Summary

We have outlined an extension of the REX semiempirical molecular orbital method to periodic systems. The method provides a simple and systematic approach to the description of the spin–orbit splitting of energy bands. The method is illustrated with results for tellurium and polonium, with trigonal-helical and simple-cubic structures, respectively; the helical structure of tellurium is described as a distortion of a simple-cubic structure, with the distortion being quenched in the case of polonium by its very large spin–orbit coupling.

Acknowledgment. I thank Y. Q. Jia of the People's Republic of China for his assistance with this project and Professor J. K. Burdett of the University of Chicago for very helpful suggestions. I also thank the University of Michigan Computing Center for the use of its facilities.

Notes

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High-Yield One-Step Synthesis of 1,4,7-Trithiacyclononane (9S3)

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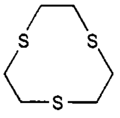
Received February 3, 1987

In 1983 Glass and co-workers reported the first complex of 1,4,7-trithiacyclononane (9S3),[1] a ligand originally synthesized



9S3

by Ochrymowycz et al. in 1974.[2,3] Intensive work by a number of groups has subsequently shown that 9S3 forms complexes with a wide variety of transition-metal ions.[1,4-11] These complexes are remarkably robust, presumably because the nine-membered ring constrains the S atoms to virtually the same positions in the free ligand[12] as in its complexes.[1,4-11] Moreover, they often have exceptional redox and electronic properties. For example, $[\mathrm{Rh(9S3)_2}]^{3+}$ readily undergoes two successive one-electron reductions to yield $[\mathrm{Rh(9S3)_2}]^{+}$ via a rare example of a stable monomeric Rh(II) complex.[10] Both the investigation of the reactivity of these unusual complexes and the obvious utility of 9S3 as a capping ligand ensure that work on this macrocycle will continue to expand at its present impressive pace.

A major impediment to work on this ligand, however, has been its preparation. Owing to the difficulty of closing a nine-membered ring, synthesis of 9S3 has been a thorny problem. The original synthesis gave 9S3 in only 0.04% yield,[2] which subsequent work raised first to 4.4%[1] and then to 20%[6]. These procedures are not suited to scaling up to multigram quantities because they require separation of 9S3 from its higher homologues and polymers by column chromatography. Recently Sellmann and Zapf[13] published an ingenious $\mathrm{Mo(CO)_3}$-mediated cyclization of 2-mercaptoethyl sulfide that gives 9S3 in high yield. Because this route involves several steps and a considerable amount of manipulation, it is inconvenient for large-scale preparation of the ligand. We report here a high-yield (50%) route that proceeds in one step from commercially available materials and can be used to prepare pure 9S3 in large quantities without column chromatography.

Experimental Section

All reagents were supplied by Aldrich Chemical Co. Ltd. and used as received, except 2-mercaptoethyl sulfide, which was vacuum distilled prior to use.

1,4,7-Trithiacyclononane (9S3). Finely powdered anhydrous cesium carbonate (13.03 g, 40 mmol) was suspended in *N,N*-dimethylformamide (DMF) (250 mL, from a freshly opened bottle) under a dinitrogen atmosphere. To the vigorously stirred suspension maintained at 100 °C was added a solution of 2-mercaptoethyl sulfide (5.56 g, 36 mmol) and 1,2-dichloroethane (3.54 g, 36 mmol) in DMF (150 mL) from a dropping funnel at a rate of 5 mL/h. After the addition was complete, stirring was continued at 100 °C for a further 12 h, after which the solvent was removed in vacuo. The residual white solid was extracted with $\mathrm{CH_2Cl_2}$ (3 × 100 mL), and the filtered extract washed with 1.0 M aqueous NaOH (2 × 100 mL) and evaporated to dryness. The resulting sticky solid was washed with water (3 × 50 mL) and dissolved in $\mathrm{CH_2Cl_2}$ (100 mL). The solution was dried over $\mathrm{MgSO_4}$ and evaporated to dryness. The residue was placed in a sublimation apparatus and heated at 90 °C under vacuum, whereupon the product crystallized as a white solid on the water-cooled cold finger (3.25 g, 50%); mp 79–80 °C. Anal. (Oxford Microanalytical Service) Calcd for $\mathrm{C_6H_{12}S_3}$: C, 40.0; H, 6.7. Found: C, 40.0; H, 6.9. IR (Nujol mull, $\mathrm{cm^{-1}}$): 2804 w, 1421 m, 1414 m, 1409 m, 1298 m, 1283 s, 1192 w, 1185 w, 1137 w, 1129 w, 987 w, 924 m, 879 s, 840 m, 825 s, 722 w, 671 m, 620 m. ^{1}H NMR ($\mathrm{CDCl_3}$, δ, vs. $\mathrm{Me_4Si}$) 3.13 s. The yield depends critically upon the rate of addition, with faster rates giving yields of approximately 35%. The ligand is soluble in dichloromethane, toluene, and diethyl ether, sparingly soluble in pentane and methanol, and insoluble in water.

Discussion

The major advantages of this procedure are the simplicity of the synthesis and the ease of the workup. All of the starting materials are commercially available, and isolation of the product by condensation from the vapor avoids recourse to column chromatography. Together these two features (especially the latter) permit ready scaling up of the procedure, so that large quantities of 9S3 can be made easily.

The synthesis makes use of the cesium carbonate mediated cyclization introduced by Kellogg and co-workers.[14,15] While there has been speculation on why $\mathrm{Cs_2CO_3}$ favors cyclization over polymer formation,[15,16] its efficacy probably results from weak ion pairing between $\mathrm{Cs^+}$ and $\mathrm{RS^-}$, which generates an exceptionally nucleophilic thiolate anion. Under high dilution conditions the enhanced nucleophilicity of $\mathrm{RS^-}$ would particularly favor intra-

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molecular (over intermolecular) S_N2 reaction of the intermediate $ClCH_2(CH_2SCH_2)_2CH_2S^-$ species that results from the attack of the first thiolate on 1,2-dichloroethane.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Relative Signs of P-P Coupling Constants in the NMR Spectra of Octahedral Metal Phosphine Complexes

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Received December 22, 1986

^{31}P NMR spectroscopy is one of the most important techniques for examining and characterizing diamagnetic metal phosphine complexes. In particular, in six-coordinate complexes, two-bond phosphorus-phosphorus coupling constants $^2J_{PP}$ across the metal center (P-M-P) are characteristic of the relative stereochemistry of the phosphine ligands as well as the nature of metal-ligand bonding in the complex.[1] Generally, the magnitude of $^2J_{PP}$(trans) is greater than $^2J_{PP}$(cis) with $^2J_{PP}$(trans) having a positive sign and $^2J_{PP}$(cis) being negative.[1,2] With the increasing availability of modern NMR facilities and the introduction of new NMR methods[3] sensitive to the relative signs of coupling constants, determination of the signs of coupling constants in metal complexes will become more frequent. The relative (and absolute) signs of interligand coupling constants are potentially important parameters which directly reflect the nature of the metal-phosphorus bonds between the coupled nuclei, and in the future the signs of coupling constants will undoubtedly be invoked to support structural assignments.

Where the specific symmetry of the metal complex leads to spin systems containing chemically but not magnetically equivalent phosphorus nuclei (e.g. AA'XX', AA'BB', AA'XX'Y, etc.) it has been possible to obtain $^2J_{PP}$ coupling constants by analysis of the complex NMR spectra. For simple spin systems, analytical solutions of the NMR spectra exist[4] and iterative computer programs[5] permit routine analysis with a high degree of automation, even for very complex spin systems.

We wish to highlight a common error in spectral analysis, before its occurrence becomes widespread: *in many instances, an NMR spectrum does not have a unique solution.* Even in complex spin systems, e.g. AA'BB' spin systems or spin systems that are second order by virtue of strong coupling between nuclei with similar chemical shifts, the spectra are not necessarily sensitive to the signs or magnitudes of each of the coupling constants in the spin system.

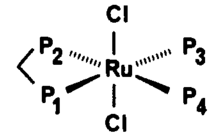
In the particular case of the analysis of an AA'BB' (or AA'XX') spin system, the symmetry of the spin system leads to an *NMR spectrum that does not have a unique solution.* From the NMR spectrum of an AA'BB' spin system, by spectral analysis alone, it is possible to determine the relative signs (i.e. like or opposite) of $J_{AA'}$ and $J_{BB'}$ and the relative signs of J_{AB} and $J_{AB'}$ but the sign relationship between these two sets of coupling constants cannot be established. Moreover, although the magnitudes of the two coupling constants $J_{AA'}$ and $J_{BB'}$ can be determined, by virtue of the symmetry of the spin system it is not possible to distinguish which coupling constant is $J_{AA'}$ and which is $J_{BB'}$. Similarly a distinction between J_{AB} and $J_{AB'}$ is impossible. Given the spectrum of an AA'BB' spin system, without any additional information, there are 16 different combinations of the coupling constants that will give identical NMR spectra. In such spin systems, in order establish the correct solution (or at least to narrow the range of possible solutions) one can rely on precedent from the analysis of the spectra of similar compounds with spin systems where no ambiguity in the analysis exists. Alternatively, additional experiments that are sensitive to either signs or magnitudes of specific coupling constants can be performed.

Table I. $^2J_{PP}$ (Hz) for Complexes **1** and **2**[a]

complex	$J_{P1,P2}$[b]	$J_{P1,P3}$ ($=J_{P2,P4}$)	$J_{P1,P4}$ ($=J_{P2,P3}$)	$J_{P3,P4}$[b]
1a	-31.2 (-37.4)	307.0	-38.4	-37.4 (-31.2)
1b	-28.7 (-35.8)	305.1	-36.4	-35.8 (-28.7)
2a	-35.1 (-17.5)	297.4	-33.2	-17.5 (-35.1)
2b	-33.3 (-16.5)	292.5	-32.8	-16.5 (-33.3)

[a] Magnitudes of $^2J_{PP}$ were taken directly from ref 6. $^2J_{PP}$(trans) is taken to be positive.[1,2] [b] $J_{P1,P2}$ and $J_{P3,P4}$ cannot be distinguished by simple spectral analysis (see text); the alternative assignment is given in parentheses.

In a recent report[6] of the synthesis of a series of octahedral ruthenium complexes, $Ru(DPPM)L_2Cl_2$ [DPPM = bis(diphenylphosphino)methane] (**1**) and $Ru(DPPE)L_2Cl_2$ [DPPE = 1,2-bis(diphenylphosphino)ethane] (**2**) (L = $PPhMe_2$ or PPh_2Me), the analysis of the resulting AA'BB' ^{31}P NMR spectra was reported to give the signs of $J_{P1,P2}$, $J_{P3,P4}$ and $J_{P1,P3}$ ($=J_{P2,P4}$) as negative with $J_{P1,P4}$ ($=J_{P2,P3}$) being positive. Although $J_{P1,P3}$ ($=J_{P2,P4}$) cannot, in theory, be distinguished from $J_{P1,P4}$ ($=J_{P2,P3}$), $J_{P1,P3}$ is clearly $^2J_{PP}$(trans) by its magnitude.



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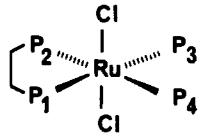

2

a. P_3, P_4 = $PPhMe_2$

b. P_3, P_4 = PPh_2Me

The relative signs reported for the coupling constants are clearly unreasonable. There can be no significant difference between the bonding in any pair of cis phosphorus atoms in these complexes and although minor differences between $J_{P1,P2}$, $J_{P2,P3}$ ($=J_{P1,P4}$), and $J_{P3,P4}$ might be anticipated, an inversion of sign would be impossible. Simulation of the reported spectra demonstrates that $J_{P1,P3}$ ($=J_{P2,P4}$) and $J_{P1,P4}$ ($=J_{P2,P3}$) necessarily have opposite sign and that $J_{P1,P2}$ and $J_{P3,P4}$ have the same sign. However, as outlined above, the spectra are insensitive to the relative signs of the set of coupling constants $J_{P1,P2}$ and $J_{P3,P4}$ with respect to the set $J_{P1,P3}$ ($=J_{P2,P4}$) and $J_{P1,P4}$ ($=J_{P2,P3}$). For those complexes of group 8 transition metals where the signs of $^2J_{PP}$ have been determined,[1] $^2J_{PP}$(trans) has a positive sign and the signs of *all* $^2J_{PP}$(cis) in **1** and **2** must therefore be negative to provide solutions to the spectra that are chemically reasonable. Additionally, from the analysis of the AA'BB' spin systems of **1** and **2** it is not possible to distinguish $J_{P1,P2}$ from $J_{P3,P4}$ so the assignment of these coupling constants must remain ambiguous (Table I).

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