Table I. Fractional Coordinates for
1α,2,2aα,3α,4,9bα-Hexahydro-9b-acetoxy-1,3-propano-5H-cyclobuta[d][2]benzazapin-5-ne, One Arbitrary Antipode of **6**.

Atom	x	y	z
C(1)	0.7053	0.1016	0.3829
C(2)	0.8203	0.0636	0.3651
C(2a)	0.8654	0.0800	0.5446
C(3)	0.8600	−.0100	0.6449
N(4)	0.9056	0.0175	0.8084
C(5)	0.8658	0.0862	0.8911
C(5a)	0.7586	0.1393	0.8261
C(6)	0.7022	0.1653	0.9411
C(7)	0.6004	0.2119	0.9027
C(8)	0.5531	0.2362	0.7485
C(9)	0.6101	0.2128	0.6337
C(9a)	0.7131	0.1646	0.6726
C(9b)	0.7678	0.1510	0.5382
C(10)	0.7471	−.0631	0.6345
C(11)	0.6753	−.0781	0.4680
C(12)	0.6238	0.0187	0.3952
C(13)	0.8666	0.3057	0.5828
C(14)	0.8702	0.4075	0.5147
O(1)	0.9137	0.1006	0.0279
O(2)	0.7928	0.2495	0.4860
O(3)	0.9225	0.2792	0.7049
Std dev[a] (average)	0.0005	0.0004	0.0006

[a] Standard deviations are based solely on least-squares parameters.

Crystal structure analysis of the O-acetyl derivative of **5b** (n = 4) confirmed the structural formula and established the relative stereoconfiguration at the point of attachment of the OH group. The details of the structure will be published elsewhere.[8]

By analogy with unacetylated **6**, **4** must be the lower homolog formed by photolysis of **1b**. The formation of **4** and **6** (unacetylated) is perfectly consistent with our previous observations; at the benzazepinone stage, **3** or **5**, it is again the γ-hydrogen which is abstracted, and the cyclobutanols **6** and **4** are formed presumably via biradical intermediates of type **7**.[9] This novel approach to the synthesis of other polycyclic benzazepines containing bridged cyclobutane systems as well as more detailed mechanistic studies are now under investigation.

(8) J. L. Flippen, *Acta Crystallogr.*, to be submitted for publication.
(9) Photochemical formation of bicyclobutanols from cycloalkyl and bicycloalkyl phenyl ketones has recently been reported: F. D. Lewis, R. W. Johns, and R. A. Ruden, *J. Amer. Chem. Soc.*, 94, 4292 (1972); F. D. Lewis and R. W. Johnson, *ibid.*, 94, 8914 (1972).

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Hydroacylation. The Synthesis of Ketones from Olefins Using Metal Hydride Reagents

Sir:

Hydroformylation, an extensively employed and well-studied synthetic sequence, proceeds *via* olefin insertion into a metal hydride bond followed by CO insertion into the resulting metal carbon bond to yield metal acyl which then undergoes C–H reductive elimination of aldehyde (olefin → alkyl → acyl → aldehyde).[1] Or, more simply, hydroformylation can be considered to be the stepwise addition of H– and –C(O)H to an olefin. We now wish to report that ketones, too, can be synthesized through a stoichiometric procedure mechanistically analogous to hydroformylation in which, formally, H– and –C(O)R are added, stepwise, to olefins. Hydroacylation as described herein provides a facile route to ketones from terminal olefins rapidly, under neutral reaction conditions, at room temperature, and with inexpensive reagents.

Several organometallic-based ketone syntheses have recently been reported in which metal alkyls are formed under necessarily strongly basic conditions by reaction of an alkyllithium reagent with a metal halide at low temperature[2] or of a metalloanion with an alkyl halide.[3] In both procedures acyl halide is oxidatively added to the metal alkyl; reductive elimination gives the ketone. The scope of the former is limited by the availability of the alkyllithium reagent, that of the latter by susceptibility of the alkyl halide to nucleophilic attack by the metalloanion. In contrast to these routes, hydroacylation involves formation of the metal alkyl under *neutral* reaction conditions through insertion of olefin into a metal–hydride bond. We have demonstrated that hydroacylation succeeds even in cases where the position of the equilibrium for reversible M–H β-insertion into the olefin overwhelmingly *disfavors* the metal alkyl.[4] In this scheme, too, oxidative addition of acyl halide is followed by reductive elimination of ketone.

The results of hydroacylation involving either cobalt or rhodium hydrides are summarized in Tables I and II. These procedures are briefly described below. In a typical experiment, $HRh(CO)L_3$ (**1**)[4] (75 mg, 0.082 mmol) was stirred in 15 ml of benzene under 40 psi of ethylene for 20 min at room temperature. The reaction mixture was depressurized, a slight molar excess of benzoyl chloride was added, and the mixture was stirred for 12 hr at 20° (again under 40 psi of ethylene). Depressurization followed by evaporative distillation of volatiles yielded propiophenone (76%). The residue of distillation, $L_2Rh(CO)Cl$, could be recycled to **1** almost quantitatively (see reaction 1).

$$CH_2{=}CH_2 + HRh(CO)L_3 \rightleftharpoons [CH_3CH_2Rh(CO)L_n] \qquad (1)$$

L = PPh₃
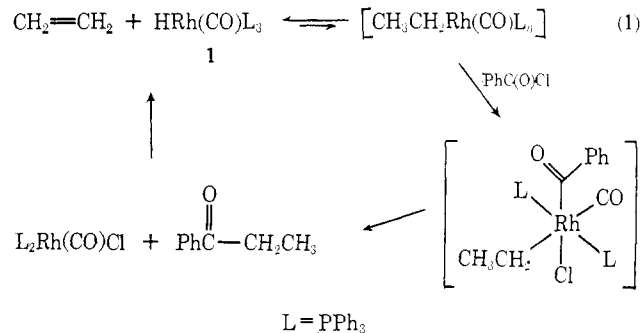
(1) See, for example, C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1966.
(2) L. S. Hegedus, S. M. Lo, and D. E. Bloss, *J. Amer. Chem. Soc.*, 95, 3040 (1973).
(3) J. P. Collman, S. R. Winter, and D. R. Clark, *J. Amer. Chem. Soc.*, 94, 1788 (1972).
(4) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

Table I
$$\text{olefin} + HRh(CO)L_3 + RC(O)Cl \xrightarrow[20°]{12\ hr} \text{ketone} + L_2Rh(CO)Cl$$

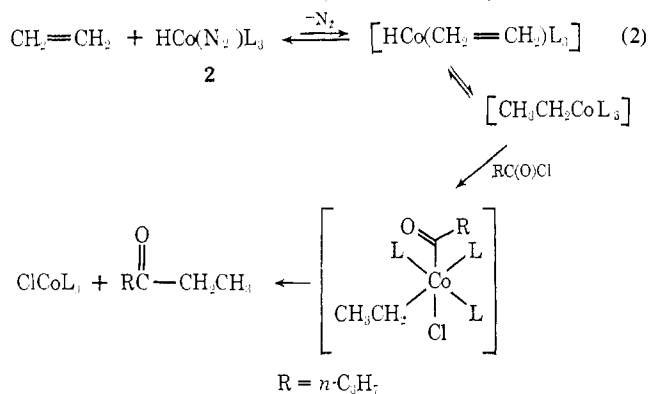| Olefin		Added Reagents	Solvent	RC(O)Cl	Ketone (%)ᵃ
CH₂=CH₂	1 atm	1 atm CO	Benzene	PhC(O)Cl	Propiophenone (29)
	20 psi		Benzene		(39)
	40 psi		Benzene		(76)
	80 psi		Benzene		Polymer only
	40 psi	4 equiv L	Benzene		Propiophenone (86)
	40 psi		THF		(70)
	40 psi	4 equiv L	THF		(87)
	40 psi	10 equiv L	THF		(50)
	40 psi	4 equiv L	Benzene	CH₃C(O)Cl	2-Butanone (2)
	40 psi	4 equiv L	THF	n-C₃H₇C(O)Cl	3-Hexanone (1)
	40 psi	4 equiv L	Et₂O		(20)
	40 psi	4 equiv L	Et₂O	n-C₇H₁₅C(O)Cl	3-Decanone (25)
1-Hexene			Benzene	CH₃(CO)Cl	2-Octanone (0)
		1 atm CO			(2)
2-Butyne		4 equiv L	Benzene		3-Methyl-3-penten-2-one (0)

ᵃ Yields, based on metal hydride, were determined by vpc using an 8 ft × ¹/₄ in. column packed with 5% Carbowax 20M or Chromosorb P (60/80 mesh).

Table II
$$\text{olefin} + HCo(N_2)L_3 + RC(O)Cl \xrightarrow[25°]{10\ min} \text{ketone} + L_3CoCl$$

Olefin	Added reagents	Solvent	RC(O)Cl	Ketone (%)ᵃ
CH₂=CH₂ (40 psi)		Benzene	PhC(O)Cl	Propiophenone (75)
		THF		(39)
		Et₂O		(30)
	4 equiv L	Benzene		(75)
		Benzene	n-C₃H₇C(O)Cl	3-Hexanone (86)
		Et₂O		(59)
		Benzene	n-C₇H₁₅C(O)Cl	3-Decanone (85)
1-Pentene		Benzene	CH₃C(O)Cl	2-Heptanone (20)
		Et₂O		(3)
		Benzene	PhC(O)Cl	Caprophenone (11)
2-Butyne		Benzene	CH₃C(O)Cl	3-Methyl-3-penten-2-one (12)

ᵃ Yields, based on metal hydride, were determined by vpc using an 8 ft × ¹/₄ in. column packed with 5% Carbowax 20M or Chromosorb P (60/80 mesh).

Experiments involving HCo(N₂)L₃ (2)[5] were performed in similar fashion. Addition of olefin to a red benzene solution of 200 mg of 2 (0.232 mmol) resulted in an immediate color change to red-brown. Addition of RC(O)Cl to this red-brown solution produced a rapid (<10 min) color change to emerald green. In the case of ethylene and butyryl chloride, 3-hexanone (86%) was obtained on evaporative distillation of volatiles. The residue from distillation contained L₃CoCl[6] and a small amount of L₂CoCl₂[7] (see reaction 2). As can be

$$CH_2=CH_2 + HCo(N_2)L_3 \underset{-N_2}{\overset{-N_2}{\rightleftharpoons}} \left[HCo(CH_2=CH_2)L_3\right] \quad (2)$$

$$\left[CH_3CH_2CoL_3\right]$$

$$\downarrow RC(O)Cl$$

$$ClCoL_3 + RC{-}CH_2CH_3 \longleftarrow \begin{bmatrix} O{=}\overset{R}{C} \\ L{-}\overset{|}{Co}{-}L \\ CH_3CH_2\ \overset{|}{\underset{Cl}{}}\ L \end{bmatrix}$$

R = n-C₃H₇

seen by comparison of Tables I and II, hydroacylation yields using the inexpensive, easy to prepare, and reactive cobalt species 2 are in general superior to those using the rhodium species 1. Examination in detail of procedures involving either hydride and ethylene has provided insights into the mechanism of hydroacylation which point to ways to improve the synthetic utility of the process in general. Examples of the process using other unsaturated substrates indicate the scope of the reaction.

The yield of various ketones from hydroacylation depends on several factors among which are the rate of metal alkyl formation from the metal hydride, the equilibrium concentration of alkyl vs. hydride under the reaction conditions, and the relative reactivity of these two species toward the acyl halide. For 1, we have observed an increased yield of ketone when moderate amounts of excess triphenylphosphine are added to the initial reaction mixture. A similar dependence on added L for formation of ethylrhodium(I) species from rhodium(I) hydrides and ethylene has been noted in another context.[4] No dependence of the yield of ketone on added L was observed when 2 was employed.[8] Metal alkyl and metal hydride can both react with acyl chloride. We have observed that benzoyl chloride

(5) Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organometal. Chem.*, **59**, 353 (1973), and references cited therein.

(6) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969).

(7) Blue L₂CoCl₂ is formed slowly by reaction of L₃CoCl and RC-(O)Cl.

(8) The difference in ketone yields from either hydride may result from the ease with which a ligand is dissociated from the hydride (N₂ for 2, L for 1) and the subsequent competition between the olefin and other ligands present for this vacant coordination site.

reacts far slower with **1** than does acetyl chloride.[9] A higher observed yield of benzoyl ketone (compared with acetyl species) is therefore consistent with the assertion that the less reactive (more selective) acylating reagent, benzoyl chloride, can better discriminate between the more reactive (toward oxidative addition) metal alkyl and the less reactive hydride. Thus, metal alkyl can successfully compete with metal hydride for reaction with RC(O)Cl even though the former is present in low concentration relative to the latter.[4] The need, therefore, to produce a stable (with regard to β-H elimination) metal alkyl is not stringent though ketone yield does depend on the rate of and equilibrium value for (reversible) formation of the alkyl.[10]

For either hydride **1** or **2**, the coordination ability of the olefin (which is the immediate precursor of the metal alkyl) is reflected in the yield of ketone produced from it.[11] Yields of ethyl ketones from ethylene are high. Yields of ketones derived from sterically more demanding olefins are somewhat lower.[8,11] However, the fact that the hydroacylation procedure succeeds even as well as it does with these substrates, especially with the cobalt hydride, is encouraging, for it testifies to the existence of a favorable pathway for the general transformation. We are continuing our work along the lines of developing hydridometal species which are even more reactive toward olefin insertion than is **2** and are also exploring the use of metal hydrides which may be accommodated in catalytic hydroacylation procedures.

(9) See also, M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, **93**, 1368 (1971).
(10) Several metal hydrides have been studied in this regard: R. A. Schunn, *Inorg. Chem.*, **9**, 2567 (1970).
(11) The decreasing stability of Rh(I)–olefin complexes with increasing size of alkyl substitution on the olefinic bond has been noted: F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973).

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Mechanism of Fluxional Rearrangement in Cyclooctatetraenetricarbonylmolybdenum. A Random Process *via* a Symmetrical Transition State

Sir:

The possibility of inferring mechanistic conclusions about fluxional and other stereochemically nonrigid molecules from the way in which nmr line shapes change with temperature was first recognized and reduced to practice[1] in 1966. Many such studies have since been made,[2,3] and certain broadly useful principles have been discovered.[4] Among these is the widely useful one that, among *transition metal com-*

(1) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).
(2) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).
(3) K. Vrieze and P. W. N. M. van Leeuwen, *Progr. Inorg. Chem.*, **14**, 1 (1971).
(4) F. A. Cotton in "Dynamic Nuclear Magnetic Resonance Spectroscopy," L. M. Jackman and F. A. Cotton, Ed., Academic Press, in press.

pounds, the rearrangement pathway is generally based on 1,2 shifts. In any event, random·processes appear to be extremely rare.

One of the clearest cases of 1,2 shifts is found in the 1,3,5,7-tetramethylcyclooctatetraenetricarbonylmetal compounds, **1**, where the metal is Cr, Mo, or W. For these the lowest energy process (occurring between about -20 and $+50°$) is that depicted schematically[5] as **1a** $\rightleftharpoons$ **1b**. At higher temperatures there is a second
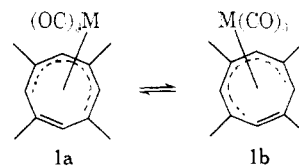
process which appeared to be leading to complete site exchange when its effects were combined with those of the first process, but definite identification of the second process was not possible. Because of the complex nature of the proton nmr spectra of the unsubstituted compounds,[6] *i.e.*, the $(C_8H_8)M(CO)_3$ species, **2**, unambiguous line-shape analysis of these was not feasible, and hence the rearrangement pathway for them could not be inferred directly. It was suggested,[2] however, that one might extrapolate from the process **1a** $\rightleftharpoons$ **1b** to the conclusion that an infinite sequence of (omnidirectional) 1,2 shifts would account for the complete averaging[6] of proton environments in compounds **2**.

Using ^{13}C nmr we have now directly attacked the problem of the rearrangement pathway in the compounds **2**. The results and conclusions are *not* in accord with the hypothesis just stated, and new insight into the behavior of fluxional organometallic molecules is thereby obtained.

At temperatures below about 0° (in 1/1, v/v, CDCl$_3$–toluene), $C_8H_8Mo(CO)_3$ shows four separate sharp signals of equal intensity for the ring carbon atoms at 131.7, 104.9, 101.8, and 88.5 ppm downfield from TMS. This is in accord with the structure of the molecule as indicated by X-ray crystallographic data on $C_8H_8Mo(CO)_3$[7] and $(1,3,5,7-Me_4C_8H_4)Cr(CO)_3$.[8] As the temperature is raised all four signals broaden and collapse *at the same rate.* This result *rules out the occurrence of 1,2 shifts,* since it is easy to show that for 1,2 shifts two lines should have initial rates of broadening that are twice as great as for the other two.

It is also easy to shown that 1,4 and 1,5 shifts are ruled out. Among discrete 1,*n* type shift processes, then, only 1,3 shifts, which are consistent with uniform rates of broadening of all four lines, remain. However, we do not consider that they provide a physically acceptable explanation. It does not seem credible that the relative motion of ring to metal atom required for a 1,3 shift could occur without passage through an intermediate configuration so close to the immediately adjacent minimum-energy configuration as to cause the system to drop into that configuration, *i.e.*, to execute a 1,2 shift. If, on this basis, we reject 1,3 shifts also,

(5) F. A. Cotton, J. W. Faller, and A. Musco, *J. Amer. Chem. Soc.*, **90**, 1438 (1968).
(6) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3444 (1966); S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965).
(7) J. S. McKechnie and I. C. Paul, *J. Amer. Chem. Soc.*, **88**, 5927 (1966).
(8) M. J. Bennett, F. A. Cotton, and J. Takats, *J. Amer. Chem. Soc.*, **90**, 903 (1968).