Supplementary Material (ESI) for Chemical Communications

An *N*-Heterocyclic Carbene as a Bidentate Hemilabile Ligand: A Synchrotron X-ray Diffraction and Density Functional Theory Study

Vladimir K. Dioumaev, David J. Szalda, Jonathan Hanson,

James A. Franz, and R. Morris Bullock*

All manipulations were performed in Schlenk-type glassware on a dual-manifold Schlenk line or in an argon-filled Vacuum Atmospheres glovebox. NMR spectra were obtained on a Bruker Avance 400 FT NMR spectrometer (400 MHz for ^{1}H). All NMR spectra were recorded at 25 °C unless stated otherwise. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. External standards of trifluorotoluene (set as δ = -63.73) and 85 % H_3PO_4 (set as δ = 0) were used for referencing ^{19}F and ^{31}P NMR spectra. $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded with broadband ^{1}H decoupling unless stated otherwise. For quantitative ^{1}H NMR measurements the relaxation delay was set at 30 seconds. GC-MS spectra were recorded on an Agilent Technologies 5973 mass selective detector connected to an Agilent Technologies 6890N gas chromatograph equipped with an HP-5ms column (5 % phenyldimethylpolysiloxane). Infrared spectra were recorded on a Mattson Polaris spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc. (Woodside, NY).

Hydrocarbon solvents were dried over Na/K-benzophenone. Benzene-d_6 was dried over Na/K. 3-pentanone was dried over CaH_2. H_2 was used as received. Compounds 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes), $CpMo(CO)_2(PPh_3)H$,[1] $CpMo(CO)_2(PMe_3)H$,[2]

$CpW(CO)_2(PPh_3)H$,[1] $CpW(CO)_2(PMe_3)H$[2] were synthesized according to the literature procedures. A sample of $Ph_3C^+B(C_6F_5)_4^-$ was donated by Albemarle Chemical Company.

Ab initio calculations were carried with Gaussian 98 set of programs,[3] and density function theory calculations were done using the B3LYP[4-7] implementation with the LANL2DZ basis set which combines the Los Alamos electron core pseudopotentials and the Dunning-Hay D95 basis set for C, H, N, and O.[8-11]

Synthesis of *cis*-$CpMo(CO)_2(IMes)H$ from $CpMo(CO)_2(PPh_3)H$. In a glovebox $CpMo(CO)_2(PPh_3)H$ (480.0 mg, 1.000 mmol), IMes (306.0 mg, 1.000 mmol), and 10 mL of toluene were placed in a glass tube equipped with a Teflon valve. The light yellow solids dissolved to produce a dark purple mother liquor. A new light yellow precipitate formed almost immediately. The tube was heated at 95 °C for 3 hours. The product was recrystallized from toluene-hexanes (1 : 3) to yield 449 mg (86 %) of pure $CpMo(CO)_2(IMes)H$ as light yellow crystals. ^1H NMR (THF-d_8) δ 7.16 (s, 2H, =C*H*), 7.02 (s, 4H, *m-H*-Mes), 4.62 (s, 5H, *Cp*), 2.34 (s, 6H, *p-Me*-Mes), 2.09 (s, 12H, *o-Me*-Mes), -4.73 (s, 1H, Mo*H*). ^{13}C NMR (THF-d_8) δ 243.3 (d, $^2J_{CH}$ = 11 Hz, Mo-*C*O), 200.2 (d, $^2J_{CH}$ = 12 Hz, N*C*N), 139.5 (m, *i-Mes*), 139.2 (q, $^2J_{CH}$ = 6 Hz, *p-Mes*), 136.9 (q, $^2J_{CH}$ = 6 Hz, o-*Mes*), 130.0 (dm, $^1J_{CH}$ = 156 Hz, *m-Mes*), 124.3 (dd, $^1J_{CH}$ = 196 and $^2J_{CH}$ = 12 Hz, =*C*H), 89.0 (dp, $^1J_{CH}$ = 174 and J_{CH} = 6 Hz, *Cp*), 21.2 (qt, $^1J_{CH}$ = 126 and $^3J_{CH}$ = 4 Hz, *p-Me*-Mes), 18.8 (qm, $^1J_{CH}$ = 128 Hz, *o-Me*-Mes). IR (THF-d_8) ν(CO) = 1918 (vs) and 1843 (vs) cm^{-1}. IR (hexanes) ν(CO) = 1930 (vs) and 1858 (vs) cm^{-1}. Anal. Calcd. for $C_{28}H_{30}N_2O_2Mo$: C, 64.37; H, 5.79; N, 5.36. Found: C, 64.13; H, 6.05; N, 5.34.

Synthesis of $CpW(CO)_2(IMes)H$ from $CpW(CO)_2(PMe_3)H$. In a glovebox $CpW(CO)_2(PMe_3)H$ (346.0 mg, 0.900 mmol), IMes (275.0 mg, 0.900 mmol), and 1 mL of toluene were placed in a glass tube equipped with a Teflon valve. The light yellow solids dissolved to produce a dark purple mother liquor. A new light yellow precipitate formed almost immediately. The volatiles were removed in vacuo, and the residue was heated in dynamic vacuo for 10 minutes at 120 °C to remove free phosphine and reestablish the equilibrium in favor of $CpW(CO)_2(IMes)H$. The product was recrystallized from toluene-hexanes (1 : 1) to yield 416 mg (76 %) of pure $CpW(CO)_2(IMes)H$ as light yellow crystals with 0.5 equiv. of crystallization solvent ($C_6H_5CH_3$) per W. ^1H NMR (C_6D_6) δ 6.80 (s, 4H, *m-H*-Mes), 6.19 (s, 2H, =C*H*), 4.60 (s, 5H, *Cp*), 2.12 (s, 6H, *p-Me*-Mes), 2.10 (s, 12H, *o-Me*-Mes), -5.93 (s, $^1J_{WH}$ = 45 Hz, 1H, W*H*). ^1H NMR (THF-d_8, -100 °C) δ 7.40 (s, 2H, =C*H*), 7.06 (s, 4H, *m-H*-Mes), 4.71 (s, 5H, *Cp*), 2.34 (s, 6H, *p-Me*-Mes), 2.12 (br s, 6H, *o-Me*-Mes), 2.01 (br s, 6H, *o-Me*-Mes), -6.43 (s, $^1J_{WH}$ = 45 Hz, 1H, W*H*). ^{13}C NMR (C_6D_6) δ 238.1 (m, W-*C*O), 184.1 (d, $^2J_{CH}$ = 14.8 Hz, N*C*N), 139.1 (m, *i-Mes*), 138.9 (q, $^2J_{CH}$ = 6 Hz, *p-Mes*), 136.6 (q, $^2J_{CH}$ = 6 Hz, o-*Mes*), 129.9 (dm, $^1J_{CH}$ = 157 Hz, *m-Mes*), 122.9 (dd, $^1J_{CH}$ = 195 and $^2J_{CH}$ = 12 Hz, =*C*H), 87.4 (d quintet, $^1J_{CH}$ = 177 and J_{CH} = 7 Hz, *Cp*), 21.4 (qt, $^1J_{CH}$ = 126 and $^3J_{CH}$ = 5 Hz, *p-Me*-Mes), 19.1 (qm, $^1J_{CH}$ = 127 Hz, *o-Me*-Mes). $^{13}C\{^1H\}$ NMR (THF-d_8, -100 °C) δ 247.4 (br s, W-*C*O), 232.3 (br s, W-*C*O), 181.5 (s, N*C*N), 139.4 (s, *p-Mes* or *i-Mes*), 138.9 (s, *p-Mes* or *i-Mes*), 137.1 (br s, o-*Mes*), 136.6 (br s, o-*Mes*), 129.8 (br s, *m-Mes*), 124.1 (br s, =*C*H), 88.0 (s, *Cp*), 21.3 (br s, *p-Me*-Mes), 19.4 (br s, *o-Me*-Mes), 18.9 (br s, *o-Me*-Mes). IR (toluene) ν(CO) = 1915 (vs) and 1824 (vs) cm^{-1}. IR (THF-d_8) ν(CO) = 1913 (vs) and 1822 (vs) cm^{-1}. IR (CD_2Cl_2) ν(CO) = 1906 (vs) and 1810 (vs) cm^{-1}. Anal. Calcd. for $C_{31.5}H_{34}N_2O_2W$ (with 0.5 equiv. of crystallization solvent, $C_6H_5CH_3$, per W): C, 57.63; H, 5.22; N, 4.27. Found: C, 57.52; H, 5.07; N, 4.14.

Synthesis of *cis*-$CpW(CO)_2(IMes)H$ from $CpW(CO)_2(PPh_3)H$. In a glovebox $CpW(CO)_2(PPh_3)H$ (608 mg, 1.07 mmol), IMes (333 mg, 1.09 mmol), and 3 mL of toluene were placed in a glass tube equipped with a Teflon valve. The yellow solids dissolved to produce a brown-red mother liquor. A new light yellow precipitate formed within 10-20 minutes. The color faded slowly to yellow-gray, indicating completion of the reaction after two days at 23 °C. The product was washed with 2 x 7 mL of hexanes and recrystallized from toluene-hexanes (1 : 1) to yield 568 mg (87 %) of pure $CpW(CO)_2(IMes)H$ as light yellow crystals. The product was identified by comparison to an authentic sample of $CpW(CO)_2(IMes)H$, which was synthesized by an independent route.

Synthesis of $[CpMo(CO)_2(IMes)]^+[B(C_6F_5)_4]^-$. In a glovebox $CpMo(CO)_2(IMes)H$ (52.4 mg, 0.100 mmol) was added slowly to a stirred solution of $Ph_3C^+B(C_6F_5)_4^-$ (96.6 mg, 0.105 mmol) in 5 mL of toluene. A dark purple precipitate formed. The stirring was continued for 40 minutes. The bright yellow mother liquor was discarded, and the precipitate was washed with toluene until the washings were colorless (5 x 3 mL). The product was washed with hexanes (3 x 3 mL) and dried in vacuo to yield 112 mg (87 %) of dark purple crystals of pure $CpMo(CO)_2(IMes)^+B(C_6F_5)_4^-$ with 0.5 equiv. of crystallization solvent ($C_6H_5CH_3$) per Mo. The product was insoluble in common non-coordinating NMR solvents. For spectra in THF-d_8 see $[CpMo(CO)_2(IMes)(THF\text{-}d_8)]^+[B(C_6F_5)_4]^-$. IR (Nujol) ν(CO) = 1999 (vs) and 1905 (vs) cm^{-1}. Anal. Calcd. for $C_{55.5}H_{33}BF_{20}N_2O_2Mo$ (with 0.5 equiv. of crystallization solvent, $C_6H_5CH_3$, per Mo): C, 53.47; H, 2.67; N, 2.25. Found: C, 53.18; H, 2.77; N, 2.43. Single crystals of $CpMo(CO)_2(IMes)^+B(C_6F_5)_4^-$ were grown directly from the reaction mixture by slow diffusion of reagents.

***cis*-$[CpMo(CO)_2(IMes)(THF\text{-}d_8)]^+[B(C_6F_5)_4]^-$.** ^1H NMR (THF-d_8) δ 7.83 (s, 2H, =C*H*), 7.13 (s, 4H, *m-H*-Mes), 5.14 (s, 5H, *Cp*), 2.36 (s, 6H, *p-Me*-Mes), 2.11 (s, 12H, *o-Me*-Mes). $^{13}C\{^1H\}$ NMR (THF-d_8) δ 251 (m, Mo-*C*O), 187.3 (s, N*C*N), 149.3 (dm, $^1J_{CF}$ = 246 Hz, *o*-C_6F_5), 141.0 (br s, *p-Mes* or *i-Mes*), 139.2 (dm, $^1J_{CF}$ = 243 Hz, *p*-C_6F_5), 137.4 (br s, *p-Mes* or *i-Mes*), 137.2 (dm, $^1J_{CF}$ = 244 Hz, *m-C*$_6$F$_5$), 136.5 (br s, o-*Mes*), 130.3 (br s, *m-Mes*), 127.6 (br s, =*C*H), 125 (br m, *i-C*$_6$F$_5$), 96.9 (s, *Cp*), 21.0 (s, *p-Me*-Mes), 18.7 (br s, *o-Me*-Mes). ^{19}F NMR (THF-d$_8$) δ –132.9 (d, 8F, $^3J_{FF}$ = 10 Hz, *o*-C$_6$*F*$_5$), –165.1 (t, 4F, $^3J_{FF}$ = 21 Hz, *p*-C$_6$*F*$_5$), –168.6 (t, 8F, $^3J_{FF}$ = 18 Hz, *m*-C$_6$*F*$_5$). IR (THF) ν(CO) = 1977 (vs) and 1882 (vs) cm^{-1}.

Synthesis of $[CpW(CO)_2(IMes)]^+[B(C_6F_5)_4]^-$. In a glovebox CpW(CO)$_2$(IMes)H (244.0 mg, 0.400 mmol) was added slowly to a stirred solution of $Ph_3C^+B(C_6F_5)_4^-$ (387.0 mg, 0.420 mmol) in 10 mL of toluene. A dark purple precipitate formed. The stirring was continued for 30 minutes. The bright yellow mother liquor was discarded, and the precipitate was washed with toluene until the washings were colorless (5 x 3 mL). The product was washed with hexanes (3 x 3 mL) and dried in vacuo to yield 490 mg (91 %) of dark purple crystals of pure $[CpW(CO)_2(IMes)]^+[B(C_6F_5)_4]^-$ with 1 equiv. of crystallization solvent ($C_6H_5CH_3$) per W. The product was insoluble in common non-coordinating NMR solvents. For spectra in THF-d$_8$ see $[CpW(CO)_2(IMes)(THF\text{-}d_8)]^+[B(C_6F_5)_4]^-$. IR (Nujol) ν(CO) = 1980 (vs) and 1890 (vs) cm^{-1}. IR (CF$_3$Ph) ν(CO) = 1983 (vs) and 1900 (vs) cm^{-1}. Anal. Calcd. for $C_{59}H_{37}BF_{20}N_2O_2W$ (with 1 equiv. of crystallization solvent, $C_6H_5CH_3$, per W): C, 51.33; H, 2.70; N, 2.03. Found: C, 51.24; H, 3.35; N, 2.02. Single crystals of $CpW(CO)_2(IMes)^+B(C_6F_5)_4^-$ were grown directly from the reaction mixture by slow diffusion of reagents.

***cis*-$[CpW(CO)_2(IMes)(THF\text{-}d_8)]^+[B(C_6F_5)_4]^-$.** ^{1}H NMR (THF-d$_8$, -30 ˚C) δ 7.99 and 7.87 (d, $^1J_{HH}$ = 2 Hz, 1H, =C*H*), 7.26, 7.19, 7.16, and 7.03 (s, 1H, *m-H*-Mes), 5.36 (s, 5H, *Cp*), 2.41, 2.31, 2.30, 2.23, 2.14, and 2.02 (s, 3H, *p-Me*-Mes and *o-Me*-Mes). ^{13}C{^{1}H} NMR (THF-d$_8$, -40 ˚C) δ 247.1 and 246.2 (s, W-*C*O), 179.6 (s, N*C*N), 149.0 (br d, $^1J_{CF}$ = 240 Hz, *o-C*$_6$F$_5$), 141.3 and 140.0 (s, *p-Mes* or *i-Mes*), 139.1 (dm, $^1J_{CF}$ = 242 Hz, *p-C*$_6$F$_5$), 137.9 (s, *p-Mes* or *i-Mes*), 137.0 (dm, $^1J_{CF}$ = 244 Hz, *m-C*$_6$F$_5$), 137.5, 136.7, 136.5, and 135.8 (s, o-*Mes*), 130.7, 130.3, 130.2, and 129.4 (s, *m-Mes*), 128.4 and 126.6 (br s, =*C*H), 125 (br m, *i-C_6*F_5), 95.4 (s, *Cp*), 21.1 and 21.0 (s, *p-Me*-Mes), 19.7, 18.9, 18.7, and 18.6 (s, *o-Me*-Mes). ^{19}F NMR (THF-d_8, -30 ˚C) δ –133.5 (d, 8F, $^3J_{FF}$ = 11 Hz, *o*-C_6F_5), –164.9 (t, 4F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), –168.5 (t, 8F, $^3J_{FF}$ = 18 Hz, *m*-C_6F_5). IR (THF-d_8) ν(CO) = 1962 (vs) and 1859 (vs) cm^{-1}.

Example of catalytic hydrogenation at 54.4 atm (800 psi). In a glove box $CpW(CO)_2(IMes)^+B(C_6F_5)_4^-$ (53.0 mg, 0.040 mmol) and 3-pentanone (1.20 mL, 11.3 mmol) were placed in a stainless steel high-pressure autoclave. H_2 was added at 54.4 atm, and the reaction was carried out at indicated temperature in a constant-temperature bath. Prior to removal of each sample for analysis, the bottom of the autoclave was cooled at -196 ˚C, and the pressure was slowly vented. The sample for NMR analysis was taken in a glove box under an argon atmosphere, and the autoclave was resealed and re-pressurized with H_2.

Example of catalytic hydrogenation at 4 atm. In a glove box $CpW(CO)_2(IMes)^+B(C_6F_5)_4^-$ (26.5 mg, 0.019 mmol) and 3-pentanone (600 μL, 5.65 mmol) were placed in a glass tube (125 mL capacity) equipped with a Teflon valve. The solution was freeze-pump-thawed, frozen again, and the entire tube was submersed in liquid nitrogen. The tube was then filled with about 1 atm H_2, sealed, and warmed to room temperature. As a result the tube contained 20 mmol of H_2 (ca. 4 atm at room temperature). The reaction was carried out at indicated temperature in a constant-temperature bath. Aliquots were removed by cooling the tube to -196 ˚C, evacuating H_2, refilling the tube with Ar, and taking it into the glovebox. After removal of an aliquot (ca. 60 μL), the tube was again freeze-pump-thawed, filled with H_2 at -196 ˚C and re-sealed.

Table of Results for Hydrogenation of 3-pentanone in neat substrate with 0.34 mol % of catalyst

catalyst	*T*, °C	pressure, atm	time, h	TON[a]
2Mo	23	4	24	0.9 (0)
2Mo	23	4	240	0.9 (0)
2Mo	50	4	24	0.8 (0)
2Mo	50	4	240	1.0 (0)
2W	23	4	24	2.1 (0)
2W	23	4	238	10.0 (0)
2W	50	4	23	15.1 (0.4)
2W	50	4	164	29.9 (0.7)
2W	23	54.4	24	7.8 (0.2)
2W	23	54.4	240	86.0 (6.0)
2W	50	54.4	24	15.9 (3.8)
2W	50	54.4	168	60.9 (12.6)

[a] Turnover number (TON) is the total number of moles of 3-pentanone hydrogenated per mole of catalyst. It includes TON for the formation of the direct hydrogenation product, 3-pentanol, and the secondary condensation product, $(Et_2CH)_2O$. Each equivalent of the ether is counted as two turnovers of the catalyst, since it is formed from two equivalents of the alcohol. The number in parenthesis is a TON for the ether alone.

Gaussian-98 summary for W model. (Note three methyls on one mesityl ring replaced by H and para-methyl group on remaining mesityl ring replaced with H.)

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 2\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/LANL2DZ FREQ\\2 methyl group
 s on W compound\\1,1\W,0.6721629286,0.731009158,0.0997377779\C,0.24581
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1237,0.4817873571,-1.7461870014\C,2.6994035554,1.5834455709,-0.8941628
708\C,2.9459154937,1.0675552786,0.4333846962\C,2.3333519347,-0.7112492
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006652\
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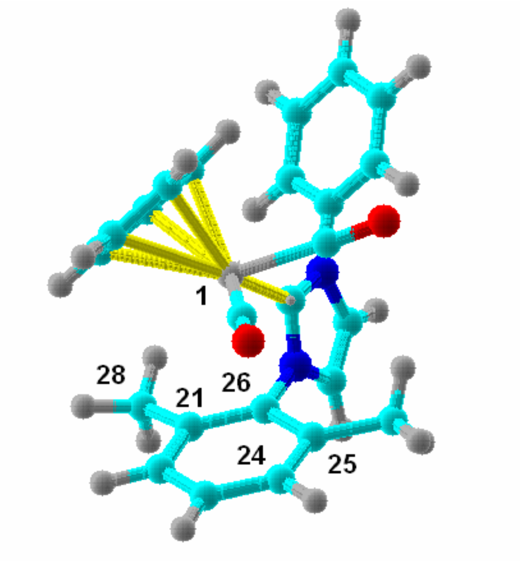

Figure 1. Calculated structure of the W model

Gaussian-98 summary for Mo model (Note three methyls on one mesityl ring replaced by H and para-methyl group on remaining mesityl ring replaced with H.)

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 02\0\\#N GEOM=ALLCHECK GUESS=TCHECK RB3LYP/LANL2DZ FREQ\\2 methyl grou
 ps on Mo compound\\1,1\Mo,0.7554016631,0.851669544,0.0955888214\C,0.303
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,2.8578387508\H,2.2206863185,-5.6572786306,0.4496459268\H,0.584782879,
-4.1866058516,-0.7339698817\H,-1.2191717616,2.7324271866,-3.9550505482
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\H,-2.4809950425,4.4162229727,-2.6308091218\H,-3.4686855911,3.80840318
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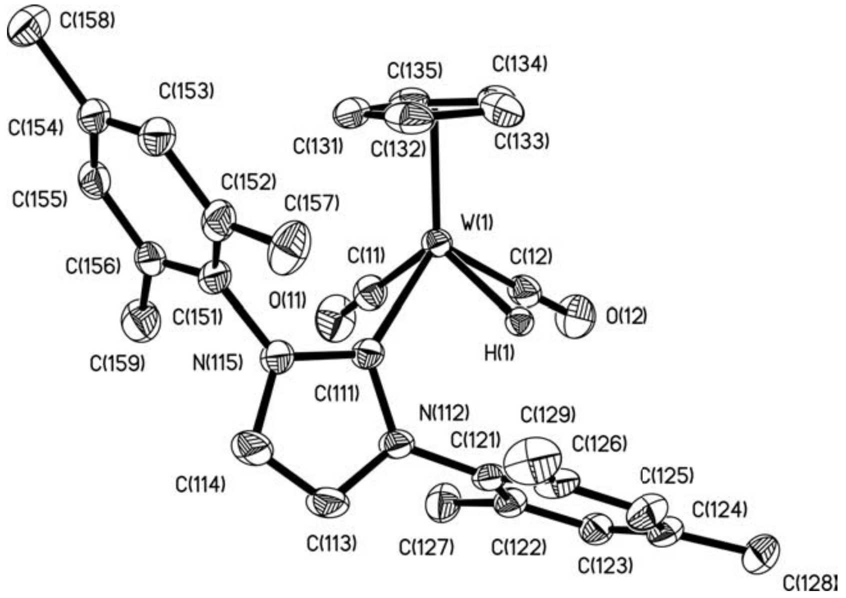
4233,0.6915967709,0.7372197203\H,-3.7677266772,2.2889412992,1.37352724
81\H,-0.2689536362,-0.6737307171,-2.8367153773\H,-1.597817392,-0.41305
29408,-3.9674451292\H,-0.1295252454,0.5511139048,-4.1169630586\O,0.029
2331409,3.8918060105,0.72224377\\Version=SGI64-G98RevA.7\HF=-1254.3092
553\
```

Crystal Structure of $CpW(CO)_2(IMes)H$ (1W)

Crystallographic data for **1W**: 0.33 × 0.33 × 0.27 mm; triclinic; $P\bar{1}$; a = 8.9340(18) Å, b = 11.258(2) Å, c = 13.631(3) Å, α = 80.97(3) °, β = 72.96(3) °, γ = 70.79(3) °; V = 1235.0(4) $Å^3$, Z = 2 and ρ_{calc} = 1.641 g/cm^3; $2\theta_{max}$ = 54.94 °; $Mo_{K\alpha}$ radiation (λ = 0.71073 Å); θ - 2θ scan; T = 293(2) K; 5652 reflections, all 5652 unique reflections were used in the refinement; no polarization correction; empirical absorption correction (psi scan); Patterson (SHELXL-97); refinement by full-matrix least squares based on F^2 (SHELXL-97); 299 parameters; hydrogens unrefined; R_1 = 0.0284 and wR_2 = 0.0656 for 4355 reflections for which $I > 2\sigma(I)$; residual electron density +0.999 and -0.605 $e/Å^3$.



ORTEP diagram of complex **1W** (30% probability ellipsoids). Selected bond lengths (Å) and angles (°): W(1)–C(11) 1.936(6), W(1)–C(12) 1.927(5), W(1)–C(111) 2.183(5), C(11)–W(1)–C(12) 77.7(2), C(11)–W(1)–C(111) 80.3(2), C(12)–W(1)–C(111) 109.68(19), N(112)–C(111)–W(1) 128.8(3), N(115)–C(111)–W(1) 129.3(3). Closest W • • • $C_{mesityl}$ non-bonding distances: W(1) • • • C(121) 3.637(5), W(1) • • • C(151) 3.663(5).

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