A Beneficial Kinetic Effect of a η^5-C_5Me_4H Ligand

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Supporting Information

Experimental Procedures

General Methods. All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous and anaerobic conditions either under high vacuum or an inert atmosphere of prepurified dinitrogen. Purification of inert gases was achieved by passing them first through a column containing MnO and then a column of activated 4 Å molecular sieves. Conventional glove box and Schlenk techniques were utilized throughout. The gloveboxes utilized were Innovative Technologies LabMaster 100 and MS-130 BG dual-station models equipped with freezers maintained at –30 ^{o}C. All glassware was heated in an oven to 275 ^{o}C to remove any moisture and then cooled to room temperature under vacuum. Small-scale reactions and NMR spectroscopic analyses were conducted in J. Young NMR tubes equipped with Kontes greaseless stopcocks. Pentane, diethyl ether (Et_2O), benzene, and benzene-d_6 were dried over sodium/benzophenone ketyl and freshly distilled prior to use. Complexes **1*** and **1'** were prepared according to the published procedures.[1] All other chemicals were ordered from commercial suppliers and used as received.

Unless otherwise specified, all IR samples were prepared as Nujol mulls sandwiched between NaCl plates, and their spectra were recorded on a Thermo Nicolet Model 4700 FT-IR spectrometer. NMR spectra were recorded at room temperature on Bruker AV-300 or AV-400 instruments, and all chemical shifts and coupling constants are reported in ppm and in Hz, respectively. ^{1}H NMR spectra were referenced to the residual protio isotopomer present in C_6D_6 (7.16 ppm). ^{13}C NMR spectra were referenced to C_6D_6 (128.4 ppm). When necessary, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and ^{13}C APT experiments were carried out to correlate and assign ^{1}H and ^{13}C NMR signals. Low-resolution mass spectra (EI, 70 eV) were recorded by the

staff of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer. Elemental analyses were performed by Mr. David Wong of the UBC microanalytical facility.

Preparation of Cp'W(NO)(C_6H_5)(η^3-MeCHCHCH$_2$) (2a' and **2b').** In a glove box a 4 dram vial was charged with a sample of **1'** (46 mg, 0.099 mmol) that was dissolved in freshly distilled benzene (5 mL). The reaction mixture was allowed to sit undisturbed at room temperature for a period of 48 h, during which time the initially orange solution had turned dark brown. The solvent was then removed from the final reaction mixture in vacuo, the resulting oily brown residue was redissolved in a minimum of 3:1 pentane/Et_2O, and the solution was chromatographed on an alumina column (1 x 4 cm) using a 2:1 mixture of pentane/Et_2O as the eluant. The yellow band that developed was eluted and collected, and the solvent was removed from the eluate in vacuo to obtain a yellow oil. Crystals containing both **2a'** and **2b'** (24 mg, 51% yield) were grown by dissolving the yellow oil in a minimal amount of pentane and storing the solution at –30 °C.

IR (C_6D_6) (cm^{-1}) 1590 (s, ν_{NO}). MS (LREI, probe temp 100 °C) *m/z* 467 [M^+]. Anal. Calcd for $C_{19}H_{25}NOW$: C 48.84, H 5.39, N 3.00. Found: C 48.53, H 5.36, N 2.98.

NMR data for **2a′**: ^{1}H NMR (300 MHz, C_6D_6) Selected signals: 1.88 (d, $^3J_{HH}$ = 5.5, 3H, allyl *Me*), 3.50 (d, $^3J_{HH}$ = 7.0 1H, allyl C*H*$_2$), 4.85 (s, 1H, Cp′*H*), 5.06 (m, 1H, allyl C*H*). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 10.6, 9.7, 9.4, 9.2 (C_5*Me*$_4$H), 16.9 (allyl *Me*), 56.1 (allyl *C*HMe), 73.5 (allyl *C*H$_2$), 114.1 (allyl *C*H), 123.6 (aryl *C*), 127.3 (aryl *C*), 143.7 (aryl *C*), 155.2 (ipso *C*).

NMR data for **2b′**: ^{1}H NMR (400 MHz, C_6D_6) δ 0.53 (d, 1H, allyl C*H*$_2$), 1.02 (d, $^3J_{HH}$ = 5.5, 3H, allyl *Me*),1.66 (m, 1H, allyl C*H*Me), 3.26 (d, $^3J_{HH}$ = 7.0, 1H, allyl C*H*$_2$), 4.65 (s, 1H, Cp′*H*), 5.06 (m, 1H, allyl C*H*). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 11.7, 11.2, 11.1, 10.9 (C_5*Me*$_4$H), 17.3 (allyl *Me*), 42.1 (allyl *C*H$_2$), 93.4 (allyl *C*HMe), 111.6 (allyl *C*H), 123.2 (aryl *C*), 128.4 (aryl *C*), 142.7 (aryl *C*), 161.8 (ipso *C*).

Preparation of Cp*W(NO)(C_6H_5)(η^3-$CH_2CHCHMe$) (2a* and **2b*).** Complex **1*** (88 mg, 0.185 mmol) was transferred into a 4 dram vial and then dissolved in C_6H_6 (ca. 2 mL) to obtain an orange solution. The reaction mixture was left at room temperature for 24 h during which time it became brown. The solvent was removed in vacuo, the resulting oil was dissolved in pentane, and the solution was transferred to the top of an alumina column (0.5 x 5 cm). A yellow band was eluted from the column with a 3:1 mixture of pentane/Et_2O to obtain a dark yellow eluate. Removal of solvent from the eluate under reduced pressure afforded a yellow solid (69 mg, 77 % yield). A ^{1}H NMR spectrum of the solid revealed the presence of compounds **2a***, **2b***, **3***, and **4***. Slow recrystallization of the solid from pentane at -30 °C afforded large orange crystals consisting of only compound **2a***.

Characterization data for **2a***: IR (cm^{-1}) 1604 (s, ν_{NO}). MS (LREI, *m/z*, probe temperature 150 °C) 481 [M^+, ^{184}W] ^{1}H NMR (400 MHz, C_6D_6) δ 1.24 (m, 1H, allyl C*H*Me), 1.45 (s, 15H, C_5Me_5), 1.88 (d, $^3J_{HH}$ = 5.9, 3H, allyl *Me*), 2.01 (d, $^3J_{HH}$ = 13.7, 1H, allyl CH_2), 3.58 (d, $^3J_{HH}$ = 7.4, 1H, allyl CH_2), 5.08 (ddd , $^3J_{HH}$ = 13.7, 9.8, 7.4, 1H, allyl C*H*), 7.11 (m, 2H, aryl *H*), 7.21 (m, 2H, aryl *H*), 7.74 (m, 1H, aryl *H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 10.3 (C_5Me_5), 17.3 (allyl *Me*), 57.7 (allyl *C*HMe), 75.6 (allyl *C*H_2), 107.9 (C_5Me_5), 115.3 (allyl *C*H), 124.3 (aryl *C*), 127.6 (aryl *C*), 144.2 (aryl *C*), 158.1 (ipso *C*). Anal. Calcd for $C_{20}H_{27}NOW$: C, 49.91; H, 5.65; N, 2.91. Found: C, 49.16; H, 5.60, N, 2.90.

NMR data for **2b***: ^{1}H NMR (400 MHz, C_6D_6) δ 0.53 (d, $^3J_{HH}$ = 9.4, 1H, allyl CH_2), 1.12 (d, $^3J_{HH}$ = 6.3, 3H, allyl *Me*),1.66 (m, 1H, allyl C*H*Me), 1.43 (s, 15H, C_5Me_5), 2.38 (d, $^3J_{HH}$ = 6.7, 1H, allyl CH_2), 5.17 (ddd, $^3J_{HH}$ = 13.3, 9.4, 6.7, 1H, allyl C*H*), 7.09 (m, 2H, aryl *H*), 7.23 (m, 2H, aryl *H*), 7.73 (m, 1H, aryl *H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 10.6 (C_5Me_5), 18.0 (allyl

Me), 44.2 (allyl *C*H_2), 93.9 (allyl *C*HMe), 107.8 (*C*$_5$Me$_5$), 113.2 (allyl *C*H), 126.1 (aryl *C*), 129.6 (aryl *C*), 143.6 (aryl *C*), 164.8 (ipso *C*).

Spectroscopic Detection of Cp'W(NO)(H)(η^3-CH(Me)CHCHPh) (3') and Cp'W(NO)(H)(η^3-CH$_2$CHC(Me)Ph) (4'). Complexes **3'** and **4'** were generated in situ by the thermolysis of **1'** (46 mg, 0.099 mmol) in C_6D_6 at 35 °C for 36 h in a J. Young NMR tube equipped with a Kontes stopcock. The ^{1}H NMR spectrum of the final mixture exhibited signals due to hydride ligands at δ -0.56 ($^1J_{WH}$ = 124 Hz) and 0.02 ($^1J_{WH}$ = 127 Hz) that can be assigned to **3'** and **4'**, respectively, by analogy to **3*** and **4*** (vide infra).

Preparation of Cp*W(NO)(H)(η^3-CH(Me)CHCHPh) (3*) and Cp*W(NO)(H)(η^3-CH$_2$CHC(Me)Ph) (4*). Complexes **3*** and **4*** were prepared by the thermolysis of **1*** (121 mg, 0.255 mmol) in C_6H_6 (4 mL) at 45 °C for 24 h. The solvent was removed from the final reaction mixture in vacuo to obtain an oily residue that was transferred to the top of an alumina column (0.5 x 6 cm) made up in pentane. A dark yellow band was eluted from the column with a 5:1 mixture of pentane/Et_2O to obtain a yellow eluate. The solvents were removed from the eluate under vacuum, the resulting residue was dissolved in a minimal amount of pentane, and the solution was maintained at -30 °C for 2 h to induce the deposition of a yellow solid that contained **3*** and **4*** in a 1:3 ratio (80 mg, 65 % yield). Yellow hedgehog crystals of **4*** were obtained by recrystallization of this solid from pentane at -30 °C over 3 d.

Characterization data for **4***: IR (cm^{-1}) 1588 (s, ν_{NO}). MS (LREI, *m/z*, probe temperature 150 °C) 481 [M$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6) δ -0.05 (s, $^1J_{WH}$ = 127, 1H, W*H*), 1.59 (s, 15H, C$_5$*M*e$_5$), 2.17 (s, 3H, allyl *Me*), 2.50 (d, $^3J_{HH}$ = 7.8, 1H, allyl C*H*$_2$), 2.82 (d, $^3J_{HH}$ = 13.3, 1H, allyl C*H*$_2$), 3.50 (dd, $^3J_{HH}$ = 13.3, 7.8, 1H, allyl C*H*), 7.01 (m, 2H, aryl *H*), 7.12 (m, 2H, aryl *H*),

7.49 (m, 1H, aryl *H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 10.7 ($C_5\mathit{Me}_5$), 24.4 (allyl *Me*), 42.7 (allyl $\mathit{C}H_2$), 94.7 (allyl *C*H), 98.2 (allyl *C*),104.6 (C_5Me_5), 126.7 (aryl *C*), 128.7 (aryl *C*), 129.0 (aryl *C*), 146.9 (ipso *C*). Anal. Calcd for $C_{20}H_{27}NOW$: C, 49.91; H, 5.65; N, 2.91. Found: C, 49.05; H, 5.54; N, 2.94.

Selected signals due to **3***: ^{1}H NMR (400 MHz, C_6D_6) δ -0.63 (s, $^{1}J_{WH}$ = 124, 1H, W*H*), 1.69 (s, 15H, $C_5\mathit{Me}_5$), 5.22 (dd, $^{3}J_{HH}$ = 12.9, 9.4, 1H, allyl C*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 10.9 ($C_5\mathit{Me}_5$), 105.1 (C_5Me_5), 106.1 (allyl *C*H).

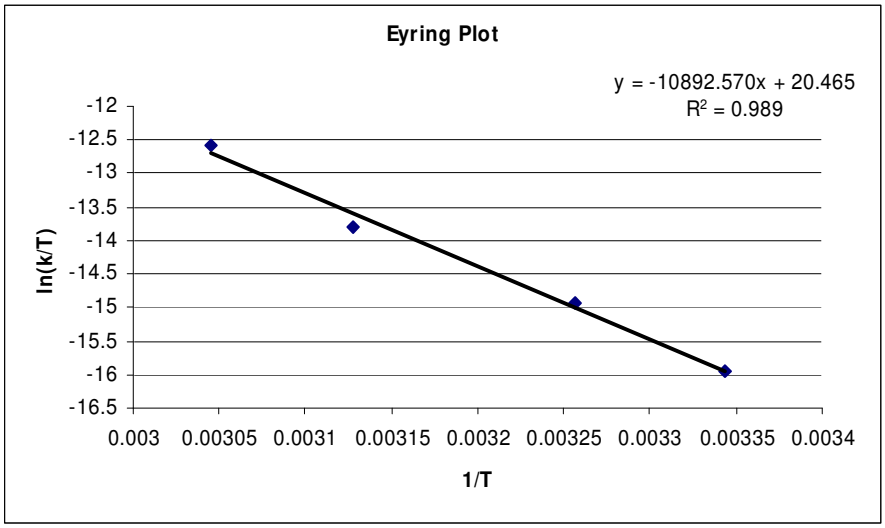
Monitoring the conversions of 1 to 2a and 2b. In a glove box, complex **1** [either **1'** (40 mg, 0.087 mmol) or **1*** (50 mg, 0.105 mmol)] was dissolved in C_6D_6 (0.8 mL) to obtain a yellow-orange solution that was then transferred into a J. Young NMR tube equipped with a Kontes greaseless stopcock. The ^{1}H NMR spectrum of the solution was recorded periodically, and the area under the doublet at δ 3.61 (d, 1H, allyl CH_2) for **1'** and the meso peak at δ 4.97 (ddd, 1H, allyl CH) of **1*** was integrated against the signal at 7.16 ppm corresponding to the residual protio isotopomer present in C_6D_6 which was referenced to 10. These NMR monitoring experiments were performed at approximately 10-degree intervals ranging from 25 °C to 55 °C for each complex and were continued over a period of 24 h at each temperature in order to determine the rate constant, k, at that temperature.

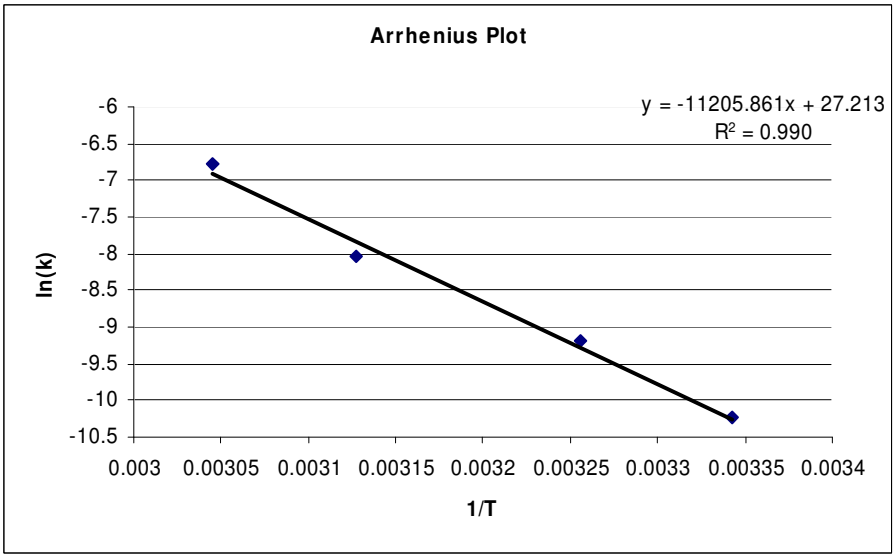
Kinetics Data for Complex 1'

T (K)	1/T (K^{-1})	k (s^{-1})	ln(k/T)	ln(k)
299.1	0.003343	3.566E-05	-15.94236	-10.24148
307.1	0.003256	1.010E-04	-14.92766	-9.20039
319.8	0.003127	3.210E-04	-13.81161	-8.04407
328.4	0.003045	1.142E-03	-12.56947	-6.77515

Activation Parameters

$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	E_a
90.6 ± 6.6 kJ/mol	-27.4 ± 3.4 J/((K)(mol))	93.2 ± 6.6 kJ/mol



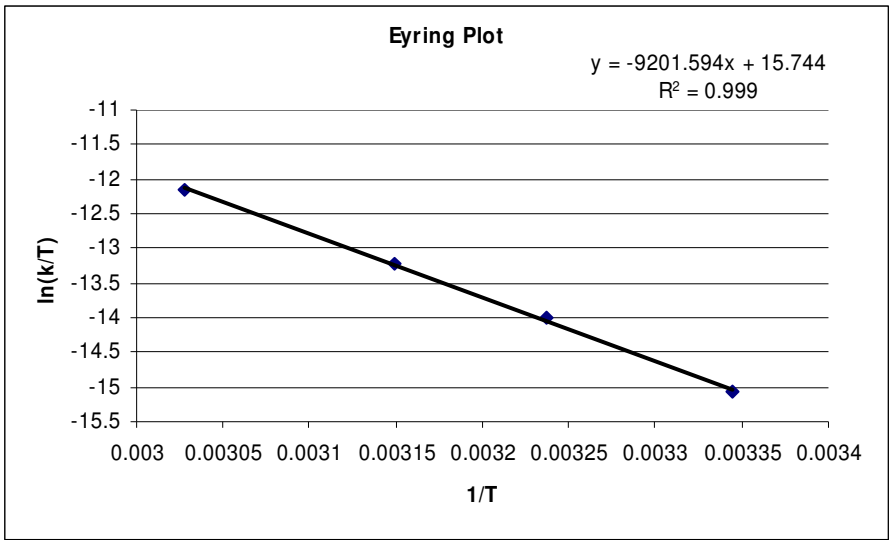


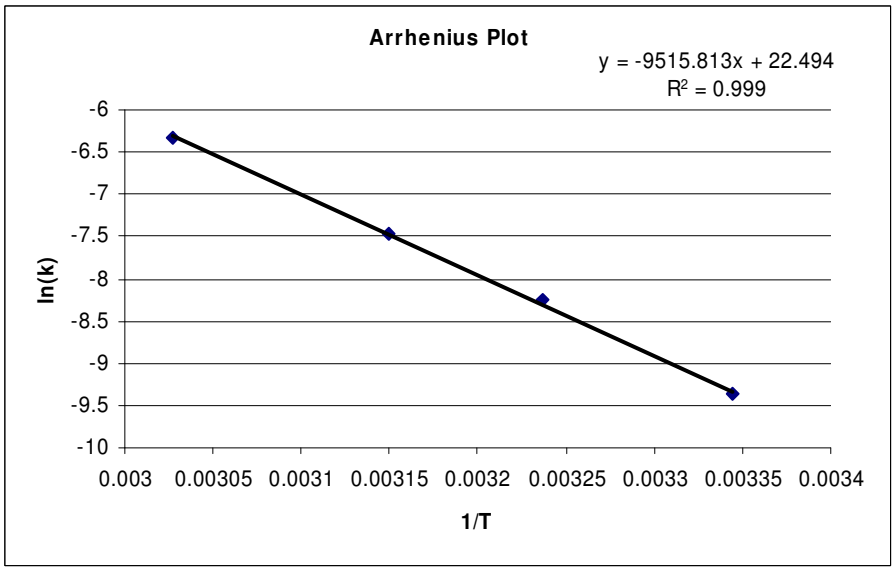
Kinetics Data for Complex 1*

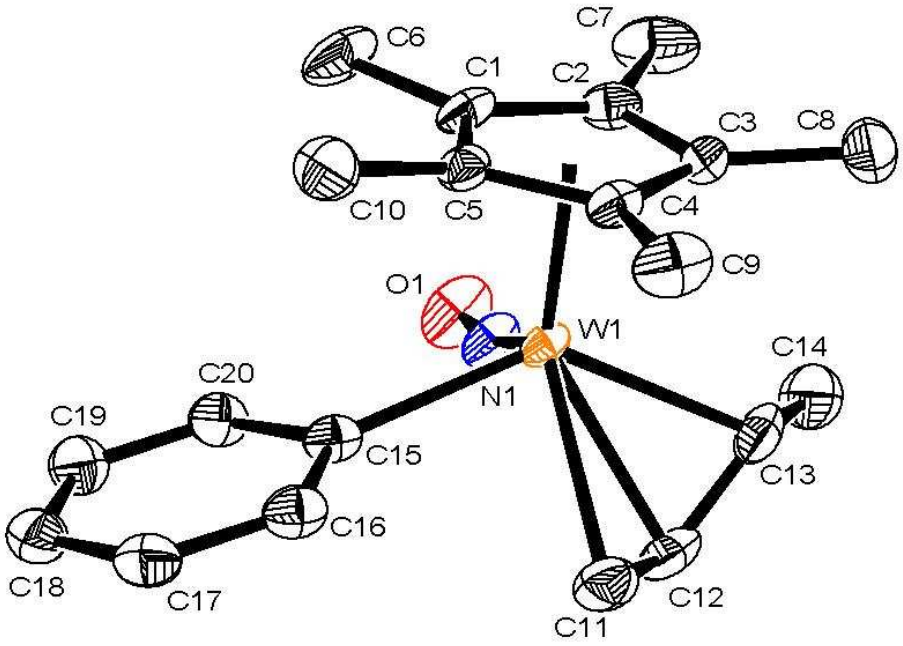
T (K)	1/T (K^{-1})	k (s^{-1})	ln(k/T)	ln(k)
299.0	0.003344	8.51E-05	-15.07213	-9.371684
308.9	0.003237	0.000259	-13.99170	-8.258682
317.5	0.00315	0.000575	-13.22162	-7.461141
330.3	0.003028	0.00176	-12.14244	-6.342441

Activation Parameters

$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	E_a
76.5 ± 1.9 kJ/mol	-66.6 ± 3.0 J/((K)(mol))	79.1 ± 1.9 kJ/mol







Solid-state molecular structure of 2a* with 50% probability thermal ellipsoids shown.

Selected interatomic distances (Å) and angles (deg): W(1)-C(11) = 2.378(5), W(1)-C(12) = 2.339(5), W(1)-C(13) = 2.277(5), W(1)-C(15) = 2.216(5), W(1)-N(1) = 1.779(4), N(1)-O(1) = 1.220(5), C(11)-C(12) = 1.380(9), C(12)-C(13) = 1.424(9), C(13)-C(14) = 1.476(9), C(11)-C(12)-C(13) = 118.7(5), W(1)-N(1)-O(1) = 167.8(4).

X-ray Crystallography. Data collection for each compound was carried out at –170 ± 2 °C on a Bruker X8 or DUO APEX diffractometer, using graphite-monochromated Mo Kα radiation.

Data for **2a′** and **2b′** were collected to a maximum 2θ value of 58.4° in 0.5° oscillations. The structure was solved by direct methods[2] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 9277 observed reflections and 407 variable parameters.

Data for **2a*** were collected to a maximum 2θ value of 63.3° in 0.5° oscillations. The structure was solved by direct methods[2] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 5994 observed reflections and 214 variable parameters.

Data for **4*** were collected to a maximum 2θ value of 66.4° in 0.5° oscillations. The structure was solved by direct methods[2] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically; hydrogen atom H1 was refined isotropically, and all other hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 6792 observed reflections and 218 variable parameters.

All calculations were performed using SIR-92,[2] SHELXL-97,[3] and the WinGX package.[4] For each structure neutral-atom scattering factors were taken from Cromer and Waber.[5] Anomalous dispersion effects were included in F_{calc};[6] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[7] The values for mass attenuation coefficients are those of Creagh and Hubbell.[8] X-ray crystallographic data for the structures are presented in Table 1.

Table 1. X-Ray Crystallographic Data for Complexes **2a′** and **2b′**, **2a***, and **4***.

	2a′ and **2b′**	**2a***	**4***
	Crystal Data		
Empirical formula	$C_{19}H_{25}NOW$	$C_{20}H_{27}NOW$	$C_{20}H_{27}NOW$
Crystal Habit, color	Needle, yellow	Plate, orange	Plate, yellow
Crystal size (mm)	0.05 × 0.20 × 0.70	0.10 × 0.20 × 0.30	0.15 × 0.20 × 0.52
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	Pbca	P–1	Pbca
Volume ($Å^3$)	6961.9(6)	909.55(17)	3663.9(4)
a (Å)	14.2940(8)	8.4341(9)	9.3285(6)
b (Å)	13.8238(7)	8.4965(9)	15.5488(9)
c (Å)	35.2329(17)	14.4435(15)	25.2601(16)
α (°)	90	85.138(5)	90
β (°)	90	88.498(5)	90
γ (°)	90	61.891(4)	90
Z	16	2	8
Density (calculated) (Mg/m^3)	1.783	1.757	1.745
Absorption coefficient (mm^{-1})	6.639	6.355	6.310
F_{000}	3648	472	1888
	Data Collection and Refinement		
Measured Reflections: Total	39364	21333	27804
Measured Reflections: Unique	9277	5994	6792

Final R Indices[a]	R1 = 0.0253, wR2 = 0.0499	R1 = 0.0377, wR2 = 0.0872	R1 = 0.0270, wR2 = 0.0589
Goodness-of-fit on F^2 [b]	1.287	1.226	1.010
Largest diff. peak and hole ($e^- Å^{-3}$)	1.575 and –1.609	9.664 and –5.073	2.985 and –1.893

[a] R1 on $F = \Sigma \mid (|F_o| - |F_c|) \mid / \Sigma |F_o|$ ($I_o > 2\sigma I_o$); wR2 = $[(\Sigma (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$ (all data); $w = [\sigma^2 F_o^2]^{-1}$; [b] GOF = $[\Sigma (w (|F_o| - |F_c|)^2) /$ degrees of freedom $]^{1/2}$.

References

(1) Tsang, J. Y. K.; Buschhaus, M. S. A.; Graham, P. M.; Semiao, C. J.; Semproni, S. P.; Kim, S. J.; Legzdins, P. *J. Am. Chem. Soc.* **2008**, *130*, 3652.

(2) SIR-92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr*. **1993**, *26*, 343.

(3) SHELXL-97: Sheldrick, G.M. *Acta Cryst*. **2008**, *A64*, 112.

(4) WinGX-V1.70: Farrugia, L. J., *J. Appl. Crystallogr*., **1999**, *32*, 837.

(5) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

(6) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(7) Creagh, D. C.; McAuley, W. J. *International Tables of X-ray Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C.

(8) Creagh, D. C.; Hubbell, J. H. *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C.