hydride reduction[6a] of the predescribed endomesylate provided the known dihydro derivative.[8,9] **Tetrahydrotriquinacene**: *exo*-9-Hydroxy-2,3,8,9-tetrahydrotriquinacen-2-one[8] was transformed into its tetrahydropyranyl ether and the enolate anion of this derivative was condensed with diethyl chlorophosphate.[7b] The resulting enol diethyl phosphate was reduced with lithium in liquid ammonia[7b] and deprotected to give *exo*-2,3-dihydrotriquinacen-2-ol.[7b,10] Following exhaustive catalytic hydrogenation, the saturated exo alcohol was oxidized with the chromium trioxide-pyridine complex in dichloromethane and reduced with lithium aluminum hydride to the endo isomer.[10] Conversion to the mesylate and E_2 elimination on activated alumina delivered the known hydrocarbon,[11] which was brought to analytical purity by preparative VPC as before.

Heats of Hydrogenation. The heats of hydrogenation of triquinacene and its di- and tetrahydro derivatives were measured as follows. By use of a calorimeter for catalytic hydrogenation of alkenes as previously described,[12] aliquot portions of a solution in hexane of triquinacene or of its di- or tetrahydro derivative were injected into the calorimeter in alternation with injections of a thermochemical standard, 1-hexene. The standard molar heat of hydrogenation ($\Delta H_{h,m} = -30.25$ kcal mol^{-1})[13] permits calculation of $\Delta H_{h,m}$ of the new compounds from the measured ratio of heats produced within the calorimeter.[12,13] For the current experiments, injections were made by using a GLC syringe with a mechanical stop set at 80 μL. Optimum reproducibility is said to be 0.6% by the manufacturer and was verified before proceeding with these experiments. Reaction times plus instrumental response times were about 10 s. Total run times were 100 s. Gas chromatographic analysis of the calorimeter fluid after nine or more hydrogenations had been run showed a single clean product peak at long retention times. Analysis of samples of calorimeter fluid intentionally contaminated with triquinacene showed a split peak with the satellite at a shorter retention time than the product peak. We estimate that 1% of unreacted triquinacene could have been detected in the calorimeter fluid, had it been present.

Thus, we see that triquinacene is unequivocally stabilized by 4.5 kcal mol^{-1} relative to reference species that lack the cyclic array of three π-bonds. The heats of formation of solid and gaseous hexahydrotriquinacene have been reported in the literature,[14] -38.0 (± 0.8) and -24.5 (± 0.9) kcal mol^{-1}. These experimental results, the numbers we have measured, and the by now standard assumption[12a] that heats of hydrogenation of hydrocarbons in dilute hexane solution are equivalent to those in the gas phase result in heats of formation of gas-phase triquinacene (**1**), dihydrotriquinacene (**2**), and tetrahydrotriquinacene (**3**) of 53.5 (± 1.0), 30.5 (± 1.0), and 3.0 (± 1.0) kcal mol^{-1}.

The provocative findings, just described, make clear that the low-temperature X-ray analyses of triquinacene[15] prove misleading in not reflecting structural features suggestive of enhanced electronic interaction. In this connection, the crystallographic data for C_{16}-hexaquinacene,[16] a substrate believed to be more ideally tailored to homoconjugation,[17] implicate possible repulsive interactions between its three double bonds. Clearly, the thermochemical test must be applied systematically to series of compounds of this type and such investigations are currently in progress. These

data will constitute useful conceptual building blocks for more complete thermochemical understanding of spherically shaped polyquinanes and ultimately of dodecahedrane, a consummate example of this class of organic compounds.

A General Method for the Selective Binding and Activation of One Aldehyde Enantioface: Synthesis and Reactivity of Rhenium Aldehyde Complexes [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(η^2-RCH=O)]$^+$PF$_6^-$

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A general conversion of achiral aldehydes to chiral alcohols of high optical purity would be of immense utility in organic synthesis. Numerous catalytic[2] and stoichiometric[3] reactions have been described that effect such transformations with varying degrees of generality and success. We now report that the easily generated, chiral rhenium Lewis acid [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)]$^+$ selectively binds one aldehyde enantioface and that these aldehyde complexes undergo essentially stereospecific nucleophilic attack. Furthermore, the rhenium Lewis acid can be recycled without racemization.

I. Binding. Methyl complex (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_3$) (**1**)[4] and HPF$_6$·Et$_2$O were reacted (CH$_2$Cl$_2$, -78 °C) to give the recently reported coordinatively unsaturated *pyramidal* cation [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)]$^+$PF$_6^-$ (**2**).[5] Addition of isobutyraldehyde, benzaldehyde, and phenylacetaldehyde (3 equiv, -78 °C) to **2** gave η^2-aldehyde complexes [(η^5-C$_5$H$_5$)Re(NO)-(PPh$_3$)(η^2-RCH=O)]$^+$PF$_6^-$ (**3a-c**; Scheme I) in 83-73% yields after recrystallization.[6] The uncommon[7] η^2-coordination mode was assigned on the basis of the CO ^{13}C NMR resonance (81-89 ppm) and the absence of an IR $\nu_{C=O}$. Crude and recrystallized **3a-c** were by all criteria diastereomerically pure, *indicating se-*

(9) (a) Srinivasan, R. *J. Am. Chem. Soc.* **1970**, *92*, 7542. (b) Paquette, L. A.; Kramer, J. D.; Lavrik, P. B.; Wyvratt, M. J. *J. Org. Chem.* **1977**, *42*, 503.

(10) Kelly, R. C. Ph.D. Thesis, Harvard University, 1965.

(11) Paquette, L. A.; Lavrik, P. B.; Summerville, R. H. *J. Org. Chem.* **1977**, *42*, 2659.

(12) (a) Rogers, D. W.; Dagdagan, O. A.; Allinger, N. L. *J. Am. Chem. Soc.* **1979**, *101*, 671. (b) Rogers, D. W.; Crooks, E. L. *J. Chem. Thermodyn.* **1983**, *15*, 1087. (c) Rogers, D. W.; Siedman, B. A. *Talanta*, in press.
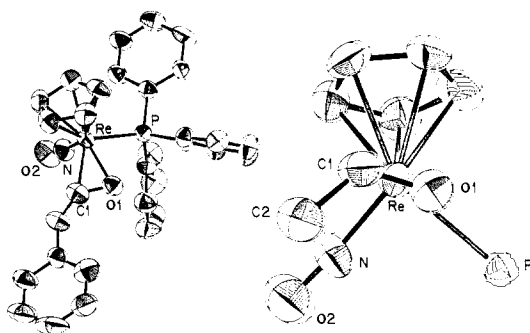
(13) Rogers, D. W. *J. Phys. Chem.* **1979**, *83*, 2430.

(14) Clark, T.; Knox, T. McO.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404. However, also see: Schulman, J. M.; Disch, R. L. *Tetrahedron Lett.* **1985**, *26*, 5647.

(15) Stevens, E. D.; Kramer, J. D.; Paquette, L. A. *J. Org. Chem.* **1976**, *41*, 2266.

(16) Christoph, J. G.; Muthard, J. L.; Paquette, L. A.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1978**, *100*, 7782.

(17) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600; **1979**, *101*, 6991.

(1) (a) University of Utah. (b) Montana State University.

(2) (a) Koenig, K. E. In *Asymmetric Synthesis*; Academic: Orlando, 1985; Vol. 5, pp 79-80. (b) Harada, K. *Ibid.* pp 357-359. (c) Knivtovics, P.; Bakos, J.; Heil, B. *J. Mol. Catal.* **1985**, *32*, 111. (d) Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R. *J. Am. Chem. Soc.* **1986**, *108*, 6071.

(3) See, inter alia: (a) Mukaiyama, T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K. *J. Am. Chem. Soc.* **1979**, *101*, 1455. (b) Mazaleyrat, J. P.; Cram, D. J. *Ibid.* **1981**, *103*, 4585. (c) Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *Ibid.* **1984**, *106*, 6717. (d) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31; see pp 39-40. (e) Midland, M. M.; McLoughlin, J. I. *J. Org. Chem.* **1984**, *49*, 4101.

(4) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(5) Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672.

(6) New compounds characterized by microanalysis, IR, and NMR (^{1}H, ^{13}C, ^{31}P) as described in the supplementary material.

(7) η^2-RCH=O complexes: (a) Kaiser, J.; Sieler, J.; Walther, D.; Dinjus, E.; Golić, L. *Acta Crystallogr., Sect. B* **1982**, *B39*, 1584. (b) Creswick, M. W.; Bernal, I. *Inorg. Chim. Acta* **1983**, *71*, 41. (c) Gauntlett, J. T.; Taylor, B. F.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1815. See also: (d) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253.

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Figure 1. Structure of the cation of $[(\eta^5\text{-}C_5H_5)\text{Re(NO)(PPh}_3)(\eta^2\text{-}C_6H_5CH_2CH=O)]^+PF_6^-$ (**3c**): left, full view; right, Newman-type projection with phenyl rings omitted. Important bond lengths (Å) and angles (deg): Re–Cl, 2.155 (12); Re–O1, 2.062 (9); Cl–O1, 1.318 (11); Re–N, 1.766 (9); Re–P1, 2.437 (3); N–O2, 1.135 (12); O1–Re–Cl, 36.3 (3); Re–O1–Cl, 75.7 (7); Re–Cl–O1, 68.0 (6); N–Re–P1, 88.7 (3); Re–N–O2, 173.2 (12).

Scheme I. Formation and Reactions of Optically Active Aldehyde Complexes
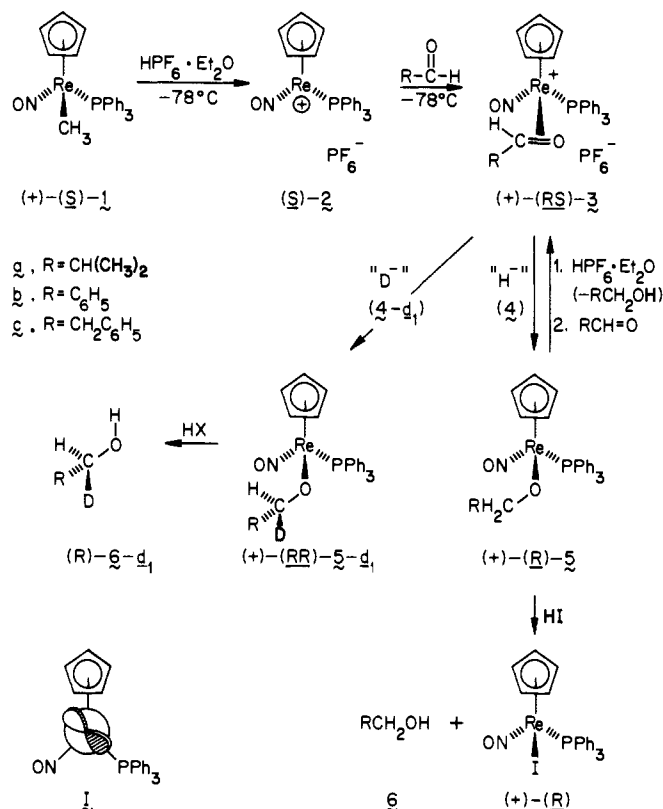
lective complexation of one aldehyde enantioface.[8]

The η^2-aldehyde ligands were expected to adopt conformations that (1) maximized overlap of their π^* orbitals with the rhenium fragment HOMO I (Scheme I)[9] and (2) placed their larger RCH= terminus *anti* to the bulky PPh$_3$ ligand.[10] This was confirmed by an X-ray crystal structure of phenylacetaldehyde complex **3c** (Figure 1). This structure also shows that (*S*)-**2**

preferentially binds the *si* aldehyde enantioface to give a *RS* diastereomer.[8c,11] This places the aldehyde alkyl substituent *syn* to the small NO ligand. If the *re* face were bound, the alkyl substituent would be *syn* to the medium-sized η^5-C$_5$H$_5$ ligand. When the above reactions were repeated with (+)-(*S*)-**1**,[13] ≥98% ee, aldehyde complexes (+)-(*RS*)-**3a–c** formed with $[\alpha]^{25}_{589}$ 229°, 230°, and 135° (Scheme I).[11]

II. Activation. Formyl complex $(\eta^5\text{-}C_5H_5)\text{Re(NO)(PPh}_3)$-(CHO) (**4**)[4] reduced (*RS,SR*)-**3a–c** (CH$_2$Cl$_2$ or THF, –60 to –20 °C) to alkoxide complexes $(\eta^5\text{-}C_5H_5)\text{Re(NO)(PPh}_3)\text{(OCH}_2R)$ (**5a–c**; 68–67% after recrystallization). Complex **4** and free aldehydes did not react over the course of 24 h at 25 °C (CD$_2$Cl$_2$, CDCl$_3$), thus demonstrating that binding to **2** activates aldehydes toward attack. Complexes **5a–c** gave alcohols HOCH$_2$R (**6a–c**) in high yields when treated with acids (CH$_2$Cl$_2$, –78 to 0 °C) such as CF$_3$COOH, HI, and HBF$_4$·Et$_2$O (80–90%; GLC).

Optically active aldehyde complexes (+)-(*RS*)-**3a–c** (Scheme I) were reduced by **4** to optically active alkoxide complexes[11] (+)-(*R*)-**5a–c**, $[\alpha]^{22}_{589}$ 158°, 168°, 152°. When these were treated with HI, iodide complex (+)-(*R*)-$(\eta^5\text{-}C_5H_5)\text{Re(NO)(PPh}_3)$(I)[12] was isolated in 70–80% yields and 94–98% ee. This bounds the ee of the aldehyde and alkoxide complexes as >94% and establishes the expected overall retention of configuration from methyl complex (+)-(*S*)-**1**.[11] When (+)-(*R*)-**5c** ($[\alpha]^{25}_{589}$ 135°) was treated with HPF$_6$·Et$_2$O and then C$_6$H$_5$CH$_2$CH=O (3.0 equiv, –78 °C), HOCH$_2$CH$_2$C$_6$H$_5$ formed as above (86%) and optically active aldehyde complex (+)-(*RS*)-**3c** was obtained in 73% yield and $[\alpha]^{25}_{589}$ 132°. This indicates that optically active alkoxide complexes (+)-(*R*)-**5a–c** can be recycled to optically active aldehyde complexes with *minimal loss of stereochemistry at rhenium*.

The synthesis of optically active alcohols was attempted next. First, racemic aldehyde complexes (*RS,SR*)-**3a–c** were treated with deuterated formyl complex $(\eta^5\text{-}C_5H_5)\text{Re(NO)(PPh}_3)$(CDO) (**4**-$d_1$; 98% labeled). Deuterated alkoxide complexes $(\eta^5\text{-}C_5H_5)\text{Re(NO)(PPh}_3)\text{(OCHDR)}$ (**5a–c**-d_1) formed in >98% diastereomeric excess, as assayed by ^{1}H NMR. These reactions were repeated with optically active aldehyde complexes (+)-(*RS*)-**3a–c**, and CF$_3$COOH was added to give alcohols HOCHDR (**6a–c**-d_1). Products **6a–c**-d_1 were shown to have *R* absolute configurations and be of >97–98% ee by published ^{1}H NMR methods.[14] This establishes that deuterium is delivered to the aldehyde face *anti* to the rhenium and that the alkoxide complexes **5a–c**-d_1 prepared above are *RR,SS* diastereomers. Finally, (+)-(*RS*)-**3b** was treated with optically active deuterioformyl complexes (+)-(*S*)-**4**-d_1 and (–)-(*R*)-**4**-d_1.[13] The resulting samples of (+)-(*RR*)-**5b**-d_1 were of equal diastereomeric purity, thus establishing the reduction stereochemistry to be independent of the chirality of the hydride donor.[15]

III. Prospective. We have demonstrated that aldehyde complexes such as (*RS*)-**3a–c** exhibit the necessary properties to be of exceptional utility in asymmetric organic synthesis: selective binding of metal to one aldehyde enantioface, aldehyde activation, facile organic product liberation, and aldehyde complex regeneration. Future papers will describe similarly stereospecific reactions of (*RS,SR*)-**3a–c** with heteroatom and carbon nucleophiles, other methods for liberating alkoxide ligands from **5a–c**, and aldehyde/nucleophile reactions in which rhenium is used in catalytic quantities.

(8) (a) We have been unable to equilibrate **3a–c** to a mixture of diastereomers (40–50 °C, CDCl$_3$, CD$_2$Cl$_2$, CD$_3$CN (substitution)). The diastereomers of analogous propene and styrene complexes are easily distinguished by NMR.[8b] (b) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (c) See footnote 15 of ref 8b for rules on *R/S* nomenclature; the rhenium configuration is specified first.

(9) (a) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (b) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109.

(10) Analogous η^2-H$_2$C=O complex: Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

(11) Good precedent exists that each reaction should proceed with retention of configuration at rhenium, and *R/S* assignments have been made accordingly;[5,8b,12] $c = 0.0010–0.0007$ g/mL (CHCl$_3$) for $[\alpha]$.

(12) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

(13) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(14) (a) (*R*)-**6a**-d_1: Reich, C. J.; Sullivan, G. R.; Mosher, H. S. *Tetrahedron Lett.* **1973**, 1505. (b) (*R*)-**6b**-d_1: Nagai, U.; Kobayashi, J. *Ibid.* **1976**, 2873. (c) (*R*)-**6c**-d_1: Caspi, E.; Eck, C. R. *J. Org. Chem.* **1977**, *42*, 767.

(15) The analogous acetaldehyde and propionaldehyde complexes form diastereospecifically and give, after treatment with **4**-d_1 and CF$_3$COOH, alcohols HOCHDR of 90% ee but with configurations (*S*) *opposite* to those in Scheme I. The same dichotomy occurs with carbon nucleophiles. These data, and our interpretation, will be reported at a later date.

Supplementary Material Available: Table of data for new compounds[6] and crystallographic data on **3c** including tables of positional parameters, thermal parameters, bond lengths and angles, torsion angles and numbering schemes and packing diagram (17 pages); structure factor tables for **3c** (27 pages). Ordering information is given on any current masthead page.

High-Pressure Studies of Transition-Metal Complexes. 1. Induced Torsional Deformation in Re2Cl8^{2-}
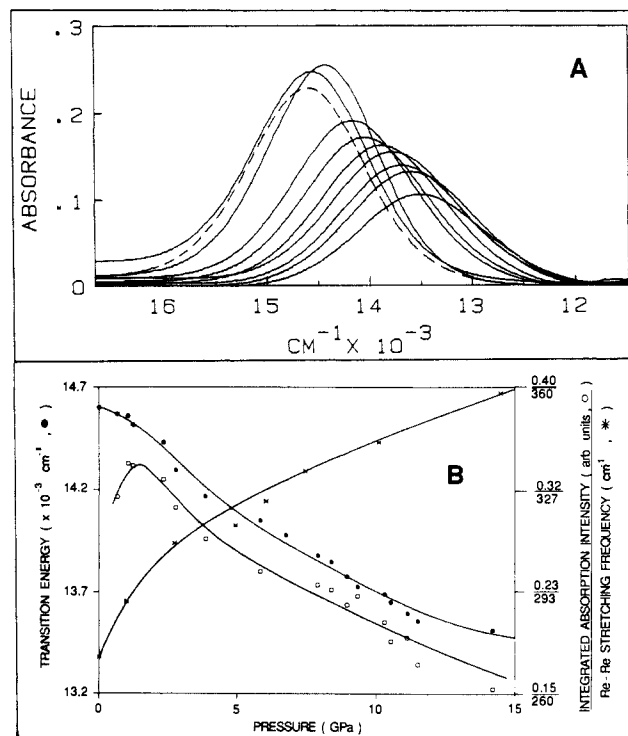
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In complexes containing a metal–metal quadruple bond, such as $Re_2Cl_8^{2-}$, the ability to vary the rotational conformation, and the metal–metal distances, between the two ML_4 units is vital to understanding the role of δ-orbital interactions in determining structure, electronic state energies, and electronic transition intensities.[1-8] Variations in rotational conformation have been obtained heretofore by incorporating bridging ligands which force the complexes to adopt partially staggered geometries. This synthetic approach has yielded a series of complexes which nearly span the entire range of X–M–M–X torsional angles ($0° \le \chi \le 40°$).[5-13] However, no means of *inducing varying degrees of torsion in a specific complex* or of systematically altering M–M distance have been reported.

Recently Carroll et al.[14] reported the pressure dependence of the electronic spectrum of $[(C_4H_9)_4N]_2Re_2X_8$ ($X = Br^-, I^-$). With increasing pressure a new, red-shifted absorption band appears which is attributed to the fully staggered conformer ($\chi = 45°$). The intensity of this band increases relative to that of the eclipsed conformer as pressure is increased, while the transition energies remain essentially unchanged. This result is interpreted as a pressure-dependent shift in a two-state equilibrium between the potential surfaces of the two conformers. The observed red shift of the $^1\delta\delta^* \leftarrow ^1\delta^2$ absorption for the staggered conformer is in qualitative accord with both theoretical predictions[3,5,6] and experimental observations[5,6] of the behavior of these complexes as $\delta(d_{xy})$ overlap goes to zero at $\chi = 45°$. Quantitatively, the red

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, Wiley: New York, 1982.
(2) Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1967**, *6*, 924.
(3) Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7007.
(4) Miskowski, V. M.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 86.
(5) Hopkins, M. D.; Zietlow, T. C.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 510.
(6) Campbell, F. L.; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 177.
(7) Campbell, F. L.; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1984**, *23*, 4222.
(8) Cotton, F. A.; Powell, G.L. *Inorg. Chem.* **1983**, *22*, 1507.
(9) Agaskar, P. A.; Cotton, F. A.; Fraser, I. F.; Peacock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1851.
(10) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.
(11) Cotton, F. A.; Fanwick, P. E.; Fitch, J. W.; Glicksman, H. D.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 1752.
(12) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.
(13) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240.
(14) Carroll, T. L.; Shapely, J. R.; Drickamer, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 3240.

Figure 1. (A) $^1\delta\delta^* \leftarrow ^1\delta^2$ electronic absorption spectra with increasing pressure for $Re_2Cl_8^{2-}$ in CH_2Cl_2. (- - -) Ambient pressure spectrum. (Scale is arbitrary for this spectrum, see text.) (—) With increasing shift of the absorption maximum to lower energy, the corresponding pressures are 1.04, 2.33, 3.86, 5.84, 7.90, 8.96, 10.3, 11.1, and 14.2 GPa, respectively. (B) Pressure dependence of the $^1\delta\delta^* \leftarrow ^1\delta^2$ transition energy maximum (●) integrated absorption intensity (O), and the Re–Re vibrational mode frequency (*). Integrated intensities were obtained from (maximum absorbance × fwhm) and are corrected for sample volume and concentration changes.

shift with pressure[14] is much smaller than that which is expected[3] or observed[5] as χ approaches 45°. Concerning the observation[14] of substantial $\delta\delta^*$ absorption intensity at $\chi = 45°$, theoretical considerations[15,16] suggest that the $\delta\delta^*$ intensity should tend toward zero for fully staggered conformers. This view is supported by expermental results which demonstrate that, in $Mo_2Cl_4(PR_3)_4$ complexes, the $\delta\delta^*$ extinction coefficient decreases from 3110 M^{-1} cm^{-1} at $\chi = 0°$ to 210 M^{-1} cm^{-1} at $\chi = 40°$.[5] Clearly, these inconsistencies need to be understood.

We now report the results of a pressure-dependent study of the electronic absorption and Raman spectroscopy of $Re_2Cl_8^{2-}$ in CH_2Cl_2 solution. The behavior observed is in marked contrast to that reported[14] for the Br^- and I^- complexes. Our results are best interpreted as arising from a gradual change in the torsional coordinate, accompanied by decreasing Re–Re distance, with increasing pressure due to pressure dependence of the shape of the ground-state potential surface.

The present studies were carried out on ~5 mM solutions of $[(C_4H_9)_4N]_2Re_2Cl_8$ in CH_2Cl_2 utilizing diamond anvil cells[17] to attain the static high pressures. Methylene chloride freezes at ~2.2 GPa (1 GPa = 10^4 atm) at room temperatures, and no discontinuities in the spectroscopic data for $Re_2Cl_8^{2-}$ were detected on passing through this phase transition. Absorption energy maxima and resonance Raman frequencies for the metal–metal stretching mode are reversible on cycling of the pressure, indicating negligible sample decomposition at high pressures. These data

(15) Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232 and references therein.
(16) It is possible that new states arising from δ-bonding interactions between d_{xy} and $d_{x^2-y^2}$ orbitals on adjacent metal centers[3] could give rise to new transitions having some intensity. However, such transitions have not been detected for rotamers with torsional angles as great as 40°.[5]
(17) Agnew, S. F.; Swanson, B. I.; Jones, L. H.; Mills, R. L.; Schiferl, D. *J. Phys. Chem.* **1983**, *87*, 5065.