

# Solid-State Chemistry of Molecular Metal Oxide Clusters. Reactions of Microporous $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$ with Small Organic Molecules

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The heterogeneous reactions of  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$  with  $\text{CO}$ ,  $\text{PF}_3$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CH}_3\text{CH}=\text{CH}_2$ ,  $c\text{-C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CH}_3\text{C}_6\text{H}_5$ , 2,3-dimethyl-1,3-butadiene, isoprene, butadiene,  $\text{Me}_3\text{SiH}$ ,  $\text{C}_2\text{F}_4$ ,  $\text{CF}_3\text{CF}=\text{CF}_2$ ,  $\text{CF}_2=\text{CFCl}$ ,  $\text{CH}_3\text{C}(\text{O})\text{H}$ , ethylene oxide,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2\text{O}$  are described. The chemistry can be described in terms of either addition of iridium to a substrate C-H bond to form intermediates that may optionally eliminate  $\text{H}_2$  or addition of  $\text{Ir}-\text{H}$  to a C=C bond. It is proposed that these reactants gain access to essentially all of the iridium sites by dissolving in the hydrophobic regions of the lattice of the low surface area iridium oxometalate.

## Introduction

We are developing the solid-state chemistry of materials derived from anionic molecular metal oxide clusters.<sup>1-11</sup> A principle focus of our research is the synthesis of materials in which highly reactive, coordinatively unsaturated transition-metal cations are stabilized in interstitial sites in lattices formed by these clusters.<sup>3,4,6,7,9-12</sup> This paper describes the reactions of  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$ , which is considered to contain four-coordinate, 14-electron iridium in discrete  $(\text{Ph}_3\text{P})_2\text{IrH}_2^+$  units with a wide variety of small organic molecules. Comparisons will be made, where possible, with the reactivity in potentially analogous fluid solution-phase systems. We note, in particular, that the molecular metal oxide cluster compound has a great proclivity toward C-H activation chemistry that does not occur in solution.

## Results

As reported previously,  $[(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_8\text{H}_{12})]_3\text{PW}_{12}\text{O}_{40}$  is obtained by the metathetic reaction of  $[(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_8\text{H}_{12})]\text{PF}_6$  with hydrated  $(\text{H}_3\text{O})_3\text{PW}_{12}\text{O}_{40}$  in acetone.<sup>6,7,10,11</sup> This compound may be reduced in a solid-gas reaction with hydrogen to produce cyclooctane and  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$  (1) (eq 1). This reaction, to a  $[(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_8\text{H}_{12})]_3\text{PW}_{12}\text{O}_{40} + 9\text{H}_2 \rightarrow$   
 $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40} + 3c\text{-C}_8\text{H}_{16}$  (1)

first-order approximation, parallels the heterogeneous reduction of  $[(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_8\text{H}_{12})]\text{BF}_4$  in acetone which yields  $[(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{acetone})_2]\text{BF}_4$ ,<sup>13</sup> but in the present case, no

extraneous solvent-derived ligands are present. Iridium EXAFS data on the analogous  $\text{PMo}_{12}\text{O}_{40}$  material reveal no Ir-Mo contacts of  $\leq 4$  Å, and so it is believed that iridium is not coordinated to the  $\text{PW}_{12}\text{O}_{40}^{3-}$  cluster by covalent Ir-O-W bonds and that, instead, 1 contains interstitial 14-electron  $(\text{Ph}_3\text{P})_2\text{IrH}_2^+$  ions. Thus, removal of cyclooctadiene by hydrogenation serves to open up a coordinatively unsaturated site on iridium that is not effectively filled by the weakly nucleophilic oxygen atoms on the surface of the  $\text{PW}_{12}\text{O}_{40}^{3-}$  cluster. Another result of this heterogeneous hydrogenation is that the crystals of the precursor suffer extensive fragmentation, and so we find it impossible to obtain single crystals of 1 of the quality needed for X-ray crystallography. The reactivity of 1 toward nucleophiles is so great that any solvents sufficiently polar to dissolve 1 yield electrically conducting solutions because they contain  $(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{solvent})_2^+$  ions; i.e., the solid-state structure is obliterated. Heterogeneous reactions of 1 with other substrates presumably lead to further breakdown of crystalline domains, and so methods other than crystallography must be used to study these systems. We rely here primarily on NMR. Our strategy is to carry out solid-gas or solid-liquid reactions of 1 with organic substrates and then to dissolve the product in a solvent, usually dimethylformamide-*d*<sub>7</sub>, knowing full well that such dissolution irretrievably destroys the *solid* product. Nevertheless, we find that solution-phase NMR data provide incisive information about reactions that have transpired at the iridium center, which is the topic of greatest interest here. Often, reactions of 1 with organic substrates yield complex mixtures, and so multinuclear and COSY NMR experiments are critically important in order to ensure that signals due to several magnetically active nuclei are all due to the same species. For the same reason, isotopically labeled reactants are used where possible. The principle value of solution-phase NMR data is that there is sufficient resolution of chemical shifts and coupling constants to make structural assignments for the species observed; a corollary is that a quite detailed discussion of such data is needed in order to establish the validity of the assignments. Such information is generally not obtainable from solid-state magic angle spinning NMR, but, in some cases, CPMAS NMR is useful in establishing that gross structural rearrangement of a reaction product has not occurred when the product is placed in solution.

**Reactions with Carbon Monoxide and  $\text{PF}_3$ .** The CO and  $\text{PF}_3$  chemistry is summarized in Scheme I. Reaction

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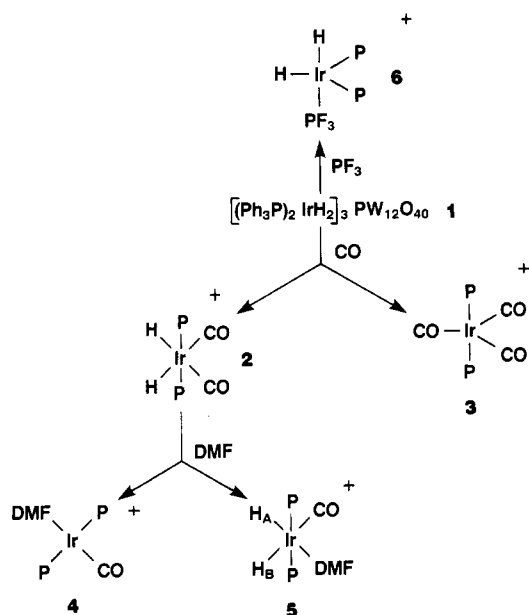
(9) Siedle, A. R.; Newmark, R. A.; Lyon, P. A.; Hunt, S. L.; Day, V. W., submitted for publication.

(10) Siedle, A. R.; Sahyun, M. R. V.; Lyon, P. A.; Hunt, S. L.; Newmark, R. A., submitted for publication.

(11) Siedle, A. R.; Newmark, R. A., *J. Am. Chem. Soc.*, in press.

(12) Siedle, A. R.; Gleason, W. B.; Newmark, R. A.; Skarjune, R. P.; Markell, C. G.; Hodgson, K. O.; Roe, A. L., submitted for publication.

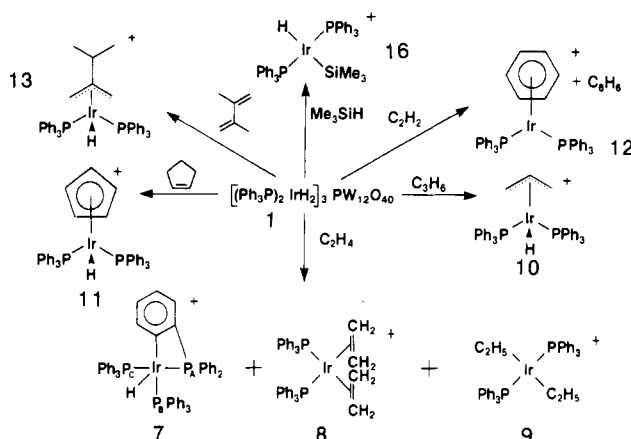
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Scheme I. CO and PF<sub>3</sub> Chemistry

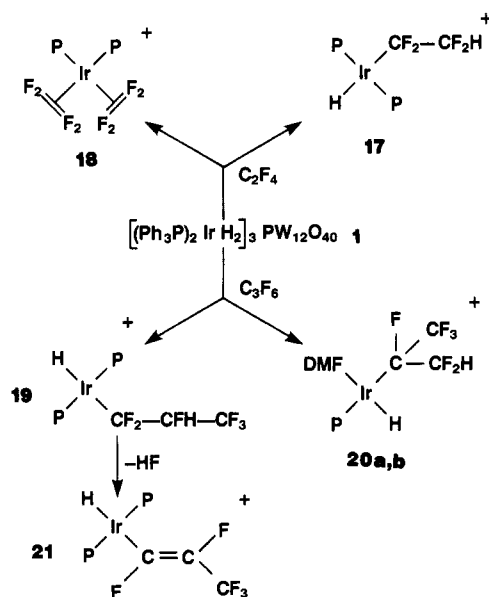
of 1 with <sup>13</sup>CO at 250-mm pressure for 16 h yields two iridium-carbonyl species according to NMR analysis of the product in propylene carbonate. The first, *trans,cis,cis*-(Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>(CO)<sub>2</sub><sup>+</sup> (2), arises from simple addition of CO to (Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub><sup>+</sup> and represents an AA'MM'X<sub>2</sub> spin system (A = <sup>1</sup>H, M = <sup>13</sup>C, X = <sup>31</sup>P). The stereochemistry is indicated by the small 14- and 6-Hz cis coupling between <sup>31</sup>P and <sup>1</sup>H and <sup>13</sup>C, respectively. Placement of two cis hydride and two cis <sup>13</sup>CO ligands in the equatorial plane is shown by 44 and 6 Hz trans and cis <sup>2</sup>J<sub>C-H</sub> coupling. In agreement with this assignment, the -9.6 ppm hydride resonance is a double triplet having 44 (*J*<sub>PC</sub>) and 15 (*J*<sub>PH</sub>) Hz splitting (the smaller <sup>2</sup>J<sub>PC</sub> was not resolved in propylene carbonate due to line broadening of the hydride resonance but was resolved in dmf). Chemical shift and coupling constant data for 2, and other materials reported here are collected in Table I. Also produced is (Ph<sub>3</sub>P)<sub>2</sub>Ir(CO)<sub>3</sub><sup>+</sup> (3). Its <sup>13</sup>C NMR spectrum shows a 170.8 ppm triplet (<sup>2</sup>J<sub>PC</sub> = 11.7 Hz). Thus, (Ph<sub>3</sub>P)<sub>2</sub>Ir(CO)<sub>3</sub><sup>+</sup> may have the TBP structure shown in Scheme I, but the species is clearly fluxional because the Ph<sub>3</sub>P (and <sup>13</sup>CO) ligand set are chemically equivalent. The reaction of 1 with CO was studied in a pulse reactor, and the products were analyzed by gas chromatography. Hydrogenation products of CO, such as H<sub>2</sub>CO and CH<sub>3</sub>OH, were not found, and so it is likely that 3 arises by displacement of hydrogen by CO.

NMR spectra of the same reaction product, dissolved in dmf, show that two additional complexes have formed as a result of reaction with the solvent. One of these, *trans*-(Ph<sub>3</sub>P)<sub>2</sub>Ir(CO)(dmf)<sup>+</sup> (4), can conceptually be derived from 3. The 171.4 ppm CO resonance is an 11 Hz triplet and the <sup>31</sup>P resonance a 28.1 ppm doublet. Similarly, *trans,cis*-(Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>(CO)(dmf)<sup>+</sup> (5), can be viewed as a solvolysis product of 2. Its <sup>1</sup>H NMR spectrum reveals two nonequivalent Ir-H protons. H<sub>A</sub>, trans to coordinated dmf, is a doublet of triplets of doublets with *J*<sub>HP</sub> = 18, *J*<sub>HC</sub> = 4.3, and *J*<sub>H<sub>A</sub>H<sub>B</sub></sub> = 4.3 Hz (confirmed by spin decoupling). The H<sub>B</sub> resonance at δ -6.28 exhibits the same multiplicity, but the *trans*<sup>2</sup>J<sub>CH</sub> coupling is much larger, 43.7 Hz. Inclusion of coordinated dmf is needed to rationalize the large chemical shift difference between H<sub>A</sub> and H<sub>B</sub> as well as the greatly different <sup>2</sup>J<sub>CH</sub> interactions. The structure is confirmed by the <sup>13</sup>C and <sup>31</sup>P spectra, cf. Table I. These complexes are illustrative of another point—definition of the number of coordinated solvent molecules (here di-

## Scheme II. Hydrocarbon Chemistry



## Scheme III. Fluoro Olefin Chemistry



methylformamide). In general, when iridium is bonded to four or more<sup>1</sup> ligands, it is not possible to unambiguously determine how many solvent molecules are bonded to the metal; 9, 16, 17, 20a,b, and 21 as written in Schemes II and III are 14-electron species, and in solution, these probably coordinate to at least one dmf molecule. Coordination or loss of dmf, which can be rapid on the NMR time scale, need not reduce the symmetry of the iridium first coordination core to which NMR is especially sensitive. When iridium otherwise has fewer than 16 electrons, as it is in 4, donation of an electron pair from a solvent-derived dmf molecule is necessary in order for iridium to attain at least a 16-electron configuration. In this and similar cases, we explicitly write coordinated solvent in the molecular formulas.

A single complex is obtained from the reaction of 1 with PF<sub>3</sub>. It arises, in contrast to CO, by formal addition of only one PF<sub>3</sub> molecule to iridium. One of several possible structures, cf. Scheme I, for (Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>(PF<sub>3</sub>)<sup>+</sup> (6) can be accommodated by the extensive NMR data, cf. Table I. *J*<sub>HH</sub> is confirmed by single frequency decoupling to be 3.5 Hz. There is another plausible structure that is consistent with the NMR data. It can be formed by opening the P-Ir-P angle in 6 to ca. 180° and introduction of a coordinated dmf molecule trans to the equatorial Ir-H, yielding a structure analogous to that of 5. It is known that in (Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>(solvent)<sub>2</sub><sup>+</sup> complexes, oxygen donor solvents

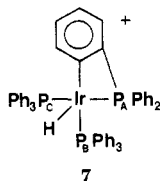
Table I. NMR Data for Organometallic Iridium Cations<sup>a</sup>

2	<sup>1</sup> H, -9.6 (IrH, dt, <sup>2</sup> J <sub>HC(trans)</sub> = 44, <sup>2</sup> J <sub>HP</sub> = 15); <sup>13</sup> C, 167.0 (dq, <sup>2</sup> J <sub>HC(trans)</sub> = 44, <sup>2</sup> J <sub>HC(cis)</sub> = <sup>2</sup> J <sub>CP</sub> = 6); <sup>31</sup> P, -0.4 (tt, <sup>2</sup> J <sub>HP</sub> = 14, <sup>2</sup> J <sub>CP</sub> = 6) <sup>b</sup>
3	<sup>13</sup> C, 170.8 (t, <sup>2</sup> J <sub>CP</sub> = 12); <sup>31</sup> P, -5.9 (q, <sup>2</sup> J <sub>CP</sub> = 12) <sup>b</sup>
4	<sup>13</sup> C, 171.4 (t, <sup>2</sup> J <sub>PC</sub> = 11); <sup>31</sup> P, 28.1 (t, <sup>2</sup> J <sub>PC</sub> = 11)
5	<sup>1</sup> H, -22.67 (IrH <sub>a</sub> , dtd, <sup>2</sup> J <sub>H<sub>a</sub>C</sub> = 4.3, <sup>2</sup> J <sub>H<sub>a</sub>P</sub> = 13, <sup>2</sup> J <sub>H<sub>a</sub>H<sub>b</sub></sub> = 4.7); -6.30 (IrH <sub>b</sub> , dtd, <sup>2</sup> J <sub>H<sub>b</sub>C</sub> = 44, <sup>2</sup> J <sub>H<sub>b</sub>P</sub> = 18, <sup>2</sup> J <sub>H<sub>a</sub>H<sub>b</sub></sub> = 4.7); <sup>13</sup> C, 178.6 (dtd, <sup>2</sup> J <sub>H<sub>b</sub>C</sub> = 44, <sup>2</sup> J <sub>H<sub>a</sub>C</sub> = 4.3, <sup>2</sup> J <sub>CP</sub> = 6.4); <sup>31</sup> P, 14.8 (ddd, <sup>2</sup> J <sub>H<sub>a</sub>P</sub> = 13, <sup>2</sup> J <sub>H<sub>b</sub>P</sub> = 18, <sup>2</sup> J <sub>CP</sub> = 6.4)
6	<sup>1</sup> H, -5.72 (IrH <sub>axial</sub> , dqtd, <sup>2</sup> J <sub>H<sub>FF</sub>3</sub> = 288, <sup>3</sup> J <sub>HF</sub> = 45, <sup>2</sup> J <sub>H<sub>FF</sub>3</sub> = 18, <sup>2</sup> J <sub>HH</sub> = 3.5), -23.63 (IrH <sub>equatorial</sub> , dtd, <sup>2</sup> J <sub>H<sub>FF</sub>3</sub> = 19, <sup>2</sup> J <sub>H<sub>FF</sub>3</sub> = 15, <sup>2</sup> J <sub>HH</sub> = 3.5); <sup>19</sup> F, -23.4 (ddt, <sup>1</sup> J <sub>FP</sub> = 1342, <sup>3</sup> J <sub>H(axial)F</sub> = 45, <sup>3</sup> J <sub>F-PPh<sub>3</sub></sub> = 5); <sup>31</sup> P, 93.2 (PF <sub>3</sub> , qdtd, <sup>1</sup> J <sub>FP</sub> = 1342, <sup>2</sup> J <sub>H(axial)P</sub> = 288, <sup>2</sup> J <sub>PP</sub> = 24, <sup>2</sup> J <sub>H(equatorial)P</sub> = 19), 7.9 (br m, PPh <sub>3</sub> )
7	<sup>1</sup> H, -23.76 (IrH, ddd, <sup>2</sup> J <sub>HP<sub>a</sub></sub> = 13.2, <sup>2</sup> J <sub>HP<sub>b</sub></sub> = 10.4, <sup>2</sup> J <sub>HP<sub>c</sub></sub> = 16.4); <sup>31</sup> P, 8.2 (P <sub>c</sub> , ddd, <sup>2</sup> J <sub>P<sub>a</sub>P<sub>c</sub></sub> = 349, <sup>2</sup> J <sub>P<sub>b</sub>P<sub>c</sub></sub> = 11, <sup>2</sup> J <sub>HP<sub>c</sub></sub> = 16), -5.9 (P <sub>b</sub> , dt, <sup>2</sup> J <sub>P<sub>a</sub>P<sub>b</sub></sub> = 19, <sup>2</sup> J <sub>P<sub>b</sub>P<sub>c</sub></sub> = <sup>2</sup> J <sub>HP<sub>a</sub></sub> = 10), -81.7 (P <sub>a</sub> , ddd, <sup>2</sup> J <sub>P<sub>a</sub>P<sub>c</sub></sub> = 349, <sup>2</sup> J <sub>P<sub>a</sub>P<sub>b</sub></sub> = 19, <sup>2</sup> J <sub>HP<sub>a</sub></sub> = 13)
8	<sup>13</sup> C, 39.1 (dd, <sup>1</sup> J <sub>CC</sub> = 41, <sup>2</sup> J <sub>CP</sub> = 5), 36.5 (dd, <sup>1</sup> J <sub>CC</sub> = 41, <sup>2</sup> J <sub>CP</sub> = 13); <sup>31</sup> P, -6.0 (m) <sup>c</sup>
9	<sup>1</sup> H, 0.48 (CH <sub>3</sub> , dq, <sup>1</sup> J <sub>HC</sub> = 124, <sup>4</sup> J <sub>HP</sub> = 5); <sup>13</sup> C, 14.8 (CH <sub>3</sub> , d, <sup>1</sup> J <sub>CC</sub> = 33), -16.9 (IrCH <sub>2</sub> , tdd, <sup>1</sup> J <sub>HC</sub> = 127, <sup>1</sup> J <sub>CC</sub> = 33, <sup>2</sup> J <sub>CP</sub> = 6); <sup>31</sup> P, -5.9 (dd, <sup>2</sup> J <sub>CP</sub> = 6, <sup>3</sup> J <sub>HP</sub> = 3) <sup>c</sup>
12	<sup>13</sup> C, 96.1 (d, <sup>1</sup> J <sub>HC</sub> = 175); <sup>31</sup> P, 1.8
13	<sup>1</sup> H, 3.04 (H <sub>anti</sub> , br s), 2.40 ((CH <sub>3</sub> ) <sub>2</sub> CH, heptet, <sup>3</sup> J <sub>HH</sub> = 7), 2.11 (H <sub>syn</sub> , d, <sup>3</sup> J <sub>HP</sub> = 9), 0.96 (CH <sub>3</sub> , d, <sup>3</sup> J <sub>HH</sub> = 7), -29.5 (IrH, t, <sup>2</sup> J <sub>HP</sub> = 16); <sup>13</sup> C, <sup>d</sup> 55.7 (allyl CH <sub>2</sub> , d, <sup>3</sup> J <sub>CP</sub> = 26), 36.5 ((CH <sub>3</sub> ) <sub>2</sub> CH), 22.7 (CH <sub>3</sub> ); <sup>31</sup> P, 7.2 (dd, <sup>2</sup> J <sub>HP</sub> = 16, <sup>4</sup> J <sub>HP</sub> = 5)
14	<sup>1</sup> H, -30.1 (IrH, <sup>2</sup> J <sub>HP</sub> = 16); <sup>31</sup> P, 11.4 (dq, <sup>2</sup> J <sub>HP</sub> = 16, apparent <sup>4</sup> J <sub>HP</sub> = 6), 7.8 (m)
15	<sup>1</sup> H, -29.2 (IrH, <sup>2</sup> J <sub>HP</sub> = 14); <sup>31</sup> P, 12.6 (dq, <sup>2</sup> J <sub>HP</sub> = 14, apparent <sup>4</sup> J <sub>HP</sub> = <sup>2</sup> J <sub>PP</sub> = 6), 6.3 (m)
16	<sup>1</sup> H, 0.03 (CH <sub>3</sub> , s), -24.2 (IrH, t, <sup>2</sup> J <sub>HP</sub> = 14); <sup>31</sup> P, 32.4 (d, <sup>2</sup> J <sub>HP</sub> = 14)
17	<sup>1</sup> H, 4.71 (CF <sub>2</sub> H, tt, <sup>2</sup> J <sub>HF</sub> = 55, <sup>3</sup> J <sub>HF</sub> = 7), -25.5 (IrH, t, <sup>2</sup> J <sub>HP</sub> = 15); <sup>19</sup> F, -67.4 (IrCF <sub>2</sub> , m), -131.3 (CF <sub>2</sub> H, dt, <sup>2</sup> J <sub>HF</sub> = 55, <sup>3</sup> J <sub>FF</sub> = 12); <sup>31</sup> P, 12.0 (td, <sup>3</sup> J <sub>FP</sub> = 25, <sup>2</sup> J <sub>HP</sub> = 14)
18	<sup>19</sup> F, -117.3, -125.2 (see text and Figure 2); <sup>31</sup> P, -1.8 (quintet, <sup>3</sup> J <sub>FP</sub> = 8)
19	<sup>1</sup> H, 3.35 (CFH, ddq, <sup>2</sup> J <sub>HF</sub> = 42, <sup>3</sup> J <sub>HF</sub> = 24, <sup>3</sup> J <sub>HF</sub> = 6), -25.3 (IrH, m); <sup>19</sup> F, -48.7 (CF <sub>2</sub> , dm, <sup>1</sup> J <sub>FF</sub> = 244), -68.0 (CF <sub>2</sub> , dm, <sup>1</sup> J <sub>FF</sub> = 244), -72.0 (CF <sub>3</sub> , qd, <sup>3</sup> J <sub>FF</sub> = <sup>4</sup> J <sub>FF</sub> = 11, <sup>3</sup> J <sub>HF</sub> = 6), -191.0 (CFH, m); <sup>31</sup> P, 11.1 (dt, <sup>3</sup> J <sub>FP</sub> = 23, <sup>2</sup> J <sub>HP</sub> = <sup>3</sup> J <sub>FP</sub> = 14)
20a	<sup>1</sup> H, 5.45 (CF <sub>2</sub> H, td, <sup>2</sup> J <sub>HF</sub> = 54, <sup>3</sup> J <sub>HF</sub> = 5), -27.36 (IrH, d, <sup>2</sup> J <sub>HP</sub> = 24); <sup>19</sup> F, -68.1 (CF <sub>3</sub> , q, <sup>3</sup> J <sub>FF</sub> = <sup>4</sup> J <sub>FF</sub> = 11), -119.9 (CF <sub>2</sub> H, dd quintet, <sup>2</sup> J <sub>FF</sub> = 272, <sup>2</sup> J <sub>HF</sub> = 56, <sup>3</sup> J <sub>FF</sub> = <sup>4</sup> J <sub>FF</sub> = 11), -127.0 (CF <sub>2</sub> H, dd quintet, <sup>2</sup> J <sub>FF</sub> = 272, <sup>2</sup> J <sub>HF</sub> = 53, <sup>3</sup> J <sub>FF</sub> = <sup>4</sup> J <sub>FF</sub> = 12), -164.4 (CF, dm, <sup>3</sup> J <sub>FP</sub> = 40); <sup>31</sup> P, -3.1 (dd, <sup>3</sup> J <sub>FP</sub> = 40, <sup>2</sup> J <sub>HP</sub> = 24)
20b	<sup>1</sup> H, 6.35 (CF <sub>2</sub> H, td, <sup>2</sup> J <sub>HF</sub> = 54, <sup>3</sup> J <sub>HF</sub> = 5), -27.52 (IrH, d, <sup>2</sup> J <sub>HP</sub> = 24); <sup>19</sup> F, -67.1 (CF <sub>3</sub> , q, <sup>3</sup> J <sub>FF</sub> = <sup>4</sup> J <sub>FF</sub> = 11), -125.20 (CF <sub>2</sub> H, dddd, <sup>2</sup> J <sub>FF</sub> = 278, <sup>2</sup> J <sub>HF</sub> = 56, <sup>3</sup> J <sub>FF</sub> = 14, <sup>4</sup> J <sub>FF</sub> = 9), -128.1 (CF <sub>2</sub> H, dd quintet, <sup>2</sup> J <sub>FF</sub> = 278, <sup>2</sup> J <sub>HF</sub> = 54, <sup>3</sup> J <sub>FF</sub> = <sup>4</sup> J <sub>FF</sub> = 13), -163.3 (CF, dm, <sup>3</sup> J <sub>FP</sub> = 40); <sup>31</sup> P, -3.7 (dd, <sup>3</sup> J <sub>FP</sub> = 38, <sup>2</sup> J <sub>HP</sub> = 24)
21	<sup>1</sup> H, -25.31 (IrH, tdd, <sup>2</sup> J <sub>HP</sub> = 14, <sup>4</sup> J <sub>HF</sub> = 6.7, <sup>3</sup> J <sub>HF</sub> = 5.5); <sup>19</sup> F, -65.0 (CF <sub>3</sub> , ddt, <sup>4</sup> J <sub>FF</sub> = 22, <sup>3</sup> J <sub>FF</sub> = 13, <sup>5</sup> J <sub>FF</sub> = 2), -100.2 (Ir-CF, dm, <sup>3</sup> J <sub>FF</sub> = 131), -167.9 (CF=CF, dm, <sup>3</sup> J <sub>FF</sub> = 131); <sup>31</sup> P, 12.4 (d of quintets, <sup>2</sup> J <sub>HP</sub> = 14, <sup>2</sup> J <sub>FP</sub> = 2)
22	<sup>13</sup> C, 65.0 (d, <sup>1</sup> J <sub>CC</sub> = 43), 71.0 (dd, <sup>1</sup> J <sub>CC</sub> = 43, <sup>1</sup> J <sub>CP</sub> = 3); <sup>31</sup> P, 28.1

<sup>a</sup>Chemical shifts in ppm and coupling constants in Hz, dmf-*d*, solvent, room temperature unless otherwise noted. <sup>b</sup>In propylene carbonate. <sup>c</sup>At -10 °C. <sup>d</sup>DMSO-*d*<sub>6</sub> solvent.

(excepting PhNO<sub>2</sub>) are associated with an Ir-H chemical shift in the range -27 to -29 ppm, whereas for complexes containing nitrogen donors, the shifts are ca. -21 ppm.<sup>14</sup> The same trend could indicate that **6** does in fact contain coordinated dmf. However, we are not certain that correlations in this series of closely related complexes can reliably be extended to other materials that, because they contain quite different ligands, e.g. CO, PF<sub>3</sub>, π-allyl and fluoroalkyl groups (vide infra), probably have very different electronic structures.

**Hydrocarbons. Ethylene.** The reactions of [(Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> with hydrocarbons are summarized in Scheme II. Of all the hydrocarbons studied, ethylene leads to the most complicated, and unexpected, reaction chemistry. The <sup>13</sup>C CPMAS NMR spectrum of the reaction product of **1** and <sup>13</sup>C<sub>2</sub>H<sub>4</sub> shows a peak at 132 ppm due to zeolitic or interlattice ethylene. Some of the zeolitic ethylene is tenaciously retained and not removed under vacuum at room temperature. Another peak, at 40 ppm, is due to π-C<sub>2</sub>H<sub>4</sub> in [(Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>x</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>y</sub>]<sup>+</sup>; this datum cannot define *x* or *y*. This ethylene complex does not survive dissolution in dmf or other polar solvents and the major product in the complicated mixture so produced is the cyclometalated species (Ph<sub>3</sub>P)<sub>2</sub>IrH[C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>]<sup>+</sup> (**7**). It



is formed at the expense of other triphenylphosphine-

containing compounds present even when Ph<sub>3</sub>P is already contained in the solvent and it accounts for 35–45% of the total <sup>31</sup>P intensity. The <sup>31</sup>P NMR spectrum of **7** in dmf at -10 °C shows a very high-field multiplet at -81.7 ppm. The chemical shift is diagnostic for phosphorus in a four-membered ring, P<sub>a</sub>.<sup>15</sup> The coupling constants are given in Table I, and the two-bond P-P coupling constants were confirmed by a <sup>31</sup>P COSY experiment. Careful examination of the NMR data for **7** prepared from <sup>13</sup>C<sub>2</sub>H<sub>4</sub> reveals no detectable (i.e. >3 Hz) coupling to any other magnetically active nuclei attached to iridium, and so it is improbable that this complex contains coordinated ethylene. The Ir-H hydride arises from a molecule of Ph<sub>3</sub>P for no P-H coupling is observed from **7** prepared from [(Ph<sub>3</sub>P-*d*<sub>15</sub>)<sub>2</sub>IrH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, but this splitting persists in the product obtained by using C<sub>2</sub>D<sub>4</sub>.

The <sup>31</sup>P NMR spectra show additional major absorptions at -6.0 and -5.9 ppm. These shift at different rates with temperature, and so two other components present in the mixture can be identified by obtaining variable-temperature spectra.

The complex *cis*-(Ph<sub>3</sub>P)<sub>2</sub>Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> (**8**) is produced in about 10% yield and has δ(<sup>31</sup>P) -6.0 at -10 °C. The coordinated ethylene molecules give rise to two <sup>13</sup>C signals at δ 36.5 (dd, <sup>1</sup>J<sub>CC</sub> = 41 Hz, <sup>2</sup>J<sub>CP</sub> = 13 Hz) and δ 39.1 (dd, <sup>1</sup>J<sub>CC</sub> = 41 Hz, <sup>2</sup>J<sub>CP</sub> = 5 Hz). Spin coupling between the two <sup>13</sup>C centers was confirmed by a homonuclear COSY experiment on a sample made by using <sup>13</sup>C<sub>2</sub>H<sub>4</sub>. The nonequivalence of the CH<sub>2</sub>=CH<sub>2</sub> carbon atoms indicates that the ethylene ligands are rotated so that the C=C bond is not parallel to the P<sub>2</sub>Ir plane. The large (156 Hz) C-H coupling constants observed in a gated decoupling experiment are consistent with a π-olefin complex rather than an iridacyclopropane. Compound **8** is in equilibrium

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with free ethylene for its characteristic  $^{13}\text{C}$  signals sharpen and become more intense on cooling while, concomitantly, the 123.6 ppm peak due to free ethylene decreases in intensity.

Another of the species identified, *trans*-( $\text{Ph}_3\text{P}$ ) $_2\text{Ir}$ -( $\text{C}_2\text{H}_5$ ) $_2^+$  (**9**), is also formed in about 10% yield and has  $\delta(^{31}\text{P})$   $-5.9$  at  $-10^\circ\text{C}$ . The peak appears as a doublet due, in part, to a 6 Hz coupling with the methylene  $^{13}\text{C}$  carbon atom. The 3 Hz fine structure actually represents a 5 Hz quartet whose outer lines are not resolved, due to spin coupling with the methyl protons in the  $\text{Ir}-\text{CH}_2-\text{CH}_3$  moiety. In agreement with this, the  $^1\text{H}$  NMR spectrum contains a 0.48 ppm doublet of quartets with  $^1J_{\text{CH}} = 124$  Hz and  $^4J_{\text{PH}} = 5$  Hz;  $^1\text{H}$  irradiation of this resonance causes collapse of the 3 Hz splitting in the  $^{31}\text{P}$  NMR spectrum. Assignment of the  $^{13}\text{C}$  NMR spectrum of **9** (Table I) was confirmed by the  $^1\text{H}$ -undecoupled spectrum. Shielding of a  $^{13}\text{CH}_2-\text{Ir}$  group is expected and accounts for the observed high-field shift. In dmf, **9** probably contains at least one coordinated solvent molecule.

Understanding of the ethylene reaction chemistry is not completely satisfactory. The initial  $\pi-\text{C}_2\text{H}_4$  complex formed in the solid-gas reaction of **1** and ethylene is destroyed when placed in solvents for the major product **7** found by fluid solution-phase NMR contains three phosphine ligands per iridium compared with two in the starting material. A complex mixture results, and only  $\leq 65\%$  of the starting phosphine ligands are accounted for. Worse yet, because **7** must clearly be formed at the expense of other components present in the reaction mixture, there is no reason to believe that **8** and **9** represent primary products of the reaction of **1** with ethylene. Reactions of **1** with  $^{13}\text{C}_2\text{H}_4$  and, sequentially, with hydrogen have been examined by  $^{13}\text{C}$  CPMAS NMR. Although ethylene is catalytically hydrogenated to ethane, a point confirmed by parallel reactions carried out in a pulsed reactor, no intermediates other than the  $\pi-\text{C}_2\text{H}_4$  complex described above are detectable.

**Propylene, 1-Hexene, and Cyclopentene.** In contrast to ethylene, the reaction of **1** with propylene is "clean" in that it yields a single product,  $[(\text{Ph}_3\text{P})_2\text{IrH}(\pi-\text{C}_3\text{H}_5)]_3\text{PW}_{12}\text{O}_{40}$  (**10**), in high (70%) yield. This product is considered to arise by oxidative addition of iridium to the  $\text{H}-\text{CH}_2$  bond in the propylene methyl group. In this context, it is significant that **10** is formed from **1** and allene only in trivial (2%) conversion and that  $\text{Ir}-\text{H}$  addition to the  $\text{C}=\text{C}$  double bond is a distinctly low-yield process. Results of studies with specifically labeled propylenes have been reported and interpreted previously.<sup>6</sup> Facile formation of the allyl compound **10** indicates the proclivity of  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$  for  $\text{C}-\text{H}$  insertion processes, and, in contrast,  $[(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{solvent})]\text{PF}_6$  reacts with propylene to form metastable  $[(\text{Ph}_3\text{P})_2\text{IrH}_2(\pi-\text{C}_3\text{H}_6)]_2\text{PF}_6$ .<sup>16</sup> Treatment of **10** with hydrogen produces propane and regenerates **1**. A plausible mechanism for catalytic hydrogenation by **1** of olefins containing allylic hydrogen atoms involves formation of a  $\pi$ -allyl intermediate, followed by hydrogenolysis of the  $\text{Ir}-\text{C}$  bond.

1-Hexene is isomerized by **1** to essentially an equilibrium mixture of *cis*- and *trans*-2-hexenes and *cis*- and *trans*-3-hexenes as summarized in Table II; no branched isomers are detected. This rearrangement logically proceeds via an allyl intermediate formed by reversible  $\text{C}-\text{H}$  addition to iridium, just as with propylene. When hydrogen is added to the system, catalytic hydrogenation to *n*-hexane

Table II. Percent of Products Obtained from 1-Hexene and 1-Hexyne Reactions

product <sup>a</sup>	reactants		
	1-hexene	1-hexene + H <sub>2</sub>	1-hexyne + H <sub>2</sub>
1-hexene	1	0.3	32
1-hexyne	0	0.0	63.0
<i>cis</i> -2-hexene	18	4.8	0
<i>trans</i> -2-hexene	58	19	0
<i>cis</i> -3-hexene	3	0.5	0
<i>trans</i> -3-hexene	19	6.9	0
<i>n</i> -hexane	0	69	5.2

<sup>a</sup> Product analysis carried out by  $^{13}\text{C}$  NMR.

also results, cf. Table II. Analysis by  $^{31}\text{P}$  NMR of the catalyst(s) recovered after isomerization or hydrogenation of 1-hexene shows the presence of **1** and, in addition, peaks at 12.6 and 6.0 ppm. The latter chemical shifts are close to those for the  $\pi$ -methallyl analogue of **10** (12.6 and 6.3 ppm, compound **15**, vide infra), and they are therefore attributed to the  $\pi$ -propylallyl intermediate  $(\text{Ph}_3\text{P})_2\text{Ir}(\pi-\text{C}_3\text{H}_7\text{C}_3\text{H}_4)\text{H}^+$ .

Cyclopentene is dehydrogenated in the presence of the hydrogen acceptor *tert*-butylethylene to produce  $[(\text{Ph}_3\text{P})_2\text{IrH}(\text{C}_5\text{H}_5)]_3\text{PW}_{12}\text{O}_{40}$  (**11**), in 90% yield. The NMR spectra of the cation in dmf [ $\delta(^1\text{H})$  5.37 (s, Cp),  $-14.9$  (t,  $^2J_{\text{PH}} = 28$  Hz);  $\delta(^{31}\text{P})$  0.4] agree with previous data.<sup>17</sup> Cyclopentane is inert and does not undergo dehydrogenation to form **11**.

**Acetylene.** The reaction of **1** with excess  $^{13}\text{C}_2\text{H}_2$  forms  $[(\text{Ph}_3\text{P})_2\text{Ir}(\eta^6-\text{C}_6\text{H}_6)]_3\text{PW}_{12}\text{O}_{40}$  (**12**), in high yield. The  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of the cation<sup>18</sup> in propylene carbonate show peaks at  $\delta$  96.1 (d,  $^1J_{\text{CH}} = 175$  Hz) and 1.8 (s), respectively. In the workup procedure, unreacted acetylene is removed by pumping. However, the product still retains zeolitic benzene,  $\delta(^{13}\text{C})$  128.3 ( $^1J_{\text{CH}} = 156$  Hz). The ratio of free to coordinated benzene, determined by integration of the  $^{13}\text{C}$  NMR spectrum, is 4:1. Therefore, acetylene cyclotrimerization is catalytic in this system. We find that **1** does catalyze the hydrogenation of 1-hexyne to 1-hexene, which is not isomerized, and hexane, cf. Table II. However, the process is quite inefficient probably because the catalytically active species is converted to an inactive  $\pi$ -arene complex.

**Benzene, Toluene, and Cyclohexane.** The reaction of **1** with benzene is degenerate in the sense that formation of no new chemical compounds is detected. However, heating **1** with  $\text{C}_6\text{D}_6$  at  $70^\circ\text{C}$  results in exchange between the arene and  $\text{Ir}-\text{H}$  hydrogen atoms. Figure 1 shows the resolution enhanced  $^{31}\text{P}$  NMR spectrum in the 24.0–24.8 ppm region of a typical reaction product as a solution in dmf. Four isotopomers of deuterated  $(\text{Ph}_3\text{P})_3\text{IrH}_2(\text{dmf})_2^+$  are observed. They are, reading from low to high field,  $(\text{Ph}_3\text{P})_2\text{IrD}_2(\text{dmf})_2^+$ ,  $(\text{Ph}_3\text{P})_2\text{IrHD}(\text{dmf})_2^+$ ,  $(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{dmf})_2^+$ , and  $(\text{Ph}_3\text{P}-2-d_1)(\text{Ph}_3\text{P})\text{IrH}_2(\text{dmf})_2^+$ . All of these species are resolved owing to a downfield, two-bond  $^{31}\text{P}$  NMR isotope effect, defined as  $[\delta(^2\text{H form}) - \delta(^1\text{H form})]$ , of  $+0.094$  ppm resulting from replacement of one  $\text{Ir}-\text{H}$  by  $\text{Ir}-\text{D}$ . Introduction of a deuterium into the ortho position of the triphenylphosphine ligand causes an upfield three-bond isotope effect on  $^{31}\text{P}$  shielding of  $-0.055$  ppm.<sup>19</sup> Thus,  $\text{Ir}-\text{H}$  to  $\text{C}-\text{D}$  exchange occurs but, at the temperature needed to observe a significant reaction rate, exchange also takes place between  $\text{Ir}-\text{H}$  and the ortho positions in the  $\text{Ph}_3\text{P}$  phenyl rings.<sup>19</sup> Similarly, exchange with cyclo-

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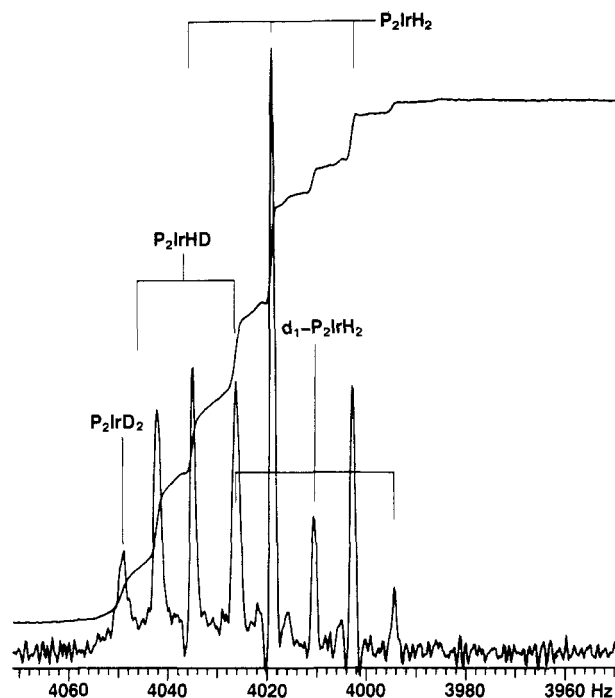


Figure 1.  $^{31}\text{P}$  NMR spectrum showing  $(\text{Ph}_3\text{P})_2\text{Ir}(\text{H},\text{D})(\text{dmf})_2^+$  isotopomers formed by exchange of **1** with  $\text{C}_6\text{D}_6$  at  $70^\circ\text{C}$ .

hexane- $d_{12}$  proceeds very slowly at  $70^\circ\text{C}$ . Rates of inter- and intramolecular exchange are comparable so that minimization of zero-point energy results in accumulation of virtually all the deuterium introduced in the phenyl C-H sites.<sup>19</sup>

$\text{C}_6\text{D}_5\text{CH}_3$  participates in a similar exchange, but  $\text{C}_6\text{H}_5\text{-CD}_3$  does not. We suggest that this selectivity for ring C-H exchange indicates electrophilic attack by iridium on the arene ring although it is emphasized that no  $\sigma\text{-C}_6\text{H}_5\text{-Ir}$  intermediate has been detected. Such a mechanism has been demonstrated for arene C-H bond activation by  $(\text{Me}_5\text{C}_5)\text{Rh}(\text{PMe}_3)$ .<sup>20</sup> Deuterium exchange between **1** and  $\text{C}_6\text{D}_6$  is suppressed by addition of hydrogen to the system, a fact that may acquire mechanistic significance when details of the reaction of **1** with  $\text{H}_2$  are understood.

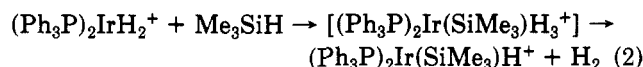
**1,3-Dienes.** The homogeneous reaction between 1,3-dimethylbuta-1,3-diene and  $[(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{acetone})_2]\text{PF}_6$  is reported to yield  $(\text{Ph}_3\text{P})_2\text{IrH}(\eta^3\text{-2,3-dimethylbutenyl})^+$  which features a  $\text{CH}_2\text{-H-Ir}$  agnostic interaction.<sup>21</sup> This diene and a toluene suspension of **1** provide a completely different material, the 2-isopropylallyl compound  $[(\text{Ph}_3\text{P})_2\text{IrH}(\eta^3\text{-2-}i\text{-C}_3\text{H}_7\text{C}_3\text{H}_4)]_3\text{PW}_{12}\text{O}_{40}$  (**13**). It may be regarded as an analogue of **10** but having an isopropyl group on the allyl C2 position, a formulation which is wholly substantiated by the NMR data (Table I). Coupling between the  $\delta$  2.11 and 3.04 syn and anti allylic protons is confirmed by a 2D COSY experiment. None of the  $\eta^3\text{-2,3-dimethylbutenyl}$  complex is detectable by  $^1\text{H}$  NMR analysis.

Isoprene (2-methyl-1,3-butadiene) and **1** react to form the analogous 2-ethylallyl complex  $[(\text{Ph}_3\text{P})_2\text{IrH}(\eta^3\text{-2-C}_2\text{H}_5\text{C}_3\text{H}_4)]_3\text{PW}_{12}\text{O}_{40}$  (**14**). The diastereotopic  $\text{Ph}_3\text{P}$   $^{31}\text{P}$  nuclei are shown by a 2D COSY NMR experiment to be coupled to one another ( $J_{\text{PP}} = 6\text{ Hz}$ ). Both signals evince long-range, poorly resolved coupling to the allylic protons. The Ir-H proton gives rise to a 16-Hz triplet due to cou-

pling to both  $\text{Ph}_3\text{P}$  ligands as shown by a 2D heteronuclear correlation (HETCOR) experiment.

Likewise, butadiene and **1** yield the  $\pi$ -crotyl complex  $[(\text{Ph}_3\text{P})_2\text{IrH}(\eta^3\text{-2-CH}_3\text{-C}_3\text{H}_4)]_3\text{PW}_{12}\text{O}_{40}$  (**15**). The  $\text{Ph}_3\text{P}$  ligands, again, are diastereotopic, cf. Table I. Both butadiene and isoprene, which are less sterically hindered than 2,3-dimethylbutadiene, undergo polymerization in the presence of **1** to form low molecular weight oligomers, the  $^1\text{H}$  resonances of which overlap with and obscure peaks due to the aliphatic and allylic CH signals from **15** and **16**. Thus, it cannot be determined whether **15** is the *syn*- or *anti*-crotyl isomer.

**Trimethylsilane.** In addition to C-H bond activation, **1** also activates the Si-H bond in trimethylsilane, cf. eq 2, in which only iridium-centered reactivity is shown, to



form  $[(\text{Ph}_3\text{P})_2\text{Ir}(\text{SiMe}_3)\text{H}]_3\text{PW}_{12}\text{O}_{40}$  (**16**). A minimalist interpretation of the NMR data (Table I) yields the square-planar *trans*- $(\text{Ph}_3\text{P})_2\text{Ir}(\text{SiMe}_3)\text{H}^+$  structure shown in Scheme II although this cation could certainly contain coordinated dmf in solution. The existence of the reversibly formed intermediate indicated in eq 2 is implied by an isotopic labeling experiment. When the reaction is carried out by using  $\text{Me}_3\text{SiD}$ , unreacted **1** contains  $(\text{Ph}_3)_2\text{IrH}_2^+$ ,  $(\text{Ph}_3)_2\text{IrHD}^+$ , and  $(\text{Ph}_3)_2\text{IrD}_2^+$  in a 75:23:2 ratio according to a  $^{31}\text{P}$  NMR analysis of the dmf solvates.

**Fluoroolefins.** The reactivity of  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$  toward tetrafluoroethylene and hexafluoropropylene, summarized in Scheme III, was of interest because fluorine substitution generally leads to increased stability of  $\pi$ -olefin and  $\sigma$ -alkyl transition-metal complexes. In addition, oxidative addition of C-H bonds to iridium cannot occur with perfluorinated substrates and reaction chemistry should be dominated by processes involving the C=C double bond.

Solid **1** reacts with  $\text{C}_2\text{F}_4$  gas to form  $[\textit{trans}-(\text{Ph}_3\text{P})_2\text{Ir}(\text{H})\text{CF}_2\text{CF}_2\text{H}]_3\text{PW}_{12}\text{O}_{40}$  (**17**) and  $[\textit{cis}-(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_2\text{F}_4)_2]_3\text{PW}_{12}\text{O}_{40}$  (**18**). Yields of **17**, logically regarded as resulting from addition of one of the two Ir-H groups in **1** to  $\text{C}_2\text{F}_4$ , are 30-40%. Compound **18** can be viewed as having been formed by formal displacement of  $\text{H}_2$  by  $\text{C}_2\text{F}_4$ ; the yield varies significantly with  $\text{C}_2\text{F}_4$  pressure, being 10% at 17 psi. High conversions to **18** were never achieved in part because use of tetrafluoroethylene at much higher than 25 psi is hazardous.

A *trans* stereochemistry for  $(\text{Ph}_3\text{P})_2\text{Ir}(\text{H})\text{CF}_2\text{CF}_2\text{H}^+$ , obtained by dissolving **17** in dmf, follows from the NMR data in Table I. The unresolved multiplet at  $\delta$  -67.4 in the  $^{19}\text{F}$  NMR spectrum is due to the  $\text{CF}_2$  group adjacent to iridium for the deshielding effect of transition metals in  $\text{M}-(\text{CF}_2)_n$  groups is well established.<sup>22</sup>

The  $^{31}\text{P}$  NMR spectrum of **18** in dmf shows a quintet centered at -1.8 ppm with  $^3J_{\text{PF}} = 8\text{ Hz}$ . We believe that  $(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_2\text{F}_4)_2^+$  has a *cis* stereochemistry and that the C-C vector in the coordinated  $\text{C}_2\text{F}_4$  is approximately perpendicular to the  $\text{P}_2\text{Ir}$  plane which also represents a mirror plane. The geminal fluorines in each  $\text{CF}_2$  group are inequivalent because one is *syn* to  $\text{Ph}_3\text{P}$  and the other is *syn* to fluorine in the adjacent  $\text{C}_2\text{F}_4$  ligand. Each coordinated  $\text{C}_2\text{F}_4$  molecule thus comprises an  $\text{AA}'\text{XX}'$  spin system due to the nonequivalence of  $^3J_{\text{FF}(\text{cis})}$  and  $^3J_{\text{FF}(\text{trans})}$ . The  $^{19}\text{F}$  NMR spectrum (Figure 2) reflects the complexity of the overall  $\text{A}_2\text{A}'_2\text{MM}'\text{X}_2\text{X}'_2$  spin system ( $\text{A}, \text{X} = ^{19}\text{F}, \text{M}$

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(21) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1981**, 506.

(22) (a) McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1964**, 4200. (b) Treichel, P. M.; Pitcher, E.; Stone, F. G. A. *Inorg. Chem.* **1962**, *1*, 511.

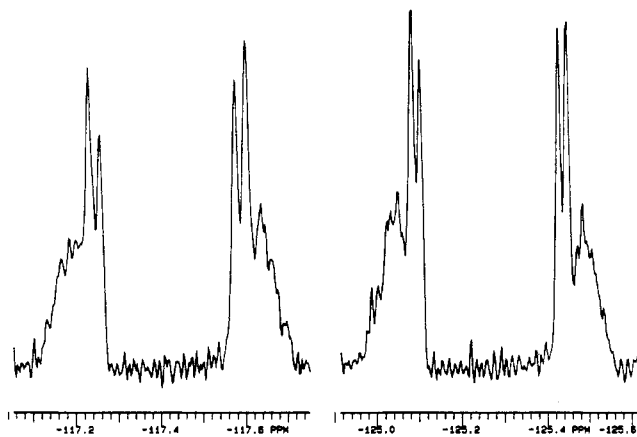


Figure 2.  $^{19}\text{F}$  NMR spectrum of  $\text{cis}-(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_2\text{F}_4)_2^+$ .

=  $^{31}\text{P}$ ) that results. The A and X multiplets have peak maxima at  $-117.3$  and  $-125.2$  ppm. The large splitting in each multiplet gives  $^2J_{\text{AX}} + ^3J_{\text{AX}} \approx 150$  Hz, but absence of other large splittings requires that  $J_{\text{AA}'}$ ,  $J_{\text{XX}'}$ , and  $J_{\text{AX}'}$  are all small. Further analysis requires  $^{31}\text{P}$ -decoupled  $^{19}\text{F}$  spectra which cannot be obtained on our instrument. Even so, because  $^3J_{\text{FF}}$  is small, the  $^2J_{\text{FF}}$  value is significant, for it is typical of a three-membered ring system, cf. 150 Hz in perfluorocyclopropane,<sup>23</sup> and we suggest that metal-fluorocarbon bonding in  $(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_2\text{F}_4)_2^+$  may appropriately be described in terms of a tetrafluoroiridacyclopropane. Consistent with this, the  $^{19}\text{F}$  pattern of 18 is substantially different from that of the  $\pi\text{-C}_2\text{F}_4$  complex  $\text{CpRh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$ .<sup>24</sup> That the 8-Hz  $^3J_{\text{FF}}$  coupling is much smaller than the 25- and 38-Hz values found in  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{F}_4)$ <sup>25</sup> is understandable in view of the quite different compositions and structures.

We have also employed  $^{19}\text{F}$  spin-lattice relaxation times ( $T_1$ ) to characterize the tetrafluoroethylene reaction products. In  $\text{trans}-(\text{Ph}_3\text{P})_2\text{Ir}(\text{H})\text{CF}_2\text{CF}_2\text{H}^+$ ,  $T_1$ 's for the Ir- $\text{CF}_2\text{-CF}_2\text{H}$  and Ir- $\text{CF}_2\text{-CF}_2\text{H}$  fluorines are 0.17 and 0.22 s, respectively. In  $\text{cis}-(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_2\text{F}_4)_2^+$ ,  $T_1$  for the chemically equivalent fluorine nuclei is 0.12 s. For comparison,  $^{19}\text{F}$   $T_1$  was determined for two exemplary small, fluorinated organic molecules in dmf solution. For [1,1,11- $\text{H}_3$ ]perfluoroundecanol,  $T_1$  ranges from 0.79 to 0.57 s:

H-CF <sub>2</sub>	-CF <sub>2</sub>	-CF <sub>2</sub>	-(CF <sub>2</sub> ) <sub>5</sub>	-CF <sub>2</sub>	CF <sub>2</sub>	-CH <sub>2</sub> OH
-137.6	-129.4	-123.4	-121.9	-123.6	-121.7	$\delta(^{19}\text{F})$
0.79	0.72	0.59	0.50	0.55	0.57	$T_1$ , s

In  $\text{cis}$ - and  $\text{trans}$ -1,2- $\text{Cl}_2\text{-c-C}_4\text{F}_6$ ,  $T_1$  for the  $\text{CF}_2$  fluorine sites ranges from 6 to 8.5 s and is  $>15$  s for the  $\text{CFCl}$  sites. Thus, the much shorter  $^{19}\text{F}$   $T_1$  values for 17 and 18 provide additional evidence these correspond to fluorinated ligands in large, complex molecules that, accordingly, have long rotational correlation times.

The reaction of 1 with hexafluoropropylene is formally analogous to that of  $\text{C}_2\text{F}_4$  in that addition of one of the Ir-H groups to the fluorocolefin occurs but there is formed a surprisingly complicated mixture of products that was successfully analyzed only after great effort. Of these, 17, 19, 20a,b, and 21 are believed to contain coordinated dmf in solution.

Addition of one of the Ir-H hydrogens to  $\text{C}_2$  yields the anticipated hexafluoro-*n*-propyl compound [ $\text{trans}$ -

$(\text{Ph}_3\text{P})_2\text{Ir}(\text{H})\text{CF}_2\text{CFHCF}_3]_3\text{PW}_{12}\text{O}_{40}$  (19). The  $\text{trans}$  stereochemistry is indicated by the NMR data in Table I. The Ir-H chemical shift in 19 is  $-25.3$  ppm, but fine coupling cannot be resolved because this peak overlaps the  $-25.3$  ppm peak of 21 (vide infra), a point confirmed by a  $^1\text{H}$ - $^{31}\text{P}$  HETCOR experiment. The  $^1\text{H}$  NMR spectrum does, however, reveal a peak at 3.35 ppm due to the CFH group [ $^2J_{\text{HF}} = 42$  (d),  $^3J_{\text{HF}} = 24$  (d),  $^3J_{\text{HF}} = 6$  Hz (q)]. The  $^{19}\text{F}$  NMR spectrum of 19 is packed with information, cf. Table I, and the F-F couplings listed have been confirmed by a  $^{19}\text{F}$  2D COSY experiment. 19 contains four types of fluorine. Two peaks at  $\delta -48.7$  and  $\delta -68.0$  are due to the diastereotopic fluorine nuclei in the  $\text{CF}_2$  group bonded to Ir; they exhibit a geminal 244-Hz F-F coupling (cf.  $-67.4$  ppm in 17). The accidental degeneracy of  $^3J_{\text{FF}}$  and  $^4J_{\text{FF}}$  (11 Hz) to the terminal  $\text{CF}_3$  is not unexpected, for  $^4J_{\text{FF}}$  are typically 10 Hz and  $^3J_{\text{FF}}$  are very sensitive to the electronegativities of substituents and range from 0 Hz in C-C-F<sub>2</sub>-CF<sub>3</sub> to 18 Hz in  $\text{CF}_2\text{H-CH}_2\text{F}$ .<sup>26</sup>

Also formed from 1 and  $\text{CF}_3\text{CF}=\text{CF}_2$  are two isomers of  $(\text{Ph}_3\text{P})\text{IrH}(\text{dmf})[\text{CF}(\text{CF}_2\text{H})(\text{CF}_3)]^+$  (20a and 20b). Surprisingly, one of the  $\text{Ph}_3\text{P}$  ligands has, for unapparent reasons, been lost and presumably replaced by a dmf solvent molecule. The Ir-H protons in both species show 24-Hz doublet splittings. 20a,b contains a hexafluoroisopropyl group bonded to iridium, and it conceptually arises, as does 19, from addition of Ir-H to the C=C double bond, but here, the hydride emerges on a terminal carbon atom, giving rise to a  $\text{CF}_2\text{H}$  group. The quaternary carbon atom in the  $\text{IrCF}(\text{CF}_2\text{H})(\text{CF}_3)$  is intrinsically chiral. Iridium too can be optically active, even when it is in a nominal square-planar coordination environment, for one of its substituents is chiral. In any event, a rigorous square-planar geometry for the metal and the ligands in its first coordination core is unlikely: the  $\text{Ph}_3\text{P}$  and dmf ligands themselves do not have mirror planes. Therefore, 20 should exist in *d,l* and meso isomers. This is reflected in the panoply of NMR data, cf. Table I. Each of the  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  resonances expected for a single species is accompanied by another nearby, equally intense peak having the same long-range splitting pattern. For example, the  $^1\text{H}$  NMR spectrum shows, in addition to the pair of 24-Hz IrH doublets (vide supra), absorptions at  $\delta 5.45$  (td, 20a,  $^2J_{\text{HF}} = 54$ ,  $^3J_{\text{HF}} = 5$  Hz) and  $\delta 6.35$  (td, 20b,  $^2J_{\text{HF}} = 54$ ,  $^3J_{\text{HF}} = 5$  Hz). It is important to note that assignment of a set of  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  to 20a or 20b is arbitrary because one cannot distinguish between the *d,l* and meso isomers. However, assignments within a set of  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  data are correct:  $^1\text{H}$ - $^{31}\text{P}$  and  $^{19}\text{F}$ - $^{19}\text{F}$  correlations have been established by 2D COSY NMR and the H-F connectivity obtained from single-frequency  $^1\text{H}$ -decoupled  $^{19}\text{F}$  spectra. It is necessary to follow the analysis of the  $^{19}\text{F}$  NMR spectra of only one isomer, 20a, to show that this species actually does contain a hexafluoroisopropyl group; corresponding data for 20b are given in Table I.

The hexafluoroisopropyl group gives rise, as expected, to four  $^{19}\text{F}$  resonances. That at  $-68.1$  ppm (q,  $^3J_{\text{FF}} = ^4J_{\text{FF}} = 11$  Hz) is assigned to the  $\text{CF}_3$  group. Two doublets of doublets of quintets at  $\delta -119.9$  (d,  $^2J_{\text{FF}} = 272$  Hz; d,  $^2J_{\text{HF}} = 56$  Hz; q,  $^3J_{\text{FF}} = ^4J_{\text{FF}} = 11$  Hz) and  $\delta -127.0$  (d,  $^2J_{\text{FF}} = 272$  Hz; d,  $^2J_{\text{HF}} = 53$  Hz; q,  $^3J_{\text{FF}} = ^4J_{\text{FF}} = 12$  Hz) are due to the diastereotopic  $\text{CF}_2\text{H}$  fluorine nuclei and they exhibit a large, 272-Hz, geminal coupling (cf. 244 Hz in 19). Finally, the deshielded  $\text{CF}(\text{CF}_2\text{H})(\text{CF}_3)$  fluorine is assigned to a multiplet at  $-164.4$  ppm that has a clear 40-Hz doublet splitting due to  $^3J_{\text{PF}}$  that correlates with the 40-Hz splitting

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(24) Cramer, R.; Kline, J. B.; Roberts, J. D. *J. Am. Chem. Soc.* 1969, 91, 2519.

(25) Green, M.; Osborn, R. B. L.; Rest, J.; Stone, F. G. A. *J. Chem. Soc. A* 1968, 2525.

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in the  $\delta$  -3.1  $^{31}\text{P}$  signal. The  $\text{CF}_3$  and  $\text{CF}_2\text{H}$  chemical shifts in **20a** are typical of aliphatic fluorine compounds.<sup>27</sup>

When the products obtained from  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$  and  $\text{CF}_3\text{CF}=\text{CF}_2$  are dissolved in dmf, a new set of  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  resonances, whose intensity increases with time, appears. These are due to the pentafluoropropenyl complex **21** that can be derived from **19** by loss of HF and that is, therefore, a secondary product. As noted above, its  $\text{IrH}$   $^1\text{H}$  chemical shift is the same as that of **19**, -25.31 ppm but it is shown by a  $^1\text{H}$ - $^{31}\text{P}$  heteronuclear correlation experiment to be uniquely coupled to the phosphines in **21** that show in the  $^{31}\text{P}$  NMR spectrum a doublet of quintets.

The  $^{19}\text{F}$  NMR spectrum establishes the structure and stereochemistry of the pentafluoropropenyl ligand in **21**. The signal at -66.0 ppm is assigned to the  $\text{CF}_3$  group. A broad doublet at  $\delta$  -100.2 ( $^3J_{\text{FF}} = 131$  Hz) is assigned on the basis of its chemical shift to the vinylic fluorine atom in the  $\text{Ir}-\text{CF}=\text{CF}(\text{CF}_3)$  group; another broad multiplet having  $^3J_{\text{FF}} = 131$  Hz is then due to the other vinylic  $\text{Ir}-\text{CF}=\text{CF}(\text{CF}_3)$  fluorine. The FF coupling constants in **21** agree well with those in  $\text{CF}_3\text{CF}=\text{CF}_2$  for which  $^3J(\text{CF}_3, \text{CF}) = 13$  Hz,  $\text{cis } ^4J(\text{CF}_3, \text{CF}) = 22$  Hz, and  $\text{trans } ^4J(\text{CF}_3, \text{CF}) = 9$  Hz.<sup>28</sup> Thus, the 13- and 22-Hz splittings in the  $\text{CF}_3$  resonance in **21** are assigned to  $^3J_{\text{FF}}$  and  $\text{cis } ^4J_{\text{FF}}$ , respectively, requiring that, as shown in Scheme III, the  $(\text{Ph}_3\text{P})_2\text{IrH}$  and  $\text{CF}_3$  groups are *trans*. The same stereochemical result follows from consideration of the 131-Hz coupling between vinylic fluorine nuclei. This value is typical of *trans* olefinic coupling, always >100 Hz, whereas *cis*  $^3J_{\text{FF}}$  are <50 Hz.<sup>28</sup> The small, 2-Hz, PF coupling is comparable to that in  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CF}=\text{CF}_2)\text{Cl}$ , 4 Hz.<sup>29</sup> Interestingly, **1** catalyzes the dimerization of  $\text{CF}_2=\text{CFCl}$  to form a mixture of *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane; no new organometallic species were detected in this reaction.

**Oxygen-Containing Substrates.** Acetaldehyde is considered to undergo reversible addition of the  $\text{C}(\text{O})-\text{H}$  to the iridium center in  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$ , and, when the reaction is carried out using  $\text{CH}_3\text{C}(\text{O})\text{D}$ , the ratio of  $(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{dmf})_2^+$ ,  $(\text{Ph}_3\text{P})_2\text{IrHD}(\text{dmf})_2^+$ , and  $(\text{Ph}_3\text{P})_2\text{IrD}_2(\text{dmf})_2^+$  isotopomers is 55:39:6. The steady-state concentration of the putative acetyliridium intermediate is likely very small, or the compound decomposes in dmf for, when the reaction is performed with  $^{13}\text{CH}_3-^{13}\text{C}(\text{O})\text{H}$ , no new iridium complexes are detectable by  $^{13}\text{C}$  or  $^{31}\text{P}$  NMR. However, substantial amounts of the cyclotrimerization product trimethyltrioxane,  $\delta(^{13}\text{C})$  98.4 and 20.8 ( $^1J_{\text{CC}} = 50$  Hz), are formed. Acetone is unreactive toward **1** at room temperature and produces neither H-D exchange or new compounds.

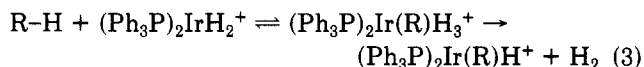
Ethylene- $^{13}\text{C}_2$  oxide reacts with **1** to form low molecular weight poly(ethylene oxide) and a compound containing coordinated ethylene oxide and no  $\text{IrH}$  hydrides,  $(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_2\text{H}_4\text{O})_2^+$  (**22**). Its  $^{13}\text{C}$  NMR spectrum discloses nonequivalent ligand carbon atoms at  $\delta$  65.0 and 71.0 ( $^1J_{\text{CC}} = 43$  Hz).

Hydrogen-deuterium exchange occurs in solid-gas reactions between **1** and  $\text{CH}_3\text{OD}$  or  $\text{D}_2\text{O}$ . In these experiments, methanol or water was contained in a side arm of a Schlenk tube so that solid **1** was exposed to only the vapors from these substrates. High-resolution  $^{31}\text{P}$  analysis revealed that the  $(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{dmf})_2^+:(\text{Ph}_3\text{P})_2\text{IrHD}(\text{dmf})_2^+:(\text{Ph}_3\text{P})_2\text{IrD}_2(\text{dmf})_2^+$  ratios produced by exchange

with  $\text{CH}_3\text{OD}$  and  $\text{D}_2\text{O}$  after 16 h were 19:42:39 and 79:15:6, respectively. The exchangeable protons in methanol are predominantly those on oxygen for a similar reaction with  $\text{CD}_3\text{OH}$  produces  $(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{dmf})_2^+$ ,  $(\text{Ph}_3\text{P})_2\text{IrHD}(\text{dmf})_2^+$ , and  $(\text{Ph}_3\text{P})_2\text{IrD}_2(\text{dmf})_2^+$  in a 90:10:0 ratio.

## Discussion

The reactions of  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$  with a wide variety of small organic molecules have been described. Four general reaction patterns may be discerned. The first involves reversible addition of Ir across a R-H bond followed, in some cases, by elimination of dihydrogen (eq 3).

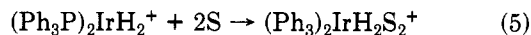


Occurrence of both steps is inferred when a new species,  $(\text{Ph}_3\text{P})_2\text{Ir}(\text{R})\text{H}^+$ , is formed. This is the case when  $\text{R} = \text{Me}_3\text{Si}$  and  $\text{CH}_2\text{CH}=\text{CH}_2$  in which case **16** and **10** are formed. Occurrence of only the first step is detectable by H-D exchange when R-D is employed for which  $\text{R} = \text{Ph}$ ,  $\text{CH}_3\text{C}_6\text{H}_4$ ,  $\text{CH}_3\text{O}$ ,  $\text{HO}$ , and  $\text{CH}_3\text{C}(\text{O})$ .

A second class of reactions involves addition of Ir-H to a C=C double bond (eq 4). This is seen in reactions  $(\text{Ph}_3\text{P})_2\text{IrH}_2^+ + >\text{C}=\text{C} < \rightarrow (\text{Ph}_3\text{P})_2\text{Ir}(\text{H})-\text{C}-\text{CH}^+$  (4)

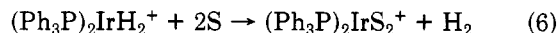
with tetrafluoroethylene and hexafluoropropylene to give **17**, **19**, and, indirectly, **20** and **21**. Propylene itself has the option of reacting by either pathway but clearly adopts the oxidative addition route of eq 3 as do cyclopentene and 2,3-dimethylbuta-1,3-diene. In the latter two examples, additional hydrogen transfer processes intervene and **11** and **13** result.

Simple addition reactions of a substrate, S, can occur, cf. eq 5. This describes the chemistry of CO,  $\text{PF}_3$ , and dmf



that leads to **2**, **5**, **6**, and  $(\text{Ph}_3\text{P})_2\text{IrH}_2(\text{dmf})_2^+$ . However, in order for this reaction to be observed under the experimental conditions used here, it is necessary that the Ir-S bond be stronger than the Ir-(solvent) bond that could form when  $(\text{Ph}_3\text{P})_2\text{IrH}_2\text{S}_2^+$  is dissolved in a polar solvent as is necessary for NMR analysis.

Formal displacement of dihydrogen by a substrate S can also occur (eq 6). In some cases, S, which is always present



in excess, may be reduced to  $\text{SH}_2$  and so coordination of S followed by intramolecular hydrogen transfer to form  $\text{SH}_2$  and coordination of additional S may occur. The only clear-cut example of hydrogen displacement occurs with CO, which yields the tricarbonyl species **3**. Because alkynes are hydrogenated, albeit sluggishly, to alkanes, the reaction of **1** with acetylene is probably best viewed as proceeding by the second pathway to produce ethane and  $(\text{Ph}_3\text{P})_2\text{Ir}(\text{C}_2\text{H}_2)_2^+$  upon which cyclotrimerization to give **12** occurs after addition of more acetylene.

It is significant that new organometallic compounds are formed in high yields in the reactions of  $[(\text{Ph}_3\text{P})_2\text{IrH}_2]_3\text{PW}_{12}\text{O}_{40}$  with organic substrates. A case in point is the reaction with cyclopentene in which the iridium cyclopentadienyl complex **11** is formed in 90% yield. This fact requires that at least 90% of the iridium centers be accessible to cyclopentene and, in general, indicates that substrates are able to extensively penetrate the lattice of **1**. Reactivity is not confined to the surface for 70% of the iridium sites cannot all be on the surface of **1** which has a surface area, measured by BET nitrogen physisorption, of only  $16 \text{ m}^2 \text{ g}^{-1}$ . These reactions, in common with many

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(28) Reilly, C. A.; Swalen, J. D. *J. Chem. Phys.* **1961**, *34*, 2122.

(29) Reference 23, p 85.

other heterogeneous processes, often lead to disorder in the lattice and formation of poorly crystalline or amorphous products. However, the reaction of 1 with cyclopentene does not lead to gross physical breakup of the solid (cf. exfoliation reactions of layered materials such as graphite and MoS<sub>2</sub>) and the surface area of 1 after conversion of 11 actually decreases to 5 m<sup>2</sup> g<sup>-1</sup>.

Previously, the platinum oxometalate compound [(Et<sub>3</sub>P)<sub>2</sub>PtH(CH<sub>3</sub>CN)]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> has been characterized as a chemically microporous solid.<sup>9</sup> This means that the solid has few or no permanent structural features such as pores or channels through which small organic molecules could gain access to the interior platinum sites. Microporosity in hydrated NH<sub>4</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> Keggin ion salts that leads to preferential reactivity of hydrophilic substrates because of their solubility in the water-filled portions of the lattice has been described.<sup>30,31</sup> Small molecules such as acetonitrile were considered to enter the solid platinum oxometalate by dissolving, on a molecular scale, in the hydrophobic regions of the lattice comprised by the ligand alkyl groups in a process analogous to swelling of organic polymers by solvent vapors.

We believe that [(Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> exhibits similar phenomena and that this is why high conversions to new organometallic species are possible in the face of a low intrinsic surface area; and that this is why the surface area does not greatly increase after such reactions. The interior of a hypothetical unit cell of 1 is expected to contain large hydrophobic regions comprised by the many phenyl rings, 12 per iridium site. Therefore, reactivity (and selectivity) at iridium may be controlled, inter alia, by solubility of a reactant in these hydrophobic regions. Recognizing that the vapor pressure of methanol is higher than that of water, we suggest that solubility in the hydrophobic portions of the lattice is the reason why CH<sub>3</sub>OD is very much more efficient than D<sub>2</sub>O in achieving H,D exchange at the IrH sites in 1.

### Experimental Section

NMR spectra were obtained on Varian XL-200 and -400 instruments operating at 200 and 400 MHz for protons. Chemical shifts are expressed relative to external (CH<sub>3</sub>)<sub>4</sub>Si (<sup>1</sup>H and <sup>13</sup>C), CFC1<sub>3</sub> (<sup>19</sup>F), or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) with positive shifts being downfield of the references. Typical <sup>31</sup>P NMR spectra were obtained with single frequency decoupling of the aryl protons in the Ph<sub>3</sub>P ligands; the decoupler power is insufficient to simultaneously decouple both these and IrH protons. As a consequence, coupling to protons in the 0–5 ppm region is attenuated.

Symmetrized two-dimensional <sup>19</sup>F COSY spectra of 19–22 were obtained at 188 MHz by using a 1024 × 1024 data matrix, 512 increments, 32 transients for each spectrum with a 1.0-s recycle time, and a 28820 Hz sweep width for a resolution of 29 Hz/point. The 2D <sup>19</sup>F COSY spectra of 17 and 18 were obtained at 376 MHz by using a 2048 × 2048 data matrix and 1024 increments for comparable resolution. Pseudoecho (Lorentz–Gauss) window functions were used for data processing. Symmetric 2D <sup>31</sup>P COSY spectra were typically obtained at 161 MHz with a 1024 × 1024 data matrix, 8700 Hz sweep width, 1.0-s delay between transients, and 512 points in the t<sub>1</sub> dimension for a resolution of 17 Hz/point.

Heteronuclear [<sup>1</sup>H]<sup>31</sup>P correlation experiments were performed by using 5-kHz sweep widths in the second dimension centered about the IrH resonance and 8-kHz sweep widths in the <sup>31</sup>P dimension, a 1.1-s recycle time, and 256 transients for each of 128 increments under typical conditions. The resolution in the <sup>31</sup>P dimension was 16 Hz. Because there is no filtering in the <sup>1</sup>H dimension, the offset was carefully adjusted so that the strong aromatic and aliphatic resonances would not overlap IrH ab-

Table III. Summary of Reaction Conditions and Yields of Organometallic Cations

product (% convn)	reactn conditns <sup>a,b</sup>
2 (49), 3 (49)	250 mm of <sup>13</sup> CO, 16 h
6 (90)	300 mm of PF <sub>3</sub> , 16 h
7 (50)	100 psi of C <sub>2</sub> H <sub>4</sub> , 72 h
10 (70)	120 psi of C <sub>3</sub> H <sub>6</sub> , 16 h
11 (70)	0.2 mL of <i>c</i> -C <sub>6</sub> H <sub>10</sub> , 0.1 mL of <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>2</sub> H <sub>5</sub> , 3 mL of toluene, 16 h, 90 °C
12 (60)	700 mm of <sup>13</sup> C <sub>2</sub> H <sub>2</sub> , 48 h
13 (95)	0.2 mL of C <sub>6</sub> H <sub>10</sub> , 1 mL toluene, 36 h
15 (60)	0.2 mL of C <sub>4</sub> H <sub>6</sub> (measured as liquid), 48 h
16 (50)	400 mm of Me <sub>3</sub> SiH, 48 h
17 (30), 18 (10)	17 psi of C <sub>2</sub> F <sub>4</sub> , 16 h
19 (33)	neat C <sub>3</sub> F <sub>6</sub> , 72 h
22 (70)	0.05 mL of <sup>13</sup> C <sub>2</sub> H <sub>4</sub> O (measured as liquid), 20 h

<sup>a</sup> Typical reactions employed 0.12–0.15 g of 1. <sup>b</sup> At room temperature unless otherwise noted.

sorptions when folded back into the proton spectrum. Very intense correlations to the folded aromatic absorptions were observed because <sup>3</sup>J<sub>PH</sub> to the six equivalent ortho positions is ca. 8 Hz. Delays in the correlation experiments were optimized for a heteronuclear coupling of 22 Hz, a compromise between the long delays needed for 16 Hz couplings and the short delays desirable for observation of signals before transverse relaxation occurs.

<sup>19</sup>F spin–lattice relaxation times were measured by using a standard +180° – τ – –90° sequence but using composite pulses for the 180° pulse. Spectra were taken for nine values of τ ranging from 0.1 to 2.0 s with a 7.0-s recycle time.

Reactions of 1 with gases and low boiling liquids were conducted in Schlenk tubes having a volume of ca. 8 mL and fitted with 10-mm J. Young vacuum stopcocks. The substrates were introduced under pressure (CO and PF<sub>3</sub>) or by transfer on a diffusion-pumped vacuum line (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>F<sub>6</sub>, Me<sub>3</sub>SiH, CH<sub>3</sub>C(O)H). Pressures <1 atm were measured with a capacitance manometer. *Caution!* Reactions carried out above atmospheric pressure must be carried out in well-shielded apparatus. Reactions with substrates liquid at room temperature (e.g. cyclopentene) can be carried out as a well stirred suspension of 1 in toluene or neat (benzene, toluene). Tetrafluoroethylene, freed of limonene polymerization inhibitor by passage over activated carbon, is a special case. *Caution!* C<sub>2</sub>F<sub>4</sub> can form explosive mixtures with air; the energy yield is far too high for any cavalier handling of C<sub>2</sub>F<sub>4</sub>. This fluorocarbon was used in a stainless-steel vacuum system, and reactions were conducted in a glass-lined metal reactor. Tetrafluoroethylene can undergo vigorous self-polymerization at pressures above 2.7 atm. Reaction conditions and conversions to products are summarized in Table III. Products were isolated by removal of solvent (if any) and excess reactant under vacuum. Solutions in dry (4A molecular sieves), degassed dmf-*d*<sub>7</sub> were then prepared under nitrogen. Yields reported in Table III are expressed as percent conversion of the (Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub><sup>+</sup> units to the species indicated. We have no definitive diffraction data to support the claim that new, discrete crystalline phases are formed in these reactions in which, operationally, one type of cation of 1 is replaced by another. The potential for cation–cation disorder is plain. We focus here only on the new organometallic cations produced.

**Synthesis of [(Ph<sub>3</sub>P)<sub>2</sub>Ir(C<sub>6</sub>H<sub>12</sub>)]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.** To a solution of 1.13 g of [(Ph<sub>3</sub>P)<sub>2</sub>Ir(C<sub>6</sub>H<sub>12</sub>)]PF<sub>6</sub> (twice recrystallized from acetone–diethyl ether) (1.17 mmol) in 40 mL of acetone was added dropwise with stirring 1.2 g of hydrated (H<sub>3</sub>O)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> in 5 mL of acetone. The pink product precipitated and was collected on a filter and then washed with 3 mL of fresh solvent. The yield, after vacuum drying, was 1.84 g (87%).

**Synthesis of [(Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (1).** A 0.2-g sample of [(Ph<sub>3</sub>P)<sub>2</sub>Ir(C<sub>6</sub>H<sub>12</sub>)]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was placed in a glass tube that was connected to a vacuum system. The container was evacuated to <10<sup>-5</sup> mm and then backfilled to 700 mm with hydrogen. Formation of 1 can be followed visually as the pink color of the cyclooctadiene complex is replaced by the very pale yellow color of the product. After 15 min, the hydrogen was pumped away; the residue was kept under dynamic vacuum for 16 h to remove

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cyclooctane. Proton NMR analysis indicates the presence of ca. 0.3 molecule of lattice acetone/(Ph<sub>3</sub>P)<sub>2</sub>Ir unit. Additional characterization data, including elemental analyses, NMR, and X-ray powder diffraction results, are given in ref 6. Compound 1 often contains small amounts, ca. 5%, of an impurity having  $\delta(^{31}\text{P}) -7.5$  (d,  $J_{\text{HP}} = 21$  Hz) and  $\delta(^1\text{H}) -27.4$  (t, 21) (in dmf). This we attribute to a decomposition product of (Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub><sup>+</sup> for it is present in reactions carried out at elevated temperatures and is a major product formed when 1 is heated at 180 °C in a sealed tube.

**Registry No.** 1, 115794-94-0; 2, 115777-39-4; 3, 115805-05-5; 4, 120410-53-9; 5, 120410-55-1; 6, 115805-07-7; 7, 120410-57-3; 8, 120410-59-5; 9, 120410-61-9; 10, 115731-73-2; 11, 115777-38-3; 12,

115777-37-2; 13, 120410-63-1; 14, 120410-65-3; 15, 120410-67-5; 16, 120410-69-7; 17, 115777-41-8; 18, 115805-09-9; 19, 120410-71-1; 20, 120410-73-3; 21, 120410-75-5; 22, 120410-78-8; CO, 630-08-0; PF<sub>3</sub>, 7783-55-3; C<sub>2</sub>H<sub>4</sub>, 74-85-1; C<sub>2</sub>H<sub>2</sub>, 74-86-2; C<sub>3</sub>H<sub>6</sub>, 115-07-1; C<sub>6</sub>H<sub>6</sub>, 71-43-2; CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>, 108-88-3; CH<sub>2</sub>=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=CH<sub>2</sub>, 513-81-5; CH<sub>2</sub>=CHC(CH<sub>3</sub>)=CH<sub>2</sub>, 78-79-5; CH<sub>2</sub>=CHCH=CH<sub>2</sub>, 106-99-0; Me<sub>3</sub>SiH, 993-07-7; C<sub>2</sub>F<sub>4</sub>, 116-14-3; C<sub>3</sub>F<sub>6</sub>, 116-15-4; CF<sub>2</sub>=CFCl, 79-38-9; CH<sub>3</sub>C(O)H, 75-07-0; CH<sub>3</sub>OH, 67-56-1; CH<sub>2</sub>=CH(C-H<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, 592-41-6; CH=C(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, 693-02-7; [(Ph<sub>3</sub>P)<sub>2</sub>Ir-(C<sub>6</sub>H<sub>12</sub>)<sub>2</sub>]PF<sub>6</sub>, 61817-47-8; (H<sub>3</sub>O)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, 1343-93-7; [(Ph<sub>3</sub>P)<sub>2</sub>Ir-(C<sub>6</sub>H<sub>12</sub>)<sub>2</sub>]PW<sub>12</sub>O<sub>40</sub>, 115731-66-3; (Ph<sub>3</sub>P)<sub>2</sub>IrD<sub>2</sub>(dmf)<sub>2</sub><sup>+</sup>, 115731-71-0; (Ph<sub>3</sub>P)<sub>2</sub>IrHD(dmfd)<sub>2</sub><sup>+</sup>, 115731-70-9; (Ph<sub>3</sub>P)<sub>2</sub>IrH<sub>2</sub>(dmfd)<sub>2</sub><sup>+</sup>, 115731-69-6; (Ph<sub>3</sub>P-2-*d*)(Ph<sub>3</sub>P)IrH<sub>2</sub>(dmfd)<sub>2</sub><sup>+</sup>, 120410-76-6; C<sub>6</sub>D<sub>6</sub>, 1076-43-3; cyclopentene, 142-29-0; ethylene oxide, 75-21-8.

## Asymmetric Synthesis. Molecular Graphics and Enantioselection in Asymmetric Catalytic Hydrogenation

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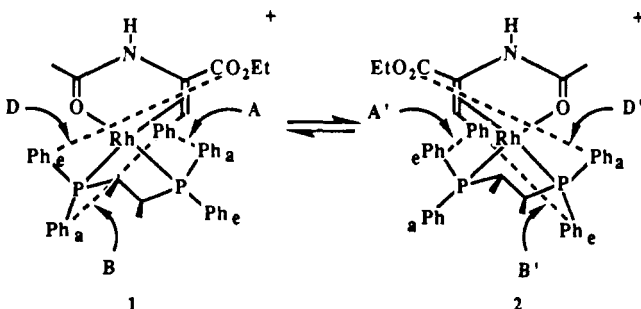
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Molecular graphics and associated energy calculations are used to analyze the addition of H<sub>2</sub> to the major and minor diastereomer precursors for asymmetric catalytic hydrogenation of ethyl *N*-acetyl- $\alpha$ -aminocinnamate with [Rh((*S,S*)-chiraphos)]<sup>+</sup>. It is found that, of the eight possible modes of H<sub>2</sub> addition, six paths generate impossibly large atom-atom interactions between the substrate and the *P*-phenyl groups suggesting that it is improbable that these paths engage in asymmetric hydrogenation. The two remaining paths, one for each isomer, appear to be devoid of strong atom-atom interactions. The details of the molecular graphics analysis are presented, and it is suggested that the approach provides a systematic, formal method of molecular model building which may prove superior to the current intuitive use of molecule models for assessing steric interactions. Molecular graphics may be helpful in designing asymmetric catalysts.

### Introduction

Asymmetric catalytic hydrogenation of amino acid precursors by chiral bidentate (phosphine)rhodium(I) catalysts is one of the most efficient synthetic methods of generating amino acids.<sup>1,2</sup> The mechanism of catalysis is understood in great detail<sup>3-5</sup> but the precise structural origins of the enantioselection remains a matter of speculation. The following features are established for the reduction of ethyl *N*-acetyl- $\alpha$ -aminocinnamate (see 1 and



2) by the [Rh((*S,S*)-chiraphos)]<sup>+</sup> catalyst ((*S,S*)-chiraphos = Ph<sub>2</sub>PCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)PPh<sub>2</sub>). First, the ee is >95%. Second, chelated (*S,S*)-chiraphos exists in the conformation shown in 1 and 2<sup>6,7</sup> where the *P*-phenyl groups are arranged in axial (a) and equatorial (e) dispositions. Third, the substrate is bound to the metal as a bidentate chelate

via the olefin and the acyl oxygen atom, 1 and 2.<sup>3</sup> Fourth, the major diastereomer is in rapid equilibrium with the minor isomer 2 and the equilibrium is displaced strongly to 1. Fifth, the minor isomer 2 is the more reactive isomer so that the prevailing enantiomer of the product originates from the minor isomer. Sixth, the addition of H<sub>2</sub> to these two isomers is both the turnover limiting as well as the enantioselective step at 25 °C and 1 atm of H<sub>2</sub>. Since the addition of H<sub>2</sub> is the first irreversible step involving diastereomeric transition states, the structural origins of the enantioselectivity are completely defined by this step.<sup>8</sup>

This note describes a highly approximate method for analyzing the steric interactions of the enantioselective step. The method employs computer-driven molecular graphics and van der Waals (VDW) energy minimization for identifying these interactions. The process we describe amounts to a sophisticated method of model building

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