Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. Nell, C. Swor, E. A. Henle, L. Zakharov, N. I. Rinehart, A. Nathan and D. Tyler, *Dalton Trans.*, 2016, DOI: 10.1039/C6DT00758A.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

View Article Online
DOI: 10.1039/C6DT00758A

Synthesis of Tetraphosphine Macrocycles Using Copper(I) Templates†

*Bryan P. Nell, Charles D. Swor, E. Adrian Henle, Lev N. Zakharov, N. Ian Rinehart, Aditya Nathan, and David R. Tyler**

Department of Chemistry and Biochemistry, University of Oregon, Eugene, OR, 97403, USA

E-mail: dtyler@uoregon.edu

KEYWORDS: phosphines; macrocycles; Cu(I) template; tetradentate ligands; ambiphilic secondary phosphines

Abstract

The synthesis of phosphine macrocycles is a relatively underdeveloped area and no standard synthetic routes have emerged. Accordingly, two general synthetic routes to tetradentate phosphine macrocycles were investigated. Both routes use Cu(I) ions as template ions because, unlike other metals such as Pd(II) and Pt(II), the Cu(I) ions can be removed from the macrocyclic complex without degrading the macrocycle ligand. The first route involves the coupling of two bidentate secondary phosphines bonded to Cu(I) using 1,3-dibromopropane or 1,4-dibromobutane. Using this route, tetradentate phosphine macrocycles with either $-(CH_2)_3OCH_3$ or Ph groups bonded to the P atoms were synthesized. Macrocycle phosphines containing the $-(CH_2)_3OCH_3$ groups were investigated for their potential water-solubility, but experiments showed these phosphines were not water soluble. The second synthetic route involved the alkylation of an open-chain, mixed tertiary-secondary, tetradentate phosphine coordinated to Cu(I). Following formation of the macrocyclic ligand, the Cu(I) template was removed by reaction with aqueous KCN to yield

View Article Online
DOI: 10.1039/C6DT00758A

the free macrocyclic phosphine. This route was demonstrated for the preparation of the macrocyclic phosphine ligand 1,5,9,13-tetraphenyl-1,5,9,13-tetraphosphacycloheptadecane. Following demetallation, this macrocyclic ligand was coordinated to Fe(II) and Co(II) to form the corresponding macrocyclic phosphine complexes.

View Article Online
DOI: 10.1039/C6DT00758A

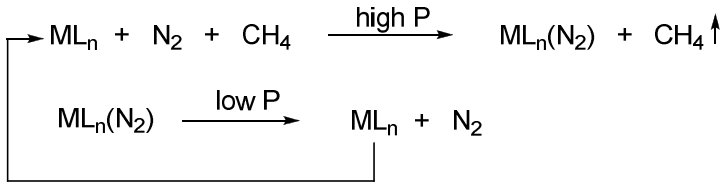
Introduction

Almost 15% of worldwide natural gas reserves are contaminated with high levels of dinitrogen (N_2).[1–3] Dinitrogen acts as a diluent in natural gas, lowering the energy density and limiting the gas's use as a fuel. In general, levels less than 4% N_2 are required for natural gas used as fuel.[4] N_2 and methane are difficult to separate because N_2 is chemically inert and also because methane and dinitrogen have similar physical properties. Industrial nitrogen rejection (the process of removing nitrogen from natural gas) uses cryogenic distillation to separate the gases, but this technique is energy-intensive and requires large capital costs, making it economically feasible only for large gas fields.[3] Recent efforts have focused on membranes for the separation.[5,6]

In previous work, we showed that complexes of the type *trans*-Fe$(P_2)_2X_2$ (where P_2 is a water-soluble bidentate phosphine) can act as absorbents in aqueous solution for separating N_2 from methane in a pressure-swing scheme (Scheme 1).[7] Unfortunately, in prolonged tests of the water-soluble *trans*-Fe$(DMeOPrPE)_2Cl_2$ complex in a pressure swing process over a continuous six-week period, the phosphine ligands slowly dissociated from the complex (Figure 1; DMeOPrPE = 1,2-bis[(dimethoxypropyl)phosphino]ethane). The eventual product was Fe$(DMeOPrPE)_3^{2+}$ (Figure 1),[7,8] which has no open coordination sites available for nitrogen coordination, and so the pressure-swing system eventually failed. To achieve a longer lasting absorbent, we decided to replace the two bidentate phosphine ligands with a tetradentate phosphine macrocycle ligand. The binding constants of macrocyclic ligands are very large (the "macrocycle effect"[9]), and the resulting Fe-macrocycle complex should be considerably more robust than complexes with two bidentate phosphines such as *trans*-Fe$(DMeOPrPE)_2Cl_2$.

View Article Online
DOI: 10.1039/C6DT00758A

Scheme 1. Solution phase pressure-swing process for separating N_2 from methane.



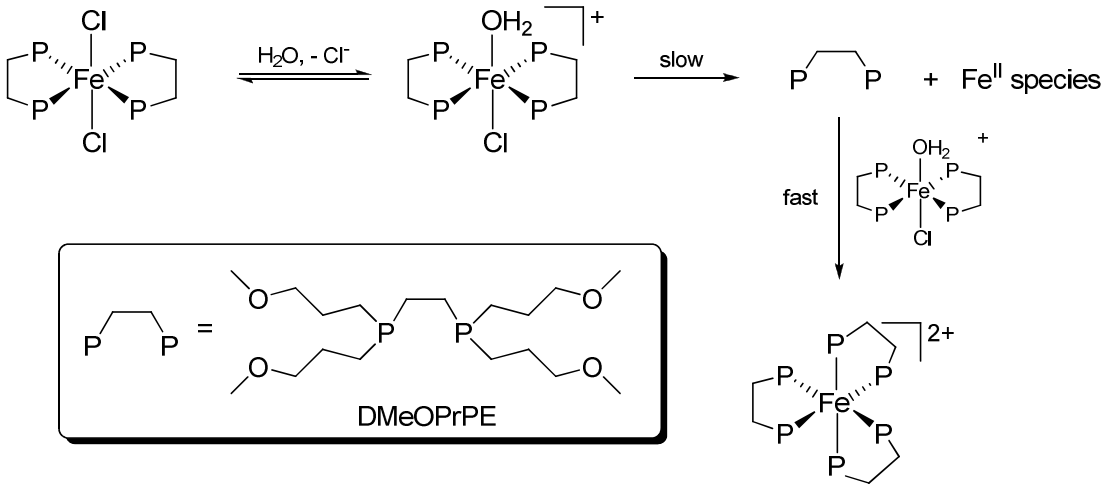


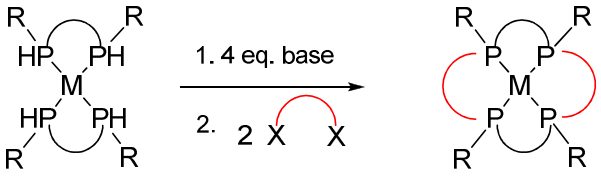
Figure 1. Degradation of $Fe(DMeOPrPE)_2Cl_2$ in water (DMeOPrPE = 1,2-bis[(dimethoxypropyl)phosphino]ethane).

The synthesis of phosphine macrocycles is a relatively underdeveloped area and no general synthetic routes to these molecules have emerged.[10] One approach to macrocyclic phosphines is a template synthesis in which two secondary bidentate phosphines are coordinated to a common metal center and then covalently linked (Scheme 2). This approach has been reported to yield macrocyclic complexes, typically using d^8 square planar metal centers (Ni(II), Pt(II), Pd(II)) as

View Article Online
DOI: 10.1039/C6DT00758A

templates.[10–14] Unfortunately, when using these metal ions as the template, it is generally not possible to separate the metal ions from the macrocyclic ligands without degrading the macrocyclic ligand in the process. There are, however, several reports of Cu(I)-based template systems where the Cu metal center has been successfully removed using either H_2S or CN^-.[15,16] In this paper, we report the synthesis of tetradentate phosphine macrocycles with hydrophilic groups using this synthetic approach.

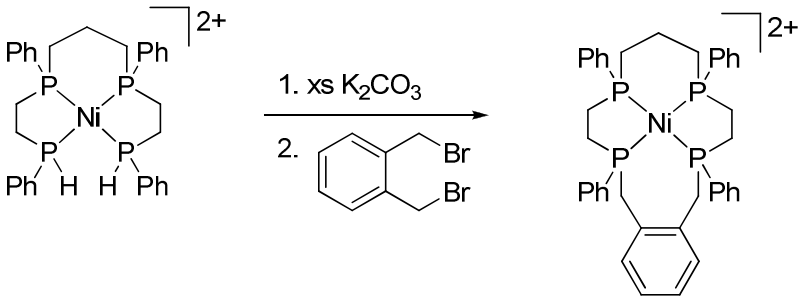
Scheme 2. Generic synthetic approach to tetradentate phosphine macrocycles using templated bidentate secondary phosphines.



A second approach to the preparation of tetraphosphine macrocycles involves linking the free ends of an open-chain tetradentate phosphine ligand bonded to a metal template. This method was demonstrated once with a Ni(II) template (Scheme 3),[14] and in this paper we extend the method to the use of a Cu(I) template. Both macrocycle synthetic routes developed in this paper are, in principle, general and should be useful for the preparation of tetradentate macrocyclic phosphines beyond the ones reported here.

View Article Online
DOI: 10.1039/C6DT00758A

Scheme 3. Preparation of a tetraphosphine macrocycle with a Ni(II) template using an open-chain tetradentate phosphine ligand.[14]

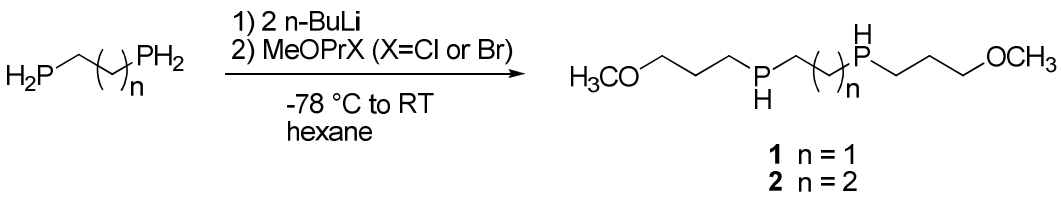


Results and Discussion

Synthesis of the bidentate and tetradentate ligands. Secondary phosphines **1** and **2** were prepared as previously described by us (Scheme 4).[17] Both **1** and **2** are clear, colorless, viscous oils. To our knowledge, these are the first examples of hydrophilic secondary phosphines. Note the reactions in Scheme 4 are not stereospecific, and the three expected stereoisomers (*R,R*(meso); *S,R*; and *R,S*) were not separated. The ambiphilic methoxypropyl functional group causes these ligands to be miscible in a wide range of solvents, from water to hexanes. Over-alkylation of the primary phosphines in Scheme 4 is a concern, but monitoring the reactions by ^{31}P NMR spectroscopy revealed that over-alkylation can be prevented by keeping the reaction temperature at -78 °C. Furthermore, because of the extra molecular mass of the methoxypropyl group, the desired product can be separated from any under- or over-alkylated products by fractional vacuum distillation.

View Article Online
DOI: 10.1039/C6DT00758A

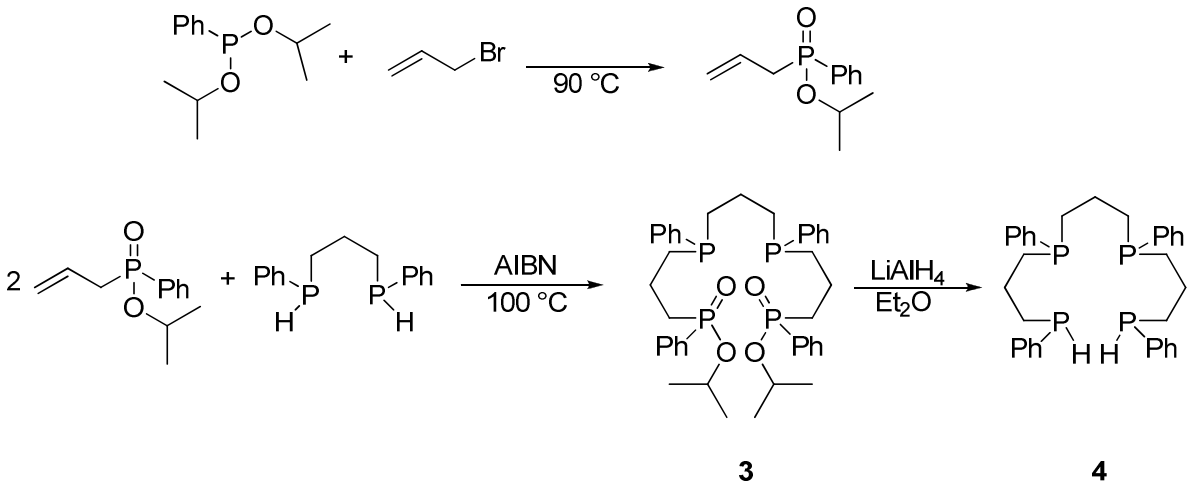
Scheme 4. Synthesis of the hydrophilic secondary phosphines **1** and **2**.



To investigate synthetic routes like that in Scheme 3 involving a linear tetradentate phosphine, ligand **4** (Scheme 5) was prepared according to literature methods as a mixture of stereoisomers by reduction of the corresponding bis-phosphinate (**3**).[18] The related new ligand with $-(CH_2)_3OCH_3$ groups (**6**; Scheme 6) was prepared by an analogous route. Both **4** and **6** were isolated as colorless, extremely viscous liquids. Unfortunately, ligand **6** was not water-soluble, and preliminary testing of the products that formed in its reactions with Cu(I) salts showed that it formed complexes that were also water-insoluble (and also very viscous liquids). In contrast, the reaction of ligand **4** with Cu(I) salts gave solid products (see the next section); for experimental convenience it was therefore decided to pursue linear tetradentate macrocycle ligands with phenyl groups rather than $-(CH_2)_3OCH_3$ groups.

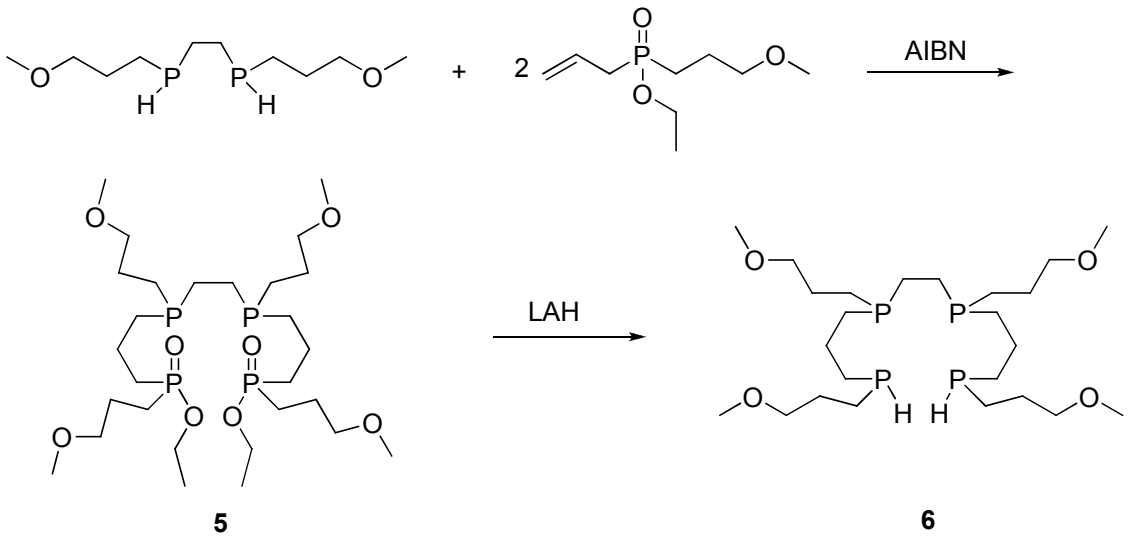
Scheme 5. Preparation of the tetradentate mixed tertiary/secondary phosphine ligand **4**.

View Article Online
DOI: 10.1039/C6DT00758A



3 4

Scheme 6. Preparation of the tetradentate mixed tertiary/secondary phosphine ligand **6**.



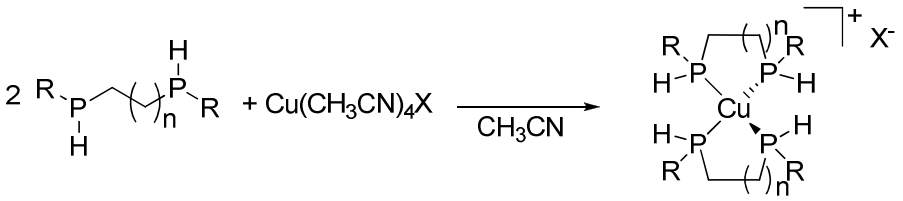
5 6

Synthesis and characterization of $Cu(P_2)_2^+$ (P_2 = a bidentate phosphine ligand). The Cu(I) template complexes of ligands **1** and **2** were synthesized by reacting the ligands with $Cu(CH_3CN)_4X$ (X = OTf^- or PF_6^-) in CH_3CN. The products were characterized as complexes **7** and **8** in Scheme 7. Coordination of the phosphines was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy, which showed that the chemical shifts of the coordinated phosphines moved ~20 ppm downfield from that of the free ligands (-41.1 ppm for **7** vs. -59.5 ppm for uncoordinated **1** and -50.5 ppm for **8** vs. -

View Article Online
DOI: 10.1039/C6DT00758A

69.6 ppm for uncoordinated **2**). The ^{31}P NMR signals were significantly broadened because of coupling with NMR-active, quadrupolar ^{63}Cu and ^{65}Cu nuclei (both spin 3/2, 69% and 31% abundance, respectively).[19,20] Note that Cu-P coupling is generally only observed for highly symmetric $Cu(PR_3)_4^+$ complexes.[20–22] In some copper-phosphine complexes the broadening can be minimized by obtaining the spectrum at high temperature,[21–23] but the spectra of complexes **7** and **8** did not change between 25 °C and 90 °C. The $[Cu(P_2)_2]^+$ formulas were supported by ESI-MS analysis (**7:** m/z 539, calculated and observed; **8:** m/z 567, calculated and observed; see the ESI). The identity of these products was further confirmed by correct elemental analyses (see Experimental Section).

Scheme 7. Synthesis of the $Cu(P_2)_2^+$ templates.



	n	R	X
7	1	$CH_3O(C_3H_6)$	PF_6
8	2	$CH_3O(C_3H_6)$	OTf
9	1	Ph	PF_6
10	2	Ph	OTf

Complexes **7** and **8** were isolated as viscous liquids, and repeated attempts at obtaining solid samples or single crystals for X-ray structural analysis were unsuccessful. In order to obtain Cu(I) template complexes that were solids instead of viscous liquids for subsequent experiments, complexes of the hydrophobic ligands MPPE (1,2-bis[(phenyl)phosphino]ethane) and MPPP (1,2-bis[(phenyl)phosphino]propane) were also synthesized (complexes **9** and **10**, respectively; Scheme 7). These complexes were isolated as crystalline solids and characterized by ^{31}P NMR spectroscopy,

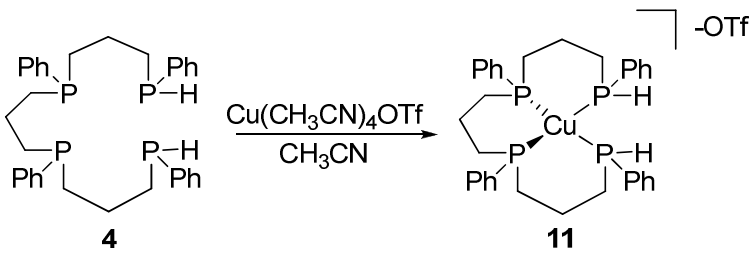
View Article Online
DOI: 10.1039/C6DT00758A

ESI-MS, and elemental analysis. Although previous reports of related complexes state they are air-stable, some oxidation was observed when these products were exposed to air, as evidenced by a blue coloration when they were dissolved in solution. The complexes were therefore handled under an inert atmosphere.

Synthesis and characterization of Cu(4)$^+$ (11). Ligand **4** reacted with one equivalent of $[Cu(CH_3CN)_4]OTf$ in CH_3CN to yield a solid product characterized as [Cu(**4**)]OTf (**11**) (Scheme 8). The $^{31}P\{^1H\}$ NMR spectrum of the product exhibited two broad peaks centered at -15 and -40 ppm, corresponding to the tertiary and secondary phosphorus atoms of the ligand, respectively. As discussed above, the broadness is consistent with coordination of the phosphine to quadrupolar $^{63}Cu/^{65}Cu$ nuclei. As also noted above, Cu-P coupling is usually observed only for highly symmetric $Cu(PR_3)_4^+$ complexes.[20–22] In complex **11**, the tetrahedral geometry about Cu(I) is likely distorted by the propylene bridges between the phosphorus atoms causing a less than ideal tetrahedral bite angle, and consequently no Cu-P coupling is observed. Overall, the ^{31}P NMR spectroscopy does not reveal much structural information except for the types of coordinated phosphine present (tertiary and secondary). The ESI-MS of the complex displayed the anticipated *m/z* at 623 ($C_{33}H_{40}CuP_4^+$) with the expected isotope pattern (Figure S35). The complex also has the correct composition by elemental analysis.

Scheme 8. Preparation of the Cu(I)-tetradentate phosphine complex (**11**).

View Article Online
DOI: 10.1039/C6DT00758A

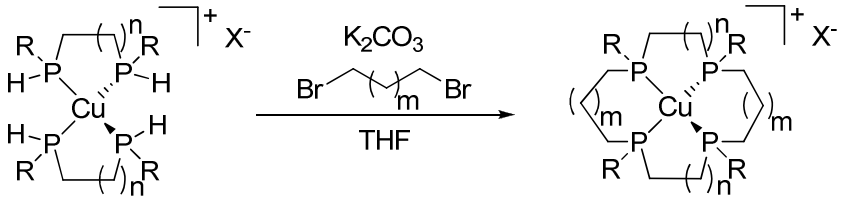


4 **11**

Macrocyclization of the $Cu(P_2)_2^+$ complexes. Complexes **7 - 10** reacted with 2 equivalents of 1,3-dibromopropane in the presence of K_2CO_3 in THF to form products characterized as the macrocycle complexes **12**-**15**, respectively (Scheme 9). Alkylation of the coordinated secondary phosphines was suggested by the downfield shifts in the ^{31}P NMR spectra (e.g., -2 ppm for **12** vs. -41 ppm for **7**). The reactions to make **12** and **13** (from **7** and **8**, respectively) took over two days to reach completion, whereas complexes **14** and **15** (from **9** and **10**, respectively) needed only four hours. We hypothesize that complexes **9** and **10** reacted faster with base than complexes **7** and **8** because the electron-withdrawing phenyl groups in **9** and **10** make the P-H bond more acidic relative to **7** and **8**, which have electron-donating $-(CH_2)_3OCH_3$ groups. ESI-MS of complexes **12**-**15** all showed molecular ion peaks consistent with the masses of the macrocyclic complexes (Table S1), indicating complete alkylation with the 1,3-dibromopropane. In addition to the macrocycles formed using 1,3-dibromopropane, the 16- and 18-membered macrocyclic complexes **16** and **17** were prepared from **9** and **10**, respectively, using 1,4-dibromobutane.

View Article Online
DOI: 10.1039/C6DT00758A

Scheme 9. Macrocyclization of $Cu(P_2)_2^+$ templates with K_2CO_3.



7-10

	n	m	R	X
12	1	1	$CH_3O(C_3H_6)$	PF_6
13	2	1	$CH_3O(C_3H_6)$	PF_6
14	1	1	Ph	PF_6 or OTf
15	2	1	Ph	OTf
16	1	2	Ph	OTf
17	2	2	Ph	OTf

Complex **15** was analyzed by single crystal X-ray diffraction, which shows the tetrahedral coordination of the macrocyclic ligand (Figure 2). The four phosphorus atoms have alternating R and S stereochemistry, giving the complex the relatively rare S_4 symmetry; the complex is thus not optically active.

View Article Online
DOI: 10.1039/C6DT00758A

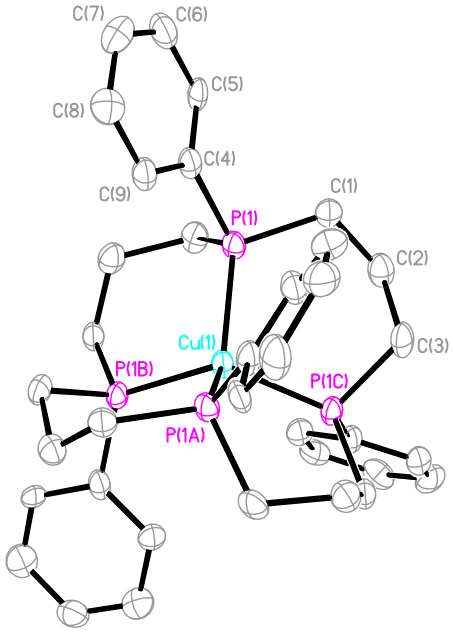


Figure 2. ORTEP drawing of the cation of **15** with thermal ellipsoids drawn at the 50% level. The H-atoms are omitted for clarity.

The ^{65}Cu NMR spectrum of complex **15** in DMSO-d_6 (with a Cl^- counterion in place of OTf^-) is shown in Figure 3. The spectrum shows a quintet centered at 293.8 ppm, consistent with coupling of the Cu center to four nearly equivalent P atoms. (Modeling the spectrum gave the following Cu-P coupling constants: $J^1_{Cu\text{-}P}$ = 824.4, 824.4, 821.8, and 821.8 Hz.)

View Article Online
DOI: 10.1039/C6DT00758A

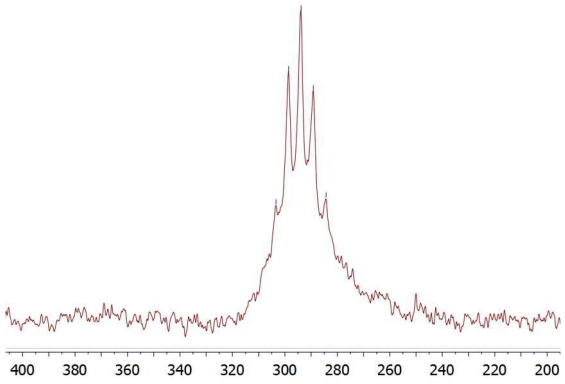


Figure 3. 600 MHz ^{65}Cu NMR spectrum of complex **15** in DMSO-d_6. The counterion is Cl^- rather than OTf^-.

Several experimental notes are of interest with regard to the preparation of complexes **12** - **17**. If KO^{t}Bu is used as the base instead of K_2CO_3, the reaction is much faster and is done within minutes instead of hours or days. The spectroscopic data of the products obtained from the experiments with KO^{t}Bu matched those obtained when K_2CO_3 was used as the base. Mass spectrometry showed that if a stoichiometric excess of the 1,3-dibromopropane or 1,4-dibromopropane is added or if the reaction is too concentrated, multiple alkylations are possible. For example, when complex **10** is alkylated with an excess of 1,3-dibromopropane or 1,4-dibromobutane, the ESI mass spectrum of the products showed the formation of a coordinated open-chain ligand with hanging propyl- or butyl-bromides (Figure 4; see the ESI for the ESI-MS). Precise control of the stoichiometry and dilute reaction solutions eliminated these side-products from forming, as indicated by mass spectrometry. Finally, it is noted that a potential problem with the synthetic route in Scheme 9 is the possibility of forming double-chelate products (Scheme 10). However, no example of this reactivity has ever been found,[11–13] and it was not observed in this study.

View Article Online
DOI: 10.1039/C6DT00758A

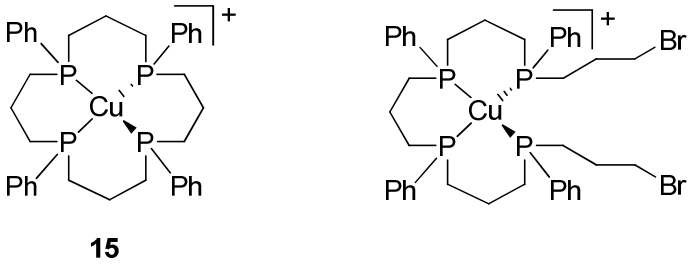
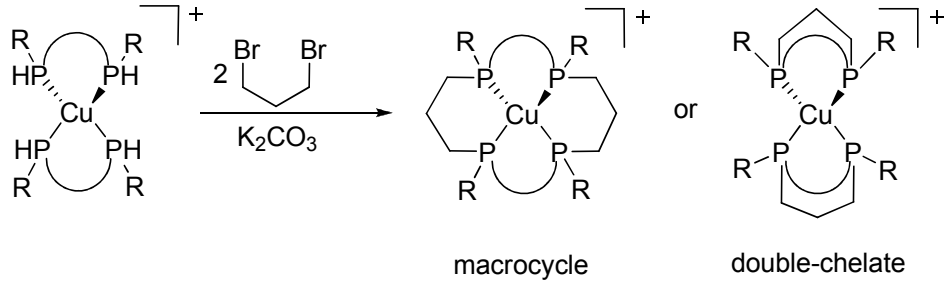


Figure 4. Products formed in the macrocyclization reaction of **10** with 1,3-dibromopropane. Double alkylation (shown on the right) is an observed side-product in ESI-MS.

Scheme 10. Possible side-reaction to form a double-chelate complex in the macrocyclization of a bis-bidentate secondary phosphine.

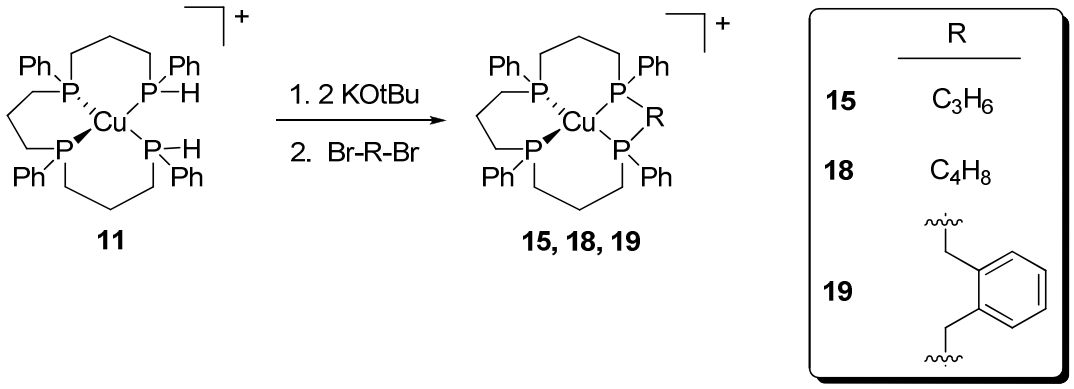


Macrocyclization of [Cu(4)]OTf (11). Complex **11** was converted to macrocyclic complexes using the general route devised above for the $Cu(P_2)_2^+$ complexes. Deprotonation of complex **11** with two equivalents of KOtBu in THF immediately gave a bright yellow solution, presumably the diphosphide species. Reaction of this species with 1,2-dibromoethane did not give a clean reaction. However, with either 1,3-dibromopropane, 1,4-dibromobutane, or *o*-dibromoxylene, the macrocyclic complexes **15, 18,** and **19**, respectively, were obtained (Scheme 11). All of the complexes were isolated as yellow powders that displayed broad peaks in the

View Article Online
DOI: 10.1039/C6DT00758A

region for coordinated tertiary phosphines in the $^{31}P\{^{1}H\}$ NMR spectra (Table 1), consistent with alkylation of the two secondary phosphines to give an all-tertiary phosphine product. Because no Cu-P coupling was observed in the ^{31}P NMR spectra, the complexes likely have a distorted tetrahedral geometry about Cu.[20–22,24–26] The identity of the products was confirmed by the disappearance of the P-H stretch in the IR spectrum (2314 cm^{-1}), the correct m/z value in the mass spectrum with the expected isotope patterns (see ESI and Experimental section), and by accurate elemental analyses (Table 1). Unfortunately, repeated attempts to grow X-ray quality crystals were unsuccessful, perhaps due to the lack of stereospecificity of the phosphine ligands.

Scheme 11. Macrocyclization of **11**.



11 **15, 18, 19**

Table 1. Characterization data for complexes **11** and **15, 18,** and **19**.

Compound	$^{31}P\{^{1}H\}$ NMR (ppm)	ESI-MS: m/z (expected)	Elemental Analysis Actual (Calc'd)		
			C	H	P
11	-15, -40	623 (623)	52.80 (52.82)	5.18 (5.21)	15.87 (16.02)

View Article Online
DOI: 10.1039/C6DT00758A

15	-14.7, -20.9	663 (663)	54.46 (54.60)	5.52 (5.45)	15.07 (15.23)
18	-18.4	677 (677)	54.89 (55.17)	5.60 (5.63)	14.60 (14.98)
19	-14, -21	725 (725)	57.65 (57.63)	5.22 (5.30)	14.27 (14.15)

As in the reactions of the $Cu(P_2)_2^+$ complexes, it is important to carefully control the stoichiometry of the macrocyclization reactions with **11**. For example, with a slight excess of 1,3-dibromopropane, ESI-MS showed that, in addition to the expected macrocyclic complex, a side-product resulting from alkylation by two separate molecules also formed, analogous to the over-alkylated product in Figure 4.

Demetallation reactions. In order to examine the conditions of Cu(I) removal, demetallation trials were first carried out with $[Cu(MPPE)_2]PF_6$ (**9**). Dissolving this complex in dichloromethane or toluene and stirring with a saturated aqueous KCN solution overnight or heating to 70 °C for 15 minutes yielded the free ligand in the organic layer, as indicated by ^{31}P NMR spectroscopy.[12,16] The same procedure was then carried out with complexes **15**, **18**, and **19** (Scheme 12). The products obtained after removal of the solvent were colorless, oily residues (**20**) or semi-solids (**21, 22**). Phosphines **20 - 22** displayed sharp peaks in their $^{31}P\{^1H\}$ NMR spectra (Table 2). These peaks, indicative of tertiary phosphines, are much sharper than those in complexes **15**, **18**, and **19**, indicating the absence of Cu coordination. In the ^1H NMR spectra, the aromatic protons of the phenyl rings give rise to a group of signals at 7.3 ppm and the aliphatic protons have broad signals from 1.2 to 2.1 ppm. In addition, the P-H signals present in ligand **4** were not in the ^1H NMR spectrum of **20 - 22**, a result consistent with full alkylation of the phosphines.

View Article Online
DOI: 10.1039/C6DT00758A

Scheme 12. Demetallation of complexes **15**, **18**, and **19** using KCN.

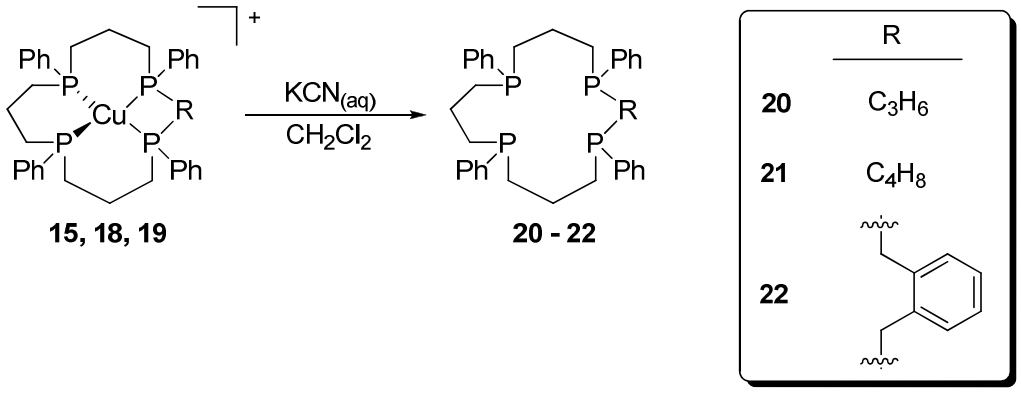


Table 2. NMR data for phosphines **20 - 22**.

Compound	$^{31}P\{^{1}H\}$ NMR (ppm)	Integrals from ^{1}H NMR: actual (expected)	
		Aromatic	**Aliphatic**
20	-26.8	20 (20)	23.7 (24)
21	-26.3, -27.3	20 (20)	27.4 (26)
22	-23.2, -26.7	24 (24)	25.3 (22)

It is interesting to note that a singlet is observed for phosphine **20**. Because the open-chain ligand precursor **4** can have many possible stereoisomers, a simple NMR spectrum of **20** is not necessarily expected. Four isomers are possible for the macrocyclic phosphine ligand (Figure 5), of which two isomers will have a singlet in the ^{31}P NMR spectrum (Figure 5, **A**, **D**). Curiously, other phosphine macrocycles, both coordinated and free, have been prepared where a singlet has been observed for isomers **B** and **C**.[27,11,12] (For this to occur, however, all the P resonances must be coincident with no P-P coupling.) Alternatively, the symmetric A_4 spin-

View Article Online
DOI: 10.1039/C6DT00758A

system could be a result of stereoselective inversion of the coordinated phosphide anions, formed as an intermediate in Scheme11, to yield a preferred geometry.[28,29 i ii]

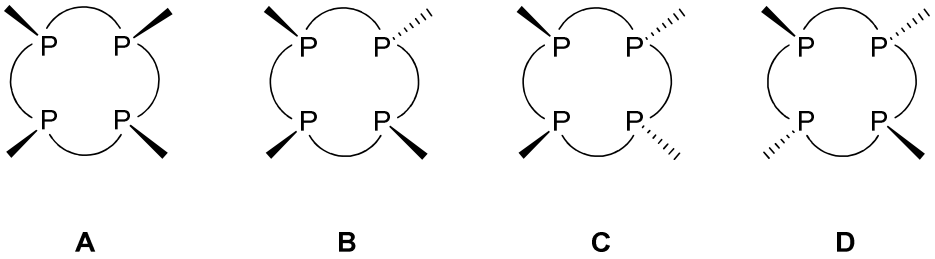


Figure 5. Possible stereoisomers of tetraphosphine **20**.

Because the exceptionally oily nature of **20** - **22** prevented their more detailed characterization, metal complexes containing the ligands were synthesized as a way to help confirm the identities of the ligands. The coordination complexes of **21** with Co(II) and Fe(II) are described in the following section.

The demetallations of macrocycle ligands derived from complexes **12** – **17** were carried out using the same procedure as described above for complexes **15**, **18**, and **19**, e.g., Scheme 13. The free ligands obtained in these reactions were also viscous liquids. Details are found in the Experimental section.

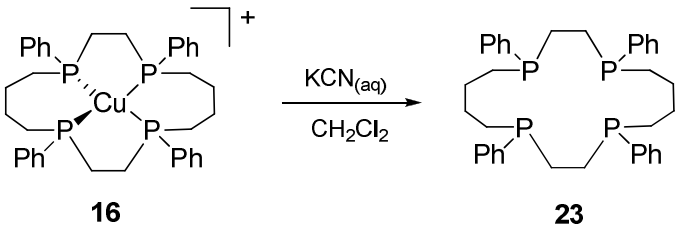
---

[i] Phosphine **21** displays two equally intense singlets at -25.6 ppm and -26.8 ppm. Two peaks are expected because there are two different phosphorus environments but the two peaks could also arise from two isomers of **21**. Because **21** is less symmetric than **20**, there are 7 possible diastereomeric pairs (two meso forms and five pair of enantiomers; see the ESI).

[ii] Phosphine **22** displayed sharp peaks in the expected region in the ^{31}P NMR spectrum, but the number of peaks indicated some degradation of the phosphine during demetallation.

View Article Online
DOI: 10.1039/C6DT00758A

Scheme 13. Demetallation of complex **16** using KCN.

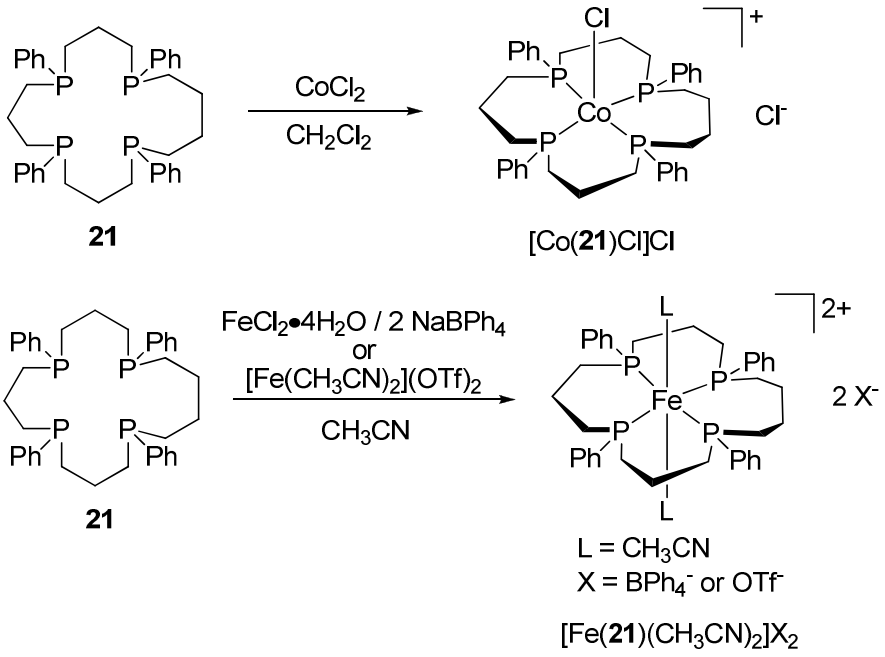


16 **23**

Coordination chemistry of ligands 21 and 23. Reaction of **21** with anhydrous $CoCl_2$ in CH_2Cl_2 gave an emerald green solution from which a green solid was isolated (Scheme 14). The product showed an *m/z* 708 in the ESI-MS, corresponding to the calculated value for [Co(**21**)Cl]$^+$, and the expected isotope pattern for this formula was also observed (see the ESI). The green product had broad NMR signals, consistent with a paramagnetic species, which is expected for a Co(II) complex. The complex has a μ_{eff} of 1.54 B.M., consistent with 1 unpaired electron[30] and also consistent with the magnetic moments found with other Co(II) tetraphosphorus complexes.[24–26,31] The electronic spectrum has two peaks in the visible region, similar in appearance to other five-coordinate $[Co(P)_4Cl]^+$-type complexes (P = a phosphine) (Table 3).[24,27,25,26,31–33] (It is also noted that similar five-coordinate complexes form when CoX_2 is reacted with phosphines. For example, 1,3-bis(dimethylphosphino)propane (dmpp) reacts with CoI_2 to form $[Co(dmpp)_2I]I$.[32]) Finally, the elemental analysis of the green powder gave a formula of [Co(**21**)]Cl_2•$4H_2O$, consistent with the proposed formula. (The elemental analysis is also consistent with the formula [Co(**21**)$_2$][$CoCl_4$], which has been found for selected phosphorus-containing macrocycle ligands.[27])

View Article Online
DOI: 10.1039/C6DT00758A

Scheme 14. Reactions of **21** with $CoCl_2$ and $FeCl_2 \cdot 4H_2O$.



View Article Online
DOI: 10.1039/C6DT00758A

Table 3. Electronic spectra of $[Co(P)_4Cl]X$-type complexes.

Complex	λ_{max} (ε)
[Co(**21**)Cl]Cl	611(397), 660(372)
[Co(**23**)Cl]Cl	589 (78), 681 (117)
$[Co(PPh(OEt)_2)_4Cl]BPh_4$[24]	588 (570), 630 (490)
$[Co(dmpp)_2Cl]BPh_4$[32]	610 (419), 690 (319)
$[Co(MC)_2][CoCl_4]$[27]	575 (240), 675 (400)
$[Co(dppp)_2Cl]Cl$[33]	600 (600), 680 (730)

QP = tris-(o-diphenylphosphinophenyl) phosphine

dmpp = 1,3-bis(dimethylphosphino)propane

MC = Macrocycles with two phosphorus atoms, acting as a bidentate ligand

Reaction of ligand **23** with anhydrous $CoCl_2$ in CH_2Cl_2 also gave an emerald green solution from which a solid green product, characterized as [Co(**23**)Cl]Cl, was isolated. The green product had broad ^1H NMR signals and a broad ^{31}P NMR signal, consistent with a paramagnetic species. The product showed a single peak in the ESI-MS at an *m/z* of 694 amu, in agreement with $[Co(\mathbf{23})Cl]^+$; the isotope pattern of the peak at 694 is also consistent with $[[Co(\mathbf{23})Cl]^+$ (see the ESI).

Reaction of **21** with simple FeX_2 salts did not yield any identifiable products. However, reaction of **21** with $FeCl_2 \bullet 4H_2O$ and two equivalents of $NaBPh_4$ in CH_3CN, gave an orange solid identified as $[Fe(\mathbf{21})(CH_3CN)_2](BPh_4)_2$ (Scheme 14). (The same product was also obtained using $[Fe(CH_3CN)_2](OTf)_2$ as the starting material.) The ESI-MS showed peaks at 670 and 335 *m/z*,

View Article Online
DOI: 10.1039/C6DT00758A

corresponding to $[m\text{-}2(BPh_4)]^+$ and $[m\text{-}2(BPh_4)]^{2+}$, respectively (see the ESI). Elemental analysis of the orange product indicated a formula of $[Fe(\mathbf{21})(CH_3CN)_2](BPh_4)_2 \cdot 2CH_3CN \cdot 3.5CH_2Cl_2$. Repeated attempts to remove the solvent molecules by prolonged heating *in vacuo* were unsuccessful.

The IR spectrum of the orange powder has weak C≡N stretches at 2251 and 2284 cm^{-1} (unbonded and bonded acetonitrile, respectively),[34] and a very strong stretch at 2091 cm^{-1}, which is tentatively assigned to ν(N≡N).[35,36] To check this assignment, the complex was prepared in an argon-filled glovebox. An IR spectrum (ATR method) of the resulting product showed a 64% reduction in the intensity of the stretch at 2091 cm^{-1} relative to other peaks in the spectrum. When the complex was exposed again to N_2 for three minutes in $CDCl_3$ solution, there was a 12% increase in the intensity of the 2091 cm^{-1} band (relative to the other bands in the spectrum, which were assumed not to change in intensity). These preliminary experiments suggest that the complex binds N_2 strongly enough to displace an acetonitrile ligand.

Computational Results. To gain better insights into the relative stabilities of the four stereoisomers depicted in Figure 5, the four stereoisomers of complex **15** were optimized and their single-point energies computed by DFT (B3LYP/6-31G(d)) in Gaussian 09.[37] The calculated energies (Table 4) indicate that the most stable isomer has an *anti-syn-anti* conformation (structure D in Figure 5). Note this structure is the one obtained in the X-ray crystal structure of complex **15**. The higher energies of the other stereoisomers appear to come from distortions in the Cu(I) coordination geometries. For example, isomer C has a nearly square planar geometry around the Cu center. The complete computational results will be presented in a subsequent paper.

View Article Online
DOI: 10.1039/C6DT00758A

Table 4. Relative energies of the four stereoisomers depicted in Figure 5.

Geometry	ΔE (kJ/mol)
A	61.2
B	7.9
C	93.9
D	0

Key points and conclusions. Two methods were investigated for the preparation of tetradentate phosphine ligands. The first method is shown in Scheme 9 and involves the coupling of two bidentate secondary phosphines bonded to Cu(I). The second method is shown in Scheme 11 and involves the coupling of secondary phosphorus atoms in a linear tetradentate phosphine, again bonded to Cu(I). The Cu(I) ion was chosen as the template because prior work showed that it was generally difficult, if not impossible, to remove Pd(II) and Pt(II) templates without also degrading the macrocycle ligand. This study showed that Cu(I) can be straightforwardly removed by stirring with KCN. Fe(II) would be the perfect template ion for these reactions because then it would not be necessary to remove the template and replace it with Fe(II) for use in the pressure-swing process (Scheme 1). However, our prior work showed that Fe(II) is not a satisfactory template for the synthesis of macrocycles via Schemes 9 and 11.[17]

The macrocycle ligands isolated in this study (**20** - **23**) were viscous oils. Characterization by X-ray crystallography was, therefore, not possible. However, the Co and Fe complexes of these ligands were powders in some cases, and this trait permitted the characterization of the complexes.

View Article Online
DOI: 10.1039/C6DT00758A

The pressure-swing nitrogen separation process outlined in Scheme 1 uses N_2-binding Fe complexes that are water-soluble by virtue of having water-soluble phosphine ligands. The bidentate phosphine ligand DMeOPrPE (containing $-(CH_2)_3OCH_3$ groups; Figure 1) is water soluble, and we expected macrocycle ligands with this R group to also be soluble. Unfortunately, neither the macrocycles with this R group nor their complexes are water-soluble so new phosphines are currently being synthesized with alternative water-solubilizing R groups. Note that conventional water-solubilizing groups such as $-SO_3^-$ and –OH are not viable because our prior work showed that these groups can coordinate to metal centers and block N_2 binding.[7] As noted above, preliminary work shows that the Fe(**21**)$(CH_3CN)_2^{2+}$ complex binds N_2, and work is continuing on this reaction and its use in a pressure-swing natural gas purification scheme.

EXPERIMENTAL SECTION

Materials and Reagents. Unless otherwise noted, all experimental procedures were performed under an N_2 atmosphere using standard Schlenk and glovebox techniques. Commercially available reagents were used as received. HPLC-grade THF was dried and deoxygenated by passing it through commercial columns of CuO then alumina under an argon atmosphere. Deuterated solvents were obtained from Cambridge Isotope Laboratories and degassed using three freeze-pump-thaw cycles. $[Fe(CH_3CN)_2](OTf)_2$,[38] and **14**[15] were synthesized according to literature methods. $[Cu(CH_3CN)_4]OTf$ was prepared from a modified procedure.[39] Ligands **1** and **2** were prepared as previously described.[17] The ligands MPPP[40] and **4**[18] were synthesized according to literature methods.

Instrumentation. Air-sensitive NMR samples were sealed in N_2-filled J-Young tubes. NMR spectra were obtained on either a Varian Unity/Inova 300 spectrometer at an operating

View Article Online
DOI: 10.1039/C6DT00758A

frequency of 299.94 MHz (^{1}H) or 121.42 MHz (^{31}P), a Varian Unity/Inova 500 spectrometer operating at a frequency of 500.62 MHz (^{1}H) or 202.45 MHz (^{31}P), or a Bruker 600 spectrometer at an operating frequency of 600.15 MHz (^{1}H), 242.94 MHz (^{31}P), or 170.46 MHz (^{65}Cu). The ^{1}H and ^{13}C NMR spectra were referenced to residual solvent peaks, and the ^{31}P NMR spectra were referenced to external 1% H_3PO_4 in D_2O. ESI mass spectra were obtained using a Thermo Finnigan LCQ Deca XP Plus ESI Mass Spectrometer using THF or CH_3CN as the solvent. Infrared spectra were recorded using a Thermo-Scientific Nicolet 6700 FT-IR spectrometer. UV-vis spectra were collected on an Agilent 8453 spectrophotometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

X-ray Crystallography. Diffraction intensities for complex **15** were collected at 150 K on a Bruker Apex2 CCD diffractometer using MoKα radiation, λ= 0.71073 Å. The space group was determined based on systematic absences. Absorption corrections were applied by SADABS.[41] The structures was solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. All H atoms were refined in calculated positions in a rigid group model. The anion $CF_3SO_3^-$ in the structure is highly disordered and was treated by SQUEEZE.[42] Corrections of the X-ray data by SQUEEZE (146 electron/cell) is close to the required value of 134 electron/cell for two $CF_3SO_3^-$ anions in the full unit cell. Diffraction data were collected up to $2\theta_{max}$ = 56.0°, but only data up to $2\theta_{max}$ = 50.0° have been used in the final refinement. Diffraction intensities at high angles were weak and as a result there is a relatively high peak, 2.147 eÅ^{-3}, on the residual density. The structure was refined as a racemic twin. The Flack parameter, 0.48(7), is close to 0.5, indicating a possible centro-symmetrical space group, but we think that the crystal is a racemic twin consisting of two domains with opposite configuration of the Cu-cations. All calculations were performed by the Bruker SHELXL-2013 package.[43]

View Article Online
DOI: 10.1039/C6DT00758A

Synthesis of isopropyl allyl(phenyl)phosphinate. Allyl bromide (6.01 g, 49.7 mmol, 2.40 eq.) was added to a 50 mL Schlenk flask containing diisopropyl phenylphosphonite (5.02 g, 20.7 mmol, 1.00 eq) and the mixture was heated to 70 °C for 12 hr. After heating, the product was distilled under reduced pressure (85-90 °C @ 250 mTorr) to yield a clear oil. Yield: 4.91 g (96.7 %). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -38.8 (s). ^{1}H NMR ($CDCl_3$): δ 7.77 (m, 2H), 7.47 (m, 3H), 5.72 (dddt, J_{HH} = 17.4, 10.6, 7.5 Hz, J_{PH} = 5.7 Hz, -CH_2CH=CH_2, 1H), 5.06 (m, 2H), 4.61 (d of sept, J_{HH} = 6.2 Hz, J_{PH} = 8.6 Hz, -$CH(CH_3)_2$, 1H), 2.73 (dd, J_{HH} = 7.5 Hz, J_{PH} = 18.4 Hz, -CH_2CH=CH_2, 2H), 1.36 (dd, J_{HH} = 6.2 Hz, -$CH(CH_3)_2$, 3H), 1.19 (dd, J_{HH} = 6.2 Hz, -$CH(CH_3)_2$, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 132.2, 131.9, 128.4, 127.5, 120.3, 69.9, 36.6 (d, J_{PC} = 97 Hz), 24.6, 24.1.

$[Cu(MeOPrPE)_2]PF_6$ (7). A CH_3CN solution of **1** (0.019 g, 0.080 mmol) was added to $Cu(CH_3CN)_4PF_6$ (0.015 g, 0.040 mmol). The reaction mixture was stirred for 1 hour at room temperature after which the solvent was removed under reduced pressure. Yield: 0.025 g (93.0%) of an off-white viscous oil. ^{31}P NMR (THF): δ -41 (br, $\Delta\nu_{1/2}$ (linewidth at half maximum) = 2350 Hz). ESI-MS: 539 amu (m^+). Anal. Calcd for $C_{20}H_{48}F_6CuO_4P_5$: C, 35.07; H, 7.06; P, 22.61. Found: C, 34.98; H, 7.13; P, 22.49.

$[Cu(MeOPrPP)_2]OTf$ (8). A CH_3CN solution of **2** (0.0698 g, 0.277 mmol, 1.92 equiv) was added to a CH_3CN solution of $Cu(CH_3CN)_4OTf$ (0.0542 g, 0.144 mmol, 1 equiv) and stirred for 1 hour. The solvent was removed under reduced pressure to yield an off-white viscous oil. ^{31}P NMR (THF): δ -50.5 (br). ESI-MS: 567 amu (m+). Anal. Calcd for $C_{23}H_{52}F_3CuO_7P_4S$: C, 38.52; H, 7.31; P, 17.28. Found: C, 38.46; H, 7.28; P, 17.04. The complex was also synthesized as the PF_6^- salt: ^{31}P NMR (THF): δ -30.5 (br, $\Delta\nu_{1/2}$ = 2150 Hz).

$[Cu(MPPE)_2]PF_6$ (9). This complex was prepared in a manner similar to **7** using MPPE (0.0211 g, 0.0860 mmol) and $Cu(CH_3CN)_4PF_6$ (0.0170 g, 0.0460 mmol). Yield: 0.281 g (97.3 %) of a

View Article Online
DOI: 10.1039/C6DT00758A

white granular solid. ^{31}P NMR (THF): δ -31 (br, $\Delta\nu_{1/2}$ = 2140 Hz). ESI-MS: 555 amu (m^+). Anal. Calcd for $C_{28}H_{32}CuF_6P_5$: C, 47.98; H, 4.60; P, 22.09. Found: C, 47.95; H, 4.67; P, 22.01. The analogous triflate complex was also prepared, using $Cu(CH_3CN)_4OTf$ instead of $Cu(CH_3CN)_4PF_6$. The spectroscopic data were identical.

[Cu(MPPP)$_2$]OTf (10). This complex was prepared in a manner similar to **8**, using MPPP (0.383 g, 1.47 mmol) and $Cu(CH_3CN)_4OTf$ (0.278 g, 0.740 mmol). Yield: 0.5177 g (95.9%) of a white granular solid. ^{31}P NMR (THF): δ -43 (br, $\Delta\nu_{1/2}$ = 2220 Hz). ESI-MS: 583 amu (m+). Anal. Calcd for $C_{31}H_{36}F_3CuO_3P_4S$: C, 50.79; H, 4.95; P, 16.90. Found: C, 50.76; H, 4.81; P, 16.77.

General method for macrocyclization with K_2CO_3. $Cu(P_2)_2X$ (X = OTf or PF_6) was dissolved in THF and excess K_2CO_3 was added in one portion. The solution immediately turned bright yellow and was stirred at room temperature for 10 minutes. The desired dihalide (two equivalents) was diluted with THF and then added dropwise. The reaction mixture was stirred overnight, during which time the reaction became lighter yellow with a white precipitate. The reaction was filtered over celite and the solvent removed in vacuo. The remaining yellow residue was redissolved in dichloromethane and filtered again over celite. Removal of the solvent yielded the product as a yellow powder.

Synthesis of 12. This complex was prepared following the general method above, using $[Cu(MeOPrPE)_2]PF_6$ (0.155 g, 0.227 mmol) and 1,3-dibromopropane (0.990 g, 0.490 mmol). Yield: 0.973 g (56 %) ^{31}P{^{1}H} NMR ($CDCl_3$): δ -2 ppm (br, $\Delta\nu_{1/2}$ = 2150 Hz). ESI-MS: 619 amu (m+).

Synthesis of 13. This complex was prepared following the general method above, using $[Cu(MeOPrPP)_2]PF_6$ (0.251 g, 0.352 mmol) and 1,3-dibromopropane (0.149 g, 0.738 mmol). Yield: 0.1661 g (56 %). ESI-MS: 647 amu (m+).

View Article Online
DOI: 10.1039/C6DT00758A

Synthesis of 15. This complex was prepared following the general method above, using $[Cu(MPPP)_2]OTf$ (0.301 g, 0.334 mmol) and 1,3-dibromopropane (0.139 g, 0.688 mmol). Yield: 0.214 g (65 %) $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -15 (br, $\Delta\nu_{1/2}$ = 2550 Hz), -21(br, $\Delta\nu_{1/2}$ = 2340 Hz) ppm. ESI-MS: 663 amu (m+).

Synthesis of 16. This complex was prepared following the general method above, using $[Cu(MPPE)_2]OTf$ (0.304 g, 0.432 mmol) and 1,4-dibromobutane (0.104 mL, 0.871 mmol). Yield: 0.275 g (95.8 %) $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 6 (br, $\Delta\nu_{1/2}$ = 2450 Hz). ESI-MS: 663 amu (m+). Anal. Calcd for $C_{37}H_{44}CuF_3O_3P_4S$: C, 54.6; H, 5.45. Found: C, 48.86; H, 4.92. This rather poor elemental analysis is likely due to residual KBr left over from the reaction. Anal. Calcd for $C_{37}H_{44}CuF_3O_3P_4S$•0.8 KBr: C, 48.92; H, 4.88.

General method for macrocyclization with KO^{t}Bu. $Cu(P_2)_2X$ (X = OTf or PF_6) was dissolved in THF and 4 equivalents of KO^{t}Bu were added in one portion. The solution immediately turned bright yellow and was stirred at room temperature for 10 minutes. The desired dihalide (two equivalents) was diluted in THF and added dropwise. The reaction mixture was stirred and became cloudy and lighter yellow after a few minutes. The reaction was stirred for at least four hours. The reaction was filtered over celite and the solvent removed in vacuo. The remaining yellow residue was redissolved in dichloromethane and filtered again over celite. Removal of the solvent yielded the product as a yellow powder.

Synthesis of 17. This complex was prepared following the general method above with KO^{t}Bu, using $[Cu(MPPP)_2]OTf$ (0.0535 g, 0.0730 mmol), KO^{t}Bu (0.0319 g, 0.284 mmol) and 1,4-dibromobutane (0.0160 mL, 0.134 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -13 (br, $\Delta\nu_{1/2}$ = 2800 Hz), -45 (br, $\Delta\nu_{1/2}$ = 3050 Hz). ESI-MS: 691 amu (m+). This complex can also be prepared using the general route using K_2CO_3. The spectroscopic evidence is identical.

View Article Online
DOI: 10.1039/C6DT00758A

General procedure for demetallation. In a typical procedure, the Cu-macrocyclic phosphine complex was dissolved in CH_2Cl_2 (3-5 mL) and stirred vigorously at room temperature with a saturated aqueous solution of KCN (2 mL) overnight. The aqueous layer was removed and the organic layer was dried over $MgSO_4$ and filtered through a plug of alumina. The solvent was removed *in vacuo* to yield a waxy residue that was taken on directly to prepare metal complexes or used as a CH_2Cl_2 solution directly.

Ligand 23. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -20.4 ppm (s). ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.03 (m, 20H), 2.77 – 0.84 (m, 29H). HR FAB-MS: 601 amu $[m+H]^+$.

Synthesis of Co(23)Cl_2. A solution of ligand **24** in THF was added to a suspension of $CoCl_2$ in THF. The solution immediately turned emerald green upon addition of the ligand to the metal. Removal of the solvent yielded a green powder. ^{31}P NMR (202 MHz, $CDCl_3$) δ 9 – -33 (m). ESI-MS: 694 amu $[m-Cl]^+$. UV-vis (CH_3CN, nm): 681, 589.

Synthesis of [Cu(4)]OTf (11). Ligand **4** (0.202 g, 0.360 mmol, 1 equiv) was dissolved in CH_3CN and added dropwise to a stirred solution of $[Cu(CH_3CN)_4]OTf$ (0.137 g, 0.364 mmol, 1.01 equiv) in CH_3CN. The solution was stirred for 20 minutes at room temperature and the solvent removed *in vacuo* to yield a waxy white solid. The solid was triturated with ether to yield an off-white powder. Yield: 0.2750 g (98.7%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -15 (br, $\Delta\nu_{1/2}$ = 2630 Hz), -40 (br, $\Delta\nu_{1/2}$ = 2420 Hz). ESI-MS: 623 amu (m+). Anal. Calcd for $C_{34}H_{40}CuF_3O_3P_4S$: C, 52.82; H, 5.21; P, 16.02. Found: C, 52.80; H, 5.18; P, 15.57.

General Method for Macrocyclization of 11. A THF solution of KO^{t}Bu was added dropwise to **11** dissolved in THF and the solution turned a bright yellow color. After stirring for 15 minutes, a THF solution of the corresponding α-ω dihalide was added dropwise. The yellow color faded to a dull yellow color with KBr precipitate. The solution was filtered through a 0.25 micron

View Article Online
DOI: 10.1039/C6DT00758A

syringe filter or a celite plug and the solvent removed. The yellow residue was redissolved in CH_2Cl_2 and filtered again. Removal of the solvent yielded a waxy yellow solid that was triturated with ether to yield a yellow powder.

Synthesis of 15 from 11. (0.602 g, 0.778 mmol, 1.00 equiv); KO^{t}Bu: (0.187 g, 1.67 mmol, 2.14 equiv); 1,3-dibromoproane: (0.157 g, 0.778 mmol, 1.00 equiv) Yield: 0.328 g (51.8%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.7 (br, $\Delta\nu_{1/2}$ = 2550 Hz), -20.9 (br, $\Delta\nu_{1/2}$ = 2430 Hz). ESI-MS: 663 amu ([m-OTf]$^+$). Anal. Calcd for $C_{37}H_{44}CuF_3O_3P_4S$: C, 54.64; H, 5.45; P, 15.23. Found: C, 54.46; H, 5.52; P, 15.07.

Synthesis of 18. (0.0583 g, 0.0750 mmol, 1 equiv); KO^{t}Bu: (0.0169 g, 0.151 mmol, 2.01 equiv); 1,4-dibromobutane (0.0164 g, 0.0760 mmol, 1.01 equiv) Yield: 0.0489 g (78.4%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -18.4 (br, $\Delta\nu_{1/2}$ = 3490 Hz). ESI-MS: 677 amu (m+). Anal. Calcd for $C_{38}H_{46}CuF_3O_3P_4S$: C, 55.17; H, 5.60; P, 14.98. Found: C, 54.89; H, 5.63; P, 14.60.

Synthesis of 19. (0.033 g, 0.043 mmol, 1.0 equiv); KO^{t}Bu (0.011 g, 0.099 mmol, 2.3 equiv); *o*-dibromoxylene (0.011 g, 0.043 mmol, 1.0 equiv) Yield: 0.016 g (41.8 %). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14 (br, $\Delta\nu_{1/2}$ = 2350 Hz) and -21(br, $\Delta\nu_{1/2}$ = 2350 Hz). ESI-MS: 725 amu (m+). Anal. Calcd for $C_{42}H_{46}CuF_3O_3P_4S$: C, 57.63; H, 5.30; P, 14.15. Found: C, 57.65; H, 5.22; P, 14.27.

Synthesis of 20-22 (described for 21). In a typical procedure, complex **18** was dissolved in CH_2Cl_2 (3-5 mL) and stirred vigorously at room temperature with an aqueous solution of KCN (2 mL) overnight. The aqueous layer was removed and the organic layer was dried over $MgSO_4$ and filtered through a plug of alumina. The solvent was removed *in vacuo* to yield a waxy solid or residue that was taken on directly to prepare metal complexes or used as a CH_2Cl_2 solution directly.

20: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -26.8 (s). ^1H NMR ($CDCl_3$): δ 1.07-2.53 (m, 24H), 6.78-8.05 (m, 20H, aromatic).

View Article Online
DOI: 10.1039/C6DT00758A

21: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -26.3 (s), -27.3 (s). ^{1}H NMR ($CDCl_3$): δ 1.5-2.3 (m, 26H), 7.2-7.6 (m, 20H, aromatic).

22: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -23.2 (s), -26.7 (s). ^{1}H NMR ($CDCl_3$): δ 1.5-2.3 (m, 22H), 7.2-7.6 (m, 24H, aromatic).

Synthesis of $[Fe(21)(CH_3CN)_2](BPh_4)_2$. To a suspension of $FeCl_2{\cdot}4H_2O$ (0.0013 g, 0.0070 mmol, 1.0 equiv) and $NaBPh_4$ (0.0045 g, 0.013 mmol, 1.9 equiv.) in CH_3CN was added **21** as a CH_2Cl_2 solution (0.0040 g, 0.0070 mmol, 1.0 equiv.). The solution immediately turned light orange and was then stirred for 1 h; the solution was filtered through celite and the solvent was then removed *in vacuo*. The orange residue was washed with ether to yield an orange powder. ESI-MS: 670 $[m\text{-}2(BPh_4)]^{+}$, 335 $[m\text{-}2(BPh_4)]^{2+}$. Anal. Calcd for $C_{89}H_{94}FeB_2P_4N_2$: C, 76.84; H, 6.67; N, 2.01; P, 8.91. Found: C, 65.60; H, 6.07; N, 3.40; P, 6.86. (with 2.4 CH_3CN and 3.4 CH_2Cl_2 as solvents of crystallization, Calcd: C, 65.57; H, 6.11; N, 3.46; P, 6.96.)

Synthesis of $[Co(21)]Cl_2{\cdot}4\ H_2O$. To a suspension of $CoCl_2$ (0.0211 g, 0.162 mmol) in CH_2Cl_2 was added **21** (0.103 mmol) in CH_2Cl_2. The solution turned from a bright blue suspension to an emerald green solution. The reaction mixture was filtered and the solvent removed *in vacuo*. The resulting residue was washed with ether to yield a dark green powder. Yield: 0.0595 g (77.3%). ESI-MS: 708 $[m\text{-}Cl]^{+}$ Anal. Calcd. for $C_{37}H_{46}CoP_4Cl_2$: C, 59.67; H, 6.23. Found: C, 54.39; H, 6.83. (with four water of hydration, Calcd: C, 54.42; H, 6.67). UV-vis (CH_2Cl_2): 611, 660 nm. μ_{eff} = 1.57 B.M.

Acknowledgment

Acknowledgment is made to the National Science Foundation (CHE-0809393) for the support of this research.

View Article Online
DOI: 10.1039/C6DT00758A

†Electronic supplementary information available: ^{1}H, ^{31}P, and ^{13}C NMR spectra for the phosphines and metal complexes reported herein, mass spectra and selected isotope patterns for complexes **7-23**; and crystallographic data for **15**.

References

1. A. Finn, *Hydrocarbon Eng.*, 2007, **12**, 49–52.

2. M. Mitariten, *Hydrocarbon Eng.*, 2004, **9**, 53–57.

3. A. J. Kidnay and W. R. Parrish, *Fundamentals of Natural Gas Processing*, CRC Press, Boca Raton, 2010.

4. R. H. Hugman, E. H. Vidas, and P. S. Springer, *Chemical composition of discovered and undiscovered natural gas in the lower-48 United States. Project summary.*, Energy and Environ. Anal., Inc., 1990.

5. K. A. Lokhandwala, I. Pinnau, Z. He, K. D. Amo, A. R. DaCosta, J. G. Wijmans, and R. W. Baker, *J. Membr. Sci.*, 2010, **346**, 270–279.

6. C. C. H. Lin, J. A. Sawada, L. Wu, T. Haastrup, and S. M. Kuznicki, *J. Am. Chem. Soc.*, 2009, **131**, 609–614.

7. W. K. Miller, J. D. Gilbertson, C. Leiva-Paredes, P. R. Bernatis, T. J. R. Weakley, D. K. Lyon, and D. R. Tyler, *Inorg. Chem.*, 2002, **41**, 5453–5465.

View Article Online
DOI: 10.1039/C6DT00758A

8. J. D. Gilbertson, N. K. Szymczak, J. L. Crossland, W. K. Miller, D. K. Lyon, B. M. Foxman, J. Davis, and D. R. Tyler, *Inorg. Chem.*, 2007, **46**, 1205–1214.

9. G. Melson, *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press, New York, 1979.

10. C. D. Swor and D. R. Tyler, *Coord. Chem. Rev.*, 2011, **255**, 2860–2881.

11. T. Mizuta, A. Okano, T. Sasaki, and H. Nakazawa, *Inorg. Chem.*, 1997, **36**, 200–203.

12. D. J. Brauer, F. Gol, S. Hietkamp, H. Peters, H. Sommer, O. Stelzer, and W. S. Sheldrick, *Chem. Ber.*, 1986, **119**, 349–365.

13. R. Bartsch, S. Hietkamp, S. Morton, H. Peters, and O. Stelzer, *Inorg. Chem.*, 1983, **22**, 3624–3632.

14. T. A. DelDonno and W. Rosen, *J. Am. Chem. Soc.*, 1977, **99**, 8051–8052.

15. B. Lambert and J. F. Desreux, *Synthesis*, 2000, **2000**, 1668–1670.

16. Y. B. Kang, M. Pabel, D. D. Pathak, A. C. Willis, and S. B. Wild, *Main Group Chem.*, 1995, **1**, 89–98.

17. B. P. Nell, C. D. Swor, L. N. Zakharov, and D. R. Tyler, *J. Inorg. Organomet. Polym. Mater.*, 2015, **25**, 495–506.

18. M. Baacke, O. Stelzer, and V. Wray, *Chem. Ber.*, 1980, **113**, 1356–1369.

19. J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, 1963, **41**, 3063–3069.

20. A. Marker and M. J. Gunter, *J. Magn. Reson.*, 1982, **47**, 118–132.

21. S. J. Berners-Price, C. Brevard, A. Pagelot, and P. J. Sadler, *Inorg. Chem.*, 1986, **25**, 596–599.

View Article Online
DOI: 10.1039/C6DT00758A

22. S. J. Berners-Price, R. K. Johnson, C. K. Mirabelli, L. F. Faucette, F. L. McCabe, and P. J. Sadler, *Inorg. Chem.*, 1987, **26**, 3383–3387.

23. B. Mohr, E. E. Brooks, N. Rath, and E. Deutsch, *Inorg. Chem.*, 1991, **30**, 4541–4545.

24. A. Bertacco, U. Mazzi, and A. A. Orio, *Inorg. Chem.*, 1972, **11**, 2547–2549.

25. J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *J. Am. Chem. Soc.*, 1972, **94**, 6194–6196.

26. M. Bressan and P. Rigo, *Inorg. Chem.*, 1975, **14**, 38–42.

27. E. P. Kyba, D. C. Alexander, and A. Hoehn, *Organometallics*, 1982, **1**, 1619–1623.

28. G. T. Crisp, G. Salem, S. B. Wild, and F. S. Stephens, *Organometallics*, 1989, **8**, 2360–7.

29. W. E. Buhro and J. A. Gladysz, *Inorg. Chem.*, 1985, **24**, 3505–7.

30. G. S. Girolami, T. B. Rauchfuss, and R. J. Angelici, *Synthesis and Technique in Inorganic Chemistry: A Laboratory Manual*, University Science Books, Sausalito, California, 1999.

31. M. Bacci, S. Midollini, P. Stoppioni, and L. Sacconi, *Inorg. Chem.*, 1973, **12**, 1801–1805.

32. J. C. Cloyd Jr. and D. W. Meek, *Inorg. Chim. Acta*, 1972, **6**, 480–486.

33. W. D. Horrocks, G. R. Van Hecke, and D. D. Hall, *Inorg. Chem.*, 1967, **6**, 694–699.

34. B. N. Storhoff and H. C. Lewis Jr., *Coord. Chem. Rev.*, 1977, **23**, 1–29.

35. J. L. Crossland, D. M. Young, L. N. Zakharov, and D. R. Tyler, *Dalton Trans.*, 2009, 9253–9259.

36. F. Studt and F. Tuczek, *J. Comput. Chem.*, 2006, **27**, 1278–1291.

37. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato,

View Article Online
DOI: 10.1039/C6DT00758A

X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

38. K. S. Hagen, *Inorg. Chem.*, 2000, **39**, 5867–5869.

39. G. J. Kubas, B. Monzyk, and A. L. Crumbliss, in *onlinelibrary.wiley.com*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 1979, pp. 90–92.

40. J. Dogan, J. B. Schulte, G. F. Swiegers, and S. B. Wild, *J. Org. Chem.*, 2000, **65**, 951–957.

41. G. M. Sheldrick, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI, 1998.

42. P. Van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **A46**, 194–201.

43. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.