

23 °C),⁴ corresponding to $t_{1/2}(2) \approx 8$ min.

The foregoing results demonstrate the reaction cycle set out in the figure, whereby thiol acts as the electron donor in the reduction of sulfoxide. The system is catalytic, with ca. 4 turnovers in 108 h, but overall reaction 5 is slow by reason of the sluggish



rate of reduction of Mo(VI) by thiol. Other synthetic systems capable of the same reactions doubtless can be devised. Thus, MoO(S₂CNEt₂)₂ (3) has been isolated in good yield from the reaction of MoO₂(S₂CNEt₂)₂ (4) with PhSH,¹⁵ and 3 has been shown to reduce sulfoxides¹⁶⁻¹⁸ with formation of 4 and sulfides. The instability of 2 in the presence of excess thiol is obviated to an extent in a catalytic reaction system, where it is oxidized to 1 at the same rate at which it is formed. In the present system 1 is cleanly reduced at an appreciable rate only by arenethiols, whose relatively acidic character¹⁹ presumably promotes protonation of an oxo ligand.

The principal result forthcoming from the present work is that thiols are thermodynamically capable of reducing a Mo^{VI}O₂ species to a Mo^{IVO} state which executes reductase reactions on enzymic substrates. Electron transfer may occur via intervening redox centers (heme, Fe/S, flavin), including possibly the pterin component of the Mo cofactor.^{22,23} Inasmuch as all Mo^{IVO} complexes with a labile binding site yet tested are capable of reducing Me₂SO,⁵ it is apparent that catalysis depends critically on the potentials of the external electron donor and the Mo(VI) center. Elsewhere we have shown that coordinated thiolate sulfur (present in oxo-transferases²⁶) raises Mo(VI) reduction potentials,⁵ one apparent advantage of this effect being to render this state reducible in catalysis by physiological reagents. With the proviso that certain sulfoxide-reducing enzyme systems utilize other donors^{27,28} and that the only enzyme with a partially characterized catalytic site (liver aldehyde oxidase²⁷) known to reduce sulfoxides²⁹ may contain the Mo^{VI}OS group when oxidized, the present

results improve the viability of thiols and thioredoxin as endogenous electron donors in reductase reactions of Mo oxo-transferases.

Lastly, the ¹⁹F NMR method for following oxo transfer catalysis is particularly effective, and applications will be presented subsequently with high-turnover systems and other substrates. The present system is not intended to be catalytically useful. Rather, it is employed to demonstrate that electrons can be transferred from thiol to substrate via a currently credible representation of an oxo-transferase active site.

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Chemical Regulation of Distance: Characterization of the First Natural Host Germination Stimulant for *Striga asiatica*

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Striga asiatica, "witchweed", an obligate parasitic plant which attaches to the roots of corn, *Sorghum*, and other grasses, causes severe damage to crop yields around the world. The seeds of this parasite require a germination stimulus,¹ and once germinated *Striga* survives for less than 2 weeks in the absence of a host. In vitro, *Striga* seeds germinate only within a 0.75-cm zone of the roots of both corn and *Sorghum*² and produce roots that are no more than ~3 mm in length. Several years ago, the sesquiterpene strigol was isolated from cotton, a nonhost plant, and found to be a potent germination stimulus for *Striga*.³ However, a stable sesquiterpene which could accumulate in the soil may stimulate germination at too great a distance for host attachment.⁴ We describe here the identification of the first germination stimulant for *Striga* from the root exudate of a natural host and provide an explanation of how this compound would define the distance away from the host root at which *Striga* germination occurs.

Sorghum bicolor (L.) Moench cv. IS 8768 seeds (10 g) were grown aseptically on moist filter paper in the dark at 27 °C for 7 days. The roots were dipped in 0.5% HOAc/CH₂Cl₂ (100 mL) for 2 s,⁵ and the extract was evaporated in vacuo to give 15 mg of a biologically active crude exudate.⁶ The ¹H NMR spectrum

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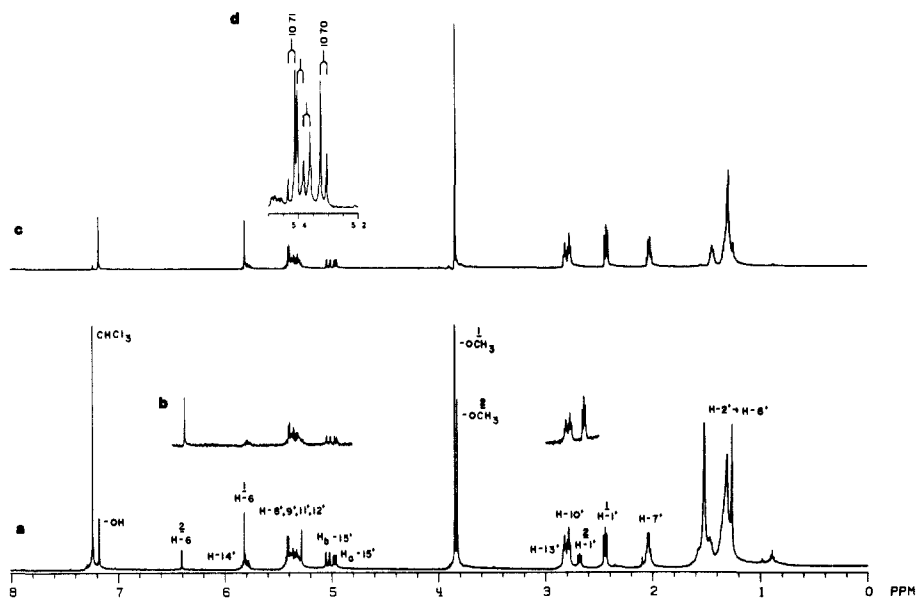


Figure 1. $^1\text{H-NMR}$ (500 MHz) spectra in 500 μL of CDCl_3 of (a) *Sorghum* crude exudate (1 mg), (b) hydroquinone **2** obtained by reducing **1** (1 mg) with zinc dust/HOAc, and (c) quinone **1** (4 mg), (d) triple-frequency irradiation of H-7', -10', and -13' simplified the vinylic region to two AB patterns with $J = 10.7$ Hz.

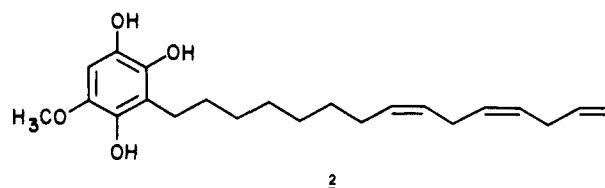
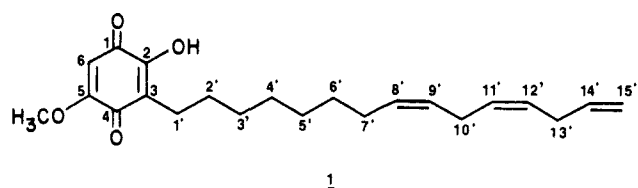
showed it to be remarkably clean (Figure 1a), and its HPLC trace (Zorbax ODS, 4.6-mm i.d. \times 25 cm, 88.0% MeOH/11.4% H_2O /0.6% HOAc, 1.5 mL/min, 280 nm) contained two major components (**1** and **2**) eluting at 6.9 and 7.6 min, respectively. When $>99\%$ pure, **1** did not induce germination of *Striga*. The biological activity of the exudate was related directly to the concentration of **2**. This compound was very unstable and on standing was rapidly converted to **1**. The germination stimulant was, therefore, isolated (9 mg) and characterized in its more stable form.

The UV spectrum (CH_2Cl_2) contained transitions at 283 (4.22), 288 (4.30), and 412 nm (2.68) suggesting a 2,5-hydroxylated benzoquinone.⁷ EI-MS (70 eV, 200 $^\circ\text{C}$) further supported this assignment with a molecular ion at m/z 358.2128, $\text{C}_{27}\text{H}_{30}\text{O}_4$ (calcd 358.2145), and a major benzylic cleavage⁸ which resulted in ions at m/z 167, 168, and 169 (base peak) corresponding to Q^+ , QH^+ , and QH_2^+ respectively. $^1\text{H NMR}$ ⁹ (Figure 1c) showed the presence of a quinonoid proton (H-6, δ 5.81, 1 H, s), a methoxy group (δ 3.84, 3 H, s), a hydroxyl substituent (δ 7.19, 1 H, s, D_2O exchangeable; ν (CH_2Cl_2) 3380 cm^{-1} , br), and a C-15 side chain containing three double bonds. A terminal olefin was evident upon irradiation of H-10' and H-13' (H-14', δ 5.80, 1 H, m, $J = 5.5$, 10.2, and 17.1 Hz; H_β -15', δ 4.97, 1 H, dd, $J = 1.7$ and 10.2 Hz; H_α -15', δ 5.03, 1 H, dd, $J = 1.7$ and 17.1 Hz).¹⁰ The other four vinylic protons appeared as a multiplet at δ 5.3–5.4. Irradiation of this region and H-14' unambiguously distinguished the methylenes at 10' and 13' (H-10', δ 2.78, 2 H, dd, $J = 5.5$ and 5.9 Hz; H-13', δ 2.82, 2 H, dd, $J = 5.1$ and 5.5 Hz)¹¹ and permitted the assignment of H-7' (δ 2.04, 2 H, dt, $J = 6.6$ and 6.9 Hz). The remaining signals corresponded to H-1' (δ 2.43, 2 H, t, $J = 7.6$ Hz) and the H-2' to H-6' methylenes (δ 1.2–1.4, 10 H m).

The olefin stereochemistry could not be readily assigned by 2D NMR experiments because of spectral overlap. However, a triple

frequency irradiation experiment (H-7', H-10', and H-13') reduced it to two isolated AB patterns with coupling constants of 10.7 Hz (Figure 1d). The *cis* olefin geometry, suggested by the small coupling constant, was confirmed by a heteronuclear correlation experiment¹² which identified two γ -gauche interactions for C-10' (δ 25.6) relative to one for C-13' (δ 31.5). In addition, a 2.7% NOE¹³ enhancement of H-7' was observed upon irradiation of H-10', unequivocally confirming a *Z* configuration about both double bonds.

Both NOE difference and 2D-exchange experiments demonstrated that the quinonoid proton (H-6) was adjacent to the methoxy substituent (22% enhancement). The rest of the substitution pattern was evident from the UV and IR spectra⁷ and the high-field-shifted ^{13}C NMR chemical shifts of the carbonyl resonances (δ 182.8, 181.6). These spectroscopic data identified compound **1** as the 2-hydroxy-5-methoxy-3-[(8'*Z*,11'*Z*)-8',11',14'-pentadecatriene]-*p*-benzoquinone.



The identity of the germination stimulant (**2**) was established from the $^1\text{H NMR}$ spectrum of the crude root exudate, which

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(10) Upon irradiation (C_6D_6) of H-10' and H-13', the multiplet at δ 5.80 simplified to two doublets with $J = 10.2$ and 17.1 Hz.

(11) Irradiation of the vinylic region simplified H-13' from a doublet to a doublet ($J = 5.5$ Hz), H-10' from a doublet to a singlet, and H-7' from a quartet of triplets to a triplet ($J = 6.9$ Hz). Irradiation of H-14' collapsed H-13' to a doublet ($J = 5.1$ Hz), while H-10' remained unchanged.

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contained additional signals (28%, δ 6.38, 1 H, s; δ 3.78, 3 H, s; δ 2.64, 2 H, t) that could be attributed to the hydroquinone form of **1** (Figure 1a). These signals disappeared as the crude exudate lost biological activity. Upon reduction of **1** with zinc dust¹⁴ or tin amalgam,¹⁵ the presence of the hydroquinone **2** in the crude exudate was confirmed (Figure 1b). The presence of **2** was further demonstrated by EI-MS analysis of the silylated crude exudate showing an ion at m/z 576 (m/z 360 + 3 Me₄Si) and by direct silylation of the second eluting component collected from HPLC under a N₂ atmosphere.

The ability of the crude root exudate to stimulate *Striga* germination is related directly to the concentration of **2**. When the concentration of the hydroquinone dropped below 10⁻⁷ M, the exudate no longer possessed activity.¹⁶ However, the biological activity could be quantitatively recovered by adding synthetic hydroquinone **2** back to the inactive exudate. The ability of *Striga* to recognize this labile hydroquinone allows it to commit itself to a host through germination only within the distance through which **2** can diffuse before being oxidized. This report documents the first characterization of a natural host-derived germination stimulant for *Striga* and demonstrates the biological commitment of this parasite to a transient species that can define viability of and distance to a potential host. The generality of this mechanism and the reasons for the exudation of such molecules from host plants are currently under investigation.

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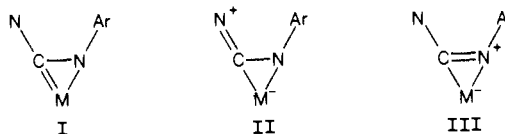
Carbon-Nitrogen Bond Formation in the Reaction between Tetrakis(dimethylamido)molybdenum(IV) and 2,6-Dimethylphenyl Isocyanide. Preparation and Characterization of the First Homoleptic Metallaamidine Complex: Mo(η^2 -Me₂NCN-2,6-Me₂C₆H₃)₄

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Transition-metal-amide bonds are known to undergo insertion reactions with a variety of unsaturated molecules such as CO₂ and CS₂.^{1,2} The reactions between tin-amide³ and more recently actinide-amide bonds⁴ and aryl isocyanides have also been reported to give insertion products. In the case of actinide chemistry, the products were spectroscopically shown to contain η^2 -R₂NCNAr ligands. The latter may be called metallaamidines having contributions from the resonance forms I, II, and III shown below.



The ligand carries a formal -1 charge and donates four electrons to the metal center as is seen for η^2 -acyl and η^2 -carbamoyl ligands, RCO and R₂NCO, respectively.⁵

We report here that the reaction between Mo(NMe₂)₄⁶ and 2,6-dimethylphenyl isocyanide yields Mo(η^2 -Me₂NCN-2,6-Me₂C₆H₃)₄. To our knowledge this report provides the first example of (1) an insertion of an isocyanide into a transition-metal-amide bond, (2) a homoleptic metallaamidine complex, M(R₂NCNAr)_x, and (3) structural characterization of the η^2 -R₂NCNAr ligand. It also provides an unusual example of a tetrakis- η^2 mononuclear species, M(η^2 -L)₄,⁷ with an interesting Mo(η^2 -CN)₄ geometry.

Hydrocarbon solutions of Mo(NMe₂)₄ react rapidly with 2,6-Me₂C₆H₃NC (4 equiv) at ambient temperatures to give Mo-(Me₂NCN-2,6-Me₂C₆H₃)₄ which was isolated as red-brown crystals in ca. 60% yields by cooling the solution to -15 °C.⁸ (Crystallization from toluene yields a 1:1 solvent to complex ratio.) The infrared spectrum of the crystalline product showed no bands assignable to ν (C≡N) in the region 2200-1900 cm⁻¹ but did show four bands, 1607, 1580, 1565, and 1555 cm⁻¹, assignable to C-N double or partial double bonds. The ¹H NMR spectrum in benzene-*d*₆ revealed eight signals of equal intensity assignable to methyl groups (NMe₂ and ArMe₂), while the ¹³C NMR spectrum revealed two resonances of equal intensity at 213 and 194 ppm assignable to NCN carbons, four amido methyl carbons (44.8, 43.6, 38.3, and 37.9 ppm), and four aryl-methyl carbons (20.5, 19.9, 19.1, and 18.1 ppm), all of roughly equal integral intensity (chemical shift values are relative to Me₄Si).

The data were consistent with formation of a product in which the aryl isocyanide had inserted into all four Mo-NMe₂ bonds yielding two different types of Me₂NCNAr ligands, each having restricted rotation about the central C-N bonds on the NMR time scale at room temperature. We resorted to a single-crystal X-ray diffraction study.⁹

The molecular structure of Mo(η^2 -Me₂NCN-2,6-Me₂C₆H₃)₄ is shown in Figure 1 and the central Mo(η^2 -C(NC₂)NC)₄ skeleton looking down the virtual C₂ axis, which bisects the C(18)-Mo-C(44) angle, is shown in Figure 2 with bond distances. There are two types of amidino ligands. One type has shorter Mo-C and Mo-N distances relative to the other, each bonded to the metal atom in a η^2 manner. The amidino ligands having the shorter Mo-C and Mo-N distances have longer η^2 -(C-N) distances than those with long Mo-C and Mo-N distances. The amido nitrogen to isocyanide carbon (Me₂N-CNAr) distances are all essentially the same, which together with the planarity of the C₂NCN moieties are indicative of extensive π -delocalization within the ligand. This is consistent with significant contributions from the resonance forms II and III. The aromatic planes are twisted out of conjugation with the Me₂N-C-N π systems as can be seen in Figure 1.

The NMR data noted previously are consistent with the observed molecular structure found in the solid state given that

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(9) Cell dimensions at -155 °C: $a = 11.233$ (1) Å, $b = 11.065$ (1) Å, $c = 19.550$ (4) Å, $\alpha = 101.19$ (1)°, $\beta = 90.19$ (1)°, $\gamma = 99.53$ (1)°, $Z = 2$, $d_{\text{calcld}} = 1.257$ g cm⁻³, and space group $P\bar{1}$. Data were collected by using Mo K α , $6^\circ < 2\theta < 45^\circ$, and of the 8466 reflections collected, 6151 were unique. There were 5443 having $F > 3\sigma(F)$ and those were used in the refinement. Final residuals are $R(F) = 0.0294$ and $R_w(F) = 0.0323$.

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