region which is characteristic of low-spin five-coordinate nickel(II) complexes.[5]

These results, however, do not prove that the products contain five-coordinate metal ions with a nitrogen (or sulfur) atom bound in one axial position. We therefore studied the reaction between $Ni(TAAB)^{2+}$ and 1,5-pentanediol (which has no donor atom that can coordinate in an axial position) and obtained a complex $Ni(TAAB)L_2$ ($L = HO(CH_2)_5O$). Since only one alkoxide ion of the diol has reacted in this case, whereas both react when a nitrogen or sulfur atom is in the center of the chain, we suggest that coordination of this central atom at the axial position holds the diol in such a position that both alkoxide ions of the diol react, giving complexes of formulation M(TAAB)LN and M(TAAB)LS. We therefore suggest that addition of one dianion from bis(2-hydroxyethyl)methylamine or bis(2-hydroxyethyl) sulfide to two *trans*-azomethine linkages of $Ni(TAAB)^{2+}$ and $Cu(TAAB)^{2+}$ has occurred, with the formation of the new and unusual type of "basket-like" macrocyclic ligand III. This demonstrates a second geometry of linkage applicable to clathro chelate formation as predicted earlier.[6] The first expected form was recently reported by Boston and Rose.[7] These examples constitute the first use of coordination template effects to synthesize ligands whose donors are arrayed three dimensionally. Earlier examples all generated monocyclic, not polycyclic, ligands.

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Molecular Oxygen Complexes of Bis(triphenylphosphine)platinum(0)

Sir:

When the bis(triphenylphosphine)platinum(0)–ethylene complex[1] is dissolved in oxygen-saturated toluene, thin yellow plates of the complex $[P(C_6H_5)_3]_2PtO_2 \cdot C_6H_5CH_3$ are obtained,[2] the crystals being only moderately stable in air.

We have undertaken an X-ray structure analysis of this complex. Crystallographic data are: system monoclinic; $a = 9.4$, $b = 23.5$, $c = 20.5$ Å; $\beta = 113.5°$ (accuracy not determined); $Z = 4$ molecules per cell; space group, $P2_1/c$. No crystals were found which were of high enough quality for diffractometer study and so an approximate structure was obtained by photographic methods. The instability of the complex meant that several crystal specimens had to be used during data collection; 2000 independent intensity data were collected and the structure was refined by full-matrix least squares with isotropic thermal parameters to an R of 0.12. The structure could not be refined anisotropically; nonpositive definite temperature factors were observed for seven light atoms, a feature we attribute to unsatisfactory intensity data. Accordingly the bond lengths probably cannot be relied on to better than 0.05 Å.

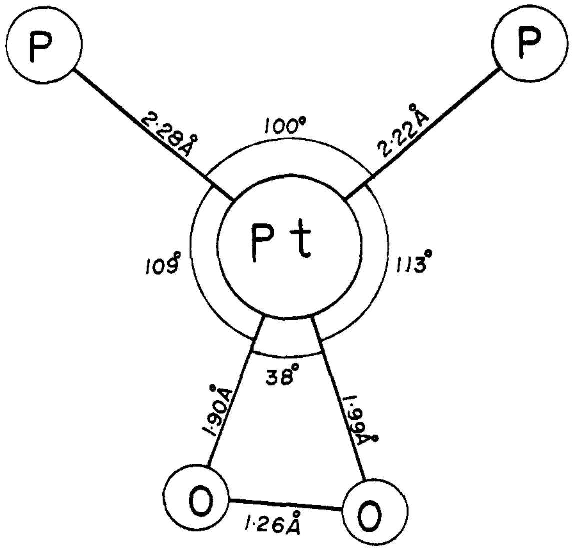

Figure 1.

Figure 1 shows the approximate configuration in the neighborhood of the Pt atom. All the atoms in this diagram are near-coplanar as evidenced by the sum of the bond angles at the Pt atom.

We have since obtained much better quality crystals of the oxygen complex $[P(C_6H_5)_3]_2PtO_2 \cdot 2CHCl_3$ by use of chloroform in place of toluene and these crystals, although still somewhat unstable, are satisfactory for diffractometer study. Preliminary crystal data are: system monoclinic; $a = 15.54$, $b = 13.52$, $c = 19.19$ (all ±0.05) Å; $\beta = 98.95 \pm 0.3°$; $Z = 4$ molecules per cell; possible space group C2, Cm, Cc, C2/m, C2/c. Because the crystals last only about 1 day when exposed to X-rays, we have concentrated on the collection of intensity data and are leaving refinement of the cell parameters until the end of data collection.

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Configurational Assignment to *dl* and *meso* Sulfides, Sulfoxides, and Sulfones

Sir:

No simple method has heretofore been reported whereby absolute *dl* and *meso* assignments to sulfides, sulfoxides, and sulfones of the type $[(R_1)(R_2)(R_3)C]_2X$ have been made. Assignments to sulfide dicarboxylic acids of this type have been made *via* tedius optical resolution techniques,[1] and the first report of an unambiguous assignment to a crystalline sulfone by X-ray

(1) Pertinent references are given by A. M. Brink and E. Larsson, *Acta Univ. Lund*, (II) No. 10 (1967); No. 29 (1966).