

ORGANOMETALLICS

Organometallics, 1997, 16(9), 1825-1827, DOI:[10.1021/om970118x](https://doi.org/10.1021/om970118x)

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1997 American Chemical Society

Experimental

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen or argon. General procedures routinely employed in these laboratories have been described in detail previously.¹ The organometallic reagent $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\text{CPh}=\text{CH}_2)$ (**1**) was prepared according to the reported literature procedure.² Ethyl acetate and acetonitrile (Aldrich) were distilled from CaH_2 . Wet acetonitrile was prepared by deaerating HPLC-grade solvent obtained directly from the Aldrich or by adding microliter amounts of distilled, deionized water to rigorously-dried acetonitrile. Acetonitrile- d_3 (CIL) was dried over CaH_2 and vacuum-transferred. Deuterated water (CIL) was deaerated under a flow of argon immediately prior to use.

Preparation of $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-OC}(\text{Me})(\text{OEt})\text{CH}=\text{CPh})$ (2**)** $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\text{CPh}=\text{CH}_2)$ **1** (135 mg, 0.25 mmol) was dissolved in EtOAc (10 mL) in a thick-walled bomb. The deep red solution was heated at 45 °C for 24 h, during which time the colour of the solution changed to purple. The solvent was removed in vacuo and the purple residue extracted with a minimum of CH_2Cl_2 . The extract was filtered through a plug of celite (1.5 × 0.5 cm) supported on a frit and the volume reduced. An equal volume of hexanes was added and the solution cooled to -30 °C overnight. Complex **2** (112 mg) was isolated as dark purple needles via removal of the supernatant and subsequent drying under vacuum.

Preparation of $\text{Cp}^*\text{W}(\text{NO})(\eta^3\text{-HNC}(\text{Me})=\text{NC}(\text{=CH}_2)\text{CH}=\text{CPh})$ (3**)**. Complex **1** (270 mg, 0.5 mmol) was dissolved in MeCN (20 mL) in a thick-walled bomb and the solution was heated for 24 h at 50 °C. After this time the blood-red solution was pumped to dryness and triturated with pentane (3 × 5 mL) followed by washing with diethyl ether (3 × 5 mL). The washings were discarded and the dark red residue was pumped to dryness. A minimum volume of CH_2Cl_2 /hexanes (1:1) was added and the resultant solution was filtered through celite (1 × 2 cm plug). The filtrate was reduced in volume and

cooled to -32 °C overnight. Complex **3** was isolated as a dark red powder after removal of the supernatant and drying under vacuum (207 mg).

NMR Tube Thermolysis of 1 in MeCN-*d*₃. Cp*W(NO)(η³-DNC(CD₃)=NC(=CD₂)CH=CPh) **3-*d*₆** was prepared by the same method as for **3** except that **1** (30 mg, 0.056 mmol) was dissolved in MeCN-*d*₃ (0.5 mL) in an NMR tube and heated for 24h at 45 °C. The solvent was removed in vacuo and the red solid was redissolved in CDCl₃. Characterization of **3-*d*₆** was afforded by comparison of its ¹H NMR spectra to that of **3**.

Preparation of Cp*W(NO)(OH)(η²-HN=C(Me)CH=CPh) (4**)** (135 mg, 0.25 mmol) was dissolved in wet MeCN (10 mL) in a thick-walled bomb and the solution was heated for 24h at 45 °C. Over this time period the solution turned a light orange color and a red crystalline solid deposited in the bottom of the bomb. The orange supernatant was removed by pipette and the crystals dried under vacuum. The supernatant was filtered through a celite plug (1.5 × 0.5 cm) and the volume of the filtrate was reduced in vacuo. The resultant dark orange solution was then cooled to -32 °C overnight and a second fraction of **4** was isolated as orange microcrystals after removal of the supernatant and drying under vacuum (107 mg).

Preparation of Cp*W(NO) (OD)(η²-DN=C(Me)CH=CPh) (4-*d*₂**).** Compound **4-*d*₂** was prepared in a manner similar to **4** except that **1** (135 mg, 0.25 mmol) was dissolved in dry MeCN (10 mL) and the red solution was then doped with D₂O (5 μL, 0.28 mmol). Orange **4-*d*₂** was isolated by removal of the solvent. Characterization was afforded by dissolving the sample in CDCl₃ and comparing the results to the ¹H NMR spectroscopic properties of **4**.

NMR Tube Reaction of **4 with D₂O.** Complex **4** (20 mg, 0.040 mmol) was dissolved in MeCN-d₃ (0.5 mL) in an NMR tube and D₂O (10 mL, 0.56 mmol) was added. The resulting solution was heated at 45 °C overnight and then its ¹H spectrum was recorded, indicating quantitative formation of **4-d₂** by comparison to the ¹H NMR spectroscopic data for that an authentic sample of **4-d₂**.

Kinetic Studies. The kinetics studies were performed using a HP8452 UV-vis spectrometer equipped with a thermostatted cell holder connected to a VWR 1150 constant-temperature bath, accurate to within ± 0.25 °C. Typical kinetic runs monitored the product band at 336 nm, over not less than 3.5 half-lives, arising from the thermolysis of 0.1 - 1 mg of complex **1** dissolved in 3 mL of solvent. Absorbance values for t_∞ were obtained by computer optimization of the residual, R, for the regression line fitted to the data through a first-order analysis. Reported errors in k_{obs} are the standard deviation in the slope for the computer-optimized regression line.

Table S1. Numbering Scheme, Yield, and Analytical Data for Complexes **2-4**.

Complex	compd	colour	anal. found (calcd)		
	no.	(yield, %)	C	H	N
Cp*W(NO)(η ² -OC(Me)(OEt)CH=CPh)	2	purple (84)	48.77 (49.00)	5.35 (5.42)	2.47 (2.60)
Cp*W(NO)(η ³ -HNC(Me)=NC(=CH ₂)CH=CPh)	3	dark red (78)	48.90 (49.52)	5.09 (5.10)	6.69 (7.88)
Cp*W(NO)(η ³ -DNC(CD ₃)=NC(=CD ₂)CH=CPh)	3-d₆	dark red (95) ^a	n/a ^b	n/a	n/a
Cp*W(NO)(OH)(η ² -HNC(Me)CH=CPh) •0.5MeCN	4	orange (80)	47.52 (47.15)	5.27 (5.22)	7.04 (6.60)
Cp*W(NO)(OD)(η ² -DNC(Me)CH=CPh)	4-d₂	orange (98) ^a	n/a ^b	n/a	n/a

^a yield as indicated in the ¹H NMR spectrum of the reaction mixture. ^b NMR tube reaction.

Table S2. Mass Spectroscopic Data and IR Spectral Data for Complexes **2-4**.

Compd no	MS (m/z) ^a	probe temp ^b (°C)	IR (Nujol, cm ⁻¹)
2	539	200	1532 (ν _{NO})
3	533 ^c	80	^d 3268 (ν _{NH}) 1614 (ν _{C=N}) 1590 (ν _{C=C}) 1517 (ν _{NO})
3-d₆	539	n/a	n/a ^e
4	510	150	3562 (ν _{OH}) 1532 (ν _{NO})
4-d₂	512	120	2630 (ν _{OD}) 2282 (ν _{ND}) 1531 (ν _{NO})

^a Values for the highest intensity peak of the calculated isotopic cluster (¹⁸⁴W). ^b Probe temperatures. ^c High-resolution EI mass spectrum (150 °C). found (calcd): 533.16608 (533.16638), [C₂₂H₂₇N₃O¹⁸⁴W, P⁺]; 503.16662 (503.16837), [P⁺-NO]. ^d KBr pellet ^e NMR tube reaction.

Table S3. ^1H and ^{13}C NMR Spectroscopic Data for Complexes **2-4**.

compd no	^1H NMR ^a δ / ppm	^{13}C NMR ^a δ / ppm
2	7.50 (d, 2H, $^3J_{\text{HH}} = 8.4$ Hz, Ph o-H) 7.19 (vt, 2H, $^3J_{\text{HH}} = 7.2$ Hz, Ph m-H) 7.18 (s, 1H, CPh=CH) 7.17 (vt, 1H, $^3J_{\text{HH}} = 7.2$ Hz, Ph p-H) 4.49 (dq, 1H, $\text{OCH}_a\text{H}_b\text{CH}_3$) 4.35 (dq, 1H, $\text{OCH}_a\text{H}_b\text{CH}_3$) 2.32 (s, 3H, OCMe) 1.59 (s, 15H, C_5Me_5) 1.14 (t, 3H, OCH_2CH_3)	250.7 (CPh=CH) 204.7 (OC(Me)(OEt)) 150.1 (Ph i-C) 136.2 (d, $^1J_{\text{CH}} = 158.6$ Hz, CPh=CH) 128.5, 127.9, 127.2, (C_6H_5) 112.7 (C_5Me_5) 69.8 (t, $^1J_{\text{CH}} = 133.7$ Hz, OCH_2Me) 26.2 (q, $^1J_{\text{CH}} = 127.4$ Hz, OC(Me)(OEt)) 21.4 (q, $^1J_{\text{CH}} = 127.7$ Hz, OC(Me)(OCH_2Me)) 9.4 (q, $^1J_{\text{CH}} = 127.7$ Hz, 127.5, C_5Me_5)
3	7.43 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, Ph o-H) 7.26 (vt, 2H, $^3J_{\text{HH}} = 8.4$ Hz, Ph m-H) 7.11 (vt, 1H, $^3J_{\text{HH}} = 7.5$ Hz, Ph p-H) 6.83 (s, 1H, CPh=CH) 4.73 (br s, 1H, HNC(Me)=) 4.45 (s, 1H, NC=CH $_a\text{H}_b$) 4.28 (s, 1H, NC=CH $_a\text{H}_b$) 2.11 (s, 3H, HNC(Me)=) 1.73 (s, 15H, C_5Me_5)	191.8 (CPh=CH) 171.1 (NHC(Me)=) 156.1 (NC=CH $_2$) 150.9 (Ph i-C) 138.8 (d, $^1J_{\text{CH}} = 127.7$ Hz, CPh=CH) 127.7 (Ph) 125.4 (Ph) 111.8 (C_5Me_5) 90.6 (NC=CH $_2$, $^1J_{\text{CH}} =$ Hz) 22.8 (HNC(Me)=) 9.9 (C_5Me_5)
3-d₆	7.43 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, Ph o-H) 7.26 (vt, 2H, $^3J_{\text{HH}} = 8.4$ Hz, Ph m-H) 7.11 (vt, 1H, $^3J_{\text{HH}} = 7.5$ Hz, Ph p-H) 6.83 (s, 1H, CPh=CH) 2.11 (s, 3H, HNC(Me)=) 1.73 (s, 15H, C_5Me_5)	^b
4	8.69 (br s, 1H, NH) 7.55 (d, 2H, $^3J_{\text{HH}} = 6.9$ Hz, Ph o-H) 7.27 (vt, 2H, $^3J_{\text{HH}} = 7.2$ Hz, Ph m-H) 7.18 (vt, 1H, $^3J_{\text{HH}} = 6.9$ Hz, Ph p-H) 7.06 (d, 1H, $^4J_{\text{HH}} = 3.5$ Hz, CPh=CH) 2.25 (s, 3H, HN=CMe) 1.67 (s, 15H, C_5Me_5) 1.20 (br s, 1H, OH)	229.5 (s, CPh=CH) 182.6 (s, HN=CMe) 150.9 (s, Ph i-C) 135.2 (d, $^1J_{\text{CH}} = 155.8$ Hz, CPh=CH)) 127.8 (d, $^1J_{\text{CH}} = 156.7$ Hz, Ph) 127.7 (d, $^1J_{\text{CH}} = 156.7$ Hz, Ph) 127.3 (d, $^1J_{\text{CH}} = 158.8$ Hz, Ph) 112.0 (C_5Me_5) 23.6 (q, $^1J_{\text{CH}} = 132.0$ Hz, HN=C(Me)) 9.7 (q, $^1J_{\text{CH}} = 127.4$ Hz, C_5Me_5)

^a Sample spectra recorded in CDCl_3 unless otherwise noted. ^b Spectrum not recorded.

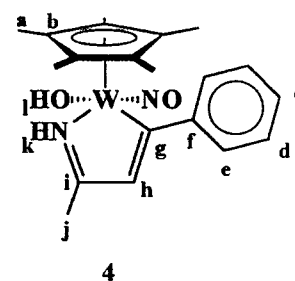
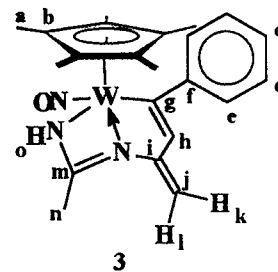
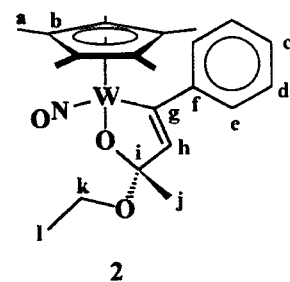
Table S3 continued:

compd no.	^1H NMR ^a δ / ppm	^{13}C NMR ^a δ / ppm
4-d₂	7.55 (d, 2H, $^3J_{\text{HH}} = 6.9$ Hz, Ph o-H) 7.27 (vt, 2H, $^3J_{\text{HH}} = 7.2$ Hz, Ph m-H) 7.18 (vt, 1H, $^3J_{\text{HH}} = 6.9$ Hz, Ph p-H) 7.06 (d, 1H, $^4J_{\text{HH}} = 3.5$ Hz, CPh=CH) 2.25 (s, 3H, NH=CMe) 1.67 (s, 15H, C ₅ Me ₅)	^b

^a Sample spectra recorded in CDCl₃ unless otherwise noted. ^b Spectrum not recorded.

Table S4. NOEDIFF Spectral Data for Compounds 2-4.

compound no.	Irradiation / δ	Enhancement / δ
2	7.18 (H_h)	2.32 (H_j), 1.59 (H_a), 7.50 (H_e)
	4.43 (H_k)	2.32 (H_j), 1.14 (H_l)
	2.32 (H_j)	1.59 (H_a), 7.18 (H_h)
	1.14 (H_l)	2.32 (H_j), 4.43 (H_k)
3	6.83 (H_h)	7.43 (H_e), 4.45 (H_k)
	4.73 (H_o)	2.11 (H_n)
	4.45 (H_k)	6.83 (H_h), 4.28 (H_l)
	4.28 (H_l)	4.45 (H_k), 2.11 (H_n)
4	2.11 (H_n)	4.73 (H_o), 4.28 (H_l)
	8.69 (H_k)	2.25 (H_j)
	7.06 (H_h)	7.55 (H_e), 2.25 (H_j)
	2.25 (H_j)	8.69 (H_k), 7.06 (H_h)

**Table S5** ^1H - ^{13}C HMQC Spectral Data for Compound 3.

^1H / δ	couples to	^{13}C / δ
1.73 (H_a)		9.9 (C_a)
2.11 (H_n)		22.8 (C_n)
4.45 (H_k), 4.28 (H_l)		90.6 (C_j)
6.83 (H_h)		191.8 (C_h)
7.43 (H_e), 7.26 (H_d)		127.7 (C_e , C_d)
7.11 (H_c)		150.9 (C_c)

Table S6. ^1H - ^{13}C HMBC Spectral Data for Complex **3**.

$^1\text{H} / \delta$	couples to	$^{13}\text{C} / \delta$
7.43 (H_e)		191.8 (C_g)
7.26 (H_d)		150.9 (C_f)
6.83 (H_h)		191.8 (C_g), 156.1 (C_i), 150.9 (C_f)
4.45 (H_k)		138.8 (C_j)
4.28 (H_l)		156.1 (C_i), 138.8 (C_j)
2.11 (H_n)		171.1 (C_m) ^a

^a Coupling between H_o and C_m through N was not observed.

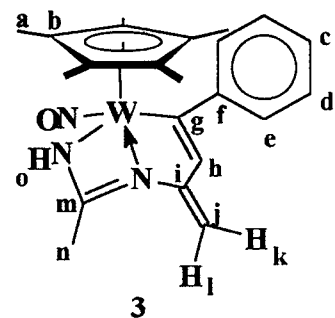


Table S7 X-ray Crystallographic Data for Complex 4

Crystal Data	
Empirical formula	C ₂₂ H ₂₉ N ₃ O ₂ W
Crystal Habit, color	Prism, Orange
Crystal size	0.50 x 0.18 x 0.18 mm
Crystal system	Monoclinic
Space group	P2 ₁ /n
Volume	2159.21(9) Å ³
a	8.4729(2)
b	21.2313(5)
c	12.1060(3)
β	97.483(1)
z	4
Formula weight	551.33
Density (calculated)	1.696 Mg/m ³
Absorption coefficient	5.371 mm ⁻¹
F(000)	1088
Data Collection	
Diffractometer	Siemens SMART Platform CCD
Wavelength	0.71073 Å
Temperature	173(2) K
θ range for data collection	1.92 to 25.03°
Index ranges	-10<h<9, -25<k<25, -14<l<10
Reflections collected	11123
Independent reflections	3800 (R _{int} = 0.0378)
Solution and Refinement	
System used	SHELXTL-V5.0
Solution	Direct methods
Refinement method	Full-matrix least-squares on F ²
Weighting scheme	w = [2(Fo ²)+(AP) ² +(BP)] ⁻¹ , where P = (Fo ² +2F _c ²)/3, A = 0.0139, and B = 3.9846
Absorption correction	Semi-empirical
Max. and min. transmission	0.66286 and 0.39415
Data / restraints / parame	3800 / 0 / 288
Final R indices [I>2σ(I)]	R ₁ = 0.0223, wR ₂ = 0.0489
R indices (all data)	R ₁ = 0.0271, wR ₂ = 0.0512
Goodness-of-fit on F ²	1.125
Largest diff. peak and hole	0.576 and -0.730 eÅ ⁻¹

Table S8. Fractional Atomic Coordinates and Anisotropic Thermal Parameters for Complex 4

atom	x	y	z	U(eq)	SOF
W (1)	7071 (1)	960 (1)	8942 (1)	17(1)	1
N (1)	5463 (4)	942 (1)	10177 (3)	22(1)	1
C (1)	5211 (4)	1443 (2)	10738 (3)	24(1)	1
C (2)	3908 (5)	1489 (2)	11466 (4)	32(1)	1
C (3)	6258 (4)	1960 (2)	10602 (3)	25(1)	1
C (4)	7271 (4)	1883 (2)	9822 (3)	21(1)	1
C (5)	8387 (5)	2412 (2)	9685 (3)	23(1)	1
C (6)	9946 (5)	2312 (2)	9460 (3)	26(1)	1
C (7)	10986 (5)	2816 (2)	9401 (3)	33(1)	1
C (8)	0494 (5)	3435 (2)	9557 (3)	34(1)	1
C (9)	8951 (5)	3537 (2)	9753 (3)	33(1)	1
C (10)	7914 (5)	3039 (2)	9823 (3)	28(1)	1
O (1)	6739 (3)	15 (1)	9237 (2)	24(1)	1
N (2)	9149 (4)	852 (1)	9318 (3)	22(1)	1
O (2)	10600 (3)	753 (1)	9458 (3)	35(1)	1
C (11)	4765 (4)	1265 (2)	7623 (3)	27(1)	1
C (12)	5265 (5)	668 (2)	7317 (3)	30(1)	1
C (13)	6856 (5)	721 (2)	7056 (3)	26(1)	1
C (14)	7316 (4)	1367 (2)	7169 (3)	20(1)	1
C (15)	6014 (4)	1704 (2)	7518 (3)	20(1)	1
C (16)	3165 (5)	1447 (3)	7932 (4)	48(1)	1
C (17)	4284 (7)	74 (2)	7242 (5)	54(2)	1
C (18)	7812 (7)	204 (2)	6601 (4)	49(1)	1
C (19)	8830 (5)	1641 (2)	6851 (3)	32(1)	1
N (101)	9330 (6)	1036 (3)	4090 (4)	70(2)	1
C (101)	9349 (6)	967 (2)	3167 (4)	41(1)	1
C (102)	9389 (7)	878 (3)	1980 (4)	54(1)	1

References and Notes

- (1) Legzdins, P.; Rettig, S. J.; Ross, K. J.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 5579.
- (2) Debad, J. D.; Legzdins, P.; Lumb, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 3288.