A sulfur mimic of 1,1-bis(diphenylphosphino)methane: a new ligand opens up†

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A simple method for synthesizing diphosphine monosulfide species was developed utilizing lithium sulfide and chlorophosphine starting materials. This afforded 1,1,2,2-tetracyclohexyldiphosphine monosulfide (1), as well as 1,1,2,2-tetracyclohexylidiphosphine monosulfide (2), which could be used as convenient ligand precursors. Upon addition of 1 or 2 to the ruthenium compound Ru(C6Me6)2(cod)Cl, the diphosphine monosulfides rearranged to give bidentate bis(ditertiaryphosphino)thioether ligands in Ru(C6Me6)2([PPh2CH2PPh2]2)Cl (3) and Ru(C6Me6)2(PCy2SCy2)Cl (4).

Bidentate phosphorus ligands have been widely employed by inorganic chemists in the synthesis of a large variety of metal complexes.1 A particularly noteworthy member of this class of ligands is 1,1-bis(diphenylphosphino)methane (dppm), which has been used, along with its alkyl and aryl substituted analogues, to generate monometallic2 and bimetallic (A-frame) compounds,3 as well as larger metal clusters.4 Moreover, many of these dppm-containing species were found to be active catalysts for hydroformylation and hydrocyanation reactions, as well as other chemical transformations.5–7

A related class of ligands is constituted by bis(ditertiaryphosphino)-thioethers, which have a sulfur atom replacing the methylene backbone. Typically, synthetic strategies utilizing low temperatures and/or large fluorinated or aliphatic substituents on the phosphorus centres have been employed to stabilize the free thioether species, but despite these efforts, a diphosphine monosulfide byproduct is also commonly seen.8–42 In addition, although much has been done in synthesizing and isolating these types of molecules there are few examples of their metal complexes. To our knowledge only Burg et al. and Arnold et al. have reported nickel25,41 and molybdenum–carbonyl23,43 complexes, respectively.

Although bis(ditertiaryphosphino)thioethers superficially resemble dppm, their stability and electronic properties are unlikely to be the same. P–S bonds are chemical analogues of P–O bonds and it is known that phosphines and phosphites have drastically different properties.44,45 Phosphites are less sigma donating and are more pi acidic, while phosphines have the opposite properties.44 Moreover, P–C bonds are much more stable than P–O bonds, which are sensitive to hydrolysis, alcoholysis, and alkoxide substitution reactions.45 As such, bis(ditertiaryphosphino)thioethers may have unique bonding properties that could be useful in tuning the electronic nature of a variety of transition metal catalysts.

In this paper we present a very simple method for synthesizing the previously reported diphosphine monosulfide species 1,1,2,2-tetracyclohexyldiphosphine monosulfide, 1, which was formerly synthesized using thiourea and chlorodiphosphine.24,39 One equivalent of lithium sulfide was dissolved in acetonitrile, and two equivalents of chlorodiphosphine were added, which afforded 1 as a white powder in high yields (87%, see Fig. 1). The 31P{1H} NMR spectrum of 1 was very diagnostic with two doublets at +247 Hz (in agreement with literature values), indicating the presence of a P–P bond.25,39 The structure of 1 was also determined by single crystal X-ray diffraction (XRD, see Fig. S1, ESI†), which matched the results reported by Aluri et al. with a P–P bond length of 2.226(2) Å and a P–S bond length of 1.953(2) Å (see Table S1 (ESI†) for other notable bond lengths and angles).46

Using the same synthetic methodology employed in the production of 1, an analogous alkyl substituted compound, 1,1,2,2-tetracyclohexylidiphosphine monosulfide, 2, was generated as

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** Synthesis of the monosulfides 1 and 2, as well as ruthenium complexes 3 and 4.
a white powder in moderate yields (70%) utilizing chlorodicyclohexylphosphine as a starting material. The $^{31}$P($^1$H) NMR spectrum of 2 was very similar to that of 1 with two doublets at 59.1 and −14.0 ppm and a $J_{PP}$ coupling constant of 302 Hz. The XRD structure of the cyclohexyl-substituted analogue was also similar to that of the phenyl-substituted compound with a P–P bond length of 2.225(4) Å and a P–S bond length of 1.972(2) Å (see Fig. 2, and see Table S2 (ESI†) for other notable bond lengths and angles).

Unexpectedly, given that a chromium complex bearing a 1,1,2,2-tetraphenyldiphosphine monosulfide ligand is known in the literature,47 diphosphine monosulfides 1 and 2 were found to be convenient precursors for metal complexes bearing bis(diphenylphosphino)thioether (dppte) and bis(dicyclohexylphosphino)thioether (dcpte) ligands, respectively. Treatment of RuCp*(cod)Cl convenient precursors for metal complexes bearing bis(diphenyl-substituted compound with a P–P bond length of 2.225(4) Å and a P–S bond length of 1.972(2) Å (see Fig. 2, and see Table S2 (ESI†) for other notable bond lengths and angles).

Unsurprisingly, given that a chromium complex bearing a diphosphine monosulfide precursor, attempts were made to

Based on our coordination studies we propose that the ligand precursors 1 and 2 exist in equilibrium with their corresponding thioether constitutional isomers in solution (see Fig. 4). Initially, the diphosphinothioether likely forms from an intermediate monophosphine monosulfide species, but the diphosphino monosulfide form is significantly more stable. This drives the equilibrium far to the right, and therefore only 1 and 2 are seen.

When the RuCp*(cod)Cl complex is introduced into the system, we believe that the diphosphine monosulfides coordinate to the metal first. There is precedent in the literature for this type of structure in the form of the chromium complex discussed previously.47 Once coordinated, the diphosphine monosulfide ligands can still interconvert into their thioether isomers and “open up”. When this happens, however, the metal centre traps the thioether as a bidentate ligand, and the equilibrium (Fig. 5) is forced to the right. As such, this reaction is likely to be very general and a wide variety of metal precursors should be suitable for this ligand architecture. The most crucial requirement, though, is that the metal has at least one vacant site to facilitate initial coordination of the diphosphine monosulfide precursor, and then the ability to make another site available to trap the thioether species.

Our group has recently reported the synthesis of ruthenium phosphido complexes with bidentate phosphine donors and their reactions with molecular oxygen.49,50 In an effort to generate similar phosphido species with a dppe ligand, attempts were made to
replace the chloride in 3 with a secondary phospine resulting in a synthetic procedure that has been successfully employed for the synthesis of other phosphido products from analogous ruthenium starting materials. The method utilized stoichiometric amounts of AgOTf as a halogen abstracting agent, but in the dppte case, an excess of AgOTf was necessary to ensure the removal of all of the chloride ligand. This in turn required an excess of diphenylphosphine as the silver cations in solution competed with the ruthenium centre for the monodentate phospine (see Fig. 6A). Separation of the silver and ruthenium species was not trivial and required several recrystallization steps, which led to unacceptable yields of the target complex (less than 10%).

In light of these poor results, an alternative synthetic scheme was developed exploiting RuCp*(cod)Cl as the starting material. In the first step, the chloride ligand was abstracted with AgOTf and diphenylphosphine was installed in its place (see Fig. 6B). A $^{31}$P NMR spectrum (decoupled) of the reaction mixture revealed two species in solution, at 31.6 and 30.5 ppm, both with a large P–H coupling, 374 and 347 Hz, respectively. Upon addition of 1, the signal at 31.6 ppm disappeared over time to give a new product, which showed a doublet, and a doublet of doublets at 32.4 and 29.4 ppm, respectively, while the other signal persisted in solution along with unreacted 1. The signal at 30.5 ppm has since been identified as $[\text{RuCp*}((\text{HPP}_{2})_{2})\text{OTf}]$ (see ESIf for a crystal structure of S1 and a more detailed account of the synthesis of 5), which, based on our proposed mechanism for the formation of the bidentate ligand, explains why this species was inert to ligand substitution; the diphenylphosphine monosulfide 1 was unable to displace a diphenylphosphine ligand. The doublet and doublet of doublets, on the other hand, were very diagnostic for the desired product: the doublet represented the equivalent phosphorus nuclei from the bidentate ligand, while the doublet of doublets corresponded to diphenylphosphine, which displayed a strong P–H coupling of 356 Hz (the P–H proton was also evident in the $^{1}$H NMR). Recrystallization of the reaction mixture allowed for separation of the desired product $[\text{RuCp*}((\text{PPh}_{2})_{2}\text{S})(\text{HPPh}_{2})]\text{OTf}$, 5, in poor yields (45%) as a yellow crystalline solid (see Fig. 6).

The XRD structure of 5 revealed a piano-stool structure with the bidentate and diphenylphosphine ligands cis to one another (see Fig. 7). The dppte ligand had a P(1)–Ru(1)–P(2) bite angle of 74.90(6)°, which is smaller than the bite angle seen in 3, but still larger than that of dppm.2 The P(1)–S(1)–P(2) bond angle, on the other hand, was found to be 82.46(9)° in 5, which is larger than that of 3, but still much smaller than the molybdenum carbonyl species and monometallic dpmm complexes found in the literature (see Table S3 [ESI†] for other notable bond lengths and angles).2,41

It should be noted that the $^{31}$P($^{1}$H) NMR spectrum of 5 varies significantly depending on the NMR solvent. Both the chemical shift and the $J_{PP}$ coupling constants change upon moving from deuterated THF to deuterated MeOH. Both sets of signals shift downfield to 36.3 and 34.4 ppm in the more polar solvent, for the doublet of doublets and the doublet, respectively. The S1P phosphorus nucleus seems to be more affected by the different solvents, and the doublet of doublet shape becomes more apparent in MeOH-d4; $J_{PP}$ changes from 36 and 35 Hz to 37 and 33 Hz. The diphenylphosphine ligand produces a doublet of doublets rather than a triplet pattern because of residual coupling to the P–H proton due to the extremely high $J_{PH}$ (a decoupling problem).

With 5 in hand, deprotonation of the diphenylphosphine ligand was attempted in THF with an excess of KH. The reaction, however, did not proceed cleanly and did not yield the desired phosphido species. Deprotonation with KOtBu gave even poorer results and resulted in complete decomposition of the ruthenium dppte complex.

We have developed a simple and effective way of preparing alkyl- and aryl-substituted ligand precursors in the form of diphenylphosphine monosulfides, and demonstrated that in the presence of a metal these compounds ‘open up’ to give the desired bidentate ligand. This valuable discovery makes a previously unattainable class of dpmm-like ligands, with varied substituents on the phosphorus donors, readily available, even those thought to be inaccessible due to the instability of the free diphenosphinothioether. In addition, we have characterized three metal complexes bearing these ligands and explored their stability with respect to different solvents and basic conditions. It was found that they tolerated a wide range of solvents, but were unstable in the presence of a strong base. More research is needed to explore the chemistry of this underutilized class of ligands.

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**Notes and references**

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