

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.3-15 DISTANCE AND ANGLE VARIATIONS IN CYCLIC SULFUR-NITROGEN MOLECULES INVOLVING DELOCALIZED BONDING. By A. W. Cordes and W. T. Pennington, Chemistry Department, University of Arkansas, Fayetteville, Arkansas 72701 USA and R. T. Oakley, Chemistry Department, Guelph University, Guelph, Ontario N1G 2W1, Canada.

An analysis will be presented of the variations observed for apparently chemically-equivalent bond distances and bond angles in cyclic molecules containing segments of alternating sulfur and nitrogen atoms. The analysis takes into account a series of sulfur-nitrogen compounds recently prepared, including heterocyclic molecules containing titanium, sulfur, and nitrogen in the ring. One of the latter structures, that of $(C_5H_5)_2TiS_3N_4$, contains an eight-membered

-TiNSNSNSN- ring which is nearly planar for the seven atom S-N portion of the ring. Because this structure has twelve molecules in a unit cell of symmetry $P2_1/C$,

it provides interesting data on the typical variations observed in these distortable rings. Examples of unexpected distortions in other sulfur-nitrogen rings can be discussed in terms of second order Jahn-Teller effects. The conclusions of this analysis will address the possible pitfalls in making bonding rationales for sulfur-nitrogen ring molecules on the basis of solid-state structures.

09.3-16 STRUCTURES AND REACTIONS OF COORDINATED HEXAFLUOROBUT-2-YNE. By A. Jarvie, Lj. Manojlović-Muir, J.C. Miller, and K.W. Muir, Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland.

The complexes $[CpMX(hfb)_2]^+$, where M = Mo or W, X = anionic ligand, and hfb is the electron-withdrawing alkyne hexafluorobut-2-yne, have proved a fertile source of organometallic species of novel structure. Previous work in this laboratory has shown that nucleophiles such as PEt_3 and $CNBU^+$ add to coordinated hfb rather than to the metal, with formation of η^2 -vinyl complexes. When X = SPr^+ a species isomeric with the starting complex can be isolated containing an η^3 - Pr^+S -hfb ligand.

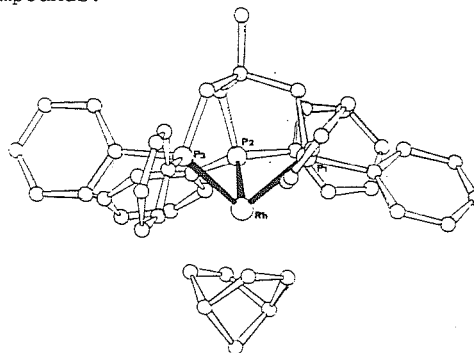
We shall report the structures of new complexes of this type including those of (1) the adduct of $[WBr_2(CO)(hfb)_2]$ and $P(OR)_3$ and (2) an isomer of $[CpMo(S_2CNMe_2)(hfb)_2]$ thought to contain a rare example of coordinated tetrakis(trifluoromethyl)-cyclobutadiene.

In addition we shall present comparative structural details of the hfb-W interactions in these complexes, showing how they relate to the electronic configurations of the metal atoms.

09.3-17 A Rh(I) COMPLEX WITH THE TRIPOD-LIKE TRIDENTATE PHOSPHINE 1,1,1-TRIS(DIPHENYLPHOSPHINOMETHYL)ETHANE.

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The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, has been employed in several metal complex systems since it was first reported in 1962 (W. Hewertson and H.R. Watson, J. Chem. Soc. (1962) 1490). Its geometry is such that it can only occupy three facial sites of a coordination polyhedron. Since it occupies three sites of a coordination sphere, the steric relationships of the remaining ligands are often fixed. As a consequence of its tridentate character and specific geometry, complexes with a degree of substitution and stereochemistry, not otherwise attainable with three unidentate ligands, may be realized. Several Rh(I) and Rh(III) complexes of this ligand are in course of study. Some of them are polynuclear with hydrido bridges. Here the structure of $[Rh(\text{triphos})(NBD)] [CF_3SO_3]$, where NBD is norbornadiene, is reported and will be discussed with those of related compounds.



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| Rh-P(1) | 2.313(2) Å | P(1)-Rh-P(2) | 91.14(7)° |
| Rh-P(2) | 2.399(2) | P(1)-Rh-P(3) | 87.76(7) |
| Rh-P(3) | 2.321(2) | P(1)-Rh-MP(1) | 144.5 |
| Rh-MP(1) | 2.069 | P(1)-Rh-MP(2) | 94.8 |
| Rh-MP(2) | 2.116 | P(2)-Rh-P(3) | 87.03(7) |
| | | P(2)-Rh-MP(1) | 123.8 |
| | | P(2)-Rh-MP(2) | 115.0 |
| | | P(3)-Rh-MP(1) | 99.0 |
| | | P(3)-Rh-MP(2) | 157.7 |
| | | MP(1)-Rh-MP(2) | 66.6 |

MP = midpoint of the coordinated double bond.