secondary or tertiary carbocations were detected by NMR, even at reduced temperatures.[28]

Long-lived alkyl-substituted cyclopentenyl cations are proposed to form from propene in HY by deprotonation of oligomeric dienes. Such ions apparently have no catalytic role. It is significant that the only free carbocations observed in this work are those that are incapable of bonding to the framework as alkoxy species. However, the alkoxy intermediates identified in this contribution are likely to be labile at higher temperatures, and a small concentration of (momentarily) free ions could be invoked to rationalize scrambling of isotopic labels[29] or cracking of alkanes[30] on solid acid catalysts at elevated temperatures.

One implication of this investigation is that the role of the zeolite framework in stabilizing alkoxy intermediates should be considered in future efforts to develop new catalysts. Also, the novel experimental methodology introduced in this contribution should be useful in the study of many highly reactive catalyst/adsorbate systems. Several analogous investigations are underway in our laboratory.

Acknowledgment. This research was funded by the National Science Foundation (Grant CHE-8700667). We thank Ray Gorte of the University of Pennsylvania for sharing with us some of his results on 2-methyl-2-propanol on ZSM-5 prior to publication and Jack Lunsford for his comments on the draft of this paper.

Registry No. Propene, 115-07-1.

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(28) Yannoni and co-workers have shown that carbocations generated in the solid state by codeposition of alkyl chlorides and SbF_5 can be observed by ^{13}C CP/MAS NMR at temperatures comparable to those used in the present study. For example, see: Yannoni, C. S.; Myhre, P. C. *J. Am. Chem. Soc.* **1981**, *103*, 230.

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Solid-State Chemistry of Molecular Metal Oxide Clusters. Ortho Metalation and Hydrogen Transport in $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ Probed by ^{31}P NMR Long-Range Deuterium Isotope Effects

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Abstract: Deuterium isotope effects on ^{31}P shielding that are large relative to the accuracy with which they can be measured are reported. In $(Ph_3P)_2IrH_2(dmf)_2^+$, substitution of one ^2H for one ^1H at the Ir–*H* or at the ortho position in the Ph_3P ligand leads to two- and three-bond isotope shifts of +0.094 and −0.110 ppm, respectively, with the effect being defined as $[\delta(^2H\ \text{form}) - \delta(^1H\ \text{form})]$. The ortho-deuterium effects on ^{31}P for Ph_3P, Ph_3PO, $Ph_3PMe^+I^-$, and $(Ph_3P)_2Ir(C_8H_{12})^+$ are −0.110, −0.096, −0.035, and −0.077 ppm, respectively. These long-range isotope effects are used to demonstrate a thermally activated, solid-state exchange of deuterium between iridium and only the ortho positions of the Ph_3P ligands in $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$. There occurs, additionally, an intermolecular hydrogen–deuterium exchange process. Slow exchange with c-C_6D_{12} leads to incorporation of the deuterium label in the Ph_3P rings.

We are developing the solid-state physical and reaction chemistry of materials derived from molecular metal oxide clusters of the Keggin-ion type, exemplified by $PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$.[1-8] An issue of particular interest is the reactivity of coordinatively unsaturated organometallic cations that can be stabilized as interstitial species in lattices comprised of such oxide cluster anions. The compound $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ (**1**) participates in unusually facile intermolecular C–H activation processes,[5,6] but this reactivity can be modulated by phenomena peculiar to the solid state. In this paper, we describe long-range deuterium NMR isotope effects on ^{31}P chemical shielding and then use these to probe *intra*molecular C–H activation in **1**. This chemistry can readily occur in the solid state because ligand phenyl groups in the lattice have sufficient motional freedom to participate in an ortho- or cyclo-metalation reaction. In addition, the data indicate that intermolecular, intralattice hydrogen transport is also involved in redistribution of the deuterium label, a process that, to our knowledge, is without precedent in homogeneous organometallic chemistry.

Long-Range NMR Deuterium Isotope Effects. We begin by describing some effects of substituting deuterium for hydrogen at positions two and three bonds removed from a magnetically active nucleus, here ^{31}P. These effects, though perhaps deceptively small, are quite large relative to the experimental errors associated with determining ^{31}P NMR chemical shifts at high magnetic fields. Furthermore, although the absolute magnitude of ^{31}P chemical shifts, expressed relative to a reference material (85% H_3PO_4), can be solvent and concentration dependent, these factors affect all isotopomers equally to within experimental error so that *relative* magnitudes of the isotope-induced shifts can readily be determined with high accuracy.[9] Consequently, these isotope effects can be very useful in determining how a deuterium label in a molecule

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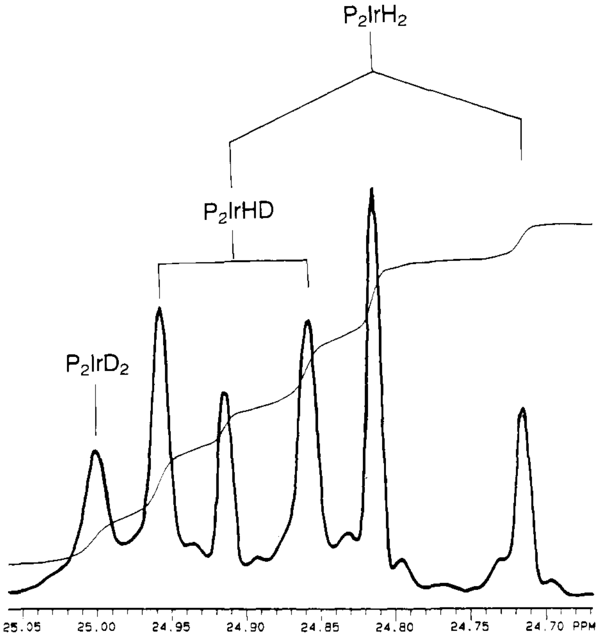

Figure 1. 161.9-MHz ^{31}P NMR spectrum of a dmf-d_7 solution of $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ after exchange with D_2 showing $(Ph_3P)_2IrH_2(dmf)_2^+$, $(Ph_3P)_2Ir(HD)_2(dmf)_2^+$, and $(Ph_3P)_2IrD_2(dmf)_2^+$.

has been redistributed as a result of chemical reactions.

As reported previously, $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ is converted, in a solid–gas reaction with dihydrogen, to cyclooctane and **1**. EXAFS data indicated that **1** contains isolated or interstitial $(Ph_3P)_2IrH_2^+$ units stabilized by a chemically noninteracting lattice of $PW_{12}O_{40}^{3-}$ clusters. When **1** is dissolved in dimethylformamide, the iridium cations become solvated and form $(Ph_3P)_2IrH_2(dmf)_2^+$,[5,6] which is a member of the well-studied $(Ph_3P)_2IrH_2(solvent)_2^+$ class.[10] Reaction of solid **1** with deuterium gas at 1 atm pressure for 19 h and subsequent removal of the gas phase by application of vacuum results in exchange with the Ir–*H* hydrogen atoms. The mechanism of this exchange reaction is still under investigation and will not be further discussed here. For present purposes, the important result is that a mixture of $[(Ph_3P)_2IrH_nD_{2-n}]_3PW_{12}O_{40}$ isotopomers is obtained. The resolution-enhanced 161.9-MHz ^{31}P NMR spectrum of the $(Ph_3P)_2IrH_nD_{2-n}(dmf)_2^+$ mixture, obtained when **1** is exchanged with D_2 then dissolved in dmf-d_7, is shown in Figure 1. The three isotopomers $(Ph_3P)_2IrH_2(dmf)_2^+$, $(Ph_3P)_2IrHD(dmf)_2^+$, and $(Ph_3P)_2IrD_2(dmf)_2^+$ are clearly resolved and recognizable from their triplet (16 Hz), doublet (16 Hz), and singlet $^2J_{P-Ir-H}$ splitting patterns (dmf-d_7 is hereinafter represented by dmf for convenience). These species have ^{31}P chemical shifts of 24.816, 24.910, and 25.004 ppm, respectively. Therefore, the two-bond deuterium isotope effect caused by substitution of D for one H at iridium in this system is +0.094 ppm. Here, we employ the convention that defines the isotope effect as [$\delta(^2H$ form) – $\delta(^1H$ form)] which is opposite to that previously used.[9] Deliberate addition of water to the sample does not change the isotopometer ratio and so the analysis is unaffected by small amounts of adventitious water that might be in the dmf solvent. Control experiments establish that the Ir–*D* does not arise by exchange with the deuterated solvent. The isotope effects observed here are comparable to the –0.127 ppm (convention undefined) value in $[(p\text{-}FC_6H_5)_3P]_2Ir(H,D)(\eta^2\text{-}O_2CCF_3)$.[11]

Three-bond deuterium isotope effects are manifest in the resolution-enhanced $^{31}P\{^1H\}$ NMR spectra of synthetic mixtures of Ph_3P and Ph_3P-d_{15} or ortho-deuterated Ph_3P-d_6 in $CDCl_3$; cf. Table I. The ortho-labeled phosphine was prepared by the regiospecific $(Ph_3P)_3RuHCl$-catalyzed exchange of Ph_3P with dideuterium.[12]

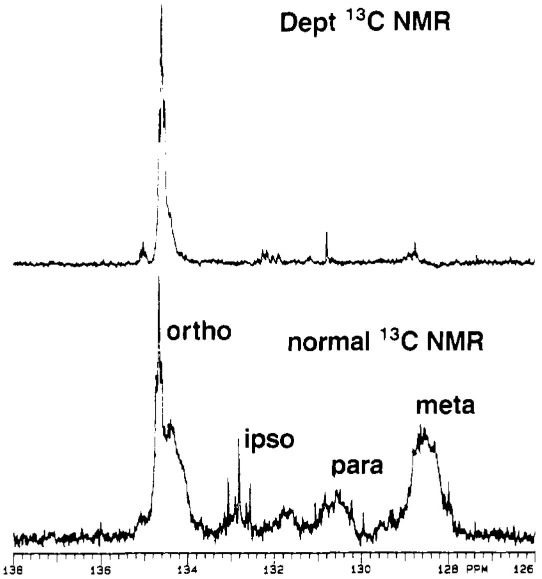

Figure 2. DEPT ^{13}C NMR spectrum of rearranged $[(Ph_3P\text{-}d_{15})_2IrH_2]_3PW_{12}O_{40}$ in dmf-d_7.

Table I. ^{31}P Isotope Shifts (ppm) in Deuterated Triphenylphosphine Derivatives

compound (solvent)	$\delta^{31}P$, ^1H form	$\delta^{31}P$, [^2H–^1H]
Ph_3P-d_{15} ($CDCl_3$)	–11.9	–0.665
Ph_3P-d_6 ($CDCl_3$)	–11.9	–0.660
Ph_3PO-d_{15} (CD_3COCD_3)	–24.5	–0.096
$[Ph_3P\text{-}d_6\text{-}CH_3]I$ (CD_3COCD_3)	20.0	–0.208
$(Ph_3P\text{-}d)_2IrH_2(dmf)_2^+$ (dmf-d_7)	24.8	–0.104
$[(Ph_3P\text{-}d_6)_2Ir(C_8H_{12})]_3$ $PW_{12}O_{40}$ (dmf-d_7)	14.7	–0.464

The spectrum of Ph_3P–Ph_3P-d_{15} shows ^{31}P resonances for these two species at –11.97 and –12.63 ppm, respectively. In a mixture of Ph_3P and Ph_3P-d_6, the ^1H and ^2H species have ^{31}P chemical shifts of –11.89 and –12.55 ppm, respectively. In both experiments, assignment of the downfield resonance to protio-Ph_3P was confirmed by observation of the ^1H decoupled spectrum in which the line width of this peak increases from 2.5 Hz (with ^1H decoupling) to 24 Hz, whereas the width of the peak due to the ^2H derivative is unchanged. The chemical shift difference between the two isotopomers is 0.665 ppm for Ph_3P-d_{15} and 0.660 ppm for Ph_3P-d_6 or, expressed alternatively, substitution of one ortho proton by a deuteron produces an upfield shift of 0.11 ppm or 18 Hz in 161-MHz spectra. Our results indicate that the meta and para contributions to the ^{31}P isotope effect are negligible although it is possible that the two are opposite and fortuitously cancel one another. However, experimentally negligible aryl carbon isotope effects occur in meta- and para-deuterated benzene derivatives[13] and it is unlikely that the effect is larger on δ ^{31}P. For comparison, we have also measured the three-bond deuterium isotope effects in $Ph_3P{=}O$-d_{15} and $[Ph_3P\text{-}d_6\text{-}CH_3]I$ in acetone which are –0.016 and –0.035 ppm per ortho deuteron, respectively; cf. Table I. This reflects the trend found in nitrogen compounds, where the magnitude of the isotope shift increases with increasing lone pair electron density at the group V atom.[14]

Similar three-bond deuterium isotope effects occur in the iridium complexes $(Ph_3P)_2IrH_2(dmf)_2^+$, $(Ph_3P\text{-}d_{15})_2IrH_2(dmf)_2^+$, and $(Ph_3P\text{-}d_6)_2IrH_2(dmf)_2^+$. These labeled species are obtained by reducing synthetic mixtures of solid $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ and $[(Ph_3P\text{-}d_{15})_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ (**2**) or $[(Ph_3P\text{-}d_6)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ (**3**) with dihydrogen, then dis-

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Table II. Frequencies (in Hz from H_3PO_4), Intensities, and Assignments for Isotopomers of $(Ph_3P)_2IrH_2(dmf)_2^+$

frequency	intensity	assignments						
3895	16	$(Ph_3P)_2$-$d_{12}IrH_2$						
3903	5		$(Ph_3P)_2$-$d_{11}IrH_2$					
3911	35	$(Ph_3P)_2$-$d_{12}IrH_2$		$(Ph_3P)_2$-$d_{10}IrH_2$				
3919	22	$(Ph_3P)_2$-$d_{12}IrHD$	$(Ph_3P)_2$-$d_{11}IrH_2$		$(Ph_3P)_2$-d_9IrH_2			
3927	28	$(Ph_3P)_2$-$d_{12}IrH_2$	$(Ph_3P)_2$-$d_{11}IrHD$	$(Ph_3P)_2$-$d_{10}IrH_2$		$(Ph_3P)_2$-d_8IrH_2		
3935	22	$(Ph_3P)_2$-$d_{12}IrHD$	$(Ph_3P)_2$-$d_{11}IrH_2$	$(Ph_3P)_2$-$d_{10}IrHD$	$(Ph_3P)_2$-d_9IrH_2		$(Ph_3P)_2$-d_7IrH_2	
3944	18	$(Ph_3P)_2$-$d_{12}IrD_2$	$(Ph_3P)_2$-$d_{11}IrHD$	$(Ph_3P)_2$-$d_{10}IrH_2$	$(Ph_3P)_2$-d_9IrHD	$(Ph_3P)_2$-d_8IrH_2		$(Ph_3P)_2$-d_6IrH_2
3952	13		$(Ph_3P)_2$-$d_{11}IrD_2$	$(Ph_3P)_2$-$d_{10}IrHD$	$(Ph_3P)_2$-d_9IrH_2	$(Ph_3P)_2$-d_8IrHD	$(Ph_3P)_2$-d_7IrH_2	
3961	10			$(Ph_3P)_2$-$d_{10}IrD_2$	$(Ph_3P)_2$-d_9IrHD	$(Ph_3P)_2$-d_8IrH_2	$(Ph_3P)_2$-d_7IrHD	$(Ph_3P)_2$-d_6IrH_2
3969	8				$(Ph_3P)_2$-d_9IrD_2	$(Ph_3P)_2$-d_8IrHD	$(Ph_3P)_2$-d_7IrH_2	$(Ph_3P)_2$-d_6IrHD
3977	6					$(Ph_3P)_2$-d_8IrD_2	$(Ph_3P)_2$-d_7IrHD	$(Ph_3P)_2$-d_6IrH_2
3985	3						$(Ph_3P)_2$-d_7IrD_2	$(Ph_3P)_2$-d_6IrHD
3994	1							$(Ph_3P)_2$-d_6IrD_2

solving the product in dimethylformamide. The ^{31}P chemical shift data for these compounds (cf. Table I) show that the effect on ^{31}P of replacing one ortho hydrogen with a deuterium atom is -0.104 ppm (vide infra). In the parent $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ cyclooctadiene compounds, the three-bond effect is -0.077 ppm per deuteron which indicates the generality of the isotope shifts.

Intramolecular C–H Activation Chemistry. Exchange of hydrogen between Ir–*H* and the ortho positions of the triphenylphosphine ligands in $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ occurs at elevated temperatures. The regiospecificity of the exchange is strikingly evident in Figure 2, which shows the "normal" and DEPT (distortionless enhancement by polarization transfer) $^{13}C\{^1H\}$ NMR spectra of a dmf solution of $[(Ph_3P\text{-}d_{15})_2IrH_2]_3PW_{12}O_{40}$ after the compound had been heated at 80 °C for 70 h. The DEPT experiment, optimized for 170-Hz polarization transfer, essentially involves pumping the ^{13}C spin manifold so that only signals due to carbon atoms bearing protons are observed.[15] Figure 2 reveals that the Ir–*H* protons are transferred almost exclusively to the triphenylphosphine ortho ring positions which are represented by the very prominent 134.3-ppm ^{13}C signal.

The resolution-enhanced ^{31}P NMR spectrum, obtained with decoupling of the aromatic protons (so as to collapse the 7.7-Hz $^3J_{P\text{-}H}$ splitting) of thermally rearranged $[(Ph_3P\text{-}d_6)_2IrH_2]_3PW_{12}O_{40}$ is shown in Figure 3. In this figure, *P has a special meaning and connotes Ph_3P-d_6. Each $(Ph_3P\text{-}d_{6-n/2})_2IrH_{2-x}D_x(dmf)_2$ species appears as a 16-Hz triplet ($x = 0$) or doublet ($x = 1$) or singlet ($x = 2$). At 9.4 T, the chemical shift difference between the Ph_3P and Ir–*H* protons, 35.4 ppm, is so large that both cannot be simultaneously decoupled on our spectrometer. Because both the downfield isotope effect associated with replacing Ir–*H* with D and the upfield isotope effect due to replacing one Ph_3P ortho C–*H* with D are both known (vide supra), it is possible to calculate the ^{31}P NMR shifts of all possible ortho-protonated $[(Ph_3P\text{-}d_{6-n/2})_2IrH_{2-x}D_x(dmf)_2^+$ isotopomers. The results of such a calculation are shown in Table II for $n < 3$. Each peak comprises absorptions from up to six different isotopomers. Insufficient data are available to calculate the concentrations of each individual species because it is not possible to unambiguously determine the IrH_2:IrHD:IrD_2 ratio. Major peaks appear to occur for the species $[(Ph_3P)_2\text{-}d_{12}]IrH_2(dmf)_2^+$, $[(Ph_3P)_2\text{-}d_{12}]IrHD(dmf)_2^+$, and $[(Ph_3P)_2\text{-}d_{12}]IrD_2(dmf)_2^+$ (cf. Figure 3); this is a significant observation that will be discussed below. A new, cumbersome notation system is now used because the H–D isotope shifts are additive and one cannot determine whether, for example, two deuterium atoms are in the same or different Ph_3P groups. Additional information cannot be obtained from spectra at higher or lower frequencies because the downfield shift due to Ir–H,D substitution, 0.094 ppm, is almost exactly the upfield ortho-deuterium effect, 0.104 ppm (vide infra). Thus, the chemical shifts of $(Ph_3P\text{-}d_1)_2IrHD(dmf)_2^+$ and $(Ph_3P)_2IrH_2(dmf)_2^+$ are the same, independent of spectrometer frequency, a point that has been confirmed by 270-MHz ^{31}P NMR spectra.

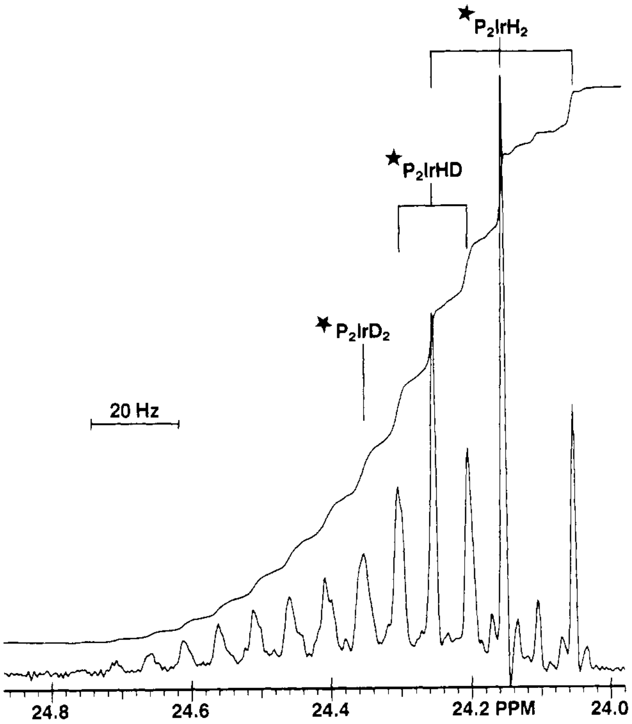

Figure 3. Resolution enhanced 161.9-MHz ^{31}P NMR spectrum, with single frequency decoupling of the aromatic protons, of rearranged $[(Ph_3P\text{-}d_6)_2IrH_2]_3PW_{12}O_{40}$ in dmf-d_7. *P indicates Ph_3P-d_6.

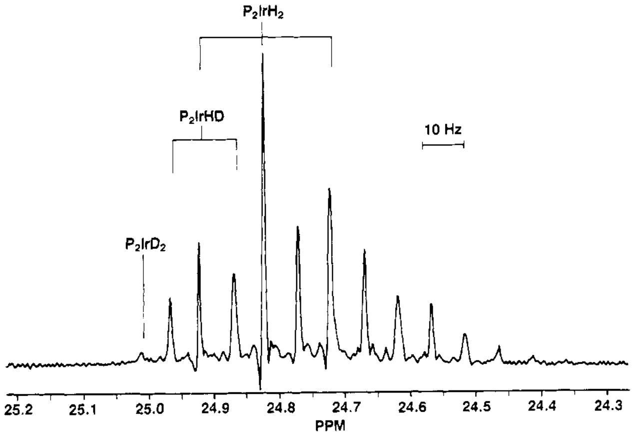

Figure 4. Resolution-enhanced ^{31}P NMR spectrum of rearranged $[(Ph_3P)_2Ir(H,D)_2]_3PW_{12}O_{40}$ (dmf-d_7 solvent).

Heating $[(Ph_3P\text{-}d_{15})_2IrH_2]_2PW_{12}O_{40}$ at 80 °C affords a rearranged material whose ^{31}P NMR spectrum is essentially identical with that of the Ph_3P-d_6 analogue which is consistent with transfer of deuterium only from the ortho ring positions to iridium. Likewise, the spectrum of $[(Ph_3P)_2IrD_nH_{2-n}]_3PW_{12}O_{40}$ (vide supra)

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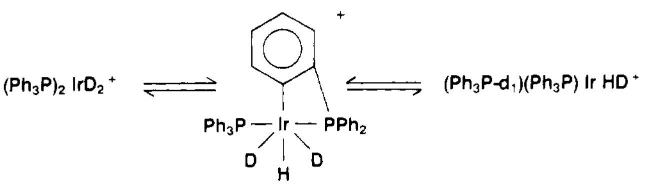
[15] See, for example: Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: Oxford, England, 1987; Chapter 6.

Scheme I



after thermal isomerization at 80 °C (Figure 4) is effectively a mirror image of the spectrum of the rearranged, ring-deuterated compound. In it are observed overlapping resonances due to isotopomers of $(Ph_3P)_2IrH_2(dmf)_2^+$, $(Ph_3P)_2IrHD(dmf)_2^+$, and $(Ph_3P)_2D_2(dmf)_2^+$ containing significant amounts of $Ph_3P\text{-}d_n$ with $n = 1$ and 2, and low levels of isotopomers up to $n = 6$.

The regiospecific transfer of deuterium between ortho Ph_3P and Ir–*H* positions in interstitial $(Ph_3P)_2IrH_2^+$ observed here is reversible in that it can proceed in either direction, i.e., with the isotopic label either on iridium or on the phenyl rings. The reaction is degenerate in that no new chemical species are produced. A classical, intramolecular ortho-metalation process (cf. Scheme I) can account for some but not all of the data. Reference to Figure 3 and Table II shows that, upon rearrangement of $[(Ph_3P\text{-}d_6)_2IrH_2]_3PW_{12}O_{40}$, deuterium is conserved within experimental error; i.e., the weighted average of deuterium atoms for the various isotopomers $[(Ph_3P)_2\text{-}d_{12-x}]IrD_xH_{2-x}(dmf)_2^+$ is 12. Intramolecular conservation of deuterium, however, is not observed. *Some species detected have more than 12 deuterium atoms and some fewer*, a result that can be rationalized only in terms of *inter*molecular H–D exchange. It is possible that deuterium transport within the lattice could occur if some intermediate were in equilibrium with $(H,D)_2$, confined by a cage effect that prevents escape of $(H,D)_2$ gas as would occur in fluid solution where dihydrogen activity is very low.

Alternatively, hydrogen transport could occur by concerted movement of protons among $(Ph_3P)_2IrH_2^+$ ions in the lattice. Facile interlattice, charge-coupled migration of H^+ between suitable acceptor sites occurs in fast-ion conductors. In this way, H,D redistribution leading to formation of molecular species having fewer or more than 12 deuterium atoms could occur. Although the fact is not necessarily of probative value here, $(H_3O)_3PW_{12}O_{40}\cdot 26H_2O$ is a fast-ion conductor.[16,17] We reasoned that, if H_2 transport were occurring, this process would be impeded by the presence of additional gas molecules having approximately the same mean kinetic diameter as H_2. When $[(Ph_3P\text{-}d_6)_2IrH_2]_3PW_{12}O_{40}$ is allowed to rearrange at 80 °C under a 40-psi atmosphere of helium, the isotopomer distribution is unchanged to within experimental error. For this reason, we believe that the transport mechanism involves intermolecular H^+ migration. It need operate over only relatively short distances which one can estimate as being two or three times the nonbonded Ir–Ir distance. Given that $d(Pt\text{–}Pt)_{min}$ in $[(Et_3P)_2PtH(CH_3CN)]_3PW_{12}O_{40}$ is 7.28 Å,[8] H^+ movement over ≤20 Å can account for the observed intermolecular hydrogen redistribution.

Although ortho-metalation chemistry in fluid solution is well known (cf. $[(c\text{-}C_6H_{11})_3P]_2IrH_2(O_2CCF_3)$, which exhibits reversible cyclometalation[11]), there appear to be few examples of the reaction in the solid state.[18,19] That facile ortho metalation proceeds so readily in solid **1** is at first sight surprising because significant motion of at least one of the phenyl rings should be required in order to reach the transition state. On the other hand, the reaction is considered to have a negative volume of activation[20] and so the internal pressure in the solid may provide a driving force. Further, well-defined examples of *inter*molecular chemistry such as we report here appear only in the condensed phase, thus indicating that solid-state organometallic chemistry can exhibit unusual features not observed in solution-phase reactions.

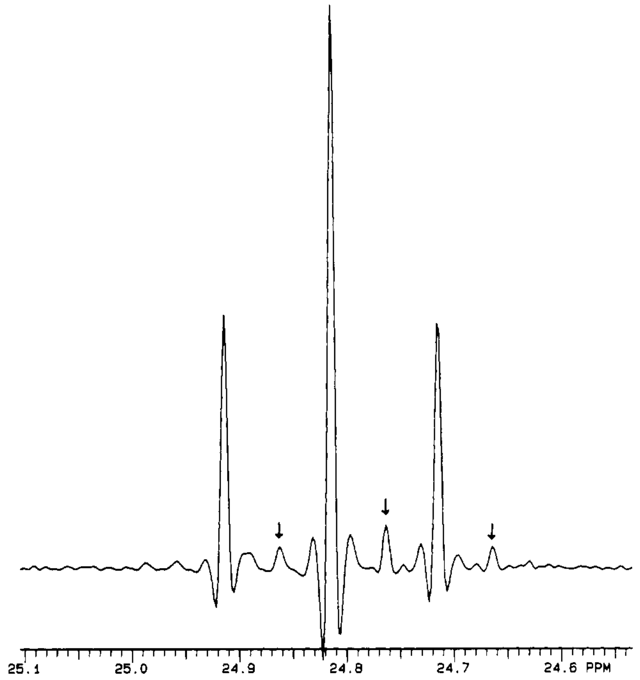


Figure 5. Resolution enhanced 161.9-MHz ^{31}P NMR spectrum of $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ after reaction with $c\text{-}C_6D_{12}$ (dmf-d_7 solvent). Arrows indicate the 1:2:1 triplet due to $(Ph_3P)(Ph_3P\text{-}d_1)IrH_2(dmf)_2^+$.

Another example of the usefulness of long-range isotope effects is found in hydrocarbon activation chemistry of **1**. Figure 5 shows the resolution-enhanced ^{31}P NMR spectrum of the reaction product (after dissolution in dmf-d_7) obtained by heating $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ with neat cyclohexane-d_{12} at 80 °C for 70 h; **1** does not dissolve in this hydrocarbon. The predominant species present is $(Ph_3P)_2IrH_2(dmf)_2^+$. However, components of a 16-Hz triplet centered at 0.052 ppm upfield from $(Ph_3P)_2IrH_2(dmf)_2^+$ is also seen, but not when $c\text{-}C_6H_{12}$ is used instead. This upfield shift is only about 50% of that calculated for the introduction of one ortho deuterium (vide supra). However, if one aromatic ring in a Ph_3P ligand in *trans*-$(Ph_3P)_2IrH_2(dmf)_2^+$ is deuterated, then the two Ph_3P groups become *chemically* inequivalent because each has a different (18 Hz at 9.4 T) relative chemical shift. But, because $J_{P\text{-}P'}$(trans) is >100 Hz, the observed spectrum is degenerate, and one observes a triplet (due to $J_{P\text{-}H}$) having a chemical shift that represents the *average* of the two nonequivalent Ph_3P ^{31}P environments. This upfield peak may therefore be attributed to $(Ph_3P)_2IrH_2(dmf)_2^+$ containing, on average, one deuterium per two Ph_3P ligands; the calculated shift is 0.055 ppm, in good agreement with the observed value of 0.052 ppm.

Thus, **1** does activate C–D bonds in cyclohexane-d_{12} at 80 °C, but the reaction is very slow. At this temperature, Ir–*H*/Ph_3P exchange is sufficiently rapid that, in effect, deuterium which initially enters the Ir–*H* site is washed into the Ph_3P phenyl rings. If such a reaction were to be followed by monitoring the Ir–*H*/Ir–*D* levels by infrared or ^1H NMR spectroscopy, one would conclude that no reaction took place. This incorrect conclusion would not change until such time as a substantial number of the ortho Ph_3P sites had incorporated the deuterium label, thus filling the exchangeable C–*H* sites and allowing deuterium accumulation in Ir–*H* sites. Probably, ortho metalation leading to metal–ring hydrogen exchange represents a general phenomena. It has recently been characterized in $(Ph_3P)_3RuHCl$,[21] and in that com-

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[19] Thermal decomposition of $(Ph_3P)_3Rh(CO)H$ in nonane, reportedly a nonsolvent, yields $(Ph_3P)_2Rh_3(\mu\text{-}PPh_2)_3(CO)_3$. Ortho metalation may be involved: Billig, E.; Jamerson, J. D.; Pruett, R. *J. Organomet. Chem.* **1980**, *192*, C49. Similar considerations apply to $Os_3(CO)_{11}$(phosphine) complexes which, on heating in nonane, give C_6H_4-bridged clusters: Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2589.

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pound, as in **1**, the equilibrium favors localization of deuterium in C–H rather than metal–H bonds. Accumulation of deuterium in C–D rather than Ir–D positions can be rationalized in terms of zero-point energy effects. Because $\nu_{C\text{-}H} > \nu_{Ir\text{-}H}$, the energy of the system is lower when the lighter nucleus (H) is placed in the lower frequency site (Ir–H).[22]

Experimental Section

^{31}P NMR spectra were recorded at 161.9 MHz on a Varian XL-400 instrument. Resolution-enhanced (Lorentz–Gauss transforms) spectra were obtained using the vendor's software. dmf refers to 99 atom % dmf-d_7 (Aldrich) that was freeze–pump–thaw degassed and stored under nitrogen over 3A molecular sieves. Positive chemical shifts are downfield of the references $(CH_3)_4Si$ (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P).

Triphenylphosphine-d_{15} was prepared from PCl_3 and C_6D_5MgBr made from 99 atom % C_6D_5Br.[23] The crude product obtained after evaporation of the ether solvent was recrystallized from methylcyclohexane to remove insoluble Ph_3PO-d_{15}. Final purification was achieved by vacuum sublimation at 95 °C. The ^{1}H NMR spectrum in C_6D_6 showed that the (ortho):(meta + para) proton ratio was 2.0:3.4, indicating essentially random distribution of residual protons in the sample. The ortho proton is a doublet (due to $^3J_{H\text{-}P} = 7.7$ Hz) at δ 7.39; ^{1}H meta and para are 7.04 and 7.03 ppm, respectively, and are resolved because there is no detectable H–H coupling due to the low ^{1}H content.

Triphenylphosphine-d_6 was prepared by the method of Parshall, Knoth, and Schunn.[12] In its $^{13}C\{^1H\}$ NMR spectrum, the ortho carbon atoms appear as a doublet ($^2J_{CP} = 19.3$ Hz) of 1:1:1 triplets ($^1J_{CD} = 24.5$ Hz). The undecoupled spectrum showed no evidence of a 159-Hz doublet due to ortho protons under conditions under which it could have been observed outside the double triplet. Deuterium exchange at the ortho positions is therefore ≥98% complete.

The validity of the ^{13}C DEPT experiment depends on accurate assignment of the various ^{13}C resonances. The ^{1}H NMR spectra of both Ph_3P and $(Ph_3P)_2IrH_2(dmf)_2^+$ are degenerate and show only two aryl multiplets in a 2:3 ratio. In each case, two possible assignments exist because the para proton is degenerate with either the ortho or meta protons. Because the PH coupling is unknown, direct assignment of the ^{1}H spectrum is not possible. Parshall et al. assigned the downfield 2H multiplet in Ph_3P to the ortho protons in a specific labeling experiment.[12] Assignments here are based on single-frequency ^{1}H decoupled ^{13}C NMR spectra; they agree with Parshall's results.[12] The ipso carbon is readily assigned on the basis of its low intensity (no NOE) as well as the absence of a large $^1J_{CH}$ splitting. The other carbon atoms give rise to signals of relative intensities 2:2:1 from which assignment of the para carbon follows unambiguously. Meta substituent chemical shifts for phosphines are always small (<2 ppm in 30 different compounds in which the phosphorus has no net formal charge), whereas ortho substituent shifts are typically 3–5 ppm.[24] Therefore, the absorption that is shifted 5.5 ppm downfield relative to C_6H_6 (128.5 ppm) is due to the ortho carbon atoms.

The $^{13}C\{^1H\}$ spectrum of $(Ph_3P)_2IrH_2(dmf)_2^+$ shows triplets due to virtual coupling to ^{31}P.[25] The C_{ortho} ^{13}C nuclei appear to be equally coupled to both ^{31}P nuclei because of the large $^2J_{PP}$ interaction, typically >100 Hz and ca. 15 Hz for mutually trans and cis phosphines, respectively, but the observed splitting is actually the average of $^2J_{PC}$ and $^4J_{PC}$ for the ortho carbon nuclei. Observation of virtual coupling requires that $^2J_{PP}$ is comparable to or greater than the P–C coupling. Spectra were calculated for $^2J_{PP}$ varying from 0 to 50 Hz with $^2J_{PC} = 10$ and $^4J_{PC} = 0$ Hz. The calculations indicate that the ortho ^{13}C signal would appear as an apparent triplet, 5 Hz for $^2J_{PP} > 25$ Hz. Additional, weak second-order absorptions at the 6% intensity level on each side of the central triplet are expected when $J_{PP} = 15$ Hz. The second-order effects become more intense as J_{PP} decreases, and the calculated spectra eventually degenerate to the anticipated 10-Hz doublet as J_{PP} approaches 0 Hz. A high-gain ^{13}C spectrum of $(Ph_3P)_2IrH_2(dmf)_2^+$ reveals no such minor features and so $J_{PP} > 30$ Hz, confirming that the Ph_3P ligands are trans, as they are in $(Ph_3P)_2IrH_2(acetone)_2^+$.[26]

The NMR spectra of Ph_3P in dmf is thus assigned as follows: ^{1}H 7.42 (m, 3 H, *m*- plus *p*-H), 7.34 (m, 2 H, *o*-H); ^{31}P −8.1 (s) ppm; ^{13}C 137.80 (d, C_{ipso}, $^1J_{PC} = 11.5$ Hz), 134.09 (d, C_{ortho}, $^2J_{PC} = 19.8$ Hz), 129.45 (d, C_{meta}, $^3J_{PC} = 19.4$ Hz), 129.29 (s, C_{para}) ppm.

Similarly, the NMR spectra of $(Ph_3P)_2IrH_2(dmf)_2^+$ are assigned as follows: ^{1}H 7.62 (m, 2 H, *o*-H), 7.52 (m, 3 H, *m*- plus *p*-H), −27.82 (t, 16.2 Hz, Ir–*H*) ppm; ^{31}P 24.8 (s) ppm; ^{13}C 134.76 (apparent t, $^2J_{PC} + {}^4J_{PC} = 12.4$ Hz, C_{ortho}), 132.96 (apparent t, $^1J_{PC} + {}^3J_{PC} = 51.4$ Hz, C_{ipso}), 131.05 (s, C_{para}), 129.01 (apparent t, $^3J_{PC} + {}^5J_{PC} = 9.8$ Hz, C_{meta}) ppm.

The ^{31}P spin–lattice relaxation times of $(Ph_3P)_2IrH_2(dmf)_2^+$, $(Ph_3P)_2IrHD(dmf)_2^+$, and $(Ph_3)_2IrD_2(dmf)_2^+$ range from 1.55 to 1.74 s, indicating that intramolecular dipolar coupling does not contribute to ^{31}P relaxation. In agreement with this, T_1 for $(Ph_3P\text{-}d_{15})_2IrH_2(dmf)_2^+$ is 1.7 s. ^{31}P NMR spectra of rearranged $(Ph_3P\text{-}d_{15})_2IrH_2(dmf)_2^+$ (cf. Figure 3) were obtained with 90° pulses and recycle times of 1.5, 3.5, 5.5, 9.5, and 17.5 s. The peak heights and line widths were identical for the latter three spectra. This indicates that the relaxation times for the various isotopomers in the mixture are similar and that the spectra are not instrumentally distorted. For Ph_3P and Ph_3P-d_{15}, T_1 is estimated to be 18 and 25 s, respectively.

$[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ was prepared by addition of hydrated $(H_3O)_3PW_{12}O_{40}$ to an acetone solution of $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ as described previously; the compound precipitated from the reaction mixture and was isolated by filtration and vacuum drying.[5,6] Conversion to **1** was effected by placing the compound in a Schlenk tube, evacuating, and backfilling to 1 atm with hydrogen. After 30 min, cyclooctane and the excess hydrogen were removed under high vacuum. The sample was then heated under vacuum for 70 h in a 80 °C oil bath. Solutions for NMR analysis were prepared in a nitrogen-filled drybox.

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