Scheme I

The process generates a novel amino acid tridentate complex and an asymmetric center at the C atom where condensation occurs. Reactions of this type have value in their capacity to expand synthetic expertise in chelate chemistry and especially for the prospects they give in synthesizing multidentate complexes.

B. T. Golding, J. MacB. Harrowfield, G. B. Robertson
A. M. Sargeson,* P. O. Whimp
Research School of Chemistry, Australian National University
Canberra, A.C.T., Australia 2600
Received February 4, 1974

Optical Activity Associated with Isolated Olefinic Bonds. II. Experimental Evidence for the Role of π-Bond Torsion in Circular Dichroism Couplets and the Question of the $\sigma_a \rightarrow \pi_x^*$ Contribution[1]

Sir:

In earlier studies of olefin circular dichroism we proposed the allylic bond polarization (ABP) model to account for the sign of the low energy portion of the couplet observed for most endocyclic olefins.[1,2] In this we followed the suggestion of Scott and Wrixon[3] ascribing the couplet to $\pi_y^* \leftarrow \pi_x \rightarrow \pi_x^*$ with $\pi_x \rightarrow \pi_x^*$ representing the low energy portion. Levin and Hoffmann recently reported calculations of $\pi \rightarrow \pi^*$ rotatory strengths of model olefins,[4] suggesting that π-bond torsion sense is the dominant factor in the CD of twisted olefins. We now wish to present new data which constitutes: (1) support for the $\pi_y^* \leftarrow \pi_x \rightarrow \pi_x^*$ assignment for cyclohexene CD couplets, (2) the first *experimental evidence* establishing the characteristics of torsion induced olefin CD, and (3) the first observations suggesting an additional CD active transition in the region of the uv dominant $\pi \rightarrow \pi^*$ transitions. We consider this new band to be the $\sigma_a \rightarrow \pi_x^*$ transition previously placed in this energy span by various calculations.[5]

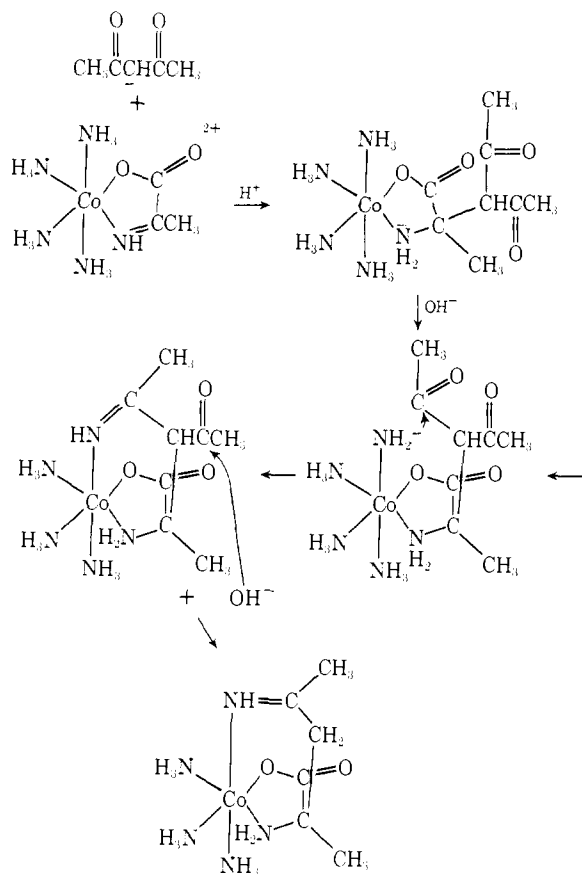The assignment of the CD couplet to the two $\pi \rightarrow \pi^*$

ment of all atomic positional parameters, anisotropic temperature factors for Co, S, O, N, and C atoms, isotropic thermal parameters for hydrogen atoms, and overall scale factor, has converged with $R = 0.040$.

The cation, which is essentially octahedral about the central cobalt atom shows the expected bond distances (see Figure 1). Two structural features are of special note. (1) The C–O distances in the coordinated carboxylate ion [*i.e.*, C(4)–O(1), 1.270 (7); C(4)–O(41), 1.233 (6) Å] are significantly different. (2) The five-membered chelate ring is markedly aplanar, with C(3) and C(4) being 0.748 and 0.350 Å, respectively, from the plane of Co, N(2), O(1), in the direction of N(1). In contrast, the chelate ring in simple α-amino acid adducts is usually close to planar.[2] In the present complex, this aplanarity is probably a consequence of the tridentate character of the ligand.

The order of events for the addition of acetylacetone has not been elucidated, but, since the acetylacetone carbanion is readily formed and such species add rapidly to the coordinated imines,[1] it seems a reasonable initial step. Base-catalyzed condensation of a carbonyl center with the less acidic ($pK_a > 14$) apical ammonia should follow (Scheme I). It also seems reasonable to assert that the acetyl group is still intact at this stage and that hydrolysis occurs after the chelation process.

All three aspects are being examined. A benzoyl group may stabilize the acylated complex and if the pH is low enough the addition of carbanion may be observed separately from the condensation with coordinated NH_3.

(2) H. C. Freeman, *Advan. Protein Chem.*, **22**, 257 (1967).

(1) For part I see N. H. Andersen, C. R. Costin, D. D. Syrdal, and D. P. Svedberg, *J. Amer. Chem. Soc.*, **95**, 2049 (1973).

(2) The ABP model[1] and the Scott–Wrixon dissignate octant rule[3] are closely related. In the ABP model attention is focused on the chiral relationship of the more polarizable allyl bonds and the π orbital rather than the carbon framework as a whole. See W. Klyne and D. N. Kirk, *Tetrahedron Lett.*, 1483 (1973), for a definition of the useful term, dissignate.

(3) (a) A. I. Scott and A. D. Wrixon, *Chem. Commun.*, 1182 (1969); (b) *Tetrahedron*, **26**, 3695 (1970); (c) *ibid.*, **27**, 4787 (1971).

(4) C. C. Levin and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 3446 (1972).

(5) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969). See also ref 3b. The lower energy Rydberg transition, $\pi_x \rightarrow 3s$, apparently occurs in this region in some solvents; however, its contribution to the CD of olefins of this report is minimal as judged by the absence of solvent effects.[6]

(6) There is some dispute as to the assignment of the low energy CD band of highly substituted olefins. Burgstahler, Barkhurst, and Gawronski have suggested that it is associated with a transition between a π state and a σ_a state ($\sigma_a \rightarrow \pi_x^*$ or $\pi_x \rightarrow 3s$).[7] The $\pi_x \rightarrow 3s$ transition has been implicated in the solvent dependent CD of $(-)$-α-pinene;[8] however, we have determined the CD spectra of a number of the endocyclic olefins of the table in a series of solvents (n-pentane, CH_3CN, perfluoroheptane, and hexafluoro-2-propanol) and find no significant polarity or density dependence for λ_2, $\Delta\Delta\epsilon$, or Δ_{ij}.[9] On this basis we conclude that the $\pi_x \rightarrow 3s$ transition is not a major contributor to either band of the CD couplets observed.

(7) A. W. Burgstahler, R. C. Barkhurst, and J. R. Gawronski in "Modern Methods of Steroid Analysis," E. Heftmann, Ed., Academic Press, New York, N. Y., 1973. The authors acknowledge the receipt of this manuscript prior to publication.

(8) A. E. Drake and S. F. Mason, *J. Chem. Soc., Chem. Commun.*, 253 (1973).

(9) N. H. Andersen and Y. Ohta, submitted for publication.

transitions arose from a tabulation of the CD data available to us[6] (see Table I). In no case has the first CD

Table I. Comparison of λ_1 and λ_2 as Observed in the CD of Endocyclic Olefins Showing Double Extrema and the Expectation Values (λ) of the Uv_{max} and the $\pi_x \rightarrow 3s$ Shoulder

Substitution	CD λ_1 (%)[a] (nm)	Uv λ_{max}[b] (nm)	CD λ_2 (%)[a] (nm)	$\pi_x \rightarrow 3s$[b]	n[c]
Di	185 ± 5 (?)	~ 188	200 ± 3 (100)	~ 208	11
Tri	189 ± 7 (90)	~ 195	206 ± 5 (90)	~ 216	58
Tetra	199 ± 6 (100%)	~ 203	216 ± 6 (100)	~ 228	11

[a] % of examples falling in stated range. [b] The expectation values are taken from ref 5 and the work of R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, **27**, 345 (1962), on steroidal olefins. [c] The number of examples for which CD couplets have been observed. Half of these examples are unpublished ones for this laboratory, the remaining are taken from ref 1 and 3, and personal communications, and A. W. Burgstahler, J. N. Marx, and D. F. Zinkel, *J. Org. Chem.*, **34**, 1550, 3716 (1969).

Figure 1. CD spectra (180–240 nm, linear in nm, solvent is n-pentane) of (+)-3-methylcyclohexanone (V, X = O, and derived olefins X = CH_2, CHMe, and CMe_2) and (−)-norcedranone (VI, X = O, and derived olefins X = CH_2, CHMe, and CMe_2).

extremum occurred at lower energy than the uv shoulder associated with $\pi \rightarrow 3s$. Given that the apparent separation of couplets (Δ_{ij}) is necessarily greater than the energy difference ($\lambda_j - \lambda_i$), the position of the CD observed λ_2 relative to the uv λ_{max} is within expectations.[6] Furthermore, the sign of the low energy CD observed for cyclohexenes constrained to a single enantiomeric C_2-conformation is consistent with the sign rule of Levin and Hoffmann when the sense of torsion predicted by molecular models is considered.

The positive λ_2 CD band noted for the P-helicity conformation (I),[1,3c] in the absence of perturbing axial allyl substituents, is in accord with a preference for slight positive torsion toward the flexible family (which retains pseudo-C_2 ring symmetry): slight positive torsion relieves the near eclipsing interaction of the substituent R and the adjacent pseudo-equatorial bond, as the C–R and allyl (5,6) bonds become more nearly antiparallel.
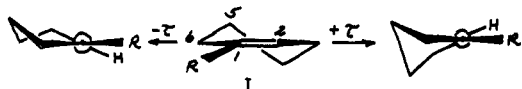
The suggestion that net π-bond torsion is requisite for the appearance of an olefin CD couplet appeared open to experimental verification in two ways: the model predicts (a) notable increases in rotatory power with increasing bulk of the vinylic substituents and (b) a mirror image relationship between E and Z isomers of exoalkylidenecyclohexanes. We now provide the results of these tests.

A series of 1,3-dialkylcyclohexanes (II) displays the predicted trend in $\Delta\epsilon$.[10,11] The related 1,4-dialkylcyclohexenes (III),[10] lacking a pseudo-equatorial substituent at C-3,[12] display only a single CD band. In this series increasing vinylic substitution does not in-

(10) Olefins of series II and III were prepared from (+)-3-methylcyclohexanone (V, X = O) by the sequence: reduction or alkyllithium addition followed by dehydration. The structures are supported by the appropriate spectroscopic data and chemical tests. Those of series II are shown as the enantiomers in order to depict P-helicity systems throughout.

(11) These flexible series were chosen since torsional accommodation of bulky vinylic substituents should occur more readily. Naturally derived *trans*-octalins show the same CD features.

(12) Twisting of the π bond, by the steric argument presented above, is particularly favorable when a C-3 pseudo-equatorial group is present. It is thus not surprising that this is a characteristic feature of cyclohexenes displaying distinct CD couplets.
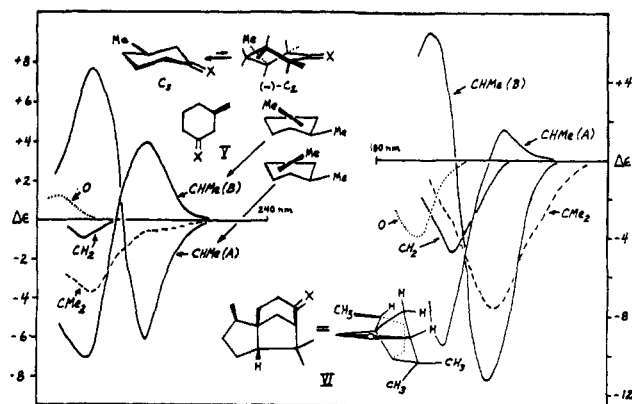
crease the rotatory power notably, suggesting that π-torsion is not a major factor. A series of α-cedrene analogs (IV)[13] provides an even stronger case for ring chirality and/or dissymmetric substituent array contributions not related to π-bond torsion. The bicyclo[3.2.1]octene system imbedded in the tricyclic skeleton constrains the cyclohexene ring to the P-helicity family, but positive torsion should be prohibited as it would increase the already substantial interaction of R_8 with the endo-Me at C-6. In keeping with our expectations for a CD not associated with π-bond torsion, $\Delta\epsilon$ does not increase notably with increasing bulk of the vinylic substituents and none of these compounds (IV) show any sign of a higher energy band of opposite sense.

	$\Delta\epsilon$ (λ)	R_1	R_2	R_4	$\Delta\epsilon$ (λ)
R = H,	+0.9 (200)				
	−1.8 (185)!	H	H	Me	+1.82 (198)
Me,	+3.5 (206)	H	Me	Me	+4.3 (200)
	−6.3 (186)	H	i-Pr	Me	+2.8 (206)
i-Pr,	+6.6 (208)	Me	H	i-Pr	+3.4 (202)
	−8.1 (189)				

R_9	R_8	$\Delta\epsilon$ (λ)
H	H	+8.2 (194)
H	Me	+8.0 (199)
H	i-Pr	+5.7 (207)
Me	Me	+6.0 (203)
i-Pr	Me	+7.1 (205)

Two cases of exoalkylidenecyclohexanes will be considered here: the olefins derived from (+)-3-methylcyclohexanone (V) and (−)-norcedranone (VI). In flexible system V the chair (C_s-V) should be the major conformer with the related C_2 system, (−)-C_2-V making some contribution—the latter may offer a rationale for the negative CD observed for the symmetric compounds (V, X = CH_2, CMe_2). The separated ethylidene isomers (V, X = CHMe), in contrast, displayed large nearly symmetrical CD couplets (see Figure 1). The E/Z assignment is based on torsion sense expected based on steric arguments analogous to those presented above. For the norcedranone series only the (+)-C_2

(13) The enantiomers are shown in order to depict P-helicity systems throughout.

form and the related chair and half-chair forms are allowed. The locally symmetric compounds (VI, X = O, CH₂, CMe₂) each show a single negative CD band. For the ethylidene isomers a torsion couplet is superimposed on this negative band (at *ca.* 202 nm in this case).[14] We suggest that this represents the first experimental evidence for the location of the $\sigma_a \rightarrow \pi_x{}^*$ transition of olefins. The $\sigma_a \rightarrow \pi_x{}^*$ transition should be highly dissymmetric but only a minor contributor to the absorption spectrum.

Thus four transitions can contribute to the CD spectra of olefins in the 185–225-nm energy span. For trisubstituted olefins CD bands appear in the following sequence: $\pi_x \rightarrow 3s$ (225–190 nm, solvent dependent), $\pi_x \rightarrow \pi_x{}^*$ (200–210 nm), $\sigma_a \rightarrow \pi_x{}^*$ (195–205 nm), and $\pi_x \rightarrow \pi_y{}^*$ (185–200 nm). In light of the enhanced separation observed in couplets, the last three transitions very likely occur within 10 nm.

The extreme complexity of this spectral region argues against strict use of any simple rule. Apparently the success of the Scott–Wrixon dissignate[2] octant rule and the APB model owes to the sign correspondence for the low energy portion of the torsion couplet and the $\sigma_a \rightarrow \pi_x{}^*$ transition in certain common olefin types (C_2-twist cyclohexenes and exomethylenecyclopentanes). At this juncture only the use of strictly analogous models can be fully justified.

Acknowledgment. This work was partially supported by NIH Grant GM-18143. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(14) The argument that this negative contribution is another transition runs as follows. Assuming that vinylic substitution does not change the relative energy of the $\pi_x{}^*$ and $\pi_y{}^*$ transitions, a rotatory contribution due to the dissymmetric substituent array represented by the skeleton (but unrelated to torsion) should influence only one portion of the couplet. In fact, the negative portion of the couplet is dominant independent of its relative energy. Even if the stated assumption were proven this argument would not be conclusive since we have not allowed for vibronic detail or variation in λ_{max} for conformational isomers.
(15) Alfred P. Sloan Foundation Fellow.

Niels H. Andersen,*[15] C. Richard Costin, James R. Shaw
*Department of Chemistry, University of Washington
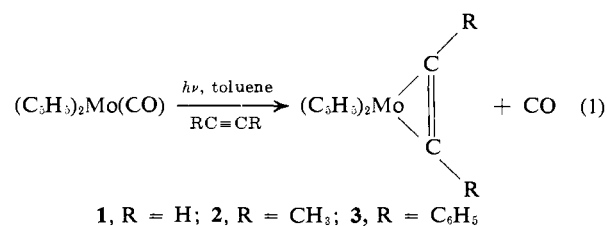Seattle, Washington 98195*

Photogeneration of Coordinatively Unsaturated Sandwich Compounds of Molybdenum and Tungsten from Their Carbonyl Complexes

Sir:

In a search for convenient avenues toward generation and study of coordinatively unsaturated complexes, we have observed that the transient species $(C_5H_5)_2Mo$ and $(C_5H_5)_2W$[1,2] are produced most conveniently by photolysis of their respective monocarbonyl complexes. Irradiation of toluene solutions of $(C_5H_5)_2Mo(CO)$ at either $-78°$ or at room temperature (high-pressure mercury lamp, 450 watt, Pyrex filter) for 4–16 hr in the presence of alkynes resulted in the formation of the respective alkyne complexes in essentially quantitative yields (eq 1). The corresponding ethylene

(1) J. L. Thomas, *J. Amer. Chem. Soc.*, **95**, 1838 (1973).
(2) J. L. Thomas and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1386 (1972).

$$(C_5H_5)_2Mo(CO) \xrightarrow[RC \equiv CR]{h\nu,\ \text{toluene}} (C_5H_5)_2Mo \diagdown \overset{R}{\underset{R}{C}} \overset{\|}{C} + CO \quad (1)$$

1, R = H; 2, R = CH₃; 3, R = C₆H₅

(4) and acrylonitrile (5) complexes[1] were obtained analogously in the presence of the respective alkenes. These products, some of which (2–5) have been previously synthesized[1–3] by other methods, are obtained virtually without side products by this photochemical method. The novel, unsubstituted acetylene complex 1 sublimes as an orange solid at 30° (10⁻³ Torr) and is characterized by singlets at τ 5.70 and 2.32 in its ¹H nmr (integrated intensities 10:1.9), a C=C stretching band at 1613 cm⁻¹, and a mass spectrum with peaks at m/e 256 (parent ion) and 230 ((C_5H_5)₂Mo⁺). The thermal stability of this complex is most unusual for a mononuclear, unsubstituted acetylene complex (*cf.* ref 4) and is undoubtedly related to the unusually strong reduction of C–C bond orders in molybdenocene π-complexes.[1] In the absence of suitable substrate molecules, photolysis of toluene solutions of $(C_5H_5)_2Mo(CO)$ yields only insoluble materials of undetermined composition, containing possibly some polymeric $[(C_5H_5)_2Mo]_n$.[1,2]

In contrast to this, benzene or toluene solutions of the tungstenocene carbonyl complex $(C_5H_5)_2W(CO)$ give essentially quantitative yields of the corresponding aryl hydride compounds 6 and 7 when photolyzed in the absence of alkene or alkyne substrates (eq 2).[5]

$$(C_5H_5)_2W(CO) \xrightarrow[C_6H_5R]{h\nu,\ \text{room temp}} (C_5H_5)_2W(H)C_6H_4R + CO \quad (2)$$

6, R = H; 7, R = CH₃
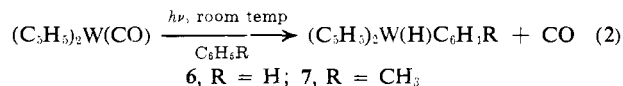
Obviously, the photogenerated species $(C_5H_5)_2W$ undergoes a facile insertion into the C–H bonds of aromatic solvent molecules, reminiscent of that of related niobium and tantalum complexes.[6] In the presence of both, arene solvent and alkyne substrate (*ca.* 1 *M*), comparable amounts of alkyne addition (2) and arene insertion (7) products are obtained from photolysis of $(C_5H_5)_2W(CO)$,[7] indicating that addition to C≡C bonds is only slightly favored over insertion to C–H bonds for tungsten, whereas in the molybdenum system the former is observed exclusively. Possible factors contributing to this gradation in carbene-like reactivity between otherwise largely analogous group VI metal complexes, and evidence concerning the role of ground- and excited-state intermediates in these reactions, will be presented in a forthcoming, more detailed account.

(3) A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **94**, 1886 (1972).
(4) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc., London*, 208 (1957).
(5) $(C_5H_5)_2W(H)C_6H_4R$ (R = H, CH₃) can be prepared by heating $(C_5H_5)_2WH_2$ in arene in the presence of isoprene or from the photolysis of $(C_5H_5)_2WH_2$ in arenes: M. L. H. Green and P. J. Knowles, *J. Chem. Soc. A*, 1508 (1971); C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1114 (1972); nmr and mass spectra of compounds 6 and 7 are in accord with these reports.
(6) E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970); F. N. Tebbe and G. W. Parshall, *ibid.*, **93**, 3793 (1971).
(7) Pure $(C_5H_5)_2W(C_2(CH_3)_2)$ (2) is prepared by photolyzing the tungstenocene monocarbonyl in liquid 2-butyne at $-78°$; in the reaction mixture, compounds 2 and 7 are identified and their ratios estimated by nmr.