

Assay of Hydride or Volatile Ligands via Outer-Sphere Oxidation

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Outer-sphere electron transfer from several transition-metal polyhydride complexes, MH_mL_n , to $Fe(bpy)_3^{3+}$ is evaluated as a quantitative procedure for determining the number, m , of hydride ligands present. The strengths and limitations of the method are discussed, and its generalization to the oxidative evolution of CO from $Co_2(CO)_8$ is demonstrated. Possible additional applications of the procedure are also described.

Introduction

The classical method for quantitative determination of carbonyl ligands in transition-metal complexes is oxidation with I_2 , frequently in pyridine solvent, followed by volumetric determination of evolved CO.^{1,2} It would be most useful to generalize such a method to the counting of hydride ligands, since both NMR integration³ and selective nuclear spin coupling⁴ methods have been shown to have their limitations. It was in recognition of this problem that Chatt and Coffey coined the whimsical name "agnohydride", referring to $Re_2H_x(PR_3)_4$.⁵ Oxidation of a hydride complex with elemental halogen is not a reliable procedure for the determination of the number of hydride ligands (as H_2) in a polyhydride complex MH_mL_n since HX may be a complicating coproduct and also since intermediate halo hydrido complexes, MH_xL_n , may resist further oxidation.^{6,7} We consider that a superior reagent for the volumetric determination of hydride ligands as H_2 is one that effects outer-sphere oxidation and thus avoids production of increasingly stable intermediates resulting from anionic ligand transfer. Outer-sphere oxidation might be expected to be followed by conversion of two hydride ligands to coordinated H_2 ; subsequent elimination of H_2 is thereby facilitated. A second need is for a potent oxidant, capable of oxidizing even formally d^2 polyhydrides such as $ReH_5(PR_3)_3$. We describe here our evaluation of $Fe(bpy)_3^{3+}$ as a reagent for this purpose.

Experimental Section

Polyhydride compounds were prepared by literature methods. The cobalt carbonyl was a commercial sample, sublimed before use. Elemental analysis was by Malissa and Reuter, Elbach, West Germany.

$Fe(bpy)_3(PF_6)_3$. As no detailed preparation is available in the literature,^{8,9} the following prescription is provided.

In air, 3.12 g (0.02 mol) of bipyridine and 1.84 g (0.0066 mol) of $FeSO_4 \cdot 7H_2O$ were added to 50 mL of H_2O , and the mixture was warmed with stirring at 50 °C until all solids were dissolved. The resulting blood red solution of $Fe(bpy)_3^{2+}$ was then filtered, and the filtrate was cooled to 0 °C in an ice bath. The solution was acidified with 1 mL of 18 M H_2SO_4 and oxidized with an excess of PbO_2 (5 g, > 3 PbO_2/Fe) until all traces of red were removed from the blue solution. A fine-porosity frit was used to remove Pb and excess PbO_2 , with the filtrates being collected at 0 °C. $Fe(bpy)_3(PF_6)_3$ was then precipitated by dropwise addition of HPF_6 to the point (~4 mL) where no additional solid formed on addition of another drop of acid.

The blue solid was isolated by filtration and placed under a nitrogen atmosphere on a Schlenk frit. The solid was washed with $EtOH$ (3 × 20 mL), CH_2Cl_2 (3 × 2 mL), and Et_2O (3 × 20 mL) (or until the washings come off colorless). It was then recrystallized from MeCN (50 mL) by slow addition of Et_2O until the solution began to turn red ($Fe(bpy)_3(PF_6)_2$). The blue, microcrystalline $Fe(bpy)_3(PF_6)_3$ was collected by filtration and washed with $EtOH$ (3 × 20 mL), CH_2Cl_2 (3 × 20 mL),

and Et_2O (3 × 20 mL) (or until the washings are colorless). After the product was dried in vacuo overnight at 100 °C, the isolated yield was 4.7 g (74%). $Fe(bpy)_3(PF_6)_3$ is stable for brief periods in air but should be stored under N_2 in the dark. It is soluble in MeCN and acetone but is insoluble in $EtOH$, CH_2Cl_2 , and Et_2O . Anal. Calcd for $C_{30}H_{24}N_6F_{18}P_3Fe$: C, 37.56; H, 2.52; N, 8.76. Found: C, 37.31; H, 2.61; N, 8.68. Material not subjected to this rigorous drying procedure has been shown to contain acetonitrile in the lattice.

The general procedure for oxidative gas evolution involves placing a weighed amount of the compound to be analyzed in a small glass vial. This vial is then placed into a larger reaction vessel together with a magnetic stir bar and excess $Fe(bpy)_3(PF_6)_3$. The excess of Fe(III) is calculated as 50–100% more than would be required to take the metal in the test compound to its highest "typical" oxidation state (e.g., Cu(II), Mo(VI), Co(III)). The reactor is then evacuated and cooled to -196 °C, and dried, freeze/thaw-degassed MeCN is condensed into the reactor. The reactor is then closed and warmed to 25 °C, and the contents are stirred until the oxidation reaction is deemed complete. Deep blue $Fe(bpy)_3^{3+}$ turns to dark red $Fe(bpy)_3^{2+}$ during this period. The reactor is then opened to a cold trap/Toepler pump/calibrated volume assembly for vacuum transfer of MeCN to the cold trap (-196 °C), followed by Toepler pumping of the residual noncondensables. Tests with known quantities of gases showed accuracy of 3–6% for the procedure. NMR monitoring of one oxidation reaction is described below.

Stoichiometric Reaction of $ReH_5(PMe_2Ph)_3$ and $Fe(bpy)_3(PF_6)_3$. To a mixture of $ReH_5(PMe_2Ph)_3$ (25 mg, 0.04 mmol) and $Fe(bpy)_3(PF_6)_3$ (79 mg, 0.08 mmol) in an NMR tube was added 0.5 mL of CD_3CN under an inert atmosphere. Immediate gas evolution was observed, accompanied by the development of an intense red color indicating the presence of $Fe(bpy)_3^{2+}$. The ^{31}P NMR spectrum showed a broad peak at -16.6 ppm, while 1H NMR showed a broad hydride resonance at -3.0 ppm assigned to the new species $ReH_3(CD_3CN)_2(PMe_2Ph)_3(PF_6)_2$. The same species is produced in 50% yield upon treatment of $ReH_5(PMe_2Ph)_3$ with 1 equiv of $HBf_4 \cdot Et_2O$ in CD_3CN . Allowing the solution to stand for several days resulted in the appearance of a new species, identified as $ReH(CD_3CN)_3(PMe_2Ph)_3(PF_6)_2$ on the basis of 1H and ^{31}P NMR comparison to previously published work.¹⁰

[*cis,mer*-IrH(MeCN)₂(PMe₂Ph)₃](BF₄)₂. Addition of 2 mmol of $HBf_4 \cdot Et_2O$ to 1 mmol of *fac*- H_3IrP_3 in CD_2Cl_2 containing 6 mmol of acetonitrile causes immediate gas evolution and production of the title compound, whose stoichiometry and stereochemistry are established by the following NMR data. 1H NMR (CD_2Cl_2): δ +2.72 (s, 3 H), +2.36 (s, 3 H), +1.64 (t, 6 H), +1.60 (t, 6 H), +1.46 (d, 6 H), -20.25 (d ($J(P-cis H) = 17$ Hz) of t ($J(p-cis H) = 14$ Hz), 1 H). ^{31}P NMR (CD_2Cl_2): δ -28.39 (d ($J(P-P) = 20$ Hz), 2 P), -41.12 (t ($J(P-P) = 20$ Hz), 1 P). ^{31}P NMR (CD_2Cl_2): δ -28.4 (d of d, 2 P), -41.1 (m, 1 P).

(HPMe₂Ph)BF₄ was prepared by reaction of equimolar PMe_2Ph with $HBf_4 \cdot OEt_2$ in pentane. The colorless precipitate was filtered out, washed with pentane (2 × 20 mL), and dried under vacuum. 40.5-MHz ^{31}P NMR (CH_3CN): -0.5 ppm; on decrease of decoupler power, this singlet becomes a doublet. 360-MHz 1H NMR (CD_3CN): phenyl multiplets and 5.1 ppm (d ($J(P-H) = 340$ Hz), P-H), 2.3 (d of d ($J = 15, 7$ Hz), P-Me). These spectral parameters duplicate those observed after oxidation of $MoH_4(PMe_2Ph)_4$ with excess $Fe(bpy)_3^{3+}$.

Results

Copper hydrides present a particularly suitable test case for a new method of hydride ligand assay. It has been shown earlier that acidolysis of $(HCuPPh_3)_6$ with D^+ yields not only HD but also H_2 .¹¹ This latter product indicates that reductive elimination

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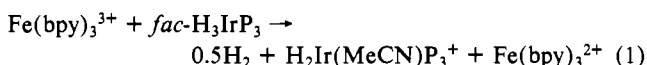
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of H₂ competes with combination of D⁺ with the Cu–H bond as a source of dihydrogen. Yet another possible source of dihydrogen from H⁺ and (LCuH)_n is H⁺-induced oxidation of Cu⁺ to Cu²⁺. Since the mechanism of acidolysis is not simple, the stoichiometry is also irrational, and previous workers were compelled to cope with this problem by combining D⁺ with (HCuPPh₃)₆, with subsequent mass spectral analysis of HD/H₂ composition. At the heart of this confusion is the utilization of an analytical reagent that can contribute in several (nonstoichiometric) ways to hydrogen evolution. Oxidatively induced reductive elimination of H₂ is evaluated here as an improved method for assaying hydride ligands.

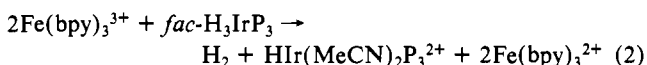
Oxidation of (HCuPPh₃)₆ with Fe(bpy)₃³⁺ (2.5 Fe/Cu) in acetonitrile rapidly evolves hydrogen. Toepler pumping of the noncondensables (–196 °C) from this reaction into a calibrated gas manifold reveals the evolution of 0.5 H₂/Cu, thus establishing a 1:1 ratio of hydride ligands to copper centers.

The copper hydride H_nCu₈(dppp)₄ (dppp = Ph₂P(CH₂)₃PPh₂) represents another informative test case.¹² The hydride resonance falls within the array of resonances of the CH₂ groups, frustrating integration. The small (unresolved) P–Cu–H coupling has prevented counting hydrides by means of the ³¹P multiplet structure. Oxidation of this eight-copper cluster with Fe(bpy)₃³⁺ (3.7 Fe/Cu) in acetonitrile evolves hydrogen in an amount corresponding to 1.1 hydride ligands per copper, thus indicating the formula H₈Cu₈(dppp)₄. This result is confirmed by successful refinement of eight hydride ligands using single-crystal X-ray diffraction data.¹³

In light of the successful assay of copper hydrides, we sought to determine the general applicability of this method toward other metal polyhydride complexes. The compound H₃IrP₃ (P = PMe₂Ph) furnishes an opportunity to test whether the number of hydride ligands per molecule must be even in order to evolve H₂ quantitatively. This question is related to whether or not H₂ elimination must be unimolecular or can be bimolecular. Reaction of *fac*-H₃IrP₃ with equimolar Fe(bpy)₃³⁺ in MeCN yields 0.48 mol of H₂/mol of Ir. Separate ¹H and ³¹P NMR experiments have identified the iridium-containing product as exclusively *cis,mer*-H₂Ir(MeCN)P₃⁺ (eq 1).¹⁴



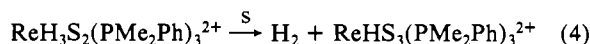
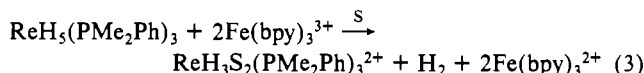
Oxidation of H₃IrP₃ with 2.1 Fe(bpy)₃³⁺/Ir over a period of 1 h resulted in evolution of 0.97 mol of H₂/mol of Ir. ³¹P and ¹H NMR spectra reveal the iridium-containing product of this oxidation to be exclusively *cis,mer*-H₂Ir(MeCN)₂P₃²⁺.¹⁵ The overall reaction is thus eq 2. The oxidative removal of only two



of three available hydride ligands occurs with the perhaps predictable retention of iridium oxidation state +3 in the isolable product. Attempts to remove all hydride ligands from *fac*-H₃IrP₃ by using an Fe³⁺:Ir ratio of 7:1 gave results consistent only with eq 2; only two hydride ligands can be eliminated. While there may be some inefficiency associated with the reaction of two cations (Fe(bpy)₃³⁺ with IrH(MeCN)₂P₃²⁺), the inability to completely remove all hydride ligands is probably due to insufficient oxidation potential to further oxidize cationic H₂Ir(MeCN)₂P₃²⁺.

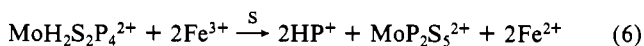
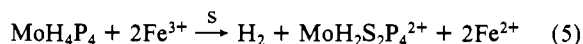
Oxidation of ReH₅(PMe₂Ph)₃ with excess (8 mol of Fe³⁺/mol of Re) Fe(bpy)₃³⁺ in MeCN yields, after 2.5 h, 1.0 mol of H₂/mol of rhenium compound employed. If the reaction is executed with an Fe:Re ratio of 2.0 but the reaction time is lengthened to 4 days,

the product, characterized by ¹H and ³¹P NMR, is the monohydride ReH(MeCN)₃(PMe₂Ph)₃²⁺.¹⁰ The seemingly paradoxical production of more H₂ from less oxidant reveals the importance of the solvent in effecting hydrogen evolution, since the longer reaction time permits *thermal* displacement of bound hydride ligands by S = MeCN (eq 3 and 4). Termination of oxidatively



induced hydrogen evolution at the trihydride stage is likely to be due to the high oxidation potential of a dication, aggravated by the kinetic (Coulomb) barrier to further reaction of such a dication with the ferric trication.

Yet another fate for bound hydride is exhibited by MoH₄P₄. Oxidation (6 Fe³⁺/Mo) of this tetrahydride in MeCN evolves 1.0 mol of H₂/mol of Mo. If the oxidation is carried out with only 2 Fe³⁺/Mo, hydrogen evolution is accompanied by production of MoH₂(MeCN)₂P₄²⁺ as the only molybdenum-containing product.¹⁶ Addition of an additional 2 mol of Fe³⁺/mol of Mo to this solution next induces dissociation of hydride ligands as *protons*. These were characterized by ¹H and ³¹P NMR as HPMe₂Ph⁺, this being the only acetonitrile-soluble phosphorus-containing material. The sequence of reactions is summarized in eq 5 and 6, where we suggest a possible fate for the molybdenum. Brønsted



acid behavior is thus evident when the dihydride dication is further oxidized (eq 6). This represents "overoxidation" of hydride ligands (past H₂ to H⁺) and thus loss of clean conversion exclusively to the preferred product H₂.

The method described here has promise for quantifying volatile ligands other than hydrides. Thus, Fe(bpy)₃³⁺ in acetonitrile liberates 8.1 mol of CO/mol of Co₂(CO)₈. The use of anhydrous (nonaqueous) conditions is recommended for CO assay in order to avoid producing any CO₂, which, as a condensable gas, would complicate quantification.

Discussion

Reliable application of the method requires attention to certain factors. While acetonitrile has been chosen as a solvent that should actively displace volatile ligands from the oxidized metal complex,¹⁷ it is advisable to examine the infrared or NMR spectrum of reaction residues to establish the absence of residual CO or H ligands. While the oxidation potential of Fe(bpy)₃³⁺ (1.21 V in MeCN)¹⁸ is substantial, there will certainly be cases where it is insufficient. Thus, when the oxidation-resistant Cr(CO)₆ (E° = +1.50 V in MeCN)¹⁹ was oxidized by tenfold excess Fe(bpy)₃³⁺, only 3.1 mol of CO was evolved/mol of chromium taken, and this after a reaction time of 24 h. While a more potent oxidant may be useful (e.g., Ir(bpy)₃⁴⁺ with E° = 2.17 V),²⁰ we currently favor the cost-effectiveness of Fe(bpy)₃³⁺. Alternatively, one could envision execution of the oxidative hydrogen evolution electrochemically, thereby greatly expanding the range of available potentials. Finally, attention is directed to the need to establish (e.g., by manometry) a reaction time appropriate to complete cessation of gas evolution.

In our experience, the choice of an outer-sphere oxidant promotes rapid reaction at or below 25 °C.²¹ Moreover, the choice

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of a substitutionally inert outer-sphere oxidant devoid of Brønsted basic (pseudo)halide ligands, X, appears to be beneficial in avoiding postoxidation transfer of hydride ligands to X⁻, which confuses quantification by producing a nonstoichiometric mixture of H₂ and HX products. It is for this reason that we have not examined Fe(CN)₆³⁻ as an oxidant.

This study discloses an analytical technique that can be useful for quantitative assay of hydride ligands. On the basis of the systems studied, the procedure appears to be most useful when the highest accessible metal oxidation state is fairly low (e.g. Cu) and thus there is no question of failing to oxidize to a d-electron configuration where hydrogen elimination becomes quantitative. In cases where hydrogen evolution is incomplete, careful attention to identification of the oxidized nonvolatile products (e.g. coordinated hydride or protonated ligand) may still permit the total number of hydride ligands to be established. The method also warrants evaluation for quantifying ligands such as CO₂, O₂, N₂,

light olefins²² and alkynes, oxalate, NO, alkyl, and even perhaps BH₄. In the last two cases, and in general, mass and/or infrared spectral analysis of the identity and purity of the evolved gas is recommended.

The mechanistic details of certain of these oxidative hydrogen evolution reactions are currently under study.

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Registry No. Fe(bpy)₃(PF₆)₃, 28190-88-7; ReH₅(PMe₂Ph)₃, 65816-70-8; [*cis,mer*-IrH(MeCN)₂(PMe₂Ph)₃](BF₄)₂, 104155-37-5; *fac*-H₃IrP₃, 12099-83-1; MoH₄P₄, 40209-71-0; Co₂(CO)₈, 10210-68-1; (HPMe₂Ph)BF₄, 104155-38-6; H⁻, 12184-88-2; CO, 630-08-0.

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Contribution from The BFGoodrich Research and Development Center, Brecksville, Ohio 44141

³¹P and ¹³C Solid-State NMR of Tertiary Phosphine-Palladium Complexes Bound to Silica

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Phosphorus-31 and carbon-13 NMR spectra with cross polarization and magic-angle spinning are used to characterize palladium-tertiary phosphine complexes and their precursors covalently bound to silica. Phosphorus-31 NMR is a good probe of complex formation and geometry, whereas ¹³C NMR is a good probe of ligand structure. The 36.44-MHz ³¹P spectrum of (≡SiOSiCH₂CH₂PPH₂)₂PdCl₂ shows two, barely resolved peaks at about 21 and 30 ppm assigned to the trans and cis complexes, respectively. These assignments are based on the chemical shifts of model compounds in both solution and the solid state. Uncomplexed phosphine and phosphine oxide are observed when complexes are prepared from phosphinated silica but not when the complexes are preformed and then attached to silica. The palladium dichloride complexes of bis(diphenylphosphino)methane, -ethane, and -propane, all of which have an approximately square-planar configuration, were examined as solid-state models for strained cis complexes on the silica surface. As in solution, the solid-state ³¹P chemical shifts of these compounds occur over a range of 127 ppm while the P-Pd-P angle varies from 73 to 91°. Hence, the ³¹P chemical shift is a very sensitive measure of strain in such complexes and confirms that the structures in solution are similar to those in the solid state. Applying these models, we find that the surface-bound complexes have mainly unstrained, trans configurations. Other species that have been examined on surfaces or as models include (dicyclohexylpropyl)phosphino complexes, for which cis and trans surface-bound complexes are observed, trimethylsilyl-capped samples, and phosphine oxides. Evidence is found for hydrogen bonding between bound phosphine oxide groups and silanol groups on the silica surface. Both the chemical shift anisotropy powder pattern and P-H cross-polarization rates indicate that the Pd-phosphine complex is rigidly bound to the silica surface.

Introduction

Considerable attention has been given recently to the chemical modification of organic and inorganic surfaces to increase their usefulness in catalytic processes. The materials resulting from such modifications are being explored as alternatives to conventional homogeneous and heterogeneous catalysts.¹ The chemical composition, conformation, and mobility of the molecular species existing at surfaces are important factors for establishing the relationship between heterogeneous catalytic processes and the corresponding ones in homogeneous solution.²

Analytical techniques for characterization of molecular structures at surfaces are few. X-ray photoelectron spectroscopy (XPS) is a powerful tool for surface characterization, but it provides atomic composition and oxidation state only. Infrared spectroscopy is commonly used to study surfaces.¹ Other techniques such as secondary ion mass spectrometry (SIMS), fast atom bombardment (FAB) mass spectrometry, and X-ray absorption

using synchrotron radiation (EXAFS) are also available.

In certain situations NMR spectroscopy can be useful for studying molecules on surfaces. NMR has the advantages of spectral simplicity and ease of interpretation, as well as sensitivity to molecular mobility. Standard high-resolution NMR has been used for some time to characterize the absorption (physisorption) of molecules on surfaces.³ This has been possible because the mobility of the adsorbed molecules on the surface or the exchange of the adsorbed molecule with unbound molecules in solution yields a relatively narrow NMR line whose features depend on the nature of the adsorption. In certain cases, swelling of the substrate can provide enough mobility to allow a standard high-resolution NMR spectrum to be obtained. It is only since the advent of solid-state

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