d also show appreciable methyl loss, despite the H rearrangement required to form $^\bullet CH_3$ from either. As expected, the largest differences are the favored formation of $C_2H_3^\bullet + C_2H^\bullet$ from **a** ($\Delta H_f^\circ = 830$ kJ mol^{-1})[8] and $2C_2H_2$ from **d**.

Neutralization Agent of IE = 6 eV. These conclusions (Figure 1) are also supported by preliminary experiments with neutralization agents that should produce C_4H_4 neutrals somewhat less excited than those produced by Na. Neutralization of $\mathbf{a}^{\bullet+}$ and $\mathbf{d}^{\bullet+}$ by triphenylamine (IE = 6.8 eV)[8] and by Hg (10.4 eV), followed by He(70% T) cationization, gave essentially the same spectra, indicating that the **a** and **d** neutrals, formed with ~160 kJ mol^{-1} (6.8 − 5.1 eV) less internal energy than that of neutrals formed with Na, indeed have energies below their dissociation barriers. However, neutralization with tetra-*p*-anisylethylene (IE = 6 eV)[20] causes the dissociation of 26% of **a** and 49% of **d**. With internal energies ~90 kJ mol^{-1} less than those from Na neutralization, the indicated product abundances (±10%) from **a** and **d**, respectively, are $C_4H_3^\bullet$, 27% and 10%; C_4H_2, 33% and 19%; C_4H, 1% and 2%; C_3H, 20% and 11%; and C_2H_2, 19% and 58%. These values are surprisingly similar to those from CAD (30% T) above.

Conclusions

The substantial differences found for $^+$NR spectra of four $C_4H_4^{\bullet+}$ isomers show not only that the cyclic cations are surprisingly stable, but that all four isomers can be characterized successfully by two independent methods. Although sodium neutralization to form unstable C_4H_4 neutrals, a method of choice for the analogous $C_4H_8^{\bullet+}$ study,[6c] produces very extensive isomerization, use of a neutralization agent of optimal ionization energy (~6 eV) also yields characteristic NR spectra for **a** and **d**. The neutralization–reionization technique with dissociation of the neutrals can also provide unique information concerning the stabilities and unimolecular reactivities of such neutral, as well as ionic, isomers. This is of special value for highly reactive species such as **c** and **d**. For example, very recent photoelectron IP measurements point to $\mathbf{c}^{\bullet+}$ as the lowest energy *cyclic* $C_4H_4^{\bullet+}$ isomer;[11f] its dominant formation from benzene$^{\bullet+}$ shown here indicates it is the lowest energy form of all $C_4H_4^{\bullet+}$ isomers, consistent with the order of ΔH_f° values of Table I.

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Registry No. $\mathbf{a}^{\bullet+}$, 59699-48-8; $\mathbf{b}^{\bullet+}$, 65513-85-1; $\mathbf{c}^{\bullet+}$, 79105-72-9; $\mathbf{d}^{\bullet+}$, 34531-09-4.

Solid-State Chemistry of Molecular Metal Oxide Clusters. Multiple, Sequential C–H Activation Processes in the Hydrogenation of Coordinated Cyclooctene. Lattice Mobility of Small Organic Molecules

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Abstract: Reaction of solid $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ with D_2 gas produces cyclooctane containing up to 16 deuterium atoms. The c-$C_8D_nH_{16-n}$ isotopomer distribution is analyzed by Poisson statistics and interpreted in terms of C–H activation involving Ir-*D*–C-*H* exchange in an intermediate species containing coordinated cyclooctene. The results are compared with those from D_2 reduction of $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ in the solid state and in acetone solution, in which cases, an additional exchange process operates. Solid-state ^{2}H NMR shows that, even at low temperatures, small organic molecules such as cyclooctane and benzene undergo nearly isotropic motion.

While homogeneous organometallic chemistry is obviously a large, well-developed and well-appreciated area of science and technology, molecular level understanding of heterogeneous processes is less advanced.[1] We are interested in developing new solid-state organometallic chemistry based on highly reactive, cationic species held in matrices comprised of anionic molecular metal oxide clusters, here exemplified by the polyoxometalate $PW_{12}O_{40}^{3-}$.[2,3] This paper describes a quite unanticipated process resulting in multiple, sequential, Ir-*D*–C-*H* exchange reactions that occur as cyclooctadiene coordinated to iridium in $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ is hydrogenated. Analogous C–H exchange occurs with $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ both in the solid state and in solution, but analysis of the products shows that, in contrast, *two* different processes are involved. Finally, we use wide-line NMR spectroscopy to demonstrate mobility of small organic molecules in materials derived from metal oxide clusters.

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[2] (a) Siedle, A. R. U.S. Patent 4,673,753, 1987. (b) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 1987. (c) Siedle, A. R.; Lyon, P. A.; Hunt, S. L.; Skarjune, R. P. *J. Am. Chem. Soc.* **1986**, *108*, 6430.

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[4] Vrieze, K. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic: New York, 1975; p 454.

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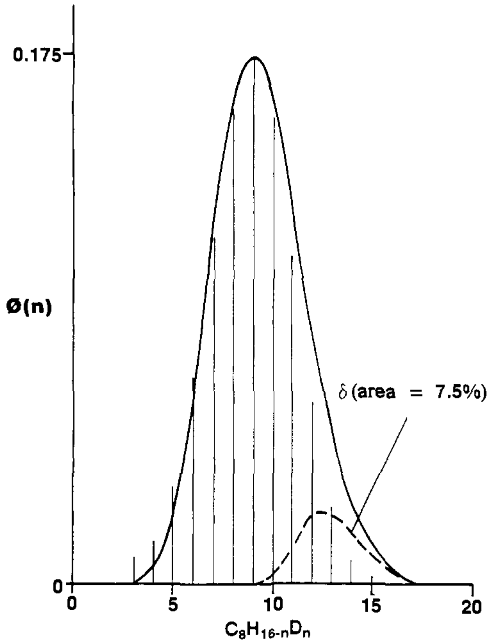


Figure 1. Distribution of c-$C_8D_nH_{16-n}$ isotopomers obtained from the reaction of D_2 with solid $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$.

C-H Activation Chemistry

It has been previously demonstrated that reaction of solid $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ (**1**) (C_8H_{12} is 1,5-cyclooctadiene) with dihydrogen (400-mm pressure, 40-min reaction time, 25 °C) produces $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ (**2**) and cyclooctane, eq 1.[3] The reaction parallels the reduction of $[(Ph_3P)_2Ir(C_8H_{12})][BF_4]$ in acetone, which leads to the solvate $[(Ph_3P)_2IrH_2((CH_3)_2CO)_2][BF_4]$, eq 2.[5]

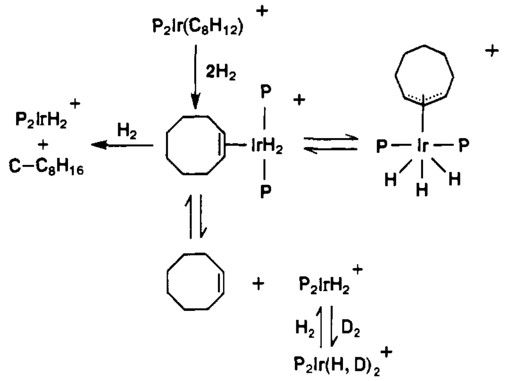
$$[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40} + 9H_2 \rightarrow [(Ph_3P)_2IrH_2]_3PW_{12}O_{40} + 3c\text{-}C_8H_{16} \quad (1)$$

$$[(Ph_3P)_2Ir(C_8H_{12})][BF_4] + 3H_2 + 2(CH_3)_2CO \rightarrow [(Ph_3P)_2IrH_2((CH_3)_2CO)_2][BF_4] + c\text{-}C_8H_{16} \quad (2)$$

In the heterogeneous reduction, no extraneous solvent molecules are available to enter the iridium coordination core. EXAFS studies on the molybdenum analogue of **2** demonstrate the absence of Mo–Ir separations of ≤4 Å, for which reason **2** is considered to contain interstitial, four-coordinate $(Ph_3P)_2IrH_2^+$ ions. The compound $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ crystallizes with about 0.9 molecule of acetone/formula weight. Most of the acetone is retained after conversion to $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$; the infrared spectra of **1** and **2** show a CO stretching band at 1708 cm^{-1} characteristic of zeolitic or lattice, rather than an η^1-acetone coordination complex.[5,7]

One would expect, on the basis of eq 1, that an analogous reaction of $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ with D_2 would yield $[(Ph_3P)_2IrD_2]_3PW_{12}O_{40}$ and c-$C_8D_4H_{12}$, but such is not the case. Analysis by resolution-enhanced ^{31}P NMR spectroscopy of the D_2 reduction product after it had been dissolved in DMF-d_7, thus converting the iridium cations into the solvates $(Ph_3P)_2Ir(H,D)_2(DMF)_2^+$, revealed that it is a mixture of isotopomers containing 46% $(Ph_3P)_2IrH_2(DMF)_2^+$, 44% $(Ph_3P)_2IrHD(DMF)_2^+$, and 10% $(Ph_3P)_2IrD_2(DMF)_2^+$. This ratio is unaffected by deliberate addition of water to the solution, and so the analysis is unaffected by adventitious moisture in the solvent. **1** also contains small amounts of zeolitic or lattice acetone, about 0.3 molecule/Ir; the acetone is introduced by the solvent in which **1** was prepared.

Scheme I



The entire reaction was repeated beginning with synthesis of **1** in acetone-d_6, but the relative amounts of the three isotopomers were unchanged. Thus, lattice acetone cannot be the source of the large amounts of Ir-*H*. This led logically to the hypothesis that the unexplained Ir-*H* might be derived from the cyclooctadiene, and so it is. Further study of this reaction has uncovered an unusual set of C-*H*–Ir-*D* exchange reactions.

Reduction of $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ with D_2 (400-mm pressure, 400-min reaction time, 65 °C) produces deuterated cyclooctanes, c-$C_8D_nH_{16-n}$, containing up to 16 deuterium atoms. Figure 1 shows the relative abundances of these isotopomers as determined by electron impact mass spectrometry. Each species has been identified by high-resolution mass spectroscopy. Careful control experiments established that the related deuterated hydrocarbon c-C_6D_{12} yields no hydrogen-containing ions whose intensity is a function of time. Thus, retroexchange with adventitious proton-containing species on the walls of the mass spectrometer does not occur to a detectable extent. More importantly, synthetic mixtures of c-C_6D_{12} and c-C_8H_{12} yielded no detectable c-$C_6D_nH_{12-n}^+$ or c-$C_8D_nH_{16-n}^+$ ions. Therefore, the analysis of isotopomer distributions is not distorted by intermolecular scrambling of the deuterium label in the mass spectrometer. Reactions carried out at 25 °C yield essentially the same result as that shown in Figure 1.

Scheme I, in which, for clarity, only events occurring at the cationic iridium center are depicted, represents one possible sequence of events that accounts for formation of all these deuterated cyclooctanes. We view the first two steps as being comprised of addition of two molecules of D_2 to $(Ph_3P)_2Ir(C_8H_{12})^+$ to give $(Ph_3P)_2IrD_2(C_8D_2H_{12})^+$, which contains reversibly coordinated cyclooctene-d_2. Cyclooctene contains four allylic hydrogen atoms, and, in the next, reversible step, transfer of one of them to iridium leads to $(Ph_3P)_2Ir(H,D)_3[(C_8(H,D)_{13})]^+$. This η^3-cyclooctenyl species is of crucial importance because its reversible formation results in C-*H*–Ir-*H* scrambling. Repetition of the addition–elimination process permutes *all* C-*H* and Ir-*H* hydrogen atoms. This is confined to one side of the ring, but syn–anti rearrangements that allow the metal to visit both sides of this ring are known to be facile in solution.[4] An analogous addition reaction between $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ and propylene has previously been shown to lead to the η^3-allyl derivative $[(Ph_3P)_2IrH(C_3H_5)]_3PW_{12}O_{40}$, which further reacts with hydrogen to form propane and $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$.[5] Continuing with Scheme I, dissociation of cyclooctene from $(Ph_3P)_2IrH_2(C_8H_{14})^+$ produces $(Ph_3P)_2IrH_2^+$, which, independently, exchanges Ir–*H* with D_2. This step introduces more deuterium into the cycle. We propose that, next, addition of an additional molecule of dideuterium to $(Ph_3P)_2Ir(H,D)_2[C_8(H,D)_{14}]^+$ results in hydrogenation of the remaining C=C bond in the coordinated cyclooctene to produce $C_8D_nH_{16-n}$ and lattice-stabilized $(Ph_3P)_2Ir(H,D)_2^+$. Precedent for the sequence thus far comes from detailed studies of the homogeneous catalytic hydrogenation of olefins by $(Ph_3P)_2IrH_2(solvent)_2^+$[6] and from a control experiment that shows the Ir-*H* protons in related $[(Ph_3P)_2Ir(H)(C_3H_5)]_3PW_{12}O_{40}$ do not exchange with D_2. Independent of mechanistic details, the reaction of D_2 with $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ exhibits two experimentally and

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[5] Siedle, A. R.; Newmark, R. A.; Brown-Wensley, K. A.; Haddad, L. C.; Skarjune, R. P.; Hodgson, K. O.; Roe, A. L. *Organometallics* **1988**, *7*, 2078.

[6] Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025, and references cited therein.

[7] Huang, Y.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298.

kinetically distinguishable steps: (1) exchange of Ir-*H* hydrogen atoms with C-*H* and (2) hydrogenation of the remaining double bond and ejection from the exchange cycle of the C_8 moiety as kinetically inert cyclooctane. The rates of these two processes are represented below as k_x and k_o, respectively. Cyclooctane is considered to be inert because control experiments show that, at room temperature, the exchange between $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ and c-C_6D_{12} is undetectably slow.

The abundances of the c-$C_8D_nH_{16-n}$ species produced, $\phi(n)$, normalized so that the sum of the parent ion intensities is unity, are plotted versus *n* in Figure 1 and shown as vertical bars. The solid line connects points representing the abundance of each species calculated from a Poisson distribution

$$\phi(n) = (\lambda^m \exp(-\lambda))/m! \qquad (3)$$

where *n* is the total number of deuterium atoms introduced in the exchange process; λ is the central tendency of the distribution, i.e.

$$\lambda = k_x/(k_x + k_o)$$

$\phi(n)$ is the (normalized) probability for a particular value of *n*; and $m = n - c$, where *c* is a constant indicative of the number of deuterium atoms incorporated into the cyclooctane product by a nonstochastic process. It is expected to be an even integer.[8] Inspection of Figure 1 shows that the data are well fit by eq 3. $\lambda = 5.4$ with $c = 4$, implying that, on average, 5.4 C-*H*-Ir-*H* exchange events occur in the cyclooctene ring before the double bond in it is reduced to form a deuterated cyclooctane. The value of the constant, $c = 4$, accommodates the two deuterium atoms incorporated in the initial formation of $[(Ph_3P)_2IrD_2(C_8D_2H_{12})]^+$ (vide supra) and the two deuterium atoms incorporated in the final reduction of the C_8 ring to form cyclooctane. The agreement indices for calculated and observed $C_8D_nH_{16-n}$ distributions are as follows: χ^2, from the χ^2 distribution; α, the "risk" or probability that the experimental curve is broader or narrower than that calculated (ideally 0.50); *r*, the correlation coefficient for the regression calculated (eq 3) on the experimental $\phi(n)$ for $n - 1$ variables.[8] With $\lambda = 5.4$, $\chi^2 = 11.35$ (ideally 12.0), $\alpha = 0.50$, and $r^2 = 0.974$. Because reduction of the two double bonds in coordinated C_8H_{12} introduces four deuterium atoms and the C-*H*-Ir-*H* exchange introduces, on average, 5.4 more, the curve in Figure 1 should and does peak near $C_8D_9H_7$. There is no systematic enhancement for species in which *n* is either odd or even, suggesting that deuterium atoms are introduced one at a time. There is a systematic deficiency of $C_8D_nH_{16-n}$ species having high (>10) values of *n*, and the total shortfall corresponds to 7.5% of total species abundance. We suggest that this may be due to a negative isotope effect and thus that Ir–H bond stretching contributes more to reaching the transition state than C–H stretching. If this indeed represents a kinetic isotope effect, it is considerably smaller than $k_H/k_D = 1.4$ observed for C–H bond insertion in coordinated arenes in $(Me_5C_5)Rh(PMe_3)(arene)$.[9]

Heterogeneous reduction of $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ differs from that of **1** in that, in addition to cyclooctane, *bi*nuclear $[(Ph_3P)_4Ir_2H_5][PF_6]$ is produced[10], and so comparison with $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ is of interest. Figure 2 shows the normalized abundances of c-$C_8D_nH_{16-n}$ species formed when $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ was treated with 400-mm pressure of deuterium at 25 °C. Again, species containing up to at least 15 deuteriums are obtained, but their distribution is quite different from that produced by the molecular metal oxide cluster derivative $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$. Analysis of the isotopomer distribution by use of Poisson statistics reveals that *two* distribution functions are required to fit the experimental curve. The one that accounts for the majority (80%) of the deuterated cyclooctanes and has a maximum at c-$C_8D_7H_9$, ϕ_1, has $\lambda = 3.6$ with $c = 4$. However, a second Poisson distribution, ϕ_2, with $\lambda = 2.5$ and $c = 2$, peaking at c-$C_8D_4H_{12}$, is evident. ϕ_1 and ϕ_2 are shown in Figure 2. The weighted sum of these two curves satisfactorily accounts for the isotopomer distribution; agreement indices for $[0.8\phi_1 + 0.14\phi_2]$ are $\chi^2 = 11.53$ (ideally 11.0), $\alpha = 0.45$, and $r^2 = 0.997$.

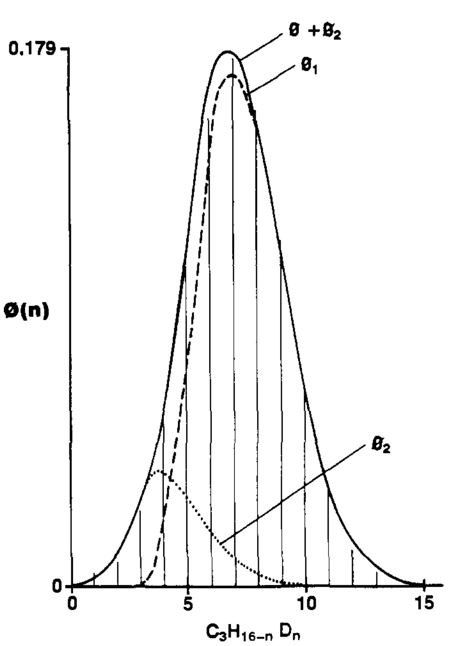

Figure 2. Distribution of c-$C_8D_nH_{16-n}$ isotopomers obtained from the reaction of D_2 with solid $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$.

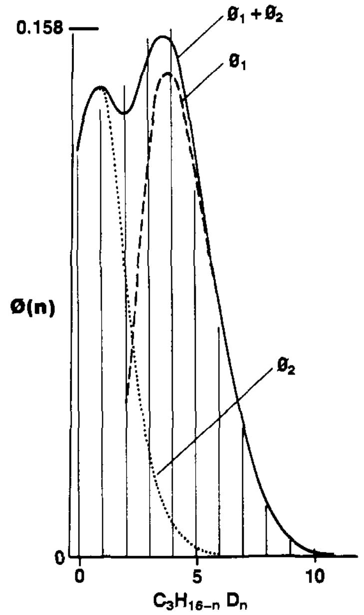

Figure 3. Distribution of c-$C_8D_nH_{16-n}$ isotopomers obtained from the reaction of D_2 with $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ in acetone.

Multiply deuterated cyclooctanes are also formed when $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ in acetone solution is reduced with D_2; cf. eq 2. The isotopomer distribution, shown in Figure 3, is again explicable in terms of two distributions or curves. ϕ_2 peaks at c-C_8DH_{15} and has $\lambda = 1.2$ with $c = 0$ while ϕ_1, peaking at c-$C_8D_4H_{12}$, has $\lambda = 2.5$ with $c = 2$. Agreement indices are as follows: $\chi_2 = 9.79$ (ideally 10.0), $\alpha = 0.47$, and $r^2 = 0.989$. Existence of a process having $c = 0$ implies formation of c-C_8H_{16}, that is, cyclooctane containing *no* deuterium. Earlier, we showed that $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ undergoes slow exchange of the Ir-*H* protons with D_2.[3] Thus, for example, in the reduction of **1**, when the reaction time is increased to 16 h and the D_2 pressure to 650

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[8] Bartsch, H.-J. *Handbook of Mathematical Formulas*; Academic: New York, 1970; p 470.

[9] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

[10] (a) Crabtree, R. H.; Felkin, H.; Morris, G. E.; King, T. J.; Richards, J. A. *J. Organomet. Chem.* **1976**, *113*, C7. (b) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

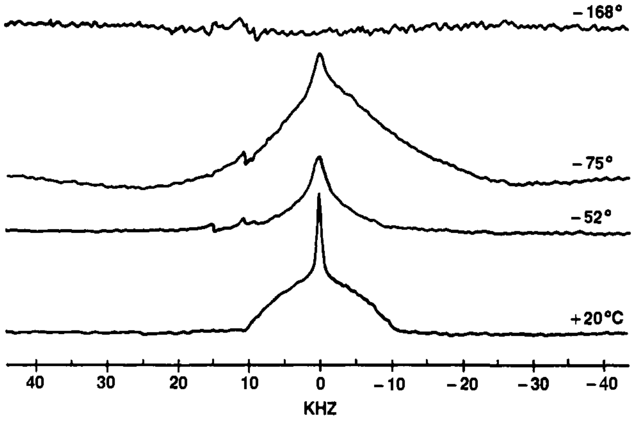

Figure 4. Variable-temperature solid-state ^2H NMR spectrum of c-$C_8D_nH_{16-n}$ in $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$.

mm, the $(Ph_3P)_2IrH_2(DMF)_2^+$:$(Ph_3P)_2IrHD(DMF)_2^+$:$(Ph_3P)_2IrD_2(DMF)_2^+$ ratio changes to 21:40:39. This exchange reaction would logically be expected to release H_2. We suggest that in the closed systems employed here (cf. Experimental Section) this exchange reaction produces H_2, which subsequently gives rise to c-C_8H_{16}.

The data show distinct differences in the reduction of $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ and $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$. This is presaged by the tendency of the seemingly analogous PF_6^- salt to give binuclear iridium species on reaction whereas this is not observed in the oxide cluster analogue. We surmise that the two-component isotopomer distributions for deuterated cyclooctanes produced from reduction of $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$, either in the solid state or in solution, reflect the operation of two distinct chemical processes, only one of which is significant for $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$. The mechanism of the second reaction leading to C-*H* is not known, but we suggest that it may involve an α-elimination process, here in a (σ-cyclooctenyl)iridium intermediate, which is analogous to that recently eludicated by several groups.[11-13] We consider it unlikely that in the PF_6^- salt one set of isotopomers is produced on the surface of the solid for the surface area is only 3 M^2 g^{-1}. However, one cannot rigorously exclude the possibility that the second exchange process is due to heterogeneity, i.e., that the solid contains two types of chemically distinct Ir sites.

Lattice Mobility of Small Organic Molecules

The production of deuterated cyclooctanes upon treatment of $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ provides an opportunity to study by solid-state deuterium NMR the mobility of cyclooctane, presumably an inert (at least at room temperature) molecule in the $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ lattice. This is possible because the line shapes are a function of the type of motion that a small molecule can undergo.[14] Figure 4 shows the variable-temperature solid-state ^2H NMR spectrum of **1** after reduction with D_2. Two overlapping peaks, distinguishable by their line widths, are apparent in the 20 °C spectrum. A narrow resonance that comprises about 20% of the intensity of the resonance is attributed to cyclooctene which is moving isotropically in the lattice. A much broader peak, having a full width at half-maximum of about 15 kHz, represents cyclooctane which, though not in a fluidlike environment, still has quite substantial motional freedom. The intensity of the narrower line decreases when the sample is subjected to pumping, and therefore, these two resonances are considered to represent two populations of cyclooctane molecules having different motional constraints. On cooling, both resonances broaden and at −186 °C broaden into the base line. The line widths of the lattice c-$C_8D_nH_{16-n}$ are narrow for a solid-state species and justify the assumption that cyclooctane is a guest in the $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ lattice. Very similar ^2H NMR spectra were observed for lattice acetone-d_6 in $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}\cdot 0.9(CD_3)_2CO$ (vide supra). The stoichiometries of compounds containing deuterated lattice molecules were determined by dissolving the compounds in dimethylformamide and integrating the ^2H spectra, with deuterium at natural abundance in the DMF as an intensity standard.

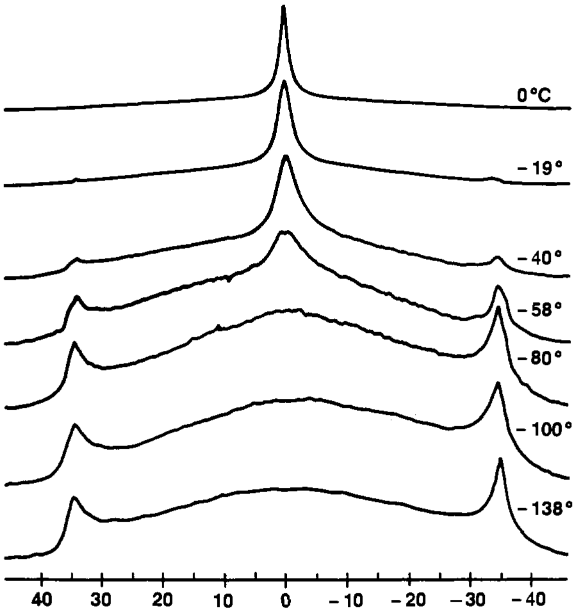

Figure 5. Variable-temperature solid-state ^2H NMR spectrum of C_6D_6 in $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$.

Subsequently, it was found that guest molecules can be introduced into $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ simply by exposing the iridium oxometalate to the appropriate vapor. Thus, when **2** is treated with CD_3OH, $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}\cdot 1.2CD_3OH$ forms. Its ^{31}P MAS NMR spectrum exhibits, in addition to the 30 ppm peak due to the $(Ph_3P)_2IrH_2^+$ moiety and a signal at −15 ppm due to the $PW_{12}O_{40}^{3-}$ cluster, an additional, sharp resonance at 0 ppm that may be due to $[(Ph_3P)_2IrH_2(CD_3OH)_n]_3PW_{12}O_{40}$ (n = 1 or 2). Indeed, **2** exchanges Ir-*H* for deuterium in CH_3OD but not CD_3OH without producing any detectable methoxyiridium species, and this exchange very likely involves coordinated methanol.[15] The solid-state ^2H NMR of this CD_3OH complex at 25 °C demonstrates a ca. 100-Hz-wide signal comprised of two closely overlapping signals attributable to isotropically moving CD_3OH in which the quadrupolar interactions are averaged. Coordinated CD_3OH, in which the CD_3 group could rotate about its C_3 axis, would give rise to a powder pattern line shape having a ca. 45-kHz wing separation.

Treatment of **2** with benzene-d_6 vapor produces $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}\cdot 3.0C_6D_6$. The variable-temperature solid-state ^2H NMR spectrum of this material is shown in Figure 5. At 25 °C, only a single, narrow resonance is seen that corresponds to isotropically moving benzene. On cooling, this signal is attenuated and replaced by a Pake pattern with a single 70-kHz splitting. This corresponds to C–D vectors oriented at 90° to the motional axis, and thus, even at −138 °C, the benzene molecules rotate about their C_6 axes. Similar results are obtained with toluene. Spectra of the 0.7 $C_6H_5CD_3$ solvate show at room temperature a 2-kHz-wide singlet that transforms to a very broad, 38-kHz total width, resonance at −150 °C. The line shape at low temperature is indicative of molecular motions having frequencies on the order of 10 kHz. These are attributed to reorientation of the toluene ring because an unencumbered CD_3 rotor should generate a 45-kHz Pake pattern even at low temperature. This interpretation is supported by ^2H spectra of the 2.1 $C_6D_5CH_3$

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solvate that display evolution of a 3.5-kHz total width flat-topped resonance consistent with ring motions of intermediate frequency. The barrier to reorientation in toluene is thus significantly higher than that of benzene, and this is explicable in terms of its greater molecular size normal to the ring.

Discussion

The compound $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ represents a prototypical catalytic system. The four-electron-donor cyclooctadiene serves as a protective group that can be removed by hydrogenolysis, thus forming $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$. In this dihydride species, iridium can be viewed as Ir(III) and the hydrides as two electron donors. There results a 14-electron species, $(Ph_3P)_2IrH_2^+$, stabilized in the lattice made up of large, anionic molecular metal oxide clusters. It has a pattern of C–H activation chemistry involving coordinated cyclooctene quite different from that occurring when the seemingly related compound $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ is reduced either in the solid state or in acetone solution.

Earlier work has described both catalytic[2] and stoichiometric[3,15] organometallic chemistry of solid materials incorporating Rh- and Ir-containing cations associated with molecular metal oxide clusters. The surface area of $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ is only 15 $M^2\ g^{-1}$,[4] and so it was not obvious how heterogeneous, stoichiometric reactions, which require that iridium centers *inside* the particles of **2**, proceed. Solid-state ^2H NMR results reported here shed some light on this question. We believe that small organic molecules, exemplified here by acetone, methanol, cyclooctane, benzene, and toluene, literally dissolve in the hydrophobic regions of the solid that are formed by the numerous phenyl rings on the triphenylphosphine ligands. Such a process depends on dispersive and perhaps entropic factors and is analogous to polymer swelling in which a low surface area organic solid can absorb large quantities of solvent. It may be related to absorption of hydrocarbons in salts of heteropoly oxometalates containing small (diameter 2.5–4 Å) unipositive cations such as H_3O^+ and NH_4^+, which have been characterized by Moffat and co-workers as being microporous solids,[16-18] but here, the cations are both much larger and nonspherical. The narrow NMR line shapes indicate that small organic molecules contained within $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ have substantial motional freedom and, at room temperature, can undergo almost isotropic, fluidlike motion. This motion has implications for synthetic and catalytic chemistry because small, asymmetric organic substrate molecules need not be constrained along a small set of rotational axes as they approach the iridium (or some other) reaction center. Thus, if one particular aspect of approach of a reacting substrate molecule is unfavorable, rotation and reapproach are possible over the time scale of a preparative reaction.

Experimental Section

$[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ (**1**) was synthesized by the metathetic reaction of $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$[19] (twice recrystallized from acetone–diethyl ether) with hydrated $(H_3O)_3PW_{12}O_{40}$ in acetone as previously described.[3] Reactions of 0.1-g samples of solid **1** and $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ with deuterium at 400-mm pressure were carried out at 65 and 25 °C, respectively, in sealed 10-mL Schlenk tubes fitted with 5-mm Young high-vacuum stopcocks. At the conclusion of the reaction, the tubes were cooled to −78 °C and the excess deuterium was pumped away. The Schlenk tubes were subsequently connected to the gas probe of a Kratos MS50 RF tandem mass spectrometer via a septum and double-ended needle. The probe was maintained at 100 °C and cyclooctane transferred to the probe by gently warming the Schlenk tube to 40 °C with a heat gun. The spectrometer source pressure during analysis was ca. 2×10^{-6} mm. Volatile species were ionized by electron impact, and positive ions were directed into the mass analyzer. The instrumental resolution was ca. 40000, and the experiment was conducted by manual peak matching.

The mass spectrometer was tuned on a perfluorokerosene (pfk) peak at m/z 111.9936, which served as the low-mass reference for peak matching the cyclooctane-derived ions. Above m/z 119, peaks were matched to the pfk 118.9920 peak, and above m/z 126, the 122.18797 peak was used. To obtain more accurate isotopomer abundance measurements, the spectrometer was immediately set for low-resolution data acquisition and full-scan spectra of the sample was obtained. Intensities of fluorine-containing ions observed in the experiment with solid $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ are not shown in Figure 2.

In a solution-phase experiment, 0.2 mL of degassed acetone (dried over CaH_2) was condensed onto 0.1 g of $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ contained in a Schlenk tube. Deuterium was added to bring the pressure to 500 mm, and the tube was then sealed by means of the vacuum stopcock. After 100 min, the contents of the tube were frozen and excess deuterium was pumped away. Volatiles were then vacuum transferred to a clean Schlenk tube.

$[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}\cdot 3.0C_6D_6$. A 0.5-g sample of $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ was placed in a Schlenk tube to which was attached a small side arm. After reduction by treatment with 25 psi of hydrogen pressure for 15 min, the sample was kept under high vacuum (ca. 3×10^{-6} mm) for 16 h. About 0.05 mL of C_6D_6 was condensed into the side arm. The reaction vessel was isolated from the vacuum system. After 24 h at room temperature, the solid was cooled to 0 °C and subjected to pumping for 1 min in order to remove loosely held benzene. The CD_3OH solvate was prepared in a similar manner.

Quantitative deuterium analyses were performed by dissolving the solvates in dimethylformamide. The proton-undecoupled 61-MHz ^2H NMR spectra, obtained with a 30-s recycle time ($\geq 5T_1$), were integrated with the 2.91 or 2.74 ppm (relative to $(CD_3)_4Si$) peaks of $(CDH_2)(CH_3)NCHO$ at natural abundance as an intensity standard.

Solid-state deuterium NMR spectra were obtained on a Varian XL-200 instrument that had been modified for operation with solid samples. The final power amplifier was replaced with an Amplifier Research Model 150 LA device to provide a 12-μs 90° pulse for ^2H. A quadrupolar echo pulse sequence[20] was used with delays between 90° pulses and acquisitions typically being about 50 μs and 50 ms, respectively. The pulse irradiation was applied at the center of the powder patterns by centering the frequency on a sample of liquid D_2O beforehand. Quadrature detection was employed in conjunction with cycling of the pulse and receiver phases. The maximum spectral width of 100 kHz combined with relatively long 90° pulses led to some distortion in line shapes, but wings were clearly identifiable in the powder patterns, with quadrupolar splittings less than ±100 kHz obtained from some of the lower temperature experiments.

In a nitrogen-filled drybox, powder samples were loaded into a sapphire cylindrical rotor fitted with Kel-F endcaps. The rotor was positioned in the stator of a Doty Scientific wide-band, variable-angle, variable-temperature solids probe. The stator angle was adjusted to 90° relative to the magnetic field direction. The temperature of the nonspinning sample was adjusted by introducing nitrogen gas, which had been cooled in a Doty liquid nitrogen heat exchanger. Temperatures were estimated with a thermocouple placed in the nitrogen stream near the sample.

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