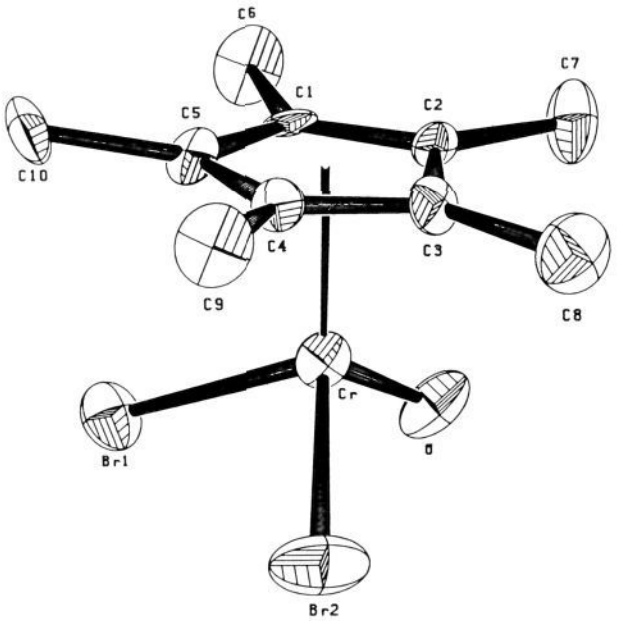

Figure 2. ORTEP view of Cp^*CrOBr_2 (**2**) with ellipsoids drawn at the 35% probability level.

between **1**, **2**, and O_2 are planned.

Magnetic susceptibility measurements (SQUID) on microcrystalline samples of **2** (μ_{eff} (300 K) = 2.02 μ_B, μ_{eff} (5 K) = 1.73 μ_B) indicate that **2** has a larger ground-state orbital contribution than vanadyl (VO^{2+}) complexes.[1,11] The IR spectrum of **2** shows a band at 934 cm^{-1} ($\nu_{Cr=O}$); isotopic labeling[12] using $^{17,18}O_2$ resulted in additional absorptions at 917 and 900 cm^{-1}. A crystallographic study shows that **2** adopts a typical piano-stool geometry with very short Cr–O[7,12a] (1.58 (2) Å) and Cr–Br (2.393 (4) and 2.375 (5) Å) distances (Figure 2).[13] The substantial contraction of the Cr–Br bonds upon conversion to the oxide indicates Cr–Br π-bonding in **2**.

The metastability of **2** is indicated by the ease with which it reverts to **1**. Proton NMR studies at 80 °C (hexamethylbenzene as internal standard) indicate that **2** gives **1** in 75% yield over the course of 1.5 h. Upon photolysis in CH_2Cl_2, **2** reverts to **1** in the same yield. Concentrated solutions of **2** tend especially to revert to **1**, and our attempts to grow crystals of **2** were often frustrated by this instability. Coordinating solvents also tend to convert **2** into Cp^*CrBr_2·L (L = THF, CH_3CN). Careful addition of Br_2 to solutions of **2** as well as electrochemical reduction of **2** at −140 mV results in concomitant deoxygenation to give **1**. In the thermal conversions (toluene) of **2** to **1**, ^{18}O-labeling studies in conjunction with GC–MS analyses[14] indicate that the final oxygen-containing species are polychromates (50%), "Cp*OH" (20%), water (10%), and oxidized solvent (e.g., $PhCH_2OH$ and PhCHO from toluene). In the photochemical conversion (CH_2Cl_2), the major oxygen-containing products are polychromates (70%) and water. Notably, O_2 is not liberated in these reactions.

The electrophilic character of **2** is indicated by its ability to oxygenate electron-rich substrates. Phosphines (PPh_3, $P(^nBu)_3$) readily abstract oxygen from **2**; ^{31}P NMR experiments show that the oxidation of PPh_3 is catalytic (CH_2Cl_2: 0.25 M PPh_3, 0.003 M **1**; initial TON ≈ 27 phosphines/20 min at 20 °C). While the metal-catalyzed oxygenation of phosphines is not unusual,[15] our observations do demonstrate the ability of **1** to *repeatedly* activate O_2 without decomposition. Compound **2** will not oxygenate Et_2S, but $CpCrOBr_2$[16] will. This indicates that the electrophilicity of this class of oxo compounds can be adjusted by substituents on the cyclopentadienyl group.

In conclusion, $[Cp^*CrBr_2]_2$ is an unusual organometallic complex which activates molecular oxygen. Work is underway to see if this family of organometallic compounds has a future either as oxidants in synthesis or as oxygen carriers.

Acknowledgment. This research was supported by the National Science Foundation (DMR 86-12860 and CHE 87-11460). D.B.M. gratefully acknowledges support through Roger Adams (University of Illinois) and 3M Fellowships. Special thanks to Stephen Doktycz for help with the GC–MS measurements.

Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles for **2** (2 pages); table of observed and calculated structure factors for **2** (5 pages). Ordering information is given on any current masthead page.

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(13) Cp^*CrOBr_2: opaque plate 0.2 × 0.3 × 0.6 mm, orthorhombic, $P2_12_12_1$, a = 6.616 (2) Å, b = 14.144 (5) Å, c = 13.664 (6) Å, V = 1278.6 (9) $Å^3$, and ρ_{calcd} = 1.886 g/cm^3 for Z = 4. Syntex $P2_1$ automated four-circle diffractometer, 26 °C, Mo ($K\bar{\alpha}$ = 0.71073 Å) $3.0 < 2\theta < 46.0°$ ($+h+k+l$) and $3.0 < 2\theta < 15.0°$ ($\mp h\mp k\mp l$), 1402 reflections (1071 unique, R_i = 0.037, 863 observed, $I > 2.58\sigma(I)$); corrected for anomalous dispersion, absorption (maximum and minimum transmission factors, 0.340 and 0.132 for μ = 70.35 cm^{-1}), Lorentz and polarization effects. Direct methods (SHELXS-86) located Br and Cr atoms; difference Fourier synthesis revealed C and O atoms. H atoms were not included in structure factor calculations. Non-H atoms were independently refined with anisotropic thermal coefficients. Variance between observed and calculated structure factors slightly dependent upon amplitude and inverse sin(θ). R = 0.077 and R_w = 0.098.

(14) Reaction solutions were analyzed by GC–MS using a methyl silicone gum column (H_2O, $PhCH_2OH$, PhCHO). After evaporation of the solvent, the residue was extracted with CH_2Cl_2 and analyzed by FD–MS (Cp^*OH). The CH_2Cl_2-insoluble solid contained the majority of the label; it was extracted with methanol and assayed for $CH_3{}^{18}OH$ by GC–MS.

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(16) Prepared from Cp_2Cr and Br_2 followed by oxygenation to give $CpCrOBr_2$. Anal. Calcd for $C_5H_5CrOBr_2$: C, 20.50; H, 1.72; Cr, 17.75. Found: C, 21.58; H, 1.78; Cr, 17.86. ^1H NMR (CD_2Cl_2, 295 K) δ 168; E_p (CH_2Cl_2, TBAHFP, Ag/AgCl) 120 mV.

Synthesis and Structure of a Tungstacyclopentatriene

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Metallacyclic compounds of the transition elements constitute an important class of organometallic species, implicated in a wide range of both stoichiometric and catalytic reactivity.[2-6] Besides

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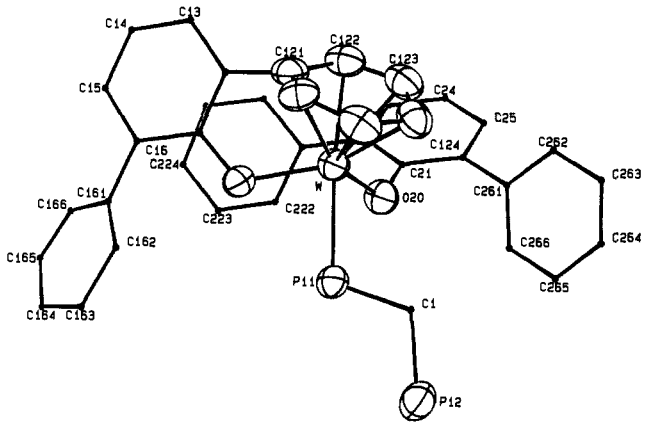


Figure 1. ORTEP view of $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(OAr\text{-}2,6,6Ph_2)(dppm)$ (**1**) emphasizing the central coordination sphere and with the dppm phenyl groups omitted. Selected bond distances (Å) and angles (deg) are as follows: W–P(11) = 2.502 (2), –O(10) = 2.038 (5), –O(20) = 1.986 (5), –C(121) = 2.190 (7), –C(122) = 2.283 (8), –C(123) = 2.301 (8), –C(124) = 2.240 (8), –C(125) = 2.299 (7), –C(126) = 2.354 (7), P(11)–W–O(10) = 79.9 (1), –O(20) = 81.0 (2), O(10)–W–O(20) = 116.8 (2), W–O(10)–C(11) = 119.0 (4), W–O(20)–C(21) = 127.0 (5).

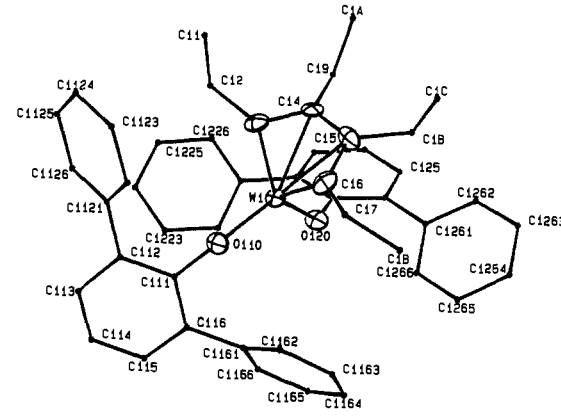
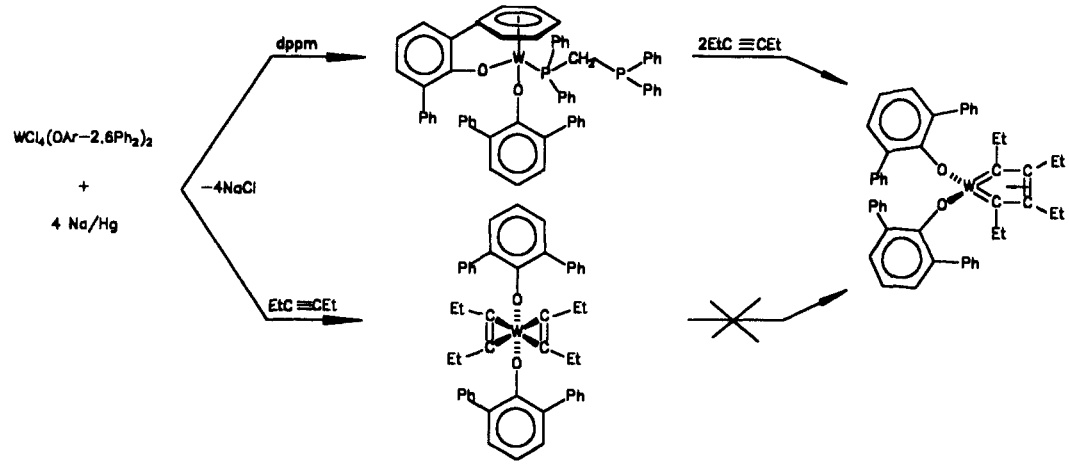


Figure 2. ORTEP view of $W(OAr\text{-}2,6Ph_2)_2(C_4Et_4)$ (**2**) (molecule 1) emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) are as follows: W(1)–O(110) = 1.854 (6), –O(120) = 1.927 (5), –C(13) = 1.891 (9), –C(14) = 2.341 (8), –C(15) = 2.389 (8), –C(16) = 1.912 (9), C(13)–C(14) = 1.42 (1), C(14)–C(15) = 1.40 (1), C(15)–C(16) = 1.42 (1), O(110)–W(1)–O(120) = 116.1 (2), W(1)–O(110)–C(111) = 154.5 (5), W(1)–O(120)–C(121) = 136.3 (5). There are no significant differences for these parameters in molecule 2 except fot the angles O(210)–W–O(220) = 121.1 (2)° and W(2)–O(220)–C(221) = 131.0 (5)°.

Scheme I



reactivity studies, these compounds have also been the focus of much theoretical attention concerning their structure and bonding.[7,8] Recently, a series of heteroatom-substituted five-membered metallacycles of the group 4[9] and group 5[9,10] metals have been isolated by the intramolecular coupling of η^2-acyl, η^2-iminoacyl, and related functional groups. The lack of planarity of the majority of these and related metallacycles has led to a number of theoretical studies.[10,11] We wish to report here a new type of early transition-metal metallacycle formed by the apparent reductive coupling of two acetylene fragments at a W(II) (d^4) metal center. Structural studies strongly implicate the description of this new ring as a tungstacyclopentatriene[7,8,10] and not as a metallacyclopentadiene[2] as has been well documented for other systems. Consistent with this formulation is the definite lack of planarity of the new metallacycle ring.

The reduction of toluene solutions of the tetrachloride $WCl_4(OAr\text{-}2,6Ph_2)_2$ ($OAr\text{-}2,6Ph_2$ = 2,6-diphenylphenoxide)[12] with sodium amalgam (4 Na per W) in the presence of dppm leads to a dark brown-green suspension. The workup of this product mixture allows the isolation of emerald green crystals of stoi-

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(13) A solution containing $W(OAr\text{-}2,6\ Ph_2)_2Cl_4$ (1.50 g, 1.8 mmol) and dppm (0.76 g, 2.0 mmol) in toluene (50 mL) was stirred vigorously over a sodium amalgam containing Na metal (0.17 g, 7.4 mmol) for 24 h. The resulting green suspension was decanted off the Hg pool and filtered, and the filtrate was concentrated to yield highly air and moisture sensitive green blocks of **1**. Typical yield = 56%. Anal. Calcd for $WP_2O_2C_{61}H_{48}$(**1**): C, 69.20; H, 4.57; P, 5.85. Found: C, 70.82% H, 5.25; P, 5.58. The ^1H NMR of **1** (C_6D_6,30 °C) shows the five nonequivalent protons of the η^6-C_6H_5 bound ring as multiplets at δ 1.71 (t), 2.77 (t), 3.15 (d), 3.38 (t), 4.62 (d); δ 1.78 (t, PCH_2P); [^1H] ^{31}P NMR (C_6H_6,30 °C) δ + 55.2 (W–*P*), –24.8 (W–PCH_2P), $^2J(^{31}P–^{31}P)$ = 65 Hz.

(14) Crystal data for $WP_2O_2C_{61}H_{48}$ (**1**) at 20 °C: a = 15.008 (2) Å, b = 39.449 (3) Å, c = 9.854 (2) Å, β = 105.86 (1)°, V = 5612 (3) Å^3, Z = 4, d_{calcd} = 1.253 g cm^{-3} in space group $P2_1/c$. A total of 7458 unique intensities were collected by using Mo Kα radiation, 4° ≤ 2θ ≤45°, of which 5247 with $I>3\sigma(I)$ were used in the final refinement. Final residuals are R = 0.042, R_w = 0.068.

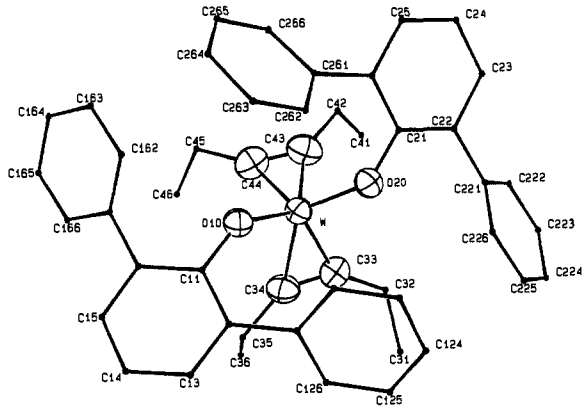

Figure 3. ORTEP view of $W(OAr\text{-}2,6Ph_2)_2(EtCCEt)_2$ (**3**) emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) are as follows: W–O(10) = 1.960 (3), –O(20) = 1.959 (3), –C(33) = 2.008 (4), –C(34) = 2.032 (4), –C(43) = 2.017 (5), –C(44) = 2.016 (5), C(33)–C(34) = 1.299 (7), C(43)–C(44) = 1.292 (7), O(10)–W–O(20) = 102.7 (1), C(33)–W–C(34) = 37.5 (2), C(43)–W–C(44) = 37.3 (2), W–O(10)–C(11) = 136.09 (2), W–O(20)–C(21) = 131.3 (2).

chiometry $[W(OAr\text{-}2,6Ph_2)_2(dppm)]$ (**1**) (Scheme I, Figure 1[13,14]) shown to be a 16-electron complex containing both a monodentate dppm ligand as well as a 2,6-diphenylphenoxide ligand chelated to the metal through an η^6-interaction with one of the side-chain aryl groups.[15] Compound **1** reacts readily with a number of unsaturated small molecules. In the case of 3-hexyne, reaction with 2 or more equiv in toluene leads to rapid formation of an orange solution whose ^1H NMR spectrum shows the presence of uncoordinated dppm along with a number of new species. The major component of the reaction mixture, **2**, (Scheme I) can be obtained as orange crystals on slow cooling.[16] A single-crystal X-ray diffraction analysis of **2** (Figure 2)[17] shows it to contain a "$W(OAr\text{-}2,6Ph_2)_2$" fragment as part of a five-membered metallacylcle ring formed by the apparent coupling together of two EtC≡CEt ligands (vide infra). A number of features of this metallacycle prove to be of particular interest. First the W–C(α) distances lie in the range 1.891 (9)–1.929 (9) Å. This distance is too short to be considered a tungsten–carbon single bond but is much more consistent with distances present in tungsten alkylidene ($W{=}CR_2$) functionalities.[18] Furthermore, there is considerable bending of the metallacycle ring with a fold angle[9] of 60.2 (4)°. This bending brings the outer two carbons of the metallacycle ring into close proximity to the metal. The distances to these carbons, 2.328 (9)–2.389 (9) Å, are slightly larger than the distances found in **1** between the tungsten metal center and the chelated η^6-arene ring carbon atoms (Figure 1). These structural parameters lead us to formulate **2** as containing a metallacyclopentatriene ring which, unlike all planar metallacyclopentadiene rings previously studied,[19] is bent. The bending of the metallacycle ring is analogous to that seen in isoelectronic, heteroatom-substituted metallacycles such as in the compounds $(OAr)_2M[R'NC(R){=}C(R)NR']$ (M = Ti, Zr, Hf) (diazametallacyclopentenes)[9] and $CpClTa[R'NC(R){=}C(R'')C(R'')]$-azametallacyclopentadienes).[10] Spectroscopic data on **2** indicates not only the presence of the bent metallacycle ring in solution but also the presence of a significant (>18 Kcal mol^{-1}) barrier to inversion of the ring.[16]

Attempts to prepare **2** by reduction of $WCl_4(OAr\text{-}2,6Ph_2)_2$ in the presence of EtC≡CEt led instead to the moderate yield formation of the bis(alkyne) complex **3** as the major product[20] (Scheme I). Careful analysis (^1H NMR) showed 15–25% of **2** to be present in the crude reaction mixture along with traces of hexaethylbenzene. A structural study of **3** (Figure 3)[21] shows the presence of the two uncoupled 3-hexyne ligands oriented parallel to each other. Spectroscopic data on **3**[22] is consistent with the acetylene groups acting as four-electron donor ligands (using Templeton's criteria)[23] as well as undergoing restricted rotation of the ^1H NMR time scale at low temperatures.

All attempts so far to intramolecularly couple the two acetylene units in **3** to form **2** have failed. Thermolysis of **3** (60 °C, days) or photolysis of **3** as well as its treatment with EtC≡CEt or dppm did not generate any significant amounts of **2**. Previous work has also shown that intramolecular coupling of acetylene units in W(II) bis-acetylene compounds is not a facile reaction.[24-28] Hence, further work is planned on elucidating the pathway whereby **2** is formed from **1** as well as the reactivity of the new type of metallacycle ring found in **2**.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8612063) for support of the research. NSF support

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(16) To a solution of **1** (0.25 g, 0.24 mmol) in toluene (25 mL) was added 3-hexyne (0.06 g, 0.73 mmol) via a syringe. An immediate color change from green to orange occurred. Removal of solvent under vacuo followed by saturation with hexane gave a clear orange solution and solid dppm. Slow evaporation of the solution produced red blocks of **2** in typical yields of 60%. Selected spectroscopic data on **2**: ^1H NMR (C_6D_6, 30 °C) two ABX_3 patterns due to the diastereotopic CH_3CH_2 groups are present at δ 3.31, 3.22 and δ 1.48, 1.10. The latter signal overlaps the corresponding methyl resonance at δ 1.09 causing a complex resonance pattern. The second CH_2CH_3 triplet is well resolved at δ 0.81. These resonances remain sharp up to 60 °C: ^{13}C NMR (C_6D_6, 30 °C) δ 249.6 ($W{=}C(\alpha)$), 91.5 (β-C), 20.1, 32.7 (CH_2CH_3), 15.9, 16.2 (CH_2CH_3).

(17) Crystal data for $WO_2C_{48}H_{46}$ (**2**) at −114 °C: a = 11.086 (2) Å, b = 18.400 (7) Å, c = 19.453 (5) Å, α = 98.96 (2)°, β = 97.14 (2)°, γ = 98.67 (2)°, Z = 4, d_{calcd} = 1.454 g cm^{-3} in space group $P\bar{1}$. A total of 9981 unique data were collected by using Mo Kα; 4° ≤ 2θ ≤ 45°, of which 7124 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are R = 0.046, R_w = 0.055.

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(19) In compound **2** the C(β)–C(β') distances are slightly shorter than the C(α)–C(β) or C(α')–C(β') distances for both molecules 1 and 2. This contrasts markedly with known planar metallacyclopentadiene structures where the pattern is reversed. See ref 8 and (a) Mague, J. T. *Inorg. Chem.* **1970**, *9*, 1610. (b) Mague, J. T. *Inorg. Chem.* **1973**, *12*, 2649. (c) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. (d) Pierpont, C. G.; Downs, H. H.; Itoh, K.; Nishiyama, H.; Ishii, Y. *J. Organomet. Chem.* **1977**, *124*, 93. (e) Gastinger, R. D.; Rausch, M. D.; Sullivan, D. A.; Palenik, G. J. *J. Organomet. Chem.* **1976**, *117*, 355. Probably the most dramatic comparison is between **2** and the tantalacyclopentadiene $Ta(OAr\text{-}2,6Pr^i_2)_3(C_4Et_4)$ reported recently by Wigley et al. Here definite Ta–C(α) single bonds are present with C(α)–C(β) = 1.33 Å (av) and C(β)–C(β') = 1.49(i) Å. See: Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics*, submitted for publication.

(20) Analysis calcd for $WO_2C_{48}H_{46}$ (**3**): C, 68.74; H, 5.53. Found: C, 68.63; H, 5.92.

(21) Crystal data for $WO_2C_{48}H_{46}$ (**3**) at 20 °C: a = 11.458 (1) Å, b = 17.961 (4) Å, c = 10.915 (2) Å, α = 104.65 (1)°, β = 115.23 (1)°, γ = 92.08 (1)°, Z = 2, d_{calcd} = 1.437 g cm^{-3} in space group $P\bar{1}$. A total of 5049 unique intensities were measured with Mo Kα, 4° ≤ 2θ ≤ 45°, of which 4449 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are R = 0.023, R_w = 0.030.

(22) Selected spectroscopic data on **3**: ^1H NMR (C_6D_6, 30 °C) δ 0.94 (q, CH_2CH_3; this resonance begins to broaden at −60 °C but limiting low-temperature spectra were not obtained), 0.54 (t, CH_2CH_3), 6.5–7.6 (m, aromatics); ^{13}C NMR (C_6D_6, 30 °C) δ 215.6 (C_2Et_2), 27.6 (CH_2CH_3), 13.7 (CH_2CH_3).

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Supplementary Material Available: Listing of positional parameters, general temperature factors, and bond distances and angles for **1-3** (51 pages); listings of structure factor amplitudes for **1-3** (118 pages). Ordering information is given on any current masthead page.

Cell-Free Biosynthesis of Nocardicin A from Nocardicin E and *S*-Adenosylmethionine

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The precursors in primary metabolism of the monocyclic β-lactam antibiotic nocardicin A (**7b**) are the L-isomers of methionine (**1**), serine (**2**), and (*p*-hydroxyphenyl)glycine (**3**, PHPG).[1,2] The possible intermediacy of tripeptide **4** or a related derivative became more likely recently with the discovery that nocardicin G (**5**), the simplest of the seven known nocardicins, gave a remarkably efficient and intact incorporation into nocardicin A,[3] whereas its 2′-epimer suffered only degradation to L-PHPG. The central role of nocardicin G as the first β-lactam-containing intermediate of the pathway and its biosynthetic relation to nocardicin A involves the ordering of an amine oxidation step to generate the C-2′ oxime,[4] the attachment of a homoserine residue from methionine, and an epimerization event in which C-9′ undergoes inversion from the L- to the D-configuration. In this communication we describe the first preparation of a partially purified cell-free system from *Nocardia uniformis* subs. tsuyamanensis (ATCC 21806) and demonstrate its effectiveness in the conversion of nocardicin E (**6**) to isonocardicin A (**7a**) in the presence of *S*-adenosylmethionine (AdoMet) and in the epimerization of the latter to nocardicin A (**7b**).

Compared to transmethylation reactions, 3-amino-3-carboxypropyl transfers from methionine are rare. However, apart from the case of nocardicin A, important examples have been demonstrated or implied in the biosynthesis of, for example, discadenine,[5] X-base,[6] Y-base[7] (modified tRNA bases), diphthamide[8] (EF-2 site of ribosylation by diphtheria toxin), nicotianine,[9] mugineic acid, and related compounds of this series.[10] Recent whole-cell experiments in *N. uniformis* with (2*S*,4*R*)- and (2*S*,4*S*)-[4-^{2}H]methionine have shown that the overall stereochemical course of 3-amino-3-carboxypropyl transfer in **7b** is inversion.[11] This finding paralleled the steric course observed in polyamine biosynthesis[12] from decarboxylated AdoMet and suggested a role for AdoMet itself in nocardicin A formation.

Cell-free extracts of *N. uniformis* were prepared under a variety of conditions. Those obtained from washed cells, harvested after the onset of nocardicin A production, by ultrasonication in the presence of added glycerol and protease inhibitors were found to be sufficiently stable to be processed through nucleic acid and ammonium sulfate precipitation steps and dialysis.[13] Incubation[14] of nocardicin E (**6**), obtained by total synthesis,[15] and AdoMet with this partially purified extract revealed an efficient, time-dependent conversion[16] of **6** to a product that appeared to be nocardicin A (**7b**) on the basis of its HPLC retention time[17] and UV spectrum. However, direct displacement of AdoMet would be expected to give isonocardicin A (**7a**, LLD) as its initial product rather than nocardicin A (**7b**, DLD). A sample of isonocardicin A[18] was found to be indistinguishable from nocardicin A[19] not only by 400 MHz ^{1}H NMR spectroscopy but also by HPLC retention time under a range of conditions. Recalling a similar analytical difficulty in discriminating between penicillin N and its LLD-diastereomer isopenicillin N, **7b** was epimerized in aqueous pyridoxal[20] to a mixture of **7a** and **7b** as evidenced by a control experiment run in deuterium oxide in which the disappearance of H-9′ was monitored by ^{1}H NMR spectroscopy.[2] Derivatization of the reaction products with 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate (GITC)[21] and HPLC analysis of the resulting thioureas as described by Neuss et al.[22] gave two resolved peaks at t_R 20 and 23 min. These were identified as corresponding to the GITC derivatives of **7a** and **7b**, respectively, on comparison with authentic samples. Similar analyses, then, of the partially purified products from the cell-free incubations of **6** and AdoMet revealed a mixture of **7a** and **7b** typically in ratios of 2:1 to 3:2, indicating the presence of an epimerase activity capable of interconverting isonocardicin A and nocardicin A. This epimerase activity was readily confirmed by incubation of pure **7b** with the cell-free system and demonstration of its equilibration to similar mixtures of **7a** and **7b**.

To establish unambiguously the intact conversion of **6** to **7a**/**7b**, a specimen of [2′-^{13}C]nocardicin E (**6**) was prepared from a

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