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^{31}P NMR ANALYSIS OF COAL MOIETIES BEARING -OH, -NH, AND-SH FUNCTIONS

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Abstract

NMR reagents for the speciation and quantitation of labile-hydrogen functional groups and sulfur groups in coal ligands have been synthesized and evaluated. These reagents, which contain the NMR-active nuclei ^{31}P, ^{119}Sn or ^{195}Pt, were designed to possess improved chemical shift resolution over reagents reported in the literature. Our efforts were successful in the case of the new ^{31}P and ^{119}Sn reagents we developed, but the ^{195}Pt work on sulfur groups was only partially successful in as much as the grant came to a close and was not renewed.

Our success with ^{31}P and ^{119}Sn NMR reagents came to the attention of Amoco and they have recently expressed interest in further supporting that work. A further measure of the success of our efforts can be seen in the nine publications supported by this grant which are cited in the reference list.

Original Hypothesis

The research described in this report was based on the premise that tagging reagents containing NMR active nuclei such as ^{31}P could be designed to conveniently speciate and quantitate labile-hydrogen heteratom functional groups in coal materials.

Introduction

Although reliable analytical techniques have been devised for the analysis of *total* organic oxygen[1-3] and sulfur[1,2,4] in coal materials, efforts to identify and quantitate the *specific* organic moieties to which these important heteroatoms are bound are comparatively poorly developed. Experiments directed at quantitating *generic* types of organically bound -OH and CO_2H and sulfur include:

- Mass balance and/or GC techniques using reagents for -SH,[1,2] -OH,[5,6] C=O,[5] and -OMe[6] groups

- Infrared analysis of derivatized -OH and -CO_2H groups using a variety of reagents[1,2] (e.g., D_3-methylation,[7] acetylation[8] and silylation[9-12]) or of unfunctionalized[9,13,14] hydroxyl groups
- ^{13}C NMR spectroscopy of acetylated -OH groups[8,14]
- Two-dimensional ^1H correlation NMR spectroscopy for underivatized ROH, R_2CO and ArOH[15a]
- ^{17}O NMR for total phenols, alcohols and ethers[15b]
- ^1H and ^{19}F NMR studies of derivatized amines in coal extracts[1]
- ^1H, ^{13}C and ^{19}F NMR studies of derivatized asphaltenes[16]
- ^{29}Si NMR spectroscopy of derivatized coal phenol fractions[17] and of ROH and ArOH in a crude oil sample[18]
- ^{29}Si, ^{19}F and ^{31}P spectroscopy of derivatized phenols in coal liquids[19]
- ^1H NMR spectroscopy of adsorbed H_2O[20] and of trimethylsilylated hydroxyls[21,22]
- ^{17}O NMR spectroscopy revealing -OH, RC(O)H and R_2CO peaks in coal-derived liquids[23]
- ^1H and ^{13}C NMR studies of phase-transfer methylated -OH, -CO_2H and NH groups[11]
- Thermokinetic reduction of sulfur compounds in coal[1,2]
- XAFS for the determination of aromatic sulfur[24] and TEM for total organic sulfur[25]
- XPS and absorption near edge structure (XANES) for the determination of sulfidic and thiophenic sulfur in coal and petroleum asphaltenes[26]
- Gas chromatography for total phenols[27a]
- GC/MS for phenols and amines[27b]

While these studies are extremely valuable, they do not identify and quantitate the specific organic moiety to which the heteroatom is bound. This situation is understandable for solid coals wherein the heteroatom may be incorporated into extremely large organic molecules which present techniques are not yet sufficiently sensitive to differentiate. A number of investigations have been aimed at identifying and in a substantial number of cases quantitating the specific organic moiety bound to heteroatoms (particularly phenols and amines) in coal derived liquids. These reports deal mainly either with chromatographic, mass spectral or NMR techniques, and they achieve their objectives with highly varying degrees of success:

- Phenols by GC,[28-31] TLC[32] and HPLC[33,34] and by ^{1}H/^{13}C NMR spectroscopies[35]
- Derivatized phenols by ^{119}Sn[36] NMR and ^{19}F NMR/GC[37,38]
- Phenols and amines by GC[39]
- Amines by GC/MS,[40] LC[41] and GC[42]
- Derivatized amines by ^{19}F NMR spectroscopy[43]

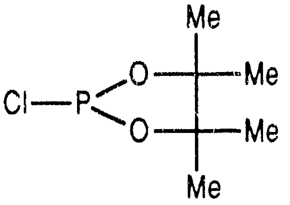
In a number of cases, partial identification of individual compounds in coal liquids has been achieved, but without quantitation:

- Phenols via GC/MS and MS/MS[44]
- Lactones and ketones by GC/FTIR/MS[45]
- Phenols, amines and thiophenols by CIMS[46]
- Phenols by negative ion MS[47]
- Phenols by LC[48a] and HPLC[48b]
- Phenols by GC/MS[49]
- Phenols, acids and amines by GC/MS[50]
- Derivatized phenols by ^{19}Si,[51,52] and ^{31}P NMR spectroscopies[56]

Approaches Used

Labile-Hydrogen Organic Functional Groups. Our own efforts, since entering this field four years ago, have centered on *designing* reactive NMR tagging reagents that impart maximum resolution of the labile hydrogen functional groups, i.e., $-CO_2H$, -OH, NH and -SH. Our objective was to synthesize reagents that would bond the NMR active nucleus directly to the heteroatom for maximum chemical shift sensitivity, unlike ^{19}F reagents which place this atom three bonds away thereby giving chemical shift ranges that are generally only ~1 ppm. Interestingly, ^{29}Si, ^{119}Sn and ^{31}P reagents studied by others do place these atoms directly on the heteroatom. However, the $^{29}SiMe_3$ tag requires DEPT and INEPTR pulse sequences to provide reliable quantitative data in its somewhat small 12 ppm range,[57] and cresol isomers cannot be differentiated with this moiety.[51] The chemical shift range for most phenols derivatized with $(Bu_3Sn)_2O$ is similar, and the conditions of derivatization (azeotropically distilling water formed in the reaction at elevated temperature in boiling toluene) are less than desirable. The range of chemical shifts for the $-P(O)(OEt)_2$ and $-P(O)Me_2$ derivatizing moieties, which also place the ^{31}P NMR tagging nucleus directly on the oxygen of phenols, was only 0.63 and 1.18 ppm, respectively.[38]

The strategy for our ^{31}P NMR tags was based on our observation that P(III) compounds tend to have more widely ranging chemical shifts than for analogous P(V) derivatives. Since the previous studies by others involved P(V) compounds with ranges of only up to ~1 ppm,[38] we evaluated a series of P(III) reagents[58-62] of which the best for phenols were **1** and **2**, giving considerably larger ^{31}P chemical



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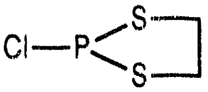

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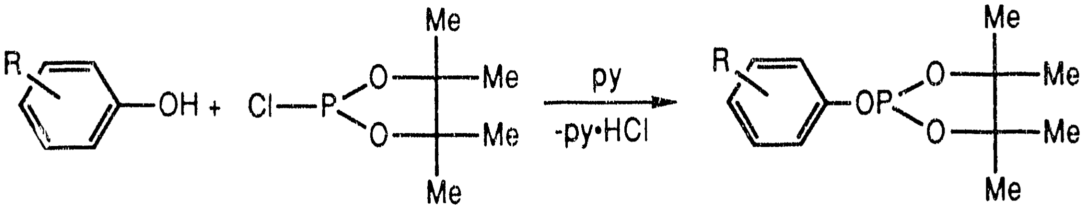
shift ranges of 5.5 and 15.3 ppm, respectively. The reaction of **1** with phenols is given as an example in reaction 1. With these reagents we were able to identify and quantitate 19 phenols in an Illinois No. 6 low-temperature condensate, which



(1)

accounts for about 60% of the phenols present.[63] Advantages of our reagents are:

- They react quickly and completely under mild conditions (below room temperature) even with sterically hindered systems. (Relevant here is the fact that $(^{19}F_3C)_2$ C=O does not react with 2,6-disubstituted phenols.)
- The chemical shift dispersion of phenols with **1** and **2** is the largest seen to date with a ^{31}P reagent. See Figure 1 for a sample ^{31}P NMR spectrum.
- The chemical shift dispersion of amines is over 55 ppm using Cl-$P(SCH_2)_2CH_2$.[62]
- These reagents result in different chemical shifts for the same phenol, thus permitting a cross-check on identification.
- If a chemical shift of a derivative overlaps that of another with one of the reagents, it is often resolved by the other reagent.

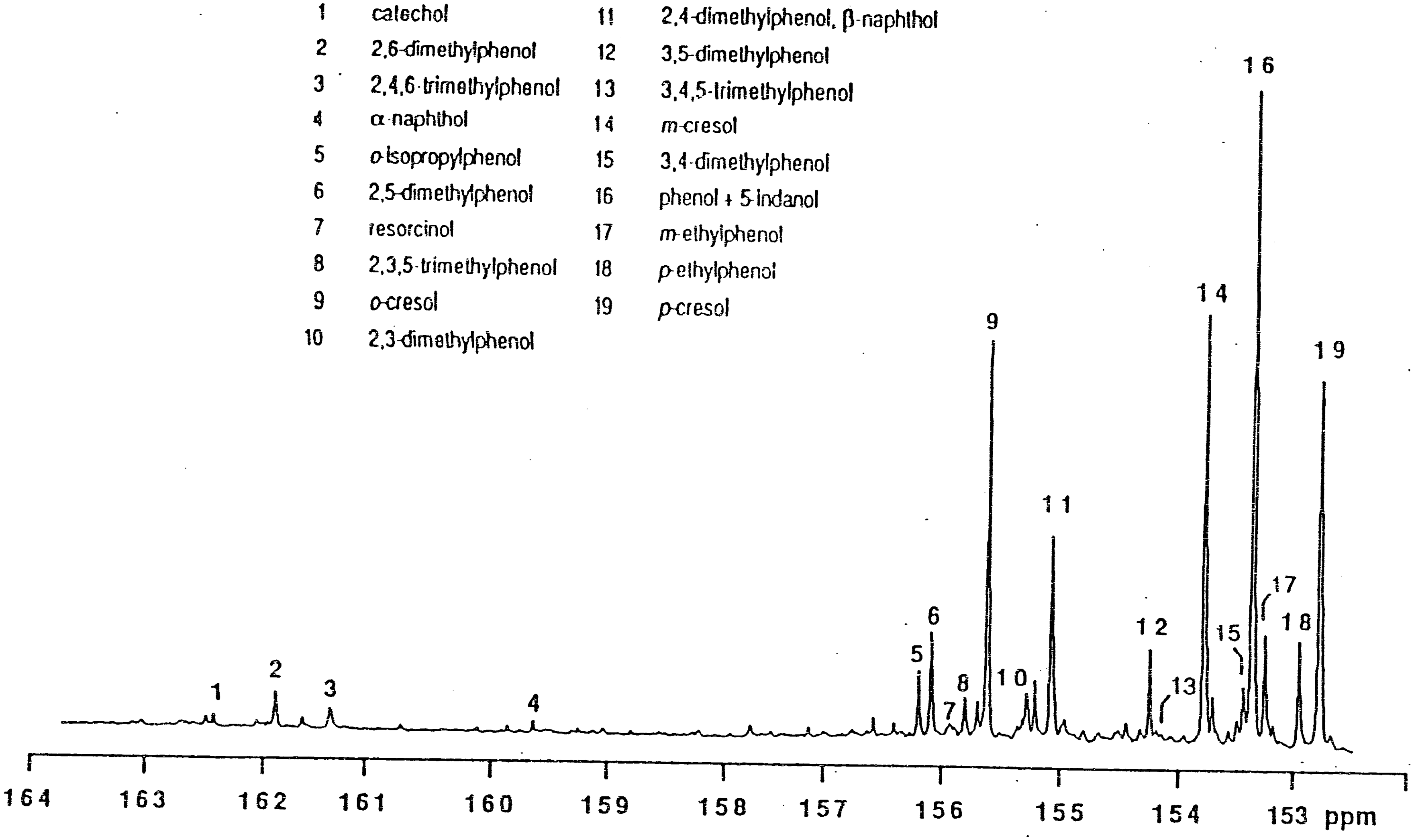
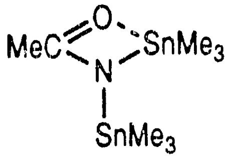


Figure 1. 200 MHz ^{31}P NMR spectrum of the phenol region of a low-temperature Illinois No. 6 condensate derivatized with reagent 2.

- Quantitation of derivatives with one reagent can be cross-checked with the other.
- Both reagents are sufficiently sensitive to resolve the chemical shifts for isomeric cresols.
- Peaks for phenols in the 0.5% concentration range can be quantitated with a precision of ±4.5 and ±3.2% with **1** and **2**, respectively.
- These reagents are quite successful in separating chemical shift ranges of three major classes of labile hydrogen functional groups as is shown in Figure 2.

This work has elicited interest on the part of Amoco and Consol. Amoco is enthusiastic about the possibility of funding further work by us which would have as one of its objectives the analysis of complex petroleum fractions. We have also submitted a proposal to Consol.

We then broadened our objective to include the design of reagent **5**, which is isostructural with the well-known silicon analog **6**, a very reactive silylating agent. Although **3** is also very reactive, an X-ray crystal structure determination revealed configuration **3** which features a long-distance Sn - - O interaction (2.737 Å)in the quasi four-membered ring.[65] Compound **4** is particularly well suited for mild derivatizations in pyridine as a solvent.[64] A second objective for our ^{119}Sn reagents was to overcome the strong sensitivity of the ^{119}Sn chemical shift to concentration. For example there is a >15 ppm ^{119}Sn chemical shift range for Me_3SnOEt in hexane over a concentration range of 0.3 to 1.3 M, rendering



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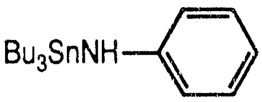

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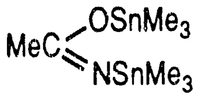

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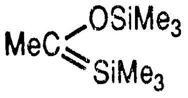

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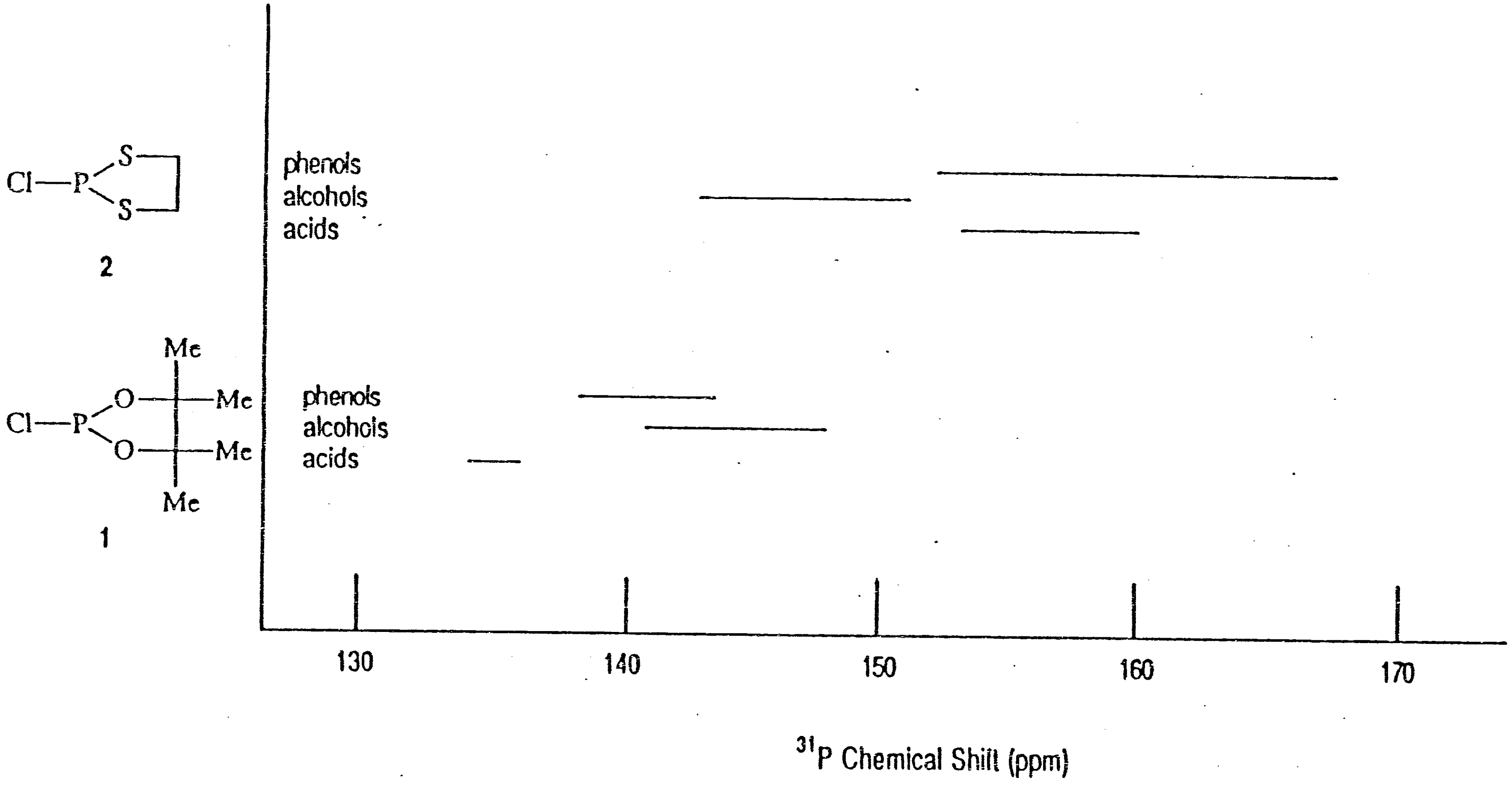
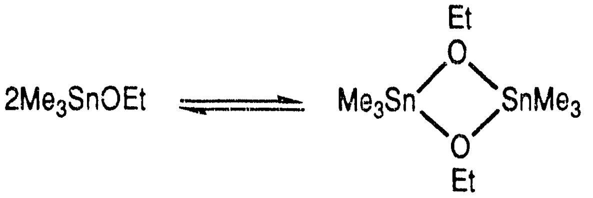


Figure 2. Chemical shift ranges for reagents 1 and 2.

assignments in mixtures of unknown concentrations impossible. We discovered that in pyridine, however, the ^{119}Sn chemical shift is insensitive to concentration. These results can be explained by equilibria of the type shown in reactions 2 and 3.[65] There are substantial advantages that accrue to reagents **3** and **4**:



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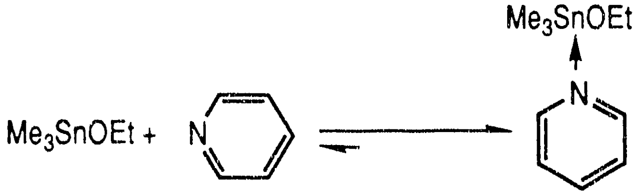
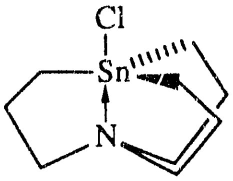


(3)

- The ^{119}Sn chemical shift ranges for derivatized model mixtures are unusually large in pyridine (typically three times as great as in hexane).
- These chemical shift ranges in pyridine for phenols and alcohols, for example, are much larger than for our best phosphorus reagent **2** by a factor of two and five, respectively.
- Phenols, alcohols and acids derivatized with -$SnMe_3$ and -$SnBu_3$ groups are *completely* separated in pyridine (see Figure 3).

It also occurred to us that structures such as **7** and **8** are robust owing to the existence of three very stable chelate rings. A reagent such as **7** or **8** has no need



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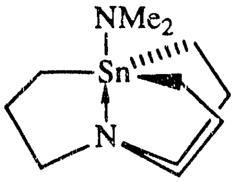

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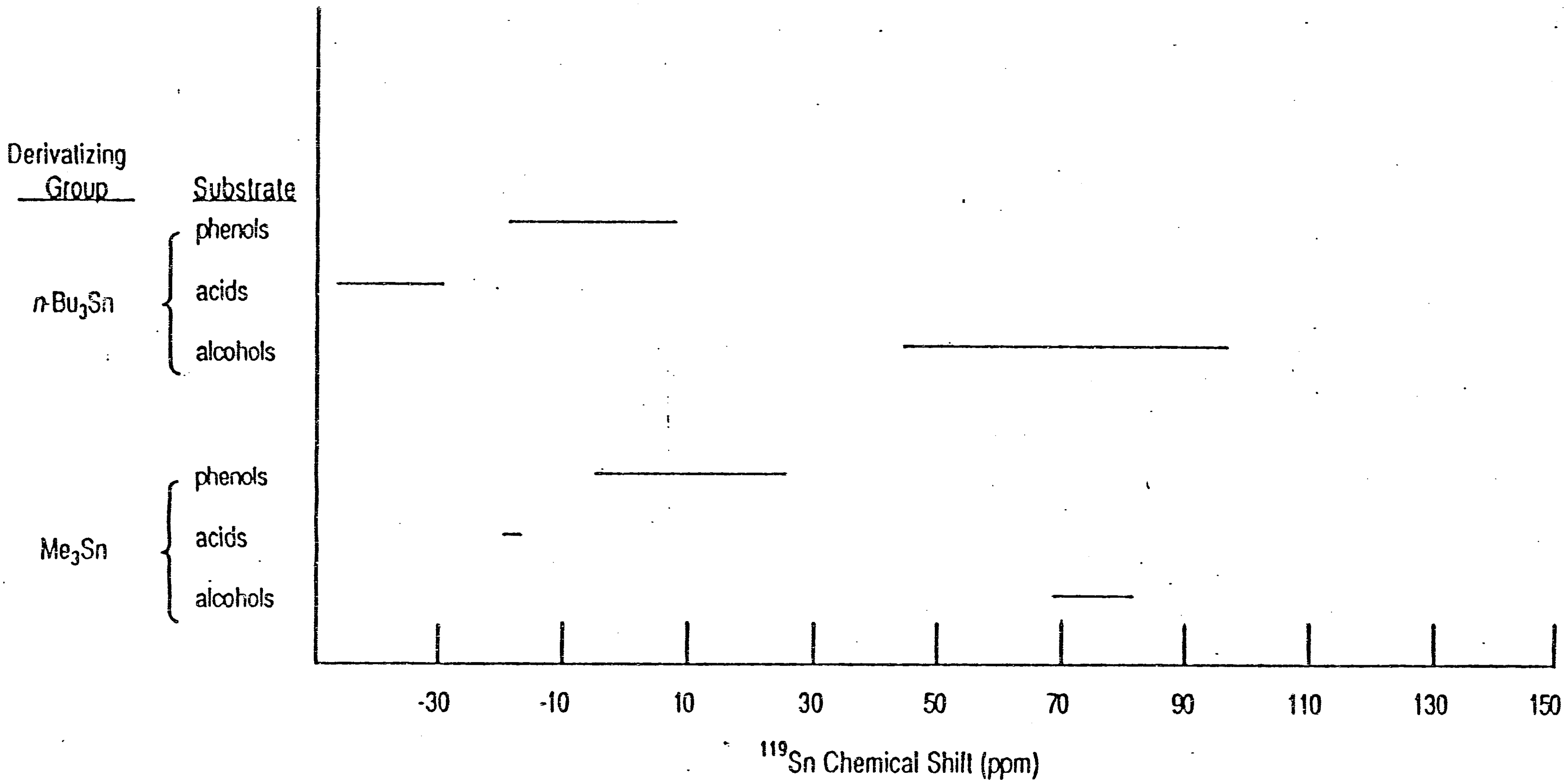
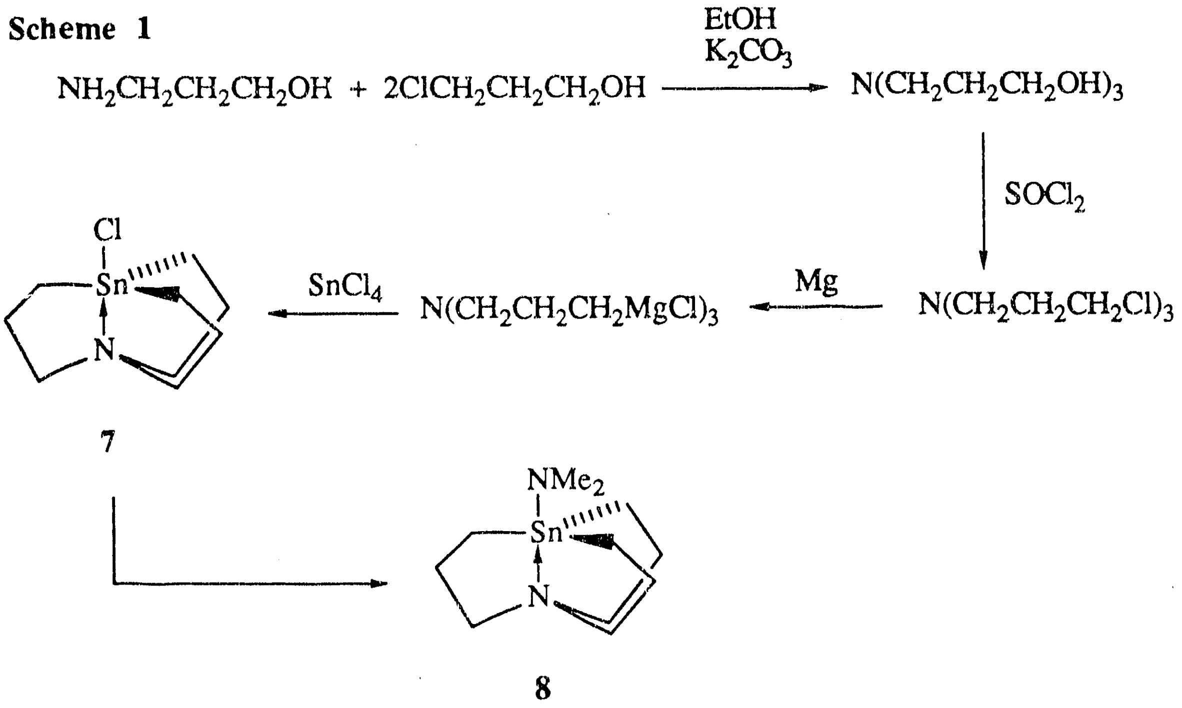


Figure 3. ^{119}Sn chemical shift ranges in pyridine.

of a solvent for coordination to the fifth coordination site since the tertiary nitrogen within the chelate ring system is already firmly attached there. As shown in Scheme 1 we have therefore synthesized **7** and have converted it in one step to the new derivatizing agent **8**, which is stable and crystalline. We have synthesized model compound derivatives of **8** in order to determine whether the ^{119}Sn chemical shifts are indeed both concentration and solvent independent.

Scheme 1



In a recent report,[66] Larsen et al. concluded from solid state ^{119}Sn Mössbauer experiments with an Illinois No. 6 sample derivatized with $(n\text{-}Bu_3Sn)_2O$ that the tin atoms replaced the labile hydrogens and that the tin (unexpectedly) was in a *five*-coordinate environment. The fifth coordination site was presumably occupied by a nearby coal heteroatom such as oxygen. Our solid state ^{119}Sn NMR results on a sample of the same coal prepared in exactly the same way indicate the presence of four-coordinate, and not five-coordinate tin. (In these experiments, Dr. John McClelland aided us in examining the derivatized coals by acoustic FTIR spectroscopy). In an effort to clarify this puzzling situation, Dr. Larsen has kindly sent us some of the same sample used in his earlier study. We have derivatized it just as he did and again our NMR results suggest that we are looking at four-coordinate tin. We have also obtained Mössbauer spectra on our samples and have concluded that, in agreement with Larsen et al., the tin would appear to be experiencing five-coordination in the coal. Coal samples derivatized with **8** (which is rigidly five-coordinate to begin with) should be subjected to ^{119}Sn NMR and Mössbauer experiments to determine whether or not CP/MAS ^{119}Sn NMR spectroscopy is a reliable indication of coordination number.

Moisture in Coal. A proper understanding of the nature of moisture in coal is essential to its efficient utilization as well as to developing a better fundamental knowledge of coal structure. In broad terms, coal moisture is often categorized "free" (i.e., surface moisture removable by mechanical means such as filtration) and "inherent" or bed moisture. Inherent moisture ranges from thermally released capillary moisture to water produced by pyrolytic decomposition of oxygen-containing functional groups.[67] Water sorption isotherm studies suggest that removal of free water is followed by capillary water which is then followed by water molecules that are sorbed in layers on surfaces of pores on the order of a few molecular diameters.[67] Monolayer water is associated with oxygen-containing functional groups by hydrogen bonding.[67] Thermally released water stemming from decomposition of oxygen-containing groups can occur well below 110 °C for low rank coals and can account for 1-2% of coal weight.[67] There is evidence that chemisorbed water (i.e., water associated with hydration of carboxylate and phenol groups can be thermally released only at temperatures above 110°[68] or in refluxing methanol.[69] Chemisorbed water associated with mineral matter may require up to 500 °C for expulsion.[70]

In addition to oven drying, azeotropic distillation, dessication and chemical titration[67,71] for the analysis of total water content, more recent methods include microwave techniques,[72] proton spin relaxation measurements,[73] proton CRAMPS NMR spectroscopy,[74] IR spectroscopy,[75] gamma ray backscattering[76] and ^{18}O isotope dilution.[77,78]

Our entry into this field came about as a result of a serendipitous discovery[79] made during our search for ^{31}P NMR tagging agents. Reagent **7** reacts with water in solution according to reaction 4.[19]

$$H_2O + 2Ph_2P(O)Cl \xrightarrow[-py\cdot HCl]{py} Ph_2P(O)OP(O)Ph_2 \qquad (4)$$

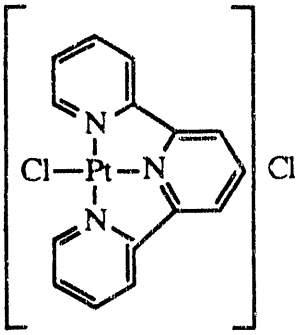
7 **8**

To our knowledge, however, ours is the first reported[80] example of water quantitation in coals using an NMR tagging technique. Reagent **7** has several advantages:

- The stoichiometry of reaction 4 leads to the formation of a product (**8**) possessing two ^{31}P nuclei, thus enhancing accuracy in the integration of the peak.
- The reaction is clean and quantitative.
- The ^{31}P NMR peak of **8** is well separated from those of peaks associated with derivatives of other labile hydrogen functional groups.
- Moisture quantitations are precise to ±1.1% for standard solutions.

Using this technique we then studied Argonne Premium Coal samples (APC's) with a series of extraction solvents in order to determine whether solvent extraction of H_2O as a function of time would tell us anything about the types of moisture contained in coal.[81] Four APC's (Beulah-Zap, Illinois No. 6, Blind Canyon and Pittsburgh No. 8) were extracted at 23 °C with pyridine, dioxane, dimethoxyethane, tetrahydrofuran, ethyl methyl ketone and acetonitrile. The moisture contents in the extracts were determined after 1/4, 1/2, 1, 2, 4 and 8 hours by ^{31}P NMR spectroscopy using the tagging reagent $ClP(O)Ph_2$. From the lowest rank coal, almost all of the water was extracted with pyridine within the first 15 minutes and for the remaining coals studied this process was complete after 8 hours. The water extracted with the least efficient extraction solvent (dioxane or dimethoxyether) within 15 minutes for each coal is considered as a reasonable estimate of the surface moisture. Higher rank coals (Pittsburgh No. 8 and Blind Canyon) contain about 50% of their total moisture as surface water, while as much as 69 and 88% such water is found for Illinois No. 6 and Beulah-Zap coals, respectively. Discrepancies between moisture contents in APC's determined by drying at 108 °C and by pyridine extraction at room temperature are accounted for by trapping as much as 25 and 15% of the coal water inside micropores of Pittsburgh No. 8 and Blind Canyon coals, respectively. There was no water left in the micropores of the Illinois No. 6 coal after drying. Upon oven drying, the Beulah-Zap coal gave ca. 4% more water than could be extracted over a period of 24 hours by pyridine. We attribute this excess moisture to decomposition of organic matter under oven drying conditions.

Sulfur Groups in Coal. Organic sulfur in coal and coal-derived materials generally takes the form of thioether (R_2S) compounds and thiophene heterocyclic systems. Although these types of compounds lack a labile hydrogen, we can take advantage of the well-known ability of the sulfur lone pair to coordinate to the platinum(II) cation. We have thus synthesized **9** and **10** as our first candidate reagents. We have successfully synthesized a series of thiol derivatives of **9** and



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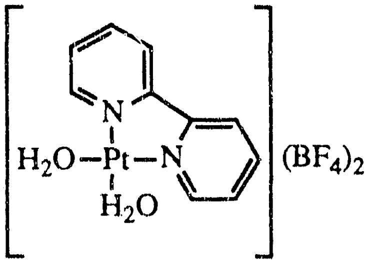

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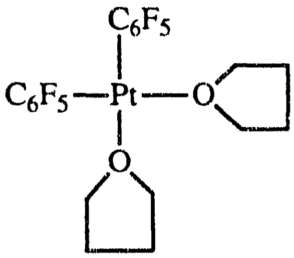

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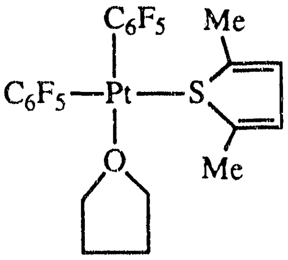
measured several of their ^{195}Pt NMR spectra.[82] It appears that differentiation may be possible, although the chemical shifts are currently quite broad. We also have synthesized **11** which has proven to be the first platinum compound capable of coordinating a thiophene (see structure below).



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