Electronic Supporting Information for:

Synthesis and reactivity of molybdenum and tungsten bis(dinitrogen) complexes supported by diphosphine chelates containing proton relays.

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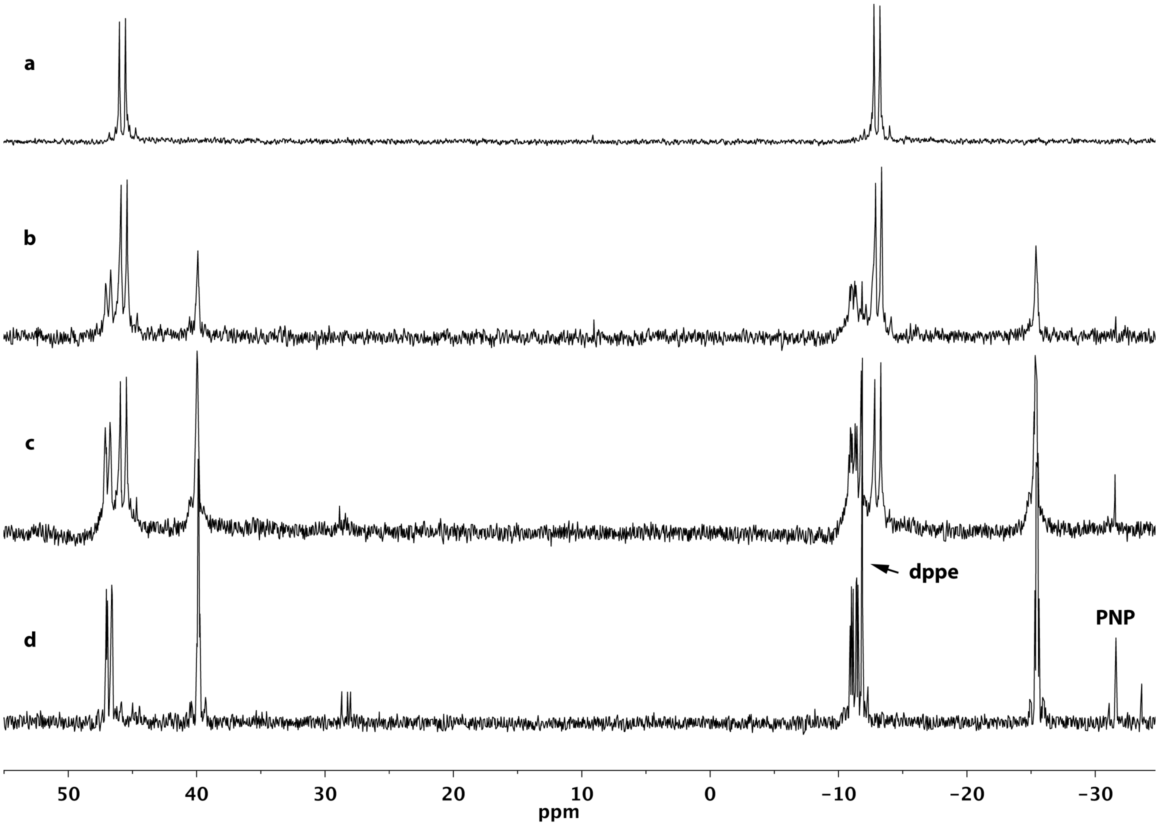


Figure S1. ^{31}P NMR spectra of *trans*-W$(N_2)_2$(dppe)(P^{Et}N^{Me}P^{Et}) (**9**) dissolved in THF-d_8 and charged with 1 atmosphere of CO gas taken at 0.5 (a), 17 (b), 42 (c), and 70.5 (d) hours. The reaction begins with pure (9) (a) before gradually converting to the *cis*-W(CO)$_2$(dppe)(P^{Et}N^{Me}P^{Et}) product and a minor quantity of free ligand likely from a non-carbonyl based degradation.

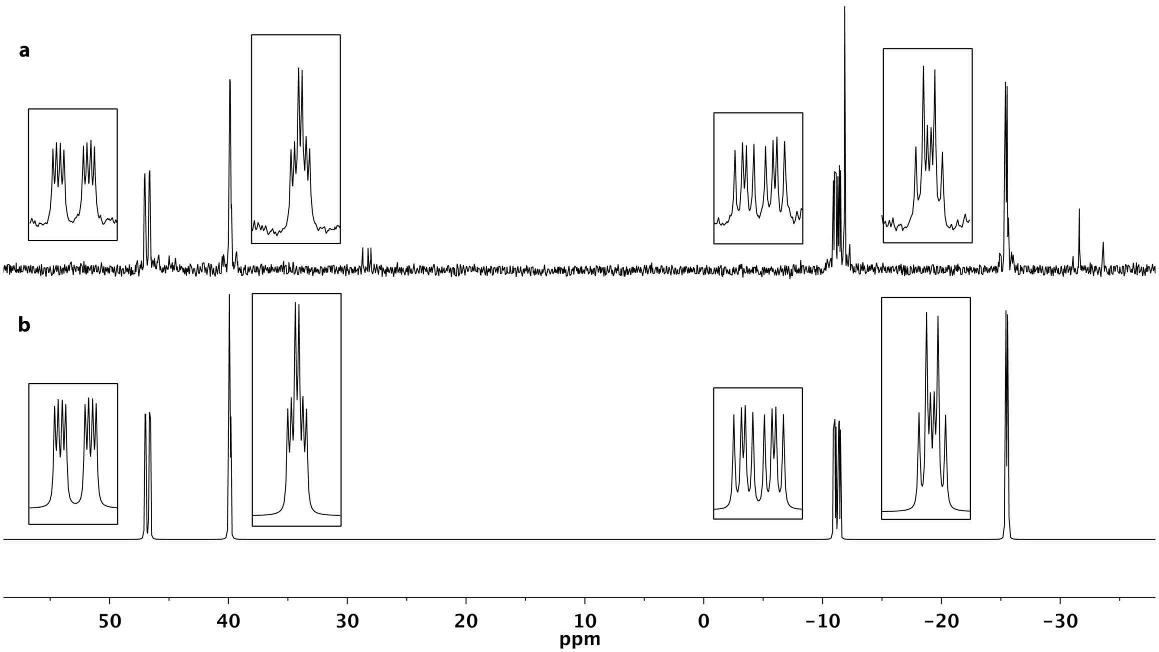


Figure S2. Measured (a, THF-d_8) and simulated (b) $^{31}P\{^1H\}$ NMR spectra of *cis*-[$W(CO)_2$(dppe)($P^{Et}N^{Me}P^{Et}$)]. Resonances at 46.8 and 39.9 ppm correspond to the dppe ligand while resonances at -11.2 and -24.5 ppm correspond to the $P^{Et}N^{Me}P^{Et}$ ligand.

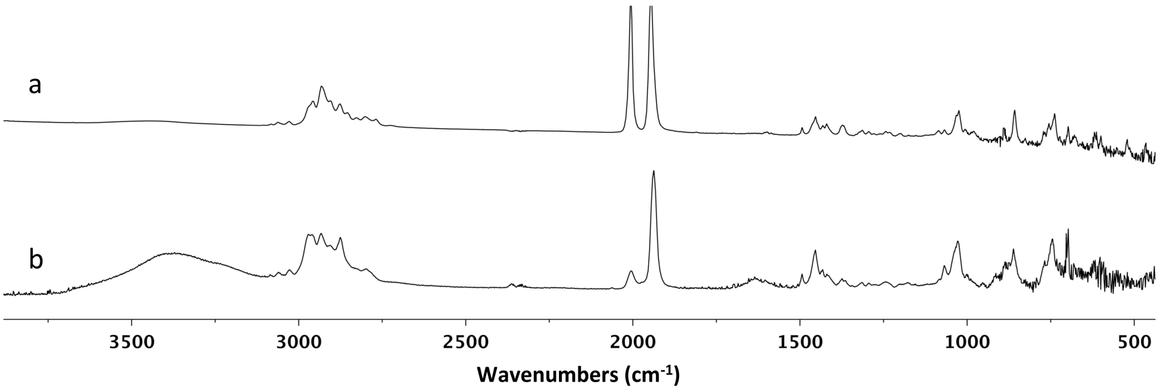


Figure S3. Infrared spectra collected in KBr pellets of *cis*-[$Mo(N_2)_2(P^{Et}N^{Bn}P^{Et})^2$] (a) and *trans*-[$Mo(N_2)_2(P^{Et}N^{Bn}P^{Et})^2$] (b)complexes. The latter (b) contains a small amount of *cis*-[$Mo(N_2)_2(P^{Et}N^{Bn}P^{Et})^2$].

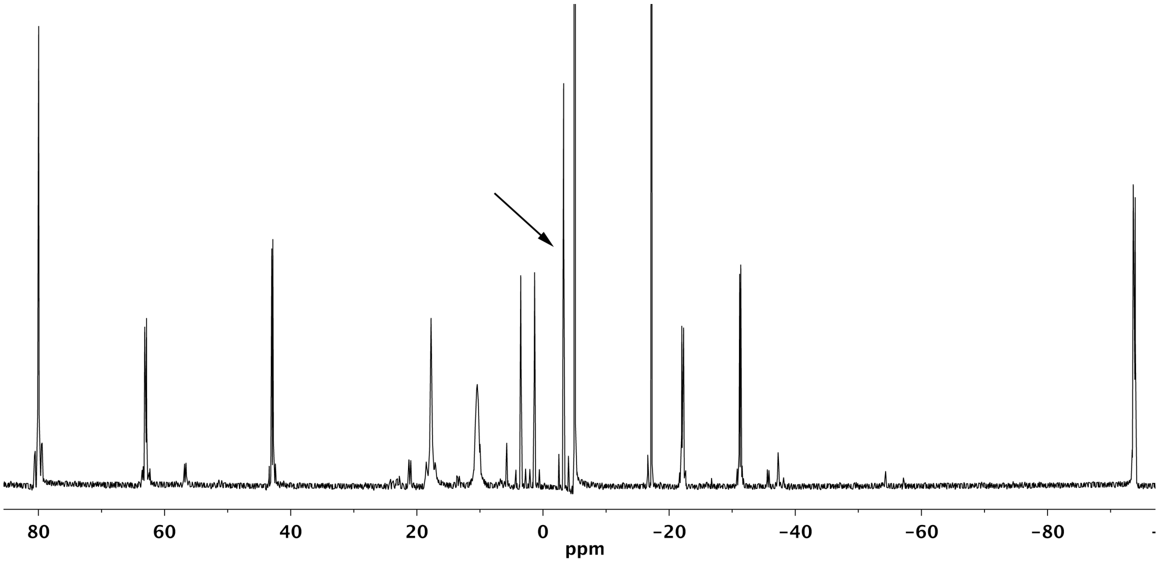


Figure S4. $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture for the synthesis of *trans*-$W(N_2)_2(dppp)_2$ (**14**) in THF. An arrow marks the desired product.

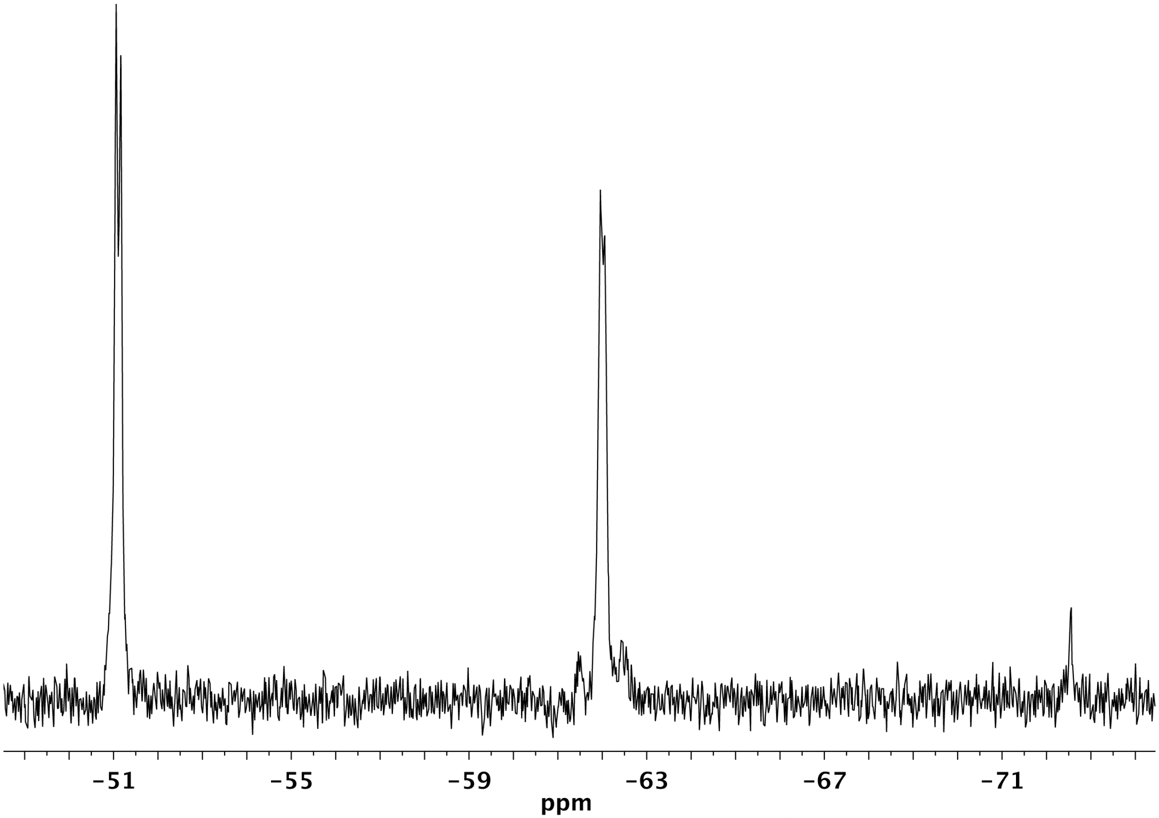
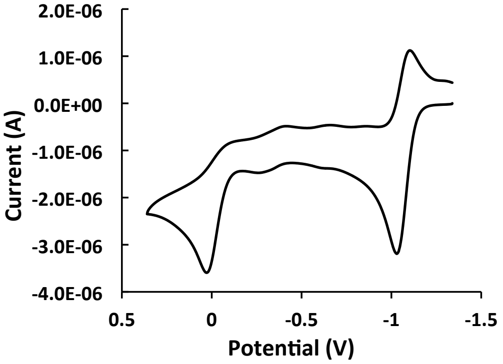
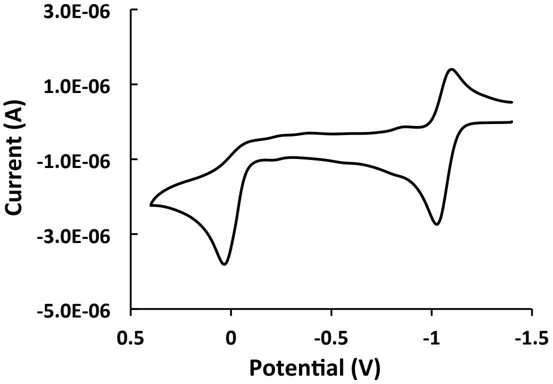


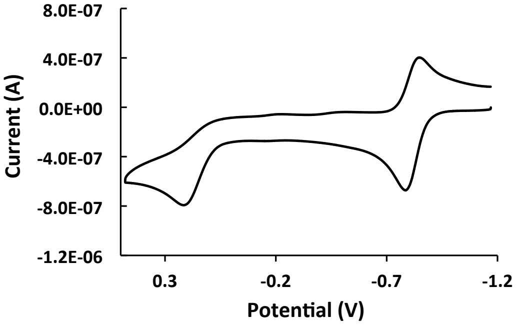
Figure S5. Three resonances are observed in the ^{15}N NMR spectrum of $^{15}N_2$-enriched *trans*-$W(N_2)_2(P^{Ph}N^{Me}P^{Ph})_2$ corresponding to the distal nitrogen (-51 ppm), proximal nitrogen (-62 ppm), and free N_2 (-72 ppm).



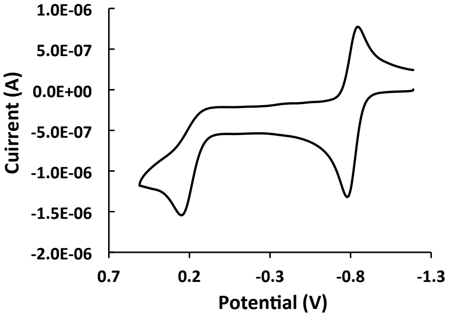
trans-$[Mo(N_2)_2(P^{Et}N^{Me}P^{Et})_2]$



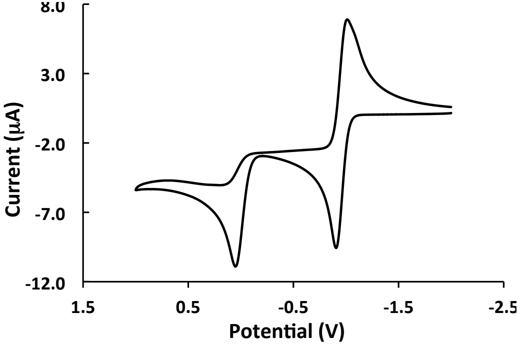
trans-$[Mo(N_2)_2(P^{Et}N^{Bn}P^{Et})_2]$



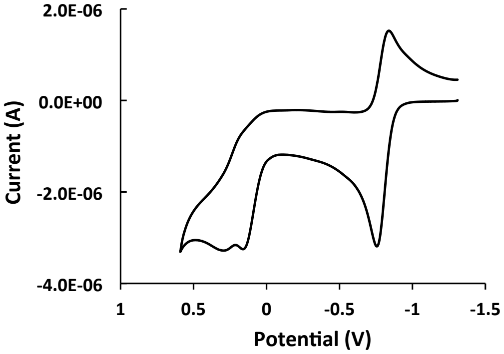
trans-$[Mo(N_2)_2(P^{Ph}N^{Me}P^{Ph})_2]$



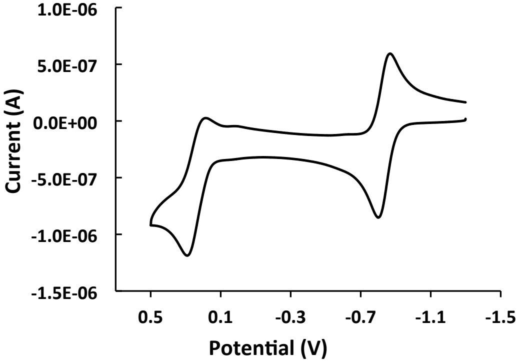
trans-$[Mo(N_2)_2(P^{Ph}N^{Bn}P^{Ph})_2]$



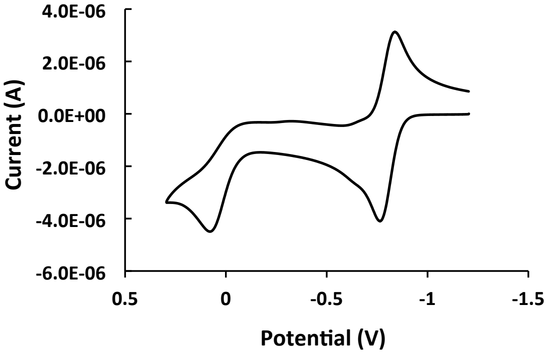
trans-$[W(N_2)_2(dppe)(P^{Et}N^{Me}P^{Et})]$



trans-$[W(N_2)_2(dppe)(P^{Ph}N^{Me}P^{Ph})]$



trans-$[W(N_2)_2(dppe)(dppp)]$



trans-$[W(N_2)_2(P^{Ph}N^{Me}P^{Ph})_2]$

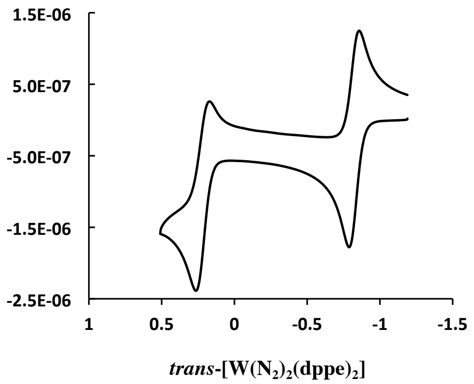


Figure S6. Cyclic voltammogram of *molybdenum and tungsten bis(dinitrogen) complexes* in THF/$^{n}Bu_4NB(C_6F_5)_4$ (0.2 M) at 0.1 V/s showing the M^{I}/M^{0} and M^{II}/M^{I} couples. The extra II/I couple on the *trans*-$[W(N_2)_2(dppe)(P^{Ph}N^{Me}P^{Ph})]$ cyclic voltammogram at 0.2 volts is the result of *trans*-$[W(N_2)_2(dppe)_2]$ impurity that could not be removed.

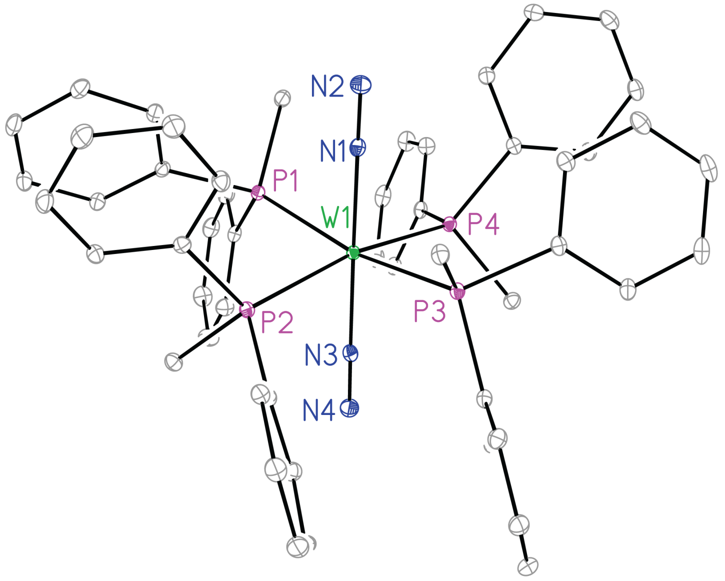


Fig. S7. Molecular structure of *trans*-$W(N_2)_2(PPh_2Me)_4$, which formed as a result of ligand redistribution upon mixing $WCl_4(PMePh_2)_2$ and $P^{Et}N^{Me}P^{Et}$ with excess Mg powder in THF. This compound has previously been reported in J. Chatt, A. J. Pearman and R. L. Richards, *J. Chem. Soc. Dalton Trans.,* 1977, 2139.

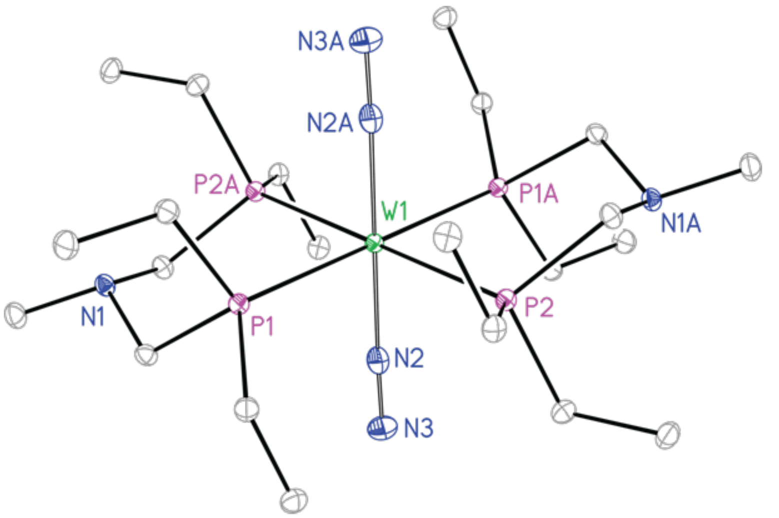


Fig. S8. Molecular structure of *trans*-$W(N_2)_2(P^{Et}N^{Me}P^{Et})_2$ without the partial occupancy chlorides.

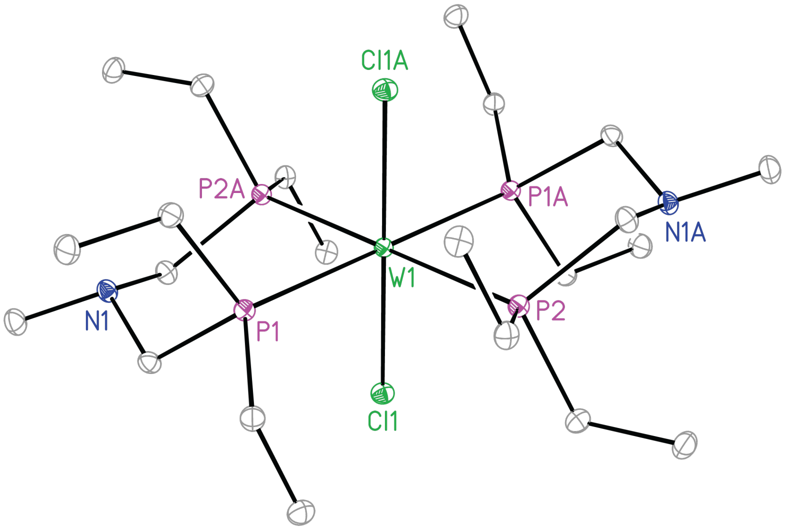


Fig. S9. Molecular structure of *trans*-$WCl_2(P^{Et}N^{Me}P^{Et})_2$ without the partial occupancy chlorides.

Table S1. Selected bond lengths (Å) and angles (°) of *cis*-$[WCl_2(P^{Et}N^{Me}P^{Et})_2]$.

W(1)–P(1)	2.4842(4)	P(1)–W(1)–P(2A)	87.129(14)
W(1)–P(2)	2.4380(4)	P(1A)–W(1)–P(2A)	98.914(15)
W(1)–P(1A)	2.4842(4)	P(1)–W(1)–P(1A)	166.11(2)
W(1)–P(2A)	2.4381(4)	Cl(a)–W(1)–Cl(1A)	80.00(2)
W(1)–Cl(1)	2.4381(4)		
W(1)–Cl(1A)	2.5244(4)	Cl(1)–W(1)–P(1)	86.917(14)
		Cl(1A)–W(1)–P(1A)	82.443(15)

Table S2. Selected bond lengths (Å) and angles (°) of $[MoBr_2(P^{Et}N^{Bn}P^{Et})]_2$.

Mo(1)–P(1)	2.5209(4)	P(1)–Mo(1)–P(2)	82.806(15)
Mo(1)–P(2)	2.5259(4)	P(1)–Mo(1)–Br(1)	82.461(12)
Mo(1A)–P(1A)	2.4410(6)	Br(1)–Mo(1)-Br(2)	87.976(7)
Mo(1)–Br(1)	2.5957(2)		
Mo(1)–Br(2)	2.5690(2)		

Table S3. Selected bond lengths (Å) and angles (°) of *trans*-[W(N_2)$_2$($P^{Et}N^{Me}P^{Et}$)$_2$] (*trans*-**12**) / *trans*-[WCl_2($P^{Et}N^{Me}P^{Et}$)$_2$].

W(1)–P(1)	2.4762(3)	P(1)–W(1)–P(2A)	83.305(10)
W(1)–P(2)	2.4645(4)	P(1A)–W(1)–P(2)	83.304(10)
W(1)–P(1A)	2.4762(3)	P(1)–W(1)–P(1A)	180.0
W(1)–P(2A)	2.4645(4)	N(2)–W(1)–N(2A)	180.0
W(1)–N(2)	1.971(9)	N(3)–N(2)–W(1)	177.1(6)
W(1)–N(2A)	1.971(9)		
		N(2)–W(1)–P(1)	88.3(2)
N(2)–N(3)	1.163(15)	N(2)–W(1)–P(1A)	91.7(2)
W(1)–Cl(1)	2.4369(7)		

Table S4. Selected bond lengths (Å) and angles (°) of *trans*-[W(N_2)$_2$(PMePPh$_2$)$_4$].

W(1)–P(1)	2.4760(4)	P(1)–W(1)–P(2)	90.469(12)
W(1)–P(2)	2.4710(4)	P(3)–W(1)–P(4)	90.991(12)
W(1)–P(3)	2.4706(4)	P(1)–W(1)–P(3)	168.294(12)
W(1)–P(4)	2.4763(4)	N(1)–W(1)–N(3)	179.35(5)
W(1)–N(1)	1.9908(13)	N(2)–N(1)–W(1)	179.52(13)
W(1)–N(3)	2.0011(13)	N(4)–N(3)–W(1)	179.40(13)
N(1)–N(2)	1.1336(18)	N(1)–W(1)–P(1)	83.99(4)
N(3)–N(4)	1.1322(18)	N(3)–W(1)–P(3)	95.26(4)

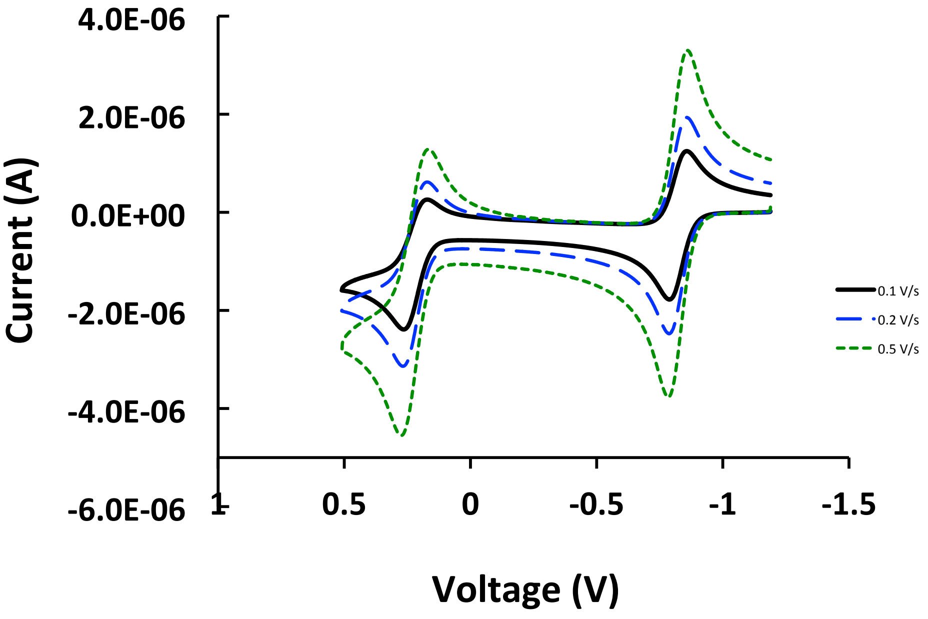


Fig. S10. Cyclic voltammographs for *trans*-W(N_2)$_2$(dppe)$_2$ in THF/^{n}Bu$_4$NB(C_6F_5)$_4$ (0.2 M) at 0.1, 0.2, 0.5 V/s. Measured i_{pa}/i_{pc} values are 0.69, 0.62, and 0.84, respectively.

Table S5. Crystallographic data for tungsten bis(dinitrogen) complexes.

	trans-W(N$_2$)$_2$(dppe)(P^{Et}N^{Me}P^{Et}) (**9**)	*trans*-W(N$_2$)$_2$(dppe)(P^{Ph}N^{Me}P^{Ph}) (**10**)	*trans*-W(N$_2$)$_2$ (dppp)$_2$•THF (**14**)	*trans*-W(N$_2$)$_2$ (P^{Ph}N^{Me}P^{Ph})$_2$•THF (**7-W**)	*trans*-W(N$_2$)$_2$(PMePh$_2$)$_4$
empirical formula	$C_{74}H_{102}N_{10}P_8W_2$	$C_{53}H_{51}N_5P_4W$	$C_{62}H_{64.97}N_4O_2P_4W$	$C_{31}H_{35}N_3P_2W_{0.5}$	$C_{58}H_{64}N_4O_{1.50}P_4W$
formula weight	1747.12	1065.72	1205.88	619.48	1148.86
color, habit	orange, blocks	orange, blocks	orange, blocks	orange, blocks	red, blocks
crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$
a, Å	10.3311(5)	23.6481(7)	9.9919(5)	13.7790(6)	11.5609(4)
b, Å	19.3128(9)	11.6215(3)	15.5200(8)	14.3548(6)	14.1387(5)
c, Å	20.2295(10)	17.3542(5)	17.6634(9)	14.2441(6)	17.2056(6)
α, deg	109.1660(10)	90	90	90	77.0490(10)
β, deg	94.039(2)	103.1780(10)	97.533(3)	101.0770(10)	72.3200(10)
γ, deg	100.228(2)	90	90	90	83.3430(10)
V(Å^3)	3715.8(3)	4643.8(2)	2715.5(2)	2764.9(2)	2607.89(16)
λ, Å (Mo, Kα)	0.71073	0.71073	0.71073	0.71073	0.71073
Z	4	4	2	2	4
density (g/cm^3)	1.562	1.524	1.475	1.488	1.463
temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
2θ range, deg	1.82 – 33.35	1.77 – 34.81	3.5 – 59.3	2.03 – 33.28	1.48 – 33.38
μ(Mo, Kα), mm^{-1}	3.315	2.668	2.293	2.255	2.383
R(F), Rw(F)	0.0274, 0.0521	0.0233, 0.0468	0.0269, 0.0589	0.0300, 0.0658	0.0218, 0.0507

Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$

Table S6. Crystallographic data for molybdenum bis(dinitrogen) complexes.

	trans-[Mo(N_2)$_2$($P^{Et}N^{Bn}P^{Et}$)$_2$] (*trans*-**5**)	*trans*-[Mo(N_2)$_2$($P^{Ph}N^{Me}P^{Ph}$)$_2$] (**7-Mo**)	*trans*-[Mo(N_2)$_2$($P^{Et}N^{Me}P^{Et}$)$_2$] (*trans*-**6**)	*cis*-[Mo(N_2)$_2$($P^{Et}N^{Me}P^{Et}$)$_2$] (*cis*-**6**)	*trans*-[Mo(N_2)$_2$($P^{Ph}N^{Bn}P^{Ph}$)$_2$] (**8**)
empirical formula	$C_{17}H_{31}Mo_{0.5}N_3P_2$	$C_{27}H_{27}Mo_{0.5}N_3P_2$	$C_{22}H_{54}MoN_6P_4$	$C_{22}H_{54}MoN_6P_4$	$C_{33}H_{31}Mo_{0.50}N_3P_2$
formula weight	387.36	503.43	622.53	622.53	579.52
color, habit	orange, plates	orange, blocks	yellow, blocks	yellow, blocks	yellow, rod
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	*P*2(1)/*n*	*P*2(1)/*c*	*P*2(1)/*c*	*C*2/*c*
a, Å	8.6590(8)	8.9918(5)	8.534(3)	19.7747(13)	23.123(4)
b, Å	11.0792(11)	13.9020(9)	18.737(6)	10.2104(7)	16.082(3)
c, Å	11.0863(11)	19.5071(12)	19.610(6)	15.5500(10)	15.539(3)
α, deg	100.9103(3)	90	90	90	90
β, deg	108.167(3)	98.521(3)	98.308(10)	101.199(2)	102.277(8)
γ, deg	93.405(3)	90	90	90	90
V(Å^3)	980.54(16)	2411.5(3)	3102.7(17)	3079.9(4)	5646.4(17)
λ, Å (Mo, Kα)	0.71073	0.71073	0.71073	0.71073	0.71073
Z	1	2	4	4	4
density (g/cm^3)	1.312	1.387	1.333	1.343	1.363
temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
2θ range, deg	1.89 – 33.37	1.81 – 33.26	1.51 – 33.44	2.10 – 33.33	1.80 – 33.26
μ(Mo, Kα), mm^{-1}	0.529	0.449	0.650	0.655	0.394
R(F), *R*w(F)	0.0263, 0.0596	0.0494, 0.0789	0.0307, 0.0648	0.0309, 0.0640	0.0448, 0.0850

Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$

Table S7. Crystallographic data for tungsten chloride and molybdenum bromide complexes.

	cis-[$WCl_2(P^{Et}N^{Me}P^{Et})_2$]	*trans*-[$W(N_2)_2(P^{Et}N^{Me}P^{Et})_2$] (*trans*-**12**)/ *trans*-[$WCl_2(P^{Et}N^{Me}P^{Et})_2$] •$PPh_3$	*trans*-[$MoBr_2(P^{Et}N^{Bn}P^{Et})_2$] (**1**)	*trans*-[$MoBr_2(P^{Ph}N^{Bn}P^{Ph})_2$]•THF (**4**)	[$MoBr_2(P^{Et}N^{Bn}P^{Et})$]$_2$
empirical formula	C_{11} H_{27} Cl N P_2 $W_{0.5}$	$C_{29}H_{42}Cl_{0.72}N_{1.54}P_3W_{0.50}$	$C_{17}H_{31}BrMo_{0.5}NP_2$	$C_{37}H_{39}BrMo_{0.5}NOP_2$	$C_{17}H_{31}Br_2MoNP_2$
formula weight	362.65	622.81	1500.73	703.51	567.13
color, habit	yellow, blocks	orange, blocks	orange, blocks	yellow, blocks	green, blocks
crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	*P*2(1)/*c*	*P*2(1)/*n*
a, Å	12.2599(4)	8.4043(8)	8.8246(4)	12.9360(3)	10.7168(4)
b, Å	15.0108(4)	11.0166(11)	10.0917(4)	27.6368(7)	13.4035(6)
c, Å	17.8358(6)	16.7489(16)	11.2789(5)	9.1815(2)	15.4417(7)
α, deg	90	88.878(3)	73.2370(10)	90	90
β, deg	106.1260(10	83.125(3)	84.9840(10)	102.7040(10)	103.0530(10)
γ, deg	90	72.038(3)	85.1490(10)	90	90
V(Å^3)	3153.19(17)	1464.3(2)	956.22(7)	3202.12(13)	2160.77(16)
λ, Å (Mo, Kα)	0.71073	0.71073	0.71073	0.71073	0.71073
Z	8	1	1	2	2
density (g/cm^3)	1.528	1.413	1.526	1.459	1.743
temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
2θ range, deg	2.86 – 27.16	1.94 – 33.46	2.11 – 33.19	1.77 – 33.33	2.04 – 34.17
μ(Mo, Kα), mm^{-1}	4.049	2.242	2.626	1.602	4.453
R(F), *R*w(F)	0.0133, 0.0328	0.0170, 0.0410	0.0189, 0.0463	0.0267, 0.0609	0.0264, 0.0576

Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\ \Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$

X-ray Crystallography Experimentals

X-ray structural analysis for ***trans*-[MoBr$_2$(P^{Et}N^{Bn}P^{Et})$_2$] (1)**: A single orange block (0.16 X 0.20 X 0.25 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 8.825(1), b = 10.092(1), c = 11.279(1) Å, α = 73.237(1), β = 84.984(1), γ = 85.149(1)°, V = 959.2(1) Å^3. 23040 reflections (R$_{int}$ = 0.0170) were collected (7248 unique) over θ = 2.11 to 33.19°. The data was consistent with the centrosymmetric, triclinic space group, $P\bar{1}$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.21. The asymmetric unit contains one MoBr$_2$(PNP)$_2$ molecule located on the inversion center, yielding Z = 1. One of the ethyl groups on the phosphine ligand was disordered over two positions, which were located from the difference map and refined. SIMU, DELU, and SAME commands were used to keep the two parts chemically equivalent. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.028 with $R1(wR2)$ 0.0187(0.0451) for [$I\theta$>2(I)] and with largest difference peak and hole of 0.508 and –0.359 e/Å^3.

X-ray structural analysis for ***trans*-[MoBr$_2$(P^{Ph}N^{Bn}P^{Ph})$_2$] (4)**: A single yellow block (0.11 X 0.11 X 0.19 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 12.936(1), b = 27.637(1), c = 9.181(1) Å, β = 102.704(1)°, V = 3202.1(1) Å^3. 55072 reflections (R$_{int}$ = 0.0280) were collected (12313 unique) over θ = 1.77 to 33.33°. The systematic absences in the reflection data were consistent with the centrosymmetric, monoclinic space group, $P2(1)/c$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.12. The asymmetric unit contains one MoBr$_2$(PNP)$_2$ molecule located on an inversion center, and one molecule of THF solvent located on a general position, yielding Z = 2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.025 with $R1(wR2)$ 0.0267(0.0609) for [$I\theta$>2(I)] and with largest difference peak and hole of 0.514 and –0.422 e/Å^3.

X-ray structural analysis for ***trans*-[Mo(N$_2$)$_2$(P^{Et}N^{Bn}P^{Et})$_2$] (*trans*-5)**: A single orange plate(0.06 X 0.12 X 0.16 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 8.659(1), b = 11.079(1), c = 11.086(1) Å, α = 100.910(3), β = 108.761(3), γ = 93.405(3)°, V = 980.5(2) Å^3. 23514 reflections (R$_{int}$ =

0.0290) were collected (7522 unique) over θ = 1.89 to 33.37°. The data was consistent with the centrosymmetric, triclinic space group, $P\bar{1}$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.05. The asymmetric unit contains one $Mo(N_2)_2(PNP)_2$ molecule located on the inversion center, yielding $Z = 1$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.053 with $R1(wR2)$ 0.0263(0.0596) for $[I\theta>2(I)]$ and with largest difference peak and hole of 0.518 and –0.616 e/Å^3.

X-ray structural analysis for ***trans*-[Mo$(N_2)_2(P^{Et}N^{Me}P^{Et})_2$] (*trans*-6)**: A single yellow block (0.08 X 0.16 X 0.20 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 19.775(2), b = 10.210(1), c = 15.550(1) Å, β = 101.199(2)°, V = 3079.9(4) Å^3. 55672 reflections (R_{int} = 0.0472) were collected (11885 unique) over θ = 2.10 to 33.33°. The systematic absences in the data were consistent with the centrosymmetric, monoclinic space group, $P2(1)/c$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.08. The asymmetric unit contains one $(PNP)_2Mo(N_2)_2$ molecule located on a general position, yielding $Z = 4$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.011 with $R1(wR2)$ 0.0309(0.0640) for $[I\theta>2(I)]$ and with largest difference peak and hole of 0.910 and –0.1715 e/Å^3.

X-ray structural analysis for ***cis*-[Mo$(N_2)_2(P^{Et}N^{Me}P^{Et})_2$] (*cis*-6)**: A single yellow block (0.08 X 0.16 X 0.20 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 19.775(2), b = 10.210(1), c = 15.550(1) Å, β = 101.199(2)°, V = 3079.9(4) Å^3. 55672 reflections (R_{int} = 0.0472) were collected (11885 unique) over θ = 2.10 to 33.33°. The systematic absences in the data were consistent with the centrosymmetric, monoclinic space group, $P2(1)/c$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.08. The asymmetric unit contains one $(PNP)_2Mo(N_2)_2$ molecule located on a general position, yielding $Z = 4$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.011 with $R1(wR2)$ 0.0309(0.0640) for $[I\theta>2(I)]$ and with largest difference peak and hole of 0.910 and –0.715 e/Å^3.

X-ray structural analysis for ***trans*-[Mo(N_2)$_2$($P^{Ph}N^{Me}P^{Ph}$)$_2$] (7-Mo)**: A single orange block (0.04 X 0.04 X 0.16 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 8.992(1), b = 13.902(1), c = 19.507(1) Å, β = 98.521(3)°, V = 2411.5(3) Å^3. 42029 reflections (R_{int} = 0.0927) were collected (9226 unique) over θ = 1.81 to 33.26°. The systematic absences in the reflection data were consistent with the centrosymmetric, monoclinic space group, $P2(1)/n$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.05. The asymmetric unit contains one Mo(N_2)$_2$(PNP)$_2$ molecule located on an inversion center, yielding Z = 2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.004 with $R1(wR2)$ 0.0494(0.0789) for [$I\theta$>2(I)] and with largest difference peak and hole of 0.582 and –1.219 e/Å^3.

X-ray structural analysis for ***trans*-[W(N_2)$_2$($P^{Ph}N^{Me}P^{Ph}$)$_2$] (7-W)**: A single orange block (0.10 X 0.16 X 0.20 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 13.779(1), b = 14.355(1), c = 14.244(1) Å, β = 101.077(1)°, V = 2764.9(2) Å^3. 38991 reflections (R_{int} = 0.0296) were collected (10506 unique) over θ = 2.03 to 33.28°. The systematic absences in the data were consistent with the centrosymmetric, monoclinic space group, $P2(1)/n$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.22. The asymmetric unit contains a W(PNP)$_2$(N_2)$_2$ molecule located on an inversion center and one molecule of THF solvent located on a general position, yielding Z = 2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.070 with $R1(wR2)$ 0.0300(0.0658) for [$I\theta$>2(I)] and with largest difference peak and hole of 2.649 and –1.032 e/Å^3. The residual electron density is along the W-N_2 bond indicating some incomplete reduction of the dichloride starting material. However, all attempts to model a partially occupied chloride along this bond have failed. This suggests that the occupancy must be less than 5% at this position and should not have a discernable affect on the bond distances in this molecule.

X-ray structural analysis for ***trans*-[Mo(N_2)$_2$($P^{Ph}N^{Bn}P^{Ph}$)$_2$] (8)**: A single yellow rod (0.04 X 0.05 X 0.20 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 23.123(4), b = 16.082(3), c = 15.539(3) Å, β = 102.28(1)°, V = 5646(2) Å^3. 51596 reflections (R_{int} = 0.0832) were collected (10782 unique) over θ = 1.80

to 33.26°. The systematic absences in the data were consistent with the centrosymmetric, monoclinic space group, *C*2/*c*. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.06. The asymmetric unit contains one $(PNP)_2Mo(N_2)_2$ molecule located on an inversion center, yielding $Z = 4$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.005 with $R1(wR2)$ 0.0448(0.0850) for $[I\theta{>}2(I)]$ and with largest difference peak and hole of 0.535 and –0.579 e/Å^3.

X-ray structural analysis for ***trans*-[W(N$_2$)$_2$(dppe)(P^{Et}N^{Me}P^{Et})] (9)**: A single orange block (0.08 X 0.14 X 0.18 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 10.331(1), b = 19.313(1), c = 20.229(1) Å, α = 109.166(1), β = 94.039(2), γ = 100.228(3)°, V = 3715.8(3) Å^3. 79213 reflections (R_{int} = 0.0314) were collected (28417 unique) over θ = 1.82 to 33.35°. The data was consistent with the centrosymmetric, triclinic space group, $P\bar{1}$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.32. The asymmetric unit contains two $(dppe)W(N_2)_2(PNP)$ molecules located on general positions, yielding $Z = 4$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.044 with $R1(wR2)$ 0.0274(0.0521) for $[I\theta{>}2(I)]$ and with largest difference peak and hole of 2.341 and –1.464 e/Å^3 due to heavy atom noise around the tungsten.

X-ray structural analysis for ***trans*-[W(N$_2$)$_2$(dppe)(P^{Ph}N^{Me}P^{Ph})] (10)**: A single orange block (0.06 X 0.12 X 0.16 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 23.648(1), b = 11.621(1), c = 17.354(1) Å, β = 103.178(1)°, V = 4643.8(2) Å^3. 63240 reflections (R_{int} = 0.0267) were collected (18422 unique) over θ = 1.77 to 34.81°. The systematic absences in the data were consistent with the centrosymmetric, monoclinic space group, *P*2(1)/*c*. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.27. The asymmetric unit contains a $[(PNP)W(N_2)_2(dppe)]$ molecule located on a general position, yielding $Z = 4$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.030 with $R1(wR2)$ 0.0233(0.0468) for $[I\theta{>}2(I)]$ and with largest difference peak and hole of 1.299 and –0.456 e/Å^3 due to heavy atom noise around the tungsten atom.

X-ray structural analysis for ***trans*-[W(N$_2$)$_2$(P^{Et}N^{Me}P^{Et})$_2$]/ *trans*-[WCl$_2$(P^{Et}N^{Me}P^{Et})$_2$] (*trans*-12)**: A single orange block (0.20 X 0.20 X 0.20 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 8.404(1), b = 11.017(1), c = 16.749(2) Å, α = 88.878(3), β = 83.125(3), γ = 72.038(3)°, V = 1464.3(2) $Å^3$. 38753 reflections (R_{int} = 0.0222) were collected (11204 unique) over θ = 1.94 to 33.46°. The data was consistent with the centrosymmetric, triclinic space group, $P\bar{1}$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.00. The asymmetric unit contains a $[W(PNP)_2L_2]$ molecule, where L is either Cl or N_2 in a ratio of 75 to 25% respectively, located on the inversion center. There is also a molecule of PPh_3 located on a general position, yielding $Z = 1$. The disorder appears to be the result of alternating, 180° rotations, of the $(Cl)(N_2)$ molecules about the inversion center throughout the crystal lattice. This structure indicates incomplete reduction of the parent dichloride complex to the dinitrogen complex. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.005 with $R1(wR2)$ 0.0170(0.0410) for $[I\theta>2(I)]$ and with largest difference peak and hole of 0.819 and –0.403 e/$Å^3$.

X-ray structural analysis for ***trans*-$[W(N_2)_2(dppp)_2]$ (14)**: A single orange block (0.15 X 0.14 X 0.10mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 36 data frames, 0.5° Φ, from three different sections of the Ewald sphere yielding a = 9.9919(5), b = 15.5200(8), c = 17.6634(9) Å, α = 90°, β = 97.533(3)°, γ = 90°, V = 2715.5(2) $Å^3$. 61951 reflections (R_{int} = 0.0441) were collected (7635 unique) over θ = 3.5 to 59.3°. The systematic absences in the diffraction data were consistent with the centrosymmetric, monoclinic space group, $P2(1)/n$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,. Bruker-AXS, 2001). The asymmetric unit contains one $W(N_2)_2(dppp)_2$ molecule, yielding $Z = 2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.066 with $R1(wR2)$ 0.0269(0.0589) for $[I\theta>2(I)]$.

X-ray structural analysis for ***trans*-$[W(N_2)_2(PMePh_2)_4]$**: A single red block (0.16 X 0.18 X 0.22 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 11.561(1), b = 14.139(1), c = 17.206(2) Å, α = 77.049(1), β = 72.320(1), γ = 83.343(1)°, V = 2607.9(2) $Å^3$. 56743 reflections (R_{int} = 0.0208) were collected (19916 unique) over θ = 1.48 to 33.38°. The data was consistent with the centrosymmetric, triclinic space group, $P\bar{1}$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.13. The asymmetric unit contains a $W(PPh_2Me)_4(N_2)_2$ molecule located on a general position and 1.5 molecules of THF solvent, yielding a Z = 4. The THF molecule located on the inversion center is disordered, which is expected considering THF doesn't contain such symmetry. All attempts to model this disorder using the PART commands and various restraints and constraints resulted in numerous non-positive definite atoms. SQUEEZE was used to remove the all the solvent from the cell. The SQUEEZE results are consistent with the model located from the difference map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.040 with $R1(wR2)$ 0.0218(0.0507) for $[I\theta>2(I)]$ and with largest difference peak and hole of 0.996 and –1.075 e/Å^3.

X-ray structural analysis for ***cis*-[WCl$_2$(P^{Et}N^{Me}P^{Et})$_2$]**: A single yellow block (0.30 X 0.30 X 0.30 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 36 data frames, 0.5° Φ, from three different sections of the Ewald sphere yielding a = 12.2599(4), b = 15.0108(4), c = 17.8358(6) Å, α = 90°, β = 106.1260(10)°, γ = 90°, V = 3153.19(17) Å^3. 19912 reflections (R_{int} = 0.010) were collected (9888 unique) over θ = 2.86 to 27.15°. The systematic absences in the diffraction data were consistent with the centrosymmetric, monoclinic space group, *C2/c*. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,. Bruker-AXS, 2001). The asymmetric unit contains one WCl$_2$(P^{Et}N^{Me}P^{Et})$_2$ molecule, yielding *Z* = 8. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was 1.125 with $R1(wR2)$ 0.0133(0.0328) for $[I\theta>2(I)]$.

X-ray structural analysis for **[MoBr$_2$(P^{Et}N^{Me}P^{Et})]$_2$**: A single green block (0.04 X 0.10 X 0.22 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiation. Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere yielding a = 10.717(1), b = 13.404(1), c = 15.442(1) Å, β = 103.053(1)°, V = 2160.8(2) Å^3. 35063 reflections (R_{int} = 0.0304) were collected (8815 unique) over θ = 2.04 to 34.17°. The systematic absences in the reflection data were consistent with the centrosymmetric, monoclinic space group, *P*2(1)/*n*. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G,.Bruker-AXS, 2001) T_{max}/T_{min} = 1.91. The asymmetric unit contains one [MoBr$_2$(P^{Et}N^{Me}P^{Et})]$_2$ dimer located on an inversion center, yielding *Z* = 2. The molecule contains a Mo-Mo bond which is supported by residual electron density along the bond axis. One of the ethyl groups on the phosphine ligand was disorder over two positions, which were located from the difference map and refined. In this case, SIMU and DELU commands resulted in non-positive definite atoms in the disordered parts so a EADP constraint was used along with a SAME command to keep the two parts equivalent. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. The goodness of fit on F^2 was

1.015 with $R1(wR2)$ 0.0264(0.0576) for $[I\theta{>}2(I)]$ and with largest difference peak and hole of 1.958 and –0.535 e/Å^3.