tions 5 and 9 (the computations show the former to be ca. 100 times slower than reaction 6) gives $d[2]/dt \simeq k_1k_3[1]/(k_2 + k_3 + k_4)$ and $d[3]/dt \simeq k_1k_4[1]/(k_2 + k_3 + k_4)$. Over the temperature range in question, $k_3/(k_2 + k_3 + k_4)$ has a temperature dependence of ca. 23 kJ·mol^{-1}, while the temperature dependence of $k_4/(k_2 + k_3 + k_4)$ is ca. −1 kJ·mol^{-1}, both agreeing quite well with the results of the more accurate numerical integration calculation.

Thus, there is no single rate-determining step in Scheme I; of course, the *rate constant* k_1 is much less than the others, but the *rates* of individual reactions are closer to each other because the concentrations of the intermediates are so small.

Acknowledgment. We thank the SERC and Dow Corning (Europe) for generous support and Dr. K. J. Hughes for valuable preliminary experiments[7] on the pyrolysis of 1.

Solid-State Organometallic Chemistry of Molecular Metal Oxide Clusters: C–H Activation by an Iridium Polyoxometalate

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Summary: Hydrogenation of $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ in a solid-gas reaction produces $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$. EXAFS studies of the molybdenum analogue indicate the presence of isolated, lattice-stabilized $(Ph_3P)_2IrH_2^+$ ions. H—D exchange with $CD_3CH{=}CH_2$ occurs via a reversible C—H addition reaction that also produces $[(Ph_3P)_2IrH(\pi\text{-}C_3H_5)]_3PW_{12}O_{40}$ and scrambles the $C_3D_3H_3$ deuterium label. Exchange with toluene is selective and involves activation of aromatic but not aliphatic C–H bonds. Slow exchange with $c\text{-}C_6D_{12}$ also occurs.

We are investigating the solid-state chemistry of materials formed from organometallic cations and anionic molecule metal oxide clusters[1,2] and have synthesized iridium oxometalates which, in their heterogeneous reactions with small organic molecules, exhibit substantial scope and diversity, here illustrated by C–H activation processes. It will be seen that incorporation of such cations into polyoxometalate lattices drastically changes the course of both preparative and reaction chemistry which are qualitatively and unexpectedly different from that observed in related homogeneous systems.

Table I. Distribution of Deuterium in $[(Ph_3P)_2Ir(H,D)(C_3H_5)]_3PW_{12}O_{40}$ and $[(Ph_3P)_2Ir(H,D)_2]_3PW_{12}O_{40}$ Formed from Labeled Propylenes

	obsd (calcd),[a] %				
substrate	$(C_3H_5)Ir{-}H$	$(C_3H_5)Ir{-}D$	IrH_2	IrHD	IrD_2
$CD_3CH{=}CH_2$	58 (50)	48 (50)	43	44	13
$CH_3CD{=}CH_2$	78 (83)	22 (17)	96	4	0
$CH_3CH{=}CD_2$	67 (67)	33 (33)	84	16	0
$c\text{-}C_3D_6$	22 (0)	78 (100)	81	18	1

[a] Assuming statistical incorporation of substrate deuterons into the product.

Metathetical reaction of $[(Ph_3P)_2Ir(C_8H_{12})]PF_6$ with hydrated $(H_3O)_3PM_{12}O_{40}$ (M = Mo, W) in acetone provides pink $[(Ph_3P)_2Ir(C_8H_{12})]_3PMo_{12}O_{40}$ (1) and $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ (2): $\delta(^{31}P)$ MAS 11, 5, −15; $E_b[Ir(4f_{7/2})] = 62.6$ eV; λ_{max} (log ϵ) 388 (3.6), 478 (3.6), 572 (2.7) nm (DMSO).[3–6] Treatment of solid 1 or 2 with hydrogen at 1 atm quantitatively yields cyclooctane and pale yellow $[(Ph_3P)_2IrH_2]_3PMo_{12}O_{40}$ (3) and $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ (4): $\delta(^{31}P)$ MAS 30, −15; $E_b[Ir(4f_{7/2})] = 62.5$ eV; surface area (N_2 adsorption) = 15.8 M^2 gm^{-1}.[6,7] Both 3 and 4 are insoluble in noncoordinating, nonreactive solvents. Dissolution in dimethylformamide produces $(Ph_3P)_2IrH_2(DMF)_2^+$ [$\delta(^1H)$ −27.8 (t, J_{PH} = 15 Hz); $\delta(^{31}P)$ 24.8]; because no hydrogen is evolved, it is improbable that 3 and 4 are dihydrogen complexes. Anion effects are already manifest for heterogeneous reduction of the BF_4^- or PF_6^- salts of $(Ph_3P)_2Ir(C_8H_{12})^+$ produces binuclear $(Ph_3P)_4Ir_2H_5^+$.[8,9]

Reduction of these derivatives of molecular metal oxide clusters parallels that of $[(Ph_3P)_2Ir(C_8H_{12})]PF_6$ in acetone which affords $[(Ph_3P)_2IrH_2(acetone)_2]PF_6$,[10] but here, it occurs in a solid–gas process in which no additional, coordinating solvents are present. Fourier transforms of the iridium L3 edge EXAFS spectrum of 3 provides a radial distribution function shifted by −0.1 Å relative to that of 1. The transform of the EXAFS of 3 displays a single

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(1) (a) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. A.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219. (b) Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Skarjune, R. P.; Hodgson, K. O.; Roe, A. L.; Day, V. W. *Solid State Ionics* **1988**, *26*, 109.

(2) Siedle, A. R. U.S. Patent 4673753, 1987.

(3) Hydrated $(H_3O)_3PW_{12}O_{40}$ was obtained from Alfa Products. ^1H NMR analysis indicates that **2** contains variable and up to 0.3 mol of acetone per $(Ph_3P)_2Ir(COD)^+$ unit. This zeolitic or lattice acetone has ν_{CO} 1708 cm^{-1} (Nujol), and it is not coordinated to iridium. In $[(Ph_3P)_2IrH_2(acetone)_2]PF_6$, ν_{CO} is 1664 cm^{-1}. When the hydrogenation of **2** is carried out in a pulsed reactor, it is seen that some of this acetone is released; the weak CO stretching band from residual acetone is not shifted. The IR spectra of **1–4** show no bands due to water.

(4) The −15 ppm signal is due to the $PW_{12}O_{40}^{3-}$ cluster. Splitting of the Ph_3P resonance is attributed to crystallographic nonequivalence of the $(Ph_3P)_2Ir(C_8H_{12})^+$ units: $\delta(^{31}P)$ (DMSO-d_6) 14.5, −14.5.

(5) Magic-angle spinning (MAS) and solution-phase chemical shifts are expressed relative to external $(CH_3)_4Si$ (^{13}C) or 85% H_3PO_4 (^{31}P). X-ray photoelectron binding energies, E_b, are referenced to the C(1s) line at 285.0 eV.

(6) Anal. Calcd for **1** (Found): C, 37.1 (36.8); H, 3.1 (2.9); Ir, 13.3 (13.0); Mo, 26.6 (27.0); P, 5.0 (4.9). Calcd for **2** (Found): C, 29.9 (29.4); H, 2.4 (2.3); Ir, 10.7 (10.3); P, 4.0 (4.1); W, 40.9 (39.9). Anal. Calcd for **3** (Found): C, 32.6 (32.5); H, 2.4 (2.5); Ir, 14.5 (14.7); Mo, 29.0 (29.3); P, 5.5 (5.7). Anal. Calcd for **4** (Found): C, 25.8 (25.8); H, 1.9 (2.1); Ir, 11.4 (11.7); P, 4.3 (4.6); W, 43.9 (42.8). The data are insensitive to small amounts of zeolitic solvent.

(7) **2**: ^1H NMR (DMSO-d_6): δ 7.3–7.7 (m, Ph, 90 H), 4.31 (s, $=CH$, 12 H), 2.43 (d, CH_2, 12 H), 2.1 (s, $CH_3)_2CO$, 5.4 H), 2.03 (d, CH_2, 12 H); ^{13}C NMR (DMSO-d_6): δ 134.12 (C2,6), 131.09 (C4), 129.26 (d, 55, C1), 128.49 (C3,5), 86.21 (=CH), 30.47 (CH_2). X-ray powder pattern: strong lines at $d_{h,k,l}$ (I/I_0) 15.992 (100), 13.483 (37), 13.081 (31), 12.316 (30), 9.528 (46), 8.788 (48), 5.245 (33) Å.

(8) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994.

(9) Crabtree, R.; Felkin, H.; Morris, G. E.; King, T. J.; Richards, J. A. *J. Organomet. Chem.* **1976**, *113*, C7.

(10) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Crabtree, R. H.; Hlatky, G.; Parnell, C. P.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354.

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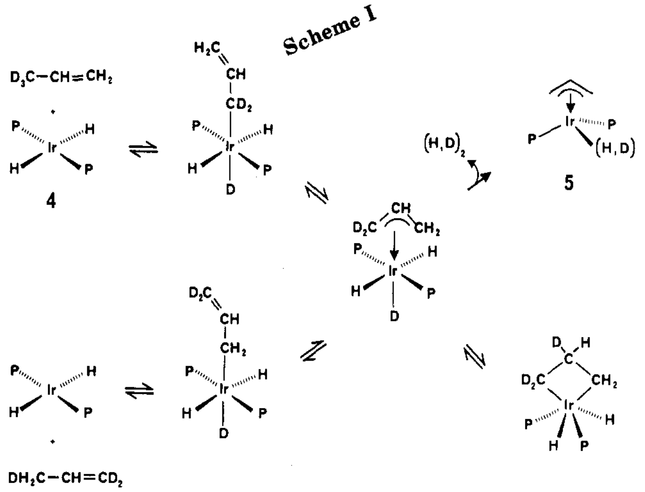
Scheme I



strong peak at 2.2 Å due to backscattering from coordinated phosphorus.[11] No peaks due to scattering from molybdenum are observed. We infer therefore that **3** contains isolated, lattice-stabilized $(Ph_3P)_2IrH_2^+$ units because coordination of iridium to the exterior oxygen atoms of the $PMo_{12}O_{40}^{3-}$ cluster should give rise to a Mo–Ir contact sufficiently short (<4 Å) to have been discerned by EXAFS. Similar lattice stabilization of 14e Rh(I) occurs in the bifunctional catalyst $[(Ph_3P)_2Rh(CO)]_4SiW_{12}O_{40}$.[1,2]

$[(Ph_3P)_2IrH_2(solvent)_2]BF_4$ (solvent = H_2O, acetone) in CD_2Cl_2 reacts with propylene to form stable $[(Ph_3P)_2IrH_2(propylene)_2]BF_4$.[8] In contrast, insertion of Ir into C–H bonds is a pervasive feature of the solid-state organometallic chemistry of **4**. Solid **4** reacts with $CH_3{}^{13}CH{=}CH_2$ at ca. 120 psi[12] at ambient temperature to form as the sole ^{13}C-containing product $[(Ph_3P)_2IrH(\pi\text{-}C_3H_5\text{-}2\text{-}^{13}C)]_3PW_{12}O_{40}$ (**5**): $\delta(^{13}C)$ MAS 101; $\delta(^{31}P)$ MAS 10, −15. Thus, no rearrangement of the C_3H_6 carbon framework occurs. The yield of **5** is ca. 70% after 16 h.[13] Subsequent treatment of **5** with H_2 produces **4** and propane. Deuterium-labeling studies reveal that this propylene reaction is surprisingly complex.

When **5** is prepared from $CD_3CH{=}CH_2$, the product contains 58% Ir–H and 42% Ir–D. This indicates that the protons and deuterons derived from the propylene are nearly completely redistributed (a random distribution would give 50% each Ir–H and Ir–D). Further, ^1H, ^2H, and ^{13}C NMR demonstrate intramolecular scrambling in the recovered $C_3D_3H_3$ and that the deuterium distribution in the 1-, 2-, and 3-positions is in a 1.01:0.32:1.66 ratio. Unreacted **4** also incorporates the deuterium label. This may be ascertained from the resolution-enhanced ^{31}P NMR spectrum, for the two-bond deuterium isotope effect on ^{31}P is −0.094 ppm. The three isotopomers $(Ph_3P)_2IrH_2(DMF)_2^+$ (43%), $(Ph_3P)_2IrHD(DMF)_2^+$ (44%), an $(Ph_3P)_2IrD_2(DMF)_2^+$ (13%) have $\delta(^{31}P)$ 24.816, 24.910, and 25.004 respectively, and are readily resolved. The results of labeling experiments with $CD_3CH{=}CH_2$, $CH_3CD{=}CH_2$, and $CH_3CH{=}CD_2$ are summarized in Table I. The striking features of the **4**/propylene chemistry are the following: (1) $CD_3CH{=}CH_2$ is, if kinetic isotope effects are neglected, most effective and $CH_3CD{=}CH_2$ least effective in incorporating deuterium into $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$; i.e., the exchange is selective; (2) deuterium transfer to iridium in $[(Ph_3P)_2Ir(H,D)(\pi\text{-}C_3H_5)]_3PW_{12}O_{40}$ is nonselective and nearly random; (3) deuterium in unreacted propylenes is extensively scrambled. These findings can be accommodated by the reactions shown in Scheme I; equilibrium among all species is not established during the experiment. A reversibly formed allyl–Ir intermediate permutes protons on C1 and C3 as shown for one exchange cycle. An iridacyclobutane is proposed to account for H,D exchange at C2 (a complete exchange cycle is not shown).[14] Compound **5** is also formed from cyclopropane-d_6 and **4**. Because no isomerization to propene occurs,[15] a different intermediate must be involved. Activation of C–H bonds, as revealed by H–D exchange, also occurs with toluene-d_8 at 70 °C. Experiments with $C_6D_5CH_3$ and $C_6H_5CD_3$ show that the exchange is selective, involving aromatic and not methyl C–H bonds. The exchange is suppressed by addition of hydrogen.[16-18] Cyclohexane-d_{12} exchanges slowly.

Molecular metal oxide clusters have an unusual ability, not exhibited by small, unipositive anions such as BF_4^- or PF_6^-, to stabilize highly reactive, coordinatively unsaturated organometallic cations exemplified by $(Ph_3P)_2IrH_2^+$. In $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$, the heterogeneous chemistry that transpires at the iridium center diverges from that reported for fluid phase systems in which solvent–metal coordination occurs. We believe the solid-state chemistry of these and similar materials to be exceptionally rich. Additional experiments are underway to further define the reactions of iridium polyoxometalates with small organic molecules.

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Registry No. **1**, 115731-65-2; **2**, 115731-66-3; **3**, 115794-93-9; w4, 115794-94-0; **5**, 115731-68-5; $[(Ph_3P)_2Ir(C_8H_{12})]PF_6$, 61817-47-8; $(H_3O)_3PMo_{12}O_{40}$, 12026-57-2; $(H_3O)_3PW_{12}O_{40}$, 1343-93-7; $(Ph_3P)_2IrH_2(dmf)_2^+$, 115731-69-6; $(Ph_3P)_2IrHD(dmf)_2^+$, 115731-70-9; $(Ph_3P)_2IrD_2(dmf)_2^+$, 115731-71-0; $[(Ph_3P)_2Ir(H)(C_3H_5)]_3PW_{12/40}$, 115731-73-2; $[(Ph_3P)_2Ir(D)(C_3H_5)]_3PW_{12}O_{40}$, 115731-75-4; $[(Ph_3P)_2Ir(H)(D)]_3PW_{12}O_{40}$, 115731-77-6; $[(Ph_3P)_2Ir(D)_2]_3PW_{12/40}$, 115731-79-8.

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[11] X-ray absorption data were collected in the transmission mode on beam line IV-1 at the Stanford Synchrotron Radiation Laboratory using a silicon (220) monochromator. Samples were kept at room temperature in a He atmosphere. Data reduction to obtain the Fourier transform was performed as outlined by: Cramer, S. P.; Hodgson, K. O.; Steifel, E. I.; Newton, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 2748.

[12] Reactions were carried out in Schlenk tubes fitted with 10-mm high vacuum stopcocks obtained from J. Young Co. *Caution*: High-pressure reactions must be conducted in well shielded equipment.

[13] NMR data for **5** in DMF-d_7: $\delta(^1H)$ 2.05 (dd, $J_{H\text{-}H2} = 8$, $J_{PH} = 6$ Hz, $H_{1,3}$ anti), 3.38 (d, $J_{H\text{-}H2} = 4$ Hz, $H_{1,3}$ syn), 5.96 (m, H_2), −28.7 (t, $J_{PH} = 15$ Hz, Ir*H*); $\delta(^{13}C)$ 57.3 ($J_{CH} = 158$, $J_{C1\text{-}C2} = 42$, $J_{CP} = 28$ Hz, $C_{1,3}$), 99.1 ($J_{CH} = 165$ Hz, C_2); $\delta(^{31}P)$ 9.9, −7.6 (cage P).

[14] Adam, G. J. A.; Davies, S. G.; Ford, K. A.; Ephritikhine, M.; Todd, P. F.; Green, M. *J. Mol. Catal.* **1980**, *8*, 15.

[15] Compound **4** induces no isomerization of cyclopropane detectable by GC/MS analysis.

[16] This observation and the fact that the IrH protons in **4** exchange with D_2 suggest that $[(Ph_3P)_2IrH_4]_3PW_{12}O_{40}$ may form. High-pressure NMR experiments to test this possibility are in progress.

[17] Heterogeneous C–H activation by MgO has been reported by: Ito, T.; Lunsford, J. H. *Nature (London)* **1985**, *314*, 1985. Hoq, M. F.; Klabunde, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 2114.

[18] Exchange between D_2 or C_2D_4 and a series of phosphine-substituted metal hydrides in benzene solution has been reported by Schunn, R. A. *Inorg. Chem.* **1970**, *9*, 2576. In these homogeneous reactions, ligand dissociation may be mechanistically significant.