

Synthesis of 1,4,7-Triphenyl-1,4,7-triphosphacyclononane: The First Metal-Free Synthesis of a [9]-aneP₃R₃ Ring

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The 1,4,7-triphenyl-1,4,7-triphosphacyclononane ([9]-aneP₃Ph₃) macrocycle was synthesized through the reaction of lithium bis-(2-phenylphosphidoethyl)phenylphosphine with 1,2-dichloroethane. [9]-aneP₃Ph₃ was subsequently coordinated to a Mo⁰ metal center and isolated as the *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ metal complex.

Herein we report the first direct synthesis of a triphosphacyclononane macrocycle without the use of a transition-metal template. Cyclononane macrocycles containing nitrogen (i.e., tacn, [9]-aneN₃H₃) and sulfur ([9]-aneS₃) are well-known and have a rich transition-metal coordination chemistry.^{1,2} For example, transition-metal complexes of tacn are used as functional models for metalloenzyme active sites and in numerous catalytic organic conversions.^{3,4} The phosphorus derivatives of the cyclononane macrocyclic compounds, however, have remained absent from study because no effective route to their synthesis has been reported.

Given the widespread use of phosphorus ligands in transition-metal homogeneous catalysis, it can be expected that triphosphacyclononane compounds hold substantial potential in this area.⁵ For example, the triphosphacyclononane compounds have the ability to facially cap metal centers,

resulting in their kinetic and thermal stability, while creating labile positions trans to the phosphorus coordination sites. The ability to electronically and sterically tune the phosphorus donor atoms adds another degree of control that is ideal for catalytic systems.

Early preparations of triphosphacyclononane macrocycles were carried out by Kyba et al. through direct solution methods; however, only 11-membered rings containing benzyl backbones were obtained.⁶ Norman et al. reported the first transition-metal template synthesis of a [12]-aneP₃H₃ macrocycle in 1982.⁷ This was followed by the pioneering work of the Edwards group in the template synthesis of numerous [12]-aneP₃R₃ derivatives that were successfully removed from the metal template and used in subsequent metal coordination and catalysis studies.⁸ Indeed, not only did the [12]-aneP₃R₃ macrocycles show interesting metal coordination properties, they were also shown to be an entirely new class of homogeneous alkene polymerization and ROMP catalysts with early transition metals.⁹

Although the [12]-aneP₃R₃ macrocycles showed usefulness for metal coordination and catalysis, the larger ring size is not ideal for a maximum metal-chelating stability. The [9]-aneP₃R₃

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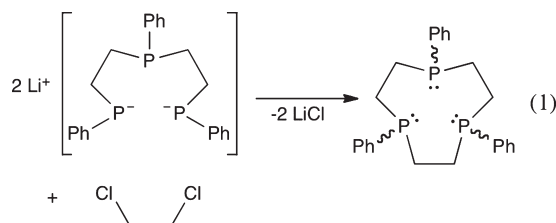
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derivatives have a more idealized geometry for metal coordination, as illustrated in both aza- and thia-crown chemistry. Consequently, where there are currently over 50 reports of the [12]-aneS₃ ligand in the literature, the [9]-aneS₃ ligand appears in over 160 papers.

To date, there are only four literature reports of 9-membered triphospha macrocyclic compounds, all of which were synthesized using Fe^{II} as a templating metal center.¹⁰ Only the 2000 Communication and 2006 full report include the synthesis of triphosphacyclononane with a hydrocarbon backbone for the 9-membered ring.^{10a,b} In all cases, however, the triphospha macrocyclic compounds could not be liberated from the transition-metal template in a form useful for subsequent metal coordination and catalysis studies.

Our method represents the first direct synthesis of a [9]-aneP₃R₃ ligand without the use of a transition-metal template. This synthesis allows for future metal coordination and catalysis studies to be conducted on this important macrocycle. Subsequent metal coordination of the newly synthesized [9]-aneP₃Ph₃ ligand to form a *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ metal complex illustrates the transition-metal coordinating ability of this novel compound.

The synthesis of [9]-aneP₃Ph₃ was accomplished through the reaction of lithium bis(2-phenylphosphidoethyl)phenylphosphine with 1,2-dichloroethane (eq 1).¹¹ The reaction was carried out under low-concentration and high-temperature conditions, which are essential for obtaining the intramolecular ring-closed product over intermolecular oligomeric and polymeric materials.



Synthesis of the [9]-aneP₃Ph₃ ring results in the formation of two isomers, as shown in Figure 1. The syn-syn isomer appears as a singlet at -15.9 ppm in the ³¹P{¹H} NMR spectrum, where the syn-anti isomer yields a double-triplet (2:1) pairing (³J_{PP} = 4.7 Hz) at -16.3 and -17.1 ppm, respectively. Integration of the ³¹P{¹H} NMR spectrum of the reaction mixture shows that the [9]aneP₃Ph₃ ring is formed in a 85% overall yield, with a 3:7 ratio of the syn-syn to syn-anti isomers, respectively. The remaining 15% of peaks in the ³¹P{¹H} NMR spectrum appear as broad, unresolved resonances, most likely because of the heavier oligomer and polymer material.

Separation of the [9]aneP₃Ph₃ rings from the reaction mixture was accomplished through solvent extraction, and the [9]aneP₃Ph₃ ring was further characterized through ¹H and ¹³C{¹H} NMR.

To obtain unequivocal structural characterization of the [9]-aneP₃Ph₃ ring, coordination to a transition-metal and

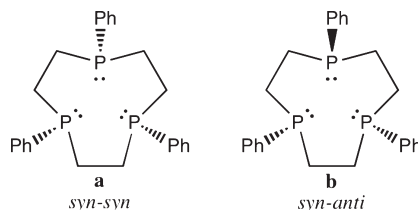
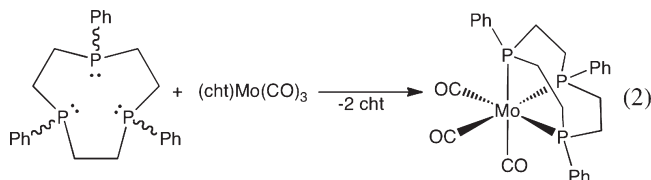


Figure 1. Isomers of the [9]aneP₃Ph₃ ring.

subsequent isolation of the metal complex were accomplished. The reaction of a [9]-aneP₃Ph₃ solution with (cht)-Mo(CO)₃ (cht = cycloheptatriene) resulted in the formation of the *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ metal complex (eq 2). The ³¹P{¹H} NMR of the reaction



mixture shows the disappearance of the peaks attributed to the [9]-aneP₃Ph₃ ring and the appearance of a new singlet at 94.0 ppm. The downfield shift observed in the ³¹P{¹H} NMR spectra is indicative of metal coordination by the phosphorus atoms. After purification, *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ was obtained in an overall 68% yield and fully characterized through spectroscopic and single-crystal X-ray analysis. Interestingly, the ³¹P{¹H} NMR integration and reaction yield indicate that both the syn-syn and syn-anti isomers react to form the facially capped metal complex. Apparently, the barrier for inversion around the phosphorus center is low enough to be overcome by the strength of metal chelation.

The X-ray structure of *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ (Figure 2) shows a distorted octahedral environment around the molybdenum metal center consisting of the facially capping [9]-aneP₃Ph₃ and three carbonyl ligands in mutually cis positions. The structural distortion around the molybdenum metal revolves mainly around the [9]-aneP₃Ph₃ ring, which shows acute P-Mo-P bite angles that average 78.42(5)° and trans C-Mo-P angles that average 170.0(2)°. The average C-Mo-C bond angles, however, are 92.9(2)°, illustrating that the carbonyl ligands maintain close to an idealized octahedral position around the metal center.

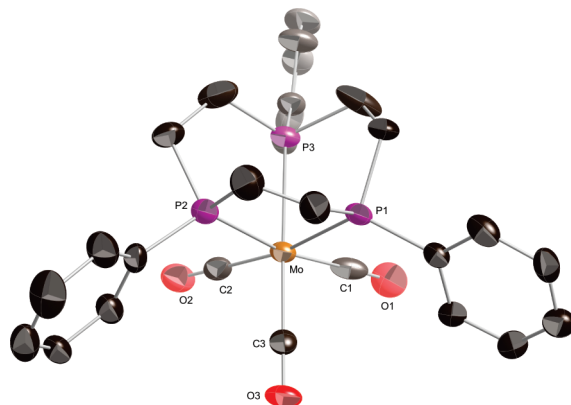


Figure 2. X-ray structure of Mo([9]-aneP₃Ph₃)(CO)₃.

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The bond distances in the *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ structure show that [9]-aneP₃Ph₃ is bound more tightly to the metal center than its [12]-aneP₃R₃ counterparts. The average Mo–P and Mo–C bond distances in *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ are 2.459(2) and 1.949(7) Å, respectively. In four previously reported *fac*-Mo([12]-aneP₃R₃)(CO)₃ structures, the average Mo–P and Mo–C bond distances are 2.497(1) and 1.972(1) Å, respectively.¹² Further, the average C–O bond distances in *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ are 1.169(6) Å, whereas those in the *fac*-Mo([12]-aneP₃R₃)(CO)₃ structure average 1.156(1) Å. The shorter Mo–P bond distances in the [9]-aneP₃Ph₃ structure indicate that the ring is more tightly bound than that in the [12]-aneP₃R₃ complexes. This is additionally supported by the fact that our [9]-aneP₃Ph₃ structure shows an increase in π -back-bonding to the carbonyl ligands, illustrated by the shorter Mo–C and longer C–O bonds observed in the *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ structure over the *fac*-Mo([12]-aneP₃R₃)(CO)₃ counterparts.

The IR data for *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ also supports the observation of increased π -back-bonding to the carbonyl ligands relative to the [12]-aneP₃R₃ complexes. In 10 reported [12]-aneP₃R₃Mo complexes, the ν (CO) frequencies range between 1954 and 1910 cm^{−1} and between 1864 and

1813 cm^{−1}.¹² The IR data for *fac*-Mo([9]-aneP₃Ph₃)(CO)₃ shows ν (CO) frequencies of 1902 and 1795 cm^{−1}. The stronger bonding of the [9]-aneP₃Ph₃ ring (relative to [12]-aneP₃R₃) results in better σ donation to the metal and, hence, increased π -back-bonding to the carbonyl ligands, supporting the X-ray crystallographic data.

In summary, we have successfully synthesized the first [9]-aneP₃R₃ phosphacrown compound without the use of a transition-metal template. The [9]-aneP₃Ph₃ ring was bound to a molybdenum metal center, which demonstrated greater structural distortion and stronger binding than the [12]-aneP₃R₃ analogues. Work continues in our laboratory to separate the two [9]-aneP₃Ph₃ ring isomers and to conduct additional metal coordination studies.

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Supporting Information Available: Further details of the synthesis and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 764783 contains the supplementary crystallographic data for *fac*-Mo([9]-aneP₃Ph₃)(CO)₃. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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