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

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Advanced Coal Research at U.S. Colleges and Universities

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Quarterly Report

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OBJECTIVE

The purpose of this research is to develop a convenient, reliable and rapid NMR method for the determination of labile-hydrogen functional groups and organic sulfur compounds which are components of coal and coal-derived materials. For this purpose, the former functional groups, including water molecules, are derivatized with reagents containing NMR-active nuclei such as ^{31}P or ^{119}Sn, while sulfur groups are derivatized with ^{195}Pt NMR tagging reagents. Knowledge of the heteroatom composition of coals is necessary for the development of increasingly sophisticated coal processing technologies.

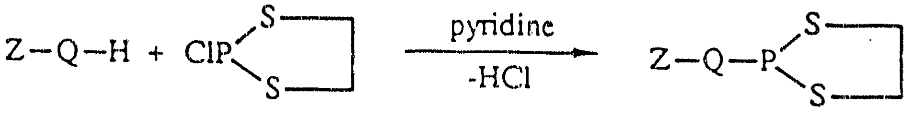
INTRODUCTION

Heteroatoms such as oxygen, sulfur, and nitrogen in coal are important in determining the processing methodology to be utilized. Because of this, a knowledge of the forms in which these heteroatoms occur in coal is required.[1] Thus, for example, oxidation of coal during weathering has a potentially serious economic impact on coal recovery by surface-based coal cleaning processes,[2] and also on its caloric content.[3] Moreover, the phenolic and carboxylic acid functionalities created during weathering have an adverse effect on froth flotation owing to the influence these groups have on the wettability and electrokinetic properties of coal.[4]

Fourier transform phosphorus-31 nuclear magnetic resonance (NMR) spectroscopy has long been routine for the qualitative detection of various species in both liquid and solid materials that are not nearly as complex as coal materials.[5] However, the development of NMR tagging reagents capable of resolving closely related species and quantitating them is still in an embryonic stage of development. Nuclei consisting of ^{31}P, ^{119}Sn and ^{195}Pt are highly sensitive to their chemical environments, displaying wide chemical shift ranges with relatively narrow absorptions in solution. In the solid state, chemical shifts are generally broader by at least an order of magnitude than in solution, owing to chemical shift anisotropy.

A. ^{31}P NMR Tagging Reagents

Although line-narrowing techniques are continually being developed in NMR laboratories to solve the broadness problem in solid state spectra, our approach has been to design reagents potentially capable of yielding chemical shift separations in the derivatives that are sufficiently large to provide resolved spectra at least for classes of compounds. This strategy led to an examination of the phospholanyl framework (1 in Figure 1) as an NMR tagging agent. By varying the heteroatoms in this ring system as well as the substitution patterns shown in Figure 1, we were able to select 3 and 8 as reagents suitable for reacting with a wide range of model compounds in pyridine solution at room temperature to give stable derivatives.[6,7] This is shown schematically in reaction 1 for reagent 8.

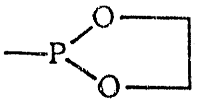


(1)

8

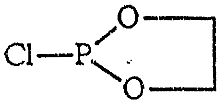
Z = alkyl, aryl; Q = CO_2, O, S, NZ

The above investigations enabled us to make substantial progress on the qualitative[8] and quantitative[9] analysis of coal condensates and extracts.



a phospholanyl framework

1



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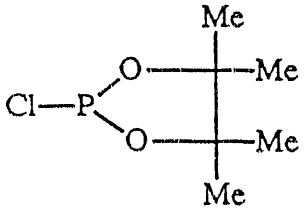

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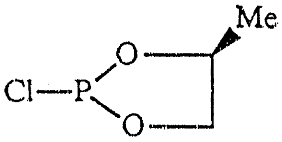

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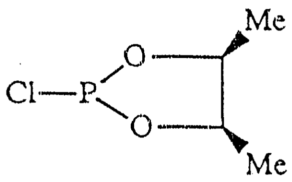

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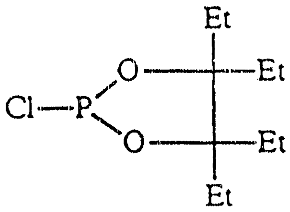

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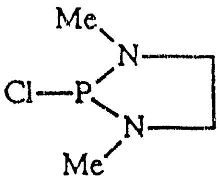

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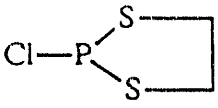

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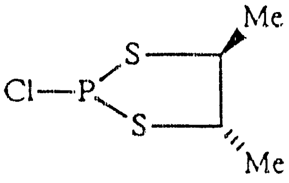

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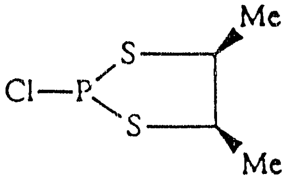

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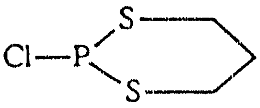

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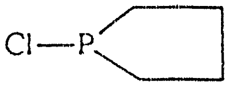

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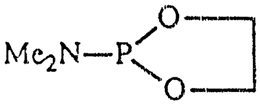


13

$ClPPh_2$

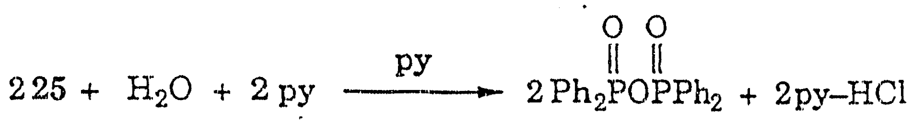
24

$ClP(O)Ph_2$

25

Figure 1. Structures of Phosphorus-Containing Reagents.

We have found that **2** and **3** react with moisture in coal extracts. This serendipitous discovery has allowed us to determine (for the first time by an NMR method) the moisture contents of extracts.[10] More recently, we have found that these reagents also undergo deleterious side reactions with water and so **24** and **25** were investigated. Reagent **25** now appears to be the best candidate uncovered thus far.[11] Thus, **25** reacts cleanly at room temperature according to reaction 2 in which the phosphorus-containing product incorporates two ^{31}P nuclei for every

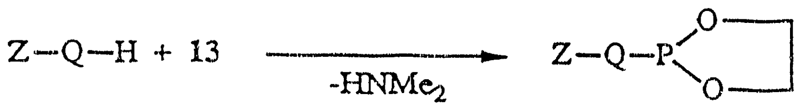


$$2\,25 + H_2O + 2\,py \xrightarrow{py} 2\,Ph_2\overset{O}{\overset{\|}{P}}O\overset{O}{\overset{\|}{P}}Ph_2 + 2\,py\text{–}HCl \qquad (2)$$

water molecule reacted. The latter circumstance allows more precise values of low water contents to be realized owing to better integration of the ^{31}P NMR peak. We have measured a series of model pyridine/H_2O mixtures by our technique. Interestingly, some of the -20 mesh samples analyze for more moisture (by up to ~1%) by the ASTM method than their -100 mesh counterparts. Dr. Vorres has suggested that this may be due to the additional time involved in processing the finer-mesh samples during which partial drying can occur.[12] Also notable is our observation that for most of the samples studied so far, the moisture contents by our method are higher by about 1% than by the ASTM method.[13] This may be an indication that tightly bound water is being released by pyridine. Because moisture in solid coal affects its beneficiation, cleaning, and value as a fuel, a knowledge of the amount of moisture, its distribution (surface versus bulk) and its nature (chemisorbed versus physisorbed) is required. Our NMR method is a potentially valuable one for attacking this problem.

Using our NMR water analysis reagent **25** we have examined the rates at which water is extracted from Argonne Premium Coal samples (APC's) as a function of the swelling capability of the extracting solvent. 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 1/2, 1/4, 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 dimethoxyethane) within 15 minutes for each coal is considered 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% of 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 up ca. 4% more water than could be extracted over a period of 25 hrs. by pyridine. We attribute this excess moisture to decomposition of organic matter under oven drying conditions.

Because of our concern that the liberation of HCl in the reaction of solid coals with reagents such as **2**, **3**, and **8** might be giving rise to the ^{31}P NMR peaks observed in unexpected regions of the spectrum, we synthesized **13**. Reagent **13**, which would yield presumably innocuous Me_2NH in reaction 3, also gives rise to the unexpected upfield peaks.

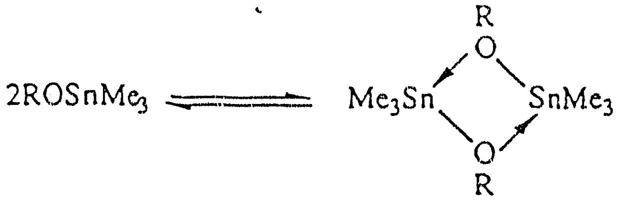


(3)

To test the hypothesis that a reaction(s) other than simple metathesis is occurring, we reacted *n*-Bu_3P with an oven-dried sample of Illinois No. 6 coal. To our surprise we found an unexplainable upfield ^{31}P NMR resonance (2.7 ppm) which is still puzzling us. If we are able to learn what is going on here, however, we may have a valuable new solid coal characterization tool.

B. ^{119}Sn NMR Tagging Agents

In our search for satisfactory ^{119}Sn NMR tagging reagents we investigated compounds **14-21**.[14,15] Compounds such as these display considerable ^{119}Sn chemical shift dependence in noncoordinating solvents owing to dimer formation:



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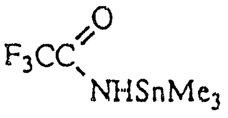

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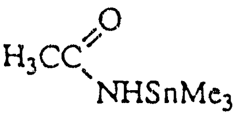

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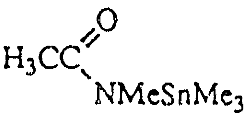

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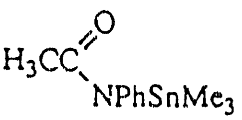

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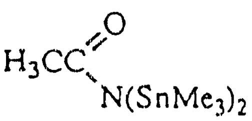

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Me_2NSnMe_3 19

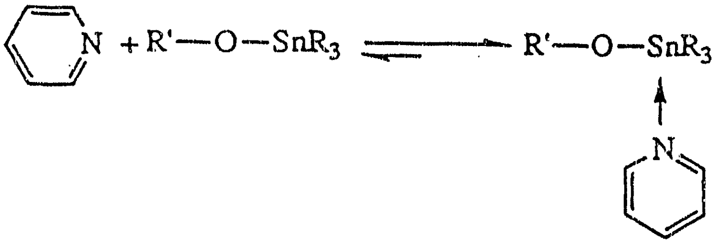
$PhNHSnMe_3$ 20

$PhN(SnMe_3)_2$ 21

$PhNHSn(i\text{-}Pr)_3$ 22

$PhNHSn(n\text{-}Bu)_3$ 23

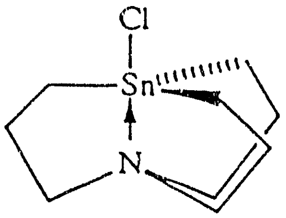
It was encouraging to observe, however, that in pyridine, these shifts are not only quite concentration independent (due to solvent coordination as in reaction 5) but are also considerably better separated for model compounds than the ^{31}P shifts associated with our current phosphorus reagents. From our reactivity studies of these new reagents and our structural determination of **18** by X-ray means,[15] we are now much better prepared to search for the optimum ^{119}Sn NMR tagging reagent.



(5)

Reagent **23** was found to possess the shortcoming that the ^{119}Sn chemical shifts of the model compounds are not sufficiently concentration independent to allow precise assignments of chemical shifts. This poses particular problems in identification of the different phenols and carboxylic acid present in unknown mixtures (e.g., coal liquids). The problem is apparently that equilibrium 5 does not lie sufficiently far to the right to prevent some averaging of the chemical shifts of the four and five-coordinate tin species.

In casting about for ways to solve this problem, we were struck with the fact that structures such as **29** and **30** are robust owing to the existence of three very stable chelate rings. A reagent such as **30**, for example, has no need 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 synthesized **29**, converted it in one step to the new derivatizing agent **30**, which is stable and crystalline.



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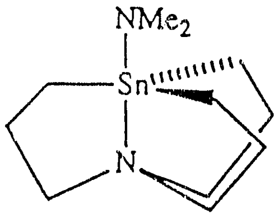

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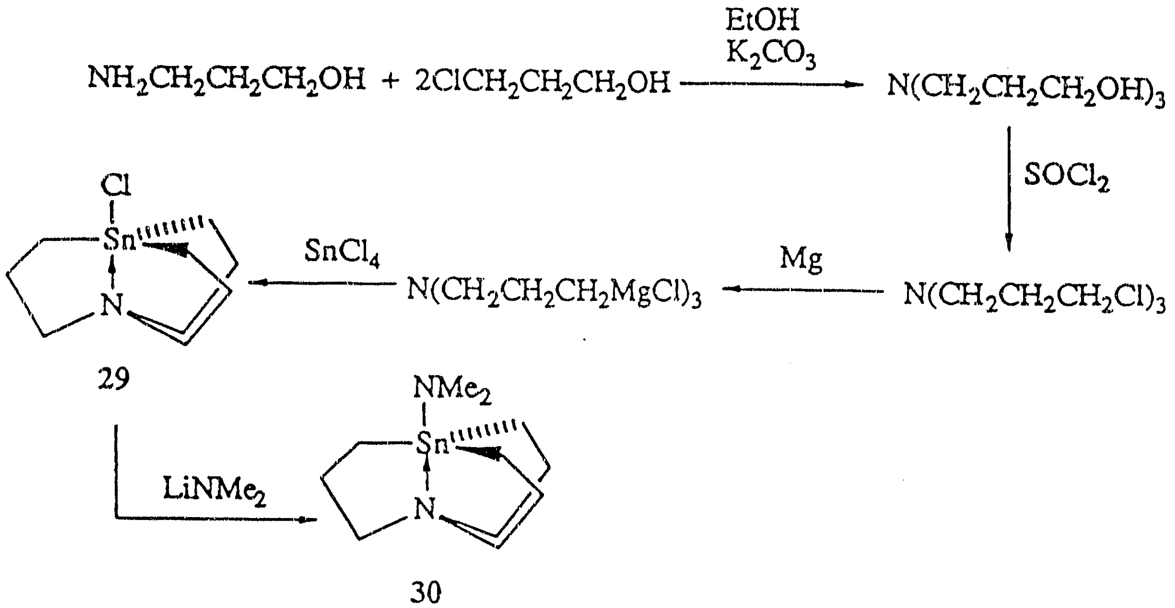
Scheme 1



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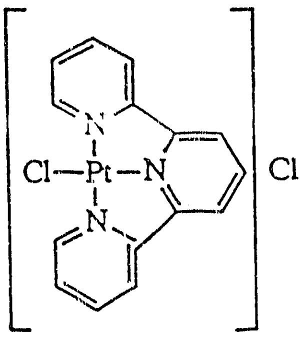
We have shown that $PhNHSnBu_3$ (**23**) differentiates derivatized phenols and carboxylic acids very nicely at low temperature where exchange of derivatized acids does not interfere. This successful experiment allowed us not only to speciate but also to preliminarily quantify for the first time a model mixture of phenols and carboxylic acids with quite reasonable precision (±6% avg.). We have now extended this approach to additional model compounds.

In a recent report,[16] Larsen et al. concluded from solid state ^{119}Sn Möessbauer experiments with an Illinois No. 6 sample derivatized with $(n\mathrm{Bu}_3\mathrm{Sn})_2\mathrm{O}$ 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.

The ^{119}Sn Möessbauer spectra of our solid coal samples derivatized with **23** have been obtained. My collaborator, Prof. Gary Long, is of the opinion that Larsen's data are largely reproducible and that five-coordinate tin seems to be indicated.

C. ^{195}Pt NMR Tagging Reagents

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 **26** and **27** as our first candidate reagents. We have successfully synthesized a series of thiol derivatives of **26** and measured



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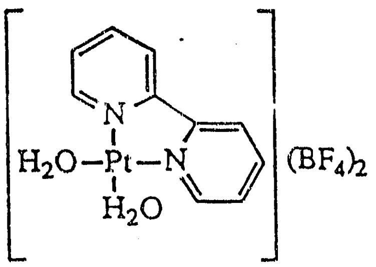

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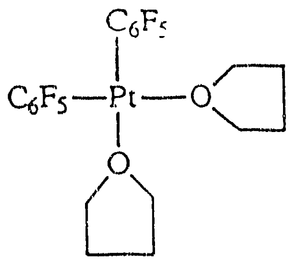

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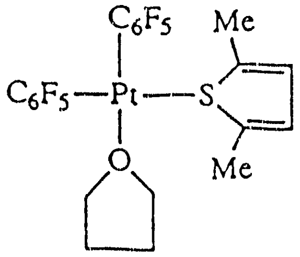
several of their ^{195}Pt NMR spectra. It appears that differentiation may be possible, although the chemical shifts are currently quite broad. We also have synthesized **28** which has proven to be the first platinum compound capable of coordinating a thiophene (see structure below).



ACCOMPLISHMENTS

A. ^{31}P NMR Tagging Reagents

Very strong evidence that our development of ^{31}P NMR tagging reagents is providing useful results is indicated by the:

1. Amoco's promise to provide $20,000 for the same purpose as well as collaborating on the CP/MAS ^{31}P NMR analysis of derivatized solid coal samples. In addition, Amoco has promised $35,000 in in-kind services at Amoco's laboratories for our work.

2. The willingness of CONSOL to provide up to $25,000 for testing our method on coal liquefaction samples.

Because of the highly applied nature of this work, I am unable to attract qualified post docs or any of our graduate students to do these analyses. This program needs some funding for the research components which the training of our future coal scientists require. Unless we are able to find such support quickly, I cannot appropriately utilize the offered funds.

The manuscript of the solvent extraction of H_2O in Argonne Premium coals last quarter was completed and submitted to Energy and Fuels.[13]

B. ^{119}Sn NMR Tagging Reagents

We have synthesized a set of model compound derivatives of **30** and have measured their chemical shifts. We have also derivatized an Illinois No. 6 sample with **30** and have submitted it for Möessbauer analysis to Prof. Gary Long, and for CP/MAS ^{119}Sn NMR spectroscopy for comparison of the result obtained with **23**.

C. ^{195}Pt NMR Tagging Reagents

A paper we submitted last quarter on the ^{195}Pt NMR chemical shifts of platinum thiolato complexes has been provisionally accepted.[17]

The determination of the crystal structure of the first thiophene platinum complex (referred to in the Introduction part C) is still in progress in a collaborative effort with Prof. Jacobson.

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