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Synthesis of planar macrocyclic tetradentate phosphine–Mo complexes†

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The synthesis of transition-metal complexes bearing a macrocyclic tetradentate phosphine ligand is relatively undeveloped. Herein, an open-chain tetradentate phosphine ligand with two P-containing rings was synthesized and coordinated to a Mo-oxo template. After deprotonation and cyclization with suitable alkyl chains, a series of planar macrocyclic tetradentate phosphine–Mo complexes was obtained without stereoisomers.

It is well known that phosphines are excellent ligands which impart many interesting properties to their metal complexes;[1–5] in particular, the macrocyclic effect[6] of the cyclic phosphine ligand makes the complex more stable.[7] For example, Mock and coworkers reported the first 16-membered tetradentate macrocyclic phosphine chromium complexes *trans*-[$Cr(N_2)_2(PPh_4NBn_4)$] for activation of dinitrogen molecules.[8,9] An extensive development of the chemistry of phosphorus containing macrocyclic compounds in the past years was stimulated by the use of these compounds for the design of new types of supramolecular and coordination systems.[10]

Macrocyclic phosphine complexes can be synthesized *via* two major strategies. One involves the synthesis of macrocyclic phosphine ligands followed by their coordination to a metal center. While in the other strategy, which is normally called template synthesis, components are coordinated to the target metal prior to the final cyclization. Despite the development of the synthesis of macrocyclic phosphine ligands in recent years,[11–13] macrocyclic phosphine complexes of group 6 transition-metals are rare. Helm reported a metal-free synthesis of a [9]-aneP_3R_3 ring and the further coordination of such a ligand to $Mo(CO)_3$.[14] By placing reactive groups in close proximity to each other, template synthesis has demonstrated superior selectivity and relatively high yields.[12] Norman first employed a Mo(0) template to prepare the macrocyclic triphosphine–molybdenum complex *fac*-[$(CO)_3Mo(PHC_3H_6)_3$] *via* intramolecular hydrophosphination reactions of coordinated primary alkenyl phosphines.[15] This method was followed by Edwards' group in the template synthesis of a series of 1,5,9-triphosphacyclododecane complexes with both molybdenum and chromium.[16–20] Influenced by the ring size, macrocyclic tridentate phosphine ligands ([9]-aneP_3R_3 to [12]-aneP_3R_3) in the aforementioned complexes exclusively exhibit a facial coordination geometry. Macrocyclic tetradentate phosphine ligands offer the possibility of fully encircling a metal center. The first example of a tetraphosphine macrocyclic complex was reported in 1977 by Rosen using a Ni(II) template.[21] Unfortunately, no crystallographic characterization was performed, nor was there any information about the stereoisomers in this pioneering work. Recently, Tyler reported a macrocyclic tetradentate phosphine complex with Cu(I) in a tetrahedral geometry.[22] To date, most of the currently synthesized macrocyclic tetradentate phosphine complexes have been based on Cu(I), Ni(II), Pd(II) or Pt(II).[22–27] Synthesis of planar macrocyclic tetradentate phosphine complexes with group 6 transition-metals has remained absent since no effective route has been established.

Moreover, compared with oxa-, aza-, and thia-carbocyclic systems, the synthesis of cyclic phosphine ligands especially planar macrocyclic tetradentate phosphine is still difficult.[28] This may also be related to the stereochemistry at the phosphorus atoms. Unlike tertiary amines, the inversion barrier of phosphines is sufficiently high (29–36 kcal mol^{-1}), so they do not undergo inversion at room temperature.[29] This means that the macrocyclic phosphines with asymmetric phosphine groups ($PR_1R_2R_3$) are chiral, resulting in multiple possible stereoisomers for each macrocycle (Scheme 1).[12,30,31] For instance, the bisphosphane complex of Pd(II) undergoes reaction with 2 equiv. of acetylacetone in ethanol to form two isomeric cycloadducts which are derived from the (*RSSR*)-form

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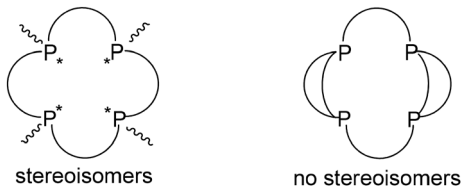
† Electronic supplementary information (ESI) available: Experimental procedure, NMR spectra and X-ray diffraction data. CCDC 2433616–2433620 for **P2**, **Mo1**, **Mo2**, **Mo3**, and **Mo4**. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5dt00984g

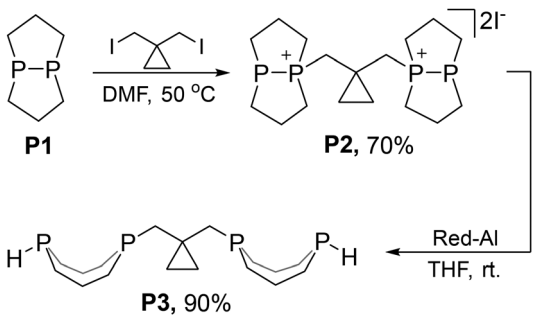


Scheme 1 Stereochemistry of macrocyclic tetradentate phosphine ligands.

and the (*RSRS*)-form of the starting compound, respectively. In the (*RSSR*)-form derived product, the methyl groups of two adjacent P atoms are oriented above the equatorial plane and the other two methyl groups are oriented below the plane. However, in the (*RSRS*)-form derived product, the methyl groups of all four P atoms are above the equatorial plane.[32] Introduction of a side ring can effectively avoid stereoisomerism (Scheme 1). Herein, we report the synthesis of a series of Mo complexes bearing a planar macrocyclic tetradentate phosphine ligand with two side rings.

Starting from compound **P1**,[33] the quaternary phosphonium diiodide [PP^{Cpr}PP]I_2 (**P2**)[33,34] (PP^{Cpr}PP = 4-{[(octahydro[1,2]diphospholo[1,2-*a*][1,2]diphosphol-4-ium-4-ylmethyl)cyclopropyl]methyl}-octahydro-[1,2]diphospholo-[1,2-*a*][1,2]diphosphol-4-ium) was synthesized in a good yield by alkylation with 1,1-bis(iodomethyl) cyclopropane (Scheme 2). ^{31}P{H} NMR spectroscopy of the phosphonium salt **P2** exhibits two doublets of triplets at 79.6 ppm and −50.0 ppm ($^{1}J_{PP}$ = 252.0 Hz, $^{4}J_{PP}$ = 14.3 Hz), respectively, corresponding to the two different types of P atoms. Four P atoms in **P2** form an AA′BB′ spin system. Four coupling constants are used to determine the NMR pattern in such a system. With $|J_{AB}| = {}^{1}J_{PP}$ = 252.0 Hz and $|J_{AA'}| = {}^{4}J_{PP}$ = 14.3 Hz (coupling between P2 and P3 along the carbon chain), and the other two coupling constants close to zero, P atoms in **P2** will give two doublets of triplets. Crystals of compound **P2** suitable for X-ray analysis were grown by recrystallization using methanol (Fig. 1).

Treatment of compound **P2** with sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) broke the P–P bonds, leading to the 1,5-diphosphocane moieties in [HPP^{Cpr}PPH] (**P3**) (HPP^{Cpr}PPH = 1-{[(1,5-diphosphocan-1-ylmethyl)cyclopropyl]methyl}-1,5-diphosphocane). ^{31}P{H} NMR of **P3** shows two doublets at −34.9 ppm and −73.6 ppm. The resonance at



Scheme 2 Synthesis of compound **P3**.

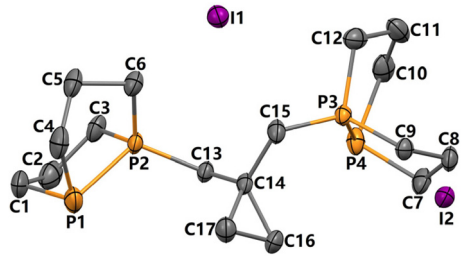
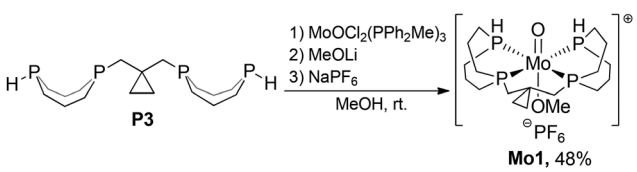


Fig. 1 X-ray structure of compound **P2**. Thermal ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–P2 2.193(2), P3–P4 2.186(2), P3–C12 1.811(7), P4–C7 1.863(7), C14–C17 1.509(9), P3–C9 1.810(6), C9–C8 1.522(9), C9–P3–C12 109.9(3), C9–P3–C15 112.9(3), C12–P3–C15 111.9(4), C9–P3–P4 100.2(2), C12–P3–P4 100.9(3), C15–P3–P4 119.9(2), C13–P2–C6 116.4(3), C13–P2–C3 109.6(3), C6–P2–C3 112.2(3), C13–P2–P1 118.3(2).

−73.6 ppm becomes a broad doublet with $^{1}J_{PH}$ = 199.1 Hz in the proton coupled ^{31}P NMR, which clearly proves that P–H bonds are present in **P3**. Correspondingly, P–H bonds of **P3** in ^{1}H NMR are a doublet at 3.30 ($^{1}J_{PH}$ = 196.4 Hz) ppm, which collapses to a singlet in ^{1}H{P} NMR. When ligand **P3** was added to the suspension of $Mo(O)Cl_2(PPh_2Me)_3$ (**Mo0**)[35,36] and MeOLi in MeOH at room temperature, the green solid of **Mo0** gradually disappeared during the reaction, accompanied by the formation of a yellow solution (Scheme 3). After the anion exchange with $NaPF_6$, ^{31}P{H} NMR of this yellow solution displays two resonances, indicating a typical AA′BB′ spin system. Again, the signal at −36.1 ppm shows a P–H coupling constant of $^{1}J_{PH}$ = 314.8 Hz in the proton coupled ^{31}P NMR and the P–H gives a doublet with a coupling constant of $^{1}J_{PH}$ = 316.3 Hz at 5.88 ppm in the ^{1}H NMR, suggesting the presence of P–H bonds in this complex; thus, a Mo-oxo complex [(HPP^{Cpr}PPH)Mo(O)(OMe)][PF_6] (**Mo1**) with a tetradentate phosphine ligand was proposed. Gratifyingly, yellow crystals of **Mo1** were grown by layering *n*-hexane on top of the dichloromethane solution. An X-ray crystallography study reveals a pseudo octahedral geometry at the Mo center, with the tetradentate phosphine ligand in the equatorial plane and a methoxy group *trans* to the oxo ligand (Fig. 2, left). The O–Mo–O is linear (O1–Mo1–O2 179.06(9)°). The Mo–O single bond (Mo1–O2 1.9487(19) Å) is longer than the Mo=O double bond (Mo1–O1 1.719(2) Å). The lengths of the Mo–P bonds in **Mo1** are similar (2.46–2.50 Å). In contrast, since the planar macrocycle has not been formed, the bite angle of the two secondary phosphine ligands (P1–Mo1–P4 (111.01(3)°)) is larger than other three bite angles.



Scheme 3 Synthesis of complex **Mo1**.

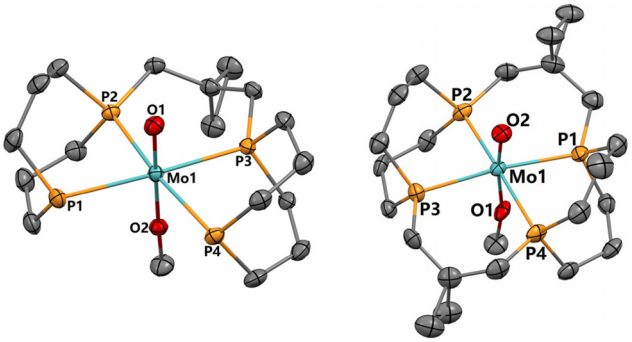
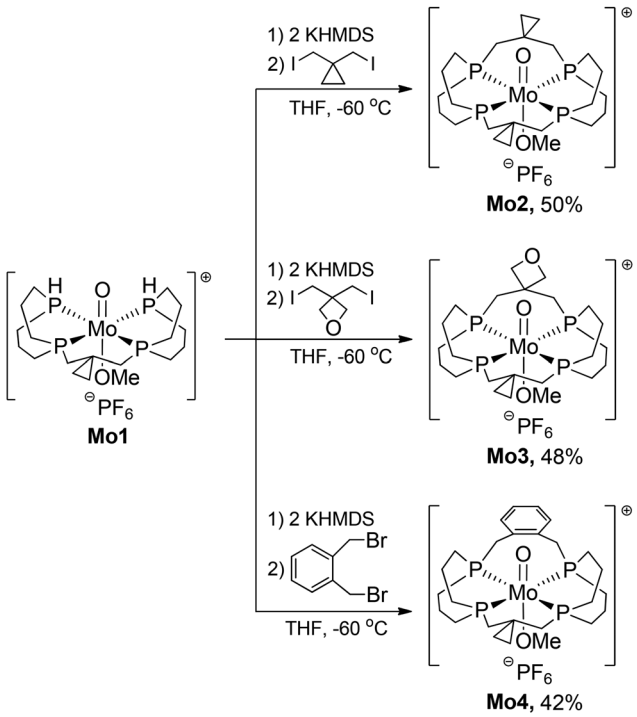


Fig. 2 X-ray structures of complex **Mo1** (cation, left) and **Mo2** (cation, right). Thermal ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) of **Mo1**: Mo1–O1 1.719(2), Mo1–O2 1.9487(19), Mo1–P1 2.5203(8), Mo1–P2 2.4863(7), Mo1–P3 2.4609(7), Mo1–P4 2.5086(8), O1–Mo1–O2 179.06 (9), O1–Mo1–P1 94.44(7), O1–Mo(1)–P2 93.07(7), O2–Mo1–P1 86.50(6), O2–Mo1–P2 87.16(6), P1–Mo1–P2 77.42(3), P1–Mo1–P3 169.74(3), P1–Mo1–P4 111.01(3), P2–Mo1–P3 93.99(3); **Mo2**: Mo1–O1 1.712(13), Mo1–O2 1.971(12), Mo1–P1 2.438(6), Mo1–P2 2.437(5), O1–Mo1–O2 178.2(9), O1–Mo1–P1 95.2(6), O2–Mo1–P1 84.0(6), P1–Mo1–P2 97.6(5), P1–Mo1–P3 170.1(7), P1–Mo1–P4 79.5(6).



Scheme 4 Synthesis of complexes **Mo2**, **Mo3** and **Mo4**.

Unlike the secondary phosphine ligands in Ni(II) or Pd (II),[25,37] which could be deprotonated with a weak base such as triethylamine or K_2CO_3, the ligand in complex **Mo1** could only be deprotonated by a very strong base like KHMDS, although the Mo moiety was overall cationic before deprotonation. The deprotonation of complex **Mo1** in THF at −60 °C, followed by the addition of 1 equiv. of 1,1-bis(iodomethyl)cyclopropane gave a yellow solid. The P atoms of this solid resonate as only a singlet at 5.0 ppm in the $^{31}P\{H\}$ NMR, indicating the formation of the desired macrocyclic complex [($PP^{Cpr}PP^{Cpr}$)Mo(O)(OMe)][PF_6] (**Mo2**) ($PP^{Cpr}PP^{Cpr}$ = dispiro-[cyclopropane-1,11′-1,5,9,13-tetraphosphatricyclo-[11.3.3.3^{5,9}]docosane-3′,1″-cyclopropane]) (Scheme 4). The formation of the planar tetradentate structures was also confirmed by X-ray diffraction (Fig. 2, right). In the solid state of **Mo2**, the four Mo–P bonds have almost the same length (2.44 Å), while the bite angles of the diphosphocane moieties (P2–Mo1–P3 81.8(5)° and P1–Mo1–P4 79.5(6)°) are slightly smaller than the other two bite angles (P1–Mo1–P2 97.6(5)° and P3–Mo1–P4 99.4(6)°). $^1H\{P\}$ NMR of **Mo2** exhibits broad signals of the protons except the protons of the methoxy group. This phenomenon is attributed to not only the fluxional processes of the molecule, but also the coupling of the protons with very close chemical shifts.

Similarly, after the deprotonation of **Mo1**, the addition of 1 equiv. of 3,3-bis(iodomethyl)oxetane or α,α′-dibromo-*o*-xylene produced [($PP^{Cpr}PP^{Oxt}$)Mo(O)(OMe)][PF_6] (**Mo3**) ($PP^{Cpr}PP^{Oxt}$ = dispiro-[oxetane-3,11′-1,5,9,13-tetraphosphatricyclo-[11.3.3.3^{5,9}]-docosane-3′,1″-cyclopropane]) or [($PP^{Cpr}PP^{Xy}$)Mo(O)(OMe)][PF_6] (**Mo4**) ($PP^{Cpr}PP^{Xy}$ = spiro[1,5,9,18-tetraphosphatetracyclo[16.3.3.3^{5,9}.0^{11,16}] heptacosa-11(12),13,15-triene-3,1′-cyclopropane]) (Scheme 4), respectively. In these cases, P atoms in each molecule become two inequivalent groups, forming AA′BB′ spin systems as observed in the $^{31}P\{H\}$ NMR spectra. Note that in **Mo3** and **Mo4**, the chemical shift differences of inequivalent P atoms are much smaller than the J_{PP} coupling, complicated patterns are seen and the coupling constants cannot be simply read from the spectra. Intriguingly, protons of the methoxy group in **Mo4** shift to the high field in the ^1H NMR spectra (δ = 2.16 ppm), suggesting the presence of a strong shielding effect. Yellow crystals of **Mo3** (Fig. 3, left) and

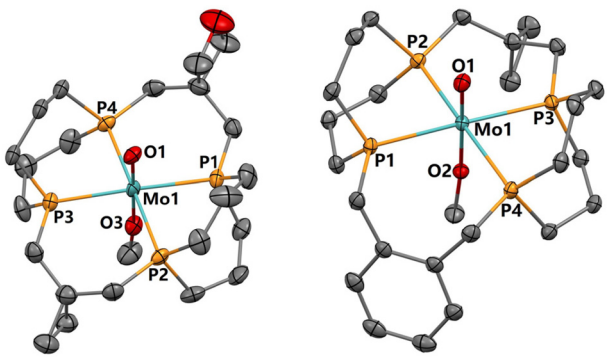


Fig. 3 X-ray structures of complex **Mo3** (cation, left) and **Mo4** (cation, right). Thermal ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) of **Mo3**: Mo1–O1 1.764(4), Mo1–O3 1.925(4), Mo1–P1 2.4433(13), Mo1–P2 2.4293(15), O1–Mo1–O3 179.5(2), O1–Mo1–P1 92.96(14), O1–Mo1–P2 91.87(14), O3–Mo1–P1 87.32(13), O3–Mo1–P2 87.74(14), P1–Mo1–P2 81.20(6), P1–Mo1–P3 175.67(7), P1–Mo1–P4 98.73(6), P2–Mo1–P3 98.83(5); **Mo4**: Mo1–O1 1.7142(13), Mo1–O2 1.9696(12), Mo1–P1 2.4616 (5), Mo1–P2 2.4627(5), O1–Mo1–O2 177.80(6), O1–Mo1–P1 91.69(5), O1–Mo1–P2 95.01(5), O2–Mo1–P1 87.00(4), O2–Mo1–P2 86.48(4), P1–Mo1–P2 79.101(15), P1–Mo1–P3 172.039(16), P1–Mo1–P4 103.944(15), P2–Mo1–P3 96.715(15).

Mo4 (Fig. 3, right) were obtained by vapor diffusion of diethyl ether into a dichloromethane or *N*,*N*-dimethylformamide solution. X-ray diffraction analysis reveals that the lengths of the Mo–P bonds and the bite angles in **Mo3** are similar to those in **Mo2**. However in **Mo4**, owing to the different lengths of the chains of the macrocycle, the bite angle of P1–Mo1–P4 (103.944(15)°) is significantly larger than that of P2–Mo1–P3 (96.715(15)°). Additionally, the C atom of the methoxy group in **Mo4** is located 3.84 Å above the face of the benzene ring, which is an NMR shielding region. This rationalizes the unusually low chemical shift of its protons.

In conclusion, a new class of planar macrocyclic tetradentate phosphine–Mo complexes was synthesized for the first time though templating. Thanks to the two side rings in the structure, these complexes did not generate stereoisomers during the synthesis. Further studies on the reactivity of these complexes are in progress in our lab.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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