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Photochemical Synthesis and Reactions of $FeH(C_6H_4PPhCH_2CH_2PPh_2)(PPh_2CH_2CH_2PPh_2)$

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The irradiation of solutions of *cis*-$FeH_2(DPPE)_2$ (**1**), DPPE = 1,2-bis(diphenylphosphino)ethane, with ultraviolet or visible light is an efficient method for preparing $FeH(C_6H_4PPhCH_2CH_2PPh_2)(DPPE)$ (**2**). The 366-nm quantum yield for loss of hydrogen from **1** is 0.25 ± 0.05, and the chemical yield of crystalline **2** is 90%. Hydrogen (1 atm) reacts with solutions of **2** at 50 °C to give **1** quantitatively and can be released irreversibly at 25 °C by the photoconversion of **1** to **2**. This cycle can be repeated without degeneration of the system. Protonation of **2** with formic acid gives **1** and CO_2 and with fluoroboric acid under N_2 gives *trans*-$[FeH(N_2)(DPPE)_2]BF_4$. The decarbonylation of acetaldehyde by **2** provides a direct synthesis of $Fe(CO)(DPPE)_2$. Products containing ortho-metalated $PEtPh_2$ result as both H_2 and N_2 are photoeliminated from $Fe(N_2)H_2(PEtPh_2)_3$.

The photoinduced elimination of cis hydride ligands as dihydrogen from transition-metal complexes has proven to be a very general photochemical reaction.[1] Recent work has also demonstrated that this is a convenient method of generating coordinatively unsaturated compounds that undergo potentially important reactions such as N_2 and CO_2 fixation,[2] saturated carbon–hydrogen bond cleavage,[3] and water splitting as a source of hydrogen.[4] We are investigating the photochemical syntheses of very reactive, low-valent phosphine complexes of iron by this route. Here we report that *cis*-$FeH_2(DPPE)_2$ (**1**) is a useful source of the complex $FeH(C_6H_4PPhCH_2CH_2PPh_2)(DPPE)$ (**2**), which contains an ortho-metalated phosphine ligand.

The great reactivity of **2** toward the oxidative addition of sp hybridized carbon–hydrogen bonds has been demonstrated.[5] Compounds HX, X = acetylides and cyanide, add to **2** as in eq 1; the trialkyl phosphite derivatives of **2**, $Fe(P(OR)_3)(DPPE)_2$, are catalysts for the hydrocyanation of ethylene.[6]

$$HX + \mathbf{2} \rightarrow trans\text{-}Fe(H)(X)(DPPE)_2 \qquad (1)$$

Compound **2** also cleaves the activated carbon–hydrogen bonds of cyclopentadiene[5] and β-diketones[7] and catalytically activates silicon–hydrogen bonds to alcoholysis.[8] We demonstrate here that **2** can also serve as a hydrogen storage material and as a convenient precursor to carbonyl and dinitrogen complexes.

Experimental Section

Oxygen and water were excluded during all operations by using vacuum lines or a glovebox supplied with purified nitrogen. Solvents were dried over and distilled from sodium–benzophenone ketyl and were degassed before use. The best yields of the yellow solids *cis*-$FeH_2(DPPE)_2 \cdot 2C_7H_8$[9] and $FeH_2(N_2)(PEtPh_2)_3$[10] were obtained by conducting the published procedures in a darkened room.

The ^{31}P NMR spectra were recorded at 32.3 MHz with a Bruker WP80 spectrometer. Chemical shifts were measured relative to $P(OCH_3)_3$ in an insert tube but are reported relative to 85% H_3PO_4 with use of $\delta(P(OCH_3)_3) = +139.8$ in C_6D_6. Solid samples for UV–vis spectra were placed in degassable 10-mm quartz cells in a glovebox. Then a solvent was vacuum distilled from $LiAlH_4$ onto the sample, and the spectrum was recorded on a Cary 14 spectrophotometer. These dilute solutions had to be prepared and handled while excluding light and oxygen. Gas evolution was measured with use of a Toepler pump and gas buret system. Samples for hydrogen uptake were sealed in breakable ampules, suspended in a pure hydrogen atmosphere in a thermostated, constant-pressure, gas-uptake apparatus and then dropped to break the ampule and initiate uptake.[11]

Ultraviolet irradiation of solutions was conducted with a 450-W Hanovia medium-pressure mercury lamp; a plastic filter ($\lambda \geq 400$ nm) was used during visible irradiations. For quantum yield measurements, the 366-nm line was isolated by interposing suitable Corning glass filters between the lamp and solution; the intensity was determined by ferrioxalate actinometry to be $(1.2 \pm 0.2) \times 10^{-6}$ einstein/min. The photochemical conversion of a benzene solution (2.5×10^{-3} M) of $FeH_2(DPPE)_2$, $\epsilon_{500} = 60$, to a solution of **2**, $\epsilon_{500} = 460$, was monitored simultaneously by visible spectral changes at 500 nm and by hydrogen evolution measurements. The 366-nm quantum yield for product formation (**2** and H_2) was $\phi = 0.25 \pm 0.05$ at 5% conversion. A less accurate value of $\phi = 0.4 \pm 0.2$ was obtained by measuring hydrogen evolution from a reference solution of $[Pt_2H_3(DPPM)_2]PF_6$ ($\phi = 0.7 \pm 0.1$)[12] under identical photolysis conditions.

Microanalyses were performed by the Canadian Microanalytical Service.

Photochemical Preparation of $FeH(C_6H_4PPhCH_2CH_2PPh_2)(DPPE)$ (2). Method A. Yellow *cis*-$FeH_2(DPPE)_2 \cdot 2C_7H_8$ (0.75 g, 0.72 mmol) was dissolved in 30 mL of degassed benzene in a narrow Pyrex Schlenk tube. The solution was stirred, held at 25 °C, and slowly purged with pure nitrogen as it was irradiated ($\lambda > 280$ nm) for 1 h. The resulting orange solution was evaporated under vacuum. The residue was soluble in ether (5 mL) long enough to be quickly filtered but then reprecipitated as orange crystals of the product. After this suspension was cooled for 30 min at −40 °C, the very oxygen-sensitive crystals (0.55 g, 90%) were collected, washed with ether, and dried in vacuo. Their IR and ^1H and ^{31}P NMR spectral properties were identical with those reported;[5,13] see Figure 1. Anal. Calcd for $C_{52}H_{48}FeP_4$: C, 73.24; H, 5.67. Found: C, 73.10; H, 5.65.

If "red $FeH_2(DPPE)_2$"[5] is used, then a red residue is obtained after photolysis and evaporation. This residue is composed of ether-soluble **2** and an insoluble, unidentified red material with an IR peak at 1790 cm^{-1}, which is also present in the starting red dihydride sample.

Method B. A thin film (0.3 mg cm^{-2}) was deposited onto the sides of an evacuable Pyrex flask by slowly evaporating under vacuum a solution of the complex (85 mg) in 10 mL of benzene while rotating the flask. The flask was irradiated for 15-min periods; after each period the volume of hydrogen evolved was measured. After 60 min of irradiation gas evolution had almost ceased and the ratio H_2:Fe = 0.54 was determined. The ^{31}P NMR spectrum of the orange product

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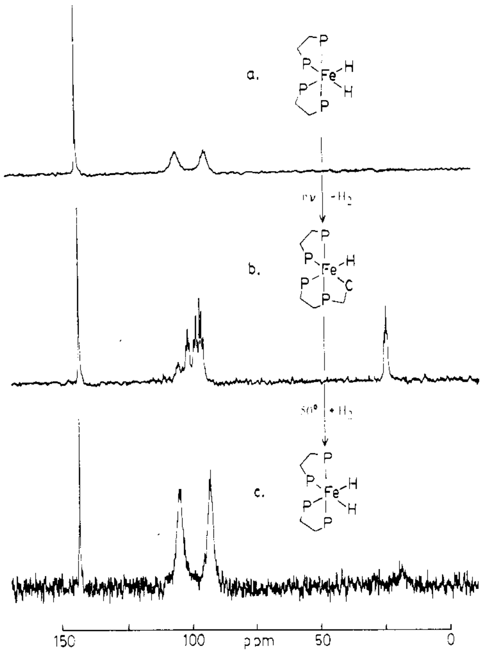

Figure 1. $^{31}P\{^1H\}$ NMR spectra referenced to 5% $P(OCH_3)_3$ in C_6D_6 in an insert tube (peak at 139.8 ppm): (a) $FeH_2(DPPE)_2$ in benzene; (b) solution of **2** obtained after 60 min of UV irradiation with an N_2 purge; (c) the product, complex **1**, after the H_2 uptake measurement of 0.97 mol/mol of Fe (a small amount of oxidation occurred (peak at 17.8 ppm) while the sample was handled).

indicated a 50:50 mixture of compounds **1** and **2**. Reaction of this film at 25 °C with carbon monoxide (1 atm) for 1 h gave a mixture of $Fe(CO)(DPPE)_2$, $\nu(CO)$ = 1834 cm^{-1}, and $Fe(CO)_3(DPPE)$, $\nu(CO)$ = 1978, 1935, 1910 cm^{-1} (in Nujol).[5]

Solid-State Photolysis of $FeH_2(N_2)(PPh_2Et)_3$. A thin film of the yellow solid was deposited on a flask by method B above. After 2 min of visible irradiation, 0.28 mol of gas/mol of iron was collected and analyzed by GC as 70% N_2 and 30% H_2. After 2.5 h 0.8 mol of gas (75% N_2, 25% H_2) was evolved. By continued irradiation, 1.4 mol of gas/mol of iron could be obtained. The IR spectrum in Nujol of the brown air-sensitive product showed bands due to the starting complex $\nu(NN)$ = 2055 cm^{-1}, $\nu(FeH)$ = 1850 cm^{-1}, free phosphine $\nu(CH)$ = 1590 cm^{-1}, and ortho-metalated phosphine $\nu(CH)$ = 1538 cm^{-1}. This solid reacted with carbon monoxide over 24 h to give $Fe(CO)_3(PPh_2Et)_2$, $\nu(CO)$ = 1880, 1860 cm^{-1}, as the major CO-containing product.[14]

Hydrogen Storage Cycles. A yellow solution of **1** (0.16 g, 0.154 mmol) was degassed and irradiated for 1 h. The solution was freeze–thaw degassed, and the hydrogen evolved was measured: 0.153 mmol, 99 ± 3% yield. This solution was reacted with pure hydrogen (1 atm) for 60 min at 50 °C and then degassed and irradiated as above to give 0.152 mmol of hydrogen, 97 ± 3% yield. This cycle can be repeated at least three times without degeneration. The cycle was also followed with use of a gas-uptake apparatus. A pure sample of **2** (85 mg) reacted with 600 torr of hydrogen in 45 min at 52 °C and took up 0.96 ± 0.5 mol of H_2/mol of Fe; the spectrum in Figure 1c demonstrates that only **1** is produced.

Reaction of 2 with Formic Acid. The ^1H NMR spectrum of the red solution of **2** (54 mg, 0.06 mmol) and HCOOH (3.2 μL, 0.06 mmol) in C_6D_6 obtained after 5 min of reaction showed a multiplet at $\delta = -13.1$ due to $FeH_2(DPPE)_2$[15] and a quintet at δ −32.2, J_{PH} = 47 Hz, assigned to the hydride resonance of *trans*-FeH(OOCH)-$(DPPE)_2$.[16] After 20 min the solution turned yellow and only hydride resonances due to **1** remained. A red solid obtained by evaporating the red solution rapidly turned yellow; an IR spectrum of the yellow solid showed $\nu(FeH)$ = 1850 cm^{-1} due to **1** and $\nu(CO)$ = 1650–1600 cm^{-1} due probably to $FeH(OOCH)(DPPE)_2$[17] and $Fe(OOCH)_2(DPPE)_2$.[18]

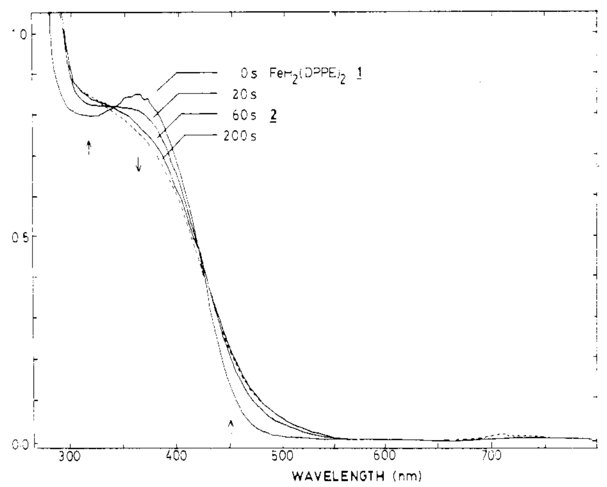

Figure 2. Electronic absorption spectral changes accompanying the photolysis ($\lambda > 260$ nm) of a 2.1×10^{-4} M solution of $FeH_2(DPPE)_2$ in benzene ($\epsilon_{363} = 4.0 \times 10^3$); isosbestic points occur at 345 and 422 nm. After 60 s the spectrum of **2** ($\epsilon_{363} = 3.7 \times 10^3$) is obtained. After 200 s (dotted line) some decomposition occurs.

Preparation of $[FeH(N_2)(DPPE)_2]BF_4$. The addition of excess fluoroboric acid (38% in H_2O) to a solution of **2** (0.1 g, 0.1 mmol) in 5 mL of benzene stirred under N_2 resulted in a yellow precipitate after 5 min. The crystals were filtered off, washed with ether, and recrystallized from methylene chloride/ether: yield 80%; $\nu(NN)$ = 2120 cm^{-1} (Nujol); $\delta(^{31}P\{^1H\})$ = 91.2 (singlet; in CH_2Cl_2). Some properties of the perchlorate and tetraphenylborate salts of this compound have been reported.[19]

Preparation of $Fe(CO)(DPPE)_2 \cdot 0.5C_6H_6$. Cold acetaldehyde (45 μL, 1.0 mmol), compound **2** (240 mg, 0.28 mmol), and 3 mL of benzene were sealed into a flask and reacted for 60 h at 25 °C. The resulting orange solution was filtered, concentrated to 1.5 mL, and then treated with 1.5 mL of ether and cooled to −40 °C. The oxygen-sensitive orange crystals were collected, washed with ether, and recrystallized from benzene/ether to yield 130 mg (50%) of $Fe(CO)(DPPE)_2 \cdot 0.5C_6H_6$: $\nu(CO)$ = 1818 cm^{-1} (strong, Nujol);[20] $\delta(^{31}P\{^1H\})$ = 86.1 (singlet; in C_6H_6). Anal. Calcd for $C_{56}H_{51}FeOP_4$: C, 73.13; H, 5.59. Found: C, 73.23; H, 5.84.

Results and Discussion

Photochemical Preparation of $FeH(C_6H_4PPhCH_2CH_2PPh_2)(DPPE)$ (2). Benzene solutions of *cis*-$FeH_2(DPPE)_2$ (**1**) are very sensitive to ultraviolet and visible light and under irradiation irreversibly evolve 1.0 mol of hydrogen at 25 °C to give complex **2** containing an ortho-metalated phosphine ligand.[5] The yield of **2** is quantitative as determined by ^{31}P NMR, UV–vis, and gas evolution measurements.

The ^{31}P NMR spectra (Figure 1) demonstrate that the broad resonances of the fluxional compound **1** at 101.8 and 90.8 ppm are cleanly replaced during irradiation by the ABCD spin system reported earlier for **2**;[5] the multiplet centered at 23.7 ppm is characteristic of the phosphorus atom in the four-membered ring. If air is rigorously excluded, the reaction

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[16] The reactions of carboxylic acids with **2** give *trans*-hydridocarboxylato complexes with δ(FeH) at approximately −32. The adduct with succinic acid has δ(FeH) = −31.09, J_{PH} = 49 Hz: Azizian, H.; Morris, R. H., unpublished results.

[17] The complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2(O_2CH)$ has $\nu(OCO)$ at 1620 and 1293 cm^{-1}: Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297.

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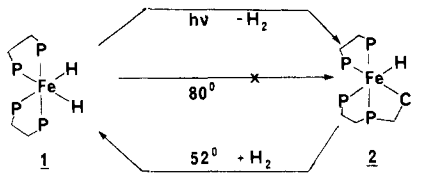
Scheme I



produces clean UV–vis spectral changes with isosbestic points at 345 and 422 nm as shown in Figure 2. However, at these low concentrations of 10^{-4} M prolonged irradiation leads to partial decomposition of the product because of reactions with trace impurities, a problem not encountered at concentrations of 10^{-2} M or greater. The 366-nm quantum yield for hydrogen loss from **1** was determined to be 0.25 ± 0.05. A thermal back-reaction with hydrogen is negligibly slow under these conditions (vide infra). Solutions of complex **1** do not lose H_2 thermally even at 80 °C under an argon purge.

On a preparative scale, air-sensitive orange crystals of **2** can be isolated in 90% yield after 1 h of UV photolysis in benzene while purging with N_2. The ease of preparation of $FeH_2(DPPE)_2$[9] and its efficient photochemical conversion to **2** make this a more convenient preparation of **2** than ones involving the photolysis[13] or pyrolysis[5] of the ethylene complex, $Fe(C_2H_4)(DPPE)_2$. The latter compound must be prepared at low temperatures by the reduction of $Fe(ACAC)_3$ with ethylaluminum reagents in the presence of DPPE[5,13] or by metal-vapor syntheses.[6,21]

On exposure to sunlight, the surfaces of crystals of **1** stored under N_2 rapidly turn the orange color of **2** and IR bands characteristic of **2** grow in at 1890 and 1556 cm^{-1}. These data were interpreted earlier as the formation of either an iron trihydride complex[22] or an isomer of $FeH_2(DPPE)_2$ with a red color due to an orientation of the phenyl groups different from that of **1**.[5] In fact, H_2 is photoeliminated from **1** in the solid state and, if a thin film of **1** is used, conversions to **2** of 0.5 have been verified by gas evolution and ^{31}P NMR studies. There is no evidence for the formation of $Fe(N_2)(DPPE)_2$ during photolysis of **1** under N_2, even at −50 °C in solution. A metal-vapor synthesis of this dinitrogen complex has been reported.[21]

The irradiation of $FeH_2(N_2)(PPh_2Et)_3$ as a solid was also briefly investigated since conflicting reports suggest that either $Fe(N_2)(H)(C_6H_4PPhEt)(PEtPh_2)_2$[23] or $FeH_2(PEtPh_2)_3$[24] are products. Our studies indicate that both H_2 and N_2 are lost even at low conversions to give products where ortho metalation of ligands has occurred, as we have observed for the DPPE complex.

Reaction of 2 with Hydrogen. A Hydrogen Storage System. Pure hydrogen (600 torr) reacts irreversibly with a 10^{-2} M solution of **2** in benzene at 52 °C in 45 min to give **1** quantitatively as shown by gas uptake measurements and ^{31}P NMR spectra in Figure 1. Thus complexes **1** and **2** represent a potential hydrogen storage system (Scheme I) where **2** readily takes up H_2 to store it as **1**. Hydrogen is irreversibly released on demand in a high quantum yield process, $\phi_{366} = 0.25$, by irradiation of **1** with UV light or with sunlight. This system can be cycled several times with no obvious side reactions. Geoffroy and Pierantozzi reported a similar cycle based on the $IrClH_2(PPh_3)_3$–$IrCl(PPh_3)_3$ system with $\phi = 0.56$ at 254 nm.[25] It is also noted that ethylene can be stored as $Fe(C_2H_4)(DPPE)_2$ and released photochemically in a cycle involving complex **2**.[13]

Protonation Reactions of 2. Compound **1** can also be regenerated from **2** in Scheme I by reaction of **2** with 1 equiv of formic acid in benzene at 25 °C. The dihydride results from the elimination of CO_2 from the intermediate *trans*-$FeH(OOCH)(DPPE)_2$ formed by reaction 1 above and identified by a transitory quintet at −32.2 ppm in the ^1H NMR spectra of the reaction. A broad infrared absorption at 1600–1650 cm^{-1} observed during the reaction is consistent with a monodentate metal formate species.[17] The complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2(O_2CH)$ extrudes CO_2 when heated to 50 °C.[17] Metalloformates are being studied as possible intermediates in the water-gas shift reaction.[26] A mixture of products including **1** and possibly $Fe(OOCH)_2(DPPE)_2$[18] is obtained if excess acid is added to **2**.

The dinitrogen complex *trans*-$[Fe(N_2)H(DPPE)_2]BF_4$ is readily prepared by protonating **2** with HBF_4 in the presence of N_2. The nitrogen stretching frequency at 2120 cm^{-1} is identical with that of $[Fe(N_2)H(DPPE)_2]BPh_4$ prepared from $FeHCl(DPPE)_2$.[19] We are investigating other routes to dinitrogen complexes that follow from the facile photochemical syntheses of compounds like **2**. We have not observed any reaction of **2** with water.

Decarbonylation of Acetaldehyde by 2. The reaction of CH_3CHO with **2** in benzene at 25 °C provides a direct route (eq 2) to $Fe(CO)(DPPE)_2{\cdot}0.5C_6H_6$ (**3**). The reaction of **2** with

$$\mathbf{2} + CH_3CHO \rightarrow Fe(CO)(DPPE)_2 + CH_4 \qquad (2)$$

CO in solution or the solid state produces $Fe(CO)_3(DPPE)$ as well as $Fe(CO)(DPPE)_2$ although **3** has been isolated from carefully controlled reactions of CO with **2** or with $Fe(N_2)(DPPE)_2$.[5,21] The carbonyl stretch is found at 1834 cm^{-1} in toluene but ranges in the solid state from 1850 to 1810 cm^{-1} depending on the solvents of recrystallization.[20] A similar solid-state effect has been reported for ν(FeH) of $FeH_2(DPPE)_2$.[13] The unusually low ν(CO) of **3** and its air sensitivity suggest that it is a very electron rich carbonyl complex. The ^{31}P NMR spectrum of **3** is a sharp singlet due to a fluxional behavior common to five-coordinate complexes although its chemical shift of 86.1 ppm differs inexplicably from the value of 96.3 ppm reported earlier.[5]

Reaction 2 likely proceeds by a slow reductive elimination of the phenyl group in **2** to give $Fe(DPPE)_2$, which rapidly oxidatively adds the sp^2 hybridized carbon–hydrogen bond of CH_3CHO to give the unobserved intermediate *cis*-$FeH(COCH_3)(DPPE)_2$. Similar intermediate and pathway have been demonstrated for the decarbonylation of propionaldehyde by hydrido(2-napthyl)bis[bis(dimethylphosphino)ethane]iron(II), $FeH(Np)(DMPE)_2$.[27] Coordination of the carbonyl to $Fe(DPPE)_2$ prior to C–H cleavage may be required since the bulkier isobutyl aldehyde does not react with **2**.

Conclusions

The photochemical preparation of **2** described here allows an easy entry into $Fe(DPPE)_2$ chemistry. Some examples of this rich chemistry reported here are the use of **1** and **2** as a photochemical hydrogen storage system and the use of **2** as a powerful reagent for oxidative-addition reactions with acids and acidic carbon–hydrogen bonds. It has previously been demonstrated that the more electron-rich compound $FeH(Np)(DMPE)_2$ is even more reactive.[27] For example, the latter reacts with aromatic C–H bonds and the sp^3 hybridized bonds of acetone and acetonitrile whereas **2** does not. The photo-

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chemistry of more electron-rich iron dihydride complexes is currently being studied.

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Registry No. **1**, 32490-69-0; **2**, 19392-92-8; $Fe(CO)(DPPE)_2$, 60105-56-8; $Fe(CO)_3(DPPE)$, 14881-58-4; $Fe(CO)_3(PPh_2Et)_2$, 36870-06-1; *trans*-$FeH(OOCH)(DPPE)_2$, 83463-70-1; $Fe(OOCH)_2(DPPE)_2$, 83463-71-2; $[FeH(N_2)(DPPE)_2]BF_4$, 83463-69-8; $FeH_2(N_2)(PPh_2Et)_3$, 22087-95-2; acetaldehyde, 75-07-0.

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Synthesis and Characterization of $(R_3PH)_3Mo_2Cl_8H$ ($R = C_2H_5$ or C_3H_7): Distinction between Phosphines and Phosphonium Ions Using Secondary Ion Mass Spectrometry

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The reaction between the dinuclear quadruply bonded $Mo_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine) and gaseous hydrogen chloride in ethanol in the presence of the tertiary phosphines PEt_3 or P-*n*-Pr_3 affords the (μ-hydrido)-dimolybdenum(III) complexes $(R_3PH)_3Mo_2Cl_8H$. The characterization of these complexes has included measurement of their secondary ion mass spectra (SIMS). A study of the SIMS spectra of complexes of molybdenum and rhenium that contain trialkylphosphine ligands has shown that it is possible to differentiate between phosphonium ions ($[R_3PH]^+$) and neutral PR_3 ligands in these complexes. Such a distinction did not exist between complexes containing the analogous $(Ph_3PH)^+$ and PPh_3 moieties.

Introduction

The technique of secondary ion mass spectrometry (SIMS) has found application in the analysis of surface structure of catalytic importance. Its recent utilization in the study of organic,[1,2] biological,[3,4] inorganic,[5-7] and organometallic[7] complexes has also demonstrated the potential of SIMS for the analysis of molecular species. Structural information of nonvolatile species is attainable from such studies via the appearance of molecular species M^+ and cationized adducts such as $[M + H]^+$ and $[M + C]^+$, where the cationizing agent C is often an alkali-metal additive or Ag from the silver support typically employed in such analyses. This technique complements field desorption mass spectrometry[8] as a means of mass analyzing nonvolatile samples and is suited to the characterization of inorganic and organometallic species as recently demonstrated.[7,9] The present study arose out of our spectroscopic characterization of the products that emanate from the reaction between the quadruply bonded dimolybdenum complex $Mo_2(mhp)_4$, where mhp represents the anion of 2-hydroxy-6-methylpyridine, and gaseous hydrogen chloride in the presence of tertiary phosphines.[10-12] The question that was posed to us during this investigation concerned the use of SIMS to differentiate phosphonium ions ($[R_3PH]^+$) from neutral phosphine ligands (PR_3) in complexes that might be difficult to analyze by conventional techniques. Since the direct sputtering of cations is an ionization process of high efficiency in the SIMS experiment,[13] we were particularly interested in whether large relative differences in the $[R_3PH]^+$ ion abundances could be used to distinguish between cationic and neutral phosphine species in transition-metal complexes. The possibility of using SIMS to identify transition-metal phosphines is of additional note since it could conceivably provide a means of characterizing heterogenized homogeneous catalysts derived from complexes containing phosphine ligands. Drawing upon complexes prepared for the first time in the present work, together with various phosphine complexes of molybdenum and rhenium that were already available in our laboratory from previous studies, we have carried out such an investigation and herein describe the pertinent details.

Experimental Section

Materials. Hydrogen chloride gas was purchased from Matheson and used without further drying. Alkylphosphines were purchased from Strem Chemicals. The following compounds were prepared according to literature procedures: $Mo_2Cl_4(PR_3)_4$, where R = Et, *n*-Pr, or *n*-Bu,[14] $MoCl_4(PEtPh_2)_2$,[15] $MoCl_4(PEtPh_2)_2$,[15] $[Mo(CNCMe_3)_6(PEt_3)](PF_6)_2$,[16] $Mo_2(mhp)_4$,[17] where mhp is the anion of 2-hydroxy-6-methylpyridine, $Re_2Cl_6(PR_3)_2$, where R = Et or Ph,[18] $ReCl_3(PMe_2Ph)_3$,[19] $ReOCl_3(PPh_3)_2$,[20] $Re_2H_8(PPh_3)_4$,[21] $ReH_5(PPh_3)_3$, $ReH_5(PPh_3)_2(PEt_2Ph)$, and $ReH_5(PPh_3)_2py$.[22]

Reaction Procedures. All reactions were carried out under a nitrogen atmosphere, and all solvents were dried and deoxygenated prior to use by purging with N_2 gas.

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