electropositive elements might be expected to have this sign. This is so for ^2J(X–C–H) in $(CH_3)_4X$ and related compounds (X = C, Si, Sn, or Pb, allowance being made for the negative magnetogyric ratios of the magnetic Si and Sn isotopes). However, it has been found[27] that the negative sign for the geminal H–H coupling applies only if the intervening atom is small (*e.g.*, C), but with other intervening atoms the coupling constant becomes positive and increases with increasing atomic number. A similar result also applies to geminal carbon to hydrogen couplings. Thus the reduced[28] *Pb*–Pb–*C* coupling constant should be positive and larger than the *Sn*–Sn–*C* one. This is the case.

The ^1H and ^{13}C chemical shifts of hexamethyldilead differ only slightly from those found for $(CH_3)_4Pb$ and may well depend on the conditions of measurement. The large high-field shift of the ^{207}Pb resonance is consistent with the corresponding value of +113 ppm for the ^{119}Sn shift in hexamethylditin, the extremely large range[30] of ^{207}Pb chemical shifts being borne in mind. It is generally considered that the local paramagnetic term is the dominant contributor to lead shielding,[31] and this depends *inter alia* on the reciprocal of ΔE (the separation between the ground and excited states) in such a way that small values of ΔE should correspond to low-field resonances. The cream color of $(CH_3)_6Pb_2$ suggests that ΔE is relatively small; hence dominance by the paramagnetic term should lead to a ^{207}Pb chemical shift in $(CH_3)_6Pb_2$ to the *low field* of $(CH_3)_4Pb$. The results for ^{59}Co and ^{195}Pt chemical shifts may be compared here.[32,33]

We therefore conclude that ^{207}Pb chemical shift differences between related lead compounds are not necessarily dominated by the paramagnetic term and the neighboring anisotropy effect of the $(CH_3)_3Pb$ group may be more important in hexamethyldilead.

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[27] H. Dreeskamp and C. Schumann, *Chem. Phys. Lett.*, **1**, 555 (1968).

[28] The reduced coupling constant is defined[29] by $K_{AB} = 2\pi J_{AB}/\hbar\gamma_A\gamma_B$.

[29] J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

[30] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 1714 (1960).

[31] W. G. Schneider and A. D. Buckingham, *Discussions Faraday Soc.*, **34**, 147 (1962).

[32] S. S. Dharmatti and C. R. Kanekar, *J. Chem. Phys.*, **31**, 1436 (1959).

[33] W. McFarlane, *Chem. Commun.*, 393 (1968).

Stereochemically Nonrigid Organometallic Molecules. XX.[1] Proton Nuclear Magnetic Resonance Study of the Fluxional Behavior of Some Substituted (1,2,7-*Trihapto*benzyl)-(*pentahapto*cyclopentadienyl)dicarbonyl Compounds of Molybdenum and Tungsten[2,3a]

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received October 3, 1968

Abstract: Several new fluxional molecules containing substituted 1,2,7-*trihapto*benzyl groups bound to the $(C_5H_5)Mo(CO)_2$ and $(C_5H_5)W(CO)_2$ residues have been prepared and their proton magnetic resonance spectra studied with the objective of elucidating the pathway and evaluating the activation parameters concerned in the fluxional behavior of this class of molecules. The molecules are less difficult to prepare and more stable than previously reported. The chief qualitative conclusion, derived from the study of the 3,5-diisopropylbenzyl compound, is that the $(C_5H_5)Mo(CO)_2$ residue has access to all four equivalent (including enantiomorphically related) positions of attachment to the benzyl group. A plausible pathway would be *via* a *monohapto*- (*i.e.*, σ-) $C_6H_5CH_2Mo(C_5H_5)(CO)_2$ intermediate, in which rotation about the C_1–C_7 bond of the benzyl group can occur.

The first example of a compound containing a benzyl group bonded to a metal atom in a manner which could be formally considered to involve the $C_6H_5CH_2$ group serving as a 3-electron donor to the metal atom (or the $C_6H_5CH_2^-$ anion serving as a 4-electron donor to a cation) was reported in 1966 by King and Fronzaglia.[4] The compound in question is $(C_6H_5CH_2)(C_5H_5)Mo(CO)_2$ and King and Fronzaglia proposed that the benzyl group is attached to the molybdenum atom through an allylic sequence of three carbon atoms, one of which is the exocyclic methylene carbon atom. In short, the suggested structure was that which would be designated in a recently proposed notation[5] as (1,2,7-*trihapto*benzyl)(*pentahapto*-

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[1] Part XIX: F. A. Cotton and C. Reich, *J. Am. Chem. Soc.*, **91**, 847 (1969).

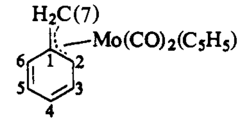
[2] A more conventional but less precise name for these compounds would be (π-benzyl)(π-cyclopentadienyl)dicarbonylmetal compounds.

[3] (a) This work was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society, to whom grateful acknowledgment is made. (b) National Science Foundation Predoctoral Fellow, 1966–1969.

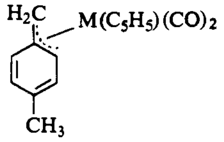
[4] R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

[5] F. A. Cotton, *ibid.*, **90**, 6230 (1968).

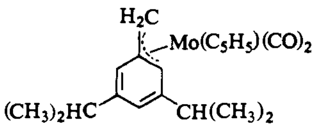
cyclopentadienyl)dicarbonylmolybdenum, or (h^3-CH_2-C_6H_5)(h^5-C_5H_5)$(CO)_2Mo$. A schematic representation is shown as I.



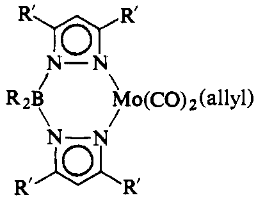
I



IIa, M = Mo
b, M = W



III



IV

Of even greater interest, however, was the observation that the proton magnetic resonance (pmr) spectrum of the benzyl group showed a pronounced temperature dependence, changing from a pattern consistent with I at −30° to a simpler pattern at +64°. The high-temperature pattern, its relationship to the low-temperature pattern, and the detailed nature of the line-shape changes at intermediate temperatures led to the conclusion that some process (or processes) of intramolecular rearrangement leading to time-average equivalence of the three pairs of protons on opposite edges of the benzyl group was accelerating markedly over the temperature range studied. Several hypotheses as to the rearrangement pathway were described, but no case was pressed for any particular one.

It is worth noting that the observations on this compound constitute one of the earliest reported descriptions of a fluxional organometallic molecule[6] in which the limiting low-temperature spectrum and the spectral changes leading thereto were observed. However, no detailed analysis leading to a more thorough empirical description of the process or to a closer definition of the mechanism was presented. The system seemed to us to merit this kind of study, and the investigation reported here was therefore undertaken.

In conjunction with the chemical and pmr studies described here, an X-ray crystallographic study of the 4-methyl analog of I was carried out;[7] it showed that structures of type I do occur in the $C_5H_5Mo(CO)_2$–benzyl compounds and revealed structural details of importance in discussing rearrangement pathways. The detailed, three-dimensional structure is shown in Figure 1.

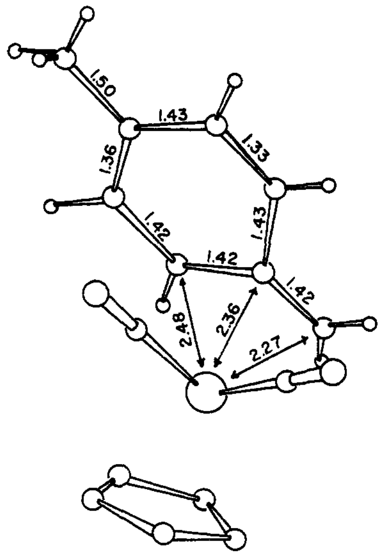


Figure 1. A quasi-perspective view of the (h^3-4-$CH_3C_6H_4CH_2$)-(h^5-C_5H_5)$(CO)_2Mo$ molecule, showing details of the stereochemistry and the more important interatomic distances (data from ref 7).

Preparation of Compounds

The three compounds of main interest in this work are all new ones, having substituents on the benzyl ring. Using the numbering scheme shown in I, they may be designated as the 1,2,7-*trihapto*-4-methylbenzyl derivatives of the $(C_5H_5)Mo(CO)_2$ and $(C_5H_5)W(CO)_2$ groups, IIa and IIb, respectively, and the 1,2,7-*trihapto*-3,5-diisopropylbenzyl derivative of $(C_5H_5)Mo(CO)_2$, III. All were obtained by way of the appropriate *monohapto*-benzyltricarbonyl intermediates following the general preparative route of King and Fronzaglia.[4]

For the molybdenum compounds, IIa and III, we found that conversion of the *monohapto*benzyltricarbonyl compounds to the *trihapto*benzyldicarbonyl compounds was conveniently accomplished by thermal decarbonylation. Only a few hours heating was required in any preparation, whereas King and Fronzaglia[4] indicated as the method of choice ultraviolet irradiation for 5 days to prepare I. For the tungsten compound, IIb, the photochemical method was found to be superior to simple heating.

Each of the dicarbonyl compounds we have prepared and studied shows only two sharp CO stretching bands in the infrared spectrum at 25°. Thus, unlike the simple allyl complex,[8,9] $C_3H_5Mo(CO)_2(C_5H_5)$, these compounds appear to be isomerically pure in solution at room temperature.

Nuclear Resonance Studies

Plan of Attack. Before reporting the experimental results and considering their interpretation, it is necessary to explain the preliminary analysis upon which the design of the experiments was based.

A benzyl group, $C_6H_5CH_2$, possesses two planes of symmetry, one containing all of the atoms and the other perpendicular to the first and passing through the atoms C_1, C_4, and C_7. As Figure 1 shows, the metal atom of the $(C_5H_5)Mo(CO)_2$ group does not lie in either of these planes. In order to discuss its location (and the locations of certain ring substituents) relative to the benzyl skeleton, we shall use the terms *face* and *edge* and avoid the equi-

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[6] *Cf.* F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968), for a survey of fluxional organometallic molecules and definitions of various terms used here.

[7] F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 5418 (1968).

[8] R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

[9] A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

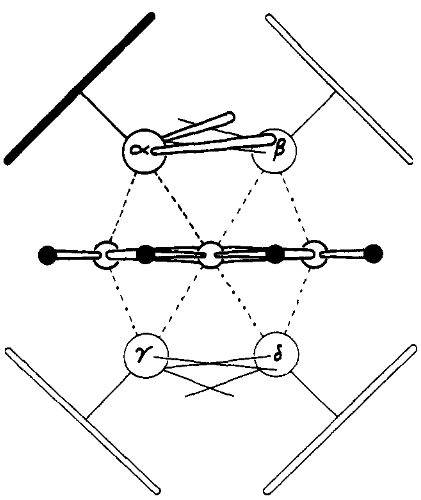

Figure 2. A schematic drawing in which both the C_5H_5 ring and the benzyl group are seen edge-on, showing the four chemically equivalent locations of the $(C_5H_5)(CO)_2Mo$ group relative to the benzyl group. The initial position, α, is represented in heavy lines. Other positions, β, γ, δ, are shown in lighter lines.

vocal term side. The two surfaces of the $C_6H_5CH_2$ group (*i.e.*, the two sides of the first symmetry plane mentioned above) will be called the *faces* of the benzyl group. The sets of atoms (*cf.* I) C_7, C_1, C_2, C_3 and C_7, C_1, C_6, C_5 define what we shall call the *edges* of the benzyl group. In Figure 1 we see the Mo atom lying in a position defined (in part) by the specification of one of the two faces and one of the two edges. It is also important to note that the structure is further characterized by a particular rotational orientation of the $(C_5H_5)Mo(CO)_2$ group relative to the benzyl group, taking a line through the Mo atom and perpendicular to the mean plane of the benzyl group as the axis of rotation.

It is seen in Figure 2 that there are four equivalent positions for the $(C_5H_5)Mo(CO)_2$ group relative to the benzyl group. The two positions in each of the pairs (α, δ) and (β, γ) are equivalent in the fullest sense, because the corresponding molecular configurations are interchangeable by rotations of the entire molecule as a rigid body; the α and δ configurations are enantiomorphous to the β and γ configurations, respectively. It should also be noted that in order to change one of the configurations to an enantiomorphous one, not only must the location of the metal atom be changed, *e.g.*, from α to β, but an internal rotation of the $(C_5H_5)(CO)_2MO$ group relative to the benzyl group must also occur.

For brevity in the following discussion, the entire $(C_5H_5)(CO)_2Mo$ or $(C_5H_5)(CO)_2W$ group will be denoted **M**, and the statement that **M** occupies site α (or β, γ, δ) will imply that it has the rotational orientation as well as the positional coordinates appropriate to that site.

It was the objective of this investigation to determine how many of the four sites α, β, γ, δ are accessible to the **M** group with sufficient frequency to produce observable effects in the pmr spectra. To put it another way, let us assume that a molecule starts with **M** in site α. There are three distinct types of site exchange possible, *viz.*, α ↔ β, α ↔ γ, and α ↔ δ, and each will have detectably different effects in suitably designed pmr experiments. We wished to know the relative importance of these three types of shift and have therefore planned and carried out experiments intended to provide such information.

One particular distinction we wished to make among the several possible site exchange processes was between the α ↔ β type, in which **M** always remains over the same face, and any other type or combination of types in which **M** would go from one face to the other. We shall designate these two classes of shift as *suprafacial* and *antarafacial* shifts, respectively. It would appear that the published results of King and Fronzaglia *can* be explained by the simple postulate of suprafacial (α ↔ β) shifts, but the observations *are not inconsistent with* certain antarafacial shift processes or with complex combinations of both suprafacial and antarafacial shifts.

It is clear that in order to determine by pmr studies whether antarafacial shifts occur frequently, the benzyl ring must be provided with one or more proton-bearing substituents capable of sensing differences between the environments over the two faces of the benzyl group. Two additional requirements are (1) that the substituent(s) be placed sufficiently far from the region of bonding of the benzyl group to **M** that it will not seriously influence the nature of the fluxional process and (2) that the equivalence of the two edges of the benzyl group be preserved. These restrictions leave as the only practical possibilities the introduction of one substituent in the 4 position or two identical substituents in the 3 and 5 positions. The use of the 3 and 5 positions was considered preferable since the effect of environmental differences on the two faces originating in the region of C_7, C_1, C_2, C_6 might be too attenuated for a substituent at the 4 position.

Finally, there remained the question of what substituent to use. Several possibilities involving rigid bodies constrained to keep some hydrogen atoms permanently over each face of the benzyl group were considered but rejected. Such molecules were necessarily large and elaborate, thereby introducing serious synthesis problems and possibly solubility difficulties. Instead, isopropyl groups were used in the 3 and 5 positions. It is now well known that when a $-CXY_2$ group is bound to some dissymmetric group the two Y groups cannot achieve equivalence in any rotational conformation *or as a result of internal rotation*, however rapid. The simplest alkyl CXY_2 system would be the ethyl group ($X = CH_3$, $Y = H$), but here the geminal H–H coupling superimposed on the quartet splitting due to the CH_3 group leads to a complex broad resonance,[10] which would be unsuited to our purposes. The isopropyl group, however, is well suited to our objectives since CH_3–CH_3' coupling will be negligible and the methyl resonances will be split only into doublets by the unique proton. There are several recent examples of this kind of use of isopropyl groups to detect inversion of dissymmetric moieties to which they are attached; in particular, it was the elegant study[11] by Whitesides, supplemented by discussions with Professor Whitesides, which led to our adoption of the isopropyl substituents.

If only suprafacial shifts occur in the 3,5-diisopropyl compound, then, in terms of the labeling scheme shown in Figure 3, there will be only g ↔ h and g′ ↔ h′ exchanges. Thus, the four separate methyl (doublet) resonances which

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(10) See, for example, the resonance observed in an early study of this phenomenon by J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

(11) G. M. Whitesides and W. M. Bunting, *J. Am. Chem. Soc.*, **89**, 6801 (1967).

Table I. Activation Parameters[a] for Site Exchanges

Compound	Solvent	Protons[b]	Log A	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
IIa	$CDCl_3$	a, b	16.6±0.2	19.2±0.3	18.6±0.3	15.6±1.3
IIa	$CDCl_3$	c, d	16.2±0.3	18.8±0.4	18.2±0.4	14.0±1.3
IIb	$CD_3C_6D_5$	a, b	13.5±0.2	15.9±0.2	15.3±0.2	1.3±1.1
III	$CDCl_3$	c, d	14.9±0.3	18.7±0.4	18.1±0.4	7.5±1.3
III	$CD_3C_6D_5$	c, d	14.6±0.3	18.3±0.5	17.7±0.5	6.2±1.3
III	$(CD_3)_2CO$	c, d	14.9±0.3	19.1±0.4	18.4±0.4	7.6±1.3

[a] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated at the temperatures giving mean residence times of 0.01 sec. [b] As identified by lower case letters in Figures 3 and 5.

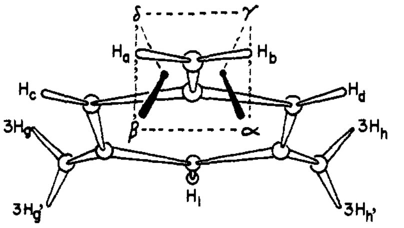

Figure 3. A diagram showing how the various protons in the 3,5-diisopropylbenzyl compound are labeled.

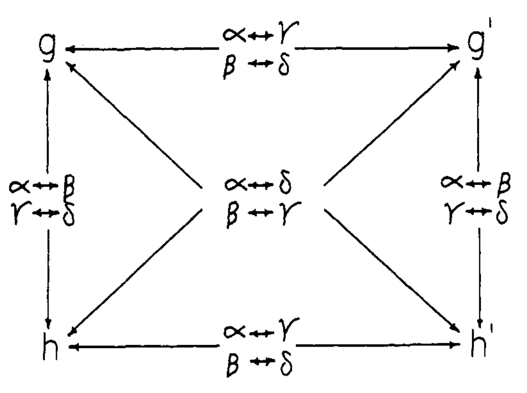

Figure 4. A diagram summarizing the site exchanges of isopropyl methyl protons which will be effected by each of the three types of shift in the location of the $(C_5H_5)(CO)_2Mo$ group.

should be seen in the limiting low-temperature spectrum will coalesce to two doublet resonances if only suprafacial shifts occur. If only antarafacial shifts of the α ↔ γ type occur, only the site exchanges g ↔ g' and h ↔ h' will take place. Again, the resonances of the low-temperature spectrum will coalesce to two doublet resonances. If antarafacial shifts of the type α ↔ δ occur, then the only exchanges will be g ↔ h' and g' ↔ h. These results are summarized in Figure 4. A combination of any two (or all three) of these types of shifts will lead to permutation of all sites and hence to coalescence of the spectrum to one doublet.

Data for the 4-Methylbenzyl Compounds. The pmr spectra of the molybdenum and tungsten compounds were recorded at frequent temperature intervals from −30 to +60°. Three of these spectra for the molybdenum compound are presented in Figure 5. These spectra are entirely analogous to those reported by King and Fronzaglia[4] for the unsubstituted molybdenum compound. As may be seen from assignments shown in the figure, the observations at −30° are consistent with the molecular structure shown in Figure 1 while those at +60° can only be explained by assuming that at this temperature one or more processes of rearrangement are interchanging the environments of the two edges of the benzyl ring fairly rapidly. Assuming that no rotation of the methylene group about the C_1–C_7 bond occurs, such an interchange could be accomplished by α ↔ β shifts alone, or by α ↔ δ shifts alone. Of course a random mixture of these two kinds of shifts or a random mixture of all three kinds of shifts (*i.e.*, α ↔ γ shifts as well) would also account for the observed coalescences. α ↔ γ type shifts alone cannot account for the observations.

An approximate line-shape analysis was performed on the spectra of compound IIa. Because of the overlapping of peaks, and the presence of spin–spin splittings showing second-order effects, the procedures (described in the Experimental Section) were necessarily less rigorous and less accurate than those used in simpler and more favorable cases. The resonances for the methylene protons and those for the ring protons *ortho* to the methylene group were each treated separately to give data on the rates of the two different site exchanges at various temperatures. It was found that each set of points gave a straight Arrhenius plot. From these plots the activation parameters given in Table I were derived. It is clear that there is no significant difference between the two sets of parameters, and this is strikingly demonstrated by the upper part of Figure 6 which shows the two sets of points lying on the line defined by the mean values of log A and E_a for the two sets of protons.

Thus the rearrangement pathways responsible for the observed site exchanges, a ↔ b and c ↔ d, must either be one and the same, or they must be very similar. From the uncertainties in the data and in the derived parameters of activation, we estimate, at about the 90% confidence level, that the rates of the two processes do not differ by more than a factor of ~4 anywhere in the temperature range studied.

A similar line-shape analysis, using only one of the site exchanges, for the tungsten compound gave appreciably different activation parameters. The differences from the parameters for the molybdenum compound are certainly real, even if there are systematic errors in our procedure for evaluating these parameters, since the sets of spectra for the two compounds are qualitatively very similar so that systematic errors in the procedure should influence both sets of results about equally. The tungsten compound rearranges more slowly despite having an activation energy ~3 kcal/mole lower because it also has a much lower frequency factor. We are not at present disposed to offer any rationalization of these results.

Data for the Diisopropylbenzyl Compound. Proton

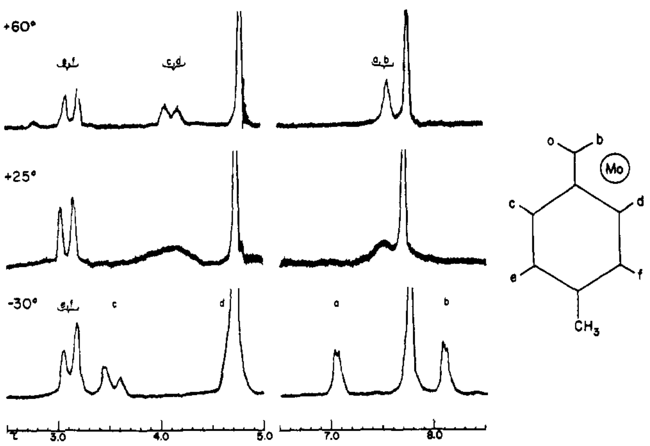

Figure 5. Proton magnetic resonance spectra of (1,2,7-h^3-4-$CH_3C_6H_4CH_2$)(h^5-C_5H_5)$(CO)_2$Mo at 60 Mc. Approximately 0.1 *M* solutions in $CDCl_3$ were used. Small peaks are identified according to the diagram at the right. The large peaks at τ ~4.7 and ~7.7 are due to C_5H_5 and CH_3, respectively.

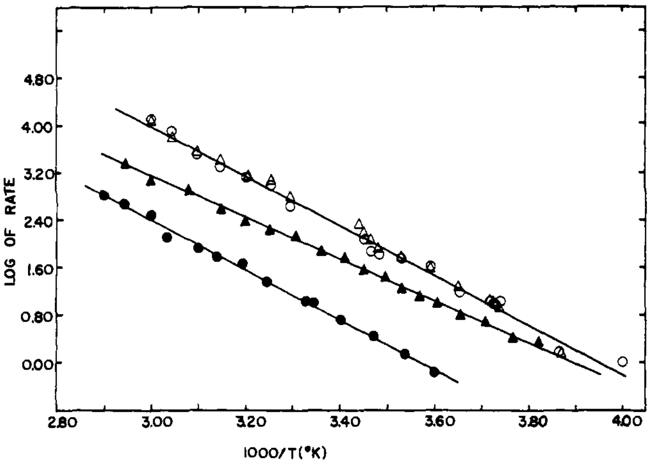

Figure 6. Arrhenius plots for the site exchange processes observed in this study. Open circles and triangles are for the ring (c, d) and methylene (a, b) protons, respectively, of $(CH_3C_6H_4CH_2)(C_5H_5)$-$(CO)_2$Mo. Filled triangles are for the methylene (a, b) protons of the tungsten analog. Filled circles are for the ring protons (c, d) of the 3,5-diisopropyl compound in acetone-d_6.

magnetic resonance spectra for this compound at three temperatures are shown in Figure 7. Because there are no protons at the 3 and 5 ring positions, the protons at the 2 and 6 positions (the c and d protons of Figure 3) now give rise to singlets in the low-temperature spectrum which collapse and eventually coalesce as the temperature rises. The methylene protons (a, b) also give separate resonances at low temperature which collapse and finally coalesce at higher temperatures. The unique ring proton (i) of course gives a sharp singlet at all temperatures. The behavior of all these resonances closely parallels that of the corresponding ones in the 4-methyl compound. Moreover, using the c, d resonances a line-shape analysis gave activation parameters (see Table I and Figure 6) for $CDCl_3$ solutions which are quite similar to those for (p-$CH_3C_6H_4$-CH_2)$(C_5H_5)(CO)_2$Mo in the same solvent. It seems clear that introduction of the isopropyl groups does not seriously alter the fluxional nature of the molecule.

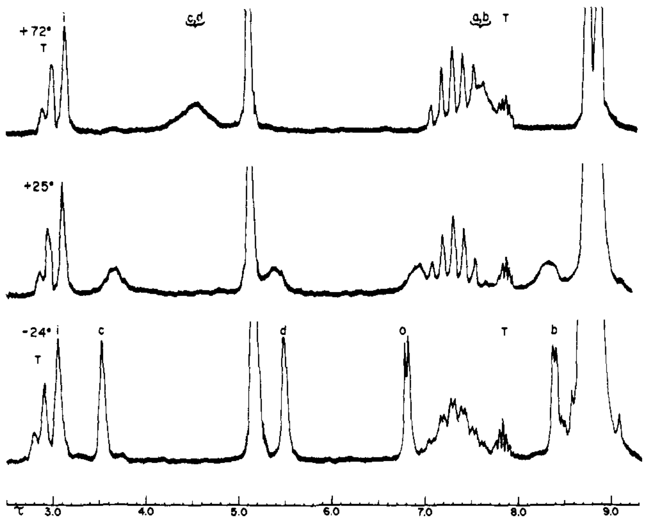

Figure 7. Proton magnetic resonance spectra of (1,2,7-h^3-3,5-$(C_3H_7)_2C_6H_4CH_2$)(h^5-C_5H_5)$(CO)_2$Mo at 60 Mc. Approximately 0.1 *M* solutions in toluene-d_8 were used. Peaks marked T are due to traces of toluene-d_7. Other small peaks are identified by letters corresponding to Figure 3. The strong lines at τ ~5.1 and ~8.8 are due to C_5H_5 and the isopropyl methyl groups, respectively. The broad multiplet at τ ~7.3 is due to the single protons of the isopropyl groups.

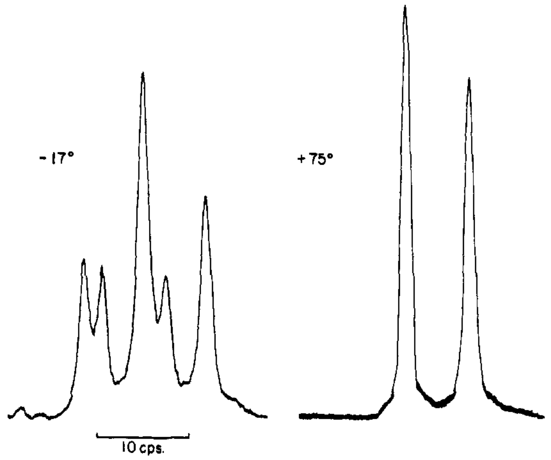

Figure 8. Enlarged records of the isopropyl methyl resonances in the low-temperature and high-temperature limiting spectra in toluene-d_8.

The effect of solvents on the fluxional behavior was also studied using the diisopropyl compound. No significant difference in behavior was found using the three solvents $CDCl_3$, $CD_3C_6D_5$, and $(CD_3)_2CO$. This lack of significant solvent dependence, which is qualitatively apparent when spectra in the different solvents are compared, is shown quantitatively by the activation parameters listed in Table I. These parameters are the same within the experimental uncertainties for all three solvents. Thus, it would seem that solvent molecules play no intimate part in the transition state for rearrangement.

We turn now to the temperature dependence of the isopropyl methyl resonances. Figure 8 shows these in the low- and high-temperature limits. At low temperature (−17°), the pattern is consistent with an instantaneous structure of the kind we have been assuming. Each of the four sets of methyl protons is coupled to the unique proton of its own isopropyl group by ~6.8 cps. The chemical shift difference between the g and g′ protons is too small to resolve. Therefore, these give rise to a symmetrical doublet, each component of relative intensity 3. The h and h′ sets differ in chemical shift by ~2.0 cps; therefore, these protons give rise to a doublet (separation ~2.0 cps) of doublets (separation ~6.8 cps). The second highest component of this set is overlapped by the lower field component of the g, g′ doublet.

In the high-temperature spectrum (+75°) we find only a doublet with separation ~6.8 cps. Each component of this doublet is at least as narrow as were the individual components of the low-temperature multiplet. Thus, no resolvable chemical shift differences occur in the high-temperature spectrum. This indicates that all four sets of methyl proton environments g, g′, h, and h′ have become equivalent.

It is already known from the study of the 4-methyl compound that the fluxional pathway was such as to give time-average equivalence to the two edges of the ring. It is now seen that the two faces also acquire time-average equivalence. If this were not the case, each peak in the high-temperature spectrum would show a small splitting of about 1 cps (the average of the h, h′ splitting (~2 cps) and the g, g′ splitting (~0 cps)). Unless there is some curious and, so far as we know, unprecedented, decrease in the h, h′ chemical shift difference as the temperature rises, the absence of any such secondary splitting in the high-temperature spectrum is direct and unambiguous proof that the $(C_5H_5)(CO)_2Mo$ group has access to all four positions, α, β, γ, δ, and passes among them rapidly, ≥ 10 jumps/sec, at a temperature of ~75°.

The previous three paragraphs and Figure 8 pertain to results obtained for toluene-d_8 solutions. We have emphasized these results since the h, h′ chemical shift difference was greater in that solvent than in any other one used. In fact, analogous studies were carried out in three other solvents, namely, $CDCl_3$, $(CD_3)_2CO$, and C_6H_5Cl. In these solvents the h, h′ separations at low temperature were in the range 1.6–2.0 cps. In all cases, however, the high-temperature spectrum consisted of a doublet essentially identical with that shown in Figure 8 for the toluene solution at +75°. Even granting that in *one* solvent there might be some remarkable temperature dependence of the h, h′ chemical shift difference, such that it would decrease by a factor of ~0.2 on going from ~ −20 to ~ +75°, it seems unlikely in the extreme that this would happen in all four of the solvents used.

Discussion

As noted earlier, in the discussion underlying Figure 4, any *two* of the three kinds of shift (*i.e.*, those shown vertically, horizontally, and diagonally in the figure) will suffice to give the $(C_5H_5)(CO)_2M$ moiety access to all four positions, α, β, γ, and δ. While there is no direct experimental evidence which requires any more detailed conclusion than this, we believe that it is reasonable to hypothesize a more specific pathway of rearrangement.

None of the experimental facts would seem to be at variance with the notion that these molecules pass randomly from one to another of the four equivalent (or enantiomorphous) configurations of the type shown in detail in Figure 1 by way of a 7-*monohapto*benzyl intermediate. The latter must be assumed to be (a) short-lived and not directly observable, and (b) capable of undergoing fairly fast rotation about the C(1)–C(7) bond. Thus, starting from the α configuration of the *trihapto*benzyl structure, the molecule would rearrange to the *monohapto*benzyl intermediate, undergo simultaneously rotations about the C_1–C_7 and C_7–Mo bonds, and revert to a *trihapto*benzyl configuration with about equal probability of the new one being any one of the four.

It will be noted on examining this suggestion in detail that an α → δ shift proceeding in this way would interchange the environments of the two edges of the phenyl ring but would not interchange the environments of the two benzyl protons (H_a and H_b). Thus, if the shifts of $(C_5H_5)(CO)_2M$ among the α, β, γ, and δ positions were random, the rate of a, b exchange would be only two-thirds that of the rate of c, d exchanges. Although it was shown that the rates of these exchanges are the same within experimental error at all temperatures, the errors are such that a ratio of 2/3 in these rates could not be distinguished from a ratio of unity. In fact, the ratio of rates would have to be less than ~1/4 before there would be any real chance of observing a statistically significant difference.

The *trihapto–monohapto–trihapto* pathway involves an intermediate which is coordinately unsaturated, having a so-called 16-electron configuration.[12] This is not an unreasonable thing to postulate. It is simply an intramolecular type of dissociative ligand exchange. Coordinately unsaturated intermediates have previously been postulated for carbonyl insertion reactions of other complexes,[13] and for the rearrangement of certain π-allyl complexes involving rhodium.[14] Of direct relevance to the present case, there was recently reported a class of π-allyl complexes of molybdenum, *viz.*, the dipyrazolylborate compounds, IV, containing bulky R′ groups[15] which appear to be well-documented, stable 16-electron complexes. The compound believed to be (1,2,3,9,10-*pentahapto*indenyl)dicarbonyliodomolybdenum has also been put forward[16] as an example of a molybdenum complex with a 16-electron valence shell.

Finally, it may be noted that there is a feature peculiar to this type of "allyl" complex which may help significantly to lower the activation energy for rearrangement by the *tri-*, *mono-*, *trihapto* pathway; this is a feature not present in simple allyl complexes of $(C_5H_5)(CO)_2Mo$, and the latter have not, in fact, been observed to undergo any rearrangement leading to an A_4X spectrum.[9] The crystallographic study[7] of $(h^3\text{-}CH_3C_6H_4CH_2)(h^5\text{-}C_5H_5)(CO)_2Mo$ revealed a marked alternation of C–C bond lengths around the benzene ring, as may be seen in Figure 1. This indicates that the *trihapto* attachment of a benzyl group significantly lessens the benzenoid resonance.[17] If

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[12] The lack of solvent effect on the rate implies that the decrease in coordination by the benzyl group is not compensated by solvent molecules.

[13] R. F. Heck in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

[14] *Cf.* K. Vrieze and H. C. Volger, *J. Organometal. Chem.*, **9**, 527 (1968).

[15] S. Trofimenko, *J. Am. Chem. Soc.*, **90**, 4754 (1968).

[16] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 475 (1965).

[17] The structure of the C(3)–C(4)–C(5)–C(6) portion of the benzene ring appears to resemble very closely that of a localized cisoid 1,3-butadiene group. Efforts were made to detect chemical behavior consistent with this description. The compound $(h^3\text{-}CH_3C_6H_4CH_2)(h^5\text{-}C_5H_5)(CO)_2Mo$ was treated with maleic anhydride, tetracyanoethylene, and the dimethyl ester of acetylenedicarboxylic acid. In no case, however, could we isolate and identify a product which would have been produced by a Diels–Alder addition.

the molecule passes from the state with a *trihapto* ring to an intermediate or transition state configuration with a *monohapto* ring, this resonance stabilization is recovered, thus making the *monohapto* configuration more energetically accessible.

Experimental Section

The preparation and all handling of organometallic compounds were carried out in an atmosphere of prepurified nitrogen, since the (h^3-$CH_2C_6H_5$) compounds are somewhat air sensitive as solids and extremely so when in solution. All solvents were dried in an appropriate manner, distilled, and stored under nitrogen. The (h^1-$CH_2C_6H_5$) compounds were also kept in the dark. Melting points of (h^3-$CH_2C_6H_5$) compounds were determined in sealed, nitrogen-filled capillaries.

(*Monohapto*-4-methylbenzyl)(*pentahapto*cyclopentadienyl)tricarbonylmolybdenum. A procedure similar to that of King and Fronzaglia[4] for the *monohapto*benzyl compound was employed, using 0.130 mol of $NaMo(CO)_3C_5H_5$ and 23.9 g (0.170 mol) of *p*-$CH_3C_6H_4CH_2Cl$ in 500 ml of tetrahydrofuran. The crude product was recrystallized from methylene chloride–petroleum ether (35–50°) at −78° to yield 18.4 g (40%) of bright yellow solid, mp 94–96° (with slight decomposition).

Anal. Calcd for $C_{16}H_{14}MoO_3$: C, 54.87; H, 4.03. Found: C, 54.7; H, 3.99.

The infrared spectrum (cyclohexane solution) showed strong bands at 2015 and 1935 cm^{-1} (± 5 cm^{-1}). The pmr spectrum consisted of a multiplet at τ 2.96 (4 H) and singlets at τ 4.83 (5 H), 7.08 (2 H), and 7.73 (3 H).

(*Trihapto*-4-methylbenzyl)(*pentahapto*cyclopentadienyl)dicarbonylmolybdenum. In a 50-ml three-neck flask furnished with an inlet for nitrogen and a small air-cooled condenser which led to a vacuum pump was placed 1.00 g (2.9 mmol) of (h^1-$CH_3C_6H_4CH_2$)(C_5H_5)-$(CO)_3Mo$. The flask was maintained under vacuum (0.05 torr) while immersed in an oil bath at 105° for 1.3 hr. Nitrogen was admitted, the flask was allowed to cool, and the dark red pyrolysate was dissolved in benzene. This solution was chromatographed on silica gel (Merck silicic acid), eluting with 1:3 benzene–petroleum ether. Collection of the eluate was begun after infrared spectra showed all of the unreacted starting compound to have been eluted. The dark red zone was collected in the bottom of a sublimer and solvent concurrently removed in a stream of nitrogen. The residue was sublimed at 77° (0.04 torr) over a period of 7 hr yielding 0.105 g (11%) of a red-orange solid (mp 98–100°).

Anal. Calcd for $C_{15}H_{14}MoO_2$: C, 55.91; H, 4.35. Found: C, 56.1; H, 4.10.

The infrared spectrum (cyclohexane) had strong bands at 1950 and 1875 cm^{-1} (± 5 cm^{-1}). The compound is stable for several months when stored at ~5° under nitrogen.

3,5-Diisopropylbenzyl Chloride. Using the method of Wiley, *et al.*,[18] 45 g (0.25 mol) of 3,5-diisopropylphenol was pyrolyzed with 140 g (0.33 mol) of triphenyldibromophosphorane at 300° for 18 hr. The crude 3,5-diisopropylphenyl bromide was distilled from the pyrolysis flask at aspirator pressure and was purified by vacuum fractionation, yielding 18.0 g (30%) of a colorless oil, bp 58–63° (0.1 torr).

Anal. Calcd for $C_{12}H_{17}Br$: C, 59.75; H, 7.12. Found: C, 60.5; H, 7.02.

The pmr spectrum of a $CDCl_3$ solution of the 3,5-diisopropylphenyl bromide had the following resonances (τ values): doublet at 2.80 (2 H), multiplet at 3.02 (1 H), heptuplet at 7.27 (2 H), and doublet at 8.86 (12 H).

3,5-Diisopropylphenyl bromide, 14.7 g (0.061 mol), dissolved in 150 ml of anhydrous ether was treated with 0.070 mol of commercial butyllithium in hexane at 0°, and after 1 hr with dry formaldehyde gas.[19] The mixture was then treated with water, the ether layer separated, and the aqueous layer extracted twice with 150-ml portions of ether. The combined ether extracts were washed with 5% HCl solution, followed by water, and dried over anhydrous $MgSO_4$. The ether was then stripped from the filtered solution and the residue vacuum fractionated to yield 8.0 g (75%) of 3,5-diisopropylbenzyl alcohol as a colorless oil, bp 95–97° (0.35 torr).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.18; H, 10.50. Found: C, 80.9; H, 10.8.

The pmr spectrum of a $CDCl_3$ solution had the following resonances (τ): singlet at 3.00 (3 H), broad singlet at 4.96 (1 H), singlet at 5.57 (2 H), heptuplet at 7.22 (2 H), and doublet at 8.82 (12 H). The ir spectrum had a strong broad band at 3340 cm^{-1}.

The 3,5-diisopropylbenzyl alcohol, 6.32 g (0.033 mol), was treated with 50 ml of thionyl chloride at 0° and the mixture was allowed to stand at room temperature for 12 hr. The excess thionyl chloride was then stripped off at aspirator pressure, and the residue was fractionated under vacuum to afford 3.90 g (56%) of 3,5-diisopropylbenzyl chloride as a colorless oil, bp 76–77° (0.45 torr).

Anal. Calcd for $C_{13}H_{19}Cl$: C, 74.08; H, 9.10. Found: C, 73.2; H, 9.23.

The pmr spectrum of a $CDCl_3$ solution had the following resonances (τ): singlet at 2.97 (3 H), singlet at 5.68 (2 H), heptuplet at 7.22 (2 H), and doublet at 8.83 (12 H).

(*Monohapto*-3,5-diisopropylbenzyl)(*pentahapto*cyclopentadienyl)tricarbonylmolybdenum. The method previously described for the *p*-methyl analog was employed with 0.020 mol of $NaMo(CO)_3C_5H_5$ and 3.50 g (0.0166 mol) of diisopropylbenzyl chloride in 90 ml of tetrahydrofuran, to yield 4.5 g (64%) of a bright yellow solid, mp 91–92° (with slight decomposition).

Anal. Calcd for $C_{21}H_{24}MoO_3$: C, 59.99; H, 5.77. Found: C, 60.1; H, 6.06.

The infrared spectrum of a cyclohexane solution had strong bands at 2010 and 1930 (doublet) cm^{-1} (± 5 cm^{-1}). The pmr spectrum of a solution in $CDCl_3$ had the following resonances (τ): doublet at 3.10 (2 H), multiplet at 3.28 (1 H), singlet at 4.85 (5 H), singlet at 7.07 (2 H), heptuplet at 7.19 (2 H), and doublet at 8.79 (12 H).

(*Trihapto*-3,5-diisopropylbenzyl)(*pentahapto*cyclopentadienyl)molybdenum. In the vessel described above for the *p*-methyl compound 1.0 g (2.4 mmol) of (h^1-$(C_3H_7)_2C_6H_3CH_2$)(C_5H_5)$Mo(CO)_3$ was pyrolyzed under high vacuum for 2.2 hr at 110°. The dark red pyrolysate was chromatographed as before and collection of eluate begun when the near absence of starting material was indicated by the ir spectrum. The dark red, viscous oil was pumped for 12 hr under high vacuum and the solid then sublimed at 78° (0.04 torr) for 36 hr to yield 0.22 g (23%) of dark red crystals, mp 69–71°.

Anal. Calcd for $C_{20}H_{24}MoO_2$: C, 61.22; H, 6.18. Found: C, 61.3; H, 5.79.

The infrared spectrum of a cyclohexane solution shows strong bands at 1955 and 1880 cm^{-1} (± 5 cm^{-1}.)

(*Monohapto*-4-methylbenzyl)(*pentahapto*cyclopentadienyl)tricarbonyltungsten. To a 50-ml tetrahydrofuran solution of 9.1 mmol of $NaW(CO)_3C_5H_5$, prepared by the method of Piper and Wilkinson,[20] was added 2.11 g (15 mmol) of *p*-methylbenzyl chloride. The mixture was stirred for 24 hr and then worked up in the same way as were the corresponding molybdenum compounds to yield 1.74 g (55%) of pale yellow solid, mp 110–112°.

Anal. Calcd for $C_{16}H_{14}WO_3$: C, 43.86; H, 3.23. Found: C, 44.1; H, 3.38.

The ir spectrum (cyclohexane) has strong bands at 2010 and 1920 cm^{-1} (± 5 cm^{-1}). The pmr spectrum in $CDCl_3$ had the following resonances (τ): multiplet at 2.93 (4 H), singlet at 4.40 (5 H), singlet at 7.01 (2 H), and singlet at 7.73 (3 H).

(*Trihapto*-4-methylbenzyl)(*pentahapto*cyclopentadienyl)dicarbonyltungsten. The *monohapto*-4-methylbenzyl compound, 1.30 g (3.0 mmol), dissolved in 8 ml of benzene was placed in a Vycor tube which was attached by a ground-glass joint to an additional joint that had been blown onto the bottom of a 50-ml three-neck roundbottom flask. This flask was equipped through two of its regular necks with a gas inlet and a small condenser leading to a gas outlet. With a slow stream of nitrogen flowing through the system, the apparatus was lowered into a large vessel of water in which there was also placed a 450-W, medium-pressure Hanovia mercury lamp, close to the Vycor tube. The *monohapto*benzyl compound was irradiated for 24 hr. The volume of the dark red solution was reduced to half by evaporation with a stream of nitrogen, and the solution was chromatographed on silica gel, with a 1:2 mixture of benzene and petroleum ether serving as the eluent. As before infrared spectra were used to monitor the eluate, and collection of an orange band was begun after it was seen that virtually all unchanged

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(18) G. A. Wiley, R. L. Hershkovitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

(19) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1941, p 188.

(20) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).

starting material had passed through. The residue from evaporation of the eluate was sublimed at 80° (0.05 torr) for 36 hr to yield 0.28 g (26%) of the orange solid product, mp 125–127°.

Anal. Calcd for $C_{15}H_{14}WO_2$: C, 43.92; H, 3.45. Found. C, 44.1; H, 3.50.

The infrared spectrum (cyclohexane) had strong bands at 1945 and 1868 cm^{-1} (± 5 cm^{-1}). This compound is very similar to its molybdenum analog except that it reacts more readily with chlorinated solvents and is, in general, less soluble in organic media.

Spectroscopic Measurements. Infrared spectra were recorded on Perkin-Elmer 237 and 337 spectrometers.

Nmr spectra were measured with a Varian Associates A-60 spectrometer. Temperature calibration was achieved by measuring the peak separation in methanol and ethylene glycol samples. The spectra were calibrated at the lowest temperature with a Krohn-Hite Model 450 oscillator and a Hewlett-Packard Model 524 electronic counter.

To assure rigorous exclusion of oxygen from nmr samples, solvents and tetramethylsilane were degassed and distilled under high vacuum directly onto the solids which had been previously placed in standard-size nmr tubes using a nitrogen-filled glove box.

Treatment of Nmr Data. The rate of rearrangement at a given temperature was estimated by comparison of experimental spectra with those calculated by the method of Kubo[21] and Sack[22] in a manner previously described[23,24] using a computer program written by Professor G. M. Whitesides of this department for the IBM 360 computer. The computer output consisted of line shapes drawn by a Calcomp plotter and these were visually compared with experimental spectra.

To achieve maximum accuracy in kinetic measurements, spectra were recorded at minimum sweep width and maximum spectrum amplitude. In instances where spectral features were difficult to discern (*e.g.*, near coalescence points) several scans were made of the spectrum. In cases where the separate resonances for each of two exchanging protons were discernible at all times during their collapse, computed spectra were fitted to give the best agreement with both signals. Where one resonance was obscured by other peaks in the spectrum during its collapse, computed spectra were fitted only to the completely visible resonance. In the case of the high-field ring protons in (h^3-$CH_3C_6H_4CH_2$)(h^5-C_5H_5)Mo(CO)$_2$, each exchanging component was simulated as a doublet (due to *ortho* coupling) with the most intense component again split into a doublet (due to what was apparently long-range coupling). Furthermore, since the high-field resonance was partially obscured by the cyclopentadienyl peak, the line width and intensity of the smaller component of the doublet were estimated from the spectrum in the fast exchange limit.

A computer program written by Mr. W. K. Bratton was used to fit Arrhenius plots by the method of least squares and to compute activation parameters.

Acknowledgment. We thank Professor George M. Whitesides for several helpful and stimulating discussions, and particularly for persuading us that the effort required to synthesize the 3,5-diisopropylbenzyl compound would probably be rewarded by useful results. We thank Professor Dietmar Seyferth for the use of some glpc equipment.

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[21] R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957).

[22] R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

[23] G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).

[24] F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, **90**, 1438 (1968).

Chemistry of Metal Hydrides.[1] V. Preparation of Platinum Hydrides from $[PtX(CO)(R_3P)_2]^+$ and $[PtX(COOR)(Ph_3P)_2]$

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Abstract: The synthesis of $[Pt_2X_2(R_3P)_4][BF_4]_2$ for X = Br or I with R = phenyl, and for X = Br with R = ethyl, is described. The rates of cleavage of these dihalo-bridged diplatinum cations with carbon monoxide to give the carbonyls, *trans*-$[PtX(CO)(R_3P)_2][BF_4]$, have been studied qualitatively. *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ reacts with water giving *trans*-$[PtHCl(Et_3P)_2]$ and carbon dioxide. The triphenylphosphine analog, *trans*-$[PtX(CO)(Ph_3P)_2][BF_4]$, where X = Cl, Br, or I, reacts readily with methanol or ethanol giving the alkoxycarbonyl $[PtX(COOR)(Ph_3P)_2]$ where R = CH_3 or C_2H_5. These alkoxycarbonyls react with water in the presence of salt catalyst giving *trans*-$[PtHX(Ph_3P)_2]$. Possible mechanisms for these conversions are discussed.

The ability of $[RhCl(Ph_3P)_2]$ and *trans*-$[IrCl(CO)(Ph_3P)_2]$ to act as catalysts for the homogeneous hydrogenation of olefins and to undergo oxidative additions is well known.[2] This reactivity led us to examine the isoelectronic cation $[PtX(CO)(R_3P)_2]^+$ for similar activity. Although such catalytic character has not as yet been observed for these platinum(II) complexes, we have found that their reactions with water and alcohols are of considerable interest. This paper describes the facile production of the hydridoplatinum(II) compounds, *trans*-$[PtHX(R_3P)_2]$, with X = halide and R = ethyl or phenyl, directly from the platinum(II) carbonyl cation by reaction with water, and indirectly *via* an alkoxycarbonyl compound.

Results and Discussion

The compounds *trans*-$[PtX(CO)(R_3P)_2][BF_4]$, where X = Cl, Br, or I with R = phenyl, and where X = Cl or Br with R = ethyl, can be synthesized by various routes.[1,3,4] It was of interest, however, to prepare these

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[1] For part IV, see H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, **91**, 596 (1969).

[2] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966), and references therein.

[3] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, **90**, 2259 (1968).

[4] M. J. Church and M. I. Mays, *Chem. Commun.*, 435 (1968).