

Supplementary Information for Insight into the Coordination Chemistry of Nitrogen-Centred Triphosphine Ligands to Tungsten(0)

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NMR Spectra

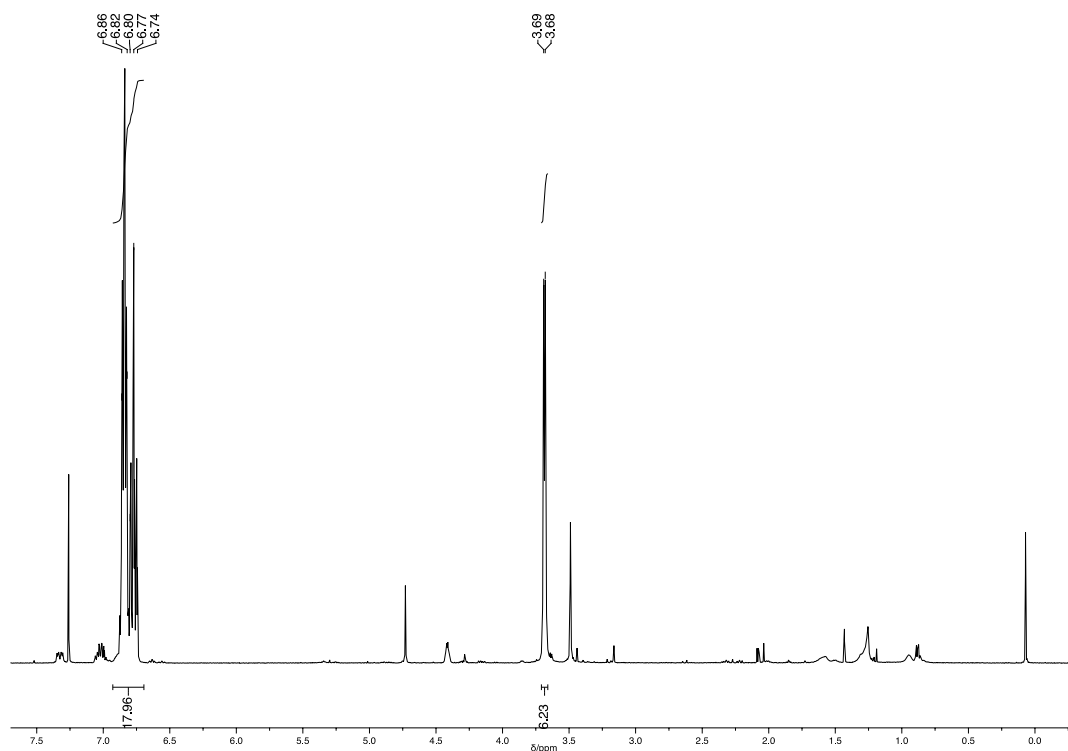


Figure S1. ^1H NMR spectrum of NP_3PhF_2 (CDCl_3 , 400 MHz)

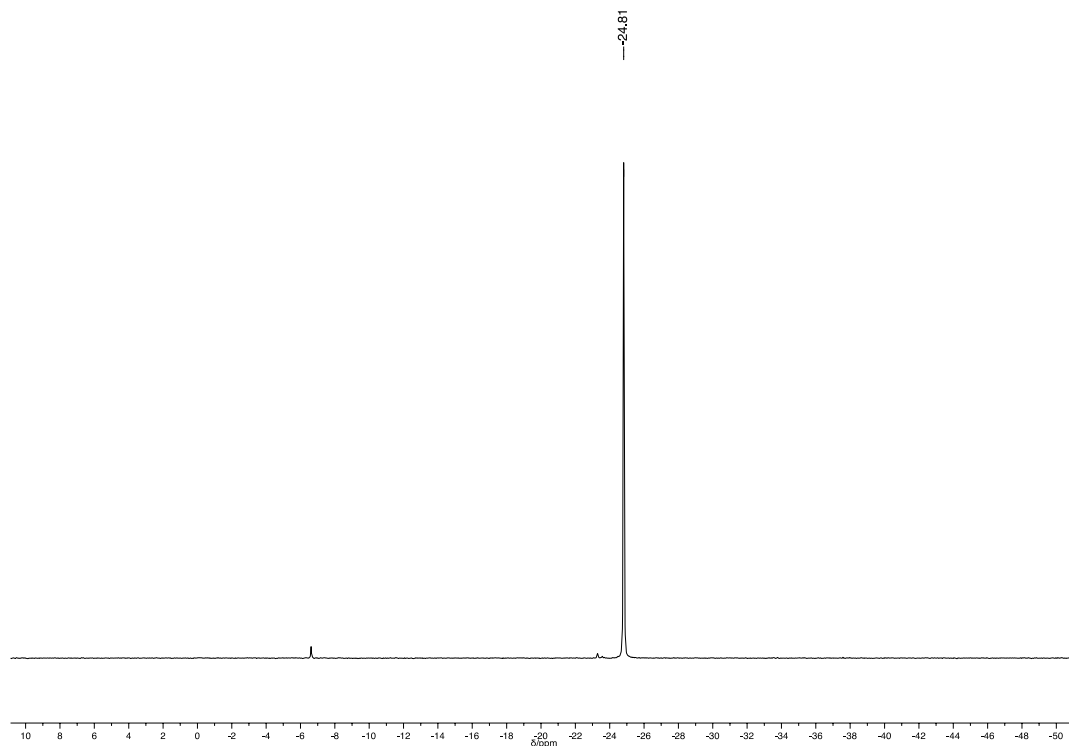


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{NP}_3^{\text{PhF}_2}$ (CDCl_3 , 162 MHz)

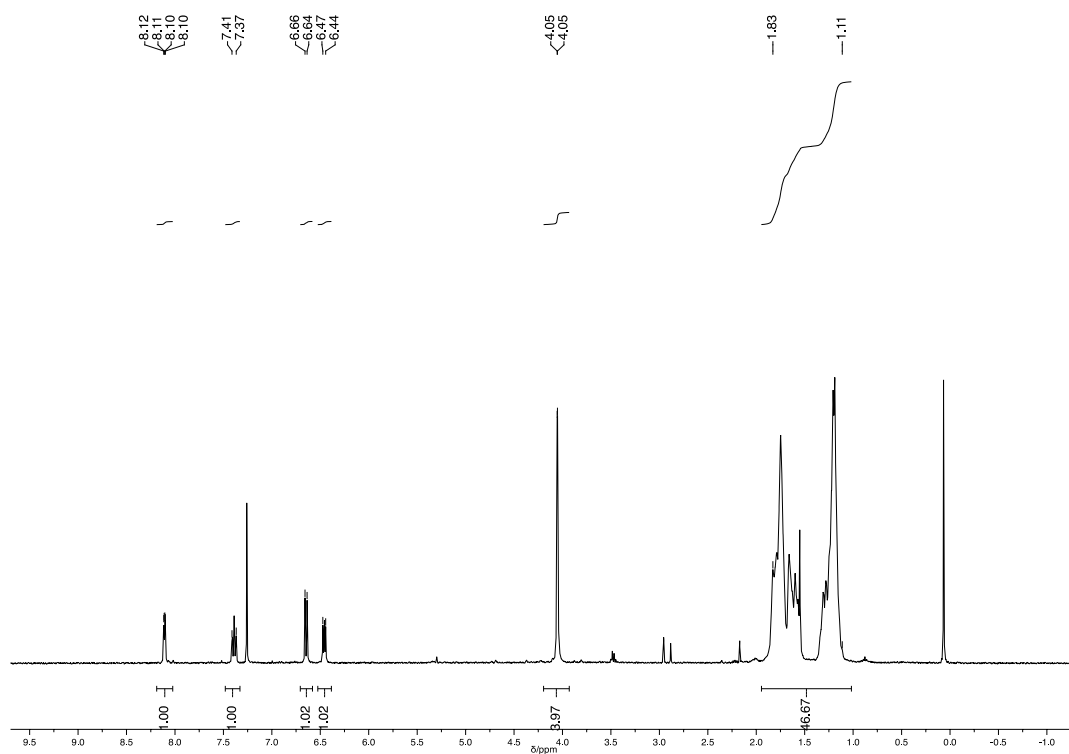


Figure S3. ^1H NMR spectrum of $\text{PPN}^{\text{C}_{\text{y}}\text{h}}$ (CDCl_3 , 400 MHz)

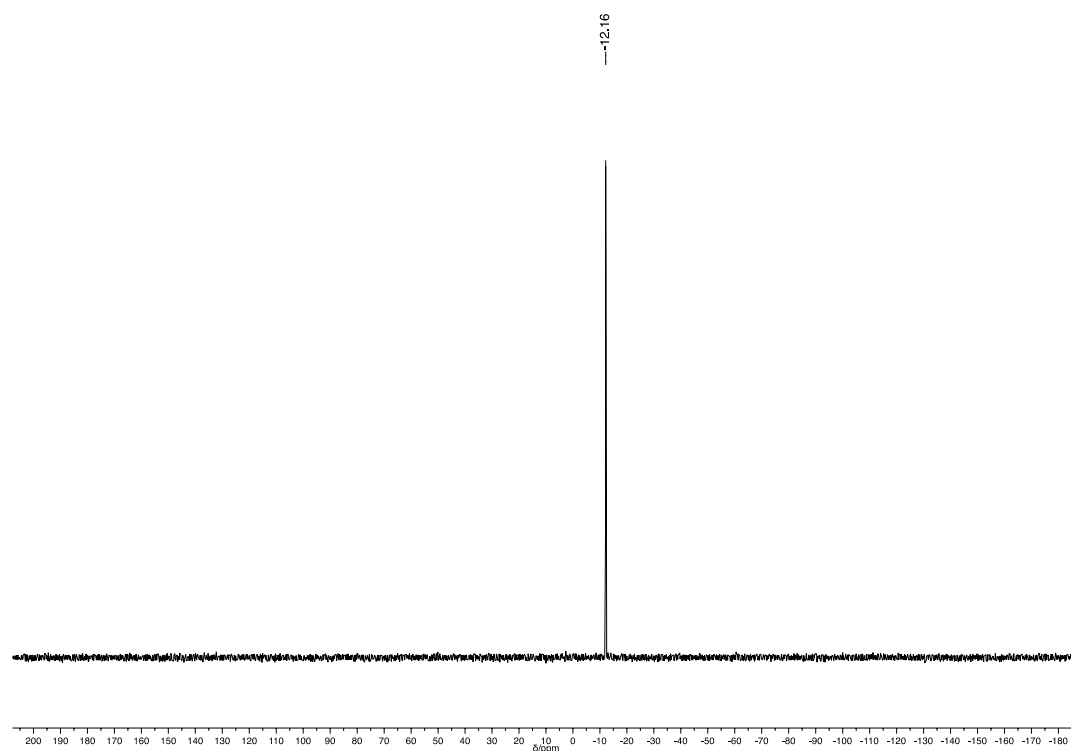


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of PPN^{Cyh} (CDCl_3 , 162 MHz)

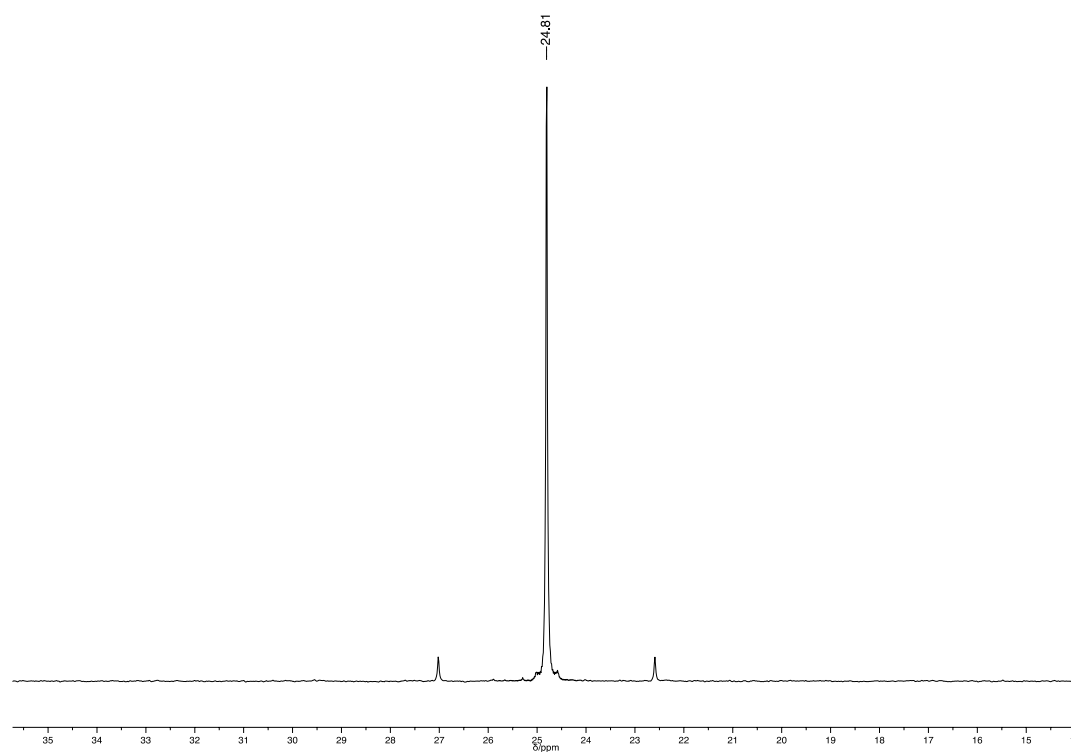


Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphine-selenide $\text{NP}_3^{\text{Ph}}=\text{Se}$ (CDCl_3 , 162 MHz)

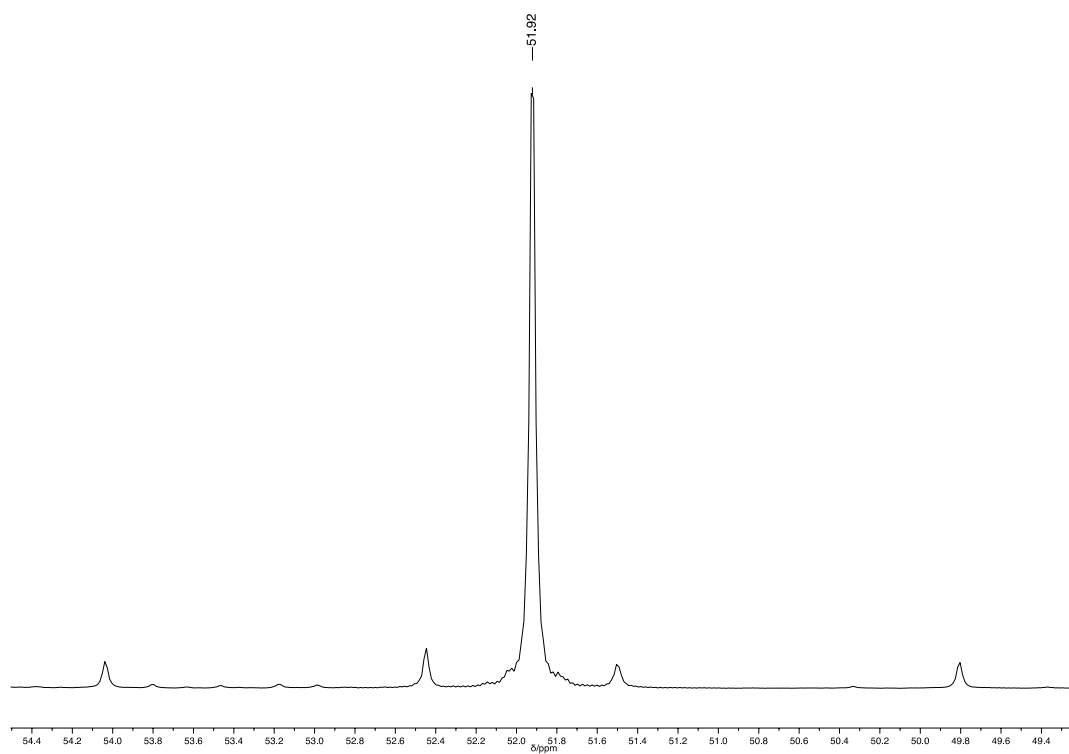


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphine-selenide $\text{NP}_3^{\text{iPr}}=\text{Se}$ (CDCl_3 , 162 MHz)

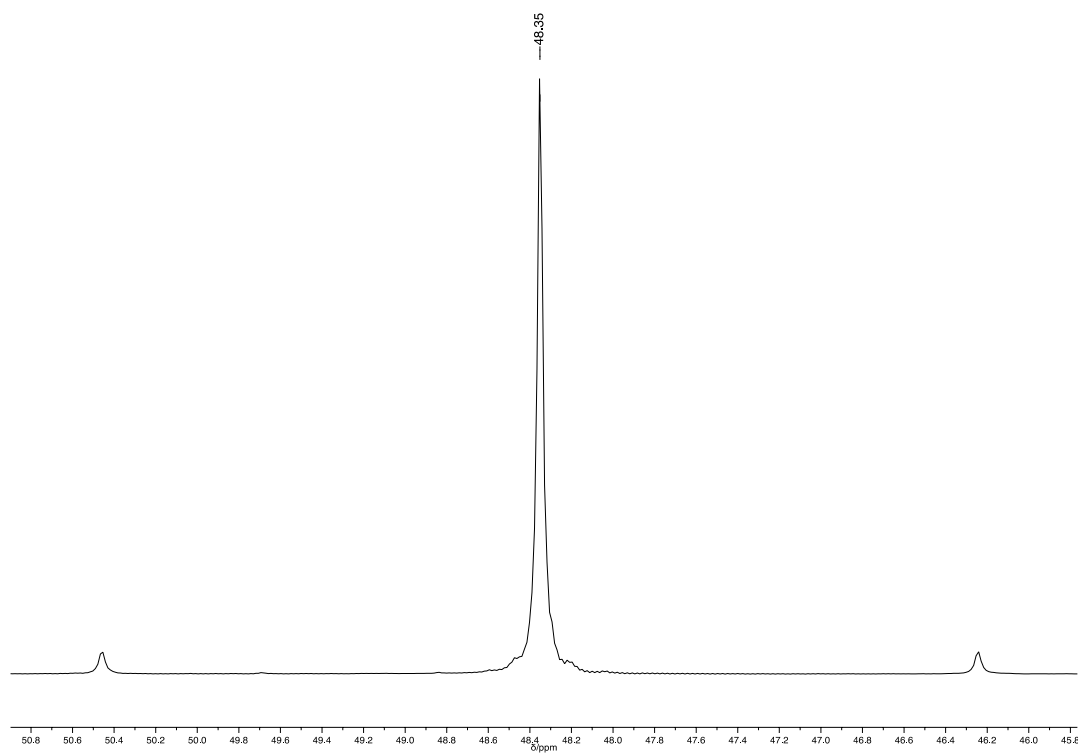


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphine-selenide $\text{NP}_3^{\text{Cyp}}=\text{Se}$ (CDCl_3 , 162 MHz)

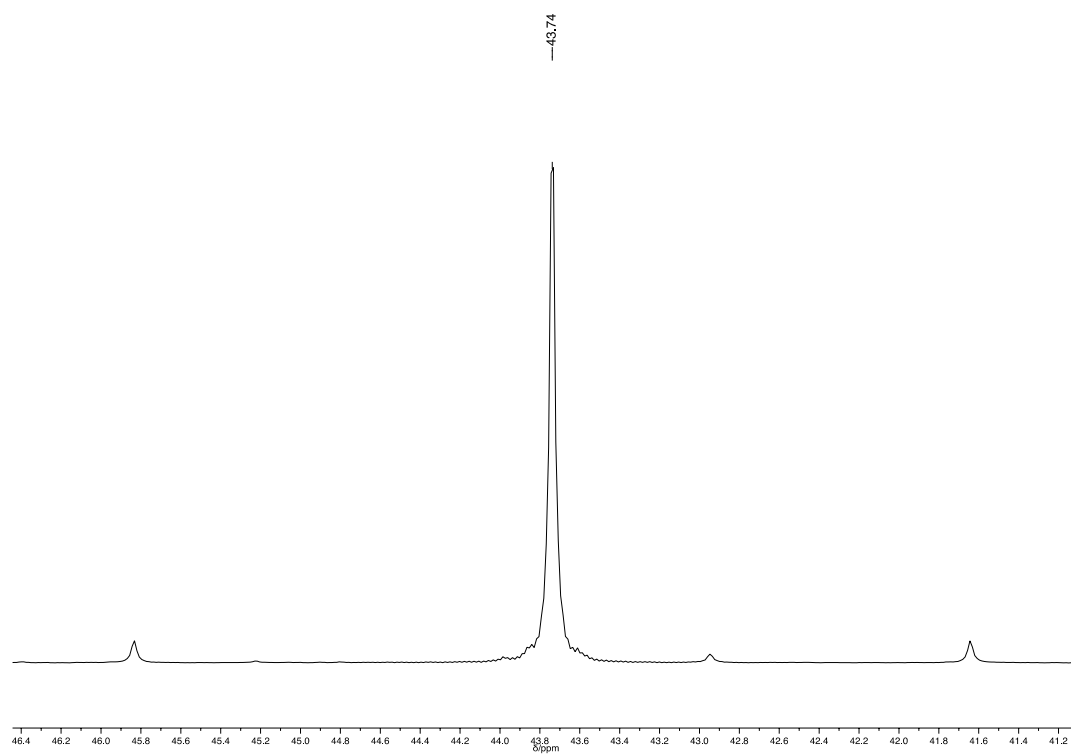


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphine-selenide $\text{NP}_3^{\text{Cyh}}=\text{Se}$ (CDCl_3 , 162 MHz)

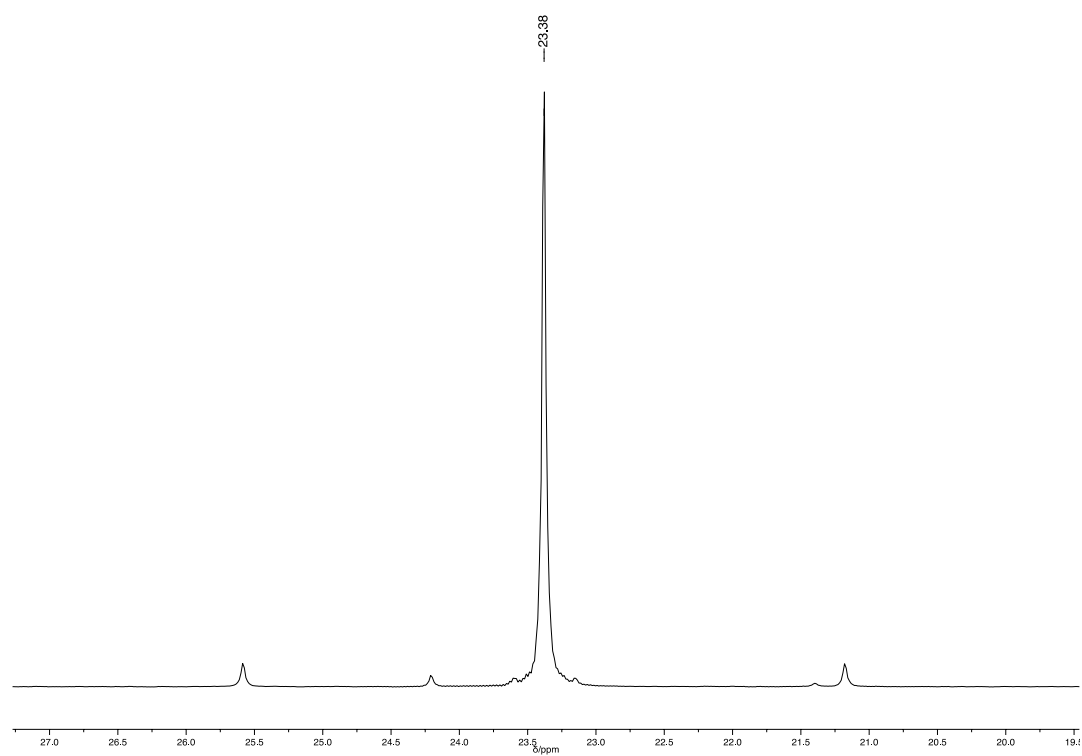


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphine-selenide $\text{MeCP}_3^{\text{Ph}}=\text{Se}$ (CDCl_3 , 162 MHz)

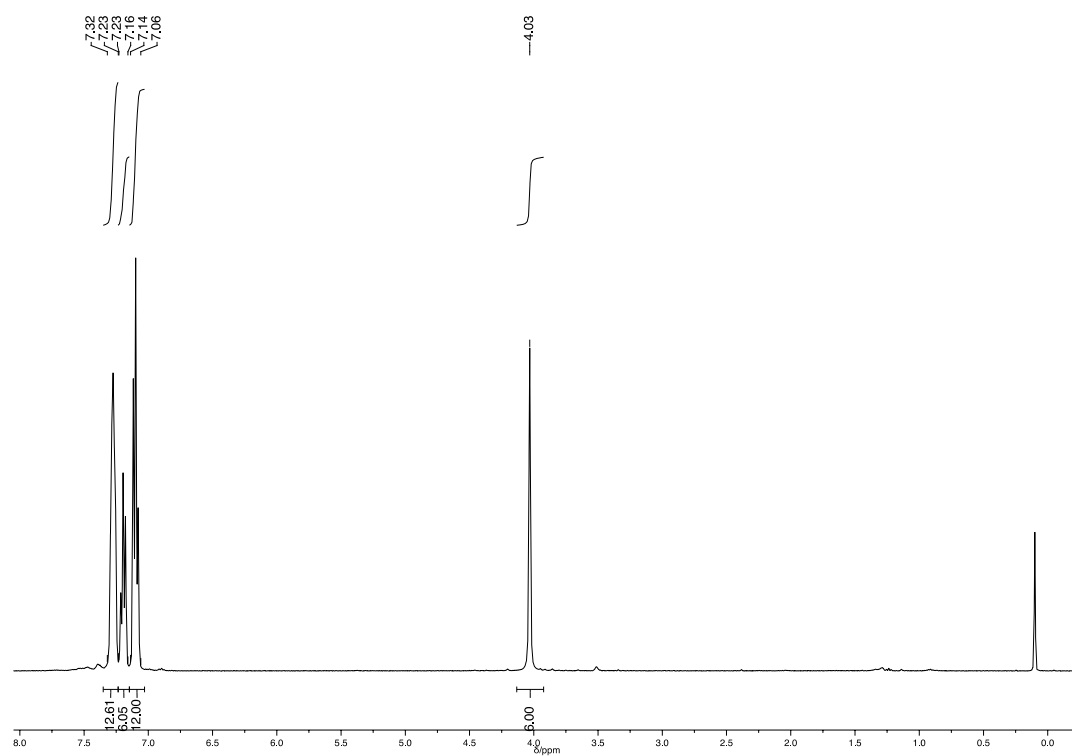


Figure S10. ¹H NMR spectrum of [W(CO)₃(κ³-NP₃^{Ph})] (**1**) (CDCl₃, 400 MHz)

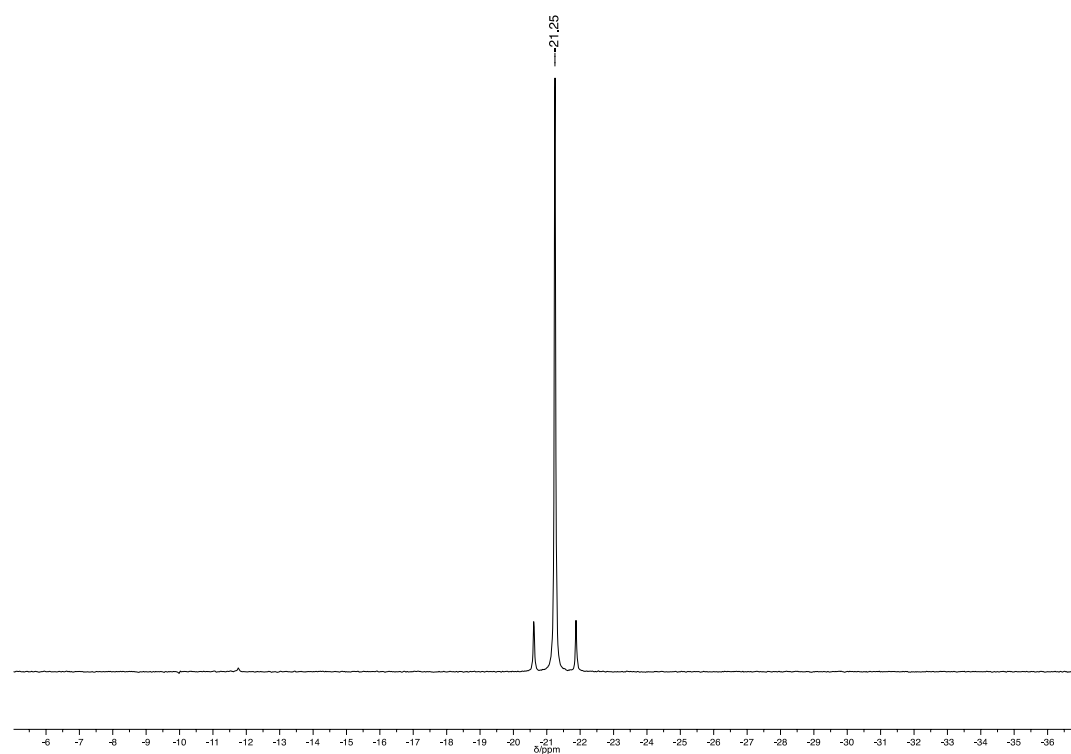


Figure S11. ³¹P{¹H} NMR spectrum of [W(CO)₃(κ³-NP₃^{Ph})] (**1**) (CDCl₃, 162 MHz)

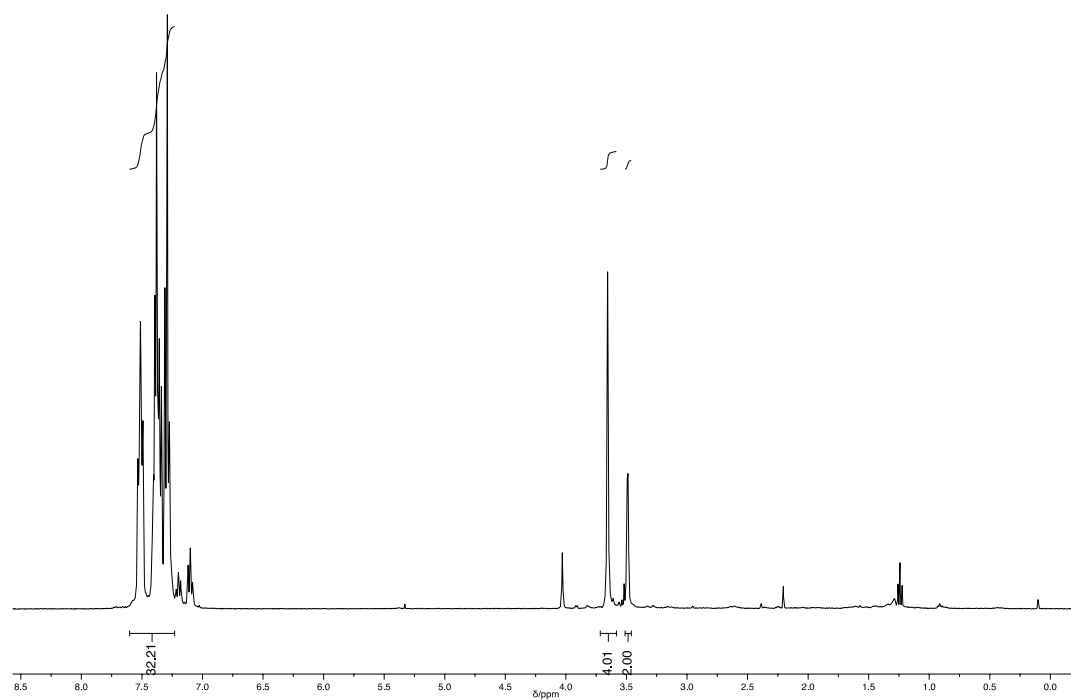


Figure S12. ¹H NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{Ph}})]$ (**2**) (CDCl_3 , 400 MHz)

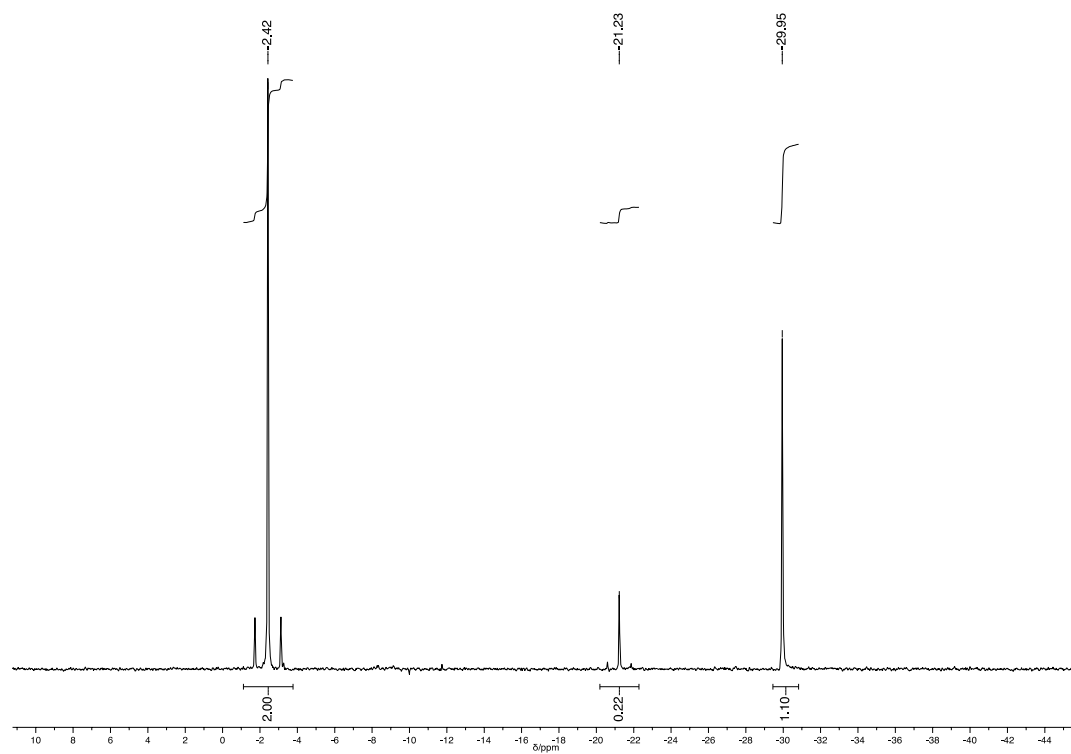


Figure S13. ³¹P{¹H} NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{Ph}})]$ (**2**) (CDCl_3 , 162 MHz)

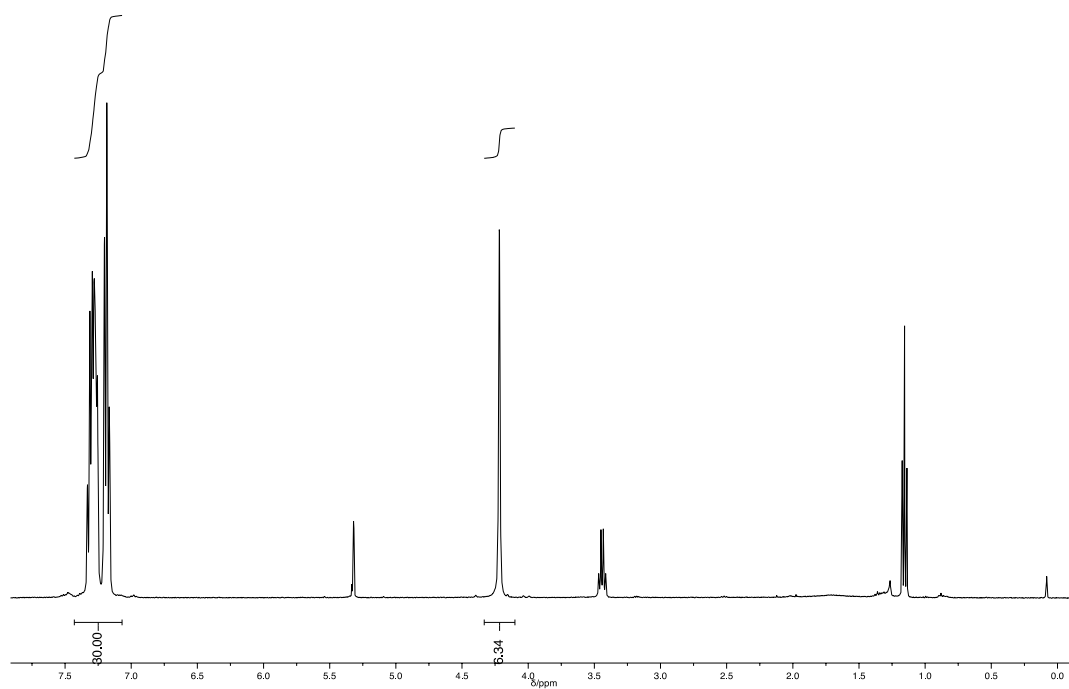


Figure S14. ^1H NMR spectrum of $[\text{W}(\text{CO})_3(\kappa^3\text{-NP}_3^{\text{Ph}})][\text{BF}_4]$ (**3**) (CD_2Cl_2 , 400 MHz)

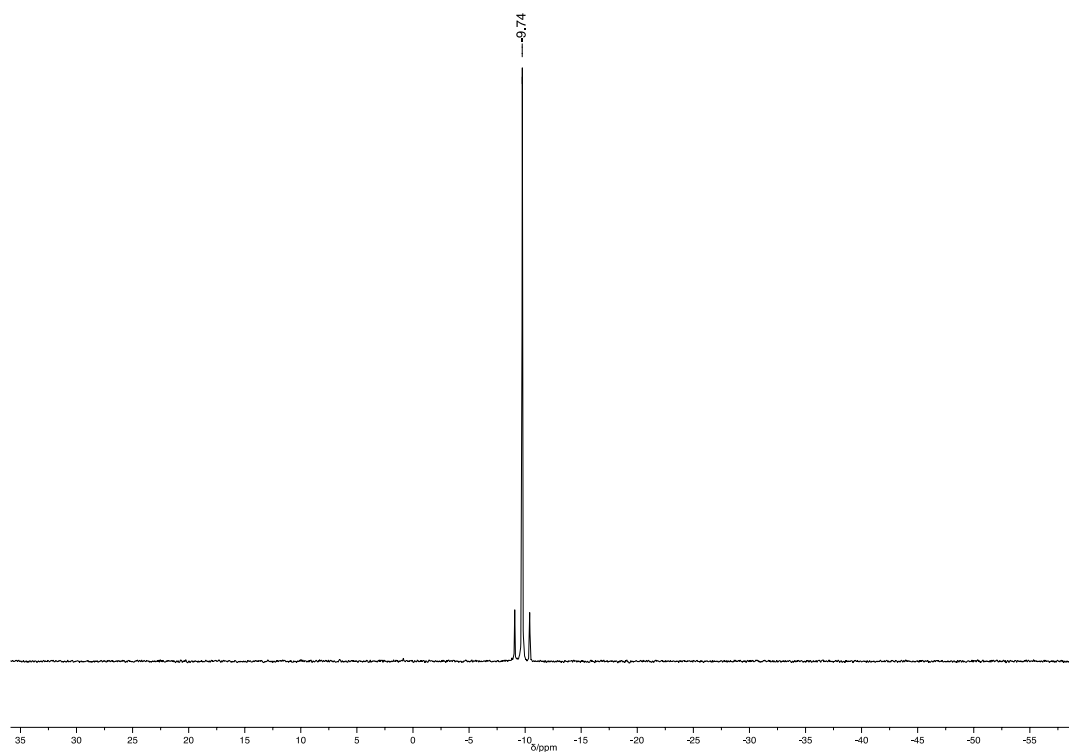


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{W}(\text{CO})_3(\kappa^3\text{-NP}_3^{\text{Ph}})][\text{BF}_4]$ (**3**) (CD_2Cl_2 , 162 MHz)

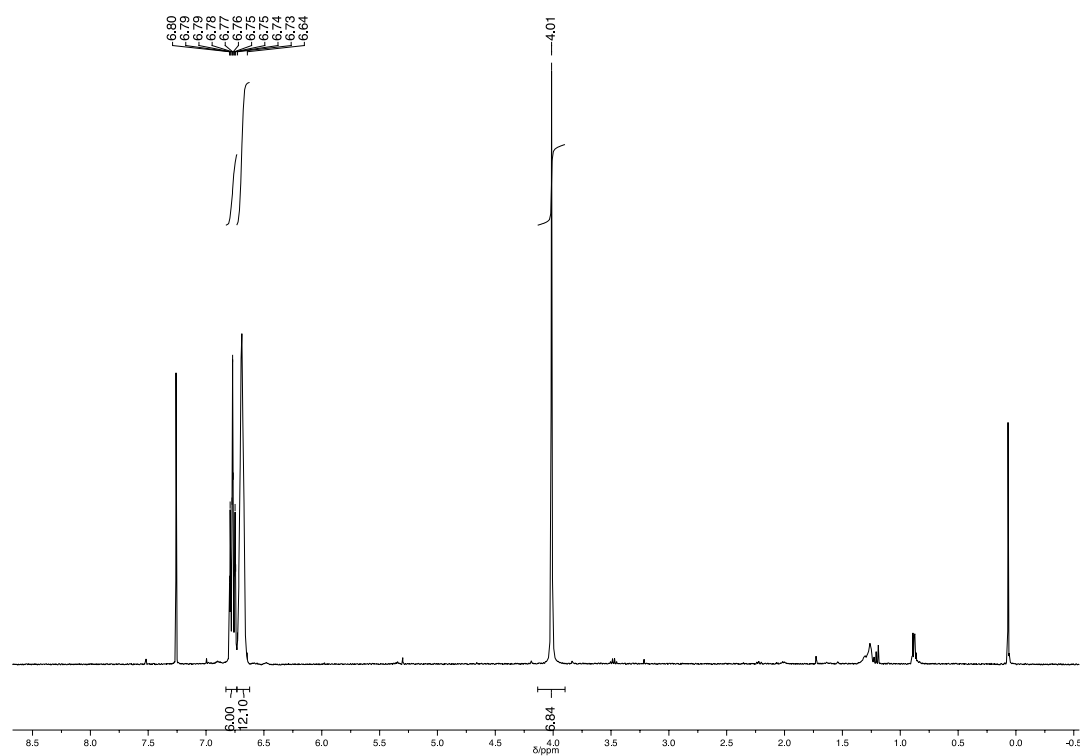


Figure S16. ^1H NMR spectrum of $[\text{W}(\text{CO})_3(\kappa^3\text{-NP}_3^{\text{PhF}_2})]$ (**4**) (CDCl_3 , 400 MHz)

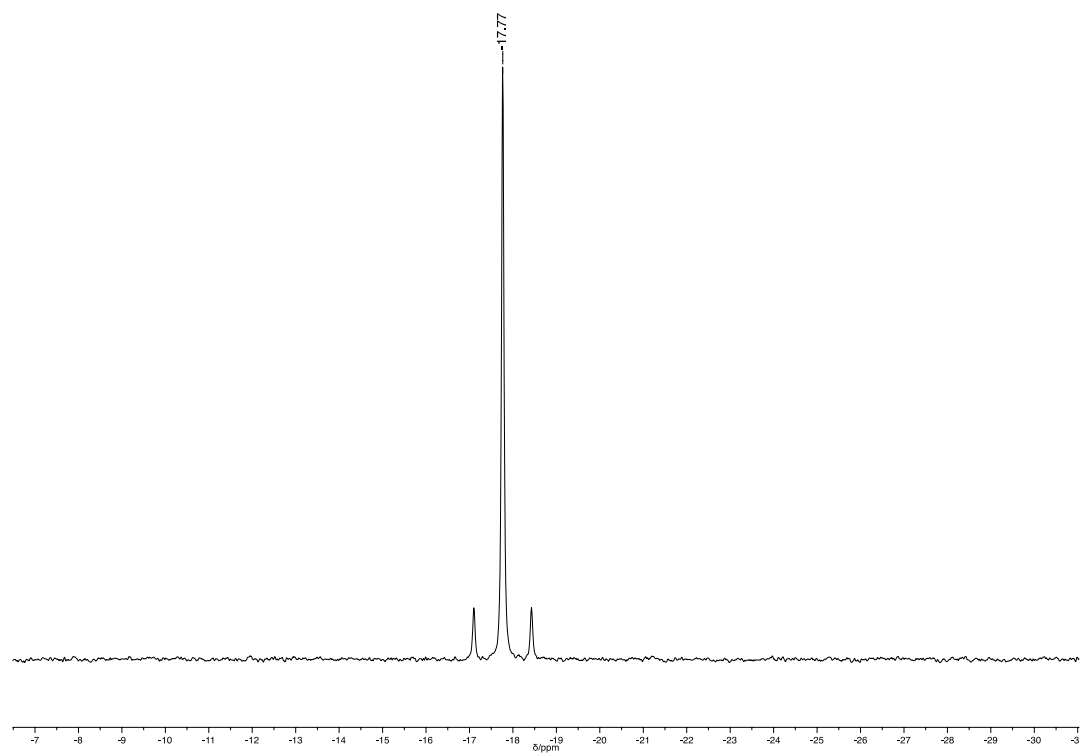


Figure S17. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{W}(\text{CO})_3(\kappa^3\text{-NP}_3^{\text{PhF}_2})]$ (**4**) (CDCl_3 , 162 MHz)

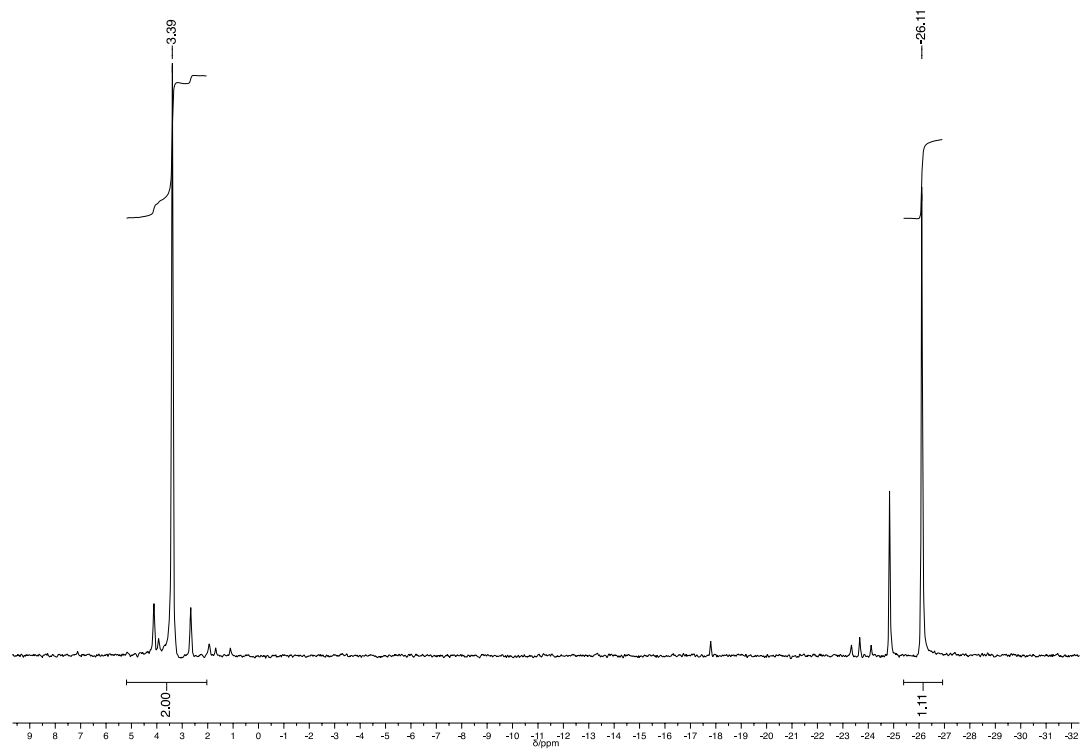


Figure S18. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{PhF}_2})]$ (**5**) (CDCl_3 , 162 MHz)

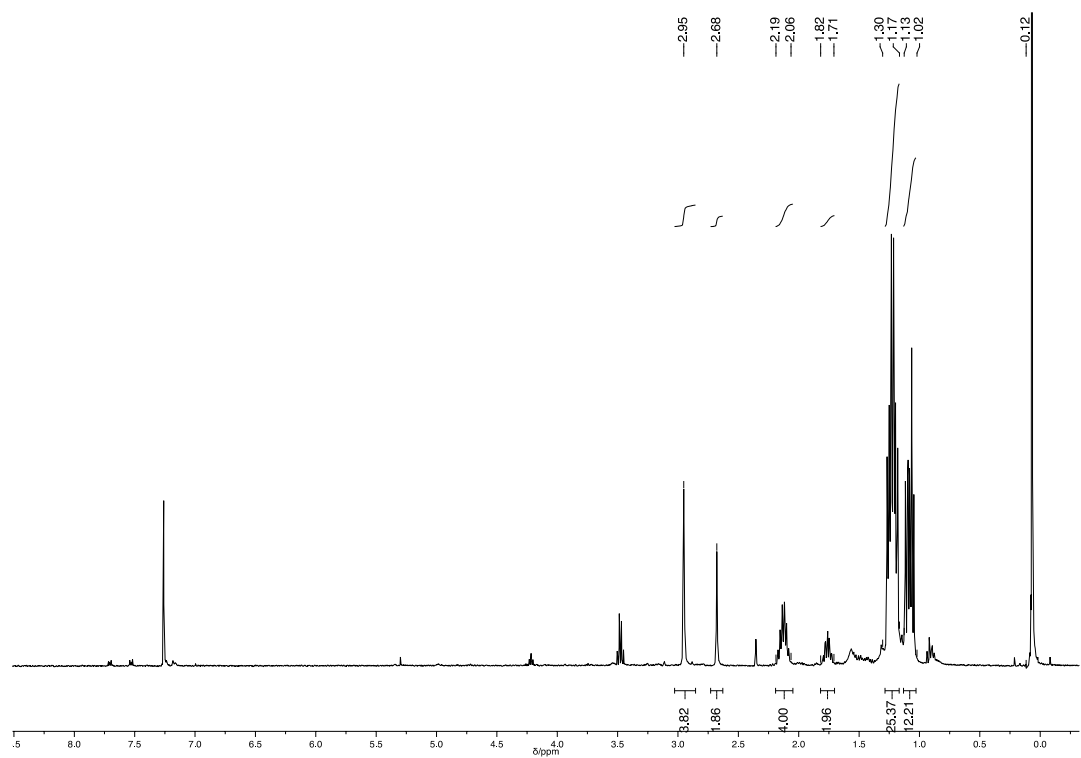


Figure S19. ^1H NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{iPr}})]$ (**6**) (CDCl_3 , 400 MHz)

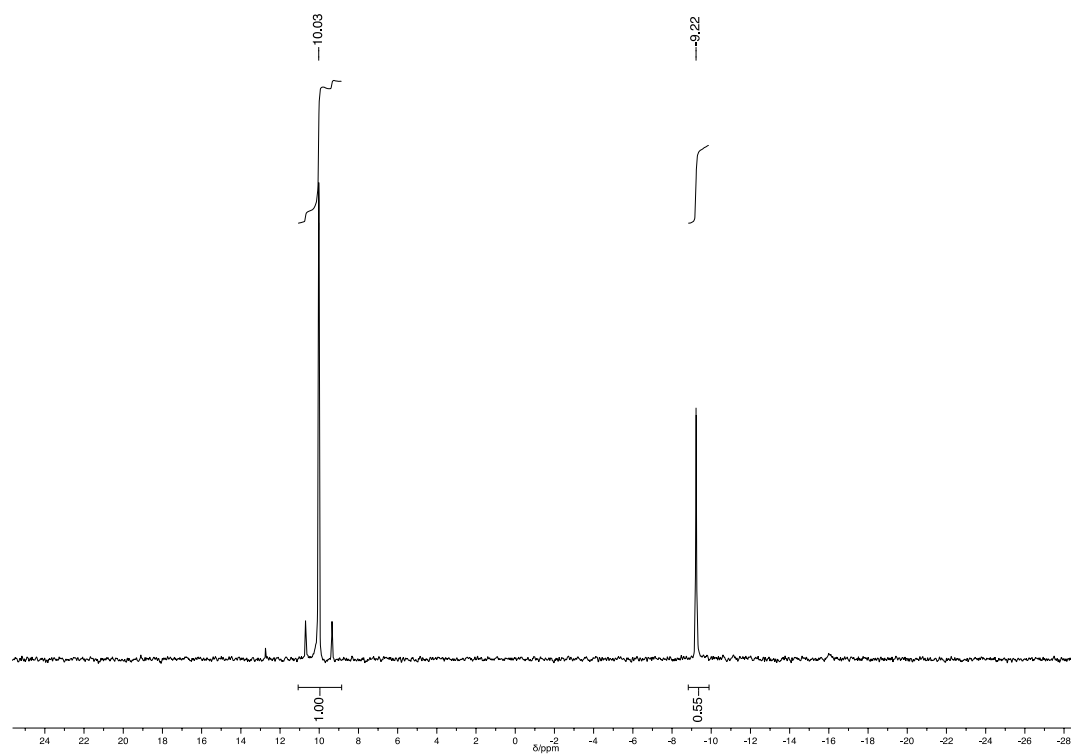


Figure S20. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{iPr}})]$ (**6**) (CDCl_3 , 162 MHz)

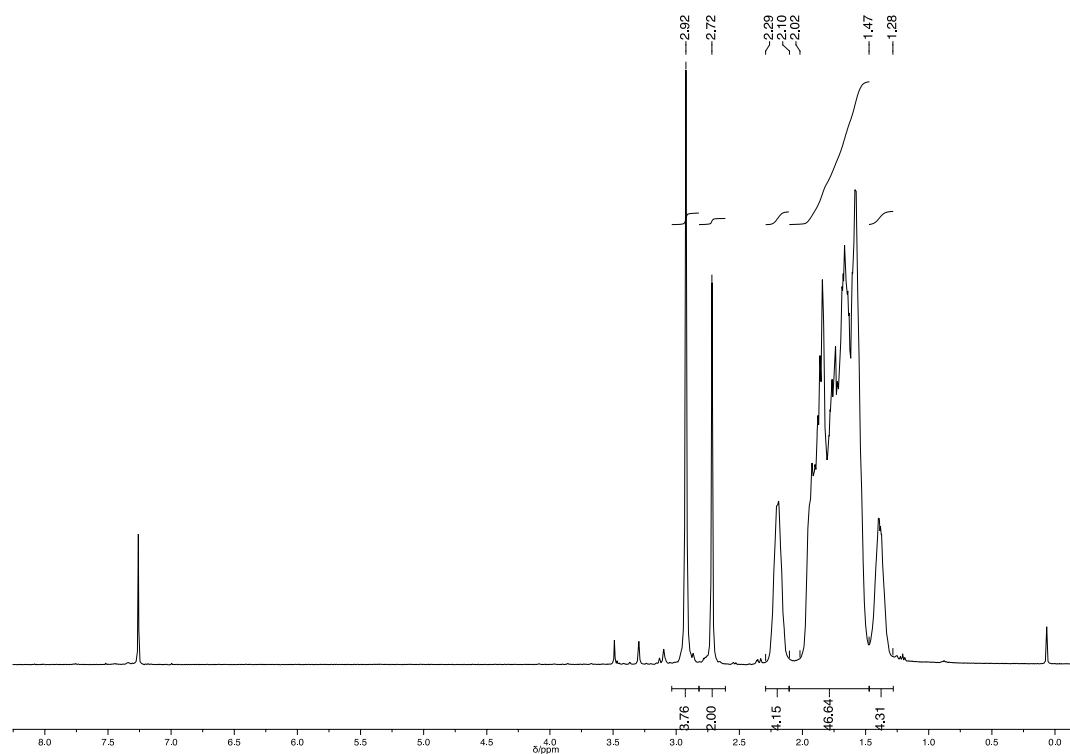


Figure S21. ^1H NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{Cyp}})]$ (**7**) (CDCl_3 , 400 MHz)

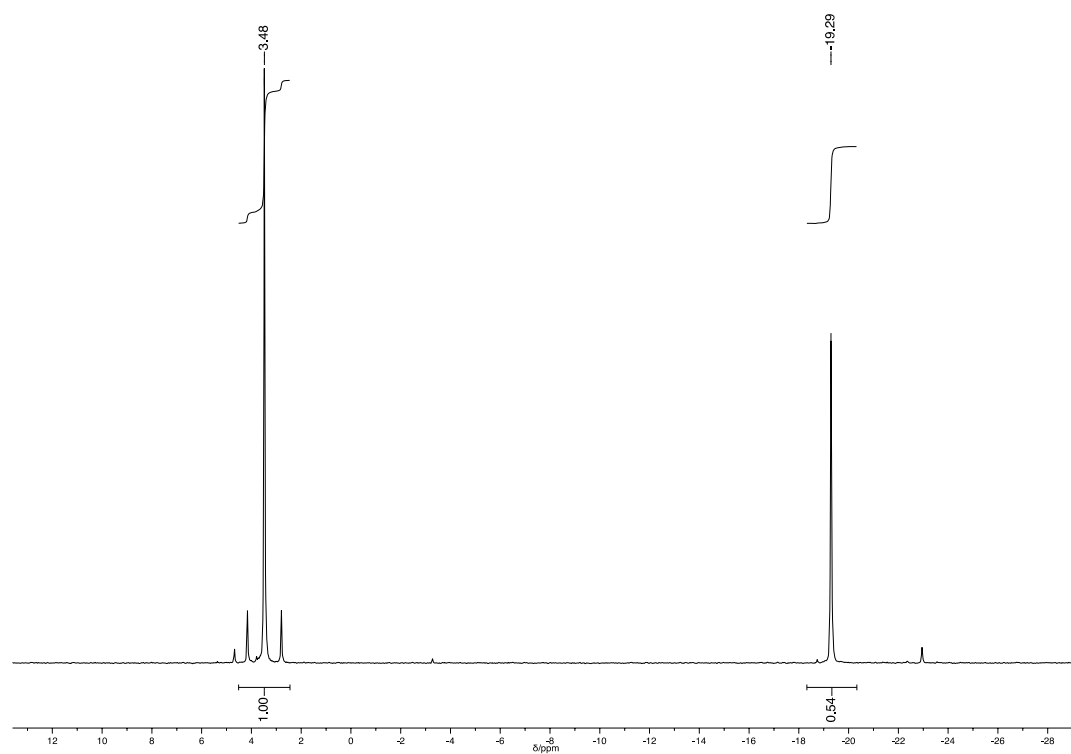


Figure S22. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{Cyp}})]$ (**7**) (CDCl_3 , 162 MHz)

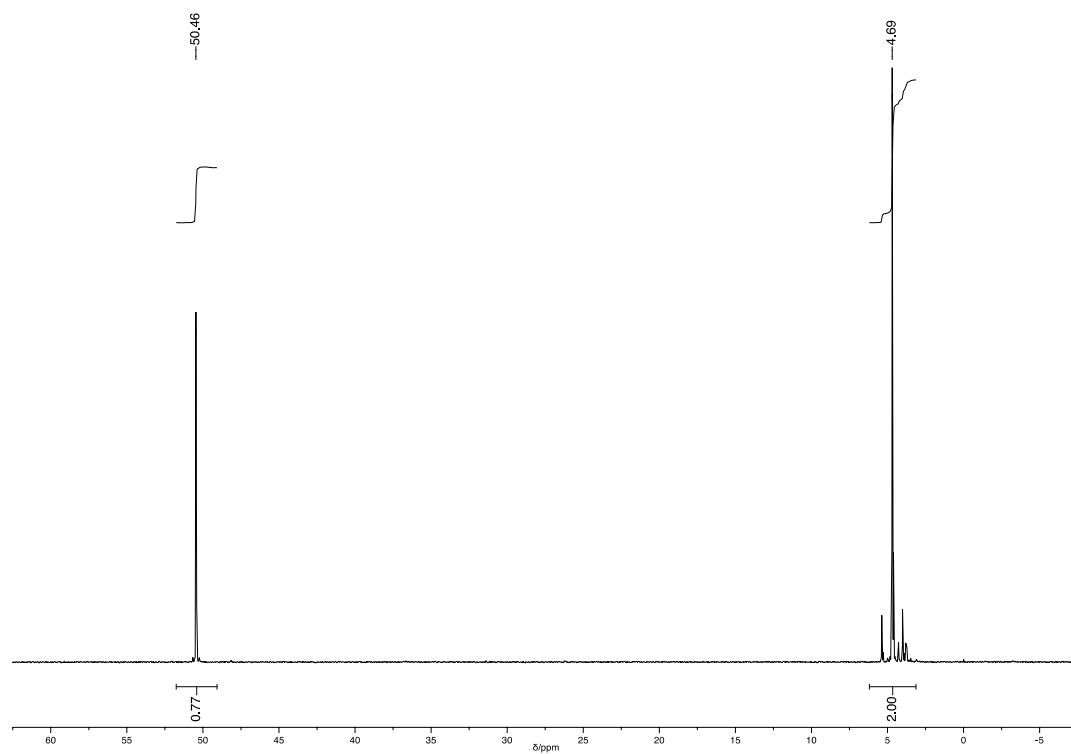


Figure S23. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2\text{-NP}_3^{\text{iPr}})]$ (**8**) (CDCl_3 , 162 MHz)

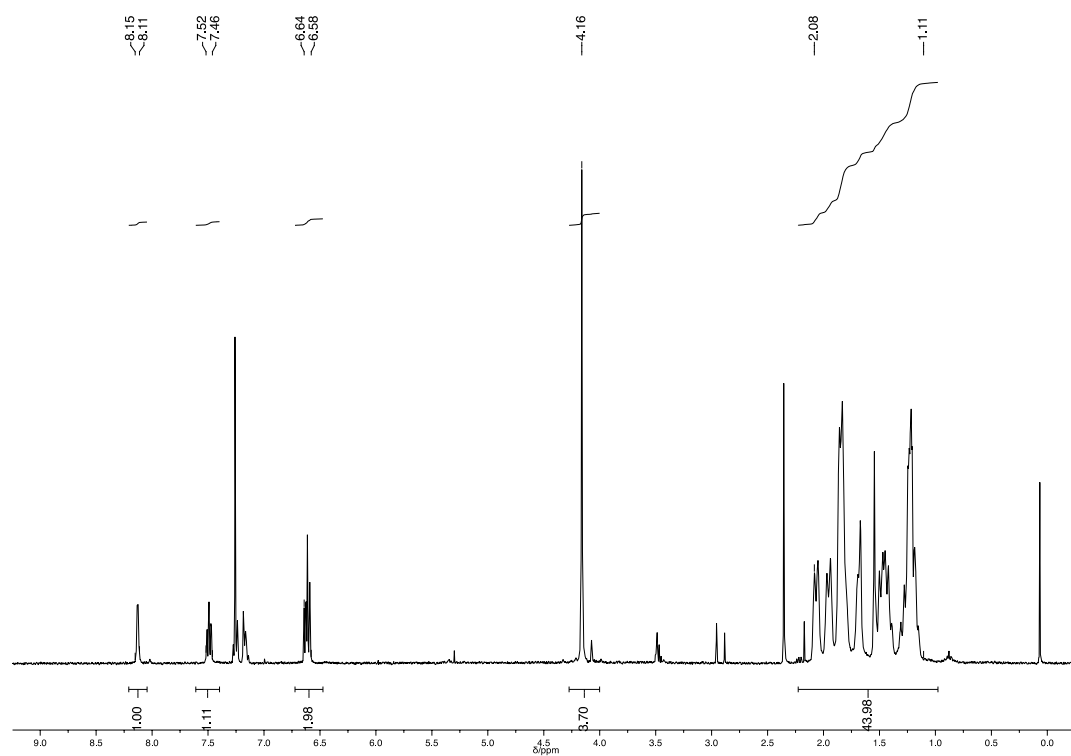


Figure S24. ¹H NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2P\text{-PPN}^{\text{Cyh}})]$ (**10**) (CDCl_3 , 400 MHz)

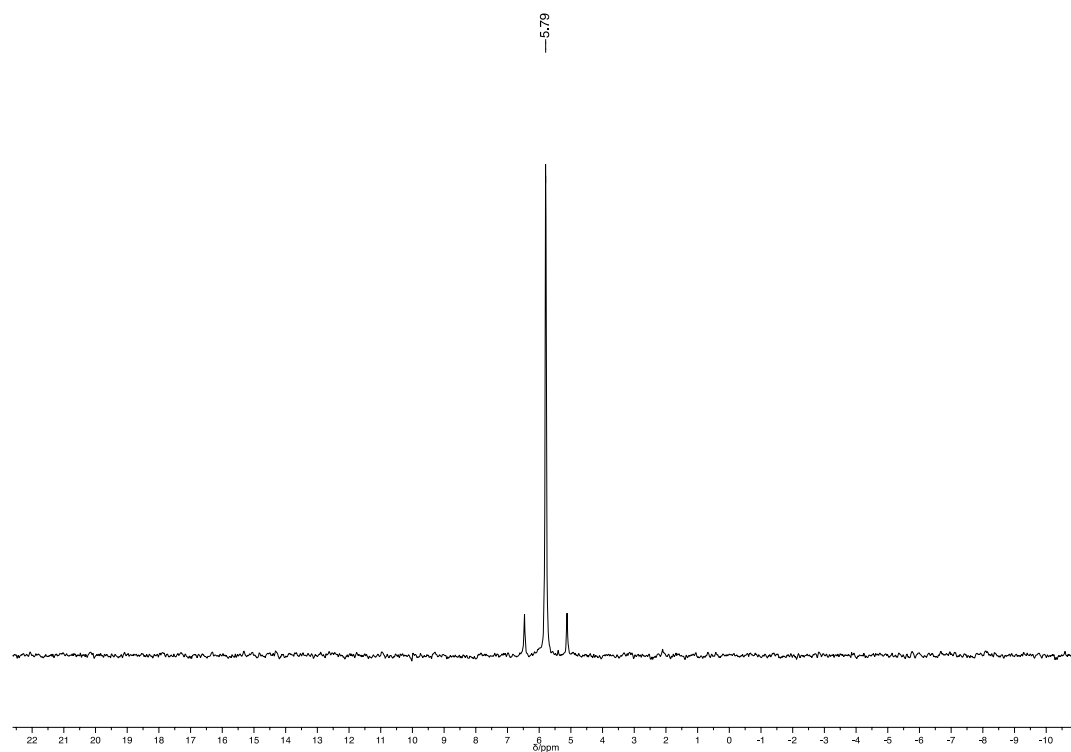


Figure S25. ³¹P{¹H} NMR spectrum of $[\text{W}(\text{CO})_4(\kappa^2P\text{-PPN}^{\text{Cyh}})]$ (**10**) (CDCl_3 , 162 MHz)

Crystallographic Data

Table S1 provides a summary of the crystallographic data for the structures of **1**, **3**, **4**, **4'**, **6**, **7**, **8** and **10**. Data were collected using Agilent Xcalibur PX Ultra A (**1**, **4**, **6**, **7** and **8**) and Xcalibur 3E (**3**, **4'** and **10**) diffractometers, and the structures were refined using the SHELXTL, SHELX-97, and SHELX-2013 program systems.¹ The absolute structures of **7** and **8** were determined by use of the Flack parameter [$x^+ = -0.009(6)$ and $-0.023(19)$ respectively]. CCDC 1412494 to 1412501.

Table S1. Crystal Data. Data Collection and Refinement Parameters for the structures of **1**, **3**, **4**, **4'**, **6**, **7**, **8** and **10**.

data	1	3	4
formula	C ₄₂ H ₃₆ NO ₃ P ₃ W	[C ₄₂ H ₃₇ NO ₃ P ₃ W](BF ₄)	C ₄₂ H ₂₄ F ₁₂ NO ₃ P ₃ W
solvent	—	1.5(CH ₂ Cl ₂)	—
formula weight	879.48	1094.68	1095.38
colour, habit	colourless needles	colourless blocks	colourless platy needles
temperature / K	173	173	173
crystal system	monoclinic	orthorhombic	monoclinic
space group	<i>P2₁/n</i> (no. 14)	<i>Pnma</i> (no. 62)	<i>P2₁/n</i> (no. 14)
<i>a</i> / Å	10.23450(11)	18.1122(4)	10.3366(2)
<i>b</i> / Å	19.2654(3)	35.0113(8)	8.3660(2)
<i>c</i> / Å	18.46010(20)	13.3447(3)	45.8955(10)
α / deg	90	90	90
β / deg	94.9551(9)	90	92.650(2)
γ / deg	90	90	90
<i>V</i> / Å³	3626.21(7)	8462.3(3)	3964.62(16)
<i>Z</i>	4	8	4
<i>D_c</i> / g cm⁻³	1.611	1.718	1.835
radiation used	Cu-K α	Mo-K α	Cu-K α
μ / mm⁻¹	7.482	3.093	7.445
2θ max / deg	147	56	148
no. of unique reflns			
measured (<i>R</i>_{int})	6984 (0.0217)	8710 (0.0535)	7582 (0.0408)
obs, F_o >	6205	6893	6523
no. of variables	451	510	560
<i>R</i>₁(obs), <i>wR</i>₂(all) [a]	0.0215, 0.0516	0.0761, 0.1669	0.0398, 0.0958

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [b] There are two crystallographically independent molecules. [c] R_{int} of zero due to structure being modelled as a twin using HKLF5 refinement.

Table S1. Part 2.

data	4'	6	7
formula	C ₄₂ H ₂₄ F ₁₂ NO ₃ P ₃ W	C ₂₅ H ₄₈ NO ₄ P ₃ W	C ₃₇ H ₆₀ NO ₄ P ₃ W
solvent	—	—	—
formula weight	1095.38	703.40	859.62
colour, habit	colourless platy needles	colourless plates	colourless platy needles
temperature / K	173	173	173
crystal system	triclinic	monoclinic	orthorhombic
space group	<i>P</i> -1 (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>Pna</i> 2 ₁ (no. 33)
<i>a</i> / Å	8.30064(15)	15.45700(18)	21.077(2)
<i>b</i> / Å	10.2472(2)	12.41049(15)	20.1866(18)
<i>c</i> / Å	23.6539(5)	32.2167(5)	8.8990(4)
α / deg	101.9521(18)	90	90
β / deg	94.4676(17)	95.3745(14)	90
γ / deg	90.3026(16)	90	90
<i>V</i> / Å ³	1961.89(7)	6152.93(14)	3786.3(6)
<i>Z</i>	2	8 [b]	4
<i>D_c</i> / g cm ⁻³	1.854	1.519	1.508
radiation used	Mo-K α	Cu-K α	Cu-K α
μ / mm ⁻¹	3.167	8.660	7.152
2 θ max / deg	58	145	147
no. of unique reflns			
measured (<i>R</i> _{int})	8502 (0.0277)	19350 (0.00) [c]	5188 (0.0146)
obs, $ F_o >$	8104	17023	5108
no. of variables	559	627	437
<i>R</i> ₁ (obs), <i>wR</i> ₂ (all) [a]	0.0431, 0.0990	0.0797, 0.2588	0.0175, 0.0464

Table S1. Part 3.

data	8	10
formula	C ₃₇ H ₆₀ NO ₅ P ₃ W	C ₃₅ H ₅₂ N ₂ O ₄ P ₂ W
solvent	—	0.5(C ₇ H ₈)
formula weight	875.62	856.64
colour, habit	pale yellow-brown plates	colourless blocks
temperature / K	173	173
crystal system	orthorhombic	monoclinic
space group	<i>Pna</i> 2 ₁ (no. 33)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> / Å	20.9984(5)	37.9478(5)
<i>b</i> / Å	20.2089(4)	10.57997(15)
<i>c</i> / Å	8.90858(17)	19.1922(3)
α / deg	90	90
β / deg	90	100.3336(14)
γ / deg	90	90
<i>V</i> / Å ³	3780.39(14)	7580.43(19)
<i>Z</i>	4	8 [b]
<i>D</i> _c / g cm ⁻³	1.538	1.501
radiation used	Cu-K α	Mo-K α
μ / mm ⁻¹	7.195	3.173
2 θ max / deg	148	66
no. of unique reflns		
measured (<i>R</i> _{int})	4377 (0.0389)	25641 (0.0350)
obs, $ F_o >$	3938	15781
no. of variables	425	867
<i>R</i> ₁ (obs), <i>wR</i> ₂ (all) [a]	0.0430, 0.1200	0.0817, 0.1077

X-ray Crystallography Discussion

The N1–H proton in the structure of **3** could not be located from ΔF maps, and so it was added in an idealized position and then refined freely subject to an N–H distance constraint of 0.90 Å. The C14-based phenyl ring was found to be disordered. Two orientations were identified of *ca.* 52 and 48% occupancy, their geometries were idealized, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). Both of the BF₄ anions have C_s symmetry with B10, F11 and F12, and B20, F21 and F22 sitting on the mirror plane. The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.² This suggested a total of 498 electrons per unit cell, equivalent to 62.3 electrons per asymmetric unit. Before the use of SQUEEZE the solvent clearly resembled dichloromethane (CH₂Cl₂, 42 electrons), and 1.5 dichloromethane molecules corresponds to 63 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric is low by 1.5(CH₂Cl₂) = C_{1.5}H₃Cl₃ (and that for the unit cell low by C₁₂H₂₄Cl₂₄) compared to what is actually presumed to be present. The final ΔF map for this structure contains an anomalously large residual electron density hole of *ca.* –5.92 eÅ⁻³ located in relatively free space with its closest contact to a non-hydrogen atom being *ca.* 1.16 Å to C46. This is probably a result of the presence of a small but significant amount of twinning, but attempts to model this did not meet with any substantive success.

The crystal of **6** that was studied was found to be a two component twin in a *ca.* 56:44 ratio, with the two lattices related by the approximate twin law [1.00 0.00 0.00 0.00 -1.00 0.00 -0.39 0.00 -1.00]. The structure was found to contain two crystallographically independent molecules, **6-A** and **6-B**, and the C23-based isopropyl group in molecule **6-B** was found to be disordered. Two orientations were identified of *ca.* 80 and 20% occupancy, their geometries were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The C23-based cyclopentane unit in the structure of **7** was found to be disordered. Two orientations were identified of *ca.* 67 and 23% occupancy, their geometries were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The absolute structure of **7** was determined by use of the Flack parameter [$x^+ = -0.009(6)$].

The absolute structure of **8** was determined by use of the Flack parameter [$x^+ = -0.023(19)$].

The structure of **10** was found to contain two crystallographically independent molecules, **10-A** and **10-B**, and the C6-based pyridyl ring was found to be disordered in both molecules. Two orientations were identified in each case corresponding to a “flipping” of the nitrogen atom position between the two possible *ortho* sites, with occupancies of *ca.* 68:32 and 63:37 for molecules **10-A** and **10-B** respectively. In both instances the geometries of the two orientations were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The included toluene solvent molecule was found to be severely disordered. Four orientations were identified of *ca.* 27, 26, 25 and 22% occupancy, their geometries were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

Figures S26–S35 show 50% probability ellipsoid ORTEP diagrams of the crystal structures of compounds **1**, **3**, **4**, **6–8** and **10**, while Tables S2–S9 provide selected bond lengths and angles for compounds **1**, **3**, **4**, **6–8** and **10**.

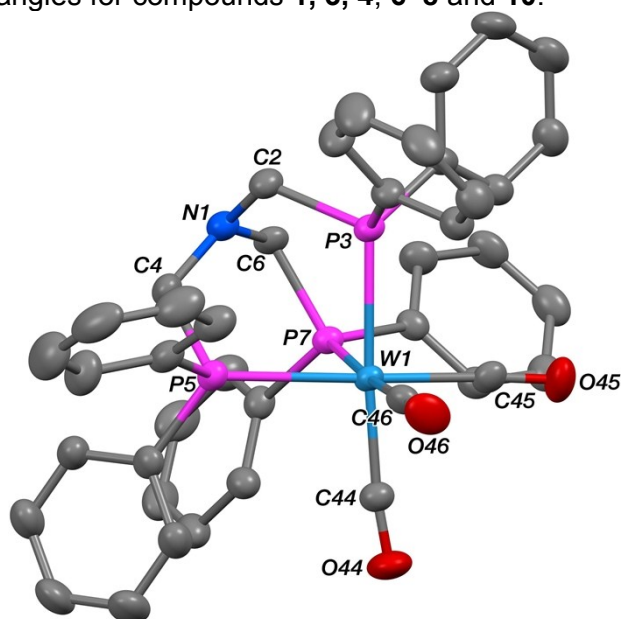


Figure S26. The crystal structure of **1** (50% probability ellipsoids)

W(1)–P(3)	2.5148(6)	P(3)–W(1)–C(45)	91.02(8)
W(1)–P(5)	2.5354(7)	P(3)–W(1)–C(46)	90.96(8)
W(1)–P(7)	2.5131(6)	P(5)–W(1)–C(44)	95.74(8)
W(1)–N(1)	3.615(2)	P(5)–W(1)–C(45)	175.94(8)
W(1)–C(44)	1.982(3)	P(5)–W(1)–C(46)	98.95(8)
W(1)–C(45)	1.975(3)	P(7)–W(1)–C(44)	97.62(8)
W(1)–C(46)	1.995(3)	P(7)–W(1)–C(45)	94.39(8)
		P(7)–W(1)–C(46)	175.53(8)
P(3)–W(1)–P(5)	87.93(2)	C(44)–W(1)–C(45)	85.44(12)
P(3)–W(1)–P(7)	84.62(2)	C(44)–W(1)–C(46)	86.76(11)
P(5)–W(1)–P(7)	81.60(2)	C(45)–W(1)–C(46)	84.99(11)
P(3)–W(1)–C(44)	175.94(8)		

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

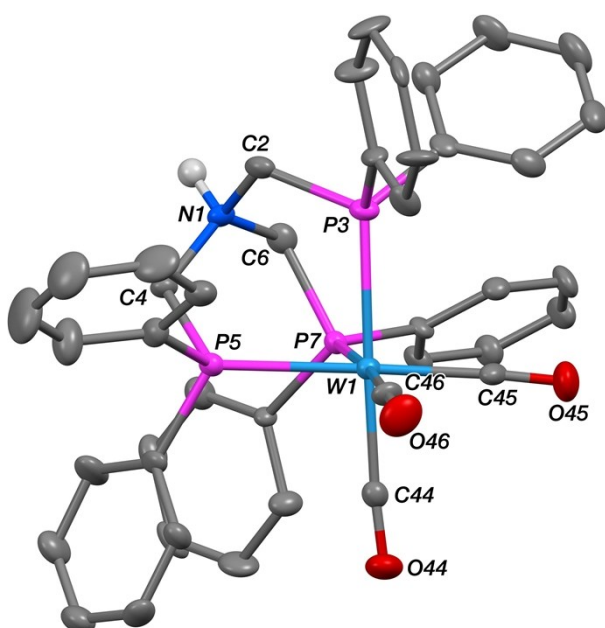


Figure S27. The structure of the cation present in the crystal of **3** (50% probability ellipsoids)

W(1)–P(3)	2.507(3)	P(3)–W(1)–C(45)	94.7(3)
W(1)–P(5)	2.488(3)	P(3)–W(1)–C(46)	95.7(3)
W(1)–P(7)	2.508(3)	P(5)–W(1)–C(44)	94.8(3)
W(1)–N(1)	3.657(8)	P(5)–W(1)–C(45)	176.5(3)
W(1)–C(44)	1.988(10)	P(5)–W(1)–C(46)	95.0(3)
W(1)–C(45)	1.985(10)	P(7)–W(1)–C(44)	93.7(3)
W(1)–C(46)	2.003(10)	P(7)–W(1)–C(45)	95.4(3)
		P(7)–W(1)–C(46)	175.9(3)
P(3)–W(1)–P(5)	86.66(9)	C(44)–W(1)–C(45)	83.8(4)
P(3)–W(1)–P(7)	86.13(8)	C(44)–W(1)–C(46)	84.6(4)
P(5)–W(1)–P(7)	81.45(8)	C(45)–W(1)–C(46)	88.0(4)
P(3)–W(1)–C(44)	178.4(3)		

Table S3. Selected bond lengths (Å) and angles (°) for **3**.

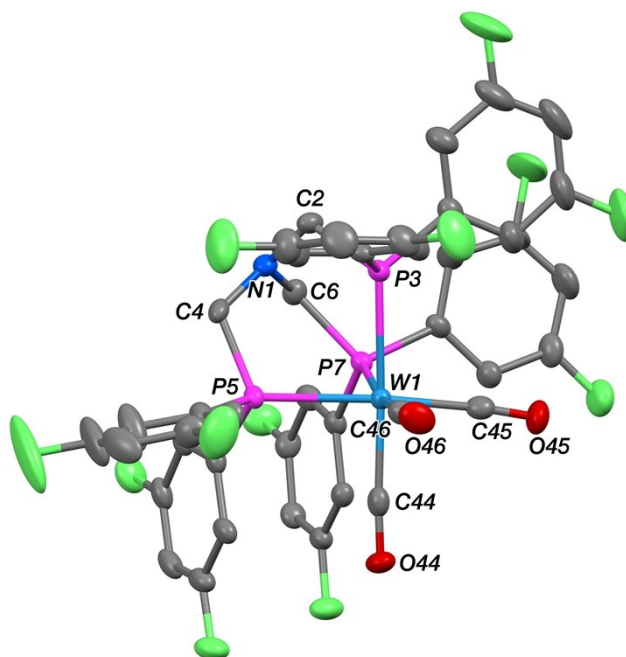


Figure S28. The crystal structure of **4** (space group: $P2_1/n$) (50% probability ellipsoids)

W(1)–P(3)	2.5038(14)	P(3)–W(1)–C(45)	97.11(17)
W(1)–P(5)	2.5059(13)	P(3)–W(1)–C(46)	86.67(17)
W(1)–P(7)	2.4961(13)	P(5)–W(1)–C(44)	89.49(16)
W(1)–N(1)	3.656(5)	P(5)–W(1)–C(45)	171.88(16)
W(1)–C(44)	1.983(6)	P(5)–W(1)–C(46)	101.41(17)
W(1)–C(45)	1.987(6)	P(7)–W(1)–C(44)	101.08(16)
W(1)–C(46)	1.994(5)	P(7)–W(1)–C(45)	93.02(16)
		P(7)–W(1)–C(46)	170.79(16)
P(3)–W(1)–P(5)	88.23(4)	C(44)–W(1)–C(45)	85.8(2)
P(3)–W(1)–P(7)	84.63(4)	C(44)–W(1)–C(46)	87.8(2)
P(5)–W(1)–P(7)	81.36(4)	C(45)–W(1)–C(46)	85.1(2)
P(3)–W(1)–C(44)	173.46(16)		

Table S4. Selected bond lengths (Å) and angles (°) for **4**.

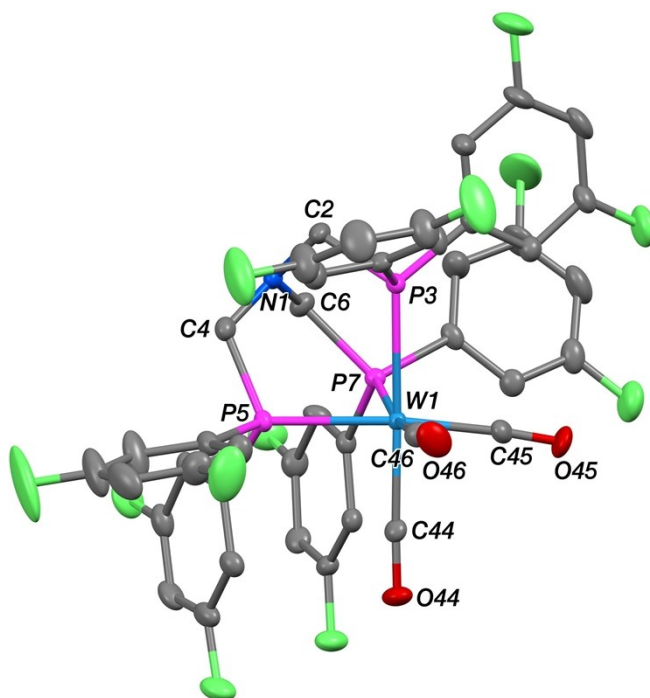


Figure S29. An alternative crystal structure of **4** (space group: *P*-1 (50% probability ellipsoids)

W(1)–P(3)	2.5036(15)	P(3)–W(1)–C(45)	97.30(18)
W(1)–P(5)	2.5054(15)	P(3)–W(1)–C(46)	85.80(18)
W(1)–P(7)	2.5072(15)	P(5)–W(1)–C(44)	89.26(18)
W(1)–N(1)	3.635(5)	P(5)–W(1)–C(45)	172.27(18)
W(1)–C(44)	1.972(6)	P(5)–W(1)–C(46)	100.11(19)
W(1)–C(45)	1.980(6)	P(7)–W(1)–C(44)	101.95(17)
W(1)–C(46)	1.987(6)	P(7)–W(1)–C(45)	95.14(18)
		P(7)–W(1)–C(46)	169.36(19)
P(3)–W(1)–P(5)	89.32(5)	C(44)–W(1)–C(45)	84.6(2)
P(3)–W(1)–P(7)	83.71(5)	C(44)–W(1)–C(46)	88.6(2)
P(5)–W(1)–P(7)	81.57(5)	C(45)–W(1)–C(46)	84.4(3)
P(3)–W(1)–C(44)	173.89(17)		

Table S5. Selected bond lengths (Å) and angles (°) for **4**'.

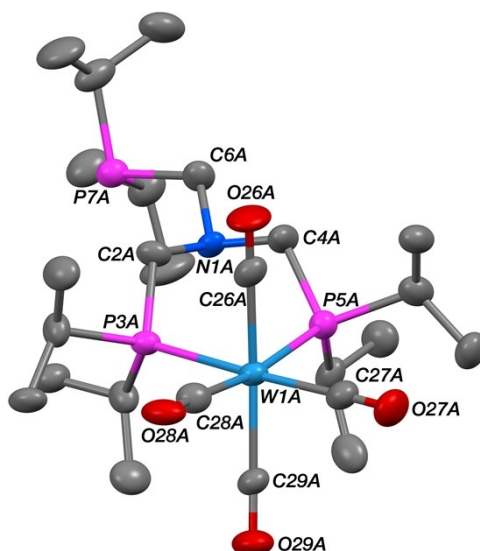


Figure S30. The structure of one (**6-A**) of the two independent complexes present in the crystal of **6** (50% probability ellipsoids)

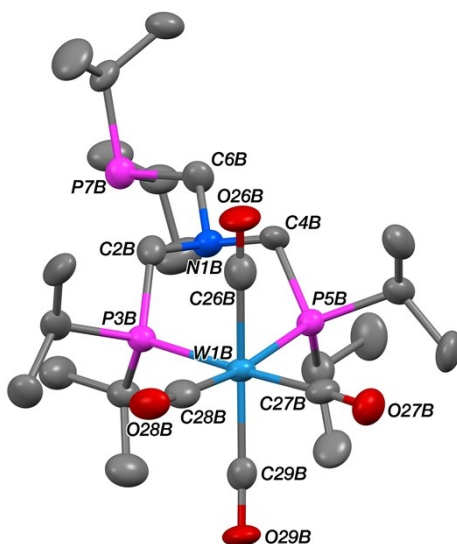


Figure S31. The structure of one (**6-B**) of the two independent complexes present in the crystal of **6** (50% probability ellipsoids)

	A	B		A	B
W(1)–P(3)	2.529(2)	2.536(2)	P(3)–W(1)–C(29)	96.8(3)	97.7(3)
W(1)–P(5)	2.548(3)	2.548(3)	P(5)–W(1)–C(26)	88.0(3)	87.7(3)
W(1)–N(1)	4.101(9)	4.094(10)	P(5)–W(1)–C(27)	94.8(3)	94.7(3)
W(1)–C(26)	2.047(12)	2.025(13)	P(5)–W(1)–C(28)	171.8(3)	172.1(3)
W(1)–C(27)	2.019(11)	1.999(10)	P(5)–W(1)–C(29)	101.9(3)	102.0(3)
W(1)–C(28)	1.994(11)	2.000(12)	C(26)–W(1)–C(27)	90.0(4)	88.8(4)
W(1)–C(29)	2.041(10)	2.006(12)	C(26)–W(1)–C(28)	84.3(4)	84.9(5)
			C(26)–W(1)–C(29)	169.1(4)	168.3(4)
P(3)–W(1)–P(5)	82.36(8)	82.33(8)	C(27)–W(1)–C(28)	88.0(4)	88.0(5)
P(3)–W(1)–C(26)	88.8(3)	90.0(3)	C(27)–W(1)–C(29)	84.8(4)	84.0(4)
P(3)–W(1)–C(27)	177.0(3)	176.8(3)	C(28)–W(1)–C(29)	85.9(4)	85.7(4)
P(3)–W(1)–C(28)	94.7(3)	94.9(3)			

Table S6. Selected bond lengths (Å) and angles (°) for **6**.

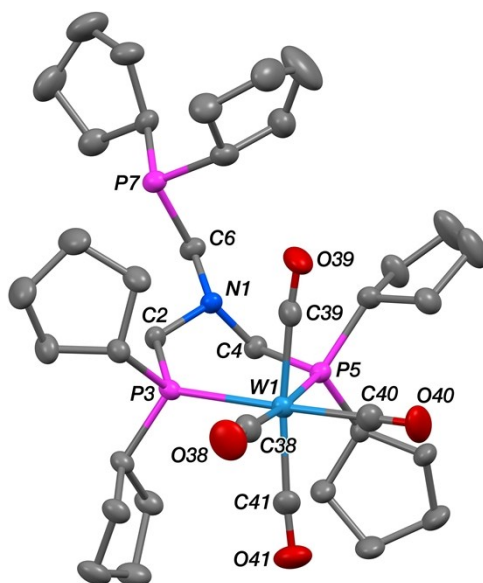


Figure S32. The crystal structure of **7** (50% probability ellipsoids)

W(1)–P(3)	2.5269(9)	P(3)–W(1)–C(41)	95.71(12)
W(1)–P(5)	2.5283(9)	P(5)–W(1)–C(38)	175.42(12)
W(1)–N(1)	3.809(3)	P(5)–W(1)–C(39)	88.41(12)
W(1)–C(38)	1.995(5)	P(5)–W(1)–C(40)	95.26(13)
W(1)–C(39)	2.020(4)	P(5)–W(1)–C(41)	92.19(11)
W(1)–C(40)	1.999(4)	C(38)–W(1)–C(39)	88.71(17)
W(1)–C(41)	2.029(4)	C(38)–W(1)–C(40)	88.08(18)
		C(38)–W(1)–C(41)	91.11(17)
P(3)–W(1)–P(5)	88.66(3)	C(39)–W(1)–C(40)	85.75(16)
P(3)–W(1)–C(38)	87.86(12)	C(39)–W(1)–C(41)	172.75(16)
P(3)–W(1)–C(39)	91.52(11)	C(40)–W(1)–C(41)	87.00(17)
P(3)–W(1)–C(40)	175.15(13)		

Table S7. Selected bond lengths (Å) and angles (°) for **7**.

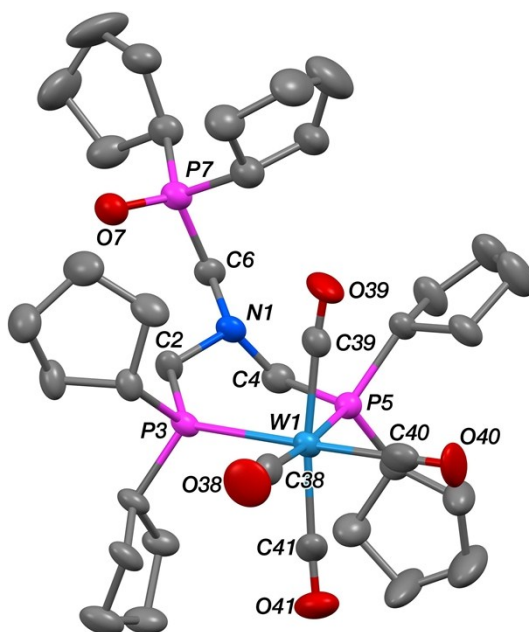


Figure S33. The crystal structure of **8** (50% probability ellipsoids)

W(1)–P(3)	2.527(2)	P(3)–W(1)–C(41)	96.1(3)
W(1)–P(5)	2.528(2)	P(5)–W(1)–C(38)	175.4(3)
W(1)–N(1)	3.826(8)	P(5)–W(1)–C(39)	87.9(3)
W(1)–C(38)	2.010(14)	P(5)–W(1)–C(40)	95.0(3)
W(1)–C(39)	2.061(10)	P(5)–W(1)–C(41)	91.4(3)
W(1)–C(40)	1.976(14)	C(38)–W(1)–C(39)	89.5(4)
W(1)–C(41)	2.050(11)	C(38)–W(1)–C(40)	88.7(5)
		C(38)–W(1)–C(41)	91.6(5)
P(3)–W(1)–P(5)	88.71(7)	C(39)–W(1)–C(40)	86.0(4)
P(3)–W(1)–C(38)	87.5(3)	C(39)–W(1)–C(41)	172.4(4)
P(3)–W(1)–C(39)	91.5(3)	C(40)–W(1)–C(41)	86.5(5)
P(3)–W(1)–C(40)	175.4(4)		

Table S8. Selected bond lengths (Å) and angles (°) for **8**.

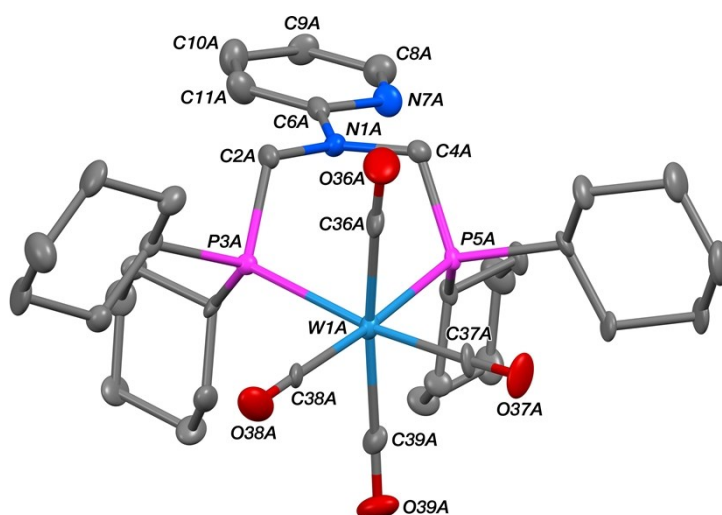


Figure S34. The structure of one (**10-A**) of the two independent complexes present in the crystal of **10** (50% probability ellipsoids)

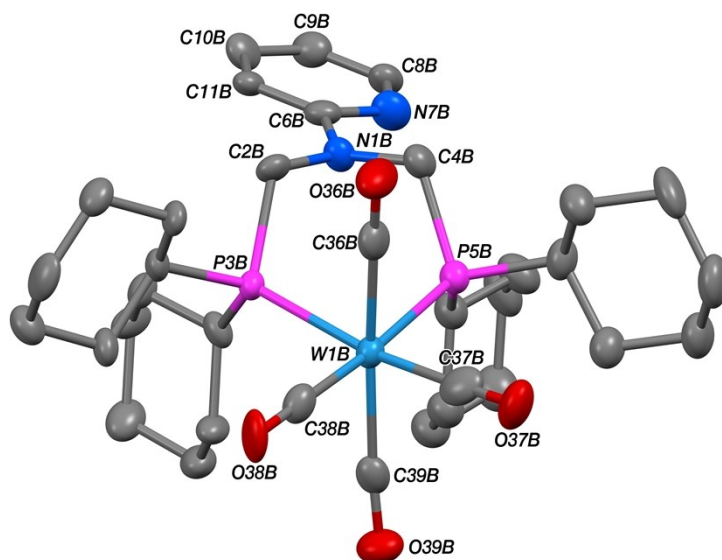


Figure S35. The structure of one (**10-B**) of the two independent complexes present in the crystal of **10** (50% probability ellipsoids)

	A		B	
W(1)–P(3)	2.5420(15)	2.5305(19)	P(3)–W(1)–C(39)	103.20(18)
W(1)–P(5)	2.5596(16)	2.559(2)	P(5)–W(1)–C(36)	88.9(2)
W(1)–N(1)	4.002(5)	4.028(6)	P(5)–W(1)–C(37)	95.40(19)
W(1)–C(36)	2.028(6)	2.012(8)	P(5)–W(1)–C(38)	175.61(16)
W(1)–C(37)	2.027(6)	1.949(10)	P(5)–W(1)–C(39)	95.57(18)
W(1)–C(38)	2.010(7)	1.941(9)	C(36)–W(1)–C(37)	84.8(3)
W(1)–C(39)	2.036(6)	2.037(8)	C(36)–W(1)–C(38)	90.3(3)
			C(36)–W(1)–C(39)	169.7(3)
P(3)–W(1)–P(5)	84.25(5)	83.75(7)	C(37)–W(1)–C(38)	88.8(2)
P(3)–W(1)–C(36)	86.44(18)	86.1(2)	C(37)–W(1)–C(39)	85.5(3)
P(3)–W(1)–C(37)	171.27(19)	170.5(2)	C(38)–W(1)–C(39)	86.0(2)
P(3)–W(1)–C(38)	91.40(16)	92.0(2)		

Table S9. Selected bond lengths (Å) and angles (°) for **10**.

Calculation of Cone Angles

Cone angles were calculated based on a method proposed by Mingos and co-workers.³ A general algorithm was developed that allowed the same geometrical description of Tolman's cone angles to be applied to crystal structures. This involved measurement of the distance, d , from a metal centred 2.28 Å from the phosphine, to each atom on each substituent; as well as the angle, α , between the phosphorus centre, metal atom and substituent atom (Figure S36). The half angle, $\theta_i/2$, is defined as the angle required for a cone which radiates out toward the substituent, i , group from the metal, and just touches the van der Waals radius of the outer most atom for that substituent. This half angle can be calculated from d and α by the trigonometric relationship shown in Equation 1 (where r_H is the van der Waals radius of the atom in question, set at 1.00 Å for hydrogen).

Figure S36. Graphic definition proposed by Mingos and co-workers³ of the van der Waals surface for phosphine ligands which results in the calculation of the "Mingos cone angle" directly from crystallographic data

$$\theta_i/2 = \alpha + 180/\pi \times \sin^{-1}(r_H/d) \quad (1)$$

After identification of the largest $\theta_i/2$ angle with respect to the metal–ligand axis, $\theta_{i_{max}}/2$, the process is repeated for each substituent on phosphorus, allowing calculation of the overall cone angle, Θ , using Equation 2.

$$\Theta = \frac{2}{3} \sum_{i=1}^3 \theta_i/2 \quad (2)$$

Equation 2 requires the phosphine to contain three discrete substituents, but NP_3^R ligands have two substituents and an arm that connects the phosphine to the apical moiety. Consequently, Equation 1 cannot be used to determine $\theta_i/2$ for each substituent. Instead, the EMP bond angle (θ_{EMP_i}) was used (where E is apical atom) as this is similar to that solution proposed by Tolman to describe bidentate diphosphine ligands.⁴ The equation required to determine the Mingos cone angle for *each coordinated phosphine group of a specific NP_3^R ligand in any given crystal structure*, $\Theta_{P_R}^{\text{Mingos}}$ (i.e. tridentate crystal structures will have three unique $\Theta_{P_R}^{\text{Mingos}}$ values per structure), becomes:

$$\Theta_{P_R}^{\text{Mingos}} = \frac{2}{3} \left(\sum_{i=1}^2 \theta_{i_{max}}/2 + \theta_{EMP_i} \right) \quad (3)$$

The overall Mingos cone angle for a specific NP_3^R ligand, $\Theta_{\text{NP}_3^R}^{\text{Mingos}}$, was found by calculating the mean average for all *individual phosphine Mingos angles*, $\Theta_{P_R}^{\text{Mingos}}$, across all crystallographically reported complexes (N) featuring that ligands (Equation 4).

$$\Theta_{\text{NP}_3^R}^{\text{Mingos}} = \sum_{P_R=1}^N \Theta_{P_R}^{\text{Mingos}} / N \quad (4)$$

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4. Tolman, C. A. *Chem. Rev.* **1977**, 77, 313–348.