that $Cp(NO)(CO)Mn\text{–}C\{O\}Ph$ does not insert CO to form a glyoxyl ligand even when maintained under 150 atm of CO.[13] We also observed that complex **3** did not insert CO to form a glyoxyl ligand when subjected to 1000 psi CO nor when the synthesis of **3** (eq 1) was conducted under 3 atm of CO. The synthesis of **4** could be envisaged to occur via NO_2^--induced oxidation of **2** to form NO^+ and $[Cp(CO)_2Mn\text{–}C\{O\}R]^-$ (**7**), followed by CO insertion and addition of NO^+ to **7**. However, this is not the case since **4** was not produced when authentic **7**[14] was allowed to react with $[NO]BF_4$.

This study has shown that the carbyne ligands in **1** and **2** are readily oxidized to form acyl ligands and also describes the first synthesis of a glyoxyl ligand from the assembly of other coordinated ligands, although we do not believe that this occurs via insertion of CO into a metal-acyl bond. The generality of this reaction is currently under exploration.

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Supplementary Material Available: Tables of crystallographic and atomic positional parameters for **4a** (3 pages). Ordering information is given on any current masthead page.

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Heteropoly "Browns" as Class I Mixed Valence (W(IV,VI)) Complexes. Tungsten-183 NMR of W(IV) Trimers

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Reduction of many heteropoly tungstates yields dark blue mixed-valence species ("heteropoly blues") in which electrons undergo "hopping" delocalization at a rate that is rapid on the ESR and NMR time scales.[1] More highly reduced polyanions, especially under acidic conditions, are transformed to brown species that are less sensitive to oxidation than the blues and which display quite different electrochemistry. Launay[2] has suggested that the brown complexes contain tungsten(IV) atoms in trigonal metal–metal bonded W_3O_{13} groups. This suggestion is supported, but not unequivocally, by X-ray photoelectron spectroscopy[3] of 6-, 12- and 24-electron reduced metatungstate anion, $[(H_2)W_{12}O_{40}]^{6-}$, and by a disordered crystal structure[4] of the 6-electron reduced salt $Rb_4H_8[(H_2)W_{12}O_{40}]_{aq}$.

In the course of our investigations of the aqueous and nonaqueous redox chemistry of highly reduced heteropolyanions, we have examined solutions of the 6-electron reduced "browns" of the three Keggin anions α-$SiW_{12}O_{40}^{4-}$, α-$BW_{12}O_{40}^{5-}$, and α-$(H_2)W_{12}O_{40}^{6-}$ by ^{183}W NMR spectroscopy.[5] The spectra not only confirm Launay's proposal concerning stoichiometry but also demonstrate other electronic and molecular structural features that distinguish the "browns" from the "blues".

Each spectrum consists of just three narrow lines (Figure 1, Table I) of intensity 1:1:2. Two of these (3 W, 6 W) have chemical shifts very close to that of the oxidized anion while the third (3 W) is deshielded by about 1500 ppm and is attributed to the W(IV) atoms. This assignment is supported by our measurement of the chemical shift of the W(IV) cation $W_3O_4(H_2O)_9^{4+}$ (also shown in Table I).[8,9] A three-line spectrum for the heteropoly anions requires that the reduced anions have C_3 or C_{3V} symmetry and that the W(IV) atoms occupy either an edge-shared or corner-shared group of the Keggin skeleton. The magnitude of the tungsten–tungsten couplings[10] unambiguously excludes the second possibility; the low-field line shows $^2J_{W-W}$ of 14–15 Hz (corner-shared) whereas the other line of intensity corresponding to three tungstens has $J = 4\text{–}6$ Hz (edge-shared). The highst field line (6 W) has both couplings as expected. The shielding pattern of the two tungsten(VI) lines ($\delta(6\ W) < \delta(3\ W)$) is analogous to that observed for the W resonances of the 1,4,9 isomer of $PV_3W_9O_{40}^{6-}$[11] in which the three vanadiums also occupy an edge-shared triad of the Keggin structure. The reverse pattern ($\delta(6\ W) > \delta(3\ W)$) is observed for 1,2,3-$PV_3W_9O_{40}^{6-}$ and –$SiV_3W_9O_{40}^{7-}$[10] in which the vanadium atoms occupy a corner-shared triad.

We note not only that all the lines are much narrower than those recently reported by Kozik et al.[12] for heteropoly blues but also that the change in chemical shift of the unreduced tungsten atoms adjacent to the tungsten(IV) atoms is very small (−1 to −6 ppm, vs. −172 ppm for unreduced tungstens in $P_2W_{18}O_{62}^{8-}$). Both of these observations underline the difference in electronic structure of the diamagnetic "blues" and the "browns". In the former, pairs of electrons defining W(V) atoms are antiferromagnetically coupled and are delocalized on the NMR time scale (class II mixed-valence behavior). The electron motion and the local paramagnetism lead to greatly reduced relaxation times and increased line widths. In contrast the spectra reported here for the "browns" are consistent with complete localization of W(IV) and W(VI) valences (class I behavior). The spectra show a modest temperature dependence of +0.1 ppm/°C for the W(VI) and +0.5 ppm/°C for the W(IV).[13]

The 6-electron reduced anions have six additional protons and Launay has argued that these constitute terminal aquo ligands on the W(IV) atoms. The following results support this view. Three (and only three) of these protons may be neutralized[6,7,14] and titration of $SiW_{12}O_{40}H_6^{4-}$ to $SiW_{12}O_{40}H_3^{7-}$ (presumed conversion of $W\text{–}OH_2$ to $W\text{–}OH$) results in a change of chemical shift of +200 ppm for the W(IV) resonance while the W(VI) resonances are unaffected.

The metatungstate anion contains two nonlabile protons within the central tetrahedron.[15] During reduction in D_2O/DCl, partial

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[5] The reduced compounds were prepared as ca. 0.15 M solutions in 0.5 M DCl/D_2O by literature methods.[4,6,7] Spectra were recorded on a Bruker AM-300 WB spectrometer at 12.505 MHz using 20-mm tubes. The upfield and downfield regions were scanned separately (SW = 2000 Hz) to minimize acoustic ringing and to optimize resolution. About 30 000 scans were taken. Chemical shifts are given relative to saturated Na_2WO_4.

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[9] W(IV) complexes have chemical shifts in the range 1100–1600 ppm. We note that for all diamagnetic tungsten oxo complexes δ_W appears to be roughly diagnostic of oxidation state: tungstates(VI), +60 – −250 ppm; $W^{III}_2(O\text{-}t\text{-}Bu)_6$, +4408; $W^{II}_2(O_2CCF_3)_4$, +6760. (Minelli, M.; Enemark, J.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.)

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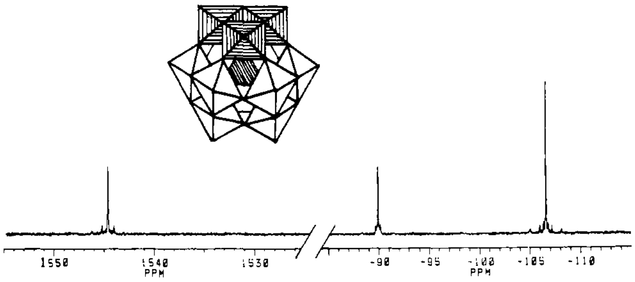

Figure 1. ^{183}W NMR spectrum, 12.505 MHz, of 0.15 M $H_4[SiW_{12}O_{40}H_6]$ in 0.5 M DCl. The W(IV) atoms occupy the crosshatched octahedra in the Keggin structure shown.

Table I. ^{183}W NMR Data for Oxidized and 6-Electron Reduced $[XW_{12}O_{40}]^{n-}$[a]

anion	chemical shift/ppm[b]	$^2J_{W-W}$/Hz[c]	line width/Hz[d]
$SiW_{12}O_{40}^{4-}$	−102.5		0.3
$SiW_{12}O_{40}H_6^{4-}$	+1544.6 (3 W)	15.1	1.2
	−89.9 (3 W)	6.4	0.9
	−106.6 (6 W)	6.4, 15.0	0.9
$BW_{12}O_{40}^{5-}$	−128.5		1.1
$BW_{12}O_{40}H_6^{5-}$	+1452.8 (3 W)	14.4	2.3
	−107.4 (3 W)	4.2	1.2
	−131.6 (6 W)	4.2, 14.4	1.0
$(H_2)W_{12}O_{40}^{6-}$	−109.5		2.3
$(H_2)W_{12}O_{40}H_6^{6-}$	+1355.4 (3 W)[e]	*f*	1.6
	−82.0 (3 W)	*f*	1.6
	−115.0 (6 W)	*f*, 14.6	2.9
$W_3O_4(H_2O)_9^{4+}$	+1138.4		3.0[g]

[a] In 0.5 M DCl. [b] ±0.1 ppm. [c] ±0.5 Hz. [d] ±0.1 Hz. [e] Resonances for HD and D_2 isotopomers are also observed; see text. [f] Coupling is not resolved. [g] In saturated *p*-toluenesulfonic acid.

exchange of H by D occurs and the resonances of the three isotopomers with internal H_2^{2+}, HD^{2+}, and D_2^{2+} are resolved at 1355.4, 1354.8, and 1354.3 ppm, respectively.[16] The corresponding effects of deuteration upon the two W(VI) resonances are not observed although these two lines are slightly broadened (Table I). These data, coupled with a much smaller isotope effect for the oxidized metatungstate anion,[17] suggest that the internal protons in the reduced anion are both covalently attached to $O(W^{IV})_3$, i.e., that this oxygen atom has become a water molecule.[18] Tourné, Tourné, and Weakley[19] have demonstrated isotope effects of a similar magnitude and direction for the resonances of a tungsten atom bound to an "internal" water molecule of $P_2W_{21}O_{71}(OH_2)_3^{6-}$.

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(16) Assignment of the three lines was confirmed by allowing the reduced solution to undergo (very slow) further exchange over a period of 2 months.

(17) Acerete et al. (Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384) tentatively proposed rapid, pH-dependent H–D exchange for $(H_2)W_{12}O_{40}^{6-}$ and concluded that $\Delta\delta_W$ for $(H_2)W_{12}O_{40}^{6-}$ and $(D_2)W_{12}O_{40}^{6-}$ was −7 ppm. It now appears that the original data reflect external protonation effects only (Acerete, private communication). We have synthesized $(D_2)W_{12}O_{40}^{6-}$. Spectra of mixtures of $(D_2)W_{12}O_{40}^{6-}$ and $(H_2)W_{12}O_{40}^{6-}$ show two lines separated by 0.1 ppm. The deuterio anion has the more highly shielded resonance.

(18) It is reasonable to expect that the oxygen bonded to the W(IV) triad would be the most basic of the interior oxygens. Chauveau et al. (Chauveau, F.; Doppelt, P.; Lefebvre, J. *Bull. Soc. Chim. Fr.* **1983**, 197) propose just the opposite, i.e., preferential protonation of W(VI) oxygens, based on ^{1}H and ^{19}F NMR of reduced fluorotungstates, $[H_2W_{12}F_nO_{40-n}]^{(6-n)}$ ($n = 1-3$). However, the data of Chauveau et al. are equally consistent with our suggestion.

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Stereocontrolled Total Synthesis of (±)-Cyanocycline A

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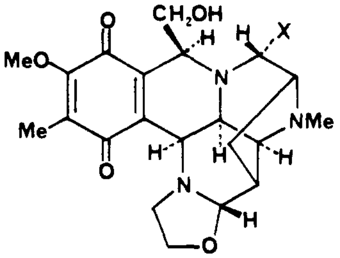
Cyanocycline A (**1**) was isolated from the fermentation broth of *Streptomyces flavogriseus* and has been shown to exhibit broad-spectrum antimicrobial and antitumor activities.[1] The structure of **1** was determined by an X-ray crystallographic analysis and was found to be identical with cyanonaphthyridinomycin,[2] which was derived from naphthyridinomycin[3] (**2**) by treatment with sodium cyanide. The challenging synthetic problems of **1** involve controlling stereochemistry of the eight chiral centers of the highly crowded hexacyclic system, in addition to the construction of such labile functional groups as quinone and oxazolidine. The first total synthesis of this formidable molecule has recently been achieved by Evans and his co-workers.[4] In this paper we describe a stereocontrolled total synthesis of cyanocycline A (**1**), which is the result of our intensive efforts directed toward syntheses of this class of quinone antitumor antibiotics.[5]



1: X = CN

2: X = OH

One of the key reactions of our synthesis is an addition of zinc dienolate derived from the dihydropyrrole **3**[6,7] to 5-(benzyloxy)-2,4-dimethoxy-3-methylbenzaldehyde (**4**)[5a] (THF, 0 °C, 30 min), which gave a diastereomeric mixture of the thermodynamically favorable γ-addition products **5** in 77% yield. Hydrogenolysis of benzyl ether (H_2 (1000 psi), 10% Pd/C, EtOH, room temperature, 96%) followed by hydrogenation of olefin (H_2 (1500 psi), 5% Rh/C, EtOAc, 80 °C, 100 min, 63%) gave the pyrrolidine **6**. Stereochemistry of the pyrrolidine ring **6** was completely controlled as evidenced by the formation of the keto ester **7** as the single isomer in a three-step sequence ((1) $PhCH_2Br$, K_2CO_3, acetone, reflux; (2) Jones oxidation, acetone, 0 °C; (3) MeI,

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(6) Prepared from *N*-*t*-Boc-dehydroalanine-*tert*-butyl ester (i) in a three-step sequence in 68% overall yield: (1) i, *tert*-butyl acetoacetate (1.5 equiv), NaOEt (0.2 equiv), EtOH, 60 °C; (2) p-TsOH (0.3 equiv), quinoline (0.6 equiv), toluene, Dean–Stark trap, reflux; (3) $LiBEt_3H$ (2.2 equiv), THF, −20 °C.

(7) Satisfactory spectroscopic data were obtained for each intermediate.

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