erally considerably less than observed for $Gd(dpm)_3$. It may be noted that the relative r_i calculated from $\langle\delta_i\rangle^{1/6}$ for $Gd(dpm)_3$, 0.57, 0.55, and 0.96, for δ_p/δ_o, δ_m/δ_o, and δ_m/δ_p, agree reasonably well with predictions from X-ray data,[4,5] whose values are 0.53, 0.54, and 1.02, respectively.

It is evident from our results that analysis of relative line widths due to shift reagents can lead to very serious errors in estimated distance ratios. This work points out the hazards of relying on structural information deduced from line widths arising from *shift* reagents. The suggested absence of exchange broadening effects for $Er(dpm)_3$ therefore indicates that the observed linewidth ratios reflect nonaxial magnetic anisotropy.

Preliminary considerations suggest that this contrast in behavior with respect to effective axial symmetry noted for the line width and shift data should not have been unexpected. The dipolar shift equation contains only odd powers of trigonometric functions of the azimuthal angle[2]; such odd functions can be averaged to zero *via* rotations as discussed elsewhere. Dipolar relaxation, on the other hand, is made up of sums of squares of matrix elements of the dipolar Hamiltonian,[17] such that even powers of these trigonometric functions will appear; such functions cannot be averaged to zero. Hence relaxation rates may be expected to reflect rhombic anisotropy under conditions where such effects vanish for dipolar shifts.

Work is in progress to define more clearly nuclear relaxation, both proton and heteronuclei,[18] in the presence of lanthanide ions. The possibility of obtaining information of the rhombic anisotropy from the experimental line width data is being explored.

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(18) J. W. Faller and G. N. La Mar, *Tetrahedron Lett.*, 699 (1974).
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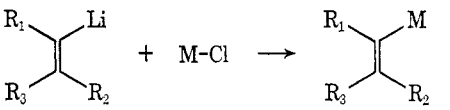
Comparative β-Hydride Eliminations from η^1-Vinyliridium(I) and -rhodium(I) Complexes

Sir:

β-Elimination and readdition of metal hydride has been shown[1] to be responsible for the formation of rearranged organic products of certain reactions involving transition metal alkyls. η^1-Vinylmetal complexes also occur as intermediates in several metal-assisted organic transformations and we have observed that such complexes can undergo two different types of β-hydride elimination sequences.

η^1-Vinylic derivatives of Ir(I) or Rh(I) can be prepared by reaction of metal(I) halide complexes and the corresponding lithium reagent[2-5] (reaction 1). Thermol-



(1)

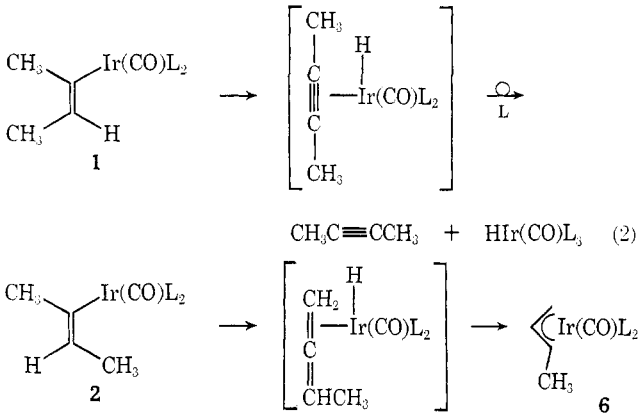
1, $R_1 = R_3 = CH_3$; $R_2 = H$; M = *trans*-$L_2Ir(CO)$
2, $R_1 = R_2 = CH_3$; $R_3 = H$; M = *trans*-$L_2Ir(CO)$
3, $R_1 = R_3 = H$; $R_2 = CH_3$; M = *trans*-$L_2Ir(CO)$
4, $R_1 = R_2 = CH_3$; $R_3 = H$; M = *trans*-$L_2Rh(CO)$
5, $R_1 = R_2 = CH_3$; $R_3 = H$; M = L_3Rh
L = PPh_3

ysis products of **1–5** depend on the (C=C) stereochemistry of the trisubstituted vinylic moiety and on the position of attachment of alkyl groups to the double bond. For **1**, a β-vinylic H cis to Ir is present; metal hydride and alkyne are formed. For **2**, **4**, and **5** (which have no *cis*-β-vinylic H) elimination of β-allylic H occurs to generate, *via* an η^2-allene complex, η^3-crotyl species **6**.[6] For **1**, in which both types of β-H are present, no η^3-crotyl complex is formed. Thus, the trend for competitive rates of β-H elimination is cis β-vinylic H > β-allylic H. If neither type of β-H is present (**3**), only intramolecular oxidative addition of a C–H bond of coordinated L occurs[2] to yield, ultimately, olefin. In no case were the products of elimination of trans β-vinylic H, γ-allylic H, or α-vinylic H observed.

A typical synthesis and thermolysis sequence occurred as follows. Compound **2** was prepared by stirring a suspension of 312 mg of $L_2Ir(CO)Cl$ (0.4 mmol) with a slight excess of *trans*-2-lithio-2-butene[7] in ether, under argon, at −30° for 0.5 hr and then at room temperature for 0.5 hr.[8] The yellow suspension of $L_2Ir(CO)Cl$ slowly dissolved and the solution became orange. Ethanol (10 ml) was added and the reaction mixture was filtered and then concentrated by partial removal of solvents *in vacuo*. Golden yellow crystals of **2** were formed and were recovered by filtration, washed copiously with ethanol, and dried *in vacuo* (ν_{CO} 1935 cm^{-1} (Nujol); nmr (C_6D_6): δ 1.45 (m, 6), 6.50 (m, 1), and complex absorption for PPh_3 (30)).[9,10] A solution of **2** in C_6D_6 was heated to 90° in a sealed tube for 8 hr during which time it slowly isomerized to **6** (reaction 2). At no time could nmr signals attributable to free or η^2-coordinated organic ligands be detected.

Complexes **1** and **3** were prepared in the same way and were spectrally comparable with **2**. In contrast with the decomposition behavior of **2**, **1** in C_6D_6 rapidly underwent cis β-vinylic H elimination to yield 2-butyne at room temperature (reaction 2). Vinylic complexes **1** and **2** all underwent β-H elimination slowly compared with their *n*-octyl analog[11] which has not yet been

(1) For example, see C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **93**, 1280 (1971), and references cited therein.
(2) J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, **94**, 6226 (1972).
(3) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).
(4) M. D. Rausch and G. A. Moser, *Inorg. Chem.*, **13**, 11 (1974).
(5) We were unable to prepare **1** by direct reaction of 2-butyne with $HIr(CO)L_3$.
(6) C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 850 (1971).
(7) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).
(8) Ether was distilled under argon from sodium benzophenone ketyl. This was made possible by admixing 10% tetraglyme with the ether.
(9) Satisfactory elemental analyses were obtained.
(10) The stereochemistry of the lithium reagent was checked by vpc determination (6 ft × 0.25 in. column packed with 5% Carbowax 20 M on 60/80 Chromosorb P) of the bromide products from reaction with 1,2-dibromoethane. Protonation of **2** (in C_6D_6) with dilute HCl yielded *trans*-2-butene as the sole organic product. (C=C) Stereochemistry is therefore maintained in the vinylation of the metal.
(11) J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, **96**, 2276 (1974).



$$CH_3C{\equiv}CCH_3 + HIr(CO)L_3 \quad (2)$$

isolated. Compound **3** (in which no accessible β-H is present) slowly produced propene as the sole organic product when heated to 80° in C_6D_6.

Reactions of Rh(I) vinylic complexes were briefly investigated. Hydride rearrangements in these systems were so rapid, however, that treatment of either $L_2Rh(CO)Cl$ or L_3RhCl with *trans*-2-lithio-2-butene yielded, on immediate work-up, products derived from isomerization to η^3-crotyl complexes[12]; only a small amount of material attributed to **4** was detected by ir.

Stereochemical factors affecting β-H elimination from Pt(II) alkyls have been noted; acyclic alkyls[13] eliminate faster than do metallocyclic ones.[14] We note that elimination from aklyliridium(I) complexes is faster than from vinylic analogs. Stereochemical arguments may play some role in assessing this difference in rates, too. However, such considerations do not appear to account for the large difference in rates observed for cis β-vinylic H *vs.* β-allylic H elimination. Bond strength arguments cannot be used to explain the observed order of rates for β-H elimination since they would predict the opposite trend. The relative stability of complexes formed by β-H elimination (η^2-acetylene *vs.* η^2-allene) may dictate the direction of reaction for η^1-vinylic systems, and this phenomenon should be added to the growing list of considerations thus far established for it.

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(12) C. A. Reilly and H. Thyret, *J. Amer. Chem. Soc.*, **89**, 5144 (1967).
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An Efficient and Mild Lactonization Method for the Synthesis of Macrolides

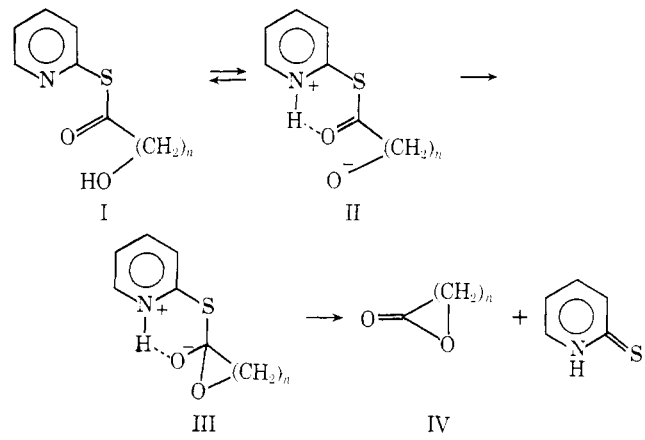
Sir:

The synthesis of naturally occurring large ring lactones, including such important substances as the erythromycins[1a] and cytochalasans,[1b] is rendered all the more formidable by the limited utility of most of the existing cyclization methods.[2-4] We describe here a new method for internal esterification of hydroxy acids to form medium and large ring lactones which appears to be highly effective and yet mild enough to be used with complex and polyfunctional substrates. The development of the method was guided by the following considerations.

(1) Because lactone formation becomes relatively slow in going from common to large ring sizes,[5] undesirably high reaction temperatures or excessively slow addition of the hydroxy acid derivative to the reaction medium would be required (for maintenance of high dilution) unless some means can be found to activate the reacting groups.

(2) One way of simultaneously activating both the carboxyl and hydroxyl groups for mutual reaction would be to utilize a carboxylic derivative which would favor proton transfer from hydroxyl to carboxylic oxygen. This idea is illustrated for the specific case of a 2-pyridinethiol ester of a hydroxy acid (I) in Scheme I.

Scheme I



The proton transfer from hydroxyl to carbonyl in I is clearly more favorable than for simple esters. The dipolar intermediate II (or hydrogen bonded equivalent) generated by internal proton transfer in I, could reasonably be expected to undergo a facile, *electrostatically driven*, cyclization to III which then would yield the

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(2) For methods involving internal esterification see (a) M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **17**, 1283 (1934); **18**, 1087 (1935) [acid catalysis]; (b) D. Taub, N. N. Girotra, R. D. Hoffsommer, C. H. Kuo, H. L. Slates, S. Weber, and N. L. Wendler, *Tetrahedron*, **24**, 2443 (1968) [carboxyl activation *via* $(CF_3CO)_2O$]; (c) E. W. Colvin, T. A. Purcell, and R. A. Raphael, *J. Chem. Soc., Chem. Commun.*, 1031 (1972) [carboxyl activation as imidazolide]; (d) M. Stoll and P. Bolle, *Helv. Chim. Acta*, **31**, 98 (1948) [heterogeneous gas-phase reaction over TiO_2]; and (e) E. W. Spanagel and W. Carothers, *J. Amer. Chem. Soc.*, **58**, 654 (1936) [thermal catalytic depolymerization of polyesters].
(3) For cyclizations generating bonds other than the ester linkage see (a) J. Carduff, G. Eglinton, W. McCrae, and R. A. Raphael, *Chem. Ind. (London)*, 559 (1960) [oxidative coupling of a diacetylene]; (b) E. J. Corey and H. A. Kirst, *J. Amer. Chem. Soc.*, **94**, 667 (1972) [cyclization of a dihalide by $Ni(CO)_4$]; (c) R. N. Hurd and D. H. Shah, *J. Org. Chem.*, **38**, 390 (1973) [Dieckmann cyclization]; and (d) H. Hunsdiecker and H. Erlbach, *Chem. Ber.*, **80**, 129 (1947) [internal nucleophilic displacement by carboxylate].
(4) For macrocycle formation by C=C cleavage of fusion bonds see (a) I. J. Borowitz, V. Bandurco, M. Heyman, R. D. G. Rigby, and S. Ueng, *J. Org. Chem.*, **38**, 1234 (1973), and earlier papers, and (b) J. Falbe and F. Korte, *Chem. Ber.*, **96**, 919 (1963).
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