

think that these complexes are also definitely not  $\eta^1$ , and extended Hückel calculations bear this out, again favoring an  $\eta^2$  structure.<sup>33</sup>

**Acknowledgment.** We thank F. Cecconi for technical assistance, G. Vignozzi and F. Nuzzi for microanalyses, and Professors Roald Hoffmann, Peter Lillya, and Paul Dobosh for helpful discussions.

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**Registry No.** [(Ph<sub>3</sub>C<sub>3</sub>)Ni(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>, 75507-34-5; [(Ph<sub>3</sub>C<sub>3</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, 79839-96-6; [(Ph<sub>3</sub>C<sub>3</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>·C<sub>6</sub>H<sub>6</sub>, 79855-23-5; [(Ph<sub>3</sub>C<sub>3</sub>)Ni(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, 77598-41-5; (C<sub>2</sub>H<sub>4</sub>)Ni(PPh<sub>3</sub>)<sub>2</sub>, 23777-40-4; (C<sub>2</sub>H<sub>4</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub>, 33395-22-1.

**Supplementary Material Available:** Listings of structure factor amplitudes for compounds 1-3 (63 pages). Ordering information is given on any current masthead page.

## Alkane Dehydrogenation by Iridium Complexes

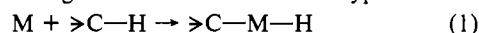
Robert H. Crabtree,\* Michelle F. Mellea, Jean M. Mihelcic, and Jennifer M. Quirk

Contribution from the Yale University Department of Chemistry, Sterling Chemistry Laboratory, New Haven, Connecticut 06511. Received May 8, 1981

**Abstract:** Cyclopentene reacts with IrH<sub>2</sub>S<sub>2</sub>L<sub>2</sub><sup>+</sup> at 40 °C (S = H<sub>2</sub>O or acetone; L = PPh<sub>3</sub>) to give CpIrHL<sub>2</sub><sup>+</sup>. The same product is formed from cyclopentane at 80 °C in the presence of 3,3-dimethyl-1-butene (**5**). Cyclooctene or cyclooctane and **5** give Ir(1,5-cyclooctadiene)L<sub>2</sub><sup>+</sup>. Evidence against colloid, radical, or carbonium ion mechanisms is given. We propose that this system constitutes the first example of a reverse hydrogenation of an alkane by a transition-metal complex.

The activation of alkanes by soluble transition-metal species has been the object of much study.<sup>1</sup> After a brief review of some of this work, we will discuss our own approach, which has led to the development of a system in which a variety of alkanes can be dehydrogenated to give  $\pi$ -coordinated ligands.

Much work has gone into attempting to activate alkanes via eq 1 with nucleophilic metal fragments. The hope has been that the metal will cleave an alkane CH bond by an "oxidative" addition. As the driving force for additions of this type has been



thought to be the dispersal of negative charge from the metal to the alkyl and hydride ligands, a nucleophilic metal has generally been considered as the best type of candidate for the reaction. In this connection, Chatt<sup>2</sup> et al. and Ittel<sup>3</sup> et al. have studied Mdmpe<sub>2</sub> (M = Fe, Ru, or Os; dmpe = 1,2-dimethylphosphinoethane), generated thermally from MArHdmpe<sub>2</sub>, and Green<sup>4</sup> et al. have studied "Cp<sub>2</sub>W" (Cp = cyclopentadienyl), generated photochemically from Cp<sub>2</sub>WH<sub>2</sub>. The ruthenium-based system is successful in activating CH bonds in free arenes, in the coordinated dmpe group, or in free CH<sub>3</sub>CN and (CH<sub>3</sub>)<sub>2</sub>CO. The tungsten system activates phenyl and benzylic CH bonds in arenes and the CH bonds of Si(CH<sub>3</sub>)<sub>4</sub>. None of these systems, however, has been reported to activate free alkanes.

A number of systems<sup>5</sup> based on simple salts of Pt and Ir are known to catalyze H/D exchange in alkanes, although there is some question as to whether or not the active species in these solutions is homogeneous.<sup>6</sup>

Radicals can abstract hydrogen atoms from alkanes,<sup>7</sup> and a number of cases are known<sup>8-10</sup> where transition-metal-centered

radicals or free radicals produced by transition-metal reagents give reactions of this type. The well-known Fenton's<sup>11</sup> reagent falls into this category.

A number of commercially important processes rely on carbonium ion rearrangements induced by Lewis-acid catalysts. These, and radical-based systems, however, offer little expectation of the sort of selectivity that might be associated with a system operating via eq 1.

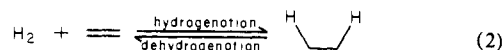
We now report fully on a stoichiometric, selective, homogeneous, alkane dehydrogenation system which we propose acts via a reverse-hydrogenation mechanism, involving eq 1 as a first step. We find that an electrophilic, rather than a nucleophilic, metal center is involved. A brief note on these results has appeared.<sup>12</sup>

Baudry, Ephritikine, and Felkin have recently reported a similar system to ours, only based on rhenium;<sup>13</sup> it may well be mechanistically related.

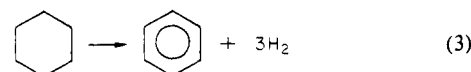
### Results and Discussion

#### The Nature of the Problem: A Comparison with Hydrogenation.

The conversion of alkanes to alkenes can be regarded as the reverse of the well-known alkene hydrogenation reaction:



Any catalyst for the forward process should also speed up the rate of the reverse reaction and might be considered as a potential candidate for alkane dehydrogenation. The thermodynamics of the process ( $\Delta H \approx -33$  kcal/mol) shows that the "equilibrium" vastly favors the alkane side. Since the entropy of the process is negative, there should be a temperature at which the equilibrium begins to favor the alkene side. Indeed, the commercially important reforming process, e.g.,



is catalyzed by metals such as Pt, Re, or Ir, that are hydrogenation catalysts, and a high temperature (e.g., 500 °C) is required.<sup>14</sup> We sought to avoid the need for high temperatures in the system we

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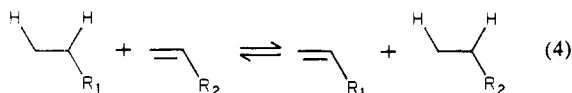
(11) Fenton, H. S. H. *J. Chem. Soc.* **1894**, 65, 899.

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set out to develop, because these would preclude the application of any such system to the selective dehydrogenation of thermally sensitive organic compounds. Clearly, we can bias the overall thermodynamics by including an alkene as a hydrogen acceptor (or oxidizing agent) in the system (eq 4). This does not, however,



help us at all with the kinetics of the process, because the initial act must still be eq 1, which may be very unfavorable for alkanes. Equation 1 is probably least unfavorable for third-row metals where the M-C and M-H bonds are believed to be stronger than in the first or second rows.<sup>15</sup> The presence of the hydrogen acceptor in eq 4 brings its own severe disadvantages, which will be further discussed below.

It might seem that selected homogeneous hydrogenation catalysts should catalyze reaction 4. If this is tried using RhCl(PPh<sub>3</sub>)<sub>3</sub> or RuHCl(PPh<sub>3</sub>)<sub>3</sub>,<sup>16</sup> for example, it is found that no alkane dehydrogenation occurs. The probable reasons are the following: (1) the alkane is such a poor ligand that it cannot compete with PPh<sub>3</sub> or with any hydrogen acceptor for the metal; (2) by the chelate effect, the metal preferentially activates a CH bond in its own ligands to give a cyclometalated<sup>17</sup> product; (3) the hydrogen acceptor is preferentially coordinated and dehydrogenated to give a stable  $\pi$  complex<sup>18</sup> (e.g., propene might give a  $\pi$ -allyl hydride complex).

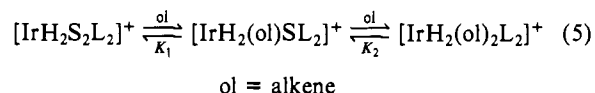
The first point, that of *access* of the alkane to the metal site, is perhaps the one which places the severest constraint on the choice of possible metal systems. Fortunately, it is a problem which we have already met in our studies of the hydrogenation of hindered alkenes.<sup>19</sup> The substrate, the hindered alkene, is a poor ligand, but still one which is much better than an alkane. Certain ideas that were useful in solving this problem have proved to be directly applicable to alkane activation. For this reason a comparison of the two problems is helpful. The classical homogeneous hydrogenation catalysts, mentioned above, are species prepared by refluxing the metal halides with excess PPh<sub>3</sub>. As such, they have a relatively high PR<sub>3</sub>/metal ratio, and rely on dissociation of PR<sub>3</sub> (or coordinated solvent) to generate active sites for substrate coordination. They are very selective for unhindered olefin substrates, because only these are able to displace the competing ligands (PR<sub>3</sub> or solvent) from the metal. Schrock and Osborn<sup>20</sup> made an important contribution by recognizing that the PR<sub>3</sub>/metal ratio could be altered in a potentially useful way by using complexes of the type [M(cod)L<sub>2</sub>]A (M = Rh or Ir; cod = 1,5-cyclooctadiene; L = PR<sub>3</sub>; A = BF<sub>4</sub>, PF<sub>6</sub>, or ClO<sub>4</sub>). In the classical hydrogenation solvents, EtOH or acetone (=S), the complexes [MH<sub>2</sub>S<sub>2</sub>L<sub>2</sub>]A could be isolated. The rhodium analogue loses S relatively easily and is an excellent hydrogenation catalyst for unhindered olefins. The iridium analogue, much more stable kinetically, is a much poorer hydrogenation catalyst and was not studied in detail.

We found<sup>19</sup> that in the iridium system, the hydrogenation rate was drastically affected by the solvent. In coordinating solvents, e.g., Me<sub>2</sub>CO, slow hydrogenation only of unhindered olefins was observed. In CH<sub>2</sub>Cl<sub>2</sub>, no solvate complexes were formed, but we observe (by <sup>1</sup>H NMR at -80 °C) that the substrate, as the best available ligand, now fills the role formerly played by the solvent, S, and the complexes [IrH<sub>2</sub>(olefin)<sub>2</sub>L<sub>2</sub>]A are formed. These can collapse directly to products and are very rapid hydrogenation catalysts even for hindered olefins. The rhodium analogues, we

find, do not give analogous complexes, and behave in CH<sub>2</sub>Cl<sub>2</sub> much as they do in EtOH or acetone. We do not understand the underlying reason for this striking difference between the rhodium and the iridium systems.

For hindered olefins, therefore, successful hydrogenation required the use of: (1) a complex having a low PR<sub>3</sub>/metal ratio (a ligand-deficient system); (2) a noncoordinating solvent; and (3) a third-row metal. We therefore applied these ideas to the problem of alkane activation.

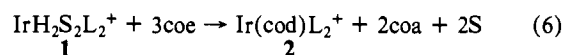
**The Iridium System in Hydrocarbon Dehydrogenation.** [IrH<sub>2</sub>S<sub>2</sub>L<sub>2</sub>]BF<sub>4</sub> (1, S = acetone (a); H<sub>2</sub>O, (b); L = PPh<sub>3</sub>) was chosen as a convenient and suitable precursor, because we knew from previous work that, in a noncoordinating solvent, the S ligands in this complex could be replaced by a variety of olefins.



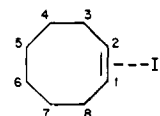
The equilibria shown in eq 5 have been observed from -80 to -20 °C in CD<sub>2</sub>Cl<sub>2</sub> by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.<sup>21</sup> Equilibrium studies give an estimate of the relative ligating power of various S groups. In the order of increasing ligating strength, these are: H<sub>2</sub>O < Bu-*t*-OH < Pr-*i*-OH < Me<sub>2</sub>CO < EtOH < MeCN. Other potential S ligands, such as Et<sub>2</sub>O, did not give complexes of type 1 at all. We used the H<sub>2</sub>O solvate 1b and the Me<sub>2</sub>CO solvate 1a in subsequent work, because we required S ligands which offered the least possible degree of competition with our substrate alkane.

Our first experiments involved alkene dehydrogenation, both to test the feasibility of the plan, and so as to have any products in hand for comparison with those we hoped to obtain from the corresponding alkanes.

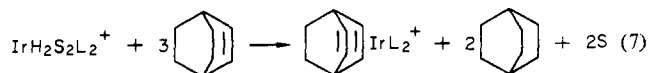
The complexes 1a and 1b react smoothly with specially purified (see Experimental Section) cyclooctene (coe) (10 mol eq) in refluxing CH<sub>2</sub>Cl<sub>2</sub> at 40 °C to give [Ir(cod)L<sub>2</sub>]BF<sub>4</sub> (2) after 60 min. The rapidity of this metalation was very encouraging. What seems to be happening is the dismutation of coe to coordinated cod and free cyclooctane (coa), which was determined by NMR and GC methods. The hydrogen abstracted from the ligand is passed, probably by a classical hydrogenation mechanism, to free olefin.



It was not yet clear whether the metal was directly attacking the unactivated 5 and 6 positions of coe, or whether this reaction only proceeded because the metal first attacked the activated allylic hydrogens in the 3 and 8 positions.



We therefore decided to study the dehydrogenation of [2.2.2]bicyclooctene, in which the application of Bredt's rule forbids the formation of an intermediate  $\pi$ -allyl. This alkene reacts with 1 under analogous conditions at a very similar rate to give the new bicyclooctadiene complex, shown in eq 7. This suggested that attack of unactivated CH bonds under relatively mild conditions was indeed possible.



A number of other olefins were studied: cyclopentene gives the new cyclopentadienyl hydride shown in eq 8. Here, two hydrogens are passed to the excess olefin, and one, presumably the last to be activated by the metal, remains bound to it in the product.

(21) Crabtree, R. H.; Quirk, J. M., manuscript in preparation.

(15) Parshall, G. W. *Acc. Chem. Res.* 1970, 3, 179; 1975, 8, 113.

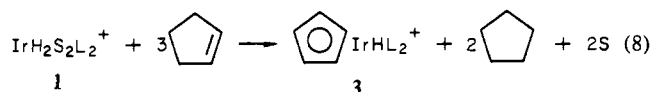
(16) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* 1966, 1711. Evans, D.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Nature (London)* 1965, 208, 1203.

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Cycloheptene gives an analogous  $\eta^5$ -cycloheptadienyl hydride and cyclohexene an  $\eta^5$ -cyclohexadienyl hydride.<sup>22</sup> All these complexes were fully characterized by microanalytical and spectroscopic methods (see Experimental Section) and presented no unusual features.

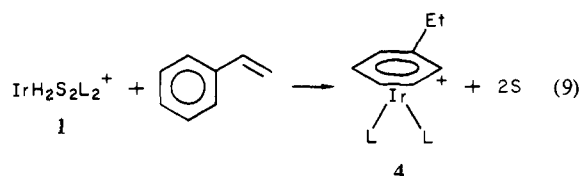
We were now able to proceed to alkane dehydrogenation with some confidence that if any products were formed at all they would be the same ones that we had observed in the reactions of the corresponding alkenes.

None of the corresponding alkenes react with the solvated iridium complexes  $[\text{IrH}_2\text{S}_2\text{L}_2]\text{BF}_4$  (**1a**, S = Me<sub>2</sub>CO; **1b**, S = H<sub>2</sub>O) in CH<sub>2</sub>Cl<sub>2</sub> at 40 °C, but on raising the temperature to 80 °C, which is most conveniently arranged by replacing CH<sub>2</sub>Cl<sub>2</sub> with (CH<sub>2</sub>Cl)<sub>2</sub> as solvent, some cyclopentadienyl complex (**3**, 7%) is formed from cyclopentane. This product could be identified among the products by <sup>1</sup>H NMR and could not be isolated in crystalline form.

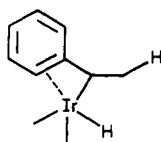
**The Choice of Hydrogen Acceptor.** The principle of the system seemed to be correct, but the yield was not yet at all satisfactory. We believed that the reason for the low yield might be that no hydrogen acceptor was present in these solutions to remove the hydrogen stripped from the cycloalkane (cf. eq 4). We therefore tried a large number of alkenes as possible hydrogen acceptors, using the cyclopentane system as an assay for activity. We found, however, that most of these olefins completely suppressed the small activity that we had previously observed. The probable reasons for this depend on the particular alkene. Those containing allylic hydrogens probably dehydrogenate to give coordinated unsaturated ligands which block the available sites at the metal. For example, cyclooctene gives only **2** in an attempted cyclopentane activation and not **3**.

Exclusion of the class of alkenes containing allylic hydrogens leaves a substantial number that are potentially metalation resistant: C<sub>2</sub>H<sub>4</sub> itself, styrene and its derivatives, and *tert*-butyl ethylene (3,3-dimethyl-1-butene) and related species. Ethylene fails, probably because its unusually high complexation constant denies the alkane access to the metal.

Styrene and a large number of its derivatives also failed, leading us to examine the reasons in detail. Styrene reacts readily with **1a** or **1b** to give an orange crystalline product which was characterized as **4**. This type of reaction does not seem to have been

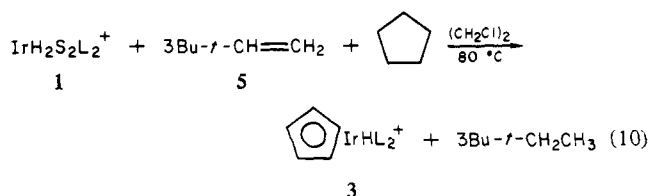


previously observed and may go via an  $\eta^3$ -benzylic intermediate of the type:



Stilbene and  $\alpha$ -methylstyrene behave in an analogous way to give the corresponding arene complexes. Tetraphenylethylene, or a mixture of *cis*- and *trans*-*t*-BuCH=CH-*t*-Bu, in contrast, proved so bulky that they failed to react with **1**.

*t*-BuCH=CH<sub>2</sub> (**5**) had the required combination of metalation resistance and steric bulk. As hydrogen acceptor, it substantially



increased the yield of dehydrogenation product. For example, 4 molar equiv of **5** increased the yield of the cyclopentadienyl complex **3** from 7% to 40% (NMR, based on Ir). The product (**3**) could now be crystallized in 32% yield from the reaction mixtures by evaporating the volatiles and treating the residues with warm methanol. The product was identical with the authentic material in all respects. Increasing the proportion of **5** in the reaction mixtures led to a fall in the yield of **3**. For example, at 8 molar equiv/Ir, the yield was 30% (NMR). On decreasing the proportion of **5** to zero, the yield fell to 7% (NMR).

In the absence of hydrogen acceptor, cyclooctane was not dehydrogenated to give **2**. The addition of 4 molar equiv of **5** per iridium gave the cyclooctadiene complex, **2**, in a yield of 70% (NMR). This product was a little more difficult to isolate than **3**, and only 47% of **2** was obtained after crystallization with warm methanol. The complex proved to be identical with the authentic material. In particular, it reacts with HCl to give IrHCl<sub>2</sub>(cod)(PPh<sub>3</sub>), the characteristic NMR spectrum of which was observed.

Cycloheptane was not dehydrogenated at all in the absence of hydrogen acceptor, but with 4 molar equiv of **5**, some of the expected cycloheptadienyl complex (12%) was detected by NMR after 12 h. This complex was not stable at 80 °C, and slowly decomposed under the reaction conditions to unidentified material. The yield of the cycloheptadienyl complex accordingly fell to zero after being refluxed for 24 h.

[2.2.2]Bicyclooctane did not give the bicyclooctadiene complex, whether **5** was present or not. We suspect that the products may derive from activation of the tertiary CH bonds. Adamantane also seems to give products of this type, which we have not yet been able to characterize.

In no case were dehydrogenated or rearranged alkanes detected in the volatile fractions by GC. Linear alkanes, such as *n*-hexane, gave neither organometallic nor organic products under these conditions.

We are currently trying to increase the activity of the system.  $[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]\text{BF}_4$  and  $[\text{Ir}(\text{cod})(\text{PR}_3)(\text{amine})]\text{BF}_4$  are both more active hydrogenation catalysts than the bis(PPh<sub>3</sub>) analogue, but no stable solvated hydrides of type **1** could be isolated in these cases, even though the solvated hydrides could be detected by NMR in acetone solution; they decomposed (but not to metal) on attempted isolation.

**Reproducibility and Mechanism.** We took great care (1) to see if these reactions were reproducible; and (2) to discover if they proceeded via eq 1 or in some other way.

For example, in examining the first point, complex **1** was carefully recrystallized. The *tert*-butylethylene (**5**), cyclopentane, and dichloroethane were carefully purified, including a fractional distillation step using a Teflon spinning band apparatus, and were stored in clean, dry glassware under nitrogen. We have found no difficulty in reproducing these results with different batches of reagents, whether or not exceptional precautions were taken (see Experimental Section).

Alkanes are well-known to enter into three general types of reaction: (1) with radicals;<sup>7</sup> (2) with carbonium ions;<sup>23</sup> and (3) with metal surfaces<sup>24</sup> (heterogeneous catalysis). It seemed possible that in spite of our having designed the system to operate via eq 1, one of these three alternative mechanisms might have been responsible for our results.

**Radical Mechanisms.** Radicals have commonly been proposed as intermediate in chemical reactions on the basis of studies such

(22) The structure of an orange complex, which we suggested (ref 12) contains a cyclohexadiene ligand, is still under study. The colorless cyclohexadienyl hydride obtained under the conditions described here is unexceptional.

(23) Olah, G. A. *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 173.

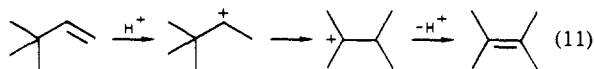
(24) Clarke, J. K. A.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125.

as the following: (1) observation of characteristic radical-derived products; (2) radical initiation and suppression studies; and (3) use of substrates particularly subject to radical rearrangements.<sup>25</sup> We have been able to apply the first of these methods to our alkane activation system. Hill<sup>18</sup> has recently shown, for example, that in his alkane activation system based on transition-metal-generated radicals, the alkyl radicals that are formed both abstract chlorine atoms from the solvent ( $\text{CH}_2\text{Cl}_2$ ) and also dimerize, to give  $\text{RCl}$  and  $\text{R-R}$ , respectively. We have carefully analyzed the volatile fractions of our system, and have failed to detect any trace of  $\text{RCl}$  or  $\text{R-R}$  by GC methods.

Few radical substrate traps or initiators lack coordinating functions which we have shown interfere with the activation process by competitive binding to the metal,  $\text{O}_2$  cannot be used as the reaction is air sensitive, and styrene deactivates the system via eq 9.

The iridium compounds with which we work are very resistant to undergoing radical reactions of any sort. They fail to react with  $\text{O}_2$ ,  $\text{MeI}$ ,  $\text{CHCl}_3$ , or  $\text{CCl}_4$ . For example, **3** can be refluxed in  $\text{CHCl}_3/\text{CCl}_4$  for several hours without change.

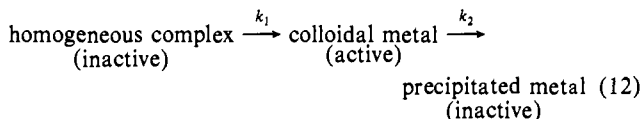
**Carbonium Ion Mechanisms.** Carbonium ions might very easily have been formed in our system by protonation of the hydrogen acceptor by trace acid. This mechanism, however, can be entirely excluded because this carbonium ion is subject to an extremely rapid skeletal rearrangement<sup>26</sup>



No trace of substances arising from this rearrangement was detected in the volatile products by GC. Indeed, deliberate addition of trace amounts of noncoordinating acids completely suppressed the reaction, probably by rearranging the *tert*-butylethylene to tetramethylethylene (2,3-dimethyl-2-butene), which is ineffective as a hydrogen acceptor.

**Heterogeneous Mechanisms.** The presence of bulk precipitated metal has vitiated the conclusions of a surprisingly large number of studies on catalysis in solutions claimed to be homogeneous. We were able to rule out definitely the presence of bulk metal by Maitlis<sup>27</sup> method (see Experimental Section).

A far more difficult problem, and one which is only just beginning to receive the attention it deserves, is that of the unperceived presence of *colloidal* metal in "homogeneous" catalysts. Such colloidal particles can be catalytically active,<sup>28</sup> and may be responsible for all of the observed catalytic action. They may or may not subsequently precipitate. It is not sufficient, therefore, merely to verify that the solutions are clear, nor to show that any bulk metal that is precipitated is catalytically inactive. This is because the sequence of events shown in eq 13 may be taking place.



Indeed, this scheme may be operative in the  $\text{PtCl}_4^{2-}$ -catalysed  $\text{H}/\text{D}$  exchange reactions mentioned previously.<sup>6</sup>

There are three approaches which may be useful in attacking this problem. The first is by a direct physical technique, dynamic light scattering.<sup>29</sup> In the dynamic light scattering experiment, not only is the scattered light detected, but the fluctuations in its amplitude are also analyzed numerically. The result is the au-

torrelation function, which can be used to characterize the scattering particles in terms of their diffusion constant, and therefore their size. The larger the particles, the slower they diffuse by Brownian motion, and the slower is the decay of the auto-correlation function. In this way, background scattering from the solvent and reagents or from adventitious dust particles can be distinguished from scattering from particles of colloidal size. Berne and Pecora<sup>29</sup> have discussed the practical and theoretical basis of the method; the reader is referred to their work for further details.

The second approach is that of selectivity. If the selectivity of the supposed homogeneous catalytic reaction is very different from that observed among all known heterogeneous catalysts, then the claim of homogeneity for the system receives powerful support.

For example, our own alkene hydrogenation catalyst<sup>19</sup> is based on similar iridium chemistry to that described in this paper. Since the activity of this catalyst resembles that of heterogeneous catalysts in its facile reduction of highly substituted alkenes, the involvement of colloidal metal remained a small but distinct possibility. In collaboration with Dr. J. W. Suggs,<sup>30</sup> however, we were able to show that the catalyst adds hydrogen to the  $\alpha$  face of a variety of steroids, the  $\beta$  isomer being undetectable.  $\text{RhCl}(\text{PPh}_3)_3$  behaves similarly, but not any heterogeneous catalyst.<sup>31</sup>

The third approach is simply to show that the supposed homogeneous system fails to catalyze a reaction which is catalyzed by authentic colloidal preparations. This method would be particularly sensitive for a trace quantity of very small and highly active colloid, which might escape detection by light scattering.

We have successfully applied all these approaches to the alkane dehydrogenation system. The light-scattering correlation functions of both the starting reaction mixtures and product solutions are flat over the whole instrumental time scale range, implying that colloids are absent. In contrast, a 1 nM preparation of a synthetic iridium colloid ( $3 \times 10^{11}$  particles/cm<sup>3</sup>; average radius, 250 Å) could easily be detected.

The colloid might still escape detection under two circumstances: (i) the particles were small (say 5 Å radius), or (ii) the colloid was only formed at the reaction temperature but redissolved before cooling to room temperature. We are currently examining the limits of detection of the dynamic light scattering method with variations in size of the colloid particle, but classical iridium colloids have a radius range of ca. 100–500 Å. The second possibility seems unlikely, because iridium is an exceptionally noble metal, much more so than Pd or Pt. It does not react with aqua regia, but only with  $\text{Na}_2\text{O}_2/\text{NaOH}$  at 200 °C or  $\text{Cl}_2/\text{NaCl}$  at 625 °C.<sup>32</sup>

The selectivity of the alkane dehydrogenation system is quite marked. For example,  $\text{Me}_3\text{CCH}=\text{CH}_2$  (**5**), but not  $\text{Me}_3\text{SiCH}=\text{CH}_2$  (**6**), is effective as a hydrogen acceptor. This may arise because **6** is less bulky than **5** and blocks the active sites by complex formation. We find, for example, that  $\text{IrH}_2\text{S}_2\text{L}_2^+$  gives only  $\text{IrH}_2\text{S}(\mathbf{5})\text{L}_2^+$  with **5** but can give  $\text{IrH}_2(\mathbf{6})\text{L}_2^+$  with **6**.<sup>21</sup>

The third approach requires the existence of a reaction which is catalyzed by the colloidal, but not by the homogeneous, system. Fortunately, nitrobenzene is reduced very effectively by iridium colloids at room temperature under  $\text{H}_2$  (1 atm),<sup>34</sup> a reaction that we have not observed with any of our homogeneous systems. The alkane dehydrogenation reaction mixtures do not reduce nitrobenzene under conditions in which a 10 mM synthetic colloid can give detectable quantities of aniline. A colloid might still have been present if it were selectively poisoned for the nitrobenzene reduction by some component of the reaction mixture which did

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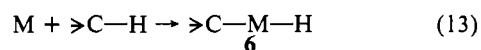
(34) Dunswoth, W. P.; Nord, F. F. *J. Am. Chem. Soc.* **1950**, *72*, 4197.

not affect its alkane dehydrogenation activity. We regard this possibility as remote, however.

Other considerations support the view that the solutions are homogeneous. (1) No bulk metal is ever precipitated from our solutions, whereas iridium organosols are rather unstable and tend to precipitate metal.<sup>35</sup> (2) The reactions are reproducible.

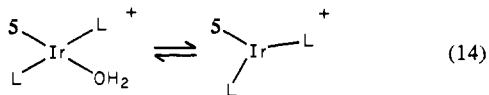
**Reverse Hydrogenation Mechanism.** We propose that the mechanism of the reaction of eq 10 involves an oxidative addition of the alkane CH bond to the metal, followed by successive dehydrogenation steps. This mechanism is the only one that appears to be consistent with all the experimental observations we have reported here and also with the general tenor of the results obtained on this system recently.<sup>19</sup> In particular, it is interesting to find that one of the most active hydrogenation catalysts known turns out also to be active in alkane dehydrogenation, the reverse reaction.

Attempts have often been made in the past to isolate the adduct **6** which is very probably an intermediate in our system.



These attempts have been uniformly unsuccessful probably because **6** is often thermodynamically unstable with respect to the alkane. We have avoided this problem, by choosing a metal system which is capable of giving rise to several successive dehydrogenation steps in the alkane. Eventually a coordinated  $\pi$  ligand is formed (cod or Cp) which is thermodynamically much more stable than the free alkane. The equilibrium of eq 13, perhaps unfavorable, may be overcome by much more favorable subsequent steps. The presence of the hydrogen acceptor further increases the driving force for these steps.

The exact coordination environment of the metal at the moment of oxidative addition to the alkane remains unclear. We know that the *tert*-butylethylene (**5**) relatively rapidly (ca. 10 min) reacts with **1** to strip it of its coordinated H<sub>2</sub>. A white complex has been isolated from these solutions, which may be an intermediate in the alkane dehydrogenation; further work is in progress. As mentioned above, **5** seems to be too bulky to give bis(olefin) complexes. The active intermediate which attacks the alkane might possibly be a Y-shaped 3-coordinate d<sup>8</sup> species:<sup>36</sup>

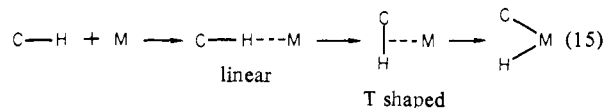


We are currently examining to what extent *tert*-butyl ethylene (**5**) may be a reagent of general utility for stripping hydrogen ligands from metal complexes; others have also used it in this context.<sup>13</sup>

**Cyclometalation.** In 1978 we observed<sup>37</sup> the facile cyclometalation of Ir(PMe<sub>2</sub>Ph)<sub>4</sub><sup>+</sup> at 80 °C. This encouraged us in our search for an alkane activation system, but also suggested that cyclometalation of the ligand might always occur in preference to attack on a free alkane. We embarked on a synthesis of a number of ligands we hoped would be metalation resistant (e.g., 1-phosphaadamantane). All of them suffered from problems, either being too difficult to make or giving complexes that are very insoluble. Fortunately, the cyclometalation problem seems not to have been severe with PPh<sub>3</sub>. This is puzzling: either cyclometalation is reversible, or it does not occur at all. Possibly the bis(phosphine) system is insufficiently bulky to promote cyclometalation; we have certainly never seen evidence for it.

**Electrophilicity of the Metal.** These cationic bis(phosphine)-iridium complexes are unusual in their willingness to add the relatively reducing addenda H<sub>2</sub>, HCl, and the C-H bond of alkanes and in their reluctance to add the more oxidizing addenda, the

CH bonds of CH<sub>3</sub>CN, arenes, CH<sub>2</sub>Cl<sub>2</sub>, and (CH<sub>2</sub>Cl)<sub>2</sub> and the C-halogen bonds of these chlorocarbons, MeI and related compounds. This feature of the iridium system allows us to use such apparently unsuitable solvents as CH<sub>2</sub>Cl<sub>2</sub> and (CH<sub>2</sub>Cl)<sub>2</sub> for our reactions. We have also suggested that the metal in Ir(cod)L<sub>2</sub><sup>+</sup> is reduced, rather than oxidized, in adding H<sub>2</sub> and that the reactivity of the system is enhanced rather than, as might be expected on classical ideas, diminished by the presence of electron-withdrawing ligands. These ideas have been discussed in greater detail elsewhere<sup>38</sup> but they point to a generally electrophilic or Lewis acid tendency in the chemistry of these systems. It seems likely that in activating the CH bonds of alkanes, abstraction of C-H bonding electrons by the metal is more important than the donation of metal nonbonding electrons into the C-H  $\sigma^*$  orbitals. If so, a T-shaped rather than a linear transition state may be involved. The latter arrangement, however, has often been observed in structural studies,<sup>39a</sup> and may be a true intermediate in the re-



action.<sup>39b</sup> These ideas may account for the failure of a variety of nucleophilic metal complex to activate alkanes, and may also help explain why we do not observe metalation of C-Cl bonds in the solvent nor C-H bonds of PPh<sub>3</sub> nor solvent. The use of ligands other than PPh<sub>3</sub> has so far met with preparative difficulties, but further work is in progress.

**Relationship to Metal Surfaces.** Our electrophilic, ligand-deficient, iridium system may provide and analogy with reactions taking place at a metal surface. It is known that certain hydrocarbon reactions, such as C-H bond breaking, occur more easily at steps and kinks than on a flat crystal surface.<sup>40</sup> Much data show that the work function of a metal decreases with increasing step density.<sup>41</sup> A metal atom at a step will therefore be more positive than one on a flat surface, a conclusion in agreement with theoretical studies<sup>42</sup> that suggest that surface atoms, and especially those of low coordination number at steps, are positive by 0.2–0.5 e with respect to the bulk. The high reactivity of metal surfaces may therefore be attributable to the ligand deficiency of the surface atoms, and to some extent to their electrophilicity. Our iridium system seems to exhibit both of these properties.

## Conclusion

We have shown that alkanes can be dehydrogenated by a suitable metal complex to give a coordinated  $\pi$  ligand, and that the reaction proceeds by a reverse-hydrogenation mechanism. Systems operating via this mechanism offer the possibility of much higher selectivity than those that involve radical or carbonium ion intermediates, and we have verified this expectation experimentally.

The use of a ligand-deficient metal allows multiple dehydrogenation steps. The electrophilic character of the metal tends to suppress additions having oxidative character, and so encourages addition of the alkane CH bond and discourages addition of PPh<sub>3</sub>, aryl CH, and solvent CH and CCl bonds. The use of a noncoordinating solvent eliminates competition for active sites with the alkane, itself a very poor ligand indeed. The use of a hydrogen acceptor encourages the reaction; but the hydrogen acceptor must not bind very strongly to the metal, nor must it be subject to

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dehydrogenation itself. A precursor  $[\text{IrH}_2\text{S}_2\text{L}_2]^+$  is used which contains very weakly bound ligands to reduce competition with the alkane to the lowest possible level. We are fortunate that our ligand-deficient species shows little or no tendency to dimerize or polymerize, a reaction which the hydrogen acceptor may well help suppress. A cyclic alkane capable of giving a stable dehydrogenated  $\pi$  complex seems to make the best substrate.

Dehydrogenated hydrocarbons are not released into solution by our system. Further work is in hand to increase its activity and to try to make it catalytic.

### Experimental Section

NMR spectra were recorded at 295 K on a Bruker HX-270 MHz instrument. Gas chromatography was performed on a Varian 920 instrument with a 3 m 5% Carbowax column. Standard Schlenk tube inert atmosphere and vacuum line techniques were used. The paraffins were shaken with concentrated  $\text{H}_2\text{SO}_4$  for 24 h twice, then distilled. Chlorinated solvents were distilled from  $\text{CaH}_2$ .  $\text{Et}_2\text{O}$  and THF were distilled from  $\text{Na}/\text{Ph}_2\text{CO}$ . Alkenes were deperoxidized (alumina column) and cyclooctene was treated five times with 1 M  $\text{AgNO}_3$  to remove traces of cyclooctadienes before distillation. In the alkane activation experiments all the liquid reagents and solvents were also fractionally distilled on a Teflon spinning-band column under  $\text{N}_2$  and stored under  $\text{N}_2$ . All reactions were run under  $\text{N}_2$ .

The complexes were made by published methods<sup>43</sup> and recrystallized before use.

**Dihydridodisolventobis(triphenylphosphine)iridium(III) Tetrafluoroborate.**  $\text{S} = \text{Me}_2\text{CO}; [\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{BF}_4$  (500 mg) was suspended in  $\text{Me}_2\text{CO}$  (10 mL) and hydrogen bubbled gently through the solution at 0 °C for 10 min. The addition of  $\text{Et}_2\text{O}$  (25 mL) precipitated a beige or yellow product. Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  gives a product identical with the authentic<sup>44</sup> material. Anal. Calcd for  $\text{C}_{42}\text{H}_{44}\text{O}_2\text{P}_2\text{F}_4\text{B}\text{Ir}\cdot\text{CH}_2\text{Cl}_2$ : C, 51.30; H, 4.60. Found: C, 51.25, H, 4.65.  $\text{S} = \text{H}_2\text{O}; [\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{BF}_4$  (500 mg) was suspended in (50 mL) of water and  $\text{H}_2$  bubbled gently through the solution until the red starting material gave way to a beige or light-yellow suspension (30 min, 20 °C). The product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the complex. NMR is reported as position ( $\delta$ ), multiplicity ( $s$  = singlet,  $d$  = doublet,  $c$  = complex) (coupling constant Hz), assignment: -29.8,  $t$  (16), IrH; 2.4,  $c$ ,  $\text{H}_2\text{O}$ ; 7.1-7.4,  $c$ , Ph. Anal. Calcd for  $\text{C}_{36}\text{H}_{36}\text{P}_2\text{F}_4\text{BO}_2\text{Ir}\cdot\text{CH}_2\text{Cl}_2$ : C, 47.96, H 4.13. Found: C, 47.70, H, 4.13.

The deuteriated analogues  $[\text{IrD}_2\text{S}_2\text{L}_2]\text{BF}_4$  were made in an analogous way from  $\text{D}_2$ .

**The Reaction of Alkenes with Dihydridobissolvato(triphenylphosphine)iridium(I) Tetrafluoroborate.** To a solution of  $\text{CH}_2\text{Cl}_2$  (30 mL) and alkene (2 mL) was added  $[\text{IrH}_2\text{S}_2\text{L}_2]\text{BF}_4$  (**1a**;  $\text{S} = \text{Me}_2\text{CO}$ ;  $\text{L} = \text{PPh}_3$ ; 200 mg). The mixture was refluxed for 4 h during which time the solution turned from colorless to the color of the product. The cooled solution was reduced to 5 mL in vacuo and  $\text{Et}_2\text{O}$  slowly added until a solid had precipitated. Recrystallization ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ) gave an analytically pure product. The products in each case together with the yield,  $^1\text{H}$  NMR spectrum, and analytical data were as follows.

From cyclopentene (or cyclopentadiene),  $[\text{IrCpH}(\text{PPh}_3)_2]\text{BF}_4$ , 83%, colorless crystals. NMR ( $\text{CDCl}_3$ ) -14.8,  $t$  (26), IrH; 5.2,  $s$ , Cp; 7.1-7.4,  $c$ , Ph. Anal. Calcd for  $\text{C}_{41}\text{H}_{36}\text{P}_2\text{F}_4\text{B}\text{Ir}$ : C, 56.62; H, 4.14. Found: C, 56.85; H, 4.61.

From cyclohexene (or 1,3- or 1,4-cyclohexadiene, but not benzene),  $[\text{Ir}(\eta^5\text{-C}_6\text{H}_7)\text{H}(\text{PPh}_3)_2]\text{BF}_4$ , 80%, colorless crystals. NMR ( $\text{CDCl}_3$ , 25 °C) -17.5,  $t$  (19, IrH; 1.45, broad,  $\text{CH}_2$ ; 2.2, 3.6, 4.0, 5.2, broad, CH. Anal. Calcd for  $\text{C}_{42}\text{H}_{38}\text{P}_2\text{F}_4\text{B}\text{Ir}\cdot 1/2\text{CH}_2\text{Cl}_2$ : C, 55.14; H, 4.25. Found: C, 54.83; H, 4.43.

From cycloheptene,  $[\text{Ir}(\eta^5\text{-C}_7\text{H}_9)\text{H}(\text{PPh}_3)_2]\text{BF}_4$ , 74%, colorless crystals. NMR ( $\text{CDCl}_3$ , 25 °C) -15.2,  $t$  (21), IrH; 1.2 and 1.5,  $c$ ,  $\text{CH}_2$  (exo and endo); 4.9, 5.1, and 5.6,  $c$ , CH; 7.1-7.4,  $c$ , Ph. Anal. Calcd for  $\text{C}_{43}\text{H}_{40}\text{P}_2\text{F}_4\text{B}\text{Ir}$ : C, 57.53; H, 4.46. Found: C, 57.92; H, 4.83.

From cyclooctene (or 1,5-cyclooctadiene),  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{BF}_4$ , 90%, red crystals. NMR ( $\text{CDCl}_3$ , 25 °C) 1.8 and 2.2,  $c$ ,  $\text{CH}_2$  (exo and endo); 4.2,  $c$ , CH; 7.1-7.4,  $c$ , Ph. Anal. Calcd for  $\text{C}_{44}\text{H}_{42}\text{P}_2\text{F}_4\text{B}\text{Ir}$ : C, 57.96; H, 4.61. Found: C, 58.12; H, 4.73.

From [2.2.2]bicyclooctene,  $[\text{Ir}(\text{C}_8\text{H}_{10})(\text{PPh}_3)_2]\text{BF}_4$ , 78%, red-brown crystals. NMR ( $\text{CDCl}_3$ , 25 °C) 1.0,  $c$ , CH; 3.7,  $c$ , CH vinyl; 4.6,  $c$ ,  $\text{CH}_2$ . Anal. Calcd for  $\text{C}_{44}\text{H}_{40}\text{P}_2\text{F}_4\text{B}\text{Ir}$ : C, 58.09; H, 4.40. Found: C, 57.85; H, 4.24.

From styrene,  $[\text{Ir}(\eta^6\text{-PhEt})(\text{PPh}_3)_2]\text{BF}_4$ , 94%, orange crystals. NMR ( $\text{CDCl}_3$ , 25 °C) 1.2,  $t$  (7),  $\text{CH}_3$ ; 2.6,  $q$  (7),  $\text{CH}_2$  4.9,  $d$  (5),  $\alpha\text{-CH}$ ; 5.4,  $dd$

(5, 7),  $m\text{-CH}$ ; 7.1  $t$ , (7),  $p\text{-CH}$ . Anal. Calcd for  $\text{C}_{44}\text{H}_{40}\text{F}_4\text{BP}_2\text{Ir}$ : C, 58.12; H, 4.45. Found: C, 58.57; H, 4.56. This complex was most conveniently isolated by removal of the volatiles after 10 min of reaction at 25 °C. The complex crystallizes in a pure state from the residual styrene but can also be crystallized from  $\text{CH}_2\text{Cl}_2/\text{hexane}$ . The NMR assignments were confirmed by decoupling studies.

**The Reactions of Alkanes with Dihydridobissolvato(triphenylphosphine)iridium(I) Fluoroborate.** To a solution of  $[\text{IrH}_2(\text{Me}_2\text{CO})(\text{PPh}_3)_2]\text{BF}_4$  (200 mg) in 1,2-dichloroethane (30 mL) was added cyclopentane (5 mL) and 3,3-dimethyl-1-butene (80  $\mu\text{L}$ ). The refluxing solution turned from very pale yellow to orange-brown after 18 h, and the volatiles were removed in vacuo. Hot methanol (5 mL, 40 °C) was added and on cooling the white complex  $[\text{IrCpH}(\text{PPh}_3)_2]\text{BF}_4$  was isolated (61 mg, 32%). Anal. Found: C, 56.94, H, 4.34. The complex was identical with that isolated from cyclopentene.

Cyclooctane gave a red solution under identical conditions, from which  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{BF}_4$  was isolated as above (90 mg, 47%). The complex was identical with the material prepared from cyclooctene. Anal. Found: C, 57.74; H, 4.43. The identity of the complex was confirmed by reaction with excess HCl introduced into the NMR sample. The characteristic resonances<sup>38</sup> of the product  $[\text{Ir}(\text{cod})\text{HCl}_2(\text{PPh}_3)]$  were observed.

Cycloheptane gave an orange-brown solution in which  $[\text{Ir}(\eta^5\text{-cycloheptatrienyl})\text{H}(\text{PPh}_3)_2]\text{BF}_4$  could be detected (NMR). This complex decomposes slowly under the reaction conditions so that the yield after 12 h (12%) fell to zero after 24 h.

Cyclohexane does not give any characterizable products, but since the expected cyclohexadienyl complex decomposes to unidentified products under the reaction conditions, this result is not surprising.

[2.2.2]Bicyclooctane gives as yet unidentified products, and not the bicyclooctene complex obtained above.

Similar results were obtained in each case with the aquo complex ( $\text{S} = \text{H}_2\text{O}$ ).

**Analysis of the Volatile Components.** The volatile fractions in the alkane dehydrogenation reactions were analyzed by GC. In each case, the only product deriving from the hydrogen acceptor was 3,3-dimethyl-1-butane. No 2,3-dimethylbutanes or -butenes were observed.

In the dehydrogenations or attempted dehydrogenations of these alkanes, no dehydrogenated product was detected in the volatiles. For example, no cyclopentene nor cyclopentadiene was formed from cyclopentane, no benzene or cyclohexene from cyclohexane, no cycloheptene from cycloheptane, and no cyclooctene, cyclooctadiene, or cyclooctatetrene from cyclooctane.

In a further set of GC experiments, but only in the case of the cyclopentane dehydrogenation, a careful search was made for cyclopentyl chloride and dicyclopentyl, which would derive from cyclopentyl radical. No trace of these compounds was detected.

**The Hydrogen Acceptor.** The following alkenes failed to act as hydrogen acceptors, no cyclopentane dehydrogenation being observed: 2,3-dimethyl-2-butene, di-*tert*-butylethylene (cis and trans), styrene, 2,6-dichlorostyrene, stilbene, tetraphenylethylene, 1,1-diphenylethylene, vinyltrimethylsilane, and vinyl-*o*-carborane. The following hydrogen acceptors gave a trace of dehydrogenation, although this was less than would have been observed (7%) in the absence of hydrogen acceptor: ethylene (<1%), 2,6-dimethylstyrene (3%).

A *tert*-butylethylene/Ir molar ratio of 4 proved to give the highest yields of cyclopentadienyl complex. When this ratio was zero, the yield fell to 7% (measured by  $^1\text{H}$  NMR on the reaction mixtures); at a ratio of 4 the NMR yield was 40% (32% isolated). At a ratio of 8, the yield fell to 30% (5% isolated). The other hydrogen acceptors were therefore all assayed using an acceptor/Ir ratio of 4. NMR yields were measured by cutting out and weighing the tracings of the appropriate resonances.

**Other Studies.** The dehydrogenation reactions fail completely in air (1 atm). Other solvents have not proved successful, for example, EtOAc gives a mixture of products that appear to contain coordinated acetato groups. Even in our hydrogenation studies, the choice of solvent was critical.<sup>19</sup> In alkane activation, this restriction seems to apply with even greater force. counterion effects were found: the hexafluorophosphate salt of **1** gave only about one third the yield of alkane dehydrogenation products than does the tetrafluoroborate.

UV irradiation of the reaction mixtures (25 °C, 360 nm Blak-Ray B 100A lamp) gave no alkane dehydrogenation; thermal reactions in the dark gave lower alkane dehydrogenation yields than under normal laboratory illumination (fluorescent tube). Further studies are in progress.

**Colloid Studies.** In the dynamic light-scattering experiment, the beam from an argon ion laser (Lexel model 95, 488 nm., 500 mW) is focused into a 5-mm diameter NMR tube, containing the sample (1 mL), positioned in a Malvern RR102 spectrometer. Light scattered 90° to the incident beam and normal to the long axis of the tube is detected by a photomultiplier tube and analyzed using a Malvern 7025 128-channel Autocorrelator. The dwell time per channel could be varied from 0.1 to

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100  $\mu$ s. The relaxation time for the decay of the autocorrelation function was measured and the corresponding translational diffusion constant calculated.<sup>29</sup> This, in turn, was related to the radius of the scattering particles by Stokes law.

A synthetic Ir colloid was prepared as described below. With a channel time of 3  $\mu$ s, this colloid gave a translational diffusion constant of  $8.58 \times 10^{-8}$  cm<sup>2</sup>/s, corresponding to a Stokes Radius of 250 Å. The preparation was diluted 10<sup>4</sup>-fold and still gave a readily detectable signal. Dilution a further 10<sup>4</sup>-fold led to the loss of signal. This allowed us to assign an approximate detection limit of 1 nM to the method.

The cooled alkane dehydrogenation solutions, in contrast, gave a completely flat autocorrelation function over the whole instrumental channel time range, implying that within the detection limits of the method, no particles were present. Further work is in progress on developing this technique as a general method for the detection of particulates in catalyst preparations.

**Preparation of the Iridium Colloid.** This preparation is a variant of that described by Dunsworth and Nord.<sup>34</sup> To an aqueous solution of poly(vinyl alcohol) (2 g of PVA in 90 mL of H<sub>2</sub>O) was added 10 mL of a solution of (NH<sub>4</sub>)<sub>2</sub>IrCl<sub>6</sub> (40% Ir, 90 mg, 0.28 mmol) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (25 mg, 0.5 mmol). The mixture was heated on a steam bath for 15 min, during which time it became gray-yellow. The cooled mixture was adjusted to pH 7 with 10% acetic acid and water added to make the whole up to 100 mL. Stable colloids could not be obtained without PVA, but the latter made very little contribution to the light scattering.

The synthetic colloids were completely clear to the eye, but the Tyndall effect light scattering could be easily seen at the focus of a small lens (2-cm diameter, 10-cm focal length) in bright sunlight.

We successfully repeated Dunsworth and Nord's<sup>34</sup> work on the reduction of nitrobenzene to aniline by the iridium colloid. Thirty cubic centimeters of H<sub>2</sub> (1 atm, 25 °C) was absorbed per minute. To the cooled alkane dehydrogenation reaction mixture in its original flask was

added nitrobenzene (1 mL) under H<sub>2</sub> (1 atm, 25 °C), and the mixture was stirred for 4 days. No trace of aniline was detected (GC), nor was metal precipitated.

The presence of bulk metal was eliminated as follows. The reaction mixtures were passed through a micropore filter, the flask washed with CH<sub>2</sub>Cl<sub>2</sub> (5 × 5 mL), and the washings filtered. The micropore filter did not show traces of bulk metal (Zeiss microscope, 100 × magnification), nor did the filter catalyze cyclohexene hydrogenation (1 atm, 25 °C, 3 days, detection by GC) when returned to the original flask. This is a variant of the Maitlis<sup>27</sup> method.

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**Registry No.** 1a, 72414-17-6; 1b, 79792-57-7; 2, L = PPh<sub>3</sub>, 38834-40-1; 3, L = PPh<sub>3</sub>, 79792-58-8; 4, 79792-60-2; 5, 558-37-2; [Ir( $\eta^5$ -C<sub>6</sub>H<sub>7</sub>)H(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, 79792-62-4; [Ir( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)H(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, 79792-64-6; [Ir(C<sub>8</sub>H<sub>10</sub>)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, 79792-66-8; [Ir( $\eta^5$ -cycloheptatrienyl)H(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, 79792-68-0; cyclopentene, 142-29-0; cyclopentadiene, 542-92-7; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; 1,5-cyclooctadiene, 111-78-4; [2.2.2]bicyclooctene, 931-64-6; styrene, 100-42-5; cyclopentane, 287-92-3; cyclooctane, 292-64-8; cycloheptane, 291-64-5.

## A Second-Order Jahn–Teller Effect in a Tetranuclear Metal Atom Cluster Compound

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**Abstract:** The bonding in the type of compound exemplified by W<sub>4</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>16</sub> (Chisholm et al., 1981) has been examined using Fenske–Hall calculations. It is shown that the low-symmetry (C<sub>1</sub>) structure of this molecule can be understood as the result of a second-order Jahn–Teller distortion of a more regular (C<sub>2h</sub>) structure; the more regular structure would require two more electrons, which would then permit the formation of the entire set of five metal–metal single bonds. Loss of two electrons from such a structure is shown to lead uniquely to the type of distortion observed and the calculations suggest that the molecule is stabilized by ca. 0.5 eV as a result of the distortion. It is noted that the analysis developed here applies directly to the newly reported compound Ba<sub>1,13</sub>Mo<sub>8</sub>O<sub>16</sub> which contains both nearly undistorted (C<sub>2h</sub>) and strongly distorted (C<sub>1</sub>) Mo<sub>4</sub> clusters.

Compounds containing triangular trinuclear metal atom clusters are being discovered and or recognized at a great rate these days<sup>1-3</sup> and the importance of these, especially among the early transition metals, is receiving increasing recognition.<sup>3</sup> One of the important structure types is that shown in Figure 1a, in which there is a capping nonmetal atom ( $\mu_3$ -X) on one side of the plane of the M<sub>3</sub> triangle and three edge-bridging nonmetal atoms ( $\mu$ -X) on the other side. In addition, there are three terminal (i.e., nonbridging) nonmetal atoms (X) also attached to each metal atom, completing a distorted MX<sub>6</sub> octahedron. This unit has the composition M<sub>3</sub>X<sub>13</sub>. It is known in the solid state context, where many of the X atoms

are shared between units, as well as in discrete molecular compounds. It is probably the structure of the aquo molybdenum(IV) species. The structure can be obtained simply by joining three MX<sub>6</sub> octahedra so that there is one vertex (the  $\mu_3$ -X or capping atom) common to all of them and three shared edges, all meeting at this unique vertex. This arrangement of fused octahedra constitutes one quarter of the Keggin structure found for a number of isopoly acids. It becomes a metal cluster structure when the metal atoms are drawn together by the formation of M–M bonds. In various cases the X atoms have been found to be O, S, F, Cl, or others and they need not all be the same in one molecule. Molecular orbital considerations, either simple<sup>5</sup> or more sophisticated,<sup>6</sup> suggest that this structure should be stable with three M–M bonds of formal order one when the cluster has 6 electrons

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