JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1997, 119(5), 1139-1140, DOI:10.1021/ja9635037

Experimental Details

General procedures routinely employed in these laboratories have been described in detail previously.[1] The organometallic reagents $Cp^*W(NO)(CH_2SiMe_3)_2$[2] and $Cp^*W(NO)(H)[\eta^2\text{-}PPh_2C_6H_4]$ (**1**)[2] were prepared by literature procedures. Trimethylphosphine (Aldrich) was dried over sodium/benzophenone ketyl, vacuum transferred and stored over sodium before use, *tert*-butyl isocyanide and cyclohexyl isocyanide (Aldrich) were dried over activated 4A molecular sieves, acetone (Aldrich) was dried over $CaSO_4$ and vacuum-transferred before use, cyclopentanone and trimethylphosphite (Aldrich) were dried over CaH_2 and vacuum-transferred, ethyl acetate and acetonitrile (Aldrich) were distilled from CaH_2, and PPh_3 (Strem) was recrystallized from hexanes. Dihydrogen (Linde, extra dry) was used as received.

Preparation of $Cp^*W(NO)(PPh_3)(CNCMe_3)$ (2). A sample of **1** (73 mg, 0.12 mmol) was dissolved in THF (10 mL) in a bomb equipped with a Kontes stopcock; *tert*-butyl isocyanide (60 mg, 0.72 mmol) was added with a pipette and the bomb was placed in a 45 °C temperature bath for 6 h. The THF and excess *tert*-butyl isocyanide were then removed under vacuum, and the residual red solid was extracted into Et_2O and filtered through Celite. Removal of the ether under vacuum and recrystallization of the residue from a minimum amount of hexanes at -30 °C yielded 68 mg (82% yield) of **2** as red crystals.

Anal. Calcd for $C_{33}H_{39}N_2OPW$: C, 56.64; H, 5.66; N, 4.03. Found: C, 57.00; H, 5.78; N, 3.97. IR (Nujol, cm^{-1}): 1844 (ν_{CN}), 1552 (ν_{NO}). ^1H NMR (C_6D_6): δ 7.75 (m, 6 H, *o*-H_{aryl}); 7.08 (m, 6 H, *m*-H_{aryl}); 7.01 (m, 3 H, *p*-H_{aryl}); 1.82 (s, 15 H, C_5Me_5); 1.11 (s, 9 H, $CNCMe_3$). ^{13}C NMR (C_6D_6): δ 226.3 (d, $^2J_{PC}$ = 6.0 Hz, $CNCMe_3$); 138.3 (d, $^1J_{PC}$ = 44.0 Hz, PC_{aryl}); 134.2 (d, $^2J_{PC}$ = 12.0 Hz, *o*-C_{aryl}); 129.3 (*p*-C_{aryl}); 128.1 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C_{aryl}); 101.9 (C_5Me_5); 59.3 ($CNCMe_3$); 31.9 ($CNCMe_3$); 10.7 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 49.0 (s, $^1J_{WP}$ = 455 Hz, PPh_3). EIMS (*m/z*, probe temperature 150 °C): 694 (P^+, ^{184}W).

Preparation of Cp*W(NO)(PPh_3)(CN{*c*-C_6H_{11}}) (3). Utilizing the procedure described above for **2**, the reaction of **1** (68 mg, 0.11 mmol) and cyclohexyl isocyanide (70 mg, 0.64 mmol) gave orange-red crystals of **3** (65 mg, 82% yield).

Anal. Calcd for $C_{35}H_{41}N_2OPW$: C, 58.34; H, 5.74; N, 3.89. Found: C, 58.46; H, 5.79; N, 3.96. IR (Nujol, cm^{-1}): 1796 (ν_{CN}), 1550 (ν_{NO}). ^1H NMR (C_6D_6): δ 7.79 (m, 6 H, *o*-H_{aryl}); 7.12 (m, 6 H, *m*-H_{aryl}); 7.04 (m, 3 H, *p*-H_{aryl}); 3.58 (m, 1 H, CNC*H*); 1.88 (s, 15 H, C_5Me_5); 1.05-2.10 (several m, 10 H, CH_2). ^{13}C NMR (C_6D_6): δ 234.6 (d, $^2J_{PC}$ = 4.2 Hz, CN{*c*-C_6H_{11}}); 138.5 (d, $^1J_{PC}$ = 44.0 Hz, PC_{aryl}); 134.1 (d, $^2J_{PC}$ = 11.7 Hz, *o*-C_{aryl}); 129.4 (*p*-C_{aryl}); 128.2 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C_{aryl}); 102.4 (C_5Me_5); 59.2 (CNCH); 35.5 (CH_2); 34.8 (CH_2); 25.8 (CH_2); 24.2 (CH_2); 24.0 (CH_2); 10.8 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 49.3 (s, $^1J_{WP}$ = 454 Hz, PPh_3). EIMS (*m/z*, probe temperature 150 °C): 720 (P^+, ^{184}W).

Preparation of Cp*W(NO)(PPh_3)(η^2-O=CMe_2) (4). **1** (0.12 g, 0.20 mmol) was dissolved in acetone (5 mL) in a bomb equipped with a Kontes stopcock; the bomb was placed in a 45 °C temperature bath for 6 h. Et_2O (5 mL) was then added, and the reaction solution was stored at -30 °C for 12 h. The yellow crystals of **4** which deposited were isolated by decantation of the remaining solution and were dried under vacuum (90 mg, 67% yield).

Anal. Calcd for $C_{31}H_{36}NO_2PW$: C, 55.30; H, 5.41; N, 1.98. Found: C, 55.61; H, 5.42; N, 2.09. IR (Nujol, cm^{-1}): 1538 (ν_{NO}). ^1H NMR (C_6D_6): δ 7.85 (br m, 6 H, *o*-H_{aryl}); 7.05 (br m, 9 H, *m/p*-H_{aryl}); 2.15 (s, 3 H, CH_3); 2.03 (s, 3 H, CH_3); 1.67 (s, 15 H, C_5Me_5). ^{13}C NMR (CD_2Cl_2): δ 135.0 (br, *o*-C_{aryl}); 130.7 (br, *p*-C_{aryl}); 128.5 (br, *m*-C_{aryl}); 107.6 (C_5Me_5); 70.3 ($^1J_{WC}$ = 51 Hz, *C*=O); 33.3 (CH_3); 30.0 (CH_3); 10.6 (C_5Me_5); the PC_{aryl} resonance was not observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 28.2 (s, $^1J_{WP}$ = 340 Hz, PPh_3). EIMS (*m/z*, probe temperature 120 °C): 669 (P^+, ^{184}W).

Preparation of Cp*W(NO)(PPh_3)(η^2-O=C{CH_2}$_4$) (5). **1** (110 mg, 0.18 mmol) was dissolved in cyclopentanone (5 mL), and the resulting solution was allowed to stand at room

temperature for 3 d. The cyclopentanone was then removed under vacuum and the orange residue was recrystallized from THF/hexanes (1:1) at -30 °C to give 85 mg (68% yield) of **5** as yellow crystals.

Anal. Calcd for $C_{33}H_{38}NO_2PW$: C, 56.99; H, 5.51; N, 2.01. Found: C, 57.39; H, 5.85; N, 1.93. IR (Nujol, cm^{-1}): 1543 (ν_{NO}). ^1H NMR (C_6D_6): δ 7.82 (br m, 6 H, *o*-H_{aryl}); 7.04 (br m, 9 H, *m/p*-H_{aryl}); 2.72 (m, 2 H, 2 C*H*H′); 2.01 (m, 1 H, C*H*H′); 1.92 (m, 1 H, C*H*H′); 1.81 (m, 1 H, C*H*H′); 1.73 (m, 1 H, C*H*H′); 1.66 (s, 15 H, C_5Me_5); 1.58 (m, 2 H, 2 C*H*H′). ^{13}C NMR (CD_2Cl_2): δ 134.6 (br, *o*-C_{aryl}); 130.7 (br, *p*-C_{aryl}); 128.6 (br, *m*-C_{aryl}); 107.6 (C_5Me_5); 80.9 ($^1J_{WC}$ = 50 Hz, *C*=O); 42.4 (CH_2); 37.1 (CH_2); 27.1 (CH_2); 25.7 (CH_2); 10.6 (C_5Me_5); the PC_{aryl} resonance was not observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 29.9 (s, $^1J_{WP}$ = 344 Hz, *P*Ph_3). EIMS (*m/z*, probe temperature 150 °C): 695 (P^+, ^{184}W).

Preparation of Cp*W(NO)(PPh$_3$)(η^2-O=C{Me}OEt) (6). Utilizing the procedure described above for **4**, the reaction of **1** (100 mg, 0.16 mmol) and ethyl acetate (5 mL) provided **6** as lemon-yellow crystals (80 mg, 70% yield).

Anal. Calcd for $C_{32}H_{38}NO_3PW$: C, 54.95; H, 5.48; N, 2.00. Found: C, 55.18; H, 5.48; N, 1.85. IR (Nujol, cm^{-1}): 1545 (ν_{NO}). ^1H NMR (C_6D_6): δ 7.86 (br m, 6 H, *o*-H_{aryl}); 7.06 (br m, 9 H, *m/p*-H_{aryl}); 3.89 (m, 1 H, C*H*H′); 3.79 (m, 1 H, C*H*H′); 2.55 (s, 3 H, CH_3CO); 1.79 (s, 15 H, C_5Me_5); 1.21 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_2CH_3). ^{13}C NMR (CD_2Cl_2): δ 134.7 (br, *o*-C_{aryl}); 130.8 (br, *p*-C_{aryl}); 128.6 (br, *m*-C_{aryl}); 108.4 (C_5Me_5); 101.8 ($^1J_{WC}$ = 54 Hz, *C*=O); 60.9 (CH_2); 26.4 (CH_3CO); 16.3 (CH_2CH_3); 10.3 (C_5Me_5); the PC_{aryl} resonance was not observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 30.6 (s, $^1J_{WP}$ = 346 Hz, *P*Ph_3). EIMS (*m/z*, probe temperature 150 °C): 700 (P^+, ^{184}W).

Reaction of 1 with PMe$_3$. **1** (52 mg, 0.085 mmol) was dissolved in THF (15 mL) in a small bomb; excess PMe_3 (ca. 1 mmol) was vacuum transferred into the solution, and the mixture was heated at 45 °C for 5 h. The THF and PMe_3 were then removed under vacuum; the remaining orange-red residue was recrystallized from Et_2O/hexanes (1:1) to give 48 mg (82% yield) of a 3:1

mixture of Cp*W(NO)(PPh_3)(PMe_3) (**7**) and Cp*W(NO)(H)(PMe_3)($C_6H_4PPh_2$) (**8**) as red and orange solids, respectively. Attempts to separate these two complexes by crystallization or chromatography have not been successful, and they have been characterized as a mixture.

Anal. Calcd for $C_{31}H_{39}NOP_2W$: C, 54.16; H, 5.72; N, 2.04. Found: C, 53.87; H, 5.57; N, 1.89. EIMS (*m/z*, probe temperature 150 °C): 735 (P^+, ^{184}W). Spectroscopic data for **7**: IR (Nujol, cm^{-1}): 1510 (ν_{NO}). ^1H NMR (C_6D_6): δ 7.76 (m, 6 H, *o*-H_{aryl}); 7.10 (m, 6 H, *m*-H_{aryl}); 6.98 (m, 3 H, *p*-H_{aryl}); 1.71 (s, 15 H, C_5Me_5); 1.15 (d, $^2J_{PH}$ = 7.8 Hz, 9 H, PMe_3). ^{13}C NMR (dioxane-d_8): δ 142.3 (d, $^1J_{PC}$ = 38.4 Hz, PC_{aryl}); 134.3 (d, $^2J_{PC}$ = 11.5 Hz, *o*-C_{aryl}); 129.1 (*p*-C_{aryl}); 128.4 (d, $^3J_{PC}$ = 8.8 Hz, *m*-C_{aryl}); 99.8 (C_5Me_5); 23.3 (d, $^2J_{PC}$ = 28.1 Hz, PMe_3); 11.1 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51.9 (d, $^2J_{PP}$ = 7.5 Hz, $^1J_{WP}$ = 477 Hz, PPh_3); -20.2 (d, $^2J_{PP}$ = 7.5 Hz, $^1J_{WP}$ = 465 Hz, PMe_3). Spectroscopic data for **8**: IR (Nujol, cm^{-1}): 1548 (ν_{NO}). ^1H NMR (C_6D_6): δ 8.04 (m, 1 H, H_{aryl}); 7.61 (m, 1 H, H_{aryl}); 7.50 (m, 1 H, H_{aryl}); 7.38 (m, 1 H, H_{aryl}); 7.16 (m, several H, H_{aryl}); 7.04 (m, several H, H_{aryl}); 6.89 (m, 1 H, H_{aryl}); 6.80 (m, 1 H, H_{aryl}); 1.84 (s, 15 H, C_5Me_5); 0.83 (d, $^2J_{PH}$ = 8.4 Hz, 9 H, PMe_3); -0.37 (d, $^2J_{PH}$ = 94 Hz, $^1J_{WH}$ = 63 Hz, 1 H, W*H*). ^{13}C NMR (C_6D_6): δ 153.9 (d, $^2J_{PC}$ = 5.5 Hz, WC_{aryl}); 141.2 (d, $^1J_{PC}$ = 34.4 Hz, PC_{aryl}); 136.1 (C_{aryl}); 136.0 (d, $^1J_{PC}$ = 20.6 Hz, PC_{aryl}); 133.2 (d, $^1J_{PC}$ = 18.3 Hz, PC_{aryl}); 128.6 (C_{aryl}); 128.2 (d, J_{PC} = 8.3 Hz, C_{aryl}); 128.1 (C_{aryl}); 127.4 (C_{aryl}); 125.1 (C_{aryl}); 124.3 (d, J_{PC} = 3.3 Hz, C_{aryl}); 106.8 (C_5Me_5); 19.6 (d, $^2J_{PC}$ = 31.7 Hz, PMe_3); 11.1 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.6 (s, PPh_3); -17.1 (s, $^1J_{WP}$ = 197 Hz, PMe_3).

Preparation of Cp*W(NO)(PPh_3)(P{OMe}$_3$) (9). A small bomb was charged with **1** (45 mg, 0.069 mmol) and THF (15 mL); to this suspension was added P{OMe}$_3$ (60 μL, 0.51 mmol) using a syringe against a flow of argon. The bomb was then placed in a temperature bath at 45 °C for 8 h. The reaction mixture was then evaporated to dryness, and the brown residue was chromatographed on alumina (2 cm) using Et_2O/hexanes (1:1) as the elutant. A bright orange band was collected, and the solvent mixture removed under vacuum to leave an orange solid. Recrystallization from hexanes at -30 °C provided orange prisms of **9** (13 mg, 26% yield).

Anal. Calcd for $C_{31}H_{39}NO_4P_2W$: C, 50.63; H, 5.34; N, 1.90. Found: C, 50.32; H, 5.32; N, 1.79. IR (Nujol, cm^{-1}): 1537 (ν_{NO}). ^1H NMR (C_6D_6): δ 7.86 (m, 6 H, *o*-H_{aryl}); 7.12 (m, 6 H, *m*-H_{aryl}); 7.03 (m, 3 H, *p*-H_{aryl}); 3.29 (d, $^3J_{PH}$ = 10.6 Hz, 9 H, P{O*Me*}$_3$); 1.80 (s, 15 H, C_5Me_5). ^{13}C NMR (C_6D_6): δ 141.1 (d, $^1J_{PC}$ = 41.7 Hz, PC_{aryl}); 134.2 (d, $^2J_{PC}$ = 11.2 Hz, *o*-C_{aryl}); 128.7 (d, $^3J_{PC}$ = 13.2 Hz, *m*-C_{aryl}); 127.8 (*p*-C_{aryl}); 100.5 (C_5Me_5); 52.0 (d, $^2J_{PC}$ = 6.5 Hz, P{O*Me*}$_3$); 10.8 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 164.3 (d, $^2J_{PP}$ = 6.2 Hz, $^1J_{WP}$ = 719 Hz, *P*{OMe}$_3$); 52.8 (d, $^2J_{PP}$ = 6.2 Hz, $^1J_{WP}$ = 461 Hz, *P*Ph$_3$). EIMS (*m/z*, probe temperature 180 °C): 735 (P^+, ^{184}W).

References

(1) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1995**, *14*, 5579.

(2) Debad, J. D.; Legzdins, P.; Lumb, S. A. *Organometallics* **1995**, *14*, 2543.

Table S1. Crystallographic data for $Cp^*W(NO)(H)(\eta^2\text{-}PPh_2C_6H_4)$ (**1**).

Formula	$C_{28}H_{30}NOPW$
Formula Weight	611.35
Crystal Color, Habit	Orange, Block
Crystal size	0.30 × 0.25 × 0.22 mm
Crystal system	Triclinic
Space group	$P\bar{1}$
a	10.3786(5) Å
b	10.8927(6) Å
c	12.7051(6) Å
α	95.549(1)°
β	97.927(1)°
γ	116.282(1)°
Volume	1255.25(11) Å^3
Z	2
Density (calculated)	1.617 Mg/m^3
F(000)	604
Wavelength	0.71073 Å
Temperature	173(2) K
θ range for data collection	1.64 to 25.04°
Index ranges	$-12 \le h \le 12$, $-7 \le k \le 12$, $-15 \le l \le 14$
Reflections collected	6399
Independent reflections	4286 (R_{int} = 0.0247)
Absorption correction	semi-empirical
Max. and min. transmission	0.41724 and 0.32194
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	4283/275/397
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0217, wR2 = 0.0527
R indices (all data)	R1 = 0.0233, wR2 = 0.0547
GOF on F^2	1.073
Largest diff. peak and hole	0.622 and -0.822 e/Å^3

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor

Atom	*x*	*y*	*z*	U(eq)	SOF
W(l)	1657(1)	3949(1)	1585(1)	28(1)	1
P(1)	1412(1)	2937(1)	3326(1)	22(1)	1
N(l)	1851(5)	5547(4)	2257(3)	50(1)	1
O(1)	2237(5)	6767(3)	2638(3)	75(1)	1
C(1)	-490(4)	1898(3)	2705(3)	27(1)	1
C(2)	-538(4)	2342(4)	1703(3)	31(1)	1
C(3)	-1934(5)	1717(5)	1016(3)	45(1)	1
C(4)	-3152(5)	757(5)	1348(4)	53(1)	1
C(5)	-3053(4)	349(4)	2340(4)	46(1)	1
C(6)	-1697(4)	912(4)	3025(3)	36(1)	1
C(7)	2091(4)	1764(3)	3815(3)	25(1)	1
C(8)	3240(4)	2223(4)	4702(3)	32(1)	1
C(9)	3779(4)	1330(4)	5031(4)	42(1)	1
C(10)	3170(5)	-24(4)	4477(4)	45(1)	1
C(11)	2019(5)	-488(4)	3603(4)	46(1)	1
C(12)	1480(4)	402(4)	3277(3)	37(1)	1
C(13)	1614(4)	4065(3)	4557(3)	23(1)	1
C(14)	2680(4)	5455(4)	4762(3)	31(1)	1
C(15)	2814(4)	6323(4)	5684(3)	36(1)	1
C(16)	1895(4)	5839(4)	6404(3)	35(1)	1
C(17)	825(4)	4455(4)	6202(3)	37(1)	1
C(18)	696(4)	3567(4)	5286(3)	31(1)	1
C(19)	4160(15)	4644(12)	1507(9)	41(3)	0.599(15)
C(20)	3420(18)	3194(12)	1172(9)	44(3)	0.599(15)
C(21)	2367(14)	2887(9)	235(9)	38(2)	0.599(15)
C(22)	2489(22)	4158(12)	-31(11)	31(3)	0.599(15)
C(23)	3611(20)	5227(8)	743(15)	34(2)	0.599(15)
C(24)	5379(11)	5452(16)	2476(8)	87(5)	0.599(15)
C(25)	3814(16)	2183(16)	1677(11)	98(6)	0.599(15)
C(26)	1374(12)	1485(9)	-448(11)	99(6)	0.599(15)
C(27)	1725(12)	4346(16)	-1046(7)	80(4)	0.599(15)
C(28)	4243(12)	6781(8)	745(11)	70(3)	0.599(15)
C(19')	3942(21)	5090(13)	1106(17)	47(5)	0.401(15)
C(20')	3842(17)	3921(24)	1526(11)	54(5)	0.401(15)
C(21')	2789(23)	2723(13)	799(19)	57(5)	0.401(15)
C(22')	2176(22)	3159(20)	-47(14)	66(6)	0.401(15)
C(23')	2852(33)	4625(20)	162(22)	52(6)	0.401(15)
C(24')	4917(26)	6585(17)	1632(23)	214(20)	0.401(15)
C(25')	4863(21)	3941(43)	2508(15)	205(20)	0.401(15)
C(26')	2546(38)	1263(19)	866(30)	230(20)	0.401(15)
C(27')	1062(19)	2267(35)	-1040(12)	234(21)	0.401(15)
C(28')	2568(29)	5548(36)	-533(26)	214(19)	0.401(15)

Table S3. Bond Lengths (Å) for **1**.

atoms	distance	atoms	distance
W(1)-C(2)	2.212(4)	W(1)-P(1)	2.5601(8)
W(1)-N(1)	1.776(3)	W(1)-H(1)	1.58(4)
W(1)-C(19)	2.38(2)	W(1)-C(20)	2.41(2)
W(1)-C(21)	2.354(12)	W(1)-C(22)	2.33(2)
W(1)-C(23)	2.36(2)	W(1)-C(19')	2.34(2)
W(1)-C(20')	2.29(2)	W(1)-C(21')	2.37(2)
W(1)-C(22')	2.39(2)	W(1)-C(23')	2.33(3)
P(1)-C(1)	1.794(3)	P(1)-C(7)	1.830(3)
P(1)-C(13)	1.819(3)	N(1)-O(1)	1.230(5)
C(1)-C(2)	1.406(5)	C(1)-C(6)	1.387(5)
C(2)-C(3)	1.410(5)	C(3)-C(4)	1.389(7)
C(4)-C(5)	1.383(7)	C(5)-C(6)	1.381(6)
C(7)-C(8)	1.391(5)	C(7)-C(12)	1.386(5)
C(8)-C(9)	1.389(5)	C(9)-C(10)	1.386(6)
C(10)-C(11)	1.381(7)	C(11)-C(12)	1.384(6)
C(13)-C(14)	1.395(5)	C(13)-C(18)	1.393(5)
C(14)-C(15)	1.382(5)	C(15)-C(16)	1.384(6)
C(16)-C(17)	1.391(6)	C(17)-C(18)	1.391(5)
C(19)-C(20)	1.403(11)	C(19)-C(23)	1.399(10)
C(19)-C(24)	1.505(10)	C(20)-C(21)	1.401(11)
C(20)-C(25)	1.502(9)	C(21)-C(22)	1.412(10)
C(21)-C(26)	1.501(9)	C(22)-C(23)	1.393(10)
C(22)-C(27)	1.499(9)	C(23)-C(28)	1.521(9)
C(19')-C(20')	1.395(13)	C(19')-C(23')	1.405(13)
C(19')-C(24')	1.506(12)	C(20')-C(21')	1.406(14)
C(20')-C(25')	1.513(13)	C(21')-C(22')	1.401(14)
C(21')-C(26')	1.509(13)	C(22')-C(23')	1.410(14)
C(22')-C(27')	1.496(13)	C(23')-C(28')	1.497(13)

Table S4. Bond Angles (°) for **1**.

atoms	angle	atoms	angle
N(1)-W(1)-C(2)	106.0(2)	N(1)-W(1)-P(1)	91.24(11)
C(2)-W(1)-P(1)	62.38(9)	N(1)-W(1)-H(1)	88.1(14)
C(2)-W(1)-H(1)	71.7(14)	P(1)-W(1)-H(1)	131.9(14)
W(1)-N(1)-O(1)	167.1(3)	W(1)-P(1)-C(1)	85.57(12)
W(1)-P(1)-C(7)	129.00(11)	W(1)-P(1)-C(13)	118.03(11)
W(1)-C(2)-C(1)	110.6(2)	W(1)-C(2)-C(3)	134.1(3)
C(1)-P(1)-C(7)	107.4(2)	C(1)-P(1)-C(13)	110.6(2)
C(7)-P(1)-C(13)	103.3(2)	P(1)-C(1)-C(2)	101.4(2)
P(1)-C(1)-C(6)	134.3(3)	P(1)-C(7)-C(8)	121.2(3)
P(1)-C(7)-C(12)	119.7(3)	P(1)-C(13)-C(14)	119.5(3)
P(1)-C(13)-C(18)	120.9(3)	N(1)-W(1)-C(19)	99.0(3)
N(1)-W(1)-C(20)	132.5(4)	N(1)-W(1)-C(21)	145.6(3)
N(1)-W(1)-C(22)	112.6(3)	N(1)-W(1)-C(23)	88.8(4)
N(1)-W(1)-C(19')	91.1(4)	N(1)-W(1)-C(20')	114.0(6)
N(1)-W(1)-C(21')	147.8(4)	N(1)-W(1)-C(22')	136.7(5)
N(1)-W(1)-C(23')	102.4(6)	C(2)-W(1)-C(19)	150.7(3)
C(2)-W(1)-C(20)	117.9(3)	C(2)-W(1)-C(21)	104.9(3)
C(2)-W(1)-C(22)	122.8(3)	C(2)-W(1)-C(23)	157.3(3)
C(2)-W(1)-C(19')	162.7(4)	C(2)-W(1)-C(20')	133.3(6)
C(2)-W(1)-C(21')	105.6(4)	C(2)-W(1)-C(22')	106.3(4)
C(2)-W(1)-C(23')	134.3(6)	P(1)-W(1)-C(19)	102.6(3)
P(1)-W(1)-C(20)	93.5(3)	P(1)-W(1)-C(21)	116.6(3)
P(1)-W(1)-C(22)	150.2(4)	P(1)-W(1)-C(23)	135.8(3)
P(1) -W(1)-C(19')	121.2(5)	P(1) -W(1)-C(20')	93.0(4)
P(1) -W(1)-C(21')	97.8(4)	P(1) -W(1)-C(22')	129.4(6)
P(1) -W(1)-C(23')	151.4(5)	C(19)-W(1)-H(1)	125.0(14)
C(20)-W(1)-H(1)	121.1(14)	C(21)-W(1)-H(1)	87.4(14)
C(22)-W(1)-H(1)	69.2(14)	C(23)-W(1)-H(1)	92.2(14)
C(19')-W(1)-H(1)	107(2)	C(20')-W(1)-H(1)	130.6(14)
C(21')-W(1)-H(1)	108(2)	C(22')-W(1)-H(1)	76(2)
C(23')-W(1)-H(1)	74(2)	C(19)-W(1)-C(20)	34.1(3)
C(19)-W(1)-C(21)	57.3(4)	C(19)-W(1)-C(22)	57.7(4)
C(19)-W(1)-C(23)	34.3(3)	C(20)-W(1)-C(21)	34.2(3)
C(20)-W(1)-C(22)	57.3(4)	C(20)-W(1)-C(23)	56.5(4)
C(21)-W(1)-C(22)	35.1(3)	C(21)-W(1)-C(23)	57.3(4)
C(22)-W(1)-C(23)	34.5(4)	C(19')-W(1)-C(20')	35.0(4)
C(19')-W(1)-C(21')	57.8(5)	C(19')-W(1)-C(22')	57.6(5)
C(19')-W(1)-C(23')	35.1(5)	C(20')-W(1)-C(21')	35.0(4)
C(20')-W(1)-C(22')	57.8(5)	C(20')-W(1)-C(23')	58.6(6)
C(21')-W(1)-C(22')	34.3(4)	C(21')-W(1)-C(23')	57.9(6)
C(23')-W(1)-C(22')	34.8(4)	C(20)-C(19)-W(1)	74.1(9)
C(23)-C(19)-W(1)	72.1(13)	C(24)-C(19)-W(1)	121.8(9)
C(19)-C(20)-W(1)	71.9(9)	C(21)-C(20)-W(1)	70.7(8)

Table S4 (continued)

atoms	angle	atoms	angle
C(25)-C(20)-W(1)	127.8(9)	C(20)-C(21)-W(1)	75.1(8)
C(22)-C(21)-W(1)	71.4(10)	C(26)-C(21)-W(1)	123.7(9)
C(21)-C(22)-W(1)	73.5(9)	C(23)-C(22)-W(1)	74.1(12)
C(27)-C(22)-W(1)	125.2(14)	C(19)-C(23)-W(1)	73.6(13)
C(22)-C(23)-W(1)	71.4(12)	C(28)-C(23)-W(1)	124.4(14)
C(20')-C(19')-W(1)	70.7(10)	C(23')-C(19')-W(1)	72(2)
C(24')-C(19')-W(1)	117.6(14)	C(19')-C(20')-W(1)	74.3(10)
C(21')-C(20')-W(1)	75.5(11)	C(25')-C(20')-W(1)	123.7(12)
C(20')-C(21')-W(1)	69.5(10)	C(22')-C(21')-W(1)	73.5(13)
C(26')-C(21')-W(1)	128.6(13)	C(21')-C(22')-W(1)	72.2(13)
C(23')-C(22')-W(1)	70(2)	C(27')-C(22')-W(1)	126(2)
C(19')-C(23')-W(1)	73.0(14)	C(22')-C(23')-W(1)	75(2)
C(28')-C(23')-W(1)	122(2)	C(6)-C(1)-C(2)	124.3(3)
C(1)-C(2)-C(3)	115.3(4)	C(4)-C(3)-C(2)	120.6(4)
C(5)-C(4)-C(3)	122.2(4)	C(6)-C(5)-C(4)	118.9(4)
C(5)-C(6)-C(1)	118.7(4)	C(12)-C(7)-C(8)	119.1(3)
C(9)-C(8)-C(7)	120.2(4)	C(10)-C(9)-C(8)	120.0(4)
C(11)-C(10)-C(9)	119.9(4)	C(10)-C(11)-C(12)	120.0(4)
C(11)-C(12)-C(7)	120.8(4)	C(18)-C(13)-C(14)	119.6(3)
C(15)-C(14)-C(13)	119.7(3)	C(14)-C(15)-C(16)	121.0(3)
C(15)-C(16)-C(17)	119.5(3)	C(18)-C(17)-C(16)	119.9(3)
C(17)-C(18)-C(13)	120.3(3)	C(23)-C(19)-C(20)	107.5(7)
C(23)-C(19)-C(24)	125.3(11)	C(20)-C(19)-C(24)	127.1(11)
C(21)-C(20)-C(19)	108.1(6)	C(21)-C(20)-C(25)	126.7(11)
C(19)-C(20)-C(25)	125.0(12)	C(20)-C(21)-C(22)	107.9(6)
C(20)-C(21)-C(26)	127.3(10)	C(22)-C(21)-C(26)	124.5(10)
C(23)-C(22)-C(21)	107.5(6)	C(23)-C(22)-C(27)	125.4(11)
C(21)-C(22)-C(27)	126.5(10)	C(22)-C(23)-C(19)	108.9(7)
C(22)-C(23)-C(28)	127.0(10)	C(19)-C(23)-C(28)	124.0(11)
C(20')-C(19')-C(23')	107.7(8)	C(20')-C(19')-C(24')	126(2)
C(23')-C(19')-C(24')	126(2)	C(19')-C(20')-C(21')	108.6(8)
C(19')-C(20')-C(25')	125(2)	C(21')-C(20')-C(25')	125(2)
C(22')-C(21')-C(20')	107.5(8)	C(22')-C(21')-C(26')	127(2)
C(20')-C(21')-C(26')	125(2)	C(21')-C(22')-C(23')	108.0(9)
C(21')-C(22')-C(27')	127(2)	C(23')-C(22')-C(27')	125(2)
C(19')-C(23')-C(22')	107.8(8)	C(19')-C(23')-C(28')	125(2)
C(22')-C(23')-C(28')	127(2)		

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(1)	39(1)	35(1)	25(1)	12(1)	16(1)	28(1)
P(1)	27(1)	0(1)	23(1)	4(1)	8(1)	12(1)
N(1)	85(3)	44(2)	58(2)	28(2)	49(2)	50(2)
O(1)	127(3)	40(2)	97(3)	30(2)	76(3)	56(2)
C(1)	30(2)	25(2)	27(2)	-3(1)	5(1)	14(1)
C(2)	36(2)	37(2)	27(2)	2(2)	10(2)	24(2)
C(3)	51(3)	59(3)	33(2)	-2(2)	-1(2)	36(2)
C(4)	33(2)	57(3)	53(3)	-15(2)	-9(2)	17(2)
C(5)	29(2)	35(2)	56(3)	-10(2)	4(2)	3(2)
C(6)	36(2)	30(2)	36(2)	0(2)	9(2)	10(2)
C(7)	30(2)	24(2)	28(2)	11(1)	15(1)	15(1)
C(8)	33(2)	32(2)	35(2)	10(2)	9(2)	18(2)
C(9)	37(2)	53(2)	49(2)	21(2)	14(2)	28(2)
C(10)	48(2)	40(2)	70(3)	30(2)	30(2)	30(2)
C(11)	52(3)	27(2)	68(3)	10(2)	24(2)	22(2)
C(12)	46(2)	28(2)	41(2)	5(2)	11(2)	21(2)
C(13)	26(2)	25(2)	23(2)	3(1)	5(1)	15(1)
C(14)	33(2)	28(2)	32(2)	4(2)	11(2)	13(2)
C(15)	42(2)	24(2)	40(2)	0(2)	5(2)	16(2)
C(16)	43(2)	43(2)	26(2)	-4(2)	2(2)	30(2)
C(17)	40(2)	51(2)	27(2)	9(2)	13(2)	25(2)
C(18)	30(2)	32(2)	29(2)	6(2)	10(1)	12(2)
C(19)	38(6)	65(6)	31(5)	7(5)	8(4)	33(7)
C(20)	73(11)	58(6)	43(7)	26(5)	37(5)	56(8)
C(21)	48(6)	27(4)	40(8)	-4(4)	30(5)	16(4)
C(22)	24(7)	48(5)	22(3)	10(5)	13(4)	15(6)
C(23)	29(8)	31(3)	51(8)	9(3)	14(4)	19(4)
C(24)	54(6)	163(12)	44(5)	-21(6)	-10(4)	63(7)
C(25)	152(12)	147(12)	123(10)	109(10)	116(10)	141(11)
C(26)	79(7)	45(5)	129(11)	-55(6)	70(7)	-9(5)
C(27)	71(7)	175(13)	31(4)	45(6)	27(4)	79(8)
C(28)	72(6)	28(4)	121(9)	12(5)	59(7)	22(4)
C(19')	27(15)	26(6)	74(23)	-18(7)	27(10)	1(7)
C(20')	30(10)	130(13)	32(8)	39(12)	22(5)	53(14)
C(21')	80(16)	30(6)	103(17)	35(7)	85(9)	38(7)
C(22')	28(8)	91(11)	23(7)	-11(8)	16(5)	-19(9)
C(23')	41(20)	82(11)	72(20)	67(12)	44(8)	43(15)
C(24')	158(22)	80(10)	242(31)	-98(15)	171(22)	-99(13)
C(25')	83(14)	516(60)	99(13)	163(24)	52(9)	181(26)
C(26')	337(41)	84(11)	448(48)	158(20)	351(38)	154(19)
C(27')	60(11)	376(39)	43(9)	100(15)	25(7)	-71(17)
C(28')	189(26)	396(39)	307(36)	335(36)	220(25)	253(30)

Table S6. Hydrogen coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

atom	*x*	*y*	*z*	U(eq)
H(1)	480(41)	3965(39)	657(30)	33
H(3A)	-2043(5)	1954(5)	321(3)	64(15)
H(4A)	-4085(5)	368(5)	876(4)	69(16)
H(5A)	-3904(4)	-308(4)	2548(4)	54(13)
H(6A)	-1594(4)	629(4)	3703(3)	65(15)
H(8A)	3658(4)	3150(4)	5084(3)	49(12)
H(9A)	4565(4)	1647(4)	5637(4)	32(10)
H(10A)	3544(5)	-633(4)	4698(4)	46(12)
H(11A)	1597(5)	-1417(4)	3225(4)	61(14)
H(12A)	683(4)	76(4)	2679(3)	35(10)
H(14A)	3311(4)	5804(4)	4270(3)	28(9)
H(15A)	3549(4)	7267(4)	5825(3)	30(10)
H(16A)	1993(4)	6448(4)	7033(3)	31(10)
H(17A)	184(4)	4116(4)	6690(3)	23(9)
H(18A)	-20(4)	2617(4)	5156(3)	37(11)
H(24A)	6328(11)	5718(16)	2265(8)	131
H(24B)	5282(11)	4872(16)	3034(8)	131
H(24C)	5321(11)	6290(16)	2761(8)	131
H(25A)	4657(16)	2176(16)	1418(11)	146
H(25B)	2975(16)	1250(16)	1476(11)	146
H(25C)	4063(16)	2461(16)	2464(11)	146
H(26A)	1800(12)	1352(9)	-1064(11)	148
H(26B)	412(12)	1426(9)	-710(11)	148
H(26C)	1261(12)	760(9)	-15(11)	148
H(27A)	2230(12)	4293(16)	-1633(7)	120
H(27B)	1741(12)	5256(16)	-934(7)	120
H(27C)	706(12)	3611(16)	-1236(7)	120
H(28A)	5289(12)	7247(8)	1082(11)	105
H(28B)	3723(12)	7159(8)	1151(11)	105
H(28C)	4122(12)	6939(8)	-1(11)	105
H(24D)	5910(26)	6867(17)	1501(23)	321
H(24E)	4947(26)	6682(17)	2411(23)	321
H(24F)	4534(26)	7179(17)	1327(23)	321
H(25D)	5854(21)	4693(43)	2555(15)	307
H(25E)	4884(21)	3046(43)	2435(15)	307
H(25F)	4510(21)	4081(43)	3163(15)	307
H(26D)	3461(38)	1209(19)	849(30)	346
H(26E)	1786(38)	614(19)	252(30)	346
H(26F)	2228(38)	1016(19)	1541(30)	346
H(27D)	1452(19)	2565(35)	-1682(12)	351
H(27E)	165(19)	2360(35)	-1044(12)	351
H(27F)	839(19)	1293(35)	-1043(12)	351
H(28D)	3186(29)	5729(36)	-1074(26)	320
H(28E)	2807(29)	6429(36)	-76(26)	320
H(28F)	1533(29)	5101(36)	-896(26)	320

Table S7. Crystallographic data for $Cp^*W(NO)(PPh_3)(CNCMe_3)$ (**2**).[a]

Formula	$C_{33}H_{39}N_2OPW$
fw	694.51
Color, habit	red, prism
Crystal size, mm	0.20 × 0.22 × 0.40
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a, Å	8.975(4)
b, Å	22.082(3)
c, Å	16.088(3)
β, deg	103.34(2)
V, Å^3	3102(1)
Z	4
ρ_{calc}, g/cm^3	1.487
F(000)	1392
μ(Mo K$_\alpha$), cm^{-1}	38.06
Transmission factors	0.87-1.00
Scan type	ω–2θ
Scan range, deg in ω	1.00 + 0.35 tan θ
Scan speed, deg/min	16 (up to 8 rescans)
Data collected	$+h, +k, \pm l$
$2\theta_{max}$, deg	45
Crystal decay, %	10.3
Total reflections	4502
Unique reflections	4194
R_{merge}	0.052
Reflns with $I \geq 3\sigma(I)$	2102
No. of variables	365
R	0.034
R_w	0.029
gof	1.38
Max Δ/σ (last cycle)	0.03
Residual density, e/Å^3	-α0.46, +0.55 (near W)

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo K_α radiation (λ = 0.71069 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 x 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and gof = $[\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

Table S8. Atomic coordinates and equivalent isotropic displacement parameters for **1**.

atom	x	y	z	B_{eq}	occ
W(1)	0.19483(6)	0.13022(2)	0.37628(3)	4.11(1)	
P(1)	0.0199(3)	0.1310(2)	0.2361(2)	4.48(7)	
O(1)	-0.0458(9)	0.1327(5)	0.4739(5)	8.1(3)	
N(1)	0.0461(9)	0.1330(4)	0.4256(5)	4.5(2)	
N(2)	0.265(1)	0.2712(5)	0.3891(7)	6.2(3)	
C(1)	0.454(1)	0.1213(6)	0.446(1)	6.3(4)	
C(2)	0.370(2)	0.0820(8)	0.4855(9)	6.5(5)	
C(3)	0.308(1)	0.0364(6)	0.423(1)	5.8(4)	
C(4)	0.357(1)	0.0508(6)	0.3483(8)	5.1(4)	
C(5)	0.440(1)	0.1072(6)	0.3625(9)	5.1(4)	
C(6)	0.552(2)	0.1734(7)	0.490(1)	13.0(6)	
C(7)	0.353(2)	0.0822(9)	0.5780(9)	15.4(7)	
C(8)	0.228(2)	-0.0206(7)	0.441(1)	13.1(7)	
C(9)	0.332(2)	0.0092(6)	0.2713(9)	9.3(5)	
C(10)	0.535(1)	0.1299(7)	0.3051(9)	9.4(5)	
C(11)	0.228(1)	0.2198(5)	0.3726(7)	4.5(3)	
C(12)	0.250(2)	0.3299(5)	0.3450(9)	5.0(4)	
C(13)	0.396(4)	0.341(1)	0.316(3)	11(1)	0.600
C(13a)	0.228(6)	0.317(2)	0.251(3)	7(1)	0.400
C(14)	0.228(4)	0.3785(10)	0.411(1)	9.1(9)	0.600
C(14a)	0.396(5)	0.359(2)	0.380(2)	5(1)	0.400
C(15)	0.111(3)	0.335(1)	0.272(2)	7.7(8)	0.600
C(15a)	0.135(5)	0.355(2)	0.376(3)	9(1)	0.400
C(16)	0.116(1)	0.1286(7)	0.1479(6)	4.7(3)	

Table S8 (continued)

atom	x	y	z	B_{eq}	occ
C(17)	0.104(1)	0.0792(6)	0.0917(8)	5.6(4)	
C(18)	0.193(2)	0.0789(7)	0.0320(9)	7.6(5)	
C(19)	0.282(2)	0.126(1)	0.0213(9)	8.4(5)	
C(20)	0.290(2)	0.1747(7)	0.078(1)	8.8(6)	
C(21)	0.210(2)	0.1761(7)	0.1400(8)	6.6(5)	
C(22)	-0.116(1)	0.0674(6)	0.2130(9)	4.8(4)	
C(23)	-0.242(2)	0.0686(6)	0.1442(9)	6.2(4)	
C(24)	-0.339(2)	0.0182(9)	0.130(1)	7.8(5)	
C(25)	-0.310(2)	-0.0318(8)	0.178(2)	9.2(8)	
C(26)	-0.187(2)	-0.0323(8)	0.246(1)	9.0(7)	
C(27)	-0.092(2)	0.0190(7)	0.2637(9)	6.7(4)	
C(28)	-0.113(1)	0.1951(5)	0.2093(8)	3.8(3)	
C(29)	-0.167(1)	0.2216(6)	0.2745(8)	4.9(4)	
C(30)	-0.275(2)	0.2673(6)	0.2563(8)	5.2(4)	
C(31)	-0.332(1)	0.2856(6)	0.1746(10)	5.9(4)	
C(32)	-0.275(1)	0.2627(6)	0.1087(8)	5.4(4)	
C(33)	-0.167(1)	0.2165(5)	0.1270(8)	4.9(4)	

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table S9. Bond lengths (Å) for **2**.

atom	atom	distance	atom	atom	distance
W(1)	P(1)	2.433(3)	W(1)	N(1)	1.704(8)
W(1)	C(1)	2.34(1)	W(1)	C(2)	2.33(1)
W(1)	C(3)	2.36(1)	W(1)	C(4)	2.38(1)
W(1)	C(5)	2.32(1)	W(1)	C(11)	2.00(1)
W(1)	CP	2.02	P(1)	C(16)	1.82(1)
P(1)	C(22)	1.84(1)	P(1)	C(28)	1.84(1)
O(1)	N(1)	1.257(9)	N(2)	C(11)	1.20(1)
N(2)	C(12)	1.47(1)	C(1)	C(2)	1.39(2)
C(1)	C(5)	1.35(2)	C(1)	C(6)	1.52(2)
C(2)	C(3)	1.44(2)	C(2)	C(7)	1.53(2)
C(3)	C(4)	1.41(2)	C(3)	C(8)	1.51(2)
C(4)	C(5)	1.44(2)	C(4)	C(9)	1.52(2)
C(5)	C(10)	1.48(1)	C(12)	C(13)	1.51(3)
C(12)	C(13a)	1.50(5)	C(12)	C(14)	1.55(3)
C(12)	C(14a)	1.46(4)	C(12)	C(15)	1.51(3)
C(12)	C(15a)	1.36(5)	C(16)	C(17)	1.41(1)
C(16)	C(21)	1.37(2)	C(17)	C(18)	1.38(2)
C(18)	C(19)	1.35(2)	C(19)	C(20)	1.40(2)
C(20)	C(21)	1.36(2)	C(22)	C(23)	1.39(1)
C(22)	C(27)	1.33(2)	C(23)	C(24)	1.40(2)
C(24)	C(25)	1.34(2)	C(25)	C(26)	1.37(2)
C(26)	C(27)	1.41(2)	C(28)	C(29)	1.38(1)
C(28)	C(33)	1.38(1)	C(29)	C(30)	1.38(1)
C(30)	C(31)	1.36(1)	C(31)	C(32)	1.38(1)

Table S10. Bond Angles (°) for **2**.

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	W(1)	N(1)	91.4(3)	P(1)	W(1)	C(11)	91.9(3)
P(1)	W(1)	CP	126.8	N(1)	W(1)	C(11)	96.6(5)
N(1)	W(1)	CP	125.9	C(11)	W(1)	CP	115.9
C(5)	W(1)	C(11)	93.7(5)	W(1)	P(1)	C(16)	113.6(3)
W(1)	P(1)	C(22)	115.9(5)	W(1)	P(1)	C(28)	117.9(4)
C(16)	P(1)	C(22)	103.4(6)	C(16)	P(1)	C(28)	103.8(6)
C(22)	P(1)	C(28)	100.2(5)	W(1)	N(1)	O(1)	169.7(8)
C(11)	N(2)	C(12)	137(1)	C(2)	C(1)	C(5)	112(1)
C(2)	C(1)	C(6)	124(1)	C(5)	C(1)	C(6)	123(1)
C(1)	C(2)	C(3)	106(1)	C(1)	C(2)	C(7)	129(1)
C(3)	C(2)	C(7)	124(1)	C(2)	C(3)	C(4)	106(1)
C(2)	C(3)	C(8)	125(1)	C(4)	C(3)	C(8)	127(1)
C(3)	C(4)	C(5)	107(1)	C(3)	C(4)	C(9)	123(1)
C(5)	C(4)	C(9)	128(1)	C(1)	C(5)	C(4)	106(1)
C(1)	C(5)	C(10)	127(1)	C(4)	C(5)	C(10)	122(1)
W(1)	C(11)	N(2)	165(1)	N(2)	C(12)	C(13)	107(1)
N(2)	C(12)	C(13a)	106(1)	N(2)	C(12)	C(14)	107(1)
N(2)	C(12)	C(14a)	103(1)	N(2)	C(12)	C(15)	114(1)
N(2)	C(12)	C(15a)	100(2)	C(13)	C(12)	C(14)	110(2)
C(13)	C(12)	C(15)	111(2)	C(13a)	C(12)	C(14a)	111(2)
C(13a)	C(12)	C(15a)	120(2)	C(14)	C(12)	C(15)	105(1)
C(14a)	C(12)	C(15a)	111(2)	P(1)	C(16)	C(17)	122(1)
P(1)	C(16)	C(21)	117(1)	C(17)	C(16)	C(21)	119(1)
C(16)	C(17)	C(18)	118(1)	C(17)	C(18)	C(19)	122(1)

Table S10 (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(18)	C(19)	C(20)	116(1)	C(19)	C(20)	C(21)	122(1)
C(16)	C(21)	C(20)	119(1)	P(1)	C(22)	C(23)	121(1)
P(1)	C(22)	C(27)	118(1)	C(23)	C(22)	C(27)	119(1)
C(22)	C(23)	C(24)	118(1)	C(23)	C(24)	C(25)	121(1)
C(24)	C(25)	C(26)	119(1)	C(25)	C(26)	C(27)	119(1)
C(22)	C(27)	C(26)	121(1)	P(1)	C(28)	C(29)	118.0(10)
P(1)	C(28)	C(33)	123(1)	C(29)	C(28)	C(33)	118(1)
C(28)	C(29)	C(30)	119(1)	C(29)	C(30)	C(31)	120(1)
C(30)	C(31)	C(32)	120(1)	C(31)	C(32)	C(33)	118(1)
C(28)	C(33)	C(32)	121(1)				

Table S11. Anisotropic displacement parameters ($Å^2$) for **2**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	0.0599(3)	0.0435(3)	0.0518(3)	0.0082(4)	0.0105(2)	0.0079(4)
P(1)	0.065(2)	0.048(2)	0.057(2)	0.000(2)	0.014(2)	-0.002(2)
O(1)	0.101(7)	0.115(7)	0.099(7)	0.012(8)	0.039(6)	0.002(7)
N(1)	0.064(6)	0.034(5)	0.077(6)	-0.001(6)	0.028(5)	0.003(7)
N(2)	0.084(9)	0.048(7)	0.096(9)	0.003(7)	0.007(7)	0.008(8)
C(1)	0.052(9)	0.06(1)	0.10(1)	0.026(9)	-0.031(8)	0.02(1)
C(2)	0.08(1)	0.10(1)	0.06(1)	0.051(10)	0.006(9)	0.01(1)
C(3)	0.07(1)	0.07(1)	0.08(1)	0.028(9)	0.009(9)	0.028(10)
C(4)	0.065(10)	0.061(10)	0.07(1)	0.036(8)	0.015(8)	0.013(8)
C(5)	0.068(10)	0.07(1)	0.050(9)	-0.013(8)	-0.003(8)	0.010(8)
C(6)	0.09(1)	0.11(1)	0.24(2)	0.04(1)	-0.08(1)	-0.08(1)
C(7)	0.26(2)	0.28(2)	0.05(1)	0.16(2)	0.05(1)	0.08(1)
C(8)	0.11(1)	0.12(1)	0.28(2)	0.05(1)	0.06(1)	0.15(1)
C(9)	0.11(1)	0.09(1)	0.13(1)	0.042(9)	-0.03(1)	-0.06(1)
C(10)	0.075(10)	0.12(1)	0.18(1)	0.03(1)	0.06(1)	0.07(1)
C(11)	0.062(10)	0.061(8)	0.045(7)	0.010(8)	0.005(7)	0.023(8)
C(12)	0.07(1)	0.040(9)	0.08(1)	-0.010(8)	0.009(9)	0.004(8)
C(13)	0.13(3)	0.07(2)	0.27(5)	0.02(2)	0.13(4)	0.03(3)
C(13a)	0.14(5)	0.04(3)	0.08(3)	0.00(3)	-0.03(3)	0.03(2)
C(14)	0.21(3)	0.04(2)	0.08(2)	0.03(2)	-0.02(2)	-0.01(1)
C(14a)	0.08(3)	0.04(2)	0.08(3)	0.02(2)	0.01(2)	0.00(2)
C(15)	0.11(2)	0.04(2)	0.09(2)	0.00(2)	-0.07(2)	0.02(1)
C(16)	0.052(7)	0.068(8)	0.050(7)	-0.017(9)	-0.004(6)	-0.001(10)
C(17)	0.08(1)	0.068(10)	0.066(9)	0.000(8)	0.029(8)	-0.010(8)

Table S11 (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(18)	0.10(1)	0.13(1)	0.07(1)	0.01(1)	0.044(10)	-0.02(1)
C(19)	0.08(1)	0.18(2)	0.08(1)	0.02(1)	0.053(9)	0.03(1)
C(20)	0.10(1)	0.11(1)	0.13(2)	-0.01(1)	0.04(1)	-0.01(1)
C(21)	0.07(1)	0.11(1)	0.07(1)	-0.01(1)	0.030(9)	0.002(10)
C(22)	0.07(1)	0.056(9)	0.06(1)	-0.004(9)	0.027(9)	0.004(8)
C(23)	0.09(1)	0.052(9)	0.08(1)	-0.008(9)	0.001(9)	-0.011(8)
C(24)	0.09(1)	0.10(1)	0.11(1)	-0.03(1)	0.03(1)	-0.05(1)
C(25)	0.10(2)	0.06(1)	0.21(3)	-0.02(1)	0.08(2)	-0.05(2)
C(26)	0.12(2)	0.07(1)	0.16(2)	0.01(1)	0.04(1)	0.03(1)
C(27)	0.09(1)	0.056(10)	0.11(1)	-0.013(9)	0.026(10)	0.009(9)
C(28)	0.045(8)	0.041(8)	0.051(9)	-0.009(7)	-0.003(7)	0.000(7)
C(29)	0.059(9)	0.055(9)	0.067(9)	0.005(7)	0.004(7)	0.005(8)
C(30)	0.07(1)	0.057(9)	0.07(1)	0.004(8)	0.021(9)	-0.007(8)
C(31)	0.07(1)	0.060(10)	0.09(1)	0.011(8)	0.008(10)	0.001(9)
C(32)	0.08(1)	0.058(10)	0.064(10)	0.007(8)	0.005(8)	0.016(8)
C(33)	0.07(1)	0.049(8)	0.069(9)	-0.001(7)	0.014(8)	-0.002(8)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S12. Hydrogen coordinates and equivalent isotropic displacement parameters for **2**.

atom	x	y	z	B_{iso}	occ
H(1)	0.6584	0.1668	0.4865	15.6	
H(2)	0.5146	0.2115	0.4615	15.6	
H(3)	0.5460	0.1750	0.5498	15.6	
H(4)	0.4050	0.1175	0.6079	18.5	
H(5)	0.2439	0.0836	0.5785	18.5	
H(6)	0.3985	0.0451	0.6068	18.5	
H(7)	0.2080	-0.0183	0.4986	15.8	
H(8)	0.1305	-0.0248	0.3990	15.8	
H(9)	0.2927	-0.0558	0.4379	15.8	
H(10)	0.2226	0.0021	0.2491	11.1	
H(11)	0.3752	0.0280	0.2266	11.1	
H(12)	0.3840	-0.0296	0.2879	11.1	
H(13)	0.6417	0.1185	0.3282	11.2	
H(14)	0.4988	0.1119	0.2482	11.2	
H(15)	0.5262	0.1740	0.3009	11.2	
H(16)	0.4799	0.3212	0.3545	13.3	0.600
H(16a)	0.1223	0.3034	0.2272	9.5	0.400
H(17)	0.3826	0.3241	0.2577	13.3	0.600
H(17a)	0.2489	0.3532	0.2209	9.5	0.400
H(18)	0.4128	0.3845	0.3140	13.3	0.600
H(18a)	0.2985	0.2844	0.2427	9.5	0.400
H(19)	0.3279	0.3965	0.4374	10.9	0.600
H(19a)	0.4789	0.3300	0.3838	6.4	0.400
H(20)	0.1592	0.4103	0.3818	10.9	0.600

Table S12 (continued)

atom	x	y	z	B_{iso}	occ
H(20a)	0.4098	0.3930	0.3430	6.4	0.400
H(21)	0.1846	0.3597	0.4549	10.9	0.600
H(21a)	0.3966	0.3748	0.4374	6.4	0.400
H(22)	0.0220	0.3477	0.2931	9.3	0.600
H(22a)	0.1331	0.3988	0.3630	11.3	0.400
H(23)	0.1299	0.3641	0.2298	9.3	0.600
H(23a)	0.0386	0.3367	0.3464	11.3	0.400
H(24)	0.0888	0.2949	0.2439	9.3	0.600
H(24a)	0.1552	0.3485	0.4365	11.3	0.400
H(25)	0.0341	0.0456	0.0947	6.8	
H(26)	0.1912	0.0429	-0.0038	9.1	
H(27)	0.3393	0.1258	-0.0239	10.1	
H(28)	0.3547	0.2094	0.0716	10.5	
H(29)	0.2197	0.2107	0.1792	7.9	
H(30)	-0.2633	0.1041	0.1068	7.4	
H(31)	-0.4306	0.0193	0.0824	9.3	
H(32)	-0.3766	-0.0674	0.1649	11.1	
H(33)	-0.1647	-0.0683	0.2828	10.7	
H(34)	-0.0061	0.0191	0.3141	8.1	
H(35)	-0.1285	0.2080	0.3336	5.9	
H(36)	-0.3100	0.2868	0.3031	6.2	
H(37)	-0.4154	0.3154	0.1624	7.1	
H(38)	-0.3088	0.2786	0.0507	6.5	
H(39)	-0.1279	0.1985	0.0805	5.9	

SHELXL-93 and CIF Achive Format

This note is intended to accompany submissions to journals for the benefit of editors and referees who may not yet be familiar with the features of the new crystal structure refinement program SHELXTL-Plus and the new International Union of Crystallography CIF archive format.

CIF (S.R. Hall, F.H. Allen and I.D. Brown, Acta Crystallogr., **A47** (1991) 655-685) is an extremely flexible format for deposition of crystallographic data and is already the method of choice for the transmission of data to the Cambridge (organic) and Inorganic structural databases. At the end of a structure refinement with SHELXTL-Plus two archive files are produced: *.cif contains the crystal data, atomic coordinates, bond lengths etc., and *.fcf contains observed and calculated structure factors, both in CIF format. The .fcf file requires no further processing but the .cif file must be edited by the user to include items such as the crystal color that even the most sophisticated program cannot deduce from the diffraction data; this editing takes the form of replacing a question mark with the appropriate information. With a little practice it is perfectly possible for humans to read CIF files, but SHELX users are encouraged to use the program CIFTAB (supplied with SHELXTL-Plus) to produce more tasteful tables of crystal data, bonds and angles, structure factors etc. for referees.

All refinements with SHELXTL-Plus are performed with F-squared rather than F. This enables ALL data to be used rather than only data with F greater than a specified threshold, with the result that the experimental information is more fully exploited. For weakly scattering crystals this can appreciably improve the precision of the structure determination. However the R-index:

$$wR2 = \sqrt{\left(\sum[w(Fo^2-Fc^2)^2] \;/\; \sum[wFo^4] \right)}$$

that (in the absence of restraints) is minimized during the refinement is for statistical reasons about twice as large as the conventional index R1 (based on F):

$$R1 = \sum \big|\, |Fo| - |Fc| \,\big| \;/\; \sum |Fo|$$

and to make it worse an R-index based on ALL data is inevitably larger than one based only on data with F greater than a given threshold. It is rumored that a leading journal (that comes out in both German and English editions) has already

rejected several papers reporting structures refined with the new program because "the R-factor was too high" !

Note that wR2 should not be confused with 'wR' or 'Rw' (both usually based on F). Since weighting schemes for F-squared and F refinements are quite different, it may not even be possible to calculate a meaningful Rw if the structure has been refined against F-squared.

For comparison with other (older) structures it is however very desirable to quote a conventional R-index (i.e. R1) calculated with a threshold of $F^2 > 2\sigma(F^2)$ [that effectively corresponds to $F > 4\sigma(F)$]. R1 also has the advantage that it is relatively insensitive to manipulation of the weighting scheme.

Some very observant referees have drawn authors' attention to the fact that they had not fixed any coordinates to define the origin in polar space groups. This is because SHELXTL-Plus automatically uses the mathematically superior 'polar axis restraints' proposed by H.D. Flack and D. Schwarzenbach (Acta Crystallogr., **A44** (1988) 499-506) that restrains a suitable weighted sum of atomic coordinates to be constant. Similarly the Flack 'racemic twinning parameter' is always estimated by the program where appropriate and reported in the .cif file (but not used in the calculation of Fc^2 unless specified by the user), so that it is unlikely that the user will fail to notice when it is necessary to determine the correct 'absolute structure' (H.D. Flack, Acta Crystallogr., **A39** (1983) 876-881).

SHELXL-93 uses scattering factors and absorption coefficients from the new Volume C of International Tables for Crystallography (1992), so there will be small discrepancies with values of mu etc. calculated by programs that still use older values.

SHELXL-93 estimates esds in bond lengths, angles and torsion angles from the full covariance matrix. The contributions of the cell esds are also included rigorously, except that the (usually unknown) correlations between the cell parameters are ignored unless defined by the crystal symmetry (e.g. the error in a cubic cell dimension affects the esd of a bond length but not of an angle). The esds in the equations of least-squares planes and in the distances of atoms from such planes are also calculated from the full matrix,

but the (small) contributions of the cell esds to these esds involve some approximations. Thus there will be discrepancies with esds calculated for checking purposes by programs that do not have access to the full covariance matrix.

References:

G.M. Sheldrick, Acta Crystallogr., A46 (1990) 467-473.

SHELXTL-Plus V5.0, Siemens Industrial Automation, Inc., Madison, WI.