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Phthalocyaninatoruthenium(II), Hexakis(dimethylsulfoxide)phthalocyaninatoruthenium(II), and Hexadis(dimethylsulfoxide-d_6)phthalocyaninatoruthenium(II), Three Highly Selective NMR Shift Reagents

by

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July 18, 1977

Phthalocyaninatoruthenium(II), Hexakis(dimethylsulfoxide)phthalocyaninatoruthenium(II), and Hexadis(dimethylsulfoxide-d_6)phthalocyaninatoruthenium(II), Three Highly Selective NMR Shift Reagents*

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*Based in part on the Ph.D. thesis of C. K. Choy, Case Western Reserve University, 1976. Diss. Abstr. Int. B Sci. Eng., 37, 6114 (1977)

ABSTRACT

The significant properties of a useful nmr shift reagent, RuPc, and two excellent nmr shift reagents, $RuPc[(CH_3)_2SO]_6$ and $RuPc[(CD_3)_2SO]_6$, are described and discussed. Some of the kinds of compounds with which the two sulfoxide reagents can be expected to work and to fail to work are given, i.e.: imidazoles, pyridines, pyrrolidenes, primary, secondary, and tertiary aliphatic amines, and primary and secondary aromatic amines; and ethers and many other oxygen function compounds, respectively. Where pertinent some of the factors relevant to the behavior of these compounds towards the two reagents are mentioned. The selectivity of the reagents and the way in which they complement and supplement the two similar iron reagents, $FePc(NH_2C_6H_5)_6$ and $FePc(ND_2C_6D_5)_6$, are emphasized.

Running head: Phthalocyaninatoruthenium(II) Shift Reagents

INTRODUCTION

Previously, work on FePc (Pc = phthalocyanine ligand, $C_{32}H_{16}N_8$) showing that this compound is a useful nmr shift reagent, and on $FePc(NH_2C_6H_5)_6$ and $FePc(ND_2C_6D_5)_6$ showing that these compounds are valuable shift reagents has been described (1-3). Exploratory work on RuPc revealing that it functions as a shift reagent has also been mentioned (1,2).

In the present paper an account of further work on this latter reagent is given. Also given is an account of work on two new reagents, $RuPc((CH_3)_2SO)_6$ and $RuPc((CD_3)_2SO)_6$. The work on these latter two reagents is emphasized because they have quite desirable properties.

EXPERIMENTAL

Reagents -- RuPc. Following Krueger (4), this compound was prepared from $RuCl_3$ and o-cyanobenzamide, and was purified by a glacial acetic acid extraction.

$RuPc((CH_3)_2SO)_6$. A mixture of RuPc (0.20 g) and dimethylsulfoxide (20 ml) was refluxed for 2 hr and filtered (no residue). The filtrate was concentrated by distilling off some of the solvent (12 ml) and then was cooled slowly. The product, composed of purple needle-shaped crystals, was filtered off, washed, and dried (0.12 g). Anal. Calcd. for $C_{44}H_{52}N_8O_6S_6Ru$: C, 48.83; H, 4.80; S, 17.17; Ru, 9.34. Found: C, 49.16; H, 4.80; S, 17.57; Ru, 9.55. An nmr spectrum of this compound showed resonances with the positions and areas to be expected of a solution containing dimethylsulfoxide and a single isomer of $RuPc((CH_3)_2SO)_2$ in a 4:1 ratio.

$RuPc((CD_3)_2SO)_6$. Using a procedure parallel to that described for the synthesis of $RuPc((CH_3)_2SO)_6$, RuPc and dimethylsulfoxide-d_6 were reacted together and the product isolated. An nmr spectrum of the product showed only phthalocyanine resonances.

Application Techniques -- RuPc. The technique used with RuPc was parallel to that used with FePc. First the shift complex was prepared and isolated by conventional means, then a small amount of it ($\sim$ 1-5 mg) was dissolved in deuterochloroform ($\sim$ 0.5 ml), and finally, if appropriate, the solution was filtered.

The procedures used to synthesize and isolate the complexes of 1,2-dimethylimidazole and N,N'-dimethylformamide are illustrative of those used to obtain the complexes. $RuPc(N_2C_3H_2(CH_3)_2)_2$. A mixture of RuPc (0.05 g), 1,2-dimethylimidazole (0.1 ml), and benzene (25 ml) was refluxed for 3 hr and filtered. The filtrate was evaporated to dryness under reduced pressure and the product, a dark-blue powder, was washed and dried (0.01 g). An nmr spectrum of this product showed resonances with the expected positions and areas and no extraneous resonances. $RuPc((CH_3)_2N\overset{O}{\overset{\|}{C}}CH_3)_6$. With the aid of an apparatus designed to permit the extraction of a solid at the reflux temperature of the solvent being used, PcRu (0.20 g) was subjected to the action of dimethylformamide (15 ml) for 8 hr. The resultant was cooled slowly and filtered. The product, composed of purple crystals, was washed and dried (0.10 g). An nmr spectrum of it showed resonances having the positions and approximate areas to be expected of a 4:1 solution of dimethylformamide and a single isomer of $RuPc((CH_3)_2N\overset{O}{\overset{\|}{C}}CH_3)_2$. It also showed some small resonances attributable to impurities.

$RuPc((CH_3)_2SO)_6$ and $RuPc((CD_3)_2SO)_6$. The technique used with $RuPc((CH_3)_2SO)_6$ and $RuPc((CD_3)_2SO)_6$ was simple and dependable. Several crystals of the reagent ($\sim$ 1-5 mg) were dissolved in a solution of the compound ($\sim$ 1-5 mg) in chloroform ($\sim$ 0.5 ml) and, if appropriate, the resultant solution was filtered.

Instruments -- The instruments used were Varian HA-100 and Varian XL-100-15 spectrometers. They were operated in both F.T. and C.W. modes.

DISCUSSION

Coordination of Ruthenium in Reagents -- The coordination arrangement about the ruthenium in crystalline RuPc may be assumed to be square or tetragonally distorted octahedral. That around the ruthenium of the sulfoxide complexes when in solution is clearly tetragonally distorted octahedral. Probably the non-nitrogen atoms of this grouping are sulfur and not oxygen atoms since a sulfoxide sulfur is a softer base than sulfoxide oxygen.

Features of Reagents -- Like its iron analog, FePc, RuPc has a number of good features. It yields in a reliable fashion spectra which are simple, well resolved, unbroadened, concentration independent, and easy to interpret. Also, it is stable to oxidation, hydrolysis, substitution, pyrolysis, and shelf storage, and is insoluble in most common solvents.

However, as matters stand, use of it requires more effort than optimal and larger amounts of the compound of interest and of it than generally desirable. These features of it can be traced back in large part to the slowness of the addition reaction central to its use.

Unlike FePc, RuPc is not commercially available. Balancing this, however, is the markedly different range of applicability of RuPc (an earlier

statement to the contrary notwithstanding (2)).

The nondeuterated sulfoxide reagent, a reagent in many respects like $FePc(NH_2C_6H_5)_6$, has, as does the iron-aniline reagent, many positive features. Foremost is the fact that it is easy to apply. This comes about to an important extent because the exchange reaction which underlies its application is sufficiently fast.

In addition, its use requires the expenditure of only small amounts of the compound of interest and of it. However, it does give spectra which are more complex than those given by RuPc.

The deuterated sulfoxide reagent is like its nondeuterated analog except that it gives, as is highly desirable, spectra free of sulfoxide resonances. On a per use basis, its cost is little more than that of the nondeuterated reagent.

In general neither of these reagents yields spectra which are as intense as those yielded by the iron-aniline and iron-aniline-d_7 reagents. However, they do give spectra which are simpler than those given by their respective analogs (because of exchange reactions the deuterated iron-aniline reagent gives spectra containing NH_2 resonances).

As far as is known, the three ruthenium reagents work with the same types of compounds, Tables 1 and 2. Of these three, clearly the two sulfoxide reagents usually are the reagents of choice. On the basis of the results of a number of experiments, the behavior of these two reagents with a variety of types of compounds can be projected with confidence.

Behavior of Sulfoxide Reagents -- Imidazoles. With many imidazoles, even those that are quite hindered, the two reagents can be expected to work well. As with the iron reagents the ruthenium reagents interact with the pyridine-like nitrogens. It is presumed that the reagent-imidazole bond formed with these reagents is longer and stronger than that with the iron-aniline reagents

and that this basically accounts for the ability of these reagents to react with hindered imidazoles. It is also presumed that π-bonding plays a significant role in this bond. A hindered imidazole with which the nondeuterated sulfoxide reagent reacts but the nondeuterated iron-aniline reagent does not is 1,2-dimethylimidazole. A second imidazole with which the reagent reacts is the 5 tautomer of 4(5)-phenylimidazole. This is significant because the nondeuterated iron-aniline reagent does not react with either tautomer of 4(5)-phenylimidazole, suggesting, as noted earlier, that the tautomeric mixture contains much more of the 4 than the 5 tautomer.

Pyridines. The reagents can be expected to function well with many pyridines. As with the imidazoles, it is presumed that the reagent-pyridine bond formed with these reagents is longer and stronger than that with the iron-aniline reagents. No doubt π-bonding plays a significant role in this bond too. A compound having a pyridine function with which the deuterated reagent reacts is 5-aminoisoquinoline. Since, as reported below, aromatic amines react with the reagents it is not unexpected that interaction between the amino function of this compound and the reagent also occurs. However, it occurs only when the reagent concentration is high and even then only to a small extent.

Primary aliphatic amines. It can be anticipated that the reagents will work with many primary amines, both hindered and unhindered. One hindered primary amine the nondeuterated reagent functions with is 1-aminoadamantane, a compound the nondeuterated iron-aniline reagent does not work with.

Secondary aliphatic amines. The two reagents can be expected to work with many secondary aliphatic amines. An amine of this type the deuterated reagent works with is diethylamine, and a like amine the nondeuterated reagent works with is di-sec-butylamine. As pointed out previously, the iron-aniline reagent does not function with the latter.

Tertiary aliphatic amines. It is thought that the reagents will work with a modest number of tertiary amines. One tertiary amine the deuterated reagent works with is N-methylpiperidine. The iron-aniline reagents do not, so far as is known, react with tertiary aliphatic amines.

Primary aromatic amines. With many primary aromatic amines, both hindered and unhindered, it can be expected that the reagents will work. An amine of this type the deuterated reagent functions with is aniline, Figure 1 . Since RuPc functions with o-toluidine it can be assumed that the reagents will work with this amine too. As far as is known, the iron-aniline reagents do not function with primary aromatic amines.

Secondary aromatic amines. Even with some secondary amines it can be expected that the reagents will work. A case in point is N-methylaniline.

Diamines. As with the iron reagents the ruthenium reagents can sometimes be expected to function predominantly or even essentially solely with just one of the amine groups of some diamines. Thus, as already mentioned under ordinary conditions the deuterated reagent interacts essentially only with the pyridyl function of 5-aminoisoquinoline. However, because the iron and ruthenium reagents do not function in a fully parallel fashion the selectivities which the two reagents show can sometimes be expected to be different.

Amides. The reagents may well prove to be of use with amides since RuPc functions very well with dimethylformamide. It is presumed on the basis of hard-soft acid-base arguments that the reagent-amide interaction in the dimethylformamide complex is an Ru-N interaction and that the interactions in other amide complexes formed would also be Ru-N interactions.

Oxygen containing compounds. It is thought that in general the reagents will not interact with the oxygens of oxygen function compounds. One compound having an oxygen function with which the deuterated reagent does not work is N-aminomorpholine.

The fact that this trifunctional compound interacts with the reagent but only through its primary amino function is of interest because it offers a good example of the selectivity that can be shown by the reagents.

CONCLUSIONS

The sulfoxide ruthenium reagents can be expected to interact with a variety of amines and with some other soft base type compounds but not with ethers and other oxygen and non-oxygen hard base compounds. They can be expected to give complexes which are of 2:1 stoichiometry and trans geometry and hence to give spectra which are easily interpretable. They can be expected to furnish a complement to the iron-aniline reagents because their behavior towards a variety of compounds can be anticipated to be different. Like the iron-aniline reagents they are simple to make, easy to store, and uncomplicated to use.

Acknowledgment

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TABLE 1

SUMMARY OF INFORMATION ON SELECTED COMPOUNDS
WITH RuPc REAGENT

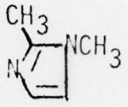
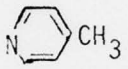
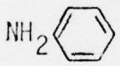
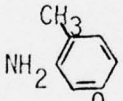
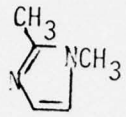
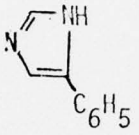
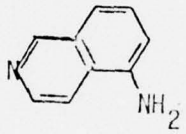
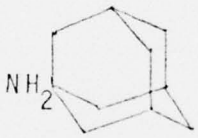
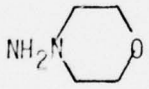
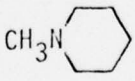
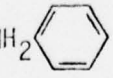
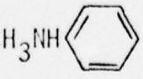
Type	Compound	Active Function
imidazole		
pyridine		
primary amine	$NH_2C_4H_9$ $NH_2C(CH_3)_3$	$-NH_2$ $-NH_2$
secondary amine		=NH
aromatic amine		$-NH_2$
		$-NH_2$
amide	$(CH_3)_2NCCH_3$	=NC-

TABLE 2

SUMMARY OF INFORMATION ON SELECTED COMPOUNDS WITH SULFOXIDE REAGENTS

Type	Compound	Reagent	Active Functions
imidazole		H	
		H	
pyridine		D	 and $-NH_2$
primary aliphatic amine		H	$-NH_2$
		D	$-NH_2$
secondary aliphatic amine	$NH(C_2H_5)_2$	D	=NH
	$NH(CHCH_3C_2H_5)_2$	H	=NH
tertiary aliphatic amine		D	≡N
primary aromatic amine		D	$-NH_2$
secondary aromatic amine		H	=NH

REFERENCES

1. J. E. Maskasky, J. R. Mooney, and M. E. Kenney, J. Am. Chem. Soc., 94, 2132 (1972).

2. J. E. Maskasky, and M. E. Kenney, J. Am. Chem. Soc., 95, 1443 (1973).

3. C. K. Choy, J. R. Mooney and M. E. Kenney, Submitted, Magnetic Resonance.

4. P. C. Krueger and M. E. Kenney, J. Inorg. Nucl. Chem., 25, 303 (1963).

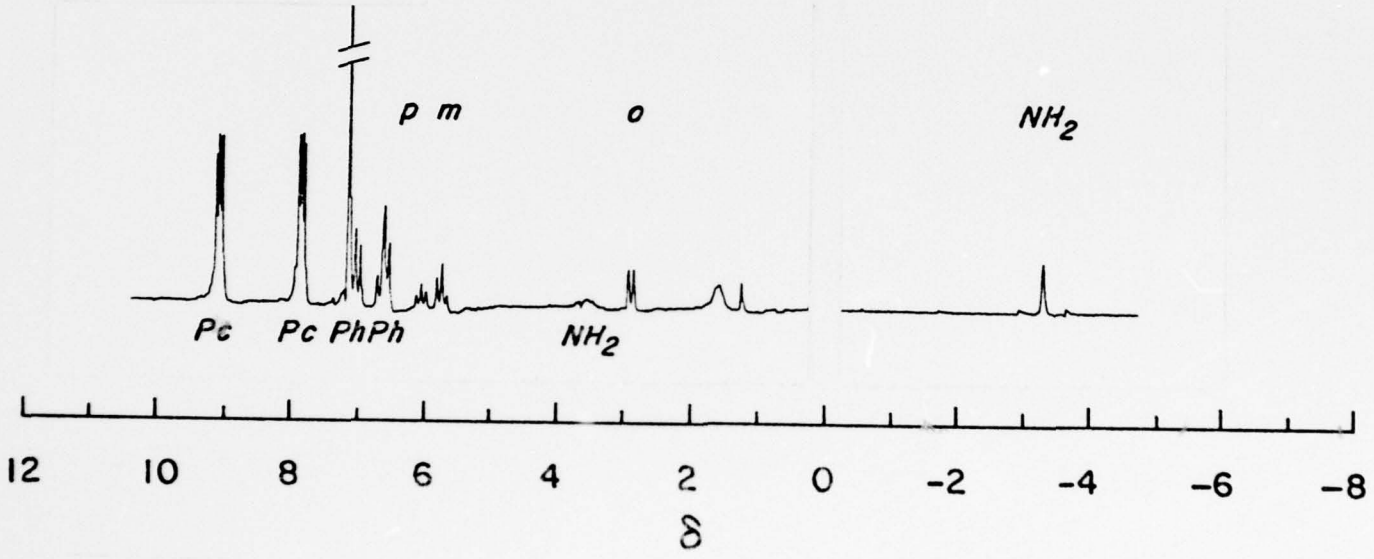


Figure 1. The spectrum of aniline in the presence of the shift reagent $RuPc(CD_3)_2SO)_6$

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