configuration XIII indicate a net charge of 0.20 e on the dioxygen ligand in the bent structure and 0.36 e in the perpendicular structure). These $Mn^{II}(O_2)$-type (Mn^{II}, d^5, $S = {}^3/_2$) configurations have not been considered in ref 2, although there is no feature of the ESR spectra which in principle is incompatible with this formalism.[30] They also meet the requirement of no spin density on O_2. If the vast majority of Mn^{II} complexes are high spin (including Mn(TPP)), there are at least two systems of Mn^{II} with a quartet ground state[31,32] including manganese phtalocyanine.[32] We also do not expect more refined calculations (of a double-ζ basis set quality or the introduction of configuration interaction between configurations of the same symmetry) to give a stationary value of the energy for the first configurations of the $Mn^{IV}(O_2{}^{2-})$ type. However, they could modify the relative stabilities of the $Mn^{II}(O_2)$- and $Mn^{III}(O_2{}^-)$-type configurations. Such calculations are now in progress.

From Table I, it also appears that for all configurations but one the bent structure is more stable than the perpendicular one. The two structures are of comparable stability (to the precision of the calculations) for the configuration XIII. However, introduction of configuration interaction will mix this configuration with the configurations IV, VII, and X for the bent structure (since IV, VII, X, and XIII belong to the $^4A'$ symmetry) and with the configurations VI and X for the perpendicular structure (VI, X, and XIII belong to the $^4B_1$ symmetry). Since the configurations IV, VII, and X of the bent structure are lower in energy than the configurations VI and X of the perpendicular structure, the same ordering is likely for the corresponding states $^4A'$ and $^4B_1$. We can therefore predict that the bent structure is more stable than the perpendicular one. This result (opposite to the conclusions of ref 2) is not unexpected since we did not find any stable configuration with dioxygen bonded as a peroxo ($O_2{}^{2-}$) ligand. If we compare the energy value of the most stable configuration for each of the two states $^4A'$ and $^4B_1$ (cf. Table I), the stabilization amounts to 33 kcal/mol.

In summary our conclusions are at odds with the interpretation of the experimental results for the Mn(TPP)O_2 system. We look forward to a more detailed experimental study of the system,[33] especially an x-ray structural determination. We are also carrying more refined calculations on this system.

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A. Dedieu,* M. M. Rohmer
*E.R. No. 139 du CNRS, Université L. Pasteur
67000 Strasbourg, France*
Received January 17, 1977

Preparation of a Tetraphosphine Macrocyclic Ligand

Sir:

The preparation of synthetic macrocycles and their subsequent ligation to various transition metals has been a fruitful area of research.[1] Macrocycles having oxygen, nitrogen, and/or sulfur donor atoms have been prepared and the chemical reactivity of their metal complexes studied.[2] To date, however, there is only one example of a macrocyclic ligand that contains a phosphorus atom[3] and the chemical reactivity of its metal complex is very much controlled by the nitrogen atoms

Scheme I
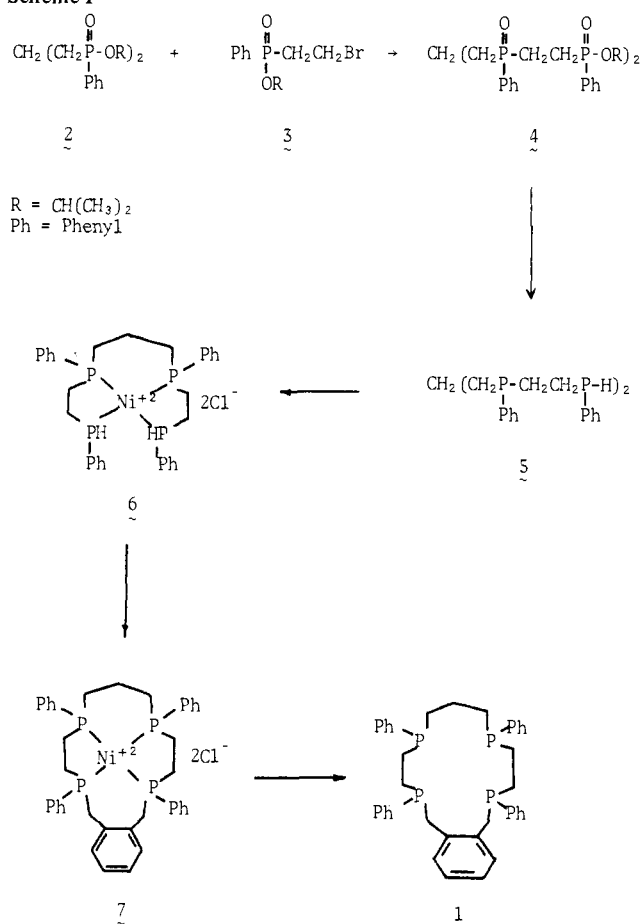
that are part of the ligating array. The dearth of information about phosphorus-containing macrocycles is surprising since it is well known that phosphines are excellent ligands which impart many interesting properties to their metal complexes.[4] In view of this, we wish to describe the first synthesis of a tetraphosphine macrocycle, 1, and in addition, we present data relating to the strong complexing ability of this macrocycle toward nickel(II).

The synthesis of the macrocycle is outlined in Scheme I. It began with the reaction of 2[5] with "Vitride" [6] and then with 3[7] in THF to produce 4[8] in 70% yield (mp 179–81 °C): ^{1}H NMR (CDCl$_3$) δ 1.25 (12 H, dd), 1.8 (12 H, m), 2.05 (2 H, m), 4.1 (2 H, m), 7.25 (20 H, m); IR (KBr) τ 3160, 3000, 2950 (C–H), 2000–1800 (arom), 1450 (Ph-P), 1420 (CH$_2$-P), 1390 (i-Pr), 1230 (P=O), 1000 (P-O). Reduction of 4 with LiAlH$_4$ in THF produced an oxygen-sensitive oil displaying characteristics indicative of the tetraphosphine 5: ^{1}H NMR (CDCl$_3$) δ 1.7 (14 H, m), 2.4 (1 H, m,[9] 5.8 (1 H, m),[9] 7.4 (20 H, m); IR (CHCl$_3$) τ 3065, 3000 (C–H), 2340 (P–H), 1450 (Ph-P). The tetraphosphine 5 was immediately treated with NiCl$_2$·6H$_2$O in ethanol to produce the stable, crystalline complex 6[8] in 85% yield: ^{1}H NMR (CDCl$_3$) δ 1.7 (14 H, m), 7.3 (20 H, m);[10] IR (CHCl$_3$) τ 3060, 3000 (C–H), 2360 (P–H), 1450 (Ph-P); UV–vis (CHCl$_3$) τ_{max} 425 nm (ϵ 1000), 375 (1500), 305 (sh, 4000), 280 (19,000). Reaction of 6 first with anhydrous K$_2$CO$_3$ in absolute ethanol and then α,α'-dibromo-o-xylene produced the desired macrocyclic complex 7[8] in 35–40% yield. The spectral properties of 7 are very similar to those displayed by 6 except that the ^{1}H NMR exhibits new multiplets at 1.8 and 7.5 ppm of four protons each while the IR attests to the disappearance of the P–H stretch and the appearance of a new CH$_2$-P stretch at 1415 cm^{-1}. In addition, a molecular weight determination by vapor phase osmometry gave an apparent

molecular weight of 762 in CHCl$_3$ (theoretical, 764) substantiating the conclusion that the template reaction leading to the macrocycle-nickel(II) complex, 7, was indeed successful. This reaction thus represents the first example of a template reaction involving a phosphine ligand at the reaction center.[11]

Final proof that the desired macrocycle was formed was provided by the reaction of the complex 7 with aqueous NaCN. After workup an air-sensitive oil was obtained in ~50% yield that showed the necessary physical and spectral characteristics of 1:[8] ^{1}H NMR (CDCl$_3$) δ 1.65 (14 H, m), 3.45 (4 H, m), 7.45 (24 H, m); IR (film) τ 3150, 3000, 2940 (C–H), 1450 (Ph-P); mol wt (CHCl$_3$) 634.6 (theoretical), 634 (obsd). The production of this material not only proves the structure of the macrocyclic complex 7, but it also provides a means by which the uncomplexed macrocycle is now available for further complexation to other important transition metals.

Once the structure of the macrocycle 1 was secure, we felt justified in examining the physical characteristics of the macrocyclic nickel(II) complexes that were available to better understand the interaction of this unique ligand with the metal. The complexes, Ni(mac)X$_2$, were prepared by metathetical reactions of the synthesized chloride and the data proves that all of the complexes studied (X$^-$ = BF$_4^-$, Cl$^-$, SCN$^-$) are 2:1 electrolytes with the nickel ion being in a square-planar array.[12] The macrocycle 1 is thus a strong field ligand, but a comparison of its ligand field strength in relation to other macrocycles is difficult to assess at present since we have been unable to induce strong monodentate ligands to form tetragonal complexes. This implies that the axial site of the complex is relatively inaccessible to nucleophilic reagents either for electronic or steric reasons. We tend to favor an electronic argument founded on the well-known back-bonding capability of a phosphine moiety and coupled with a compression by the constrained macrocycle on the d orbitals of the metal rather than a steric argument involving the axially located phenyl groups. This is partially substantiated by the reaction of cyanide ion with the metal complex; however, the magnitude, validity, and viability of these arguments will have to await future studies.[13]

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T. A. DelDonno, William Rosen*

*Department of Chemistry, University of Rhode Island
Kingston, Rhode Island 02881*
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