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Derivative Chemistry of $HCo[P(OR)_3]_4$. I. Basic Dynamic Stereochemical Processes

Sir:

Synthesis[1] of $KCo[P(OR)_3]_4$ has provided entry to two classes of $HCo[P(OR)_3]_4$ derivatives, each of importance to an understanding of basic fluxional processes; one comprises C_{3v} XML_4 molecules and the second, trihapto allyl and benzyl derivatives of $Co[P(OCH_3)_3]_3$.

A C_{3v} HML_4 molecule cannot strictly undergo a Berry rearrangement because there is a C_{2v} constraint to the reaction path.[2] A physical process applied to quasitetrahedral HML_4 molecules is the tetrahedral jump mechanism.[2] Dnmr datafor the new $XCo[P(OR)_3]_4$[3] molecules suggest that the tetrahedral jump mechanism is a probable rearrangement path for C_{3v} or pseudo-C_{3v} XML_4 aggregates.

$CH_3Co[P(OR)_3]_4$, like the parent hydrides,[2] do not show a limiting slow exchange ^{31}P or ^{13}C spectrum to −160°. These methyl derivatives cannot have the near T_d CoP_4 microsubstructure of the hydrides[2] because of $H(CH_3)$–P repulsions (precision model analysis). Nevertheless, this structural change and the larger size of the X group does not substantially raise the rearrangement barrier. A relative measure of barrier enhancement may be inferred from a study[4] that showed $CH_3Rh[P(OCH_3)_3]_4$ to have a rearrangement barrier about 2 kcal/mol higher than the analogous hydride.[2]

The mercurial $Hg\{Co[P(OCH_3)_3]_4\}_2$ is a bi(trigonal bipyramid) with axially (mercury) shared vertices. This molecule is fluxional ($AB_3 \rightleftharpoons A_4$ ^{31}P spectra) with a barrier, $E_a^{\ne}$, of ~10 kcal/mol. The coordination polyhedron about cobalt should be farther removed from quasitetrahedral than the methyl derivative. $Co_2[P(OR)_3]_8$, unlike the carbonyl analog, has a symmetrical bicapped trigonal antiprismatic Co_2P_8 framework;[5] each cobalt atom has micro C_{3v} symmetry with four P and one Co ligating atoms. A precision model of the dimer indicates that the cobalt atom should be displaced out of the equatorial P_3 plane *away* from the axial phosphorus atom and that ligand–ligand interactions are so intimate as to seriously encumber any rearrangement path. The molecule is stereochemically rigid to 100° (^1H spectra).

We suggest that a low energy rearrangement path for C_{3v} XML_4 molecules is the "tetrahedral edge traverse" outlined in Figure 1 with a reaction path constrained only to C_s symmetry. Where ϕ is close to 70.5°, X will be small, there will be the identity with the tetrahedral jump mechanism, and barriers will be very low. As ϕ increases, barriers should rise to some point midway between a ϕ of 70.5 and 90°.[6] As ϕ approaches 90°, the amorphous energy surface for the five-atom family is evident because in this region[7] barriers may fall and a lower energy quasi-Berry reaction path may become available. As ϕ becomes greater than 90°, as in $Co_2[P(OR)_3]_8$, the barrier should rise rather sharply. We plan to gather X-ray and dnmr[8] data for C_{3v} XML_4 species to test the "tetrahedral edge traverse" proposal.

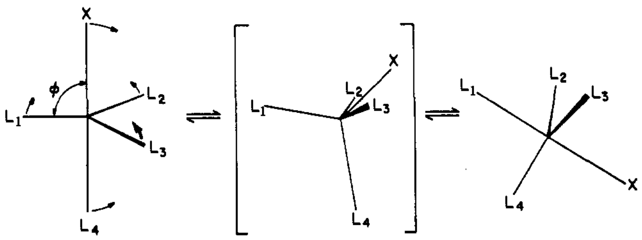

Figure 1. A representation of the tetrahedral edge traverse mechanism for C_{3v} or pseudo-C_{3v} XML_4 molecules. This simply is a more general statement of the tetrahedral jump mechanism.[2] Note that where $\phi \rightarrow 90°$ and X and L are very similar in steric and electronic character, the bracketed "transition state" is a new (labeled) trigonal bipyramid; the process then is indistinguishable from the Berry mechanism.

The ^1H spectra of h^3-$C_3H_5Co[P(OCH_3)_3]_3$ and h^3-1-$CH_3C_3H_4Co[P(OCH_3)_3]_3$ are very similar to those reported for the carbonyl analogs,[9] and there is no evidence in these spectra to 100° of a fast $\pi \rightleftharpoons \sigma$ process. A benzyl derivative is also formulated as a trihapto structure, although requisite limiting ^1H and ^{13}C spectra were not seen (*vide infra*). These molecules are fluxional with surprisingly fast ligand rotation as evidenced by the dnmr ^{31}P spectra which show A_3 (−90°) transitions to AB_2, ABC,[10] and AB_2 (−130°) for allyl, 1-methylallyl, and benzyl, respectively. The low-temperature ^{31}P spectra are best rationalized in terms of a trihapto allyl ligand either (1) above a pyramidal CoP_3 framework of C_{3v} microsymmetry or (2) as a bidentate ligand attached to two vicinal basal vertices of a square pyramid. However, these two models are so closely related by minor bending modes as to make distinctions, at least for the nmr time scale, meaningless. Conceptually, the simplest picture of the dynamic process that equilibrates P environments is a rotation[11] of the trihapto ligand in a plane normal to the Co–C_3 (centroid) axis. Alternatively, the intermediate states for such a rotation may be considered polytopal iso-

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(1) E. L. Muetterties and F. J. Hirsekorn, *J. Chem. Soc., Chem. Commun.*, in press.

(2) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 94, 5271 (1972).

(3) R = CH_3 or C_2H_5.

(4) E. L. Muetterties, to be submitted for publication.

(5) AB_3 ^{31}P spectrum and 3:1 intensity ratio for R proton resonances.

(6) ϕ in $Hg[Co(CO)_4]_2$ is 83 ± 2°: G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc. A*, 1005 (1968). We anticipate a 10–13 kcal/mol barrier which should be determinable by ^{13}C dnmr.

(7) Especially where X and L are very similar in steric and electronic character.

(8) Mechanistic distinctions cannot be made[2] from the character of line shape changes for C_{3v} XML_4.

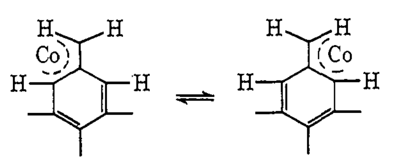
(9) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).

(10) The low-temperature spectrum is too simple for rigorous characterization as an ABC pattern, but this does not affect the stereochemical arguments because the allyl derivative provides the critical distinctions.

(11) For earlier discussion of ligand rotation see A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967); J. W. Faller and M. J. Incorvia, *J. Organometal. Chem.*, **19**, P13 (1969); J. K. Becconsall and S. O'Brien, *Chem. Commun.*, 720 (1966); J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 538 (1968).

mers in five coordination. (In this context, there is no distinction between bond rotation and a polytopal rearrangement.)

The benzyl compound must undergo an additional fast rearrangement because there is no detectable inequivalence of ortho (and of meta) carbon atoms by ^{13}C nmr even at −130°. It is proposed that the bond shift (eq 1) is rapid on the nmr time scale at −130°.[12] Although slow with respect to the nmr time scale, a $\pi \rightleftharpoons \sigma$ process[13] may be less activated in the benzyl than in the allyl derivatives because the former has a qualitatively higher reactivity toward CO displacement of one $P(OCH_3)_3$ group.[14,15]



(1)

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[12] This is also necessary to account for the low-temperature AB_2 (rather than ABC) ^{31}P spectrum.

[13] For discussion of fluxionality in a far more rigid class of *trihapto*-benzyl complexes, $(h^3\text{-}C_6H_5CH_2)(h^5\text{-}C_5H_5)Mo(CO)_2$, see discussion by F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 1339 (1969). In their carefully designed experiments, rearrangement mechanism was not established, but they suggested that a $\pi \rightleftharpoons \sigma$ process might be dominant.

[14] This research was supported by National Science Foundation Research Grant GP-9562.

[15] We are indebted to Messrs. G. Watunya and J. White for the low-temperature ^{31}P and ^{13}C spectra and Dr. P. Meakin for simulation of the ^{31}P spectra.

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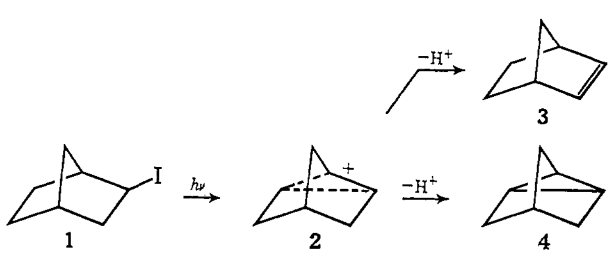
Photochemistry of Alkyl Halides. I. Ionic *vs.* Radical Behavior

Sir:

The photochemistry of alkyl iodides has been the subject of extensive study.[1] Except for the possibility of "molar elimination" of hydrogen iodide under certain conditions,[2] it is generally thought that absorption of light by the C–I chromophore results invariably in homolytic cleavage of the C–I bond and the subsequent generation of radical-derived products.[1] We wish to report the results of preliminary studies which show that the photochemical behavior of alkyl iodides in solution is richly varied and does not uniformly lead, at least ultimately, to free-radical-type products. Moreover, there is a marked contrast in behavior between alkyl iodides and the corresponding bromides.

For example, irradiation[3] of 2-*exo*-iodonorbornane (**1**),[4,5] bp 87° (16 mm), in ether solution afforded a mixture of 2-norbornene (**3**) and nortricyclene (**4**) in yields of 81 and 19%, respectively; in methanol the hydrocarbons **3** and **4** were again formed (77 and 12.5%).[6]



Additional insight was obtained by irradiation of the iodo ether **5** (X = I; Y = H_2),[7] bp 105° (4 mm), in ether solution to give a mixture of the products **9–12**[8] (Table I). Analogous behavior was exhibited by the corresponding lactone **5** (X = I; Y = O),[9] which again afforded products **9–12**.[10] A marked solvent effect was observed for both iodides; in methanol only a single principal photoproduct was formed, the ring-opened system **12**. In contrast to the iodides, the corresponding bromides **5** (X = Br; Y = H_2 and O)[7,9] afforded only the reduction products **9** (Y = H_2 and O). Similarly, 2-*exo*-bromonorbornane gave norbornane (92%) on irradiation in either ether or methanol.

Table I. Irradiation of Halides **5**

Halide **5**	Solvent	Time, hr	Yield, % **5**	**9**	**10**	**11**	**12**
X = I; Y = H_2	$(C_2H_5)O$	12	11	33	23	28	2
		$2^{a,b}$	8	9	21	30	*c*
	CH_3OH	1	3	*c*	*c*	*c*	93
X = I; Y = O	$(C_2H_5)_2O$	12	2	36	18	18	24
	CH_3OH	2	*c*	*c*	*c*	*c*	90^d
X = Br; Y = H_2	$(C_2H_5)_2O$	8^a	18	78	*e*	*e*	*e*
	CH_3OH	8^a	*e*	83	*e*	*e*	*e*
X = Br; Y = O	$(C_2H_5)_2O$	$20^{a,f}$	6	87	*e*	*e*	*g*

[a] The broad spectrum of a 450-W mercury arc was used. [b] An additional product was obtained in 26% yield. [c] Trace. [d] Isolated yield. [e] None detectable. [f] Vycor filter used. [g] Not analyzed.

There is thus a significant difference in photochemical behavior between alkyl iodides and their corresponding bromides. The photoproducts from the bromides are typical of radical-derived products.[11] However, the occurrence of Wagner–Meerwein shifts, 1,3 elimination,

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[1] For a recent review, see J. R. Majer and J. P. Simons, *Advan. Photochem.*, **2**, 137 (1964).

[2] R. Schindler and M. H. J. Wijnen, *Z. Phys. Chem.* (*Frankfurt am Main*), 34, 109 (1962).

[3] Irradiations were conducted at 253.7 nm in a quartz vessel using 50-ml solutions containing 1.0 g of halide. Mossy zinc was normally used as an anhydrous means for scavenging liberated iodine and hydrogen iodide, but similar results were obtained in the absence of zinc. Yields were determined by gas chromatographic analysis relative to a hydrocarbon standard. Except where indicated, control studies showed that no reaction occurred in the absence of light, even in the presence of added iodine or zinc iodide.

[4] Prepared by the general procedure of H. Stone and H. Shechter, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 543.

[5] Proper spectral and analytical data were obtained for all novel compounds. Novel photoproducts were further characterized by conversion to compounds of known structure.

[6] Methyl 2-*exo*-norbornyl ether was also obtained in 10% yield. However, control runs afforded this product, *but not* **3** *or* **4**, in similar yields in the dark.

[7] Prepared by treatment of 5-norbornene-2-*endo*-methanol (**12**, Y = H_2) with an excess of iodine or bromine and 1 equiv of triethylamine in methanolic solution.

[8] H. A. Bruson and T. W. Riener, U. S. Patent 2,440,220 (1948); *Chem. Abstr.*, 42, 5471 (1948); T. Shono, A. Ikeda, and Y. Kimura, *Tetrahedron Lett.*, 3599 (1971).

[9] C. D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, 77, 3583 (1955).

[10] K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **514**, 197 (1934); K. Alder and O. Diels, *ibid.*, **460**, 117 (1928).

[11] For a recently reported exception to this general behavior shown by a benzylic bromide, see S. J. Cristol and G. C. Schloemer, *J. Amer. Chem. Soc.*, **94**, 5916 (1972).