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Synthesis of 1,4,7-Triphenyl-1,4,7-triphosphacyclononane: The First Metal-Free Synthesis of a [9]-aneP_3R_3 Ring

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The 1,4,7-triphenyl-1,4,7-triphosphacyclononane ([9]-aneP_3Ph_3) macrocycle was synthesized through the reaction of lithium bis(2-phenylphosphidoethyl)phenylphosphine with 1,2-dichloroethane. [9]-aneP_3Ph_3 was subsequently coordinated to a Mo^0 metal center and isolated as the *fac*-Mo([9]-aneP_3Ph_3)$(CO)_3$ 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]-aneN_3H_3) and sulfur ([9]-aneS_3) 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 triphospha 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]-aneP_3H_3 macrocycle in 1982.[7] This was followed by the pioneering work of the Edwards group in the template synthesis of numerous [12]-aneP_3R_3 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]-aneP_3R_3 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]-aneP_3R_3 macrocycles showed usefulness for metal coordination and catalysis, the larger ring size is not ideal for a maximum metal-chelating stability. The [9]-aneP_3R_3

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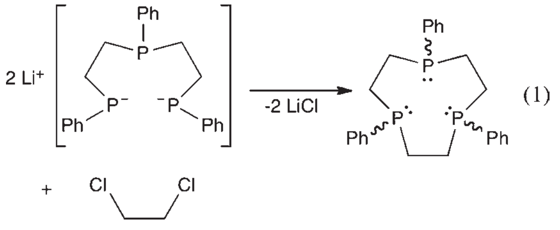
derivatives have a more idealized geometry for metal coordination, as illustrated in both aza- and thia-crown chemistry. Consequently, where there are currently over 50 reports of the [12]-aneS_3 ligand in the literature, the [9]-aneS_3 ligand appears in over 160 papers.

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]-aneP_3R_3 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]-aneP_3Ph_3 ligand to form a *fac*-Mo([9]-aneP_3Ph_3)-$(CO)_3$ metal complex illustrates the transition-metal coordinating ability of this novel compound.

The synthesis of [9]-aneP_3Ph_3 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.



(1)

Synthesis of the [9]-aneP_3Ph_3 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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows that the [9]aneP_3Ph_3 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 $^{31}P\{^1H\}$ NMR spectrum appear as broad, unresolved resonances, most likely because of the heavier oligomer and polymer material.

Separation of the [9]aneP_3Ph_3 rings from the reaction mixture was accomplished through solvent extraction, and the [9]aneP_3Ph_3 ring was further characterized through ^1H and $^{13}C\{^1H\}$ NMR.

To obtain unequivocal structural characterization of the [9]-aneP_3Ph_3 ring, coordination to a transition-metal and subsequent isolation of the metal complex were accomplished. The reaction of a [9]-aneP_3Ph_3 solution with (cht)-$Mo(CO)_3$ (cht = cycloheptatriene) resulted in the formation of the *fac*-Mo([9]-aneP_3Ph_3)$(CO)_3$ metal complex (eq 2). The $^{31}P\{^1H\}$ NMR of the reaction mixture shows the disappearance of the peaks attributed to the [9]-aneP_3Ph_3 ring and the appearance of a new singlet at 94.0 ppm. The downfield shift observed in the $^{31}P\{^1H\}$ NMR spectra is indicative of metal coordination by the phosphorus atoms. After purification, *fac*-Mo([9]-aneP_3Ph_3)$(CO)_3$ was obtained in an overall 68% yield and fully characterized through spectroscopic and single-crystal X-ray analysis. Interestingly, the $^{31}P\{^1H\}$ 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.

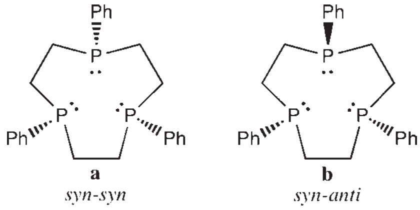
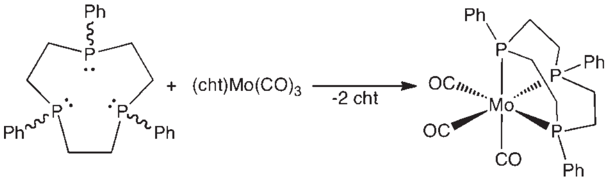


Figure 1. Isomers of the [9]aneP_3Ph_3 ring.



(2)

The X-ray structure of *fac*-Mo([9]-aneP_3Ph_3)$(CO)_3$ (Figure 2) shows a distorted octahedral environment around the molybdenum metal center consisting of the facially capping [9]-aneP_3Ph_3 and three carbonyl ligands in mutually cis positions. The structural distortion around the molybdenum metal revolves mainly around the [9]-aneP_3Ph_3 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.

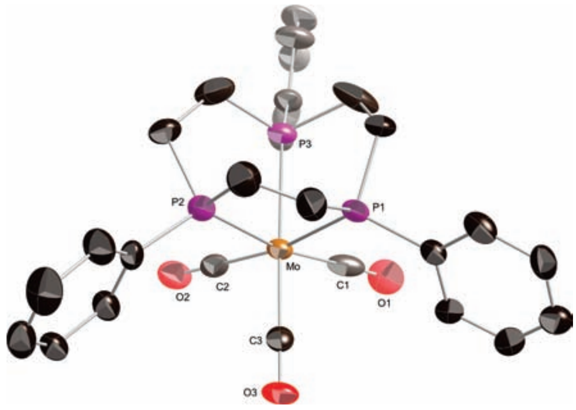


Figure 2. X-ray structure of Mo([9]-aneP_3Ph_3)$(CO)_3$.

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The bond distances in the *fac*-Mo([9]-aneP_3Ph_3)$(CO)_3$ structure show that [9]-aneP_3Ph_3 is bound more tightly to the metal center than its [12]-aneP_3R_3 counterparts. The average Mo−P and Mo−C bond distances in *fac*-Mo([9]-aneP_3Ph_3)$(CO)_3$ are 2.459(2) and 1.949(7) Å, respectively. In four previously reported *fac*-Mo([12]-aneP_3R_3)$(CO)_3$ 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]-aneP_3Ph_3)$(CO)_3$ are 1.169(6) Å, whereas those in the *fac*-Mo([12]-aneP_3R_3)$(CO)_3$ structure average 1.156(1) Å. The shorter Mo−P bond distances in the [9]-aneP_3Ph_3 structure indicate that the ring is more tightly bound than that in the [12]-aneP_3R_3 complexes. This is additionally supported by the fact that our [9]-aneP_3Ph_3 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]-aneP_3Ph_3)-$(CO)_3$ structure over the *fac*-Mo([12]-aneP_3R_3)$(CO)_3$ counterparts.

The IR data for *fac*-Mo([9]-aneP_3Ph_3)$(CO)_3$ also supports the observation of increased π-back-bonding to the carbonyl ligands relative to the [12]-aneP_3R_3 complexes. In 10 reported [12]-aneP_3R_3Mo 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]-aneP_3Ph_3)$(CO)_3$ shows ν(CO) frequencies of 1902 and 1795 cm^{-1}. The stronger bonding of the [9]-aneP_3Ph_3 ring (relative to [12]-aneP_3R_3) 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]-aneP_3R_3 phospha-crown compound without the use of a transition-metal template. The [9]-aneP_3Ph_3 ring was bound to a molybdenum metal center, which demonstrated greater structural distortion and stronger binding than the [12]-aneP_3R_3 analogues. Work continues in our laboratory to separate the two [9]-aneP_3Ph_3 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]-aneP_3Ph_3)$(CO)_3$. 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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