

the geometry of the aromatic units in the *o*-methylstyrene copolymer can be more safely based on X-ray data.¹¹

In our calculations the contribution to the CD from the perturbation of each aromatic chromophore by the chiral surrounding has been explicitly neglected (which also implies $\Delta\epsilon_A = K_{ABBB} = 0$ in eq 1). For the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition this is not a valid assumption because of the very low dipole strength of this transition. In ac-

cordance with this, the calculated CD is very small, and the observed CD therefore must be due to the local site symmetry of each aromatic chromophore.¹⁷

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Catalytic Properties of Metal Phosphides. I. Qualitative Assay of Catalytic Properties¹

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Abstract: Preparation of transition metal phosphides supported on alumina was effected by deposition of metal complexes or organometallic compounds on alumina followed by hydrogen reduction and then reaction with phosphine at $\sim 200^\circ$. A variety of catalytic reactions was utilized to probe the surface chemistry of these phosphides. In the H_2 -1-butene reaction, phosphorus introduction onto the metal surface changed the reaction course from hydrogenation to isomerization. With ruthenium phosphide surfaces, there was a relatively selective inter-action of acetylene and hydrogen to give ethylene. Yet under these same conditions ethylene and hydrogen reacted quite exothermally to give ethane. Acetylene and acetylene plus hydrogen appear to give a surface template of considerable stability; this template then appears to direct the chemical reaction. The acetylene-hydrogen produced template may be primarily σ -bonded vinyl groups which pyrolyze to acetylene and hydrogen (and ethane). Acetylene reacts with the metal phosphide surface in a complex fashion as indicated by the flash pyrolysis products from acetylene treated phosphide. These products include methane, ethane, acetylene, monovinylacetylene, butenes, pentenes, and benzene. The presence of benzene in high concentration in the acetylene reaction suggests multicenter surface sites while the lack of activity of the phosphides for butene hydrogenation indicates that the size and extent of surface metal clusters are quite small.

A systematic chemical and physical investigation of the catalytic properties of transition metal phosphides has been initiated. Preliminary studies comprise a probing of the active surface sites in phosphides through a variety of catalytic reactions. This first report presents the procedure for preparation of the metal phosphides on an alumina support and a qualitative comparison of the catalytic properties of the phosphide with the parent metal and in some instances with the metal sulfide. For further comparisons, metal antimonides were prepared and catalytically assayed.

Selection of the phosphides for detailed catalytic studies is based on two major considerations. Firstly, phosphides are a structurally diverse group although a ubiquitous feature in metal-rich phases is a trigonal prismatic M_3P polyhedron.⁴⁻⁶ Catenation of phos-

phorus atoms arises in the phosphorus-rich phases where phosphorus chains run through the structure.⁴⁻⁶ Physical properties range from metallic to near-insulator like in character.⁴⁻⁶ Because there are gross structural and electronic similarities to sulfides, a need to compare catalytic properties of phosphides and sulfides was anticipated. Secondly, an especially attractive feature of phosphides stems from a crude and perhaps invalid analogy to the importance of phosphorus ligands in homogeneous catalysis.⁷⁻¹² Phosphine and phosphite ligands are a common element in catalytically active discrete coordination complexes. These ligands through electronic and steric effects and through their lability play a critical role in enhancing the $16 \rightleftharpoons 18$ electron traverse^{10,11} for the metal complex, a traverse that is the essential feature for "oxidative addition-reductive elimination" steps involving organic substrates.⁷⁻¹² The "ligand lability" feature cannot be important in the

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metal phosphides but phosphorus may stabilize vacant surface sites adjacent to metal atoms. These vacant sites could be key features in selective interactions of organic or inorganic molecules at the surface and would increase the possibility of multiple interactions of molecules with a single surface metal atom.

Catalytic properties of some metal phosphides have been reported,¹³⁻¹⁹ but the preparative methods described for the phosphides were such that gross metal oxide surface contamination *may* have marked distinguishing catalytic features. To minimize ambiguities concerning surface composition, a preparative procedure was devised for deposition of transition metals or the precursor complex on η or γ alumina with this process and all subsequent steps effected in an inert (helium) or reducing ($H_2 + PH_3$) atmosphere. The deposited metal or metal complex was then phosphidized by treatment with PH_3 at $\sim 200^\circ$. These supported catalysts—never exposed to air—were then evaluated in a series of catalytic reactions that comprised (A) H_2 - D_2 -HD exchange, (B) olefin hydrogenation, isomerization, dimerization, and polymerization, and (C) acetylene hydrogenation. The catalysts were then compared with the catalytic properties of the alumina support, the support plus metal, support plus metal oxide, and supported metal sulfides.

Experimental Section

Materials. All gases were purchased from Air Products Co. 1-Butene was >99% pure, isobutylene was CP grade, and propylene was CP grade (98% with $\sim 2\%$ N_2). No impurities were detected by mass spectroscopy in the ethylene and butadiene. η -Alumina pellets and silica gel granules were purchased from Davison Chemical Co. γ -Alumina was purchased from Harshaw Chemical Co. Phosphine was obtained from Rocky Mountain Research, Inc. The metal carbonyls used in this work were purchased from a variety of commercial sources, and the precious metal derivatives were obtained from Engelhard Industries. Stibine, made by a literature procedure,²⁰ was carried in a stream of helium through a drying tower into the reactor. The acetylene was Matheson "Pure" grade and was further purified by a concentrated sulfuric acid scrubbing followed by passage through a trap containing KOH pellets. This treatment effectively removed impurities such as acetone, arsine, and phosphine.

Preparation of Phosphide Catalysts. Two procedures were utilized to prepare the phosphide catalysts. In the A type procedure the metal or metal precursor was deposited on the alumina support (the details of the deposition procedure for the various phosphides are described below). The phosphiding step consisted of passing a mixture of phosphine and helium (1:4 M ratio) over the catalyst containing the metal or metal precursor for a period of about 2 hr at temperatures in the range of 250–300°. An alumina control, pretreated with phosphine, was prepared by passing the phosphine-helium mixture over the alumina pellets at 325° for 3 hr (average phosphorus content after phosphine treatment was about 1–1.5%). In procedure B the alumina was treated with the metal carbonyl and phosphine in a shaker tube that was heated under

autogenous pressure to temperatures in the range of 275–300° for a period of 3 hr. Alternatively, the phosphine was excluded in the first step. After the pretreatment the pellets were recovered in an inert atmosphere and then were subjected to the standard treatment with phosphine in a quartz reactor. The substrate in most cases was η -alumina pellets ($1/8$ in.). All operations were effected in helium or nitrogen atmospheres up to the point that the catalytic evaluation was initiated.

The following are the details for the deposition of a metal or the metal precursor on the support by procedure A (glass apparatus, inert atmosphere). For nickel, the alumina was exposed to nickel carbonyl vapor diluted with helium at room temperature for a period of 2 hr. After phosphiding, the nickel and phosphorus contents were in the range of 5–6%, and X-ray analysis showed the presence of Ni_3P . In the following slurry-impregnation procedures, 60 g of alumina pellets were used. For the cobalt, the alumina pellets were slurried with a 200-ml solution of dicobalt octacarbonyl (30 g) in benzene for a 2-hr period and then dried in helium at 200°. After phosphiding the average cobalt and phosphorus contents were respectively 3 and 5%. For ruthenium, the alumina was slurried at 60° with a 100-ml solution of triruthenium dodecacarbonyl (30 g) in benzene. The recovered pellets were dried at 75° for 4 hr. After phosphiding, the average ruthenium and phosphorus contents were about 2 and 3%. For rhodium, the alumina pellets were slurried with a 100-ml solution of rhodium(III) chloride (10 g) in water for 2 hr. The recovered pellets were dried in a helium atmosphere at 75°. After the phosphine treatment, the average rhodium and phosphorus contents were 5%. For palladium, the pellets were slurried in a 200-ml solution of palladium(II) chloride (5 g) in 60° water to which sufficient hydrochloric acid had been added to effect dissolution of the palladium salt. The recovered pellets were dried at 80° under vacuum and then further treated in a helium-hydrogen atmosphere at 100–200° for 18 hr. After the phosphine treatment, the palladium and phosphorus contents were about 1%. (Another palladium phosphide was obtained by simply treating palladium sponge with the phosphine-helium mixture for 3 hr. The phosphorus content was 10%.) For platinum, the pellets were slurried with a 70-ml solution of platinum-(II) chloride (5 g) in ammonium hydroxide. The recovered pellets were dried at 120° for 18 hr and then at 200° for 1 hr (helium flow). After phosphine treatment, the platinum and phosphorus contents were about 3 and 1.5%, respectively. The modified nickel phosphides were obtained by a preliminary deposition of the metal carbonyl by the slurry technique followed by treatment of the pellets with nickel carbonyl vapor diluted with helium at 50–100° for 2 hr.

The procedure B details were as follows. About 60 g of alumina and 0.05–0.10 mol of the metal precursor were placed in a 300-ml stainless steel pressure vessel which was then evacuated. Fifteen grams of phosphine was condensed in the vessel which was then closed. The vessel was then heated at 300° for 3 hr and was agitated throughout the reaction. Molybdenum hexacarbonyl yielded a phosphide that contained on the average about 9% molybdenum and 6% phosphorus. Tungsten hexacarbonyl yielded a phosphide that contained about 7% tungsten and 8% phosphorus. Iron pentacarbonyl gave a phosphide that contained about 5% iron and 13% phosphorus.

Preparation of Sulfides and Antimonides. The sulfides were made by the technique described above for the atmospheric pressure syntheses of phosphides. The sulfiding step was effected with an H_2S -He mixture at 75–150° in a 1.5-hr period. The sulfur content of these catalysts was substantially lower than for the phosphides. Ruthenium, rhodium, nickel, and palladium all had sulfur contents in the range of 0.5–0.8% with the metal contents being about the same as found for the phosphides. The antimonides were prepared from stibine by an analogous procedure. In the antimoniding step, stibine diluted with helium was passed over the pellets at 100–150° for 1 hr. The ruthenium and nickel antimonides that were used for the studies with 1-butene had the following compositions: 0.3% ruthenium, 0.5% antimony and 6.3% nickel, 15% antimony.

Catalyst Characterization. The surface area of representative catalysts prepared on η -alumina varied from 110 to 160 m^2/g and the untreated alumina was 133 m^2/g . "Pyrolysis" of the phosphide catalysts at 100–300° produced no detectable phosphine.

X-Ray data were often uninformative because the samples were amorphous. Diffraction data indicated that the nickel phosphides were mainly Ni_2P with small amounts of NiP_2 , Ni_3P_2 , Ni_7P_3 , or possibly Ni_5P_4 , platinum phosphides where crystalline were PtP_2 , palladium phosphides were Pd_6P or Pd_5P_2 , and iron phosphides

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Table I. Hydrogen + 1-Butene Reaction

Catalyst ^a	Temperature, °C	% butane	% <i>trans</i> -2-butene	% <i>cis</i> -2-butene	% 1-butene
Ruthenium phosphide	75	Trace	23.0	12.6	64.4
	145	10.0	48.0	25.0	10.0
Ruthenium phosphide	125	Trace	21.0	12.0	67.0
	175	0.5	36.0	24.0	39.5
Rhodium phosphide	75	0	8.4	12.3	79.3
	175	0	12.3	15.4	72.3
	225	Trace	11.5	15.0	73.5
Palladium phosphide	80	38.8	24.8	14.7	21.7
	175	Trace	20.7	20.7	58.6
	225	Trace	38.2	26.2	35.6
Platinum phosphide	150	7.0	11.4	5.6	76.0
	160	10.7	14.3	8.3	66.7
Nickel phosphide	150	3.0	14.0	8.0	75.0
(Rhenium activated)	200	6.0	39.0	21.0	34.0
Molybdenum phosphide	125	0	17.0	13.0	70.0
	175	Trace	20.8	20.9	58.3
Ruthenium sulfide	75	2.6	28.4	15.7	53.3
	125	2.3	24.0	17.0	56.7
	175	2.4	29.0	18.1	50.5
Rhodium sulfide	75	3.2	50.0	25.0	21.0
	125	4.8	60.6	26.7	7.9
	175	3.1	57.1	31.9	7.9
Palladium sulfide	125	Trace	13.0	13.0	74.0
	175	Trace	44.4	33.0	22.2
Nickel sulfide ^b					
Ruthenium antimonide	110	16.8	18.6	10.6	54.0
	175	33.6	21.2	12.5	32.7
Nickel antimonide	115	23.2	5.7	2.6	68.5
	185	34.0	13.5	7.5	45.0
	175		8.0 ^d		92.0
η -Alumina control ^e	85	57.0	20.0 ^d		23.0
Ni ^c	25		3.0 ^d		27.0
	35		13.0 ^d		87.0
Rh ^c	75	6.8	66.8 ^d		24.4
	75	53.5	44.0 ^d		2.5
	80	57.0	40.3 ^d		2.7
Ru ^c	70	27.0			73.0
	90	73.4	5.3 ^d		21.3
	>100	100			
PtCl ₂ ^c	130	60.0	5.0 ^d		35.0
	145	100			
	105	2.5	12.3 ^d		85.2
Mo ^c	125	4.9	39.9 ^d		55.2

^a η -Alumina support. ^b Inactive to 175°; low conversions to 2-butene from 225 to 275° with only traces of butane. ^c High dilution of 1-butene for these "control" reactions. ^d Cis and trans. ^e Pretreated with phosphine at 250°.

were Fe₂P or FeP. Confirmatory evidence for formation of phosphides by the metal-PH₃ route was obtained by electron diffraction studies. A nickel phosphide was prepared by laying down a coating of nickel over a carbon-coated titanium grid. A phosphine-helium mixture was passed over this sample for 3 min at 200°. Electron diffraction studies indicated about 95% Ni₂P. Hence where diffraction data were definitive, metal-rich phosphides were indicated; however, the surface may well have been rich in phosphorus.

Catalyst Evaluations. Equipment and Analytical Procedure. The catalyst evaluations were carried out in quartz reactors 18 mm o.d. and about 11 in. long. The thermocouple well inside the reactor was 6 mm o.d. The usual catalyst charge was 5 g of 1/8 in. pellets. Heat was applied by an electric furnace and the temperature was measured in an inner thermocouple placed about the middle of the catalyst bed and an outer thermocouple placed to measure the temperature at the outside of the quartz reactor but very close to the catalyst bed.

With the 1-butene rearrangement, the products were passed through a Varian Model No. 1700 gas chromatograph. The column contained ethyl *N,N*-dimethylxalamate on 60-80 mesh acid-washed firebrick packed in a 6 ft length of 1/4 in. copper tubing. The coiled column, immersed in ice water, was operated with a 50 ml/min stream of helium. With ethylene and propylene, the products were passed through the gas chromatographic column described above after first going through a trap cooled in ice water. With both gases, no liquid condensates were observed. Gaseous products were characterized by mass spectroscopy, in addition to

gas chromatography. In experiments involving acetylene, a gas chromatograph column containing Poropak N 50-80 packed in a 6 ft length of 1/4 in. stainless steel tubing was used. Helium at a rate of 50 ml/min was passed through the coiled tubing heated at 75-135°. With isobutylene, a trap cooled in ice water was used to condense the dimer, which was characterized by infrared and nmr analyses.

1-Butene-Hydrogen Reaction. The gas mixture passed over the catalyst consisted of 1-butene (100 cm³/min), hydrogen (100 cm³/min), and helium (90 cm³/min). Under these conditions, most of the metal "controls" reduced 1-butene to butane very rapidly so the gas composition was changed on these "control" reactions to 1-butene (about 40 cm³/min), hydrogen (75 cm³/min), and helium (740 cm³/min). Yields listed in the table are based on the areas under the gc peaks; no other products were detected by gc. The temperature states were usually held for 20 min before advancing to the next higher temperature. The experimental results are summarized in Table I.

Dimerization of Isobutylene. The gas mixture passed over the catalyst consisted of isobutylene (150 cm³/min) and helium (150 cm³/min). The temperature states were usually held for 20 min before advancing to the next higher temperature. In all cases, controls consisting of the metal on alumina (not phosphided) and supported metal sulfides with the exception of palladium sulfide did not catalyze the dimerization, or any other reaction, of isobutylene. The experimental results are listed in Table II.

The isobutylene dimers, as characterized by ir and nmr, indicated an 80:20 mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-

Table II. Dimerization of Isobutylene

Catalyst ^a	Temp, °C	% conversion
Iron phosphide	50	12.5
	100	28.0
	200	7.0
Molybdenum phosphide	75	10.0
	125	15.0
Platinum phosphide	100	15.0
	150	12.5
Palladium phosphide	125	1.5
	175	7.0
Ruthenium phosphide	150	7.0
	200	3.0
Rhodium phosphide	150	3.0
	210	10.0
Nickel-rhenium phosphide	150	15.0
	200	12.5
Nickel-cobalt phosphide	150	12.5
	200	10.0
Tungsten phosphide	175	7.0
	225	Trace
Cobalt phosphide	175	7.0
	225	Trace
Palladium sulfide	Below 200	No activity
	200	12.0

^a η -Alumina support.

trimethyl-2-pentene. This composition corresponds very closely to the products obtained by the acid-catalyzed dimerization of isobutylene.²¹

Hydrogenation of Ethylene and Propylene. A gaseous mixture of ethylene (35 cm³/min), hydrogen (15 cm³/min), and helium (800 cm³/min) was passed over a ruthenium phosphide catalyst. There was no reaction until 125° at which point the heat of reaction was pronounced and the catalyst bed temperature rose to about 200°. A gas sample at the beginning of the temperature excursion showed ethylene and ethane to be in a 3:2 ratio. When the temperature first reached 200°, the off-gas composition was 1:3, and after 20 min at 200° it was 1:10 ethylene. Propylene showed precisely this same behavior.

Reaction of Acetylene and of Acetylene-Hydrogen with Ruthenium Phosphide. Helium (30 cm³/min) and hydrogen (30 cm³/min) were passed over a ruthenium phosphide catalyst at 100° for several minutes. After cooling the catalyst bed in helium to 50°, a mixture of acetylene (15 cm³/min) and helium (60 cm³/min) was passed over the catalyst for 1 hr. The reactor was then allowed to cool to room temperature in the He-C₂H₂ atmosphere. The catalyst was recovered without exposure to air and then placed in the spectrometer inlet. Chemisorbed species detected (relative molar amounts) at 150 and 300° pyrolysis conditions are shown in Table III (relative amounts).

Table III

	150°	300°		150°	300°
C ₆ H ₆	0.9	0.2	C ₂ H ₂	0.2	
C ₅ H ₁₀	0.2		H ₂	3.0	32.5
C ₄ H ₈	0.6		C ₄ H ₁₀	Trace	0.5
CH ₂ =CHC≡CH	0.2		C ₃ H ₆	Trace	0.5
C ₂ H ₆	1.5	3.4	CH ₄	2.0	16.5

A similar experiment was made with acetylene and hydrogen over ruthenium phosphide catalyst. Mass spectroscopic analysis at 150 and 300° detected the molecules (relative molar amounts) shown in Table IV.

Acetylene Hydrogenation. Acetylene (35 cm³/min), hydrogen (35 cm³/min), and helium (600 cm³/min) were passed over ruthenium phosphide. There was no reduction below 120°, at which point about 1% of the acetylene was converted to ethylene. At 175°, 16% of the C₂ off-gas was ethylene. By contrast, an analo-

Table IV

	150°	300°
C ₂ H ₂	1.0	
C ₂ H ₆	0.6	0.8
CH ₄		6
H ₂	3.5	26
<i>n</i> -Butane		0.2

gous ethylene-hydrogen mixture was rapidly reduced by this catalyst; the C₂ off-gas was 40% ethane at 125°, 100% at 200°. Similar results were obtained with propylene hydrogenation over the ruthenium catalyst.

Acetylene-1-Butene-Hydrogen Competitive Reaction. A gas mixture of 1-butene (35 cm³/min), hydrogen (10-15 cm³/min), and helium (800 cm³/min) was passed over the ruthenium phosphide catalyst (first entry in Table I). 1-Butene was isomerized to 2-butene at 55-75°. At 75°, acetylene (35 cm³/min) was introduced into the gas stream. No further isomerization of 1-butene to 2-butene took place, even with temperature increase to 175°. In an analogous experiment, the gas mixture of acetylene, 1-butene, and hydrogen was introduced at room temperature; no 2-butene was formed at temperatures up to 125°.

Acetylene-Ethylene-Hydrogen Competitive Reactions. Ethylene (30 cm³/min), acetylene (35 cm³/min), hydrogen (15 cm³/min), and helium (600 cm³/min) were passed over a rhodium phosphide catalyst. In the absence of acetylene, this catalyst promoted the dimerization of ethylene to a butene mixture at 175°. In the presence of acetylene, ethylene dimerization was completely suppressed at this temperature. Similar results were obtained with a ruthenium phosphide catalyst. With both catalysts, acetylene was very slowly hydrogenated to ethylene at temperatures above 125°.

Dimerization of Ethylene. Ethylene (125 cm³/min) and helium (250 cm³/min) were passed through the catalyst bed at temperatures ranging from 75 to 275°. Rhodium phosphide produced a 6% yield of 1- and 2-butenes at 175-225° while platinum phosphide only gave traces of butenes. Other phosphides or sulfides and a number of metal controls were also inactive.

Dimerization or Other Reactions of Propylene. Propylene (40 cm³/min) and helium (150 cm³/min) were passed over rhodium, ruthenium, and molybdenum phosphides at temperatures increasing from 75 to 275°. No liquid condensates were obtained; only propylene was detectable by gas chromatography. There was also no reaction when these same catalysts were preactivated with hydrogen. No reaction other than hydrogenation (75-125° range) was found when the propylene contained 10% by volume of hydrogen.

Polymerization of Ethylene under Pressure. The polymerization of ethylene was attempted in stainless steel shaker tubes (80 cm³ size). The tubes were thoroughly dried, purged with nitrogen, and charged with 1 g of catalyst. Polymerization activity was scouted at 50-250° and 100-900 atm pressure developed by ethylene injection. This series of experiments was then repeated except that 0.002 mol of hydrogen was added prior to ethylene injection. Low molecular weight polyethylene, the amounts being about two- to fivefold greater in the hydrogen-activated series, was obtained using rhodium, nickel, and platinum phosphides.

Butadiene. Butadiene (300 cm³/min) and helium (50 cm³/min) were passed over representative phosphide catalysts at temperatures increasing from room temperature to 200°. No liquid condensate was observed nor did the gas chromatograms indicate anything other than butadiene. Addition of hydrogen to the butadiene stream did not alter the results; not even hydrogenation was detectable.

Nitrobenzene Reduction. To reexamine the report of nitrobenzene reduction to aniline with phosphide catalysts,¹⁸ our ruthenium and rhodium phosphides were compared to a commercial palladium metal catalyst control. These two phosphides gave about 60% yields of aniline while the palladium control produced a 75% yield. Conditions were as described by Sweeny, *et al.*,¹⁸ except that the phosphide runs were carried out at 380° and the control run at 225°.

Hydroformylation-Carbonylation Reactions. Attempts to hydroformylate propylene with Rh, Ru, rhenium-activated Ni, or Pd phosphides as catalysts were unsuccessful with a 1:1 molar mixture of carbon monoxide and hydrogen at 150° and 35 atm. The experiments were repeated at 150° and 100 atm. Similar attempts to carbonylate acetylene were also unsuccessful.

(21) C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley, New York, N. Y., 1970, p 116.

Discussion

Introduction of phosphorus atoms into the alumina supported metallic phase invariably resulted in a reduced over-all activity toward a gaseous mixture of an olefin and hydrogen. This reflects primarily a drastic reduction in hydrogenation rate for the phosphide as compared with metal. For example, rhodium and a rhodium phosphide at 75° gave 87 and 0% hydrogenation of 1-butene, respectively. Reduced hydrogenation rates were also observed for metal phosphides where the metal alone is a poor hydrogenation catalyst; note in Table I the data for molybdenum and phosphided molybdenum.²² Ruthenium phosphide treated with a mixture of H₂ and D₂ at 50° and then pyrolyzed at 150 and at 250° in the mass spectrometer inlet yielded primarily H₂. There was very little deuterium incorporation indicating a relatively low number of active metal-hydrogen surface sites. The intrinsic hydrogen content of the phosphides seemed to be largely associated with subsurface sites. As noted below, the phosphides as prepared (hydrogen atmosphere) were active catalysts for most olefin and acetylene reactions only when hydrogen was added to the reactant stream.

All phosphides elicited the isomerization of 1-butene to *cis*- and *trans*-2-butene if and only if hydrogen was present. The alumina support, pretreated with phosphine at 325°, catalyzed no reaction between hydrogen and 1-butene. Isomerization rates for phosphides generally did not match the hydrogenation rates of the metal although a phosphided ruthenium had an activity that was about one-eighth that of the ruthenium metal control at 75°. This particular ruthenium system nicely illustrates the difference between metal and metal phosphide where the former yielded butane and no 2-butene and the latter 23% *trans*- and 13% *cis*-2-butene and a trace of butane. The analogous antimonide not only had substantially less activity for isomerization but also for hydrogenation. Only in the molybdenum system was the metal more effective in the isomerization reaction. Activity of the phosphides for olefin isomerization paralleled that for hydrogen-deuterium exchange. Ruthenium phosphide was only modestly active at 50° but at 100° converted an H₂-D₂ mixture to a near statistical H₂-HD-D₂ mixture.

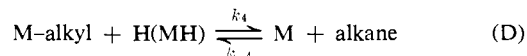
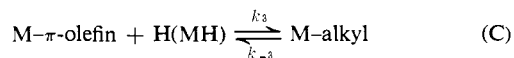
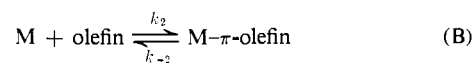
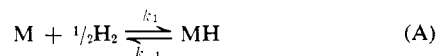
Although the phosphides catalyzed no reaction for 1-butene alone, they did catalyze dimerization of isobutylene to 2,4,4-trimethyl-1-pentene and the 2-pentene analog. Especially active in the dimerization reaction were phosphides of iron, platinum, molybdenum, and nickel. No alumina supported metal or metal sulfide was found active for this dimerization reaction.

Nickel, ruthenium, and rhodium phosphides catalyzed the hydrogenation of acetylene to ethylene at 150–200°. A consecutive reaction comprising hydrogenation of ethylene was also detected but the rate was quite low. Addition of 1-butene did not substantially affect the acetylene hydrogenation reaction but there was no evidence of butene isomerization. Addition of acetylene to a reaction system in which butene isomerization was proceeding quickly quenched the isomerization reaction. This revealing phenomenon was

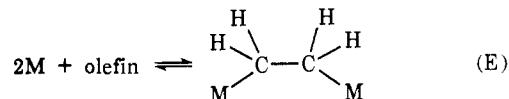
(22) Isomerization of olefins by metal sulfides, in the presence of hydrogen, has been reported. For example, see K. H. Bourne and P. D. Holmes, German Patent 1,283,221, Aug 7, 1962.

observed with ruthenium phosphide which is a very effective isomerization catalyst. Clearly acetylene ties up the surface coordination sites necessary for the butene isomerization reaction. In fact, pretreatment of the phosphide catalyst with acetylene and hydrogen at 50–100° is sufficient to block the butene isomerization until temperatures of ~125° are attained, where the characteristic isomerization reaction finally ensues. Temperatures of ~125° were necessary for reasonable rates in the acetylene hydrogenation reaction. Pretreatment of the catalyst with acetylene alone also inhibits butene isomerization. Competitive experiments also showed acetylene inhibition of ethylene dimerization and of ethylene hydrogenation; the latter is fast at 125° in the absence of acetylene.

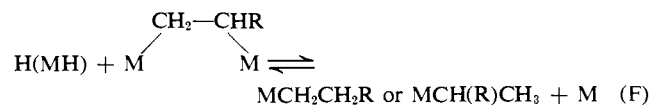
Facile hydrogenation of 1-butene may follow a conventional homogeneous³ model of



where k_4 is large with respect to k_3 and where isomerization may occur in step C. Steps B and C may be formally cast in an alternative bonding form which is strongly implicated by physical studies of ethylene on metal surfaces.^{23–25} Interaction of metal with olefin may involve a σ -bonded ethylene bridge between two metal sites or atoms.



Hydrogen atom migration to such a site could then give a singly bonded alkyl as shown in step F where



isomerization may occur. In any case, the treatment of the metal surface with phosphine should lead to a relative isolation of metal atoms by the incorporated phosphorus atoms. As surface metal clusters diminish in size and number, k_4 (step D) should decrease because of the intrinsically lower number and mobility of hydrogen atoms bonded to the surface or in positions near the surface. Step A is, for example, much slower for the phosphides than for the metals. This crude picture would suffice to explain on the basis of competitive reactions the chemistry of 1-butene and hydrogen on metal and metal phosphide. The chemistry is not simply a result of phosphorus blocking sites for 2-butene because phosphides do isomerize 2-butene, in the presence of hydrogen, although explicable at a lower rate than for 1-butene. The butene experiments

(23) R. P. Eischens and W. A. Pliskin, *Advan. Catal.*, 10, 1 (1958).

(24) L. H. Little, N. Sheppard, and D. J. C. Yates, *Proc. Roy. Soc., Sect. A*, 259, 242 (1960).

(25) (a) B. D. Barford and R. R. Rye, *J. Vac. Sci. Technol.*, 9, 673 (1972); (b) P. C. Cartier and R. R. Rye, *J. Catal.*, to be submitted for publication.

do not allow for a distinction between paths B-C and E-F nor do they set limits for the size of surface metal clusters. However, the butene surface sites are blocked by acetylene and the acetylene desorption products provide some limiting information (*vide infra*).

Hydrogenation of acetylene, primarily to ethylene, at 150–200° may be explained if it is assumed that the lifetime of a metal–vinyl surface species is much longer than that for a metal–alkyl. Blocking of butene isomerization by phosphides through treatment of the catalyst with acetylene and hydrogen supports such an assumption. The very fact that return of isomerization activity to the acetylene-treated phosphide requires high temperatures, precisely temperatures where acetylene hydrogenation occurs, is suggestive of a relatively robust M–vinyl surface species. Pyrolysis of an acetylene–hydrogen treated ruthenium phosphide yielded acetylene and hydrogen as well as ethane. Reversal of the chemisorption reaction is not inconsistent with the postulated metal–vinyl surface species. That this chemisorption process involves acetylene and hydrogen is incisively demonstrated in the acetylene–phosphide reaction discussed below where “desorption” leads to a complex array of molecules.

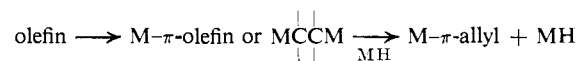
Acetylene also strongly binds sites required in butene isomerization and in ethylene hydrogenation or dimerization although no *catalytic* transformation of acetylene was observed. Acetylene pretreated ruthenium phosphide when heated in the mass spectrometer inlet at 150° gave hydrogen, methane, acetylene, monovinylacetylene, ethane, propylene, butenes, butane, pentenes, and benzene. Thus the acetylene–phosphide reaction gives rise to a surface template that thermolyzes in a complex fashion. It is evident that the phosphide reactions with acetylene and with acetylene–hydrogen are sharply distinguished. Since there is a large carbon deficit in the carbon–hydrogen balance in the products from the “acetylene template,” a carbon (graphitic) like template must remain on pyrolysis. Major products are hydrogen, ethane, butene, and benzene. Formation of butene from acetylene *might* occur at a single surface metal atom with two active sites by oxidative coupling of a bisacetylene complex to metallacyclopentadiene followed by hydrogenation. Benzene formation at a single metal atom site minimally requires two active coordination sites per metal atom. A more probable process is a two or three metal atom aggregate reaction with acetylene. Detailed spectroscopic and physical studies of acetylene and acetylene–hydrogen treated phosphided single crystal or thin films of the metal are planned to resolve this “template” question. The template, in any case, possesses considerable integrity since it does block olefin isomerization and hydrogenation reactions.

Rhodium and platinum phosphides convert ethylene to 1-butene and 2-butene. Conversions are very low. Addition of hydrogen to the reaction led to hydrogenation of the olefin, a fast reaction as compared to 1-butene hydrogenation. Treatment of a ruthenium phosphide catalyst with ethylene at 75° followed by pyrolysis gave primarily ethylene at 100° and hydrogen at 300° with the ethylene accompanied by 8% butadiene and 2% 1-butene. 1-Butene could result from a metallapentane $[M(CH_2)_4$ or $M(CH_2)_4M]$ by β -hydrogen elimination and reductive elimination of the

butenyl group and butadiene from two sequential β -hydrogen eliminations. It would then have to be assumed that a β -hydrogen elimination step can be inhibited by ethylene since no butadiene was detected in the catalyzed dimerization reaction. In any case, the catalyzed ethylene dimerization reaction is a much studied but poorly understood transformation.²⁶ None of the phosphides were found to catalyze dimerization or olefin metathesis in propylene.

Metal phosphides in combination with aluminum hydrides or alkyls have been reported¹⁴ to be catalysts for ethylene polymerization. We found the phosphides alone relatively inactive for ethylene polymerization although nickel phosphide produced a small amount of low molecular weight polymer at the upper operating conditions (250°, 1000 atm) and rhodium phosphide gave butenes in low conversions. Addition of hydrogen qualitatively changed the reaction with the production of moderate amounts of polymer (film-forming but low molecular weight) with platinum, rhodium, and nickel phosphides. This behavior is formally analogous to the earlier discussed 1-butene and 1-butene plus hydrogen reactions over metal phosphides where formation of metal–hydrogen surface sites are required for detectable isomerization rates.

In isobutylene dimerization, the role of phosphorus may be electronic because all the metal and metal sulfide “control” catalysts were inactive. The first steps may comprise



where H transfer from carbon to metal may be direct to adjacent metal atoms²⁷ or through the aegis of vacancies. Once the concentration of MH is appreciable, the probability of $MC(CH_3)_3$ formation could become high. Transfer of the *tert*-butyl carbonium ion to a carbon atom of a π -allyl(isobutylene) complex or a bis(metal)- σ -isobutylene complex would yield 2,4,4-trimethyl-1-pentene and the 2,4,4-trimethyl-2-pentene precursors. The product distribution is in any case precisely that of carbonium ion reactions of isobutylene, namely, 80% of the 1-pentene isomer.²¹ The presence of 10% hydrogen did not significantly affect the course of this dimerization reaction.

In the metal phosphides, the critical role of metal hydrogen bond formation for olefin isomerization and ethylene polymerization is reasonably well implicated from these studies. The metal–hydrogen sites must be relatively isolated on the surface under reaction conditions because the hydrogenation activity of these phosphides is so substantially reduced with respect to the parent metals but two- or three-center sites may be present (trimerization of acetylene to benzene). Indicative of the low density of coordination sites is the lack of reaction in the butadiene–hydrogen system and the very low activity of the phosphides as carbonylation catalysts for olefins. Of special note is the apparent stability of M–vinyl and M–acetylene surface species, a phenomenon that will further be explored through chemical and spectroscopic studies.

(26) (a) R. J. Kokes and J. P. Bartek, *J. Catal.*, **12**, 72 (1968); (b) French Patent 1,575,800, Oct 5, 1968; (c) Ya. T. Eidus, R. V. Avetisyan, *et al.*, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2364 (1968); (d) G. C. Bailey and J. A. Reid, U. S. Patent 2,606,940, Aug 12, 1952.

(27) The important question of size in metal clusters for the phosphides will be probed further with other types of hydrocarbon reactions.