a cyclic carbamate moiety on the pendant desosamine residue delivered the tetraol **8** in 53% yield. Selective oxidation[8] of the primary hydroxyl gave the requisite seco-acid **9** in 78% yield, thereby setting the stage to test the crucial macrocyclization step.[9]

In the event, subjection of **9** to the highly effective Yamaguchi macrolactonization protocol[9h,j] afforded a separable mixture (1:2.4:1; 96% combined yield) of the desired 14-membered lactone **10** together with two isomeric lactones. On the basis of spectral evidence, these two substances have been tentatively identified as the C(2)-epimeric seven-membered lactones **11**; however, these structural assignments must be confirmed. Cyclization of **9** could also be effected via its 2-pyridyl thioester,[9c] but lactonization under these conditions was considerably less efficient and provided primarily a mixture of the two lactones **11** together with only a small amount of **10** (49% combined yield). An authentic sample of **10** for purposes of comparison was prepared directly from **7** [$COIm_2$ (5 equiv), toluene, reflux, 20 h; 10% aqueous Na_2CO_3, room temperature, 16 h; 71%]. The formation of a seven-membered lactone as **11** from **9** was surprising, since there have been a number of reports of successful cyclizations of erythronolide seco-acid derivatives bearing unprotected hydroxyl groups at C(6) and C(12) to provide 14-membered lactones as the exclusive products.[10] Inasmuch as there were preliminary indications that **10** and **11** might interconvert under certain conditions, we were also concerned that the 14-membered lactone might arise from translactonization of the seven-membered lactone intermediate rather than by direct cyclization.[11]

In order to improve the efficiency of the macrolactonization and to circumvent the possibility of translactonization processes, the fully protected seco-acid derivative **14** was prepared in eight steps (27% overall yield) from **12**, which was an intermediate in the previous synthesis of **9** (Scheme III). The success of this sequence lay in the significant difference in the chemical reactivity of the four hydroxyl groups, which followed the order C(1) ≫ C(4″) > C(13) ≫ C(6), thereby allowing selective protection and manipulation of each hydroxyl function. When **14** was subjected to the conditions of the Yamaguchi lactonization protocol,[9h] the protected derivative of erythromycin B (**15**) was obtained in 53% yield. An authentic sample of **15** for comparison was prepared independently from erythromycin B (**1**) in eight steps,[12] and the two compounds thus obtained were identical by ^1H and ^{13}C NMR. Several preliminary attempts to effect the cyclization of **14** under conditions previously defined by Corey[9c] or Keck[9i] did not afford detectable amounts of the desired lactone **15**.

The novel macrolactonizations of **9** and **14** establish for the first time that carbohydrate residues on the hydroxyl functions at C(3) and C(5) provide sufficient restriction of rotational freedom along the C(1)–C(8) segment of the erythromycin seco-acid backbone for macrolactonization to occur. This exciting discovery should greatly simplify the synthesis of the natural antibiotics themselves and allow facile accessibility to unusual analogues. Indeed, application of this tactical device to a practical total synthesis of erythromycin B is the subject of current investigation, the results of which will be reported in due course.

Acknowledgment. We thank the National Institutes of Health (GM 31077), the Robert A. Welch Foundation, and Abbott Laboratories for their generous financial support of this research. We are also grateful to Drs. Paul Lartey, Richard Pariza, and William Baker (Abbott Laboratories) for helpful technical discussions regarding procedures required to elaborate erythromycin B (**1**) into **7** and for liberal supplies of **1**.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of intermediates in Schemes II and III and footnote 12 and of authentic samples of **10** and **15** (55 pages). Ordering information is given on any current masthead page.

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(10) See refs 3b,e,h,n–p,r,s, and 9j.

(11) More recent experiments have cast doubt on at least some aspects of this hypothesis. For example, when **10** was subjected to several conditions known to effect translactonization, there was no evidence for the formation of compounds **11**; decomposition pathway seemed dominant. However, we have not determined whether **11** might be transformed into **10**, since it is difficult to isolate either diastereoisomer in pure form.

(12) The sequence of reactions and the unoptimized yields for each step were as follows: (a) I_2, MeOH, *hν* (96%). (b) Cbz-Cl, DMAP (95%). (c) MeI, KOH, DME-DMSO (75%).[13] (d) $NaBH_4$, MeOH, 0 °C (71%). (e) $MeCH(OEt)_2$, PPTS, CH_2Cl_2 (62%). (f) H_2, 10% Pd–C, aqueous EtOH–acetate buffer (pH = 4.8) (85%). (g) $COIm_2$, toluene, reflux; 10% aqueous Na_2CO_3–THF (94%). (h) BnBr, Bu_4NI, KH, 18-crown-6, THF (92%).

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Synthesis and Reactivity of $[Re(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3]^-$ and the X-ray Structure of $Hg[Re(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3]_2$

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Recently synthesized trigonal-planar $Os(NAr)_3$ (NAr = N-2,6-C_6H_3-*i*-Pr_2)[1] has been shown to have limited reactivity.[2] Since relatively labile and reactive rhenium(V) bisimido complexes have been prepared recently,[3] we became interested in preparing what we hoped to be relatively reactive $[Re(NAr)_3]^-$. We report here the synthesis and some reactions of this species along with an X-ray study of $Hg[Re(NAr)_3]_2$.

$Re(NAr)_3Cl$[4] is cleanly reduced by 2 equiv of sodium amalgam in THF to give $[Na(THF)_2][Re(NAr)_3]$ (**1a**). $[NEt_4][Re(NAr)_3]$ (**1b**) is formed if NEt_4Cl is present. Since **1a** is soluble in toluene, sodium may be bound to nitrogen (cf. lithium salts of anionic W(VI) and Mo(VI) imido complexes[5]) or directly to rhenium (cf. **4** below). **1b** is not soluble in toluene or ether. If only 1 equiv of sodium amalgam is employed, the pentane-soluble product has the formula $Hg[Re(NAr)_3]_2$ (**1c**). We speculate that reduction to give $Re(NAr)_3$ radicals occurs first and that two of these then attack Hg to give **1c**. The structure of **1c**, as determined in an X-ray study, is shown in Figure 1.[6] The Hg–Re distance [2.621 (1) Å] is consistent with its being a single bond. The linear imido ligands (Re=N—C 173 (1)°) are arranged in a "propellar" fashion, and the two ends are staggered with respect to each other (S_6 symmetry). The Re=N bonds [1.76 (1) Å] are longer than the Os=N bonds (1.737 Å average) found in $Os(NAr)_3$. The

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(6) Crystals were mounted on glass fibers in air. Data were collected on a Rigaku AFC6R diffractometer at room temperature using Mo Kα radiation (space group $Pa\bar{3}$ with a = 19.548 (6) Å, Z = 4, FW = 1624.64, and ρ = 1.444 g cm^{-3}). A total of 4214 reflections were collected in the range $3° < 2\theta < 55°$ with 638 having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (123 variables) using the TEXSAN crystallographic software package from Molecular Structure Corporation; final R_1 = 0.034, R_2 = 0.036. Full details can be found in the supplementary material.

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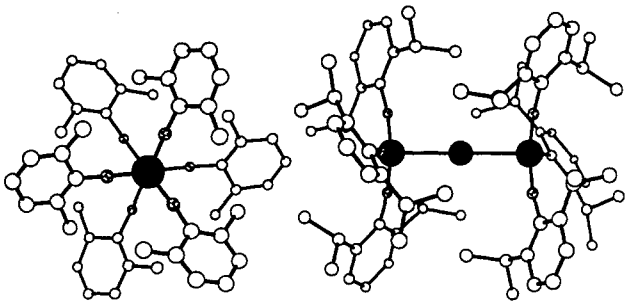
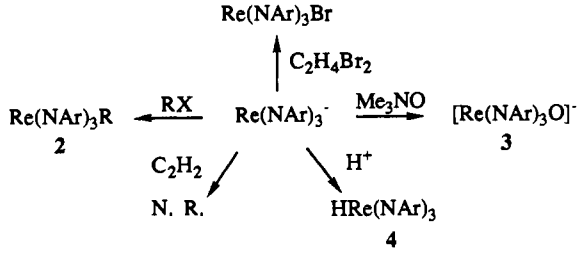


Figure 1. Two views of the structure of $Hg[Re(NAr)_3]_2$ (**1a**). Re-Hg-Re = 180.00°, Hg-Re-N = 97.4 (4)°, N-Re-N = 118.4 (2)°, Re-N-C(1) = 173 (1)°, Hg-Re = 2.621 (1) Å, Re-N = 1.76 (1) Å.

Scheme I



fact that Hg-Re-N = 97.4 (4)°, between the 90° expected for purely ionic bonding of Hg to an unperturbed trigonal-planar anion and the 109° expected for tetrahedral coordination, is evidence that the structure of the free anion probably is trigonal planar.[7] The HOMO in such a trigonal-planar species is likely to be a d_{z^2} orbital, and one pair of electrons should be in a nitrogen-centered nonbonding molecular orbital (A_2 in C_{3v}), is in $Os(NAr)_3$.[1,2]

Some reactions of **1a** or **1b** are summarized in Scheme I. Alkylations with MeI and 2,4,6-trimethylbenzyl chloride to give $Re(NAr)_3(Me)$ (**2a**) and $Re(NAr)_3(CH_2\text{-}2,4,6\text{-}C_6H_2Me_3)$ (**2b**) are very fast (~30 s at 25 °C) and take place in high yield (>90%). Although **1b** reacts with Me_3NO to give $NEt_4[Re(NAr)_3O]$ (**3**), no reaction with ethylene, acetylene, or acetone is observed. **1b** does not oxidize phosphines to give $[Re(NAr)_2(PR_3)_2]^-$ and $R_3P{=}NAr$, as does $Os(NAr)_3$,[1] consistent with the greater oxidizing ability of Os(VI) compared to Re(V). The greater nucleophilicity of $[Re(NAr)_3]^-$ compared to $Os(NAr)_3$ can be ascribed to its overall negative charge, as well as the greater ease of forming Re(VII) from Re(V) versus Os(VIII) from Os(VI).

Addition of H^+ to **1b** (as 2,6-di-*tert*-butylpyridinium triflate) affords $HRe(NAr)_3$ (**4**). In the ^1H NMR spectrum of **4** at temperatures as low as −85 °C, the imido ligands are equivalent and a sharp singlet resonance of area 1 is observed at 7.3 ppm. Upon addition of CCl_4, that resonance disappears and $Re(NAr)_3Cl$ and $CHCl_3$ are formed, a reaction typical of a transition metal hydride complex. No ν(ReH) absorption has yet been identified in the IR spectrum of **4**. Compound **4** reacts only very *slowly* with acetylene, 2-butyne, and norbornene to give $Re(NAr)_2(NHAr)(C_2H_2)$ (**5a**), $Re(NAr)_2(NHAr)(C_2Me_2)$ (**5b**), and $Re(NAr)_2(NHAr)$(NBE) (**5c**), respectively, perhaps because the reactive intermediate is "$Re(NAr)_2(NHAr)$", which is in equilibrium with **4**. NMR data for complexes of type **5** are consistent with a rigid pseudotetrahedral core geometry in which the π-bonding ligand does not rotate about the ligand(centroid)-metal axis, the two carbon atoms lie in the Re-C-C-N(amido) plane, and rotation about the Re-N bond is relatively fast on the NMR time scale. Compound **4** also reacts with PMe_3 to give $Re(NAr)_2(NHAr)(PMe_3)$ (**6**). **5** and **6** are analogous to recently reported d^2 bisimido complexes of W(IV),[8] Re(V),[3] and Os(VI).[2]

(7) An X-ray study of the PPN^+ salt of **1** is in process.
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(9) Reference deleted in press.

Hydrido/imido complexes are extremely rare. We believe $Cp^*_2Ta(NH)(H)$ to be the only other d^0 example; it is the product of oxidative addition of ammonia to "$Cp^*_2Ta(CH_3)$", which is present in small equilibrium concentration in a solution of $Cp^*_2Ta(CH_2)H$.[10]

The chemistry reported here provides further evidence for the enhanced stability of d^2 trigonal-planar trisimido species and pseudotetrahedral 14-electron molecules containing the $M(NAr)_2$ core. Other d^2 trigonal-planar molecules that have been observed or isolated recently include $Ta[OSi(t\text{-}Bu)_3]_3$[11] and W(N-*t*-Bu)$[OSi(t\text{-}Bu)_3]_2$.[12] $M(NAr)_2$ species show some characteristics of being 18-electron "metallocene-like" complexes, members of a potentially large class of species containing combinations of $2\pi,1\sigma$ ligands (η^5-C_5R_5, NR, O, and CR). Further studies will be aimed at developing the chemistry of these and other d^2 systems.

Acknowledgment. We thank the National Science Foundation (CHE 88-22508) for research support.

Supplementary Material Available: Experimental procedures, NMR data, and analytical data, a labeled ORTEP drawing of **1a**, experimental details of the X-ray study of **1a**, and tables of final positional parameters and final thermal parameters for **1a** (10 pages); table of final observed and calculated structure factors for **1a** (5 pages). Ordering information is given on any current masthead page.

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DNA Photodamage Mechanistic Studies: Characterization of a Thietane Intermediate in a Model Reaction Relevant to "6-4 Lesions"

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Received April 5, 1991
Revised Manuscript Received May 20, 1991

The (6-4) pyrimidine-pyrimidinone photoproducts and cis-syn cyclobutane dimers are the major photolesions occurring at dipyrimidine sequences in DNA when exposed to the UV portion of sunlight.[1] Whereas the mechanism of solar-induced skin cancers remains only partially understood, these lesions are widely recognized as causative of tumor development.[2] Although no experimental proof was ever produced, the mechanism of (6-4) photoproduct formation, such as in dideoxynucleotide model systems,[3] is thought to proceed via a short-lived oxetane,[4] azet-

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