Silacalix-[*n*]-phosphaarenes: Macrocyclic Ligands Based on Dicoordinate Phosphorus Centers

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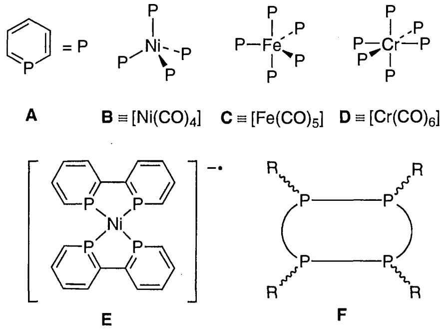
The synthesis of polyphosphinine macrocycles, which consist of a 16-membered ring with four phosphorus atoms (P_4) and a 12-membered ring with three phosphorus atoms (P_3), is described. Their high coordination ability is demonstrated by the quantitative synthesis of the rhodium and iridium cation complexes of the P_4 macrocycle and by quantitative synthesis of the $W(CO)_3$ complex of the P_3 compound. Unlike the other available macrocyclic ligands bearing oxygen, sulfur, di- or tricoordinate nitrogen, and even tricoordinate phosphorus as ligating atoms, which are all essentially σ donors, these dicoordinate phosphorus-based macrocycles have strong π-acceptor properties. Their use can be envisaged for the stabilization of negative oxidation states of transition metals or in reductive catalysis.

Carbon monoxide (CO) is probably the most important and versatile ligand in transition metal chemistry, able to stabilize metal centers in negative, zero, and positive oxidation states (*1*). This exceptional versatility is explained in terms of a synergistic σ donation and π-back donation of electrons to and from the metal (*2*). Charge decomposition analysis (*3*) shows how CO adapts to the electronic demand of the metal by varying the balance between these two effects.

Besides its toxicity and its high volatility, one of the major drawbacks of CO is that it cannot be incorporated into sophisticated structures such as polydentate or macrocyclic ligands, which can provide thermodynamic stabilization to otherwise unstable metal centers (*4*). Thus, the search for an electronic equivalent of CO with a structure that can be tailored is of high interest. Recently, besides the classical isonitriles R–N≡C where the nature of R allows fine-tuning of the ligating properties (*5*), it appeared that phosphinines **A** (Scheme 1) would be a highly advantageous alternative. Phosphinine, which displays good stability resulting from a significant aromatic character (*6*), is characterized by a very low-lying π* lowest unoccupied molecular orbital (LUMO) with a high localization at phosphorus, which implies a high π-acceptor capacity. Furthermore, its in-plane lone pair corresponds to the third highest occupied level at about –10.0 eV compared with –10.6 eV for PH_3 (*7*), suggesting a significant σ-donor capacity.

Several σ-homoleptic complexes (*8*) of phosphinine have been characterized (*9*). Not surprisingly, their structural and electronic properties were found to be very similar to the corresponding metal carbonyls (**B** to **D**). Moreover, it has been demonstrated in one particular case that the phosphinine ligand is able to stabilize a 19-electron radical anion such as **E** (*10*), thus confirming its high π-acceptor capacity. Apart from their unique electronic properties, the synthesis of dicoordinate polyphosphorus macrocycles is a valuable target, because classical tricoordinate polyphosphorus macrocycles such as **F** are plagued by conformational problems resulting from the high inversion barrier of pyramidal sp^3 phosphorus (*11*).



Scheme 1.

Having devised a versatile route to phosphinines based on the [4+2] cycloaddition of alkynes with 1,3,2-diazaphosphinines (*12*), we could envision the synthesis of polyphosphinine macrocycles (Scheme 2). The 1,3,2-diazaphosphinine **1** was first allowed to react with a threefold excess of dialkynylsilane to give **2** in 60 to 70% yield (*12*). Then, compound **2** was reacted with 2 equivalents of diazaphosphinine **1** to give **3**, which need not be isolated. The reaction was quantitative according to the ^{31}P nuclear magnetic resonance (NMR) analysis of the reaction mixture (*13*). Under high-dilution conditions (5 × 10^{-3} mol/liter),

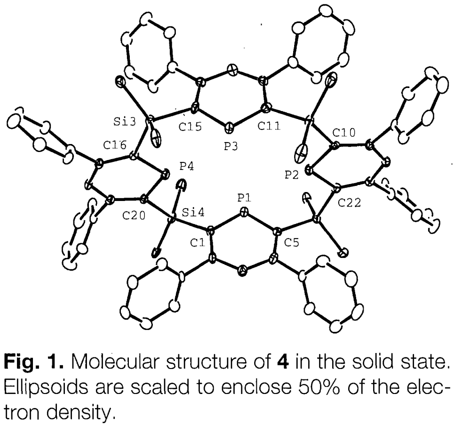


Fig. 1. Molecular structure of **4** in the solid state. Ellipsoids are scaled to enclose 50% of the electron density.

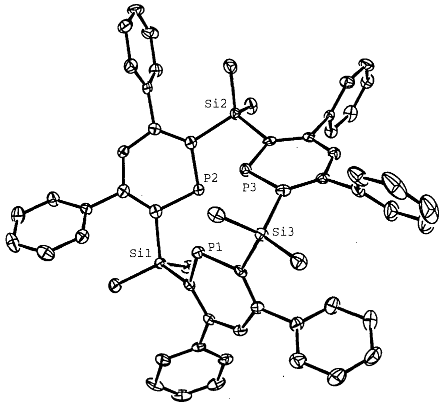


Fig. 2. Molecular structure of **5** in the solid state. Ellipsoids are scaled to enclose 50% of the electron density.

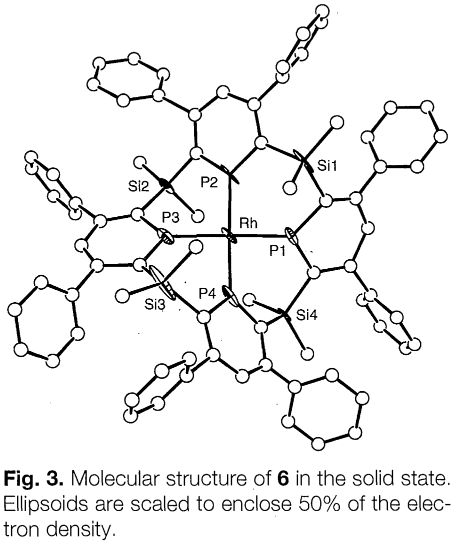


Fig. 3. Molecular structure of **6** in the solid state. Ellipsoids are scaled to enclose 50% of the electron density.

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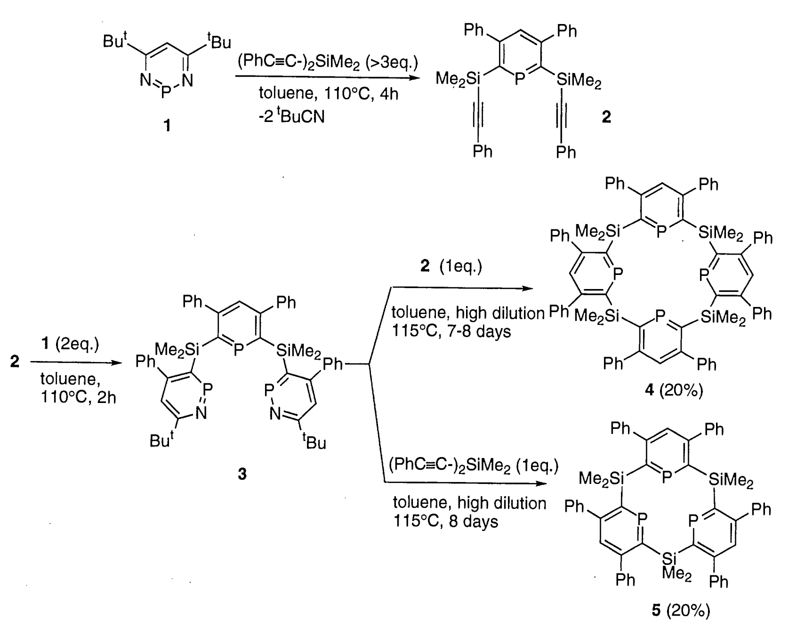
3 reacted with 2 (1 equivalent) to give the calix-[4] derivative 4 in 20% yield as a white crystalline solid, which we fully characterized by solution NMR, mass spectrometry, and elemental analysis (*14*). Apart from a very skewed central ring, the molecular structure of 4 (Fig. 1) shows no special features. Only one ^{31}P resonance and single ^{1}H and ^{13}C resonances for the two methyl groups on silicon are detected at room temperature, indicating that the conformation of the solid is not retained in solution. Under similar conditions, the reaction of 3 with the dialkynylsilane afforded the calix-[3] derivative 5 in 20% yield as a yellow crystalline solid (*15*). In the molecular structure of 5 (Fig. 2), the C–Si–C bridge angles fall in the range 104.9° to 105.8(1)°, compared with 108.0° to 109.4(2)° for 4 (number in parentheses is the standard error in the last digit), suggesting that there is some strain in the central 12-membered ring of 5. Another consequence of this strain is the lengthening of the C–Si bridge bonds, from 1.883 to 1.900(5) Å in 4 to 1.908 to 1.914(3) Å in 5.

The coordinating abilities of both 4 and 5 were then investigated (Scheme 3). The calix-[4] derivative 4 was reacted with bis-cyclooctadiene-rhodium and -iridium cations to afford the corresponding complexes 6 and 7 as red crystals in 95% yield (*16*). In the molecular structure of 6 (Fig. 3), no strain is apparent in the coordination sphere of rhodium, which displays a perfectly square planar geometry [P-Rh-P angles between 88.3° and 91.3(5)°]. The Rh-P distances [2.239 to 2.274(15) Å] are similar to those reported for the tetrakis-(2,4,6-triphenylphosphinine) rhodium cation [Rh-P = 2.2628 to 2.2918(11) Å] (*17*). As expected for a rigid structure, the methyl groups of the SiMe$_2$ bridges are inequivalent both in the ^{1}H and ^{13}C NMR spectra. The calix-[3] derivative 5 reacts with W(CO)$_5$(THF) (THF = tetrahydrofuran) at 80°C to afford the W(CO)$_3$ complex 8 in 90% yield (*18*). As in 6 and 7, the methyl substituents are inequivalent in the ^{1}H and ^{13}C spectra. In the molecular structure of 8 (Fig. 4), the P-W distances range from 2.3924(9) to 2.403(1) Å, significantly shorter than in the (2-chlorophosphinine) pentacarbonyltungsten complex [P-W = 2.457(2) Å] (*19*). There is obviously some strain in the coordination sphere of tungsten as shown by the deviation from octahedral geometry [P-W-P = 83.75(3)°, 84.93(3)°, and 85.47(4)°]. Note also that the C-P-C intracyclic angles increase significantly upon coordination from 105.8° to 106.9(1)° in 5 to 110.6° to 111.2(2)° in 8. Such an increase upon coordination has previously been observed and seems to correspond to a sizable electronic transfer from phosphorus to the metal (*9*).



Scheme 2. Synthesis of polyphosphinine macrocycles. Ph, phenyl; Me, methyl; Bu, butyl.

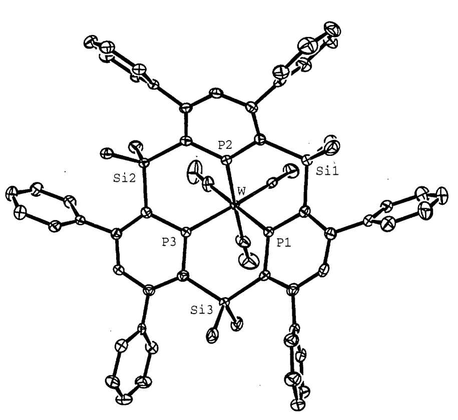
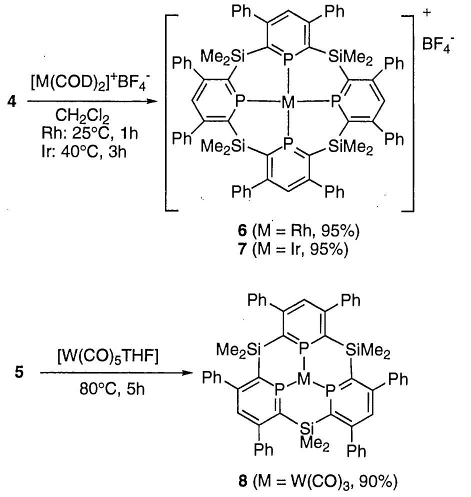


Fig. 4. Molecular structure of **8** in the solid state. Ellipsoids are scaled to enclose 50% of the electron density.



Scheme 3. Synthesis of metal complexes.

All other available macrocyclic ligands are either pure σ donors with no π-acceptor properties (with oxygen or tricoordinate nitrogen as ligating atoms) or σ donors with some π-acceptor properties (with sulfur, dicoordinate nitrogen, or, in a few cases, tricoordinate phosphorus as ligating atoms). These classical macrocycles have been mainly used to coordinate cations or to stabilize high-oxidation states and perform oxidative catalyses. One of the most famous examples is the formation of the ferryl (Fe^{IV}O)$^{2+}$ porphyrin complexes that are implicated in the reaction mechanisms of cytochromes P-450 (*20*). Manganese or iron sulfophthalocyanines are used to catalyze the oxidative degradation of chlorinated phenols (*21*). With polyphosphinine macrocycles such as 4 and 5, we enter the field of macrocyclic ligands with strong π-acceptor properties. We can thus envision the stabilization of negative oxidation states and some uses in reductive catalyses.

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13. The ^{31}P NMR for **3**: δ^{31}P = 275.9 [triplet, ^{4}J(P-P) = 12.0 Hz, phosphinine] and 304.3 (doublet, 1,2-azaphosphinine in toluene); δ is the chemical shift, and J(P-P) is the phosphorus-phosphorus coupling constant.
14. Characterization of **4**: δ^{31}P = 277.5 ($CDCl_3$); mass spectrometry, mass-to charge (m/z) ratio (ion, relative intensity): 1216 (M, 12). Elemental analysis calculated for $C_{76}H_{68}P_4Si_4$: C, 75.00; H, 5.59. Found: C, 75.14; H, 5.47.
15. Characterization of **5**: δ^{31}P = 293.1 ($CDCl_3$); m/z (ion, relative intensity): 912 (M, 100). Elemental analysis calculated for $C_{57}H_{51}P_3Si_3$: C, 75.00; H, 5.59. Found: C, 75.12; H, 5.48.
16. Characterization of **6**: δ^{31}P = 228.2, $^{1}J(^{31}P\text{-}^{103}Rh)$ = 144.5 Hz ($CDCl_3$). Elemental analysis calculated for $C_{76}H_{68}BF_4P_4RhSi_4$: C, 64.86; H, 4.84. Found: C, 64.69; H, 4.72. Characterization of **7**: δ^{31}P = 204.8 (CD_2Cl_2). Elemental analysis calculated for $C_{76}H_{68}BF_4P_4IrSi_4$: C, 61.00; H, 4.55. Found: C, 61.17; H, 4.45.
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22. We thank the CNRS and Ecole Polytechnique for financial support.

23 February 1998; accepted 23 April 1998

High-T_c Superconductors in the Two-Dimensional Limit: [(Py-C_nH_{2n+1})$_2$HgI_4]-$Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m = 1 and 2)

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The free modulation of interlayer distance in a layered high–transition temperature (high-T_c) superconductor is of crucial importance not only for the study of the superconducting mechanism but also for the practical application of high-T_c superconducting materials. Two-dimensional (2D) superconductors were achieved by intercalating a long-chain organic compound into bismuth-based high-T_c cuprates. Although the intercalation of the organic chain increased the interlayer distance remarkably, to tens of angstroms, the superconducting transition temperature of the intercalate was nearly the same as that of the pristine material, suggesting the 2D nature of the high-T_c superconductivity.

Since the appearance of layered cuprate superconductors, much attention has been given to elucidating the origin of high-T_c superconductivity, such as the interlayer coupling effect (*1–3*), in-plane charge carrier density (*4–6*), or both. According to the model of Wheatley, Hsu, and Anderson, the superconducting transition temperature T_c of a layered cuprate superconductor is expressed as

$$T_c = \lambda_o + \lambda_1 \qquad (1)$$

where λ_o is the interlayer coupling between the nearest CuO_2 planes (intrablock coupling) and λ_1 is the interlayer coupling between the next nearest planes (interblock coupling) (*1*). However, Uemura *et al.* have suggested a close correlation between T_c and 2D carrier density (n_s/m^*, where n_s is the superconducting carrier density and m^* is the effective mass) in the layered high-T_c superconductor (*4*). The issues are still controversial. To solve such problems, a way to freely modulate the interlayer distance without perturbing the superconducting oxide block is needed. Here, we developed model compounds where organic modulation layers are intercalated into Bi_2O_2 double layers of the high-T_c cuprate superconductors, $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m = 1 and 2; Bi2201 and Bi2212). In such intercalates, the interlayer distance of the superconductive CuO_2 layer can be easily controlled by changing the number of carbon atoms in the organic chain. The present organic intercalates with remarkable layer separation can be regarded as 2D limit cuprate superconductors, taking into account the small out-of-plane coherence length (ξ_c) in the pristine materials (*7*). The magnetization studies on the intercalates reveal that the high-T_c superconductivity is retained even in the nearly isolated CuO_2 plane. The organic intercalates are also regarded as weakly coupled Josephson multilayers, where the barrier width greatly influences the diamagnetic shielding fraction. In this respect, the present organic-inorganic hybrids can be an ideal model compound to investigate low-dimensional superconducting theories such as the Kosterlitz-Thouless transition (*8*) and the Lawrence-Doniach model (*9*) in high-T_c materials. Moreover, the intercalation of long-chain organic molecules can minimize the interaction between the cuprate building blocks, leading to an isolated single sheet by exfoliation. The superconducting nanoparticle, obtained in such a way, can be a precursor for the fabrication of ultrathin superconducting films.

We intercalated long-chain organic compounds into Bi-based high-T_c cuprates in the form of the complex salt bisalkylpyridinium tetraiodomercurate [(Py-C_nH_{2n+1})$_2$HgI_4]. The x-ray diffraction (XRD) analyses and the high-resolution electron microscope (HREM) images of these intercalates show that the organic spacer layers with various thicknesses are stabilized in between the Bi_2O_2 double layers of Bi-based high-T_c cuprates.

The Bi-based cuprate superconductors have weakly bound Bi_2O_2 double layers that make it possible to intercalate various guest species without introducing any substantial changes to the superconducting block (*10–14*). The pristine $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m = 1 and 2) compounds (*15*) were synthesized by conventional solid state reaction with the nominal compositions of $Bi_2Sr_{1.6}La_{0.4}CuO_x$ (Bi2201) for m = 1 and $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_y$ (Bi2212) for m = 2, where the Sr ion is partially substituted by the La ion or Ca ion to obtain single-phase samples. The intercalation of an organic chain into the pristine material was achieved with the following stepwise synthesis. First, the HgI_2-intercalated $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m = 1 and 2; HgI_2-Bi2201 and HgI_2-Bi2212) compounds were prepared by heating the guest HgI_2 and the pristine materials in a vacuum-sealed Pyrex tube, as reported previously (*13*). Then, the intercalation of the organic chain was car-

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