8298	80	3.8513	160	0.36	03060
Η	-1.85	5792	60	3.3731	710	-0.4	474710
С	-0.63	36604	40	4.4847	690	2.47	44350
Η	-0.54	4090	10	4.5152	2100	3.55	18390
С	-0.25	5697	70	4.7959	390	0.21	73750
Η	0.16	8560	0	5.13576	540	-0.71	84750
С	0.170	0740	0	5.17095	500	1.520)8810
Η	0.97	7675	0	5.85457	750	1.75	15680
Ν	1.12	7720	0	1.60464	420	-0.06	602700
Ν	0.38	0493	0	2.22260)50	4.479	97370
0	1.42	6972	0	0.82448	820	-0.96	647310
0	-0.12	2468:	50	2.9191	310	5.36	606970
Р	2.774	4187	0	2.75028	370	2.428	32430
W	0.65	3805	50	2.7470	730	1.22	26260
W	1.08	9119	90	1.1762	380	3.22	32680
С	3.304	4126	0	4.26814	470	3.343	34490
С	4.250	0633	0	5.14812	250	2.787	74140
С	2.712	2056	0	4.60956	520	4.57	10300
С	4.60	6672	0	6.32672	290	3.443	34260
Н	4.71	4587	0	4.90400	580	1.83	56610

С	3.0642790	5.7967130	5.2199990
Η	1.9621110	3.9610830	5.0112480
С	4.0139950	6.6562180	4.6655100
Η	5.3447720	6.9901210	2.9969610
Η	2.5918750	6.0445210	6.1678990
Η	4.2885460	7.5762170	5.1772210
С	4.3680750	2.1101960	1.7408020
С	5.5340490	2.0914090	2.5278910
С	4.4228010	1.5595250	0.4494650
С	6.7230570	1.5524730	2.0357380
Η	5.5109760	2.5060380	3.5320770
С	5.6136430	1.0110470	-0.0359330
Η	3.5324540	1.5391180	-0.1696090
С	6.7679270	1.0094880	0.7486750
Н	7.6140870	1.5529730	2.6604550
Η	5.6339200	0.5863180	-1.0370650
Η	7.6936570	0.5863540	0.3644770

Table S6: Cartesian coordinates for the optimized structure of 3B

Syı	nbol	Х	Y	Ζ				
С	-1.20	8091	0	3.9	798930	0.3	33466	550
Η	-2.19	95522	20	3.9	798600	0.	77832	290
С	0.53	5236	0	-1.1	504920	3.8	84602	200
Η	-0.06	62646	50	-1.	8090000	3	.2289	620
С	1.96	8243	0	-1.1	004610	3.8	87372	200
Η	2.63	7974	0	-1.6	441440	3.	22080	020
С	2.34	6486	0	-0.1	445450	4.8	85280)60
Η	3.36	2291	0	0.16	579310	5.0	6238	40
С	1.179	9738	0	0.37	35130	5.4	7924	60
Н	1.15	3552	0	1.12	249060	6.2	5726	30
С	0.042	2276	0	-0.2	322110	4.8	85012	220
Η	-0.99	92451	0	-0.	0793210	5	.1289	950
С	-0.71	9224	0	3.0	632450	-0	.6728	580
Η	-1.27	73712	20	2.2	522720	-1	.1274	990
С	-0.17	9693	30	4.9	491390	0.5	57948	390
Η	-0.21	8437	70	5.7	506880	1.	30504	430
С	0.60	53530	0	3.47	90680	-1.0	03135	590
Η	1.25	7214	0	2.98	389330	-1.′	74230	000
С	0.93	1543	0	4.61	30200	-0.2	23791	110
Η	1.88	9478	0	5.11	186480	-0.2	2301	190
N	0.92	7067	0	0.77	772760	1.1	5313	80
N	-0.08	87017	70	2.6	783110	3.	1898	140
0	1.03	1705	0	-0.1	307940	0.2	28752	210
0	-0.81	2858	30	3.3	276610	3.9	98668	880
Р	2.618	35620)	2.64	27040	2.4	1553.	30
W	0.46	52971	0	2.7	125320	1.2	26417	740
W	0.97	2495	50	0.9	897780	3.1	1447()70
С	3.09	6365	0	4.13	819310	3.3	9528	10
С	4.13	8118	0	4.99	942230	3.0	0696	10
С	2.32	5004	0	4.48	858670	4.5	1970	40
С	4.423	3378	0	6.15	520690	3.7	3487	10
Η	4.73	2302	0	4.76	511490	2.1	2831	40
С	2.60	8997	0	5.64	72780	5.2	3865	10
Н	1.47	5344	0	3.87	721700	4.7	9775	10

С	3.6651260	6.4813100	4.8590800
Η	5.2383850	6.7992040	3.4161640
Η	1.9952390	5.9028590	6.0995820
Н	3.8868100	7.3823360	5.4270110
С	4.1800330	2.0152920	1.6577370
С	5.4356120	2.1521120	2.2772900
С	4.1077750	1.2796370	0.4587210
С	6.5854140	1.6036930	1.7031270
Н	5.5184200	2.6910910	3.2163460
С	5.2570870	0.7272190	-0.1065080
Н	3.1412550	1.1025720	-0.0019920
С	6.5038870	0.8947610	0.5042390
Н	7.5454880	1.7292250	2.2002250
Η	5.1747540	0.1579910	-1.0297830
Η	7.3986270	0.4683760	0.0556920

Table S7: Cartesian coordinates for the optimized structure	e of 4	1
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Syr	nbol X Y	Z		
С	-1.4192480	4.1758540	1.7301290	
Н	-2.2339440	3.7687110	2.3151530	
С	0.7463720	-1.2491390	2.4438000	
Η	0.0079240	-1.4816140	1.6872520	
С	2.0883340	-0.8777720	2.1994300	
Н	2.5580160	-0.7845930	1.2300570	
С	2.7053540	-0.6111990	3.4688240	
Η	3.7364440	-0.3220630	3.6188130	
С	1.7418780	-0.8490780	4.4871770	
Н	1.8998750	-0.7425310	5.5526370	
С	0.5144070	-1.2219240	3.8566860	
Η	-0.4087890	-1.4794450	4.3586350	
С	-1.2953890	4.1007310	0.3055680	
Η	-2.0187220	3.6764980	-0.3780860	
С	-0.2786780	4.8309840	2.2485670	
Η	-0.0710800	5.0204470	3.2925910	
С	-0.0684690	4.7399800	-0.0541330	
Η	0.3151000	4.8542060	-1.0597920	
С	0.5720130	5.1674600	1.1412990	
Η	1.5145820	5.6929180	1.2098150	
N	0.9814290	1.7416070	-0.2045380	
N	0.3514890	2.0088420	4.6070580	
0	1.2711450	1.1341990	-1.2072600	
0	-0.0540910	2.5667110	5.5982490	
Р	2.5742620	2.6648830	2.4072940	
W	0.4801090	2.7615140	1.1798060	
W	0.9683460	1.0397040	3.2329070	
Η	-0.4468070	1.4203050	2.0810580	
С	3.1116730	4.1525700	3.3534800	
С	3.9916220	5.0699430	2.7494180	
С	2.6257480	4.4254720	4.6412300	
С	4.3745070	6.2319810	3.4184950	
Η	4.3851070	4.8704240	1.7564960	
С	3.0131870	5.5922260	5.3069290	

Η	1.9419630	3.7393710	5.1259840
С	3.8859730	6.4962360	4.7009420
Н	5.0558090	6.9296340	2.9384770
Η	2.6308550	5.7875970	6.3051720
Н	4.1858560	7.4009010	5.2230280
С	4.1591960	2.0564260	1.6892720
С	5.3009540	1.9819930	2.5087330
С	4.2477700	1.6146720	0.3603240
С	6.5011530	1.4770050	2.0095420
Н	5.2530290	2.3284970	3.5373800
С	5.4537330	1.1092700	-0.1343420
Н	3.3823870	1.6549950	-0.2898660
С	6.5808800	1.0392230	0.6847540
Н	7.3741330	1.4276530	2.6551210
Н	5.5070970	0.7744500	-1.1667630
Н	7.5167190	0.6476150	0.2951760

 Table S8: Mulliken Charges for 3

33 C -0.128596
34 H 0.213467
35 C -0.135725
36 H 0.103326
37 H 0.115301
38 H 0.101023
39 C -0.072600
40 C -0.168232
41 C -0.181251
42 C -0.126885
43 H 0.136611
44 C -0.128482
45 H 0.213515
46 C -0.135623
47 H 0.103376
48 H 0.115384
49 H 0.101102
Sum of Mulliken charges= -1.00000

- 24 O -0.420540
- 25 P 0.359555
- 26 W 0.158406
- 27 W 0.157856
- 28 C -0.071947
- 29 C -0.168510
- 30 C -0.181569
- 31 C -0.126846
- 32 H 0.136527

Table S9: Mulliken Charges for 4

1 C 0 136410	22 H 0 152662	
1 C -0.130419	35 H 0.132002	
2 H 0.182756	34 C -0.126863	
3 C -0.136373	35 H 0.201641	
4 H 0.182870	36 C -0.127743	
5 C -0.151323	37 H 0.135370	
6 H 0.185598	38 H 0.141540	
7 C -0.151093	39 H 0.135898	
8 H 0.173618	40 C -0.081216	
9 C -0.134443	41 C -0.167478	
10 H 0.181338	42 C -0.179763	
11 C -0.194137	43 C -0.125817	
12 H 0.178708	44 H 0.152551	
13 C -0.193919	45 C -0.126907	
14 H 0.178754	46 H 0.201767	
15 C -0.151463	47 C -0.127755	
16 H 0.185641	48 H 0.135347	
17 C -0.134759	49 H 0.141521	
18 H 0.181322	50 H 0.135876	
19 C -0.150896	Sum of Mulliken charges= 0	0.000
20 H 0.173547		
21 N -0.122099		
22 N -0.122019		
23 O -0.338534		
24 O -0.338400		
25 P 0.343808		
26 W 0.215734		
27 W 0.216476		
28 H -0.040534		
a a a a a a a a a a		

- 29 C -0.081455
- 30 C -0.167476
- 31 C -0.179596
- 32 C -0.125864

Table S10: Natural Charges for 3

H 20 0.25991

N 21 -0.03597

N 22 -0.03604

O 23 -0.47291

O 24 -0.47316

P 25 0.68787

W 26 0.38797

W 27 0.38822

C 28 -0.33551

C 29 -0.22488

C 30 -0.20925

C 31 -0.24425

H 32 0.23881

С	1	-0.32243	C 33 -0.23576
Η	2	0.26397	H 34 0.26509
С	3	-0.32209	C 35 -0.24590
Η	4	0.26395	Н 36 0.22365
С	5	-0.34196	Н 37 0.22974
Η	6	0.27483	H 38 0.22146
С	7	-0.33725	C 39 -0.33577
Η	8	0.25994	C 40 -0.22482
С	9	-0.35392	C 41 -0.20904
Η	10	0.25331	C 42 -0.24432
С	11	-0.36047	H 43 0.23884
Η	12	0.25734	C 44 -0.23569
С	13	-0.36031	H 45 0.26509
Η	14	0.25740	C 46 -0.24576
С	15	-0.34192	H 47 0.22368
Η	16	0.27481	H 48 0.22978
С	17	-0.35400	H 49 0.22149
Η	18	0.25332	
С	19	-0.33709	* Total * -1.00000

	C 32 -0.23133
C 1 -0.28789	Н 33 0.24493
Н 2 0.27779	C 34 -0.22685
C 3 -0.28802	Н 35 0.25671
Н 4 0.27783	C 36 -0.22300
C 5 -0.33356	Н 37 0.23982
H 6 0.28134	H 38 0.24287
C 7 -0.31738	Н 39 0.23866
Н 8 0.27679	C 40 -0.36500
C 9 -0.31433	C 41 -0.22458
H 10 0.27596	C 42 -0.21262
C 11 -0.34904	C 43 -0.23131
H 12 0.27741	H 44 0.24491
C 13 -0.34888	C 45 -0.22687
H 14 0.27740	Н 46 0.25669
C 15 -0.33394	C 47 -0.22299
H 16 0.28137	H 48 0.23980
C 17 -0.31469	Н 49 0.24286
H 18 0.27598	Н 50 0.23865
C 19 -0.31715	
H 20 0.27674	* Total * 0.00000
N 21 0.03457	
N 22 0.03479	
O 23 -0.37497	
O 24 -0.37474	
P 25 0.81437	
W 26 0.46943	

- W 27 0.46964
- Н 28 -0.12587
- C 29 -0.36508
- C 30 -0.22479
- C 31 -0.21242

	3	3B	4
V _{NO,sym} .	1612 (6)	1436 (21)	1709 (3)
V _{NO,asym.}	1591 (100)	1410 (100)	1689 (100)

Table S12: DFT/B3LYP-computed wavenumbers $v(\text{cm}^{-1})$ and relative intensities of the N–O stretches for compounds **3**, **3B** and **4**

Table S13: Topological properties of the electron density at the Bond Critical Points in complexes **3** and **4**. Values of the electron density (ρ) are given in eÅ⁻³; values of the Laplacian of ρ at these points ($\nabla^2 \rho$) are given in eÅ⁻⁵.^a

Dond	3		4	
Bond	ρ	$ abla^2(ho)$	ρ	$ abla^2(ho)$
W - W	0.642	0.754	0.500	0.513
W26 – P	0.524	3.500	0.561	2.685
W27 – P	0.524	3.494	0.561	2.687
W26 – H28			0.512	3.730
W27 – H28			0.511	3.717
W26 - N21	1.240	23.572	1.209	23.444
W27 – N22	1.240	23.573	1.209	23.454
N21 – O23	3.232	-25.295	3.432	-29.004
N22 – O24	3.232	-25.286	3.433	-29.016

^{*a*} For comparison, the values computed for the W–W bcp in $[W_2Cp_2(CO)_6]$ (W–W = 3.330 Å) were $\rho = 0.204$ eÅ⁻³and $\nabla^2 \rho = 0.003$ eÅ⁻⁵.