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Self-Assembly of a Nanoscopic Prism via a New Organometallic Pt_3 Acceptor and Its Fluorescent Detection of Nitroaromatics

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Summary: A nanoscale-sized cage with a trigonal prismatic shape is prepared by coordination-driven self-assembly of a predesigned organometallic Pt_3 acceptor with an organic clip-type ligand. This trigonal prism is fluorescent and undergoes efficient fluorescence quenching by nitroaromatics, which are the chemical signatures of many explosives.

Self-assembly is the spontaneous association of either a few or many chemical entities to form a larger aggregate under thermodynamic control. With a careful and informed choice of the starting materials, the resulting compounds can often be predicted, and therefore, design strategies can be formulated.[1] Self-assembly via the directional bonding approach is the most efficient way to the synthesis of designed coordination assemblies. The major requirement for this coordination driven self-assembly approach is the use of rigid precursors of appropriate size and shape. Square planar Pt(II) and Pd(II) have long been used as favorite metals in this area because of their rigid coordination environment, and thus, it is easy to control and predict the shapes and sizes of the final assemblies.[2] The most attractive feature of the metallasupramolecular assemblies formed by the directional bonding approach is the possibility of the introduction of functionality by introducing required functional groups or by simply tuning the structure. Of the various types of structures reported so far, 2D assemblies dominated the literature. Three-dimensional cages[2e] are relatively less compared to 2D assemblies because of the difficulty in synthesis and isolation due to very high molecular weight. M_3L_2 or M_2L_3 are the simple combinations for 3D cage construction. A few 3D cages are known with the former combination[3] (where M = bidentate acceptor and L = tridentate donor), while the latter combination (where M = tridentate acceptor and L = bidentate donor) is very rare in the literature because of the difficulty in the synthesis of shape-selective tridentate Pd/Pt acceptors.[4] This prompted us to prepare a Pt_3 organometallic planar acceptor 4,4′,4″-tris[ethynyl-*trans*-$Pt(PEt_3)_2(NO_3)$]triphenylamine (**M**) as a shape-selective linker toward the construction of a trigonal-prism (Scheme 1). Here, we report the design and synthesis of a nanoscopic prism (**1**) prepared by the self-assembly of **M** with a clip-type amide containing the ligand 1,3-bis(3-pyridyl)isophthalic amide (**L**) and the preliminary study of its fluorescent detection of nitroaromatics, which are chemical signatures of many explo-

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(5) (a) Synthesis of 4,4′,4″-Tris[*trans*-$Pt(PEt_3)_2I$(ethynylphenyl)]amine. First tri[*p*-ethynylphenyl]amine was prepared (see Supporting Information). To a 100 mL round bottom shlenk flask were added *trans*-diiodobis(triethylphosphine)platinum (750 mg, 1.094 mmol) and tri(*p*-ethynylphenyl)amine (98.9 mg, 0.312 mmol). Then 25 mL of dry, degassed toluene and 10 mL of dry diethyl amine were added under nitrogen. The solution was stirred for 10 min at room temperature before 25 mg of CuI was added in one portion. After 16 hr at room temperature, a small amount of diethylammonium iodide started precipitating out of the solution. The solvent was removed under vacuum, the resulting yellow residue was separated by column chromatography on silica gel with a solvent mixture of benzene/hexane (2:1) to obtain the product in 64% yield. Anal. Calc. (%) $C = 36.23$; $H = 5.17$; $N = 0.70$. Found: $C = 36.38$; $H = 5.37$; $N = 1.01$. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, 6H, ArH), 6.93 (d, 6H, ArH), 2.2 (q, 36H, $-CH_2$), 1.2 (t, 54H, $-CH_3$). ^{31}P NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, $^1J_{Pt-P} =$ 2874 Hz). The iodide derivative was treated with $AgNO_3$ to obtain the nitrate product (**M**). (Yield: 11.7 mg, 65%.) Anal. Calc. (%) $C = 40.16$; $H = 5.73$; $N = 3.12$. Found: $C = 40.36$; $H = 5.51$; $N = 3.32$. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.84 (d, 6H, ArH), 7.01 (d, 6H, ArH), 1.9 (q, 36H, ArH), 1.15 (t, 54H, ArH). ^{31}P NMR ($CDCl_3$, 400 MHz): δ 20.1 (s, $^1J_{Pt-P}$=3064 Hz). IR (Nujol): 2121, 1487, 1384, 1274, 1034 cm^{-1}. **Preparation of 1.** To a stirred solution of **M** (12 mg, 0.006 mmol) in acetone, the solution of **L** (2.86 mg, 0.009 mmol) in methanol was added, and this resulting solution was kept under stirring and heating in an oil bath at 50 °C overnight. The product was obtained by ether addition (96% yield). Anal. Calc. (%) $C = 45.97$; $H = 5.41$; $N = 6.16$. Found: $C = 46.26$; $H = 5.66$; $N = 6.21$. ^1H NMR ($CDCl_3$, 400 MHz): δ 10.81 (s, 6H, -NH), 9.23 (s, 3H, ArH), 9.19 (d, 6H, Py-H), 8.79 (d, 6H, Py-H), 8.3 (m, 12H, ArH), 7.61 (m, 9H, ArH), 7.15 (d, 12H, ArH), 6.91 (d, 12H, ArH), 1.9 (q, 72H, $-CH_2$), 1.1 (t, 108H, $-CH_3$).^{31}P NMR ($CDCl_3$, 400 MHz): 15.60 (s, $^1J_{Pt-P} = 2872$ Hz). (b) Crystallographic data were collected at 100(K) K using a Bruker X8 Apex II diffractometer equipped with monochromated Mo-Kα radiation ($\lambda =$ 0.71073 Å). Crystal data for linker M: C_{60} H_{102} I_3 Fe_3 N O_{26} P_6 Pt_3, MW = 1989.22, monoclinic, *P2₁/n*, $Z = 4$, $a = 16.944(5)$ Å, $b = 17.295(5)$ Å, $c = 25.961(7)$ Å, $\beta = 101.622(7)°$, $V = 7452.0(4)$ Å^3, R1 = 0.070 and wR2 = 0.1992.

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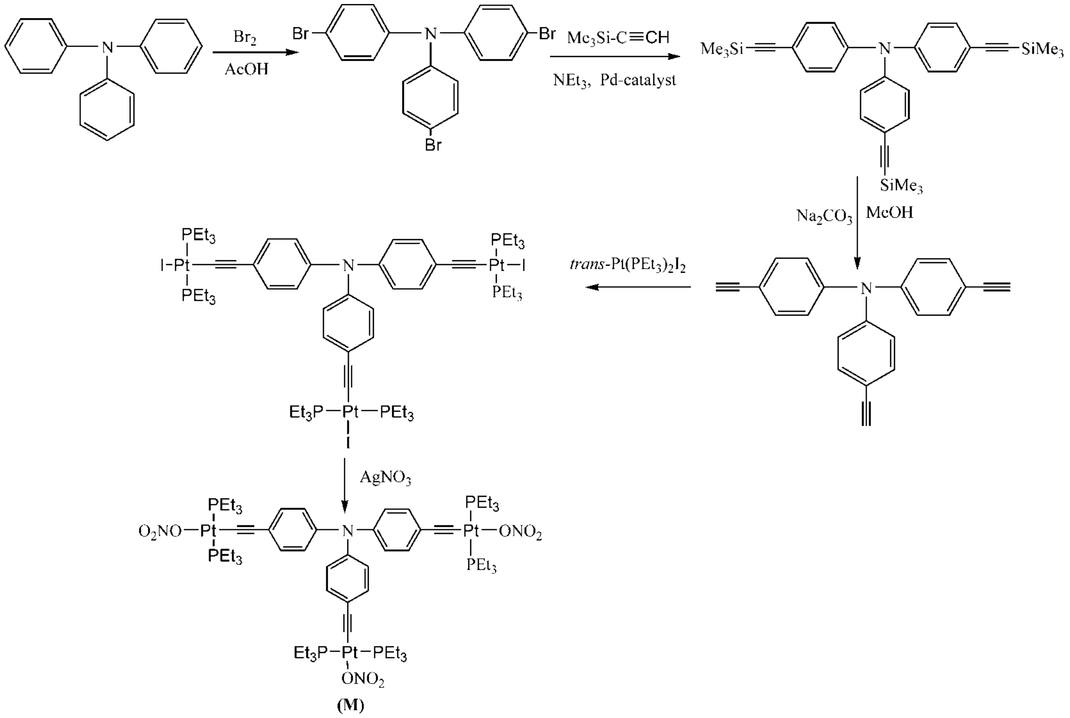
Scheme 1. Synthesis of the Organometallic Pt_3 Acceptor M



sives. Cage **1** represents the first example of a trigonal-prism obtained from a purely planar Pt_3 acceptor.

From the general concept of geometry, one can design a trigonal prism by linking two tritopic planar units with three clip-type units. On the basis of this general principle, we have prepared a new organometallic Pt_3 tritopic acceptor (**M**) following the steps shown in Scheme 1.[5a]

Ethynyl functionality was introduced to make the linker rigid and planar, and particularly to make it fluorescent since it has been found that coordination complexes containing this functional group frequently show fluorescent/luminescent behavior. The acceptor **M** was characterized fully by ^{1}H and ^{31}P NMR. Finally, the iodide form of this linker was unambiguously characterized by X-ray single crystal structure determination.[5b] A view of the molecular structure is shown in Figure 1. The crystal structure determination reveals the formation of a planar triplatinum molecule with a central nitrogen atom. The Pt−N−Pt angles lie between 117 and 121°, which is in the expected range. The geometry around the Pt centers is distorted square planar with I−Pt−P angles in the range of 89.3–92.1°, and the C−Pt−P angles between 85.7 and 91.1°. The Pt−I bond lengths (2.64, 2.64, and 2.65 Å) are similar to the distances observed in the literature for iodide trans to an acetylene group, such as $(Pt(PMe_3)_2I)CC(I(PMe_3)_2Pt$.[6]

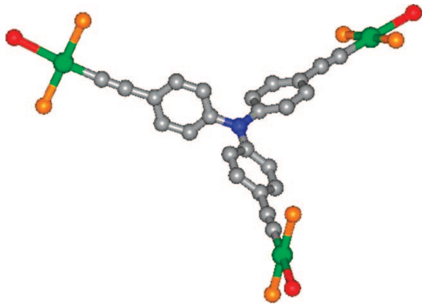
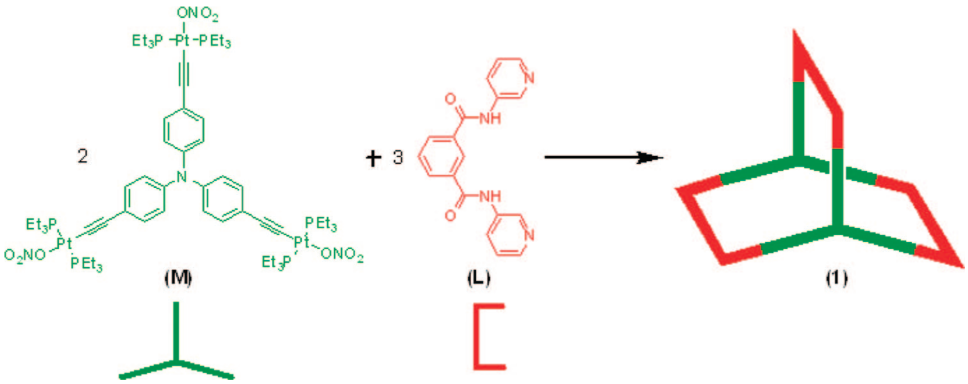


Figure 1. View of the molecular structure of the triiodide form of **M**. Ethyl groups of PEt_3 moieties are omitted for the sake of clarity. Gray = C; green = Pt; blue = N; yellow = P; red = I.

The cationic prism M_2L_3 (**1**) was prepared from the 2:3 self-assembly of **M** and the amide based clip-type donor **L** (Scheme 2). When 4,4′,4″-tris[ethynyl-*trans*-$Pt(PEt_3)_2(NO_3)$]triphenylamine (**M**)[5a] acceptor was treated with a 1.5 equivalent of the donor ligand **L**[7] in a mixture of methanol and dichloromethane for 30 min, the self-assembly of the cationic prism (**1**) as a single product occurred. An immediate visual change in color from light yellow to intense yellow was also an indication of the

Scheme 2. Self-Assembly of the Trigonal Prismatic Cage 1



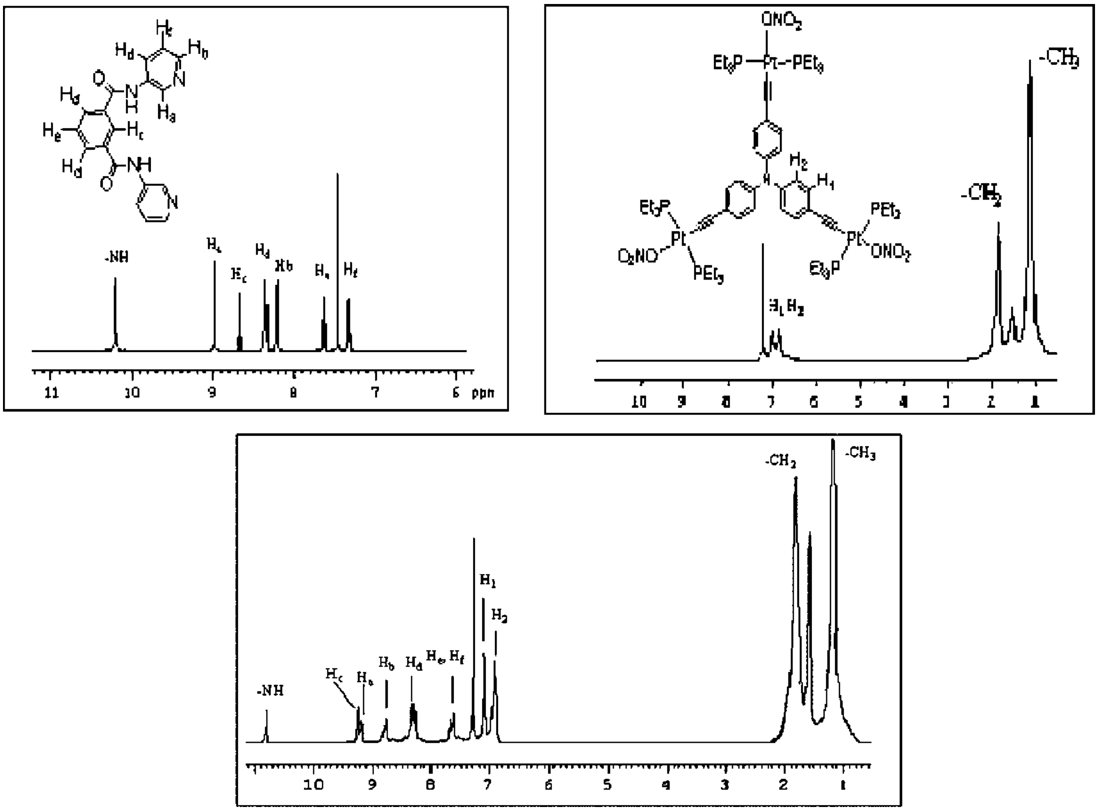


Figure 2. ^{1}H NMR of **L** (top left), **M** (top right), and **1** (bottom) in $CDCl_3$.

reaction. [2 + 3] self-assembly reaction of **M** and **L** may give either a polymeric product or a discrete prism. Solution $^{31}P\{^{1}H\}$ NMR analysis of the reaction solution showed the quantitative formation of a single, highly symmetrical species (**1**) by the appearance of a sharp singlet with concomitant ^{195}Pt satellites, shifted 5 ppm upfield ($-\Delta\delta$) relative to **M**. The upfield shift of the phosphorus signal in the ^{31}P NMR spectrum is a clear indication of the ligand to metal coordination (Supporting Information).

The ^{1}H NMR spectrum of **1** was also indicative of the symmetrical arrangement of the components and displayed significant spectroscopic differences from the precursor building blocks (Figure 2). The downfield shift of the proton signals of the protons adjacent to pyridyl nitrogen was associated with the loss of electron density on coordination by the nitrogen lone pair to the platinum metal center. NH protons of the clip **L** also showed a strong downfield shift of 0.6 ppm upon complex formation. In the IR spectrum of the prism, absorptions arising from **L** were observed.

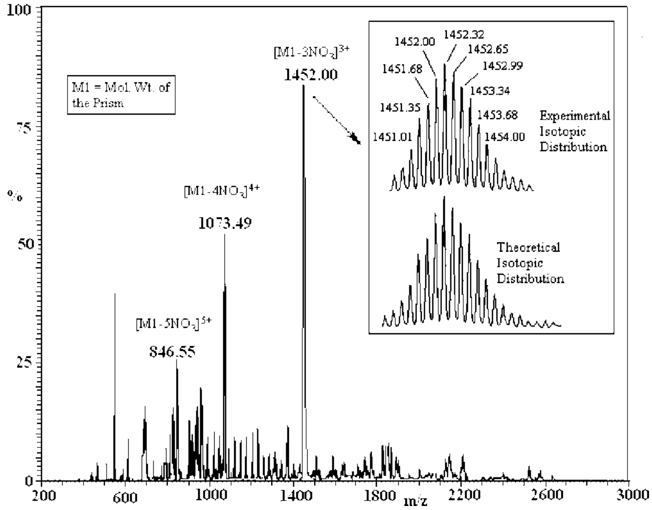


Figure 3. ESI-MS spectrum of **1** in MeOH. Inset: theoretical and experimental isotopic distribution patterns of the $[M1\text{-}3NO_3]^{3+}$ peak.

The carbonyl stretching frequency of **L** appeared at 1672 cm^{-1}, whereas the corresponding prism **1** showed carbonyl absorption at 1679 cm^{-1}. These shifts to a higher wavenumber are presumably due to the coordination of **L** to Pt. NMR spectroscopy provides insight about the metal–ligand coordination and the formation of a single product; however, it does not provide any information about the shape of this kind of product. ESI mass spectrometry has proven to be a useful tool in the corroboration of structural assignments for this kind of self-assemblies.[8] Mass-spectrometric study of **1** was performed by ESI technique, which allowed us to keep the assembly intact during the ionization process while obtaining the high resolution

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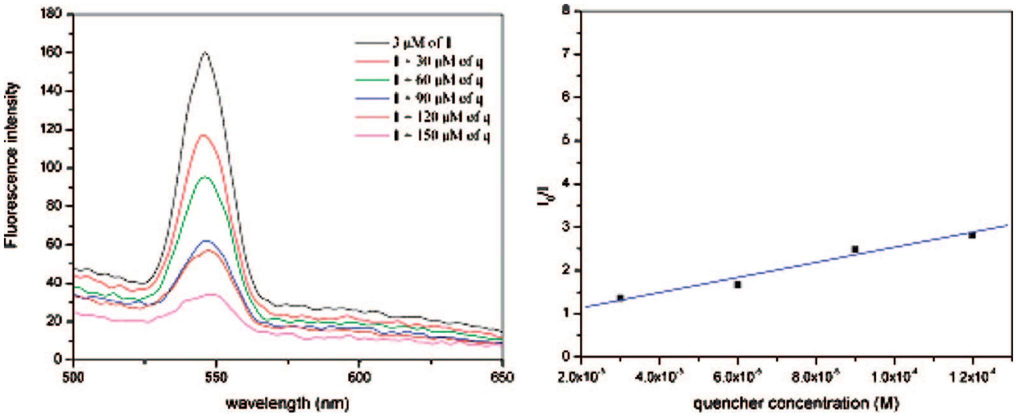

Figure 4. Fluorescent quenching of **1** by TNT (left) and Stern−Volmer plot (right).

required for unambiguous determination of the charge states. Electrospray mass spectroscopy study confirmed the formation of the cage **1** assembling two Pt_3 tritopic acceptors (**M**) and three organic clip **L** with the molecular weight of 4540.33 Da. The mass spectrum of **1** (Figure 3) showed signals corresponding to the consecutive loss of nitrate counterions, $[M1\text{-}3NO_3]^{3+}$, $[M1\text{-}4NO_3]^{4+}$, and $[M1\text{-}5NO_3]^{5+}$. For **1**, $[M1\text{-}3NO_3]^{3+}$ [*m*/*z* = 1452.00 (calcd 1451.66)]; $[M1\text{-}4NO_3]^{4+}$ [*m*/*z* = 1073.49 (calcd 1073.18)]; $[M1\text{-}5NO_3]^{5+}$ [*m*/*z* = 846.55 (calcd 845.67)]. The inset in Figure 3 displays an expansion of the $[M1\text{-}3NO_3]^{3+}$ peak along with the theoretical isotopic distribution that matched well with the experimental expansion (M1 = molecular weight of **1**). A similar result was also obtained for the $[M1\text{-}4NO_3]^{4+}$ peak. Hence, the peaks at 1452.00 and 1073.49 (*m*/*z*) are due to the +3 and +4 charge states, respectively, of cage **1**. Several attempts using different solvents and counterions to obtain single crystals yielded only powder product. However, the presence of expected peaks along with the isotopic distribution results clearly confirmed M_2L_3 composition with a molecular weight of 4540.33 Da for **1**. The only possible shape of this composition of a clip and a rigid tritopic linear unit is trigonal prism, as shown in Scheme 2.

Fluorescence-quenching-based detection of explosives represents one of the most convenient methods that have been used in defense and security. Conjugated aromatic compounds and polymers with high π-electron density are proven as efficient fluorescent sensing materials.[9] However, finite 3D cages prepared via the directional bonding approach have not been used for this purpose. We have prepared a Pt_3 organometallic ligand to introduce conjugation and aromatic functionality for the synthesis of a functional 3D supramolecule (**1**). Complex **1** shows absorptions at 275 and 368 nm in CH_2Cl_2-DMF (4:1). The quenching study was performed by picric acid and trinitrotoluene (TNT). Picric acid solution quenched the fluorescence at 413 nm (Supporting Information), whereas TNT quenched fluorescence at 546 nm (Figure 4). Analysis of the normalized fluorescence intensity (I_0/I) as a function of increasing quencher concentration ([Q]) was well described by the Stern−Volmer equation $I_0/I = 1 + K_{SV}[Q]$, for both cases. Linear Stern−Volmer behavior is consistent with the quenching that is dominated by a dynamic process. The Stern−Volmer constants (K_{SV}) in both the cases were determined from the plots. The quenching efficiencies were $48.1 \times 10^3\ M^{-1}$ and $19.6 \times 10^3\ M^{-1}$ in CH_2Cl_2-DMF (4:1) in the case of picric acid and TNT, respectively. The complex was also excited at 380 nm, and in that case, the emission peak was obtained at 440 nm, which was also gradually quenched by TNT with a concentration order of 0.1 mM. The high values of quenching efficiencies separates the quenching mechanism from that of SOPs and amplifying fluorescent polymers (AFPs),[10] which are quenched by static quenching mechanisms. The proposed quenching reaction is:

$$\mathbf{1} + RNO_2 \rightarrow \mathbf{1}^+ + RNO_2^-$$

where the nitro compound accepts an electron from the excited-state of the complex. However, the dominant interaction of the complex with the nitroaromatics is proposed to be π-stacking with partial charge transfer.

In conclusion, we herein report the synthesis and characterization of a trigonal prism (**1**) prepared via directional self-assembly of a new organometallic Pt_3 planar acceptor and an organic clip-type donor. Cage **1** represents the first example of a trigonal prism-shaped derivative of a metal-based tritopic planar acceptor. Preliminary results suggest that **1** is fluorescent and that its solution fluorescence is quenched by nitroaromatics, which are chemical signatures of explosives. The formation of the cage using both the conjugated acceptor and donor enhances the electron density and donating power of the molecule and thus increases the efficiency of fluorescence quenching by oxidative explosives. While there is enough room for improvement in the response of **1** toward other potential explosives, the Pt backbone with aromatic and ethynyl functionalities in conjugation provides excellent starting material for new explosive sensors. The use of a specially designed shape-selective metal-based linker and the preparation of functional assemblies have the potential to considerably expand the range of the directional bonding paradigm in self-assembly. Detail fluorescent quenching studies of this cage and related assemblies are under investigation.

Supporting Information Available: Crystallographic information of **M** in CIF format, synthesis of **M**, ^{31}P and ^{13}C NMR of **M** and **1**.

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