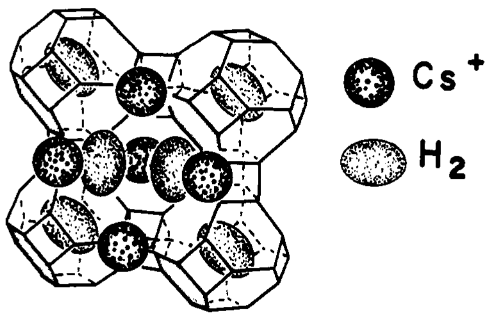


Figure 3. Proposed model for the hydrogen encapsulate of Cs_3Na_9A-type zeolite (Cs_{II}^+ indicated; Na_I^+ omitted).

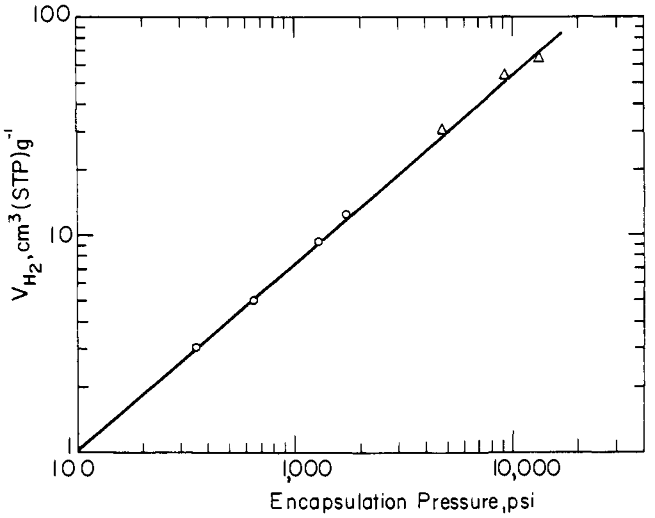


Figure 4. Dependence of V_{H_2} upon the encapsulation pressure at 300 °C (O, lower region; Δ, higher region of measurement).

ume of 155 Å^3, and each α cage, with a gross empty volume of 775 Å^3, could admit a variable number of hydrogen molecules depending on the encapsulation conditions. The change in encapsulation capacity of $Cs_{5.4}Na_{6.6}A$ (Cs_z = 5.4) with pressure is shown in Figure 4. A deviation from linear dependence of V_{H_2} upon the encapsulation pressure (p) is observed, and the empirical expression $V_{H_2} = 0.017\,p^{0.868}$, derived from the graph, holds both for the low (300-1700 psi) and the high (4000-13 300 psi) regions of measurements. At 13 300 psi, V_{H_2} = 65 cm^3 (STP) g^{-1}, corresponding to 0.6% by weight. The results obtained are in good agreement with the van der Waals equation for real gases, indicating that the stability of the Cs-A(H_2) encapsulate remains entirely unaffected by the encapsulation pressure up to 13 000 psi, and that V_{H_2} values >1% at higher pressures are feasible. This, coupled with the possibility of temperature-controlled slow release of the element, illustrates the potential importance of the principle of hydrogen encapsulation in energy and related problems.

Acknowledgment. This project was sponsored and allowed for publication by the Office of the Chief Scientist, The Ministry of Commerce and Industry, Israel. Thanks are due to Dr. I. Lewkowicz for permission to use the high pressure equipment at Soreq Nuclear Research Center, Yavne, Israel.

References and Notes

(1) D. P. Gregory, *Sci. Am.*, **228**, 13 (1973); C. A. McAuliffe, *Chem. Ind. (London)*, 725 (1975); *Chem. Br.*, **9**, 559 (1973); T. N. Veziroglu, "Hydrogen Energy", Plenum Press, New York, N.Y., 1975.

(2) D. L. Cummings and G. J. Powers, *Ind. Eng. Chem., Process Des. Dev.*, **13**, 182 (1974).

(3) J. H. N. Van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, *Philips Res. Rep.*, **25**, 133 (1970).

(4) J. J. Reilly and J. R. Johnson, *Proc. World Hydrogen Energy Conf., 1st, 1976*, **II**, paper 8B-3 (1976).

(5) W. J. Sesny and L. H. Shaffer, U. S. Patent 3 316 691 (1967).

(6) R. M. Barrer and D. E. W. Vaughan, *Trans. Faraday Soc.*, **67**, 2129 (1971), and references therein.

(7) The aluminosilicate framework of A-type zeolite is characterized by two types of polyhedra, i.e., an α cage (26-hedron of type I) and a β cage (14-hedron of type I).[10] The main intracrystalline channel system is formed by interconnection of α cages through 8 rings (d = 4.2 Å). The structure is cubic, and each α cage is connected to eight β cages through 6 rings (d = 2.2 Å). In the dehydrated, alkali-exchanged zeolite there are twelve cations per pseudocell, eight of them near the center of 6 rings (site I) and three near the 8 rings (site II). The exact dimensions of these ring apertures depend on the size of the cations in sites I and II, and, consequently, guest molecules can penetrate the α or β cages only if their kinetic diameter (σ) is smaller than the effective apertures. However, if σ is only slightly bigger than the aperture, guest molecules can be forced into the cavities by applying high pressure and elevated temperature. Quenching to room temperature results in trapping (encapsulation) of the molecules inside the cavities. The process can be reversed and the trapped molecules can be released upon heating the zeolite.

(8) Y. Amenomiya, *Chem. Tech.*, **6**, 128 (1976).

(9) The extent of ion exchange, as determined by atomic absorption and/or flame emission analysis, was 72% for K-A, 46% for Rb-A, and 45% for Cs-A, corresponding to the formulae $K_{8.6}Na_{3.4}$-A, $Rb_{5.5}Na_{6.5}$-A, and $Cs_{5.4}Na_{6.6}$-A, respectively; 0.4 M (CsCl + NaCl) solutions, containing variable relative concentrations of the two salts, were used to prepare CsNa-A samples with various Cs_z (Figure 2).

(10) D. W. Breck, "Zeolite Molecular Sieves", Wiley, New York, N.Y., 1974, pp 83-90.

(11) J. M. Hammersley and D. C. Handscomb, "Monte Carlo Methods", Methuen, London, 1964, Chapter 11, p 158.

(12) L. V. C. Rees and T. Berry, *Proc. Conf. Mol. Sieves, 1969*, 149 (1969).

(13) T. Takaishi, Y. Yatsurugi, A. Yusa, and T. Kuratomi, *J. Chem. Soc., Faraday Trans. 1*, **71**, 97 (1975); T. Takaishi, T. Ogushi, and A. Yusa, *Int. Conf. Mol. Sieves, 4th, 1977*, 95 (1977).

(14) This model is drawn after the array of 14-hedra in zeolite A.[10] It shows a "half" of an α cage surrounded by four β cages. The exact position of the H_2 molecules is unknown, and their number (5 per unit cell, corresponding to ~0.5% by weight) was chosen arbitrarily.

(15) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).

(16) Research Associate.

Dan Fraenkel,[16] Joseph Shabtai*
Department of Organic Chemistry
The Weizmann Institute of Science, Rehovot, Israel

Received April 13, 1977

The First Formally Three-Coordinate d^8 Complex: Tris(triphenylphosphine)rhodium(I) Perchlorate and Its Novel Structure

Sir:

Kinetic studies indicate that an unisolable three-coordinate d^8 compound of rhodium(I), $RhCl(PPh_3)_2$, formed dissociatively from $RhCl(PPh_3)_3$, is the raison d'être of Wilkinson's catalyst in the homogeneous hydrogenation of alkenes.[1] Thus, the successful synthesis and isolation of any three-coordinate d^8 complex would not only corroborate their previously doubted existence as intermediates but hold promise of high reactivity and considerable catalytic potential. Moreover, a very interesting structural dilemma is anticipated for d^8 metals with two vacant coordination sites. The steric predilection of three bulky ligands for trigonal planarity would mandate paramagnetism,[2] but the prevailing diamagnetism of low-valent phosphine complexes (of even d^n configuration) makes this highly unlikely. Group 8 complexes with two sites of coordinative unsaturation (so-called 14-electron compounds) are known only in a d^{10} configuration, exemplified by ML_2 complexes of the nickel triad, and show expected linear coordination.[3]

Synthetic routes to complexes of unusually low coordination number have exploited bulky phosphines,[3] sterically demanding anions,[4] and dilute low temperature matrices.[5] Our strategy has been to employ bulky phosphines under conditions which remove potentially bridging anions and donor solvents. Treatment of $RhCl(PPh_3)_3$ with $TlClO_4$ in donor solvents such as acetone, ethers, or alcohols precipitates the halide as TlCl allowing isolation of the orange crystalline complexes $[Rh(solvent)(PPh_3)_3]ClO_4$ (**1**). Evidence such as the low ν_{CO} (1665 cm^{-1}) in the acetone complex indicates that these

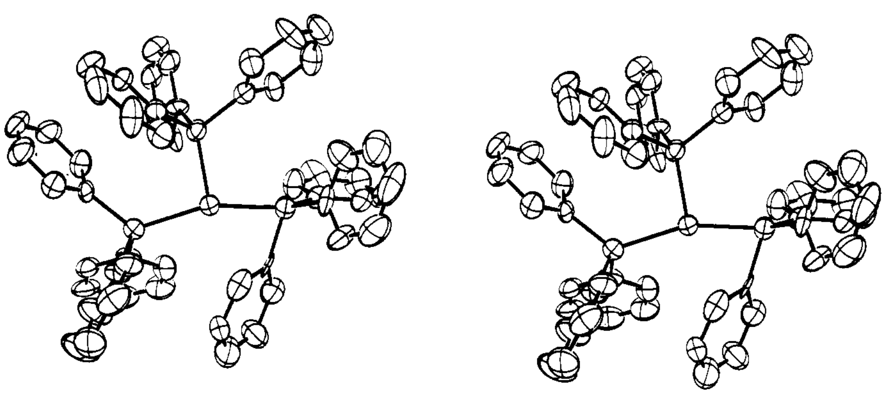


Figure 1. A stereoscopic view of the $[Rh(PPh_3)_3]^+$ cation, showing the planar, approximately T-shaped coordination about rhodium. Note the unusual manner in which the phenyl ring at the lower right is drawn in toward the rhodium atom.

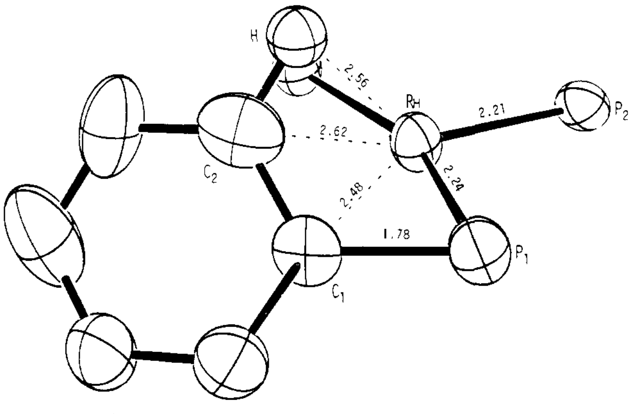


Figure 2. A close-up of the interaction region between the rhodium metal and the unique phenyl group, viewed in a direction normal to the phenyl ring. A dihedral angle of 57° exists between the $RhP_1P_2P_3$ and $P_1C_1C_2H$ planes. There are weak but perceptible interactions between Rh and the C_1 and C_2 atoms, causing the $Rh-P_1-C_1$ angle to assume a highly distorted value of 75.6 (5)°. The ortho hydrogen atom, whose calculated position is indicated in this diagram, also appears to be weakly interacting with the metal.

complexes are four coordinate with a coordinated solvent molecule and are therefore structural models for specifically solvated intermediates in catalysis by cationic d^8 complexes.[6] Of more interest, however, is that recrystallization of any of these solvated cations from oxygen-free dichloromethane gives virtually quantitative yields of a red, lattice-solvated species, $[Rh(PPh_3)_3]ClO_4 \cdot CH_2Cl_2$ (**2**).

Compound **2** crystallizes in the triclinic system with space group $P\bar{1}$; $a = 11.925$ (4), $b = 14.466$ (5), $c = 15.553$ (6) Å; $\alpha = 92.637$ (14), $\beta = 88.931$ (17), $\gamma = 112.744$ (15)°; $\rho_{calcd} = 1.34$ g/cm^3; $R = 0.075$ and $R_w = 0.081$; 3318 unique data.[7]

The crystal structure confirms the suspected $[Rh(PPh_3)_3]^+$ coordination (Figure 1). The possibility of x-ray invisible hydride ligands can be ruled out by the absence of high field ^1H NMR peaks or IR bands attributable to ν_{RhH}. Also, the red color, diamagnetism, and extreme oxygen sensitivity are consistent with the rhodium(I) d^8 formulation but collectively untenable for rhodium(II) or -(III) oxidation levels. The inner coordination sphere (Figure 2) of phosphorus donors more closely approximates a T shape than trigonal planarity ($P_1-Rh-P_2 = 102.4$ (2), $P_1-Rh-P_3 = 159.3$ (2), and P_2-Rh-P_3 97.7 (2)°. Two of the phosphines (P_2, P_3) are normal but the third is highly distorted and participates in an unprecedented $Rh \cdots C$ interaction (2.48 (2) Å) with the C_1 atom of one phenyl ring (i.e., the P-bonded carbon, or α carbon). A weaker rhodium interaction occurs with a single ortho carbon atom (C_2) at 2.62 (2) Å and its assumed hydrogen atom at 2.56 Å. The dihedral angle between the phenyl ring and the RhP_1C_1 plane is 57°. The assumption of a normal ortho hydrogen position from C_2 seems justified in that the dimensions of this unique phenyl ring are all quite typical; in particular the C_1-C_2 bond (1.41 (2) Å) is within the observed range for normal phenyl groups (1.34–1.42 Å). The acute $Rh-P_1-C_1$ angle (75.6 (5)°) best illustrates the unusual distortion about the P_1 phosphine and the other $Rh-P_1-C$ angles are correspondingly obtuse (124.3 (6), 126.7 (5)°).

The rationale behind this structure does not lie in intermolecular effects; there are no close nonbonding contacts (<3.0 Å) between the cations, ClO_4^- or CH_2Cl_2. Rather, the $[Rh(PPh_3)_3]^+$ stereochemistry seems to result from an electronically dictated distortion away from trigonal planarity towards a T shape to allow diamagnetism.[8] Related to this is the matrix-isolated d^8 complex $Fe(CO)_3$ deduced to have nonplanar stereochemistry.[5] With three-coordination, however, the rhodium atom has much of its coordination sphere vacant and seeks further electron density from the $P_1-C_1-C_2-H$ bonding framework. The highly coordinatively unsaturated tetrabenzyltitanium[9] shows a closely related interaction with $Ti \cdots\cdots$ (α carbon) distances of 2.6–2.9 Å. The presumed $Rh \cdots H$ interaction at 2.5 Å is well inside the limits considered to be attractive[3] and is similar to $RuCl_2(PPh_3)_3$.[10] The predominant interaction remains rhodium-phosphorus bonding since, although the P_1-C_1 bond is slightly compressed, the C_1-C_2 bond length is normal and the $Rh \cdots C_1$ and $Rh \cdots C_2$ interactions are considerably greater than Rh–C bonds typical of alkenes (2.1 Å)[11] or allyls (2.2 Å).[12]

It is tempting to speculate that partial metal-phenyl group interactions (both intra- and intermolecular) in triphenylphosphine complexes may be of considerable importance in the stabilization of reaction intermediates. For example, the utility of triphenylphosphine over other phosphines in certain reactions,[13] the prevalence of phenyl groups in cyclometalation reactions,[14] and the apparent advantage of phenyl substituents in chiral phosphine complexes for maximizing catalytic asymmetric induction[15] may not be totally the result of synthetic convenience.

It has occurred to us that the structure of **2** may represent an intermediate about to undergo an ortho metalation reaction. However, upon heating **2** as a solid or in solution we find no evidence of ortho metalation. Compound **2**, even as a solid, is instantly decomposed by dioxygen to triphenylphosphine oxide containing products. Donor solvents add to regenerate **1** and carbon monoxide yields $[Rh(CO)_2(PPh_3)_3]ClO_4$. Surprisingly, oxidative addition of dihydrogen does not occur at ordinary pressures, reminiscent of $Pt(PPh_3)_3$,[16] but this is considered advantageous in catalytic hydrogenation which occurs with 1-hexene at reasonable rates. The catalytic potential, reactivity, and solution structure of **2** and its related phosphine analogues is currently being explored.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE 75-03646) for research support. C.A.R. is pleased to acknowledge support from an Alfred P. Sloan Fellowship (1976-1978) and a Camille and Henry Dreyfus Teacher-Scholar Award (1976-1982). R.B. acknowledges receipt of an NIH Research Career Development Award (1975-1980). Y.W.Y. thanks the USAID for support.

Note Added in Proof. Van Gaal and van den Bekerom have published the synthesis of $RhX(PCy_3)_2$ (X = F, Cl, Br, I; Cy = cyclohexyl) deduced to be three-coordinate by NMR in the case of the fluoride and deduced to be in equilibrium with a four-coordinate dimer in the case of the chloride: H. L. M. van Gaal and van den Bekerom, *J. Organomet. Chem.*, **134,** 237 (1977).

References and Notes

(1) J. Halpern, Joint USC-UCLA-CalTech seminar at CalTech, 1976. Although its magnitude has previously been in dispute, the dissociation of $RhCl(PPh_3)_3$ is now definitively established: H. Aria and J. Halpern, *Chem. Commun.*, 1571 (1971); P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.*, **94,** 3240 (1972).

(2) In a perfectly trigonal planar ligand field the d orbitals are split $d_{xz}, d_{yz} < d_{z^2} < d_{xy}, d_{x^2-y^2}$. The highest energy degenerate pair mandates two unpaired electrons for a d^8 configuration.

(3) S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **98,** 5850 (1976), and references therein.

(4) D. C. Bradley, *Chem. Br.*, **11,** 393 (1975).

(5) M. Poliakoff, *J. Chem. Soc., Dalton Trans.*, 210 (1974).

(6) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **98,** 2134 (1976).

(7) X-ray diffraction data were collected on a Nonius CAD-3 automated diffractometer with Mo Kα radiation up to a 2θ maximum of 45°. The structure was solved by heavy-atom methods. All nonhydrogen atoms were located, and calculated hydrogen positions were included but not refined.

(8) Distortion from trigonal planarity toward a T shape splits the d_{xy} and $d_{x^2-y^2}$ energy levels.[2]

(9) I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Am. Chem. Soc.*, **93,** 3787 (1971).

(10) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4,** 778 (1965).

(11) M. A. Bennett, P. W. Clark, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 1011 (1972).

(12) M. McPartlin and R. Mason, *Chem. Commun.*, 16 (1967).

(13) The DMF preparation of Vaska's compound is successful only with triphenylphosphine.

(14) M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, **16,** 73 (1977).

(15) J. D. Morrison, M. F. Masler, and M. K. Neuberg, *Adv. Catal.*, **25,** 81 (1976).

(16) R. Ugo, G. La Monica, F. Cariati, S. Cenini, and F. Conti, *Inorg. Chim. Acta*, **4,** 390 (1970).

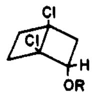
Yohannes W. Yared, Susan L. Miles
Robert Bau, Christopher A. Reed*
Chemistry Department, University of Southern California
Los Angeles, California 90007

Received June 13, 1977

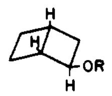
Strained Ring Systems. 17.[1]
An Unusual Inversion of Configuration in the Alkali Metal Promoted Protio-Dechlorination of 1,4-Dichloro-*endo*-2-alkoxybicyclo[2.2.0]hexanes to *exo*-2-Alkoxybicyclo[2.2.0]hexanes

Sir:

We wish to report the unique alkali metal promoted protio-dechlorination reductions of 1,4-dichloro-*endo*-2-methoxybicyclo[2.2.0]hexane (**1**)[2] in Li/*tert*-BuOH/THF



1, R = CH_3
3, R = C_2H_5



2, R = CH_3
4, R = C_2H_5

to *exo*-2-methoxybicyclo[2.2.0]hexane (**2,** 100%) and 1,4-dichloro-*endo*-2-ethoxybicyclo[2.2.0]hexane (**3**) in Na/NH_3/Et_2O (−33 °C) to the *exo*-ethoxy derivative **4** in 93%.[3] The reduction of **1** was carried out under reflux with excess lithium wire for 1 h (reduction appeared to be complete in ~0.5 h). Approximately 4 equiv of lithium were consumed. Ethers **2** and **4** were readily identified from their ^1H NMR signals of C_2 endo-H observed as broadened triplets (**2**, $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.99; **4**, $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 3.99) due to virtual coupling as seen in the exo alcohol (**2**, R = H).[4] The ^1H NMR pattern of this proton was very different from those seen in the endo alcohol[5a] and certain esters,[5b] **1**,[2] and 4-chloro-*endo*-3-methoxybicyclo[2.2.0]hexane-1-carboxylic acid.[2]

Table I. Results of the Reductions of **1** and **3** with a Deficiency of Sodium in NH_3/Et_2O[a] at −33 °C

Mole ratio of sodium/ dichloro compd	% recovered **1** or **3**[b]	% **2** or **4**[b]	% adduct **7**[c]	% polymer[d]
Na/**1** (~2/1)[e,f]	28	56 (**2**)	2 (R = CH_3)	14
Na/**3** (~1.2/1)[g,h]	50	39 (**4**)	7 (R = C_2H_5)	4

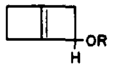
[a] 300 mL each of NH_3 and Et_2O. [b] By ^1H NMR integration vs. an internal standard. [c] By ^{13}C NMR. [d] By weight. [e] 18.2 mmol of **1.** [f] 20 mL of cyclopentadiene injected into reaction mixture 5 s after **1** was syringe injected. [g] 24.6 mmol of **3.** [h] Same as *f* with only 2-3-s delay in the injection of cyclopentadiene after **3** was added.

The question of which ring centers were involved in the apparent overall inversion of configuration at C_2 in the **1** → **2** and **3** → **4** conversions was answered by carrying out the reduction of **1** in the presence of *t*-BuOD (98% deuterium). The product was **2**-*1,4*-d_2 containing ~96% deuterium at each bridgehead position.[6] *The important point here is that no alteration at* C_2 *occurred in the reduction of* **1** *to* **2,** which is assumed to apply to the **3** → **4** reduction also.

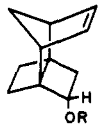
Since the olefin bicyclo[2.2.0]hex-1(4)-ene (**5**) is known to be produced by certain chemical and electrochemical reductions of 1-bromo-4-chlorobicyclo[2.2.0]hexane,[8] several attempts were made to trap the corresponding 2-alkoxy olefins **6** derived from **1** and **3**. **1** was allowed to react with Li wire in triglyme at 70 °C and 50 mm pressure[9] (**2**, bp 57 °C (58 mm)). A cooled trap containing the highly reactive Diels-Alder diene, 2,5-diphenyl-3,4-benzofuran, in THF was placed between the reaction mixture and the pump. After several hours, no evidence of olefin **6** (R = CH_3) as an adduct was found in the trap. Addition of *t*-BuOH to the deep blue reaction mixture after this time (Li wire still present) produced a small amount of **2** and a major amount of a polymer.

In separate experiments, **1** or **3** was injected into a solution of Na in NH_3/Et_2O at −33 °C followed shortly thereafter (2-5 s) by rapid syringe addition of a large excess of 1,3-cyclopentadiene.[10] In both experiments a deficiency of Na was present so as not to completely convert **1** → **2** and **3** → **4.** The results are given in Table I.

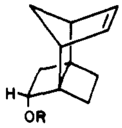
The presence of adduct **7** (R = CH_3) was deduced from the ^{13}C NMR spectra of the reaction mixture (after workup) and when much of **2** had been removed by distillation. The larger amount of adduct **7** (R = C_2H_5) in the limited reduction of **3** (Table I) allowed for its separation and collection of GLC. This collected sample (containing a small amount of **3**) exhibited the following spectral data: ^1H NMR $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.25 (m, 2), 4.27 (octet, C_7 H), 3.38 (q, OCH_2CH_3), and 2.8-1.0 (m, 10); ^{13}C NMR in agreement with **7**;[11] mass spectrum (heated inlet) *m/e* 190 ($M^{+\cdot}$). The adduct is a single isomer of 7- (**7a**) and 10-ethoxytetracyclo[$4.2.2.1^{2,5}.0^{1,6}$]undec-3-ene (**7b**) as judged from both GLC and the ^{13}C NMR spectrum. While we assume the stereochemical orientation of the alkoxy group to be exo



6



7a



7b