ESCA and showed no measurable binding-energy shifts from one dye to the next in this series.

In summary, our data show that for a symmetric cyanine dye series, the principal electronic absorption band shifts with conjugation are directly reflected in the delocalization of the nitrogen 1s core electrons in which the binding energy decreases linearly with increased conjugation. We believe that the ESCA analysis could be an important complementary tool for the assessment of solid dye films with respect to their semiconduction and photoconduction potential for various optical and electronic device coatings.

Acknowledgment. We thank Noel Turner for many helpful suggestions and Jim Murday and Forrest Carter for their continual encouragement in this work.

Registry No. 1,1′-Diethyl-2,2′-dicarbocyanine iodide, 14187-31-6; cryptocyanine, 4727-50-8; pinacyanol, 605-91-4; pseudocyanine iodide, 977-96-8.

Structure and Reactivity of the Zirconaenolate Anion $(Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)CH_3)Na\cdot 2THF$. Synthesis of Homo- and Heterobinuclear Ketene Complexes[1]

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Transition-metal acyl complexes are key intermediates in numerous stoichiometric and catalytic transformations.[2] Despite the ubiquitous use of enolate anions in organic synthesis, deprotonation of acyl ligands to form the corresponding metallaenolate anions has been only recently reported.[3] Preparation of these reactive species appears to necessitate use of a bulky, non-nucleophilic base and a metal with electron-donating ancillary ligands.[4] As previously reported, a good leaving group such as halide as a ligand on the central metal leads to neutral metal ketene complexes.[3a,5,6] Herein we report structural details of the metallaenolate (ketene) anion $(Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)CH_3)Na\cdot 2THF$ (**2a**·2THF) and describe its reactivity toward organic and metal halides.[7] The latter reactions lead to isolation of a variety of neutral binuclear ketene-bridge structures.[8,9]

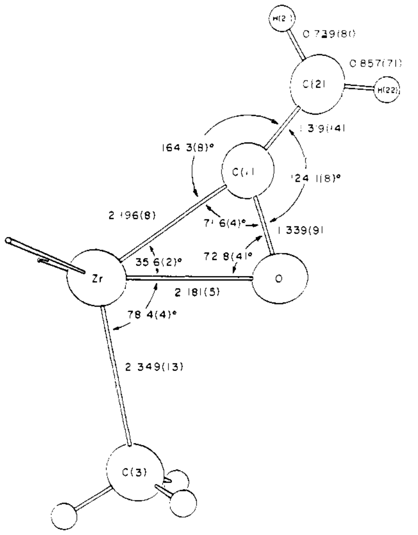
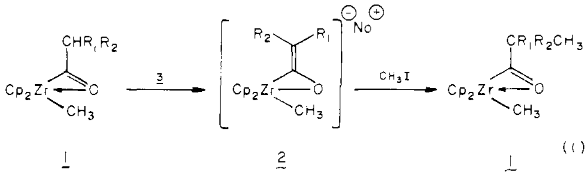


Figure 1. Molecular geometry of the equatorial ligands in **2a**·2THF.

Zirconaenolate anion **2a**·Et_2O precipitates instantly on addition of an ethereal solution of $NaN(Si(CH_3)_3)_2$ (**3**) to a stirred solution of $Cp_2Zr(COCH_3)CH_3$ (**1a**)[10] in ether at −30 °C (eq 1). The



(1)

1a, $R_1 = R_2 = H$ **2a**, $R_1 = R_2 = H$
b, $R_1 = H; R_2 = CH_3$ **b**, $R_1 = H; R_2 = CH_3$
c, $R_1 = R_2 = CH_3$ **c**, $R_1 = R_2 = CH_3$

resulting white powder is pyrophoric in air and moderately light sensitive. The complex is insoluble in pentane, ether, and benzene but dissolves readily in THF, yielding **2a**·2THF upon removal of solvent in vacuo. The latter complex is benzene soluble. Crystals of **2a**·2THF suitable for X-ray structural analysis[11] have been obtained by slow cooling of a pentane–THF solution of **2a**. The geometry of the planar $Zr(COCH_2)CH_3$ moiety is presented in Figure 1. The C(1)–O and C(1)–C(2) bond lengths are typical of single and double bonds, respectively. The $OCCH_2$ moiety is virtually identical with that in the neutral ketene complex $(\eta^5\text{-}C_5Me_5)_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)(py)$[5] (py = pyridine) except for the slightly shorter Zr–O bond in the latter (2.126 (1) Å), which may reflect the greater donor strength of CH_3 vs. the pyridine ligand. The Zr–C(3) bond length is similar to the Zr–C(methyl) distance in **1a** (2.336 (7) Å)[10] but considerably longer than in the more electron deficient $Cp_2Zr(CH_3)_2$ (2.276 (7) Å).[12] To our knowledge this is the only structurally characterized metallaenolate anion.

Although the NMR spectroscopic and structural data do not indicate high negative charge density at C(2), reaction of **2a**·2THF with CH_3I gives $Cp_2Zr(COCH_2CH_3)CH_3$[3a] quantitatively without production of ethane (^1H NMR). Alkylation of **2a**·2THF with CD_3I yields only $Cp_2Zr(COCH_2CD_3)CH_3$ (^1H NMR). Sequential alkylation and deprotonation as above leads cleanly and quantitatively to anions **2b** and **2c** (eq 1). Particular noteworthy is production of only one isomer of the zirconaenolate **2b**·Et_2O

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[1] In memory of Professor Ernst G. Straus.

[2] (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Henrici-Olive, G.; Olive, S. *Transition Metal Chem. (Weinheim, Ger.)* **1976**, *1*, 77. (d) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

[3] (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (b) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *Ibid.* **1982**, *104*, 5250. (c) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194. (d) Straus, D. A. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1983.

[4] Compare, for example: Johnson, R. W.; Pearson, R. G. *Inorg. Chem.* **1971**, *10*, 2091. Heck, R. F.; Breslow, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 2779. Malisch, W.; Blau, H.; Haaf, F. J. *Chem. Ber.* **1981**, *114*, 2956.

[5] Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

[6] For a novel synthesis of a mononuclear neutral η^2-ketene-C,O complex, see: Casey, C. P.; O'Conner, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 2919.

[7] This complex has been briefly reported with ^1H and ^{13}C NMR spectroscopic data (THF-d_8), ref 3a,d.

[8] Two examples of μ-$OCCH_2$ ketene structures are reported: (a) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679 (Ru, Ru). (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *Ibid.* **1983**, *105*, 4104. See also: Ott, K. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1983. Certain dimeric substituted ketene complexes also fall into this category: (c) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995. (d) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462. See also ref 3a,d.

[9] A structurally characterized trinuclear $(Zr_2Al)(\mu,\eta^2\text{-}OCCHCH_2C(CH_3)_3\text{-}C,O)_2$ complex has been prepared by reaction of $Al(CH_3)_2Cl$ with $(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2$ (ref 3a,d): Waymouth, R. M.; Grubbs, R. H., unpublished results.

[10] Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

[11] Complex **2a**·2THF crystallized in the space group $P\bar{1}$ with: a = 10.745(5) Å, b = 14.449 (5) Å, c = 12.060 (4) Å, α = 119.40 (3)°, β = 91.26 (4)°, γ = 114.83 (4)°, V = 1123 (1) Å^3, Z = 2.

[12] Average value from: Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Peuttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

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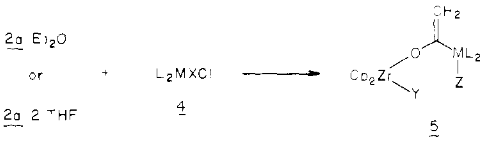
(>98% ^1H NMR).[13] The stereochemistry indicated in eq 1 is assigned by analogy with a structurally characterized neutral zirconium ketene complex formed in a similar fashion[9] and is attributed to the steric requirements of **3**. Benzyl bromide and trimethylsilyl chloride react similarly with **2a**.[14] Attempts at an aldol-type reaction of **2a** with benzaldehyde led to complex mixtures of products.

Metallaenolate (ketene) anion **2a** has been found to be of general utility in the preparation of new homo- and heteronuclear bimetallic ketene complexes of interest as models of intermediates implicated in carbon–carbon bond formation in surface-catalyzed carbon monoxide reductions.[15] Reaction of **2a**·Et_2O with zirconocene halide **4a** (eq 2) proceeds rapidly upon dissolution in



(2)

4a, L = Cp; M = Zr; X = CH_3 **5a**, Y = Z = CH_3; M = Zr
b, L = $P(CH_3)_3$; M = Pt; X = CH_3 **b**, Y = Z = CH_3; M = Pt

THF/Et_2O at −20 °C, and the binuclear ketene complex **5a** is isolated in ca. 50% yield.[16-18] The assigned structure differs from the "bridging acyl" type structures of Ru[8a] and Os[8b] μ,η^2-$OCCH_2$-*C,C* complexes, a consequence of the oxophilicity of zirconium.

Platinum halides of the type *cis*-L_2PtXCl, such as **4b** (L = $P(CH_3)_3$, X = CH_3), react cleanly with **2a**·2THF in benzene at room temperature to afford heterobinuclear bridging ketene complexes (eq 2).[19] The μ-η^2-$OCCH_2$ structure indicated in eq 2 is supported by ^1H, ^{13}C, and ^{31}P NMR spectroscopic data.[20] The inequivalence of the phosphine ligands and the different J_{HP} and J_{PPt} values establish cis orientation about Pt in **5b**.

The metallaenolate anions **2** are versatile reagents in organometallic synthesis, particularly for formation of binuclear complexes of relevance to carbon monoxide reduction systems. The reactivity of these new ketene species, including use of complexes such as **2** and **5** in stereospecific organic transformations, is presently being explored.

Acknowledgment. We acknowledge the financial support of the Department of Energy.

Supplementary Material Available: Tables of atomic coordinations, bond angles, bond distances, structure factors, and thermal parameters for **2a**·2THF (18 pages). Ordering information is given on any current masthead page.

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(13) For **2a**: ^1H NMR (THF-d_8) δ −0.68 (s, 3 H), 3.64 (d, *J* = 2 Hz,1 H), 4.55 (d, *J* = 2 Hz, 1 H), 5.43 (s, 10 H). **2b**: ^1H NMR (THF-d_8) δ −0.68 (s, 3 H), 1.82 (d, 3 H, *J* = 6 Hz), 5.07 (q, 1 H, *J* = 6 Hz), 5.45 (s, 10 H). **2c**: ^1H NMR (THF-d_8) δ −0.77 (s, 3 H), 1.68 (s, 3 H), 1.83 (s, 3 H), 5.34 (s, 10 H). By modification of reaction conditions it is possible to generate a minor isomer of **2b**.[14]

(14) Ho, S. C. H.; Grubbs, R. H., unpublished results.

(15) (a) Blyholder, G.; Emmet, P. H. *J. Phys. Chem.* **1960**, *64*, 470 and references therein. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

(16) For **5a**: ^1H NMR (C_6D_6) δ −0.17 (s, 3 H), 0.43 (s, 3 H), 4.23 (s, 1 H), 4.61 (s, 1 H), 5.65 (s, 10 H), 5.82 (s, 10 H); ^{13}C NMR (C_6D_6) δ 18.8 (q, $^1J_{CH}$ = 117 Hz), 33.0 (q, $^1J_{CH}$ = 119 Hz), 92.7 (dd, $^1J_{CH}$ = 148, 159 Hz), 107.1 (dm, $^1J_{CH}$ = 172 Hz), 113.1 (dm, $^1J_{CH}$ = 172 Hz), 208.9 (pseudotriplet, $^2J_{CH}$ = 9 Hz); IR (KBr) 1538, 1594 cm^{-1} ($\nu_{C=C}$). Anal. $C_{24}H_{28}OZr_2$ (C, H).

(17) The inequivalence of the two zirconium centers of **5a** in the ^1H NMR at room temperature stands in contrast with the formaldehyde complex $(Cp_2ZrCl)_2(\mu\text{-}OCH_2)$ (Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690) and related complexes (Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437). This might be due to the sp^2 hybridization at the oxygen-bound carbon, which inhibits formal dative Zr–O interaction. Examination at high temperature is not possible because **5a** undergoes bimolecular decomposition to $[Cp_2Zr(OCCH_2)]_n$ (identified by comparison with an authentic sample[14]) and $Cp_2Zr(CH_3)_2$ ($k = 1.1 \times 10^{-2}$ L mol^{-1} s^{-1}, 52 °C).

(18) Binuclear zirconium ketenes with Y = OCH_3, Z = CH_3 and Y = CH_3, Z = Cl have also been prepared.

(19) PtL_2XCl (L = $P(CH_3)_2Ph$, PCH_3Ph_2; X = CH_3, Cl) react to give similar ketene-bridge complexes.

(20) For **5b**: ^1H NMR (C_6D_6) δ 6.08 (s, 10 H), 5.06 (ddd, J_{HH} = 2, J_{HP} = 13, 3, J_{HPt} = 90 Hz, 1 H), 4.00 (ddd, J_{HH} = 2, J_{HP} = 3, J_{HPt} = 32 Hz, 1, H), 1.20 (d, J_{HP} = 8.5, J_{HPt} = 21.7 Hz, 9 H), 1.04 (dd, J_{HP} = 9.6, 17.5, J_{HPt} = 69.6 Hz, 3 H), 0.93 (d, J_{HP} = 7.8, J_{HPt} = 19.4 Hz, 9 H), 0.39 (s, 3 H); ^{13}C NMR (C_6D_6) δ 202.1, 152.9, 110.3, 36.4, 17.3, 15.9, 13.9; ^{31}P NMR (C_6D_6) δ −29.3 (d, J_{PP} = 12.1, J_{PPt} = 1354 Hz), −25.0 (d, J_{PP} = 12.2, J_{PPt} = 1578 Hz).

Stereocontrol of Michael Hydride Reduction by a Remote Hydroxyl Group. A Strategy for Stereorational Total Synthesis of Spatane Diterpenes

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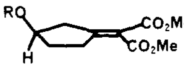
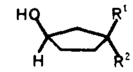
The remarkable biological activities of spatane diterpenes,[1] especially spatol (**1**),[2] make them attractive targets for synthesis. Our strategy for total synthesis of spatanes (Scheme I) envisions completion of the C_{20} skeleton from C_{15} tricyclodecane precursors such as **2a** or **2c**. The requisite stereochemistry at C-7 is assured if some derivative of the C-5 hydroxyl substituent directs syn Michael addition of hydride to C-7 in an alkylidene malonic ester as in **4** → **3**. The correct relative configurations of the C-5 hydroxyl and B-ring stereocenters is assured by exo stereoselectivity anticipated[3] in the photocycloaddition of **7**[4] with norbornenes. We now report the *first* total synthesis of a spatane diterpene, (±)-spata-13,17-dien-5-ol (**25**), and show that hydride delivery during reduction of alkylidene malonates like **4** can be directed ether syn or anti by a homoallylic hydroxyl group or the derived MEM ether, respectively.

Considering the obvious synthetic utility of stereodirected Michael additions, there are remarkably few examples of such processes. To explore the efficacy of various homoallylic substituents as stereodirecting groups, MEM ether **9a** was reduced



9a, R = MEM
9b, R = H



10t, R^1 = H, R^2 = $CH(CO_2Me)_2$
10c, R^2 = $CH(CO_2Me)_2$, R^2 = H

with $NaBH_4$ in ethanol followed by removal of the MEM protecting group.[5] A 1:5 mixture of the trans and cis hydroxy malonic esters **10t** and **10c** was obtained. Thus the MEM ether group functions as a bulky steric hinderance to syn approach of the hydride. This contrasts with the syn stereodirecting effect of an allylic MEM ether group which served as a chelating ligand during "heteroconjugate addition" of MeLi.[6] Most significantly, the stereochemical outcome was reversed by first removing the MEM protecting group. Treatment of **9b** with $NaBH_4$ in ethanol produced a 1.0:0.67 mixture of **10t** and **10c**. Further improvement in the product ratio to 1.0:0.37 was achieved by using THF as solvent. The solvent effect can be understood in terms of activation

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