C–N Bond Cleavage

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Primary Carbon–Nitrogen Bond Scission and Methyl Dehydrogenation across a W–W Multiple Bond **

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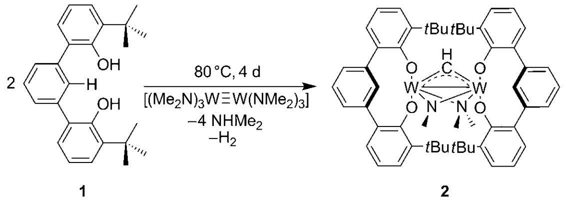
Until clean sources of renewable fuels become economically and technologically feasible, purification of coal and crude oil will remain a key industrial process.[1,2] Unfortunately, as the global energy demand increases, use of more coal and low-quality crude oil, and in particular nitrogen-rich oilsand bitumen from Canada, will inevitably follow.[3] As a consequence, more efficient and cost effective means of removing NO_x-causing compounds will be imperative. Hydrodenitrogenation (HDN)[4,5] removes nitrogen as ammonia from nitrogenous compounds in crude oil by treating with hydrogen (70 atm) at 400 °C over sulfided Co/Mo/α-Al_2O_3 or Ni/Mo/α-Al_2O_3.[6] Mechanisms proposed for this reaction suggest an aliphatic carbon–nitrogen bond cleavage event as the rate-determining step.[7,8] Recent model studies focus on C=N double-bond cleavage of aromatic N-heterocycles, because this process presents the promising opportunity of eliminating an expensive and energy intensive hydrogenation step.[9] Ultimately, an aliphatic C–N bond scission must occur, and herein we provide a relevant example of a unique C–N bond activation across a W–W dimer and the formation of a bridging methylidyne ligand by methyl dehydrogenation.[10] This sequence of reactions represents a model pathway for site deactivation of commercial HDN catalysts.

One of the challenges to understanding HDN reactions is reproducing the types of reactions that occur on a heterogeneous catalyst surface. Trianionic pincer ligands[11] provide a metal coordination environment suitable for studying reactivity[12] under homogeneous conditions, and dinuclear metal complexes[13] are a model for adjacent metal sites on a heterogeneous catalyst surface. In search of a reactive dinuclear complex, we treated $[(Me_2N)_3W{\equiv}W(NMe_2)_3]$ with the terphenyl trianionic pincer ligand precursor $\{t\mathrm{BuOCO}\}H_3$ **1** (where $\{t\mathrm{BuOCO}\}H_3 = 3,3''$-di-*tert*-butyl-1,1′:3′,1″-terphenyl-2,2″-diol) at 80 °C for four days in C_6D_6 (Scheme 1). As the reaction progresses, the color of the solution turns green, and dark-green single crystals form. An X-ray diffraction experiment performed on the crystals indicates that the solid is the ditungsten complex $[\{t\mathrm{BuOCHO}\}W(\mu\text{-NMe})(\mu\text{-NMe}_2)(\mu\text{-CH})W\{\mathrm{OCHO}t\mathrm{Bu}\}]$ (**2**; Figure 1). The product forms in 88 % yield and is the result of a C–N bond scission and double C–H bond activation with concomitant loss of both hydrogen atoms.



Scheme 1. Synthesis of $[\{t\mathrm{BuOCHO}\}W(\mu\text{-NMe})(\mu\text{-NMe}_2)(\mu\text{-CH})W\{\mathrm{OCHO}t\mathrm{Bu}\}]$ (**2**).

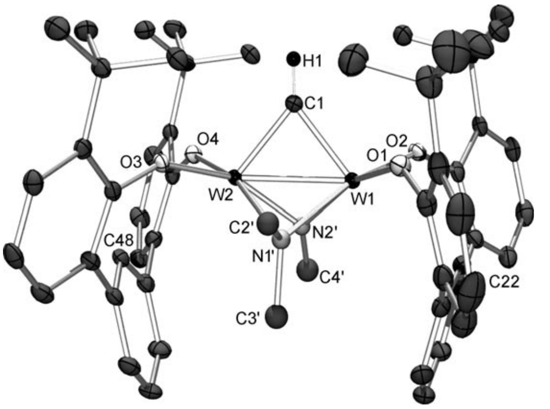


Figure 1. Molecular structure of $[\{t\mathrm{BuOCHO}\}W(\mu\text{-NMe})(\mu\text{-NMe}_2)(\mu\text{-CH})W\{\mathrm{OCHO}t\mathrm{Bu}\}]$ (**2**) with ellipsoids set at 50 % probability; hydrogen atoms (except H1), a benzene molecule, and disordered NMe groups are omitted for clarity.

The dinuclear complex **2** is C_s-symmetric, and each tungsten atom adopts a distorted square-pyramidal coordination geometry. A dimethyl amido, methyl imido, and methylidyne moiety each span the W–W core. The W^V–W^V distance is 2.49879(15) Å, which is consistent with a d^1–d^1, W–W single bond. The closest complex for comparison is $[W_2(OCH_2t\mathrm{Bu})_4(\mu\text{-OCH}_2t\mathrm{Bu})(\mu\text{-O})(py)_2(\mu\text{-C}^CC_3H_5)]$ (μ-$C^CC_3H_5$=a bridging cyclopropyl methyne), which contains three one-atom bridges (carbyne, oxo, and alkoxy) and a W–W bond of 2.4456(7) Å.[14] A similar complex $[\{W(OCMe_2CF_3)_2Cl\}_2(\mu\text{-NAr}')_2]$ has two one-atom bridges and a

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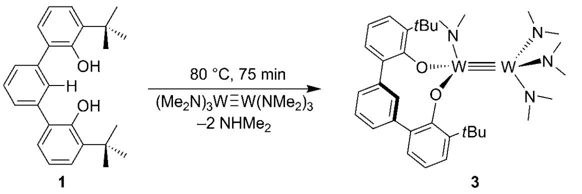
significantly longer W–W bond (2.6296(2) Å).[15] The shortest crystallographically characterized W–W distance (2.155(2) Å) was found in the quadruply bonded complex $[W_2(dmhp)_4]$.[16] Disordered μ-NMe_2 and μ-NMe ligands refine isotropically at half occupancy, and as expected, the average W–N bond for the μ-NMe_2 moiety is longer than the μ-NMe by 0.208(9) Å. The OCO ligand is bound as a dianionic bisphenolate instead of a trianionic pincer. The central aromatic rings point away from the W–W core, although each *ipso*-carbon atom remains in close proximity to its corresponding tungsten atom (W1–C22 = 2.815(2) Å, W2–C48 = 2.988(2) Å). Furthermore, each carbyne–tungsten–C_{ipso} axis is only 15.75(1)° away from linearity, suggesting that a tungsten–arene π interaction compensates for the open coordination site. Confirming the bridging atom is a carbon, crystallographic modeling of the atom as either an O or N results in poor refinement statistics, and more importantly, the proton was located in the difference Fourier map and refined without constraints to give a C1–H1 bond length of 0.88(3) Å.

The ^1H NMR spectrum of **2** in $CDCl_3$ is consistent with the solid-state C_s symmetric structure. Each half of the molecule along the W–W axis is distinct, and thus the *t*Bu protons of each diphenolate are found at 1.22 and 1.40 ppm. The μ-NMe_2 groups are diastereotopic and are at 1.65 and 1.93 ppm. A third signal at 3.99 ppm is due to the imido μ-NMe protons. An nOe of the signal at 3.99 ppm with a doublet at 7.44 ppm identifies the later as H40 (see Figure 1) and allows the absolute stereochemical assignments within the diphenolate ligand to be made. An nOe of H38 (7.32 ppm) with the signal at 1.93 ppm identifies the latter as H3′. Also observed are long-range (five bond) couplings between H4′ and C2′ and between H1 and C4′ (four bond). ^1H–^1H, ^1H–^{13}C, one-bond, and ^1H–^{13}C long-range couplings observed in the gDQCOSY, gHMQC, and gHMBC spectra allow the absolute assignment of all proton and carbon signals (Supporting Information, Table 1). The most interesting feature of the spectrum is the methylidyne proton (H1) located downfield at 19.11 ppm, which has a five-line pattern characteristic of a proton coupling to two ^{183}W nuclei. Though not located in the $^{13}C\{^1H\}$ NMR spectrum, an HMQC experiment allows indirect detection of the methylidyne carbon at 349.9 ppm and is consistent with the only other example of a bridging W-methylidyne, namely $[(tBu_3SiO)_2W(\mu\text{-}CH)(\mu\text{-}H)(\mu\text{-}O)W(tBu_3SiO)_2]$ from Wolczanski et al., which appears at 319.5 ppm.[17]

Exhaustive spectroscopic analysis indicates a dehydrogenation event must occur, as **2** does not contain a W–H bond. The IR spectrum of **2** does not reveal any bridging or terminal W–H stretching vibrations in the typical range of 1500–2000 cm^{-1}.[12] Two weak absorptions appear at 1583 and 1598 cm^{-1}, but these are ligand absorptions. The ^1H NMR spectrum (500 MHz) of **2** does not indicate the presence of a hydride signal. The spectrum does provide excellent resolution of all proton signals and their appropriate integration. The tungsten hydride in $[(tBu_3SiO)_2W(\mu\text{-}CH)(\mu\text{-}H)(\mu\text{-}O)W(tBu_3SiO)_2]$ is conspicuous at 11.77 ppm (C_6D_6).[11] A gHMBC experiment did not identify a through-bond interaction between the carbyne C–H and a W–H bond, and all attempts to locate probable hydride ligands by crystallographic methods failed. Finally, convincing evidence that no hydrides are present comes from mass spectrometry analysis, which clearly identifies the $[M+H]^+$ parent ion mass of 1199.4116 m/z for $C_{56}H_{67}N_2O_4W_2$. Periodic monitoring of the reaction conducted in a sealable tube by ^1H NMR spectroscopy does not reveal the presence of H_2. In this case, the theoretical yield of H_2 and its solubility in C_6D_6 (calculated for toluene)[19] is lower than the ^1H NMR detection limit. However, a gas chromatograph of the reaction headspace reveals the presence of H_2 at a retention time equivalent to an authentic sample.

Considering that two large diphenolate ligands bind to **2**, steric pressure may cause the unusual sequence of C–N bond cleavage and methyl dehydrogenation. However, monitoring the reaction periodically by ^1H NMR spectroscopy reveals the build-up of an intermediate at early reaction times. Upon heating the reagents, one ligand binds and displaces two equivalents of dimethylamine to form $[\{tBuOCHO\}(NMe_2)W{\equiv}W(NMe_2)_3]$ (**3**; Scheme 2). Stopping the reaction prior to subsequent bond activation events is possible by using only one equivalent of the ligand, and provides **3** in 92% yield.

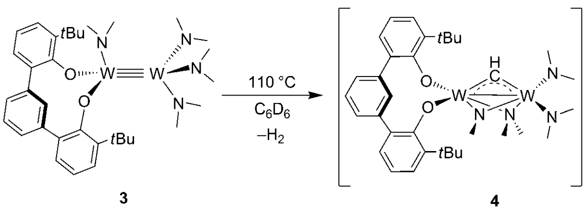


Scheme 2. Synthesis of $[\{tBuOCHO\}(NMe_2)W{\equiv}W(NMe_2)_3]$ (**3**).

Isolated **3** matches the ^1H NMR (C_6D_6) signals present at early reaction times during the formation of **2**. The molecule is C_s-symmetric in solution at ambient temperature, but unlike **2**, the mirror plane contains the tungsten atoms, resulting in only one signal for the *t*Bu protons at 1.46 ppm.

Key to the structural assignment, a broad signal appears at 3.39 ppm for the 12 NMe_2 protons that lie on opposite sides of the mirror plane. Rotation around the W–W bond must be slow at 25 °C, as the third NMe_2 group is distinct and is observed at 2.35 ppm. The fourth NMe_2 group appears at 4.09 ppm. A low-temperature NMR experiment ([D_8]toluene, −55 °C) generates a C_1-symmetric species that has non-equivalent *t*Bu groups and eight different NMe signals as a consequence of quenched W–N bond rotations. Cross-peaks in the gHMBC spectrum enable the correlation between methyl pairs on each dimethylamide, but poorly resolved ROESY nOe data prevents their absolute stereochemical assignment (see Supporting Information).

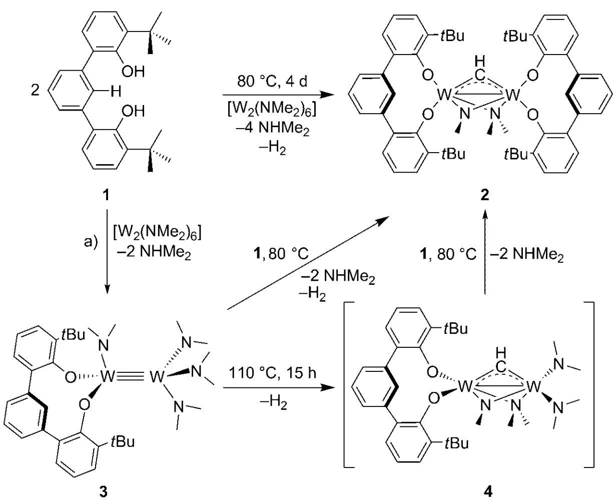
Addition of a second equivalent of ligand **1** to **3** in C_6D_6 and heating at 80 °C for 12 h leads to the exclusive formation of **2**. The fact that **3** converts into **2** upon addition of the second ligand does not impart insight into the timing of the bond cleavages. Thermolysis of **3** at 110 °C for 15 h, without additional ligand, leads to a mixture of compounds. The ^1H NMR spectrum of the mixture suggests the formation of a major compound, tentatively assigned as [{*t*BuOCHO}W(μ-NMe)(μ-NMe$_2$)(μ-CH)W(NMe$_2$)$_2$] (**4**) (Scheme 3), which exhibits a characteristic bridging methylidyne proton signal at 16.40 ppm ($J^2_{\mathrm{W-CH}} = 12$ Hz). This result indicates that the C–N bond cleavage and methyl group dehydrogenation events occur prior to addition of the second ligand. The presence of minor impurities of like solubility to **4** prevents an in-depth spectroscopic analysis of the intermediate. Nonetheless, signals that support the assignment of **4** include: 1) nine protons for each *t*Bu at 1.75 and 1.91 ppm, 2) a μ-NMe group at 4.96 ppm, 3) diastereotopic μ-NMe$_2$ protons at 3.50 and 4.21 ppm, and 4) signals for the terminal NMe$_2$ protons at 2.29 and 2.50 ppm.



Scheme 3. Thermolysis of **3** to induce CN bond cleavage and methyl group dehydrogenation to form the bridging methylidyne complex [{*t*BuOCHO}W(μ-NMe) (μ-NMe$_2$) (μ-CH) W (NMe$_2$)$_2$] (**4**).

To confirm that **4** is indeed an intermediate in the formation of **2**, addition of one equivalent of ligand **1** to **4** results in the formation of **2** (80 °C, 2 h). Monitoring the reaction by ^{1}H NMR spectroscopy indicates that all of the signals attributable to **4** decrease in conjunction with the formation of **2**; after 2 h, consumption of **4** is complete and **2** precipitates as a crystalline green solid (Scheme 4).

In summary, two adjacent metal atoms provide pathways for chemistry to occur that single metal atoms cannot. Aside from the mechanical movement of atoms from one metal center to the other, the most obvious advantage is the availability of mutliple redox equivalents. Treating [(Me$_2$N)$_3$W≡W(NMe$_2$)$_3$] with two equivalents of the diphenol {*t*BuOCO}H$_3$ (**1**) at 80 °C leads to C–N bond cleavage and methyl dehydrogenation, which is an unprecedented combination of bond activations to provide a rare example of a bridging methylidyne group. [(Me$_2$N)$_3$W≡W(NMe$_2$)$_3$] provides a total of four redox equivalents as it converts from W$^{\mathrm{III}}$–W$^{\mathrm{III}}$ into W$^{\mathrm{V}}$–W$^{\mathrm{V}}$. A single metal ion is highly unlikely to accomplish similar bond ruptures, though four-electron oxidative addition to a single tungsten center is known.[20]



Scheme 4. The overall sequence of reactions that contribute to the formation of complex **2**, including the intermediates **3** and **4**. a) The stoichiometry is 1:1 between **1** and [W$_2$(NMe$_2$)$_6$] in this reaction.

This result relates to C–N bond cleavage events that may occur on surface sites of heterogenous catalysts during hydrodenitrogenation. The C–N bond cleavage and dehydrogenation, which are not a consequence of steric pressure, occur prior to addition of the second diphenol ligand equivalent. Identification of intermediates **3** and **4** support the notion that these events can occur on surface sites and are not an attempt by the metal to relieve steric congestion. Perhaps more importantly, the formation of a bridging methylidyne in **2** represents the first evidence for an unexplored HDN catalyst site deactivation[21,22] by carbyne poisoning.

Experimental Section

2: A Schlenk tube was charged with [(Me$_2$N)$_3$W≡W(NMe$_2$)$_3$] (358 mg, 0.57 mmol), {*t*BuOCO}H$_3$ (**1**; 424 mg, 1.13 mmol), and benzene (8 mL). The solution was heated at 80 °C for 4 days and the solution color changed from yellow to intense dark green. Cooling the solution to ambient temperature causes a green crystalline precipitate to deposit. The precipitate was filtered, washed with pentane, and all volatiles were removed in vacuo to provide **2** as a green microcrystalline powder (600 mg, 88 %). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 19.11$ (t, $J^2_{\mathrm{W-H}} = 21$ Hz, 1 H, W-μ-C*H1*-W), 8.37 (t, $J = 3$ Hz, 2 H, H22,H48), 7.51 (t, $J = 6$ Hz, 2 H, H13,H39), 7.44 (t, $J = 3$ Hz, 2 H, H14,H40), 7.32 (t, $J = 3$ Hz, 2 H, H12,H38), 7.21 (t, $J = 3$ Hz, 2 H, H9,H35), 7.19 (m, 4 H, H7,H33,H21,H47), 7.16 (d, $J = 3$ Hz, 2 H, H19,H45), 6.75 (t, $J = 9$ Hz, 4 H, H8,H34,H20,H46), 3.99 (s, 3 H, μ-N(C*H*$_3$), H4), 1.93 (s, 3 H, μ-N(C*H*$_3$)$_2$, H3), 1.65 (s, 3 H, μ-N(C*H*$_3$)$_2$, H2), 1.40 (s, 18 H, C(C*H*$_3$)$_3$, H24–26,H50–52), 1.22 ppm (s, 18 H, C(C*H*$_3$)$_3$, H28–30,H54–56); ^{13}C{^{1}H} NMR (75.36 MHz, CDCl$_3$): $\delta = 349.9$ (W-μ-*C1*H-W), 161.2 (s, C17,C43), 161.1 (s, C5,C31), 141.5 (s, C15,C41), 140.7 (s, C18,C44), 140.6 (s, C11,C37), 140.3 (s, C6,C32), 131.3 (s, C13,C39), 130.7 (s, C22,C48), 128.7 (s, C10,C36), 128.2 (s, C16,C42), 126.9 (s, C9,C35), 126.6 (s, C19,C45), 125.9 (s, C12,C38), 125.4 (s, C14,C40), 125.2 (s, C7,C33), 125.1 (s, C21,C47), 120.0 (s, C20,C46), 119.9 (s, C8,C34), 55.7 (s, μ-N(*C*H$_3$), C4), 54.7 (s, μ-N(*C*H$_3$)$_2$, C3), 51.6 (s, N(*C*H$_3$)$_2$, C2), 35.5 (s, *C*(CH$_3$)$_3$, C23,C49), 35.1 (s, *C*(CH$_3$)$_3$, C27,C53), 30.4 (s, C(*C*H$_3$)$_3$, C24–26,C50–52), 30.2 ppm (s, C(*C*H$_3$)$_3$, C28–30,C54–56). ^{15}N NMR (50 MHz, CDCl$_3$): $\delta = 98.1$(*N1*), 406.1 ppm (*N2*). Selected IR data (neat): $\tilde{\nu} = 2957$ (w), 2867 (w), 1582 (m), 1423 (m), 1404 (m), 1380 (m), 1232 (vs), 1191 (s), 1087 (m), 945 (m), 875 (vs), 849 (m), 810 (m), 747 (m), and 677 cm^{-1} (m). HRMS: *m*/*z* calcd for $C_{56}H_{67}N_2O_4W_2$: 1199.4127 [$M+$H]$^+$; found: 1199.4116. Elemental analysis calcd (%) for $C_{56}H_{66}N_2O_4W_2$: C 56.11, H 5.55, N 2.34; found: C 56.04, H 5.46, N 2.29.

3: A Schlenk tube was charged with [(Me$_2$N)$_3$W≡W(NMe$_2$)$_3$] (366 mg, 0.57 mmol), {*t*BuOCO}H$_3$ (**1**; 217 mg, 0.57 mmol), and benzene (5 mL). The solution was heated at 80 °C for 75 min and a color change from gold to goldenrod (orange-yellow) was observed. The solution was cooled and filtered to remove a small amount of black precipitate, and then all volatiles were removed in vacuo to provide the product **3** as goldenrod-colored powder (491 mg, 92%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 8.82$ (s, 1H, H7), 7.34 (d, $J = 9$ Hz, 4H, H2,H4,H10,H12), 7.30 (t, $J = 6$ Hz, 1H, H17), 7.25 (d, $J = 6$ Hz, 2H, H16,H18), 6.91 (t, $J = 9$ Hz, 2H, H3,H11), 4.09 (bs, 6H, $N(CH_3)_2$), 3.39 (bs, 12H, $N(CH_3)_2$), 2.35 (bs, 6H, $N(CH_3)_2$), 1.46 ppm (s, 18H, $C(CH_3)_3$). ^{1}H NMR (500 MHz, [D_8]toluene, −75 °C): $\delta = 9.03$ (s, H7), 7.40 (d, $J = 9$ Hz, 2H, H16, H18), 7.32 (d, $J = 9$ Hz, 2H, H12, H2), 7.27 (t, $J = 9$ Hz, 1H, H17), 7.22 (d, $J = 9$ Hz, 1H, H10), 7.16(d, J=9 Hz, 1H, H4), 6.99 (t, $J = 9$ Hz, 1H, H11), 6.88 (t, $J = 9$ Hz, 1H, H3), 4.88 (s, 3H, $N(CH_3)_2$), 4.15 (s, 3H, $N(CH_3)_2$), 4.07 (s, 3H, $N(CH_3)_2$), 3.81 (s, 3H, $N(CH_3)_2$), 2.77 (s, 3H, $N(CH_3)_2$), 2.61 (s, 3H, $N(CH_3)_2$), 1.85 (s, 3H, $N(CH_3)_2$), 1.81(s, 3H, $N(CH_3)_2$), 1.73 (s, 9H, $C(CH_3)_3$, C20), 1.22 ppm (s, 9H, $C(CH_3)_3$, C22). ^{13}C {^{1}H} NMR (125 MHz, [D_8]toluene, −75 °C): $\delta = 160.9$(s, C14), 160.4 (s, C15), 141.5(s, C6, C8), 139.0 (s, C5, C9), 138.8(s, C1), 138.7(s, C13), 134.1 (s, C4), 132.3 (s, C10), 130.9 (s, C17), 129.4 (s, C7), 129.3 (s, C16, C18), 126.0 (s, C12), 125.9 (s, C2), 120.0 (s, C11), 119.0 (s, C3), 62.1(s, $N(CH_3)_2$), 60.8 (s, $N(CH_3)_2$), 59.9 (s, $N(CH_3)_2$), 58.8 (s, $N(CH_3)_2$), 42.4 (s, $N(CH_3)_2$), 41.0 (s, $N(CH_3)_2$), 40.4 (s, $N(CH_3)_2$), 37.8 (s, $N(CH_3)_2$), 35.5 (s, $C(CH_3)_3$, C19), 35.0 (s, $C(CH_3)_3$, C21), 30.2 (s, $C(CH_3)_3$, C20), 30.1 ppm (s, $C(CH_3)_3$, C22). Selected IR data (neat): $\tilde{\nu} = 2948$ (w), 2860 (w), 1579 (m), 1460 (m), 1406 (m), 1230 (vs), 1143 (w), 1090 (m), 1039 (w), 934 (m), 864 (m), 781 (m), 745 (vs), 710 cm^{-1}(m). HRMS m/z (%) calcd for $C_{34}H_{53}N_2O_4W_2$: 917.3191 $[M+H]^+$; found: 917.3164. Elemental analysis calcd (%) for $C_{34}H_{52}N_2O_4W_2$: C 44.56, H 5.72, N 6.11; found: C 44.75, H 5.66, N, 5.99.

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