Reference to the crystal structure of the divalent dimer $[cis\text{-}Pt^{II}(NH_3)_2(\mu\text{-}OH)]_2^{2+}$ [3a,c] revealed that oxidation to Pt(IV) has little effect on the geometry of the bridging four-membered ring. Comparative Pt–Pt distances and Pt–O–Pt bond angles for the two dimers respectively are 3.090 (1) Å, Pt(IV), 3.085 (1) Å, Pt(II), and 98.2 (3)°, Pt(IV), and 99 (1)°, Pt(II). Each of the water molecules of hydration shown in Figure 2 is within hydrogen-bonding distance of the bridging hydroxo group (3.332 Å) and the two terminal hydroxy ligands (O_w–O_2, 2.771 Å; O_w–$O_{3'}$, 3.067 Å).

In this work we show that it is possible to oxidize μ-hydroxo Pt(II) dinuclear compounds to dinuclear Pt(IV) species having the *cis*-diamine geometry. The antitumor and DNA binding properties of the new compounds will be reported subsequently.

Acknowledgment. This work was supported by grants from the American Cancer Society CH-296 and the Bristol Myers Co. We also wish to thank Johnson Matthey Inc. for supplying the platinum salts necessary for the synthesis of the compounds. Thanks also to C. Pfluger for help with interpretation of the X-ray structural data.

Supplementary Material Available: Tables of crystal data, bond distances, angles, atomic coordinates, and a numbered ORTEP plot of $[Pt(OH)_3(NH_2CH_2CH_3)_2]_2[NO_3][NO_2]\cdot 2H_2O$ (5 pages); table of observed and calculated structure factors for $[Pt(OH)_3(NH_2CH_2CH_3)_2]_2[NO_3][NO_2]\cdot 2H_2O$ (9 pages). Ordering information is given on any current masthead page.

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(13) The intensity of six reflections dropped uniformly as a nearly linear function of exposure time, 14% at the end of the first shell (3° ≤ 2θ(Mo Kα) ≤ 43°) and 30% at the end of the second shell (43° ≤ 2θ(Mo Kα) ≤55°). Reference to earlier work[11] and observation of the NO_3^- groups in the complex revealed that most likely one of the nitrate ions had undergone photolysis to NO_2^- in the X-ray beam.

Catalytic Effect of Nickel(II) Chloride and Palladium(II) Acetate on Chromium(II)-Mediated Coupling Reaction of Iodo Olefins with Aldehydes

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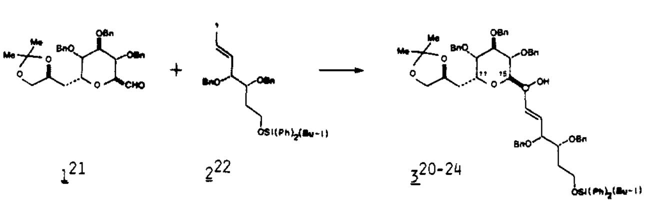
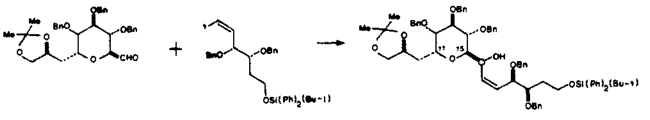
During the synthetic studies on the marine natural product palytoxin,[1-3] we were faced with a problem to transform the aldehyde **1** or its derivative into the trans-allylic alcohol **3**, which seemed possible by using routine synthetic operations. However, we soon realized that standard synthetic routes such as Wittig and aldol approaches were not as practical as we hoped.[3] Among many possibilities attempted, a coupling using organocuprates gave very promising results at least in the model series.[4] However, in spite of extensive efforts, we were unable to generate the desired organocuprate reagent from **2**.



1^{21} 2^{22} 3^{20-24}

1	2	$NiCl_2$(0.1%)-$CrCl_2$/DMSO	3 (ratio of 16α:16β stereoisomers)
1.0 eq	1.5 eq	ca. 1.5 eq	55% (1.3:1)
1.0 eq	1.5 eq	ca. 3 eq	60% (1.3:1)
1.0 eq	3.0 eq	ca. 6 eq	71% (1.3:1)
1.0 eq	10 eq	ca. 10 eq	80% (1.3:1)
1.0 eq	1.5 eq	3 eq of $Pd(OAc)_2$ (1%)-$CrCl_2$/DMSO	54% (1:1)
1.0 eq	3.0 eq	$CrCl_2$ (excess) with no added $NiCl_2$	0 ~ 80% (1.3:1)

The clue to the solution came from the work of Nozaki and his co-workers on chromium(II)-mediated addition of alkenyl halides to aldehydes.[5] After much trial-and-error experimentation, we were able to accomplish the required coupling by adding $CrCl_2$ to a DMSO solution of aldehyde **1** and trans-iodo olefin **2** at room temperature in the absence of oxygen. This reaction warrants several additional comments. First, we have examined a large number of highly oxygenated molecules, including α-oxygenated aldehydes and iodo olefins or β-iodo enones[6] and found the coupling to be remarkably effective even for multifunctional substrates. Functional groups tested include esters (methyl, ethyl), amides, nitriles, ketones, acyls (acetate, benzoate), acetals, ketals, ethers (benzyl, *p*-methoxybenzyl), silyl ethers [(*t*-Bu)(Me)$_2$Si, (*t*-Bu)(Ph)$_2$Si], alcohols, and olefins. Second, the stereochemistry of trans- as well as cis-iodo olefin is retained at least in the cases of disubstituted iodo olefins such as **2** and **4**.[7] Trisubstituted trans-iodo olefins and trans-iodo enones such as **6** and **10** gave the expected products; however, trisubstituted cis-iodo olefins and cis-iodo enones such as **9** and **12** yielded exclusively the trans olefins instead of the expected cis olefins.[8] Third, with respect to the newly introduced chiral center, this process produces a



1 4^{22} 5^{20-24}

1	4	$NiCl_2$(0.1%)-$CrCl_2$/DMSO	5 (ratio of 16α:16β stereoisomers)
1.0 eq	3.0 eq	ca. 6 eq	58% (1.6:1)
1.0 eq	3.0 eq	$CrCl_2$ (excess) with no added $NiCl_2$	0 ~ 60% (1.6:1)

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(1) For the gross structures of palytoxin, see: (a) Uemura, D.; Ueda, K.; Hirata, Y.; Naoki, H.; Iwashita, T. *Tetrahedron Lett.* **1981**, *22*, 2781 and references cited therein. (b) Moore, R. E.; Bartolini, J. *J. Am. Chem. Soc.* **1981**, *103*, 2491 and references cited therein. For the structures of minor constituents, see: Uemura, D.; Hirata, Y.; Iwashita, T.; Naoki, H. *Tetrahedron* **1985**, *41*, 1007.

(2) For the stereochemistry assignment primarily based on organic synthesis, see: Cha, J. K.; Christ, W. J.; Finan, J. M.; Fujioka, H.; Kishi, Y.; Klein, L. L.; Ko, S. S.; Leder, J.; McWhorter, W. W., Jr.; Pfaff, K.-P.; Yonaga, M.; Uemura, D.; Hirata, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7369 and preceding papers. For the sterochemistry assignment primarily based on spectroscopic methods, see: Moore, R. E.; Bartolini, G.; Barchi, J.; Bothner-By, A. A.; Dadok, J.; Ford, J. *J. Am. Chem. Soc.* **1982**, *104*, 3776.

(3) For synthetic studies on palytoxin, see: (a) Kishi, Y.; Christ, W. J.; Taniguchi, M. *Natural Products and Biological Activities*; Imura, H., Goto, T., Murachi, T., Narajima, T., Ed.; University of Tokyo Press: Tokyo, 1986; p 87 and references cited therein. (b) Still, W. C.; Galynker, I. *J. Am. Chem. Soc.* **1982**, *104*, 1774.

(4) The aldehyde **1** readily eliminates benzyl alcohol even under weakly basic conditions to yield the corresponding α,β-unsaturated aldehyde. This instability limited choices of reagents and conditions. Experimentally, we observed only organocuprates $[LiCu(CH_3)_2$, $LiCu(C_4H_9)_2$, $LiCu(c\text{-}CH{=}CHC_4H_9)_2]$ yielded the desired products in satisfactory yield. Furthermore, the addition of organocuprates almost exclusively gave the product with the desired stereochemistry at C16.

(5) Takai, K.; Kimura, K.; Kuroda, T.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 5281.

(6) This excludes α-acyloxy aldehydes; reductive elimination is the major side reaction for α-acyloxy aldehydes.

(7) Disubstituted trans-iodo enones gave exclusively expected trans enones. However, experiments using disubstituted cis-iodo enones still need to be done to conclude the stereospecificity of disubstituted β-iodo enones.

(8) The reaction of **9** with **7** in the presence of $NiCl_2$–$CrCl_2$ was very sluggish to yield only the trans olefin. It is interesting to note that the recovered iodo olefin from this reaction was pure **9**. There are examples known for the cis–trans isomerization during nickel-catalyzed reactions. See ref 17 and also: Zembayashi, M.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1975**, 1719.

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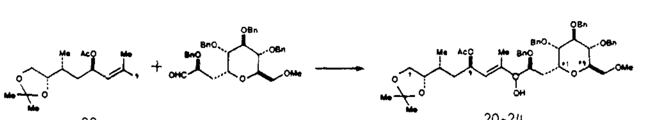
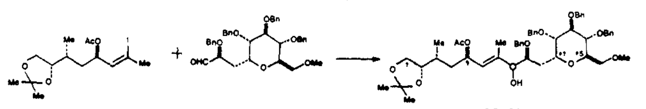


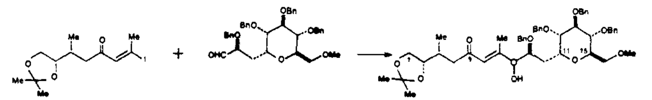
6[22] **7** **8**[20-24]

6	**7**	$NiCl_2$(0.1%)-$CrCl_2$/DMSO	**8** (ratio of 8α:8β stereoisomers)
1.5 eq	1.0 eq	ca. 1.5 eq	30% (2:1)
3.0 eq	1.0 eq	ca. 6 eq	72% (2:1)
10 eq	1.0 eq	ca. 10 eq	86% (2:1)
10 eq	1.0 eq	$CrCl_2$ (excess) with no added $NiCl_2$	0 ~ 64% (2:1)



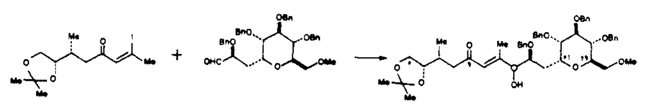
9[22] **7** **8**[20-24]

9	**7**	$NiCl_2$(0.1%)-$CrCl_2$/DMSO	**8** (ratio of 8α:8β stereoisomers)
10 eq	1.0 eq	ca. 10 eq	15% (2:1)
10 eq	1.0 eq	$CrCl_2$ (excess) with no added $NiCl_2$	0 ~ 15% (2:1)



10[22] **7** **11**[20-24]

10	**7**	$NiCl_2$(0.1%)-$CrCl_2$/DMF-$(Me)_2S$ (2:1)	**11** (ratio of 8α:8β stereoisomers)
10 eq	1.0 eq	ca. 10 eq	82% (5:1)
10 eq	1.0 eq	$CrCl_2$ (excess) with no added $NiCl_2$	0 ~ 63% (5:1)



12[22] **7** **11**[20-24]

12	**7**	$NiCl_2$(0.1%)-$CrCl_2$/DMF-$(Me)_2S$ (2:1)	**11** (ratio of 8α:8β stereoisomers)
10 eq	1.0 eq	ca. 10 eq	28% (5:1)
10 eq	1.0 eq	$CrCl_2$ (excess) with no added $NiCl_2$	0 ~ 20% (5:1)

mixture of two possible diastereomers with a moderate preference of one stereoisomer. It is worth mentioning that major products produced from α-alkoxy and α,β-bisalkoxy aldehydes have the stereochemistry opposite to cuprate or Grignard products.[9] Fourth, the reaction needs to be performed in the absence of oxygen. Fifth, DMSO was found to be critical, at least for the case of **1**, to realize the coupling reaction in high yield.[10]

The Cr(II)-mediated coupling reaction provided an excellent solution to our problem except one technical difficulty we had yet to overcome. Unlike the Cr(II)-mediated coupling of allyl halides with aldehydes,[11] the success of this coupling mysteriously depended on the source and batch of $CrCl_2$.[12] We also tested the homemade Cr(II) reagent without success.[13] These facts naturally suggested an intriguing possibility that the success of this reaction might depend on some unknown contaminant in $CrCl_2$. For this reason, we have examined the effect of transition metals for the Cr(II)-mediated coupling reaction and found that $NiCl_2$ and $Pd(OAc)_2$ have a dramatic effect. Although we have not yet established whether the effectiveness of some commercially available $CrCl_2$ is due to Ni and/or Pd salt or some other metal contaminant, *it is now possible to achieve the coupling using $CrCl_2$ from any source with excellent reproducibility*.[14-16] It is important to keep the $NiCl_2$ and $Pd(OAc)_2$ content in $CrCl_2$ low (about 0.1-1% w/w) to avoid formation of dienes from iodo olefins.[17] Since $NiCl_2/CrCl_2$ and $Pd(OAc)_2/CrCl_2$ gave very similar results for the coupling of **1** with **2**, the following examples were examined only by the former reagent system. Reactions are fast in DMF or DMF-$(Me)_2S$, which is usually the choice of solvent for coupling of iodo enones. Reactions are slower in DMSO but it often gives much cleaner results for coupling of iodo olefins.

With respect to the possible mechanism for this unique activation of an alkenyl iodide, the process may involve reduction of Ni(II) into Ni(I) or Ni(O) by Cr(II), oxidative addition of an alkenyl iodide to Ni(I) or Ni(O),[18] and then metal exchange with Cr(II) or Cr(III),[19] to generate the organometallic reagent which then couples with an aldehyde. On the other hand, Ni(II) is regenerated and recycled. A similar catalytic cycle is possible for the $Pd(OAc)_2/CrCl_2$ system as well.

The Cr(II)-mediated coupling allows a carbon-carbon bond formation between alkenyl halides and aldehydes, which can usually be achieved by traditional organometallic reagents such as Grignard, lithium, or cuprate. However, there are several unique characteristics of this reaction. Experimentally, activation of a carbon-iodine bond in the presence of an aldehyde offers an attractive convenience for many cases. In our view, this coupling reaction has demonstrated its potential and uniqueness for multifunctional substrates, for which conventional organometallic reagents are difficult to be applied. A recent example from the palytoxin project such as **13** + **14** → **15**[20] best illustrates this point.

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(9) In general, the stereoselectivity of reactions proceeding through a so-called Cram's cyclic transition state is known to be excellent in favoring formation of threo isomers; for example, see: Still, W. C.; Schneider, J. A. *Tetrahedron Lett.* **1980**, *21*, 1035 and references cited therein. It is interesting to note that the α-alkoxy group seems to have a more dominating effect over the β-alkoxy group in the case of α,β-bisalkoxy aldehydes such as **1**.[4]

(10) Extensive efforts were made to find a suitable solvent to avoid formation of α,β-unsaturated aldehyde from **1**; a substantial amount of α,β-unsaturated aldehyde was formed from **1** in DMF or DMF-$(Me)_2S$.

(11) Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3179.

(12) Activity of $CrCl_2$ purchased from ROC/RIC varied substantially; a batch in the fall of 1983 was exceptionally active, a batch in the summer of 1984 was fairly active, and batches in the summer of 1985 were inactive. $CrCl_2$ from Cerac (lot 18570-A-6+7) was fairly active. $CrCl_2$ from Aesar, Alfa, and Strem did not show activity.

(13) $CrCl_2$ was prepared by chemical ($LiAlH_4$) as well as electrochemical reduction of $CrCl_3$. We thank Professor Holm and Dr. Mukherjee for help of electrochemical reduction of $CrCl_3$.

(14) The following is a representative procedure for the coupling. The aldehyde **1** was prepared by oxidation of the corresponding primary alcohol (1.285 g, 2.35 mmol) under the Swern conditions. The crude aldehyde **1** was mixed with the iodo olefin **2** (4.766 g, 7.05 mmol) and azeotroped with toluene (×2). The mixture was dissolved in DMSO (60 mL) in a glovebox. To this solution was added $CrCl_2$ containing 0.1% $NiCl_2$ (ca. 1.75 g, 14.2 mmol) portionwise. The dark green mixture was stirred in a glovebox for 20 h at room temperature (TLC showed no aldehyde left). The reaction mixture was quenched by stirring with saturated NH_4Cl and $CHCl_3$ and then extracted with EtOAc (×3). The combined extracts were washed with brine, dried over $MgSO_4$ and evaporated. The crude products were separated by medium-pressure column chromatography (Merck silica gel; 20% EtOAc-hexanes) to give the 16α-allylic alcohol (1.026 g, 39.9% overall yield from the primary alcohol) and the 16β-allylic alcohol (0.802 g, 31.2% overall yield from the primary alcohol).

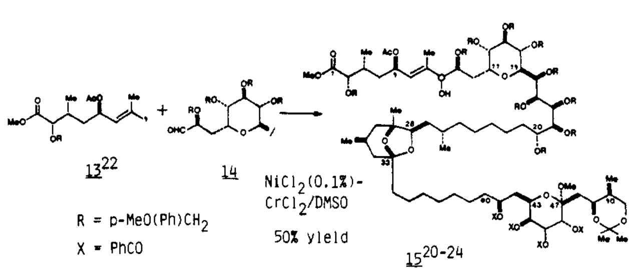
(15) We have recently learned that Dr. Takai at Kyoto University discovered a catalytic effect of $NiCl_2$ for activation of vinyl triflates by $CrCl_2$. We thank Dr. Takai for exchanging information prior to the publication: Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Uchimoto, K.; Nozaki, H. *J. Am. Chem. Soc.*, in press.

(16) Nickel and palladium are known to have a catalytic effect for various organometallic reactions. For reviews on Grignard reactions, see: (a) Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735. (b) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. Also see: Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246. For a review on cross couplings of aluminium, zirconium, and zinc reagents, see: Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. For conjugate additions of aluminium and zirconium reagents, see: (a) Ashby, E. C.; Heinsohn, G. *J. Org. Chem.* **1974**, *39*, 3297. (b) Loots, M. J.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 8045. Also see: Dayrit, F. M.; Gladkowski, D. E.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3976.

(17) At a higher content of $NiCl_2$ and $Pd(OAc)_2$ (>2%), a substantial amount of diene was formed from **2**. Dimerization of an alkenyl bromide in the presence of nickel is known; see: Semmelhack, M. F.; Helquist, P. M.; Gorzynski, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 9234.

(18) Mechanistic aspects on oxidative addition of alkenyl halides to Ni species were studied by Felkin, Kumada, Kochi, and others. For a review, see: Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 393.

(19) The iodo olefin **2** was completely consumed by about 2 equiv of $CrCl_2$ containing 0.1% $NiCl_2$ in DMSO indicating a transmetalation step involved in this process.



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(20) Cheon, S. H.; Christ, W. J.; Fujioka, H.; Hawkins, L. D.; Jin, H.; Kishi, Y.; Leder, J.; Taniguchi, M.; Ueda, K., Uenishi, J., unpublished results. The coupling of **14** with the β-iodo enone corresponding to **13** in DMF-$(Me)_2S$ was equally satisfactory to give about a 5:1 mixture of 8α- and 8β-allylic alcohols in about 50% yield.

(21) All the new compounds in this paper gave satisfactory spectroscopic data.

(22) The synthesis of this substance will be published elsewhere: Christ, W. J.; Hawkins, L. D.; Jin, H.; Kishi, Y.; Taniguchi, M., manuscript in preparation.

(23) The stereochemistry of the alcohol was established by chemical correlation with a known compound.

(24) For the numbering used in the paper, see the structure **15**.

Micelle-Mediated Resonance Raman Spectroscopy: A New Approach for Characterizing Low Levels of Luminescent Compounds

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It is well-known that the vibrational spectra produced by Raman scattering spectrometry provide abundant information on the structure of molecules and can be used to characterize them. The inherent weakness of the Raman signal is the major shortcoming of this potentially powerful technique. Two methods used to enhance Raman signals include surface enhanced Raman scattering (SERS)[1-6] and resonance Raman scattering (RRS).[7-17] While both methods can enhance Raman signals up to 6 orders of magnitude, there are a number of experimental and theoretical limitations associated with each. For example, the fluorescent background produced when exciting on the electronic absorption band of a compound generally negates enhancement advantages of resonance Raman scattering. Consequently, a significant amount of research has been done to develop techniques which partially eliminate or circumvent the problem of luminescence.[18-27]

Table I. Fluorescence Quenching in Aqueous Micellar Media

concn, ppm	rel luminescence intensity[c]
$[ZnTPPS_4]$[a]	
<1	<0.001
5	<0.001
10	5.5
50	16.2
[acenaphthylene][b]	
<1	<0.001
25	<0.001
50	<0.001
200	<0.001

[a] The zinc tetraphenylporphyrin tetrasulfonic acid ($ZnTTPS_4$) was dissolved in 5% aqueous brominated Brij 96 containing 2×10^{-3} M 5-DOXYL stearic acid and 4×10^{-3} M 4-phosphonooxy-TEMPO monohydrate. [b] Micellar solution consisted of 0.2 M thallium dodecyl sulfate and 0.7 M sodium dodecyl sulfate. [c] Measured with a Perkin-Elmer LS-5 spectrofluorimeter (λ_{ex} = 420 nm, λ_{em} = 608 nm, slits = 10 nm, setting = 1.0 full scale). One part per million $ZnTPPS_4$ in H_2O gives a fluorescence intensity of 90, while one part per million acenaphthylene in methanol gives a fluorescence intensity of 6.

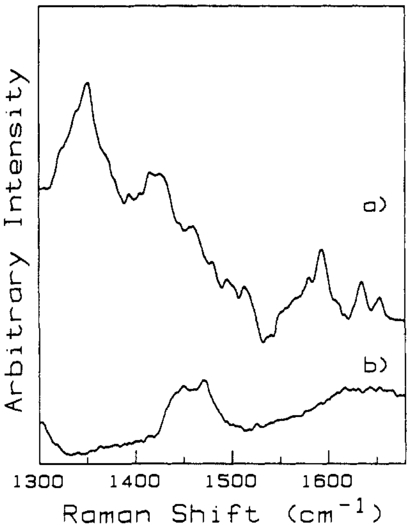

Figure 1. (a) Resonance Raman spectrum of 4.3×10^{-5} M $ZnTPPS_4$ in brominated Brij micellar cocktail. (b) Raman spectrum of micellar solution blank. Both spectra were obtained with 402-nm excitation (4-mW average power) and a spectral band-pass of ~10 cm^{-1}. Spectra are the sum of two scans. The composition of the micellar cocktail is given in Table I.

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