

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.

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(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 practice¹ 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-*

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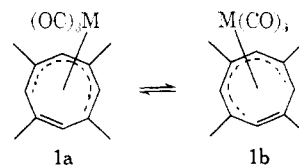
(2) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(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 $+50^\circ$) is that depicted schematically⁵ 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 averaging⁶ of proton environments in compounds **2**.

Using ¹³C 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 show 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).

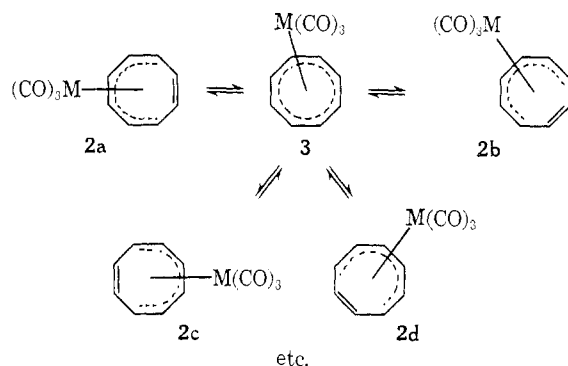
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what then can be the explanation of the observed uniform line broadening?

We propose that the rearrangement process is that shown in Scheme I. This involves a symmetrical

Scheme I



“piano-stool” intermediate, **3**, with the metal atom lying over the center of a flat (or nearly flat) octagonally (or nearly) symmetric C_8H_8 ring. In terms of bonding this is a credible intermediate, since the metal atom could still serve as an acceptor of six π electrons, a pair of electrons in a low-lying totally symmetric π MO being left as essentially nonbonding. In terms of accessibility from the ground state configuration, **3** is also satisfactory, since, in the ground state,^{7,8} the metal atom already lies rather close to the central point that will arise as the ring becomes flat and only the two carbon atoms which form the “uncoordinated” double bond need move very much as the other six are already essentially coplanar.

Obviously, one is immediately led to ask why this pathway applies for compounds **2** but not for **1**. The answer, we believe, lies in the steric effect of the four methyl groups upon a planar ring. The planar ring must be appreciably destabilized by repulsive forces upon the introduction of four methyl groups in place of four hydrogen atoms. It is possible to estimate the extent of this destabilization semiquantitatively by referring to the studies of bond shift in cyclooctatetraene⁹ and 1,3,5,7-tetramethylcyclooctatetraene.¹⁰ The bond shift processes are believed to require passage through planar transition states. For C_8H_8 the free energy of activation is <13.7 kcal mol⁻¹ whereas for 1,3,5,7-(CH₃)₄C₈H₄ it is 21.5 ± 2.0 kcal mol⁻¹. Such a difference, ca. 8 kcal mol⁻¹, could easily explain why a $C_8H_8M(CO)_3$ compound would undergo rearrangement by a process involving a planar ring in the transition state while the tetramethyl analog would execute a different process in which the planar ring is not required.

Finally, we note that scrambling of the CO groups occurs with a lower activation energy and is therefore necessarily independent of the rearrangement just discussed. It has very similar characteristics to those observed for the comparable process in $C_7H_8Mo(CO)_3$.¹¹ Up to -37° there are sharp signals at 228.2 and 213.4 ppm in an intensity ratio of 1:2. These collapse and give a single broad resonance at 16° ; the coalescence

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(10) P. Ganis, A. Musco, and P. A. Temussi, *J. Phys. Chem.*, **73**, 3201 (1969).

(11) C. G. Kreiter and M. Lang, *J. Organometal. Chem.*, **55**, C27 (1973).

temperature is $0 \pm 10^\circ$. These studies are being extended to similar molecules.¹²

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A Synthesis of Cembrene. A 14-Membered Ring Diterpene

Sir:

We wish to describe a total synthesis of cembrene (**1**), 1-isopropyl-4,8,12-trimethylcyclootetradeca-2,4,7,11-tetraene, a monocyclic diterpene hydrocarbon structure of increasing importance in nature.^{1,2} Cembrene was the first example of a rapidly expanding group of diterpenes which contain a 14-membered ring,³ including neocembrene which is a scent-trail pheromone for termites in Australia (*Nasutitermes xitiosus*).⁴ Furthermore, the bicyclic derivatives, such as verticillol from a conifer,⁵ eunicellin from Atlantic coral,⁶ and those diterpenes of the taxane type⁷ may also be re-

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