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 dust[14] 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 Me_4Si) and by direct silylation of the second eluting component collected from HPLC under a N_2 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.

Acknowledgment. We gratefully acknowledge support from the USDA (5901-0410-9-0257), the Frasch Foundation (D.G.L.), and Intsormil (USAID, PRF-4B) (LGB-paper #10,785 of the Agricultural Experimental Station, Purdue University). M.C. acknowledges support as an Aileen S Andrew Fellow and D.G.L. is an Alfred P. Sloan Foundation Fellow and a Camille and Henry Dreyfus Foundation Teacher–Scholar.

Registry No. 1, 105018-76-6; **2**, 105018-77-7.

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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: $Mo(\eta^2\text{-}Me_2NCN\text{-}2,6\text{-}Me_2C_6H_3)_4$

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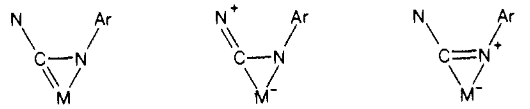
Transition-metal–amide bonds are known to undergo insertion reactions with a variety of unsaturated molecules such as CO_2 and CS_2.[1,2] The reactions between tin-amide[3] and more recently actinide–amide bonds[4] and aryl isocyanides have also been reported to give insertion products. In the case of actinide chemistry, the products were spectroscopically shown to contain η^2-R_2NCNAr ligands. The latter may be called metallaamidines having contributions from the resonance forms I, II, and III shown below.



I II III

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 R_2NCO, respectively.[5]

We report here that the reaction between $Mo(NMe_2)_4$[6] and 2,6-dimethylphenyl isocyanide yields $Mo(\eta^2\text{-}Me_2NCN\text{-}2,6\text{-}Me_2C_6H_3)_4$. 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, $M(R_2NCNR')_x$, and (3) structural characterization of the η^2-R_2NCNAr ligand. It also provides an unusual example of a tetrakis-η^2 mononuclear species, $M(\eta^2\text{-}L)_4$,[7] with an interesting $Mo(\eta^2\text{-}CN)_4$ geometry.

Hydrocarbon solutions of $Mo(NMe_2)_4$ react rapidly with 2,6-$Me_2C_6H_3NC$ (4 equiv) at ambient temperatures to give $Mo(Me_2NCN\text{-}2,6\text{-}Me_2C_6H_3)_4$ 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 $\nu(C{\equiv}N)$ 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 (NMe_2 and $ArMe_2$), while the ^{13}C NMR spectrum revealed two resonances of equal intensity at 213 and 194 ppm assignable to N*C*N 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 Me_4Si).

The data were consistent with formation of a product in which the aryl isocyanide had inserted into all four Mo–NMe_2 bonds yielding two different types of Me_2NCNAr 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 $Mo(\eta^2\text{-}Me_2NCN\text{-}2,6\text{-}Me_2C_6H_3)_4$ is shown in Figure 1 and the central $Mo(\eta^2\text{-}C(NC_2)NC)_4$ skeleton looking down the virtual C_2 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 (Me_2N–CNAr) distances are all essentially the same, which together with the planarity of the C_2NCN 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 Me_2N–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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[7] Cf. Pt(1,5-cyclooctadiene)$_2$: Green, M.; Howard, J. A. K.; Spenser, J. L.; Stone, F. G. A. *J. Am. Chem. Soc., Dalton Trans.* **1977**, 271. And the anion $Cr(O_2)_4^{3-}$: Stomberg, R. *Acta Chem. Scand.* **1963**, *17*, 1563.

[8] Dry and oxygen-free solvents and atmospheres (N_2) were used throughout.

[9] Cell dimensions at −155 °C: a = 11.233 (1) Å, b = 11.065 (1) Å, c = 19.550 (4) Å, α = 101.19 (1)°, β = 90.19 (1)°, γ = 99.53 (1)°, Z = 2, d_{calcd} = 1.257 g cm^{-3}, and space group $P\bar{1}$. Data were collected by using Mo Kα, 6° < 2θ < 45°, 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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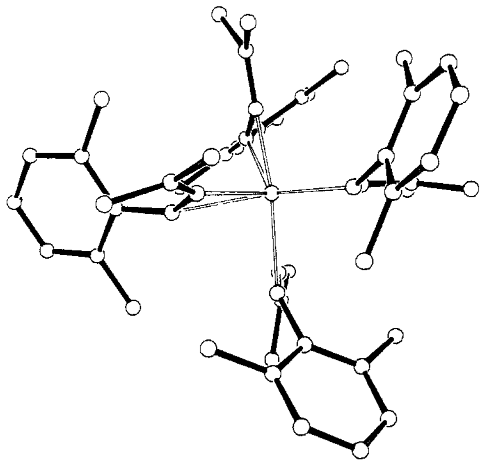

Figure 1. Ball-and-stick diagram of the $Mo(\eta^2\text{-}Me_2NCN\text{-}2,6\text{-}Me_2C_6H_3)_4$ molecule showing the alignment of the four η^2-NC ligands. Viewed down the *z* axis the NCN units are aligned in a pairwise manner along *xz* and *yz* planes.

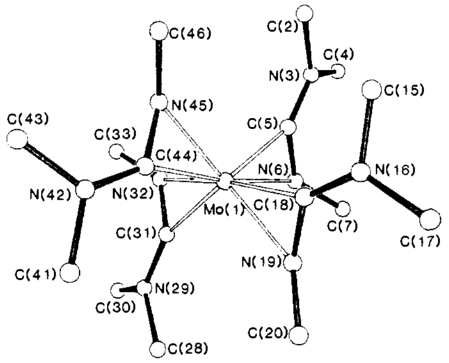

Figure 2. View of the central $Mo(\eta^2\text{-}C(NC_2)NC)_4$ moiety showing the atom number scheme. Pertinent distances (Å): for short Mo–C and Mo–N, Mo–C(18) = 2.032 (3), Mo–N(19) = 2.205 (2), Mo–C(44) = 2.024 (3), Mo–N(45) = 2.181 (2), η^2-(C–N) = 1.336 (7) (av); for long Mo–C and Mo–N, Mo–C(5) = 2.111 (3), Mo–N(6) = 2.278, Mo–C(31) = 2.116 (3), Mo–N(32) = 2.294 (2), η^2-(C–N) = 1.297 (3) (av) and Me_2N–CNAr = 1.335 (6) (av).

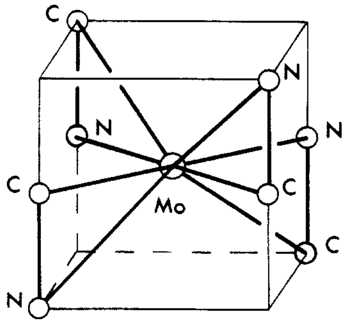

Figure 3. Central $Mo(\eta^2\text{-}CN)_4$ moiety inscribed within an idealized cube showing the cis-square-planar and pseudotetrahedral MoC_2N_2 units.

molecular motions allow the attainment of idealized C_2 symmetry. The observed restricted rotations about Me_2N–C and N–C aryl bonds presumably reflect electronic and steric factors, respectively.

Finally we note it is interesting to describe the distorted dodecahedral $Mo(\eta^2\text{-}CN)_4$ unit in terms of its relationship to an idealized metal-centered cube, MX_8, from which so many eight-coordinate structures are derived.[10] The present structure involves the fusing of a planar *cis*-MC_2N_2 unit within a MC_2N_2 tetrahedron as shown in Figure 3. The short Mo–C distances are mutually cis and trans to the long Mo–N distances. To our knowledge there are no related structures of $M(\eta^2\text{-}XY)_4$ compounds.

Further studies are in progress.[11]

Supplementary Material Available: Ball-and-stick diagram giving the atom number scheme, tables of isotropic and anisotropic thermal parameters, and complete listings of bond distances and bond angles (6 pages). Ordering information is given on any current masthead page.

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Stereochemical and Mechanistic Studies of the "Suicide" Event in Biomimetic P-450 Olefin Epoxidation

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Both cytochrome P-450 and metalloporphyrin model systems have been reported to exhibit stereospecific olefin epoxidation[1,3c] and to undergo the "suicide" porphyrin N-alkylation reaction with 1-olefins.[2,3] In this paper we report that in the previously studied model system N-alkylation[2a] is both stereospecific (syn), as observed[3c] for P-450 itself, and is olefin structure dependent. In addition, we have observed that even terminal olefins which are active toward epoxidation, styrenes and 1,1-disubstituted olefins, undergo this "suicide" event. The partitioning between epoxidation and N-alkylation is highly dependent on olefin structure but independent of olefin concentration, catalyst concentration, and the presence of a competing olefin. Unlike the natural system, where the suicide event destroys catalytic activity, the *N*-alkylporphyrins in this model system retain catalytic activity, albeit a greatly reduced activity.

Using[4] Fe(TDCP)Cl under heterogenous conditions with the oxygen atom donor pentafluoroiodosylbenzene (PFIB), we found that a variety of 1-olefins produce green pigments (Soret at 446 nm), characteristic of N-alkylation, as observed by Traylor[2a] and Mansuy.[2b] In addition, we find that methylenecyclohexane, isobutylene, styrene, 2,6-dimethylstyrene, and 3-methyl-1-butyne also yield green pigments. We have isolated the *N*-alkylporphyrins for several of these.[5,6] To our knowledge, the 1,1-disubstituted olefins and styrenes have never before been reported to produce *N*-alkylporphyrins in either P-450 or model systems. Just as in

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(4) TDCP: 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphine dianion.

(5) 21-(2-Hydroxy-3-methylbutyl)-23-H-TDCP: calcd M^+ 976, found 976. ^1H NMR ($CDCl_3$) δ 8.66 (s, β-pyrrolic, 2 H), 8.29–8.40 (m, β-pyrrolic, 4 H), 7.63–7.91 (m, β-pyrrolic, 2 H; phenyl, 12 H), 0.2–0.3 (m, $NCH_AH_BCH_X(OH)$, 1 H), –0.57 (d, CH_XOH, J = 5.7 Hz, 1 H), –1.1 to –1.0 (m, $CH(OH)CH(CH_3)_2$, 1 H), –1.19 (d, $CH(CH_3)_2$, J = 6.6 Hz, 3 H), –2.00 (d, $CH(CH_3)_2$, J = 6.3 Hz, 3 H), –2.2 to –2.1 (br s, NH, 1 H), –4.19 (d of d, $NCH_AH_BCH_X(OH)$, J_{BX} = 11, J_{AB} = 15 Hz, 1 H), –4.42 (d of d, $NCH_AH_BCH_X(OH)$, J_{AX} = 2, J_{AB} = 15 Hz, 1 H); UV max 428 (Soret), 486 sh, 521, 555, 607, 666 (weak).

(6) 21-(2-Hydroxy-2-methyl-1-propyl)-23-H-TDCP: calcd M^+ 962, found 962. ^1H NMR ($CDCl_3$) δ 8.67 (s, β-pyrrolic, 2 H), 8.32 (br s, β-pyrrolic, 4 H), 7.91–7.56 (m, β-pyrrolic, 2 H, phenyl, 12 H), –0.85 (br s, $C(CH_3)_2OH$, 7 H), –2.14 (s, NH, 1 H), –3.98 (s, NCH_2, 2 H). 21-[(1-Hydroxycyclohexyl)methyl]-23-H-TDCP: calcd M^+ 1002, found 1002. 21-(α-Hydroxy-2,6-dimethylstyryl)-23-H-TDCP: calcd M^+ 1038, found 1038.

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