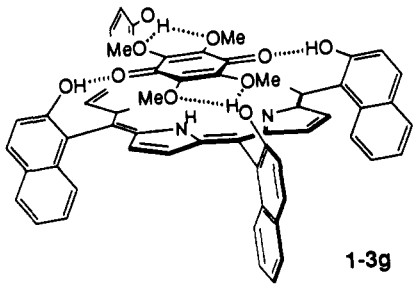

Figure 1. Schematic representation of **1–3g** complexation.

^{1}H NMR spectrum.[9] These affinities were determined by titrimetric measurement of visible spectra with clear isosbestic points in the region of 550–700 nm.

The binding constants calculated from the nonlinear curve fitting analysis and thermodynamic parameters for porphyrin **1**–quinone **3** complexation are summarized in Table I. Significant binding properties are as follows. The binding constants of quinones with **1** unambiguously increase in the order **3a** < **3b** < **3c** < **3f** < **3g** with the number of OCH_3 groups. The favorable negative changes of free energy and enthalpy increase in the same order as above. The trend of complexation is not predictable from the entropy changes for **3a–c**, **3f**, and **3g**. The positions of methoxy groups are crucial in the host–guest formation. In general, the negative gain of free energy change of the methoxy substitutions at the adjacent positions (−1.3 to approximately −1.5 kcal/mol) is about three times larger than that of substitutions at the separate positions. The remarkable enhancement of the binding constant of 2,3-dimethoxy-*p*-benzoquinone (**3c**) compared with 2,6- and 2,5-dimethoxy-*p*-benzoquinones (**3d,e**) implies that two adjacent OCH_3 substituents at 2- and 3-positions of the *p*-benzoquinone ring cooperatively act as the effective third interaction site via *bifurcated* hydrogen bonding. In contrast, the effective third and/or fourth point interactions between **3d** or **3e** and **1** seem to be much weaker than those in the former case. Simultaneous *multipoint* hydrogen bondings give rise to an extremely large binding constant for tetramethoxy-*p*-benzoquinone (**3g**) with **1** (Figure 1). It should be noted that ubiquinone (**3h**), having a long isoprenoid tail, has an appreciably high affinity with **1**.

Furthermore, it is of particular interest to compare the affinities of quinones for **1** and the previous host 5,15-*cis*-bis-(2-hydroxy-1-naphthyl)octaethylporphyrin (**2**), substituted with two hydroxynaphthyl groups at meso-positions and eight peripheral ethyl groups at β-positions. The sharp difference in binding properties between **1** and **2** is shown in Table II. In spite of no substantial difference in binding constants for **3a**, complexation of **3g** with **1** is ca. 250 times larger than that with **2**, although methoxy groups may bring about steric hindrance to 2-hydroxynaphthyl groups and a weakening charge-transfer-type interaction. It is likely that the very low binding constant for pairing of **2** and **3g** results from steric hindrance between ethyl groups of **2** and methoxy groups of **3g**. Pairing of tetramethyl-*p*-benzoquinone (**3i**) with **1** shows a marked decrease in the binding constant due to a repulsive interaction between methyl groups and 2-hydroxynaphthyl groups. The fashion of the present quinone–porphyrin **1** pairing is quite different from the system of two-point hydrogen-bonding fixation which is governed by both an electronic effect of the substituents and a charge-transfer-type interaction.[6]

Further work on the structural properties of quinone–porphyrin adducts and the kinetics of electron transfer from a photoexcited porphyrin to quinone are in progress, and details on these will appear in future publications.

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(9) For example, the following values of $\Delta\delta$, δ (**1** + **3g**) − δ(**1** or **3g**), are observed under the conditions [**1**] = [**3g**] = 2.0 mM in $CDCl_3$ at 30 °C: +1.91 (OH of **1**), −0.93 (CH_3 of **3g**).

Metal-Mediated Dimerization of 1,3-Cyclooctadiene to 2-Cyclooct-2-en-1-yl-1,3-cyclooctadiene: A Novel Bicyclic Triene[1]

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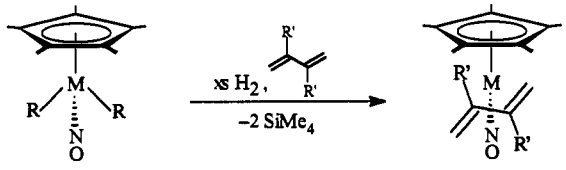
We have previously reported the synthesis and characteristic reactivity of unusual Cp′Mo(NO)(η^4-*trans*-diene) complexes [Cp′ = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5)].[2] These complexes are preparable via sodium amalgam reduction in THF of Cp′Mo(NO)I_2 in the presence of acyclic, conjugated dienes. However, this reduction method cannot be extended to encompass cyclic, conjugated dienes.[2a] Furthermore, similar reductions of Cp′W(NO)I_2 in THF in the presence of cyclic or acyclic conjugated dienes simply result in decomposition of the organometallic reactant.[2a] We now report a new method for the synthesis of Cp*M(NO)(η^4-*trans*-diene) complexes of *both* molybdenum and tungsten. This method involves treating solutions of Cp*M(NO)(CH_2SiMe_3)$_2$ [M = Mo, W] with H_2 in the presence of acyclic, conjugated dienes (eq 1).[3]



(1)

However, when 1,3-cyclooctadiene (1,3-COD) is employed as the trapping agent, it undergoes an unprecedented coupling in the metals' coordination spheres (Scheme I). The 2-cyclooct-2-en-1-yl-1,3-cyclooctadiene ligand thus formed is attached in a bis-η^2 fashion to the metal centers in the final products.[3] This hitherto unknown triene is easily liberated by treatment of these complexes with O_2.[4]

Typically, the Cp*M(NO)(CH_2SiMe_3)$_2$ reactants were exposed to an excess of diene and H_2 (1 atm) at −78 °C in Et_2O for 1 h (M = Mo) or 16 h (M = W). Chromatographic separation of the final reaction mixtures on Florisil and subsequent workup afforded yellow crystals of the various product complexes.[3] The spectroscopic properties of the new Cp*W(NO)(η^4-*trans*-diene) complexes resemble those exhibited by related molybdenum species whose molecular structures we have previously established.[2] Hence, it is likely that both of these compounds are isostructural and contain the diene ligands attached to the metal centers in a twisted, transoidal fashion.[2,6] In contrast, the spectroscopic properties of the organometallic products resulting from the re-

(1) Presented in part at the 75th Canadian Chemical Conference, Edmonton, Alberta, Canada, June 1992; Abstract 370.

(2) (a) Christensen, N. J.; Hunter, A. D.; Legzdins, P. *Organometallics* **1989**, *8*, 930. (b) Christensen, N. J.; Legzdins, P.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1991**, *10*, 3070. (c) Christensen, N. J.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 4021. (d) Christensen, N. J. Ph.D. Dissertation, The University of British Columbia, 1990.

(3) Complete experimental details and characterization data for all complexes isolated during this work are provided as supplementary material.

(4) The organometallic product of this transformation is the well-known [Cp*M$(O)_2]_2(\mu$-O).[5] Interestingly, both Cp*M(NO)($C_{16}H_{24}$) complexes are stable to reducing conditions (e.g., Na/Hg amalgam) and do not react to any appreciable extent with CO (600 psig, 5 days) at room temperature.

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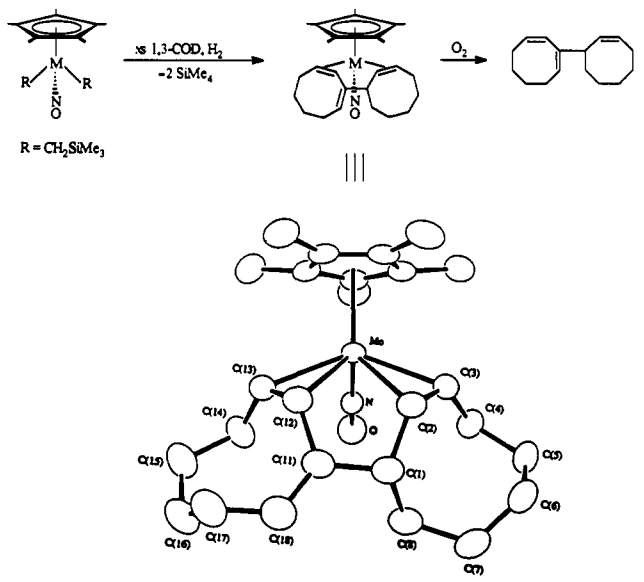
Scheme I



actions depicted in Scheme I do not permit an unambiguous assignment of their molecular structures. Consequently, we have subjected $Cp^*Mo(NO)(C_{16}H_{24})$ to a single-crystal X-ray crystallographic analysis.[7]

The carbon–carbon bond lengths within the $C_{16}H_{24}$ ligand of $Cp^*Mo(NO)(C_{16}H_{24})$ indicate the existence of three C=C linkages as shown in Scheme I, namely, C(2)–C(3) [1.392(3) Å] and C(12)–C(13) [1.383(3) Å], each of which is involved in η^2 π-bonding to Mo with an average Mo–C = 2.34 Å, and C(11)–C(18) [1.340(4) Å].[8] In solutions, the $Cp^*M(NO)(C_{16}H_{24})$ complexes display relatively complicated ^1H NMR spectra which contain complex coupling patterns for the CH and CH_2 protons of the cyclooctenyl-1,3-cyclooctadiene ligand.[3] $^{13}C\{^1H\}$ and APT data, however, prove to be more useful during structure elucidation. Thus, in addition to Cp^* signals, the APT spectra exhibit the expected nine peaks assignable to CH_2 carbons, six peaks assignable to CH carbons, and one peak attributable to the lone quaternary carbon in the $C_{16}H_{24}$ ligand. The free 2-cyclooct-2-en-1-yl-1,3-cyclooctadiene displays similar spectral features.[9]

The mechanistic details of how the triene ligand is formed during the conversions shown in Scheme I are unclear at present. $SiMe_4$ has been identified by GC and ^1H NMR spectroscopy as a byproduct in both reactions. However, the use of D_2 instead of H_2 in both conversions does not result in any incorporation of deuterium into the final organometallic products. These coupling reactions represent a novel example of the ability of a transition-metal center to promote a dimerization which would not occur without metal mediation.[10] We are currently extending this work to establish which other dienes display the same dimerization behavior as 1,3-COD and to determine which functional groups may be tolerated during such metal-mediated coupling processes.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and a postgraduate scholarship to J.D.D.

Supplementary Material Available: Experimental procedures and characterization data for all complexes and full details of the crystal structure analyses including associated tables for $Cp^*Mo(NO)(C_{16}H_{24})$ (14 pages); tables of measured and calculated structure factor amplitudes for $Cp^*Mo(NO)(C_{16}H_{24})$ (18 pages). Ordering information is given on any current masthead page.

(7) Crystals of $Cp^*Mo(NO)(C_{16}H_{24})$ are triclinic, space group $P\bar{1}$; a = 8.772(1) Å, b = 8.898(1) Å, c = 16.137(2) Å, α = 103.26(1)°, β = 103.98(1)°, γ = 94.58(1)°, V = 1177.4 Å^3, Z = 2, D_{calcd} = 1.347 g cm^{-3}, μ(Mo Kα) = 5.6 cm^{-1}; diffractometer, Enraf-Nonius CAD-4F; radiation, Mo Kα, graphite monochromator (λ(Kα_1) = 0.709 30 Å); 4° ≤ 2θ ≤ 49°; N_{obsd} = 3452 ($I_o \geq 2.5\sigma(I_o)$); N_{var} = 279; R_F = 0.023; R_{wF} = 0.031; maximum residual peak 0.37(5) e Å^{-3}.

(8) Other metrical parameters of interest are C(11)–C(12) = 1.492(3) Å, C(1)–C(2) = 1.521(3) Å, C(1)–C(8) = 1.498(3) Å, C(12)–C(11)–C(18) = 121.9(2)°, C(8)–C(1)–C(2) = 118.5(2)°.

(9) Anal. Calcd for $C_{16}H_{24}$: C, 88.80; H, 11.20. Found: C, 88.48; H, 11.17. IR (neat): 3007, 2926, 2849, 1639, 1446, 1261, 920, 846, 817, 763, 704 cm^{-1}. Low-resolution mass spectrum (probe temperature 120 °C): m/z 216 [P$^+$]. ^1H NMR (C_6D_6): δ 5.94–5.52 (m, 5 H, C*H*), 3.52 (s, 1 H, C*H*), 2.29–1.95 (m, 6 H, 3 CH_2), 1.68–1.27 (m, 12 H, 6 CH_2). $^{13}C\{^1H\}$ NMR: δ 141.69 (C_{quat}), 133.45, 132.26, 128.53, 127.08, 125.26, 43.92 (6 CH), 35.67, 29.90, 29.02, 28.05, 26.92, 26.71, 26.30, 24.77, 23.05 (9 CH_2).

(10) A recent example of metal-facilitated dimerization involves the reductive activation of benzene in $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ to obtain $[\{Mn(CO)_3\}_2\{\mu\text{-}(\eta^4\text{-}C_6H_6{:}\eta^4\text{-}C_6H_6)\}]^{2-}$ in which the Mn centers are bridged by the newly formed tetrahydrobiphenylene ligand.[11]

(11) Cooper, N. J.; Geib, S. J.; Thompson, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 8961.

Biosynthesis of the *Ephedra* Alkaloids: Evolution of the C_6–C_3 Skeleton

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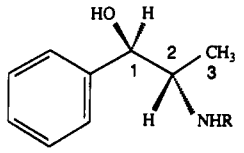
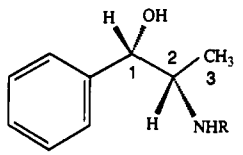
The skeleton of the *Ephedra* alkaloids, (1*R*,2*S*)-(−)-ephedrine (**1**), (1*R*,2*S*)-(−)-norephedrine (**2**), (1*S*,2*S*)-(+)-pseudoephedrine (**3**), and (1*S*,2*S*)-(+)-norpseudoephedrine (**4**), originates by union of a C_6–C_1 unit with a C_2 unit. The latter is derived from the intact CH_3CO group of pyruvic acid.[1,2] The C_6–C_1 unit is supplied by the benzylic C_6–C_1 fragment of phenylalanine,[3-5] which presumably cleaves by the ammonia lyase route,[6] since the C_6–C_1 unit of cinnamic acid[5] is incorporated and since benzaldehyde and benzoic acid[4,5] also serve as precursors. It has not been determined which of these two C_6–C_1 compounds reacts with pyruvate, nor have the C_6–C_3 intermediates on the route from the two fragments C_6–C_1 plus C_2 into the noralkaloids been identified.



1 R = CH_3

2 R = H



3 R = CH_3

4 R = H

We now report results which identify benzoic acid as the immediate precursor of the C_6–C_1 unit and which show that 1-phenylpropane-1,2-dione (**6**) and (*S*)-(−)-2-amino-1-phenylpropan-1-one (cathinone) (**7**) are the penultimate intermediates in the evolution of the C_6–C_3 skeleton of the noralkaloids.

In four experiments, solutions of (i) sodium [*carboxyl*-^{13}C]-benzoate (99% ^{13}C), (ii) [*carbonyl*-^{13}C,^{2}H]benzaldehyde (99% ^{13}C, 99.6% ^{2}H), (iii) [1,2,3-$^{13}C_3$]-1-phenylpropane-1,2-dione (**6**) (98% $^{13}C_3$), and (iv) [1,2,3-$^{13}C_3$]-(*S*)-2-amino-1-phenylpropan-1-one (**7**) (97% $^{13}C_3$) were applied to growing shoots of *Ephedra*

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‡ McMaster University.

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(4) Yamasaki, K.; Sankawa, U.; Shibata, S. *Tetrahedron Lett.* **1969**, 4099–4102.
(5) Yamasaki, K.; Tamaki, T.; Uzawa, S.; Sankawa, U.; Shibata, S. *Phytochemistry* **1973**, *12*, 2877–2882.
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