series,[11] and, in the ground state, it has a 4-fold greater restoring force than $Rh_2b_4^{2+}$.

The variation in metal–metal bond distances among the binuclear platinum and rhodium complexes is informative (Table I). We infer from the ~0.3 Å shorter ground-state M–M bond distance that diphosphite is substantially more constraining than the bridging isocyanide. As a result, the decrease in bond length upon excitation or oxidation is larger for $Rh_2b_4^{2+}$ than for $Pt_2(pop)_4^{4-}$. In each case, however, the structural and spectroscopic properties of the M–M bond in the triplet excited state closely approximate those of the corresponding dichloro $(d\sigma)^2$ d^7-d^7 species, thereby attesting to the utility of the $(d\sigma)^2$ $(d\sigma^*p\sigma)$ (i.e., single M–M bond) formulation of $^3A_{2u}$. Important additional information about M–M interactions in these binuclear complexes should be obtained from studies now underway on the products of the excited-state electron-transfer quenching reactions.

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(11) Another spectroscopic manifestation of the large Pt–Pt bond compression is the high energy (~3.8 eV)[7] of the $d\sigma \rightarrow d\sigma^*$ transition in the $^3d\sigma^*p\sigma$ state of $Pt_2(pop)_4^{4-}$ relative to $Rh_2b_4^{2+}$ (~3 eV).[2]

Synthesis of Conduritol A from Benzoquinone Using 9-[(Benzyloxy)methoxy]anthracene as a Protecting and Directing Group

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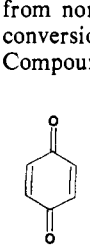
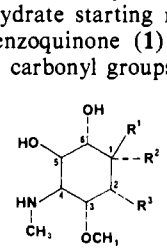
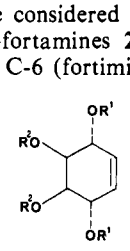
As part of our efforts[2] to synthesize aminocyclitol antibiotics[3] from non-carbohydrate starting materials, we considered the conversion of benzoquinone (**1**) to the (±)-fortamines **2**.[4,5] Compound **1** has carbonyl groups at C-3 and C-6 (fortimicin



1



2a: $R^1 = NH_2$, $R^2 = H$, $R^3 = OH$
2b: $R^1 = NH_2$, $R^2 = H$, $R^3 = H$
2c: $R^1 = H$, $R^2 = NH_2$, $R^3 = H$

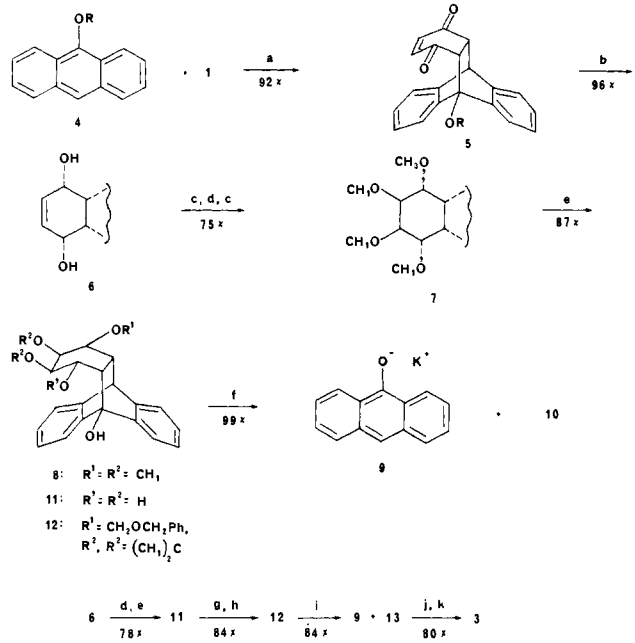


3: $R^1 = R^2 = H$
10: $R^1 = R^2 = CH_3$
13: $R^1 = CH_2OCH_2Ph$, $R^2, R^2 = (CH_2)_2C$

numbering), which might be reduced to the *cis*-3,6-dihydroxy functionality. Formal oxyamination and hydroamination of the C=C bonds of **1** would complete the functionalization. In order to implement these ideas we chose to preserve the enedione part structure of **1** by protecting one C=C bond. The protecting agent would be maximally effective if it (a) protects one C=C bond of **1** without introducing any reactive functional groups, (b) blocks one face of **1** to direct *cis* reduction at C-3 and C-6 and *cis* functionalization of the remaining C=C bond, (c) allows the differentiation of the C-3 and C-6 hydroxyls, and (d) may be removed under mild conditions. We wish to describe a protecting group that meets all these needs and, coincidentally, enables the first stereospecific synthesis of the naturally occurring cyclitol conduritol A (**3**).[6,7]

Reaction of **1** with 9-[(benzyloxy)methoxy]anthracene[8] (**4**, Scheme I, R = CH_2OCH_2Ph) gave the adduct **5**, in which one C=C bond and one face of **1** are now protected from attack by reagents. In addition, the presence of the (benzyloxy)methoxy group near one carbonyl group (*pro*-C-3, say) offers a means to distinguish it from C-6. Sodium borohydride–cerium(III) chloride[9] reduction of **5** at −78 °C gave the enediol **6**. The hydroxy groups were methylated, the remaining C=C bond was oxidized from the accessible face with osmium tetraoxide,[10] and the resulting diol was methylated to give the tetramethoxy compound **7**. This

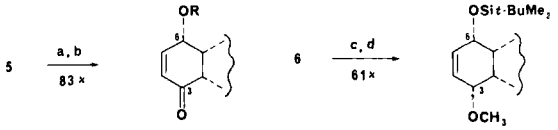
Scheme I



8: $R^1 = R^2 = CH_3$
11: $R^1 = R^2 = H$
12: $R^1 = CH_2OCH_2Ph$, $R^2, R^2 = (CH_2)_2C$

[a] Toluene, 68 °C, 15 h. [b] $NaBH_4$, $CeCl_3$, methanol, toluene, −78 °C. [c] CH_3I, NaH, THF. [d] OsO_4, NMO, acetone, water. [e] TFA, methanol, 40 °C. [f] KH, dioxane, 25 °C, 2 h. [g] Acetone, TFA, 65 °C. [h] R'Cl, NaH, THF. [i] KH, dioxane, 35 °C, 12 h. [j] Na, ammonia, ethanol, ether, −78 °C. [k] TFA, methanol.

Scheme II



14: R = H
15: R = Ac
16

[a] Bu_4NBH_4, dichloromethane, −78 °C. [b] Ac_2O, DMAP, pyridine, dichloromethane. [c] *t*-$BuMe_2SiOTf$, collidine, toluene, −100 °C. [d] CH_3I, KH, HMPA, THF, 0 °C.

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is formally the Diels–Alder adduct of **4** and tetra-*O*-methylconduritol A (**10**), but thermal retro-Diels–Alder reaction of **7** would not be expected to occur below 300 °C, since no activating groups are present on the dienophile.[11,12]

To liberate the protected C=C bond we relied instead on the remarkable "Evans accelerating effect" of the oxido group.[13,14] The requisite hydroxyl was revealed upon hydrolysis of the (benzyloxy)methyl protecting group (**7** → **8**). Treatment of a dioxane solution of **8** with potassium hydride generated the alkoxide, and fragmentation occurred *at room temperature*[15] to the potassium salt of anthrone (**9**)[16] and the olefin **10**.

To determine whether alcohol protecting groups[17] would survive the oxido-accelerated retro-Diels–Alder reaction, the pentol **11** was prepared (Scheme I), and the secondary hydroxyls were protected as the acetonide at C-4 and C-5 and the (benzyloxy)methyl ether at C-3 and C-6. Retro-Diels–Alder reaction gave the protected conduritol A derivative **13**. Either the acetonide or the (benzyloxy)methyl groups[18] could be removed from **13** selectively, and sequential deprotection afforded conduritol A (**3**) itself.[19] The overall yield of **3** from **1** was 39%.

Differentiation of the C-3 and C-6 carbonyl groups of **5** was achieved in two ways (Scheme II). Selective monoreduction of **5** using the tetrabutylammonium borohydride[21] gave a single hydroxy enone, **14**. The site of reduction was confirmed by acetylation, since the resulting acetoxy enone, **15**, showed a coupling pattern in the 360-MHz ^{1}H NMR spectrum consistent only with the structure shown. As an alternative, the enediol **6** was monosilylated using *tert*-butyldimethylsilyl triflate[22] at −100 °C, giving in 86% yield a 3:1 mixture of alcohols. Methylation of the major product afforded **16**, whose hydroxyls are now distinct and appropriately protected.

A variety of pathways may be formulated for transforming **14** or **16** to aminocyclitols **2**, and we are currently investigating these possibilities.

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Supplementary Material Available: Spectroscopic data (NMR, IR), melting points, and R_f's for new compounds (2 pages). Ordering information is given on any current masthead page.

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Two-Photon Excitation of d → d* Transitions in a Rhodium(III) Complex

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One of the challenging aspects of the study of second- and third-row transition series metal chelate complexes is the assignment of bands in absorption spectra. In particular, transitions to excited states of gerade microsymmetry, such as the metal-localized d → d*'s, are forbidden by symmetry arguments and are often obscured by symmetry-allowed (ungerade) bands of greater intensity. Since the determination of d → d* energies is of photophysical and photochemical importance, a technique that can probe these bands is of great interest. Two-photon excitation (TPE) is a nonlinear spectroscopic technique that selectively accesses gerade excited states by absorbing two photons of light simultaneously. TPE has been applied in studies of f → f* transitions in rare-earth metals[1-3] and d → d* bands in crystalline K_2PtCl_6.[4] We report the first TPE spectrum of d → d* bands in a metal chelate dissolved in a vitreous solvent, that of *cis*-dicyanobis(4,4′-dimethyl-2,2′-bipyridine)rhodium(III) chloride ($Rh(CN)_2(dmb)_2^+$).

A ~0.01 M solution of $Rh(CN)_2(dmb)_2^+$ in 4:1 ethanol–methanol was degassed by three freeze–pump–thaw cycles and sealed in a 4-mm o.d. glass capillary. An argon ion laser at 514.5 nm synchronously pumped a ring dye laser, providing a 96-MHz train of excitation pulses with peak powers of ~0.3–0.8 kW. The dye laser was continuously tunable from 570 to 620 nm, corresponding to excitation energies of 35 090–32 260 cm^{-1}. Laser light was focused on the sample, after cooling to 77 K, and phosphorescent emission from the chelate was collected at right angles, filtered with a double monochromator, and detected with an EMI 9558 cooled photomultiplier. A picoammeter voltage proportional to the photomultiplier current was sampled with a computer. Initially, the luminescence spectrum of the sample was measured by using single-photon excitation at 297 nm (obtained by frequency doubling the dye laser output). All spectral data agreed with that presented by Julander.[5] Subsequently, the one- and two-photon excited luminescence spectra were compared to confirm the origin of the emission. To generate an excitation spectrum, TPE intensities ($\lambda_{emission}$ = 471 nm) were measured at 1-nm intervals. At each wavelength the laser power was varied from zero to maximum in five evenly spaced steps. The resultant data were subjected to a linear regression of signal/average laser power vs. average laser power to verify the quadratic dependence of the luminescence intensity. An ancillary advantage of this approach is the ability to separate the total detector current into its one- and two-photon contributions.[6] The one-photon contribution was independent of the nature of the solute and was identified as residual laser scatter on the basis of polarization and optical filtering experiments. Spectral data resulting from regressions having a correlation coefficient less than 0.95 were rejected. The final TPE signal was corrected for laser pulse structure variations by utilizing a reference correction scheme.[7] Sequential two-photon processes involving real states with lifetimes greater than a few picoseconds were ruled out by ascertaining that the signal grew

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