Inorg. Chem. **1986**, *25*, 3915–3917

Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Assay of Hydride or Volatile Ligands via Outer-Sphere Oxidation

T. H. Lemmen, E. G. Lundquist, L. F. Rhodes, B. R. Sutherland, D. E. Westerberg, and K. G. Caulton*

Received June 19, 1986

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 integration[3] and selective nuclear spin coupling[4] 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, $MH_rX_sL_n$, 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*-$IrH(MeCN)_2(PMe_2Ph)_3](BF_4)_2$. 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). $^{31}P(^1H)$ 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).

$(HPMe_2Ph)BF_4$ 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 $^{31}P(^1H)$ 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

---

(1) Sternberg, H. W.; Wender, I.; Orchin, M. *Anal. Chem.* **1952**, *24*, 174.
(2) Hieber, W.; Sedlmeier, J. *Chem. Ber.* **1954**, *87*, 25.
(3) Crabtree, R. H.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1985**, *24*, 1949.
(4) Selectively hydride-*coupled* ^{31}P NMR spectra gave multiplet structure indicative of the number of hydride ligands present. However, when P–H coupling constants are small, such coupling can be difficult to resolve.
(5) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.
(6) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc. D* **1970**, 703.
(7) Sacco, A.; Rossi, M. *Inorg. Chim. Acta* **1968**, *2*, 127.
(8) Drago, R. S.; DeSimone, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 2343.
(9) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruna, H. D.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1896.
(10) Crabtree, R. H.; Hlatky, G. G.; Parnell, C. P.; Segmüller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354.
(11) Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818.

0020-1669/86/1325-3915$01.50/0

of H_2 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 Cu^{2+}. 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 $(HCuPPh_3)_6$, with subsequent mass spectral analysis of HD/H_2 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 H_2 is evaluated here as an improved method for assaying hydride ligands.

Oxidation of $(HCuPPh_3)_6$ with $Fe(bpy)_3{}^{3+}$ (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 H_2/Cu, thus establishing a 1:1 ratio of hydride ligands to copper centers.

The copper hydride $H_nCu_8(dppp)_4$ (dppp = $Ph_2P(CH_2)_3PPh_2$) represents another informative test case.[12] The hydride resonance falls within the array of resonances of the CH_2 groups, frustrating integration. The small (unresolved) P–Cu–H coupling has prevented counting hydrides by means of the ^{31}P multiplet structure. Oxidation of this eight-copper cluster with $Fe(bpy)_3{}^{3+}$ (3.7 Fe/Cu) in acetonitrile evolves hydrogen in an amount corresponding to 1.1 hydride ligands per copper, thus indicating the formula $H_8Cu_8(dppp)_4$. 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 H_3IrP_3 (P = PMe_2Ph) furnishes an opportunity to test whether the number of hydride ligands per molecule must be even in order to evolve H_2 quantitatively. This question is related to whether or not H_2 elimination must be unimolecular or can be bimolecular. Reaction of *fac*-H_3IrP_3 with equimolar $Fe(bpy)_3{}^{3+}$ in MeCN yields 0.48 mol of H_2/mol of Ir. Separate ^1H and ^{31}P NMR experiments have identified the iridium-containing product as exclusively *cis,mer*-$H_2Ir(MeCN)P_3{}^+$ (eq 1).[14]

$$Fe(bpy)_3{}^{3+} + fac\text{-}H_3IrP_3 \rightarrow 0.5H_2 + H_2Ir(MeCN)P_3{}^+ + Fe(bpy)_3{}^{2+} \quad (1)$$

Oxidation of H_3IrP_3 with 2.1 $Fe(bpy)_3{}^{3+}$/Ir over a period of 1 h resulted in evolution of 0.97 mol of H_2/mol of Ir. ^{31}P and ^1H NMR spectra reveal the iridium-containing product of this oxidation to be exclusively *cis,mer*-$HIr(MeCN)_2P_3{}^{2+}$.[15] The overall reaction is thus eq 2. The oxidative removal of only two

$$2Fe(bpy)_3{}^{3+} + fac\text{-}H_3IrP_3 \rightarrow H_2 + HIr(MeCN)_2P_3{}^{2+} + 2Fe(bpy)_3{}^{2+} \quad (2)$$

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*-H_3IrP_3 by using an Fe^{3+}: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 ($Fe(bpy)_3{}^{3+}$ with $IrH(MeCN)_2P_3{}^{2+}$), the inability to completely remove all hydride ligands is probably due to insufficient oxidation potential to further oxidize cationic $HIr(MeCN)_2P_3{}^{2+}$.

Oxidation of $ReH_5(PMe_2Ph)_3$ with excess (8 mol of Fe^{3+}/mol of Re) $Fe(bpy)_3{}^{3+}$ in MeCN yields, after 2.5 h, 1.0 mol of H_2/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 ^{31}P NMR, is the *mono*-hydride $ReH(MeCN)_3(PMe_2Ph)_3{}^{2+}$.[10] The seemingly paradoxical production of more H_2 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

$$ReH_5(PMe_2Ph)_3 + 2Fe(bpy)_3{}^{3+} \xrightarrow{S} ReH_3S_2(PMe_2Ph)_3{}^{2+} + H_2 + 2Fe(bpy)_3{}^{2+} \quad (3)$$

$$ReH_3S_2(PMe_2Ph)_3{}^{2+} \xrightarrow{S} H_2 + ReHS_3(PMe_2Ph)_3{}^{2+} \quad (4)$$

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 MoH_4P_4. Oxidation (6 Fe^{3+}/Mo) of this tetrahydride in MeCN evolves 1.0 mol of H_2/mol of Mo. If the oxidation is carried out with only 2 Fe^{3+}/Mo, hydrogen evolution is accompanied by production of $MoH_2(MeCN)_2P_4{}^{2+}$ as the only molybdenum-containing product.[16] Addition of an additional 2 mol of Fe^{3+}/mol of Mo to this solution next induces dissociation of hydride ligands as *protons*. These were characterized by ^1H and ^{31}P NMR as $HPMe_2Ph^+$, 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

$$MoH_4P_4 + 2Fe^{3+} \xrightarrow{S} H_2 + MoH_2S_2P_4{}^{2+} + 2Fe^{2+} \quad (5)$$

$$MoH_2S_2P_4{}^{2+} + 2Fe^{3+} \xrightarrow{S} 2HP^+ + MoP_2S_5{}^{2+} + 2Fe^{2+} \quad (6)$$

acid behavior is thus evident when the dihydride dication is further oxidized (eq 6). This represents "overoxidation" of hydride ligands (past H_2 to H^+) and thus loss of clean conversion exclusively to the preferred product H_2.

The method described here has promise for quantifying volatile ligands other than hydrides. Thus, $Fe(bpy)_3{}^{3+}$ in acetonitrile liberates 8.1 mol of CO/mol of $Co_2(CO)_8$. The use of anhydrous (nonaqueous) conditions is recommended for CO assay in order to avoid producing any CO_2, 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 $Fe(bpy)_3{}^{3+}$ (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 $Fe(bpy)_3{}^{3+}$, 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., $Ir(bpy)_3{}^{4+}$ with $E° = 2.17$ V),[20] we currently favor the cost-effectiveness of $Fe(bpy)_3{}^{3+}$. 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

---

(12) Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 7774.

(13) Folting, K., unpublished results.

(14) Rhodes, L. F.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259.

(15) This dication may be produced independnetly by acidolysis of *fac*-H_3IrP_3 with 2 molar equiv of $HBF_4·OEt_2$ in the presence of acetonitrile. See Experimental Section.

(16) Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185.

(17) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.

(18) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(19) Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Organomet. Chem.* **1977**, *140*, 349.

(20) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

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 H_2 and HX products. It is for this reason that we have not examined $Fe(CN)_6^{3-}$ 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 CO_2, O_2, N_2, light olefins[22] and alkynes, oxalate, NO, alkyl, and even perhaps BH_4. 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.

Acknowledgment. This work was supported by the U.S. National Science Foundation (Grant No. 83-05281) and by the Canadian Natural Sciences and Engineering Research Council. We also thank Johnson Matthey, Inc., and Rhenium Alloys for material support and Stadt Wien for the inception of the idea developed here.

Registry No. $Fe(bpy)_3(PF_6)_3$, 28190-88-7; $ReH_5(PMe_2Ph)_3$, 65816-70-8; [*cis,mer*-$IrH(MeCN)_2(PMe_2Ph)_3](BF_4)_2$, 104155-37-5; *fac*-$H_3IrP_3$, 12099-83-1; MoH_4P_4, 40209-71-0; $Co_2(CO)_8$, 10210-68-1; $(HPMe_2Ph)BF_4$, 104155-38-6; H^-, 12184-88-2; CO, 630-08-0.

---

(21) Self-exchange in the $Fe(bpy)_3^{3+/2+}$ couple proceeds near the diffusion-controlled rate.

(22) Compare the oxidative (Pb^{4+}, Ag^+, or Ce^{4+}) release of olefins from metal complexes in: Merk, W.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 4787.

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

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

Richard A. Komoroski,*[†] Angelo J. Magistro, and Paul P. Nicholas

Received December 26, 1985

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 ^{13}C NMR is a good probe of ligand structure. The 36.44-MHz ^{31}P spectrum of $(\equiv SiOSiCH_2CH_2PPh_2)_2PdCl_2$ 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 ^{31}P 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 ^{31}P 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

---

[†] Present address: Departments of Radiology and Pathology, University of Arkansas for Medical Sciences, Little Rock, AR 72205.

(1) (a) Bergbreiter, D. E. *ACS Symp. Ser.* **1982**, *No. 192*, 1. (b) Shustorovich, E.; Baetzold, R. C. *Science (Washington, D.C.)* **1985**, *227*, 876 and references therein.

(2) (a) Mazur, S.; Jayalekshmy, P.; Andersson, J. T.; Matusinovic, T. *ACS Symp. Ser.* **1982**, *No. 192*, 43. (b) Somorjai, G. A. *Science (Washington, D.C.)* **1985**, *227*, 902 and references therein.

(3) Pfeifer, H.; Meiler, W.; Deininger, D. *Annu. Rep. NMR Spectrosc.* **1984**, *15*, 291.