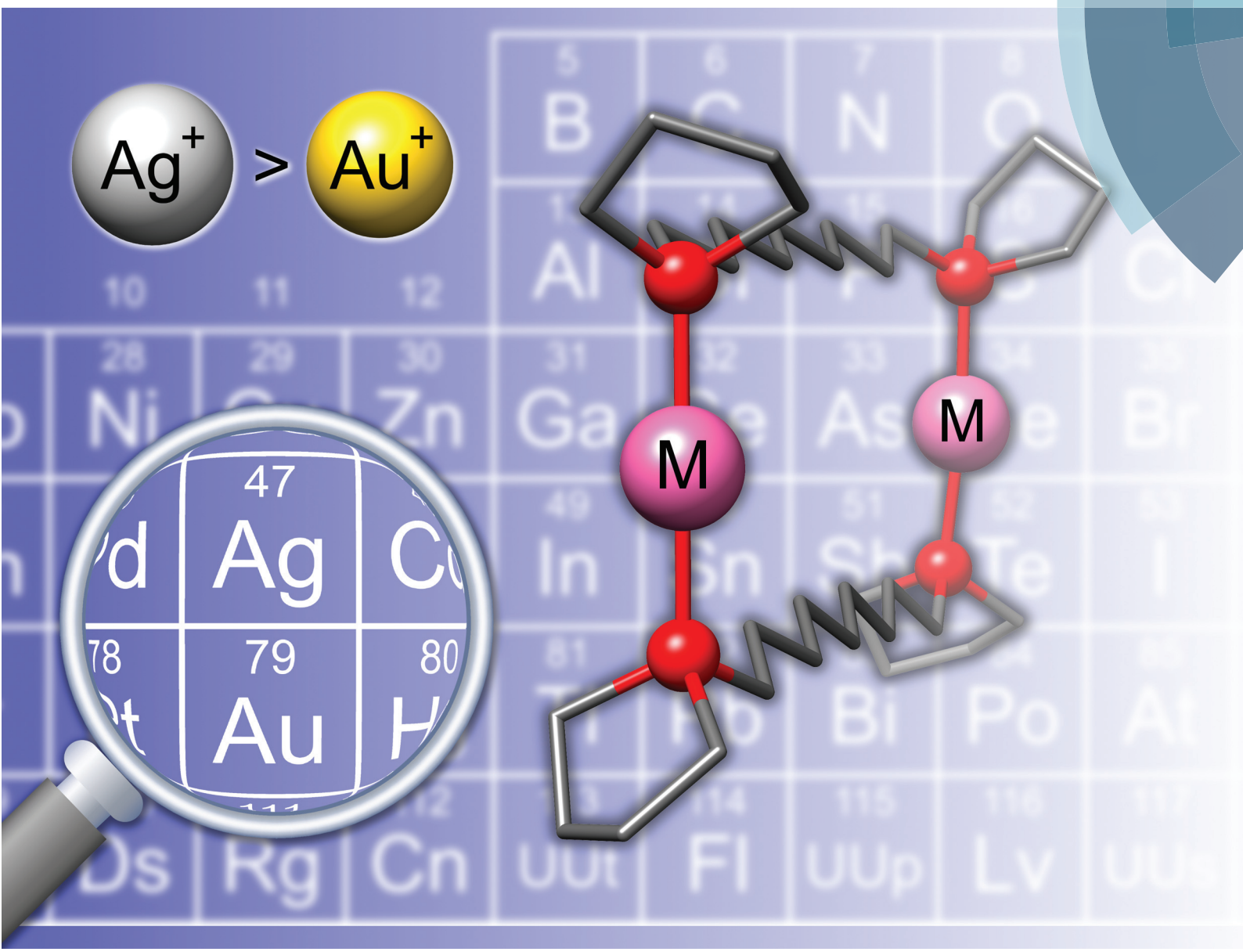
Volume 45 | Number 29 | 7 August 2016 | Pages 11583–11912

Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton



ISSN 1477-9226

ROYAL SOCIETY OF CHEMISTRY

PAPER

Evamarie Hey-Hawkins *et al.*

Selective formation of silver(I) bis-phospholane macrocycles and further evidence that gold(I) is smaller than silver(I)

175 YEARS

Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2016, **45**, 11644

Selective formation of silver(I) bis-phospholane macrocycles and further evidence that gold(I) is smaller than silver(I)†

Markus Streitberger, Andy Schmied, Reinhard Hoy and Evamarie Hey-Hawkins*

Received 9th March 2016,
Accepted 18th May 2016

DOI: 10.1039/c6dt00945j

www.rsc.org/dalton

A new synthetic approach to highly flexible bis-phospholanes from 1-benzylphospholane (**1**) as starting material is described. Silver(I) macrocycles containing 16 ($[Ag_2(\mu\text{-}\mathbf{3a})_2](BF_4)_2$, **4**), 20 ($[Ag_2(\mu\text{-}\mathbf{3b})_2](BF_4)_2$, **5**), 24 ($[Ag_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$, **6**), and 28 ($[Ag_2(\mu\text{-}\mathbf{3d})_2](BF_4)_2$, **7**) atoms in the ring were obtained in one step from $AgBF_4$ and the respective bis-phospholane $(C_4H_8P)(CH_2)_n(PC_4H_8)$ (n = 5, 7, 9, 11; **3a–d**) in excellent yields. Comparison of **6** with the previously reported isomorphous complex $[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$ gave further evidence that gold(I) is significantly smaller than silver(I). All complexes were fully characterized by NMR and IR spectroscopy, mass spectrometry, and X-ray diffraction.

Introduction

Bis-phosphines of the general type $R_2PCH_2PR_2$ (R = Ph, Me) are well known to form macrocyclic dinuclear complexes with silver(I).[1] Due to the higher stability of five- or six-membered chelate rings, bis-phosphines $R_2P(CH_2)_nPR_2$ with n = 2 or 3 form mononuclear complexes as well.[2] The coordination chemistry of bis-phosphines with larger flexible methylene spacers has been highly neglected so far. Effendy *et al.* reported a series of silver(I) complexes of $Ph_2P(CH_2)_nPPh_2$ (n = 3–6).[3] In this case, ring formation was supported by additional silver(I)–anion coordination. Dinuclear silver(I) macrocycles with bridging $Ph_2P(CH_2)_nPPh_2$ ligands are known, for example, with $AgNO_3$ for n = 3 and 4,[4] AgCl for n = 5,[5] and $AgBF_4$ with n = 3.[6] Crabtree *et al.* reported the unexpected formation of $[Ag_2\{\mu\text{-}tBu_2P(CH_2)_3PtBu_2\}_2](BF_4)_2$ as a byproduct when employing $AgBF_4$ for eliminating chlorido ligands from rhodium complexes.[7] While gold(I) complexes of highly flexible bis-phosphines with an even number of carbon atoms in the methylene spacer seem to favor polymerization,[8] the affinity of silver(I) for coordination numbers three and four enables the formation of macrocycles with 1,6-bis(diphenylphosphino) hexane and bridging perchlorate anions as well.[9] The opposite trend of greater influence of the methylene spacer was reported by Puddephatt *et al.* They combined $Ph_2P(CH_2)_nPPh_2$ (n = 1–6) with *trans*-1,2-bis(4-pyridyl)ethylene and silver(I) trifluoroacetate and obtained macrocycles for n = 1 and 5 and a one-dimensional polymeric structure for n = 6.[10] Recently, we reported the coordination behavior of highly flexible bis-phospholanes with solely aliphatic backbone towards gold(I) ions.[11]

Because the coordination chemistry of bis-phospholanes towards silver(I) has been highly neglected so far, we extended our studies on the coordination chemistry of bis-phospholanes to silver(I) tetrafluoridoborate. The weakly coordinating tetrafluoridoborate anion should allow the formation of argentophilic interactions in the solid state and thus enable comparison with the aurophilic interactions observed in gold(I) complexes.[12] Furthermore, we hoped to obtain single crystals that are isomorphous with the previously reported gold(I) complexes, to add further examples to the reported ones[13–16] to additionally support the prediction based on theoretical calculations that gold(I) is significantly smaller than silver(I).[17]

Results and discussion

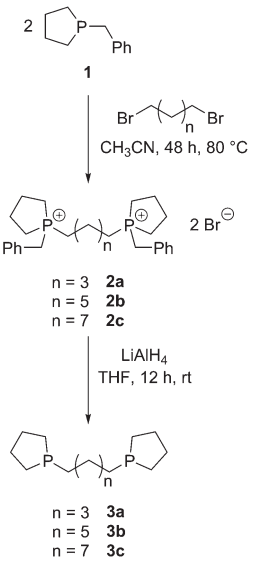
Improved synthesis of bis-phospholanes

We previously reported a three-step syntheses of the bis-phospholane ligands **3a–3d** using a modification of the procedure reported by Haddow *et al.* starting from 1-phenylphospholane.[11,18]

Treating two equivalents of 1-benzylphospholane (**1**) with 1,x-dibromoalkanes (x = 5, 7 or 9) in acetonitrile gave the bis-benzylphospholanium salts **2a–c** in quantitative yield. In contrast to their phenyl analogues, **2a–c** can be treated directly with lithium aluminum hydride to afford the corresponding bis-phospholanes **3a–c** (Scheme 1), thus avoiding the harsh

Institute of Inorganic Chemistry, Faculty of Chemistry and Mineralogy, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany. E-mail: hey@uni-leipzig.de

† Electronic supplementary information (ESI) available. CCDC 1439660–1439663. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00945j



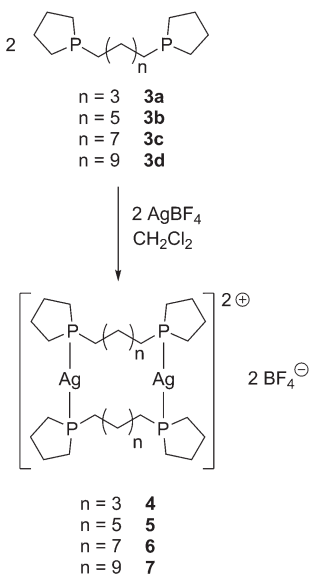
Scheme 1 New synthetic approach to bis-phospholanes **3a–c**.

conditions required for the basic hydrolysis of the phenyl analogues at high temperature, which can lead to degradation of functional groups.

Although the reductive cleavage of benzyl-substituted phosphonium salts had been described as early as 1975 by Horner *et al.*, only little attention was paid to the benzylphospholane moiety up to now.[19]

Silver(I) bis-phospholane macrocyles

Addition of $AgBF_4$ to a solution of **3a**, **3b**, **3c**, or **3d** [11] in dichloromethane led to macrocycles $[Ag_2(\mu\text{-}\mathbf{3a–d})_2](BF_4)_2$ (**4–7**) in excellent yield by self-assembly under thermodynamic control (Scheme 2).



Scheme 2 Selective formation of silver(I) macrocycles **4–7**.

Complexes **4–7** were obtained as white, light-stable solids. In the $^{31}P\{^1H\}$ NMR spectra, a downfield shift on coordination from about −27 ppm (**3a–d**) to about −1 ppm (**4–7**) occurred. In the mass spectra (ESI(+) mode) $[M - BF_4]^+$ and $[Ag(\mathbf{3a–d})]^+$ peaks were observed, indicating the presence of the macrocycles also in solution. Even though the formation of oligomers is conceivable, only macrocycles are observed, which seem to be the thermodynamic products. Coordination-driven self-assembly strategies have been previously employed to obtain well-defined macrocycles.[20] One recent example is the selective formation of a dimetallic silver(I) bis-carbene macrocycle (formed selectively in 89% yield after 20 h at 55 °C).[21] Solvent effects can also play a major role, as was shown in the solvent-dependent formation of helical polymers and discrete bi-, tri-, and tetranuclear metallacycles from AgX (X = OTf, ClO_4, PF_6, and BF_4) and 9,10-bis(diphenylphosphino)-anthracene.[22]

The complexes **4–7** are soluble in dichloromethane or chloroform, and crystals suitable for X-ray analysis could be obtained over several days from saturated dichloromethane/toluene solutions at room temperature. The crystal structures are shown in Fig. 1, and selected bond lengths and angles are given in Table 1.

All complexes show nearly linear coordination at the silver(I) ions with P–Ag–P bond angles between 170.91(7) and 176.89(1)°. Although the shortest Ag–F distances (267.9–300.5 pm) are much longer than the sum of the covalent radii, these weak electrostatic interactions cause a noticeable distortion from linearity. The Ag–P bond lengths range from 236.4(2) to 239.34(7) pm. The Ag–P bond lengths in $[Ag_2(\mu\text{-dppp})_2](BF_4)_2$ (dppp = 1,3-bis(diphenylphosphino)propane; Ag–P: 240.16(7), 239.35(7) pm) are slightly increased compared to **4–7**, while the P–Ag–P bond angles are significantly smaller (P–Ag–P: 159.66(3)°).[6] A P–Ag–P bond angle of 167.3(1)° was observed in $[Ag(PPh_3)_2]BF_4$ with small Ag–P bond lengths of 232.1(3) pm and 232.2(3) pm.[23]

In **4–7** the large P–Ag–P bond angles result from electron-rich bis-phospholane ligands stabilizing the oxidation state +I and the weakly coordinating tetrafluoridoborate anions. The electron-rich complex $[Ag_2\{\mu\text{-}t\mathrm{Bu}_2\mathrm{P}(\mathrm{CH}_2)_3\mathrm{P}t\mathrm{Bu}_2\}_2](BF_4)_2$ has large P–Ag–P bond angles as well (169.49(4)°), but due to the bulky *tert*-butyl groups long Ag–P bonds of 240.6(1) pm.[7] The use of electron-rich phosphines (PMe_3) and weakly coordinating anions (PF_6^-) resulted in an Ag–P bond length of 237.5(1) pm and a nearly linear P–Ag–P group with a bond angle of 178.70(4)° in $[Ag(PMe_3)_2]PF_6$.[24]

Schmidbaur *et al.* reported the isomorphous complexes bis-(trimesitylphosphine)gold(I) and bis(trimesitylphosphine)silver(I) tetrafluoridoborate with gold(I) being about 6% smaller than silver(I).[13] A similar trend is observed for the isomorphous complexes $[Au(PPh_3)_2]BF_4$ [16a] and $[Ag(PPh_3)_2]BF_4$ [16b] for which the Au–P bond is about 4% shorter than the Ag–P bond. A gold(I) radius nearly 7% smaller than in the isomorphous silver(I) complex was observed by Omary *et al.*, on the basis of the M–N bond lengths (M = Ag, Au) in trinuclear pyrazolato complexes.[14] Dias *et al.* reported the same trend in M–C

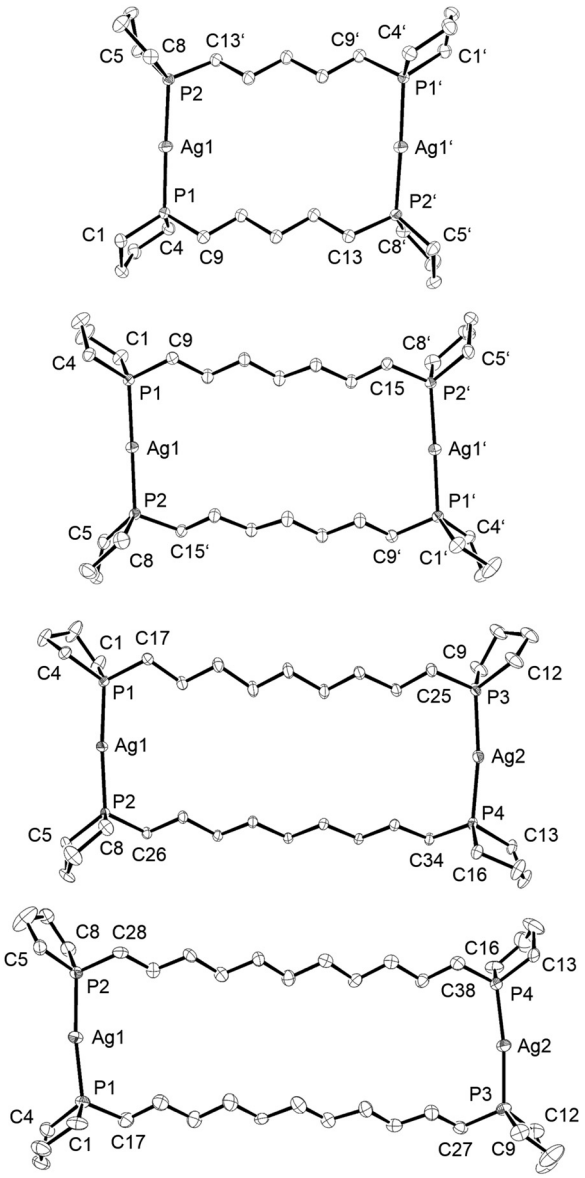


Fig. 1 Molecular structures of **4**, **5**, **6** and **7** (from top to bottom). Ellipsoids are drawn at 50% (**4**, **5**, **6**) and 30% (**7**) probability. H atoms, counterions, and solvent molecules are omitted for clarity. See ESI† for the second independent molecule of **7**.

Table 1 Selected bond lengths [pm] and angles [°] in **4**–**7**; missing values in **4** and **5** are generated by symmetry

	4	**5**	**6**	**7** [a]
Ag1–P1	237.21(8)	239.34(7)	236.3(1)	236.4(2) [238.7(2)]
Ag1–P2	237.02(8)	238.84(6)	236.4(1)	236.6(2) [238.3(2)]
Ag2–P3			237.8(1)	238.8(2) [237.5(2)]
Ag2–P4			238.7(1)	238.2(2) [237.7(2)]
P1–Ag1–P2	176.89(1)	173.49(1)	173.81(4)	170.91(7) [171.20(8)]
P3–Ag2–P4			172.44(4)	171.72(7) [174.90(7)]

[a] Values for the second independent molecule are given in brackets.

Table 2 Selected crystallographic data for **6** and $[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$ [11]

	6	$[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$
Formula	$C_{34}H_{68}Ag_2B_2F_8P_4{\cdot}0.5C_7H_8$	$C_{34}H_{68}Au_2B_2F_8P_4{\cdot}0.5C_7H_8$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
a [pm]	1034.8(5)	1037.3(5)
b [pm]	1143.1(5)	1105.6(5)
c [pm]	2051.2(5)	2090.2(5)
V [nm^3]	2.364(2)	2.388(2)

bond lengths for non-isomorphous tris(ethylene)- and tris(cyclooctyne)gold(I) and -silver(I) complexes, and supported this observation by theoretical calculations.[15]

$[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$ and **6** give further evidence that gold(I) is smaller than silver(I) (M–P 229.3(1) and 229.9(1) pm in $[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$ *versus* 236.3(1) and 236.4(1) pm in **6**) and support theoretical calculations, even though weak Ag···F Coloumb interactions are present in both structures.[11] These complexes fulfill the criteria (same ligands and counterions, same coordination number and geometry, isomorphous crystal lattice, and same experimental conditions) announced by Schmidbaur *et al.* for a scientific comparison of bond lengths.[13] Table 2 presents selected crystal data for **6** and $[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$, which underline the close crystallographic resemblance of the two complexes.

Steric interactions between the phospholane moieties are not observed. In bis(trimesitylphosphine)silver(I) tetrafluoridoborate, for example, the Ag–P bond lengths (244.09(9) pm) are increased by more than 10 pm compared to $[Ag(PPh_3)_2]BF_4$ (Ag–P: 232.1(3) pm, 232.2(3) pm), and Alyea *et al.* observed significant intramolecular methyl–methyl interactions in bis(trimesityl)silver(I) cations.[25] Furthermore, the sterically demanding mesityl groups in $[M(PMes_3)_2]BF_4$ (M = Ag, Au) prohibit any deviation from linearity.

Summary

We have presented a new and simplified route to bis-phospholane ligands using 1-benzylphospholane (**1**) as a starting material. Furthermore, the fascinating coordination behavior of **3a–d** towards silver(I) tetrafluoridoborate was investigated. A comparison of the crystal structures of the isomorphous complexes **6** and $[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$ give further evidence that gold(I) is significantly smaller than silver(I). Argentophilic interactions were not observed in the solid state.

Experimental section

Materials and methods

All reactions were carried out in a nitrogen atmosphere by using standard Schlenk techniques and anhydrous solvents, which were purified with an MB SPS-800 solvent purification

system from MBRAUN or as mentioned in the literature. Benzylphosphine,[26] 1,3,2-dioxathiepane-2,2-dioxide,[27] and **3d**[11] were prepared according to the literature. All other chemicals were used as purchased. NMR spectra were recorded at 298 K with a Bruker AVANCE DRX 400 spectrometer. The chemical shifts δ of ^{1}H, ^{13}C, ^{31}P are reported in parts per million (ppm) at 400.12, 100.63 and 162.02 MHz, respectively, with tetramethylsilane as an internal standard and referencing to the unified scale. Coupling constants J are given in Hz. FTIR spectra were recorded with a PerkinElmer Spectrum 2000 FTIR spectrometer, scanning between 400 and 4000 cm^{-1}, by using KBr pellets. Wavenumbers $\tilde{\nu}$ are reported in cm^{-1}. Mass spectra were recorded with ESQUIRE 3000 plus (ESI) and Finnigan MAT 8230 (EI) spectrometers. Elemental analyses were carried out with a Heraeus VARIO EL oven. Melting points were measured in sealed capillaries by using a variable heater from Gallenkamp.

Crystallographic data for compounds **4**, **5**, **6** and **7** were collected with an Oxford Diffraction CCD Xcalibur-S diffractometer (data reduction with CrysAlis Pro,[28] including the program SCALE 3 ABSPACK[29] for empirical absorption correction) by using MoK_α irradiation (λ = 71.073 pm) and ω-scan rotation. Structures were solved with the SIR tool.[30] Refinement was performed with SHELXL97.[31] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by constrained methods using the riding model. The refinement was carried out with the least-squares method on F^2. Final R indices were calculated as follows: $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$. Figures were drawn with ORTEP.[32] CCDC 1439660 (**4**), 1439661 (**5**), 1439662 (**6**) and 1439663 (**7**) contain the supplementary crystallographic data for this paper.

Synthesis and characterisation

1-Benzylphospholane (1). At 0 °C *n*-BuLi (58 mmol, 36 mL, 1.6 M in hexanes) was added to a solution of 7.2 g (58 mmol) benzylphosphine in hexanes (70 mL). The yellow suspension was stirred for 1 h at rt and then added to a solution of 8.8 g (58 mmol) 1,3,2-dioxathiepane-2,2-dioxide in hexanes (100 mL) *via* cannula. The mixture was stirred 3 h at rt and a second equivalent of *n*-BuLi (58 mmol, 36 mL, 1.6 M in hexanes) was added. After stirring overnight the reaction mixture was quenched with water (50 mL) and extracted with diethyl ether (2 × 50 mL). The combined organic layers were washed with distilled water and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by bulb-to-bulb distillation at 3 mbar (oil bath temperature 130 °C).

Yield: 6.6 g (64%). Colorless oil. Found C, 73.96; H, 8.24. Calc. for $C_{11}H_{15}P$: C, 74.14; H, 8.48. IR: $\tilde{\nu}$ = 2941 (s), 1698 (s), 1601 (s), 1494 (m), 1452 (m), 1265 (s), 869 (m), 769 (m), 700 (s), 656 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.25 (m, 2H), 7.15 (m, 3H), 2.65 (s, 2H), 1.65 ppm (m, 8H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 138.9 (d, J_{CP} = 4.9), 128.9 (d, J_{CP} = 5.5), 128.3 (s), 125.5 (d, J_{CP} = 2.1), 35.4 (d, J_{CP} = 20.5), 27.6 (d, J_{CP} = 4.0), 25.2 ppm (d, J_{CP} = 13.6). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = −16.7 ppm (s). MS (EI): m/z (%) = 178 $[M]^+$ (5), 150 $[M - C_2H_4]^+$ (15), 91 $[M - C_4H_8P]^+$ (100), 77 $[M - C_5H_{10}P]^+$ (5), 65 $[M - C_6H_{10}P]^+$ (15).

Preparation of phosphonium salts

Dibromoalkane (4.0 mmol) was added to a stirred solution of 1-benzylphospholane (8.0 mmol) in acetonitrile (10 mL). After stirring for two days at 80 °C, the clear solution was cooled to rt and the product precipitated. After filtration, the residue was washed with *n*-pentane (5 mL). The resulting white solids (**2a–c**) were used without further purification.

1,5-Bis(benzylphospholanium)pentane dibromide (2a). Yield: 2.3 g (96%). Mp = 241 °C. Found C, 55.17; H, 6.93. Calc. for $C_{27}H_{40}Br_2P_2$: C, 55.31; H, 6.88. IR $\tilde{\nu}$ = 3060 (m), 3029 (m), 2906 (s), 2792 (w), 1601 (m), 1494 (s), 1456 (s), 1399 (s), 1266 (m), 1111 (m), 1028 (m), 889 (m), 831 (m), 774 (m), 701 (s), 573 (m), 518 (m), 490 (s) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 7.43 (m, 10H), 3.99 (d, 4H, J_{HP} = 16.0), 2.49 (m, 4H), 2.31 (m, 8H), 1.91 (m, 4H,), 1.67 (m, 4H), 1.58 ppm (m, 6H). $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ = 131.1 (d, J_{CP} = 5.1), 130.5 (d, J_{CP} = 3.2), 130.2 (d, J_{CP} = 9.1), 129.3 (d, J_{CP} = 3.7), 31.0 (t, J_{CP} = 16.1), 28.7 (d, J_{CP} = 41.1), 26.8 (d, J_{CP} = 5.1), 21.4 (d, J_{CP} = 40.3), 21.2 (d, J_{CP} = 4.4), 21.0 ppm (d, J_{CP} = 50.2). $^{31}P\{^{1}H\}$ NMR (CD_3CN): δ = 54.2 ppm (s). MS (ESI(+), CH_3OH): m/z = 505 $[M - Br]^+$, 213 $[M - 2Br]^{2+}$.

1,7-Bis(benzylphospholanium)heptane dibromide (2b). Yield: 2.4 g (99%). Mp = 197 °C. Found C, 56.38; H, 7.49. Calc. for $C_{29}H_{44}Br_2P_2$: C, 56.69; H, 7.22. IR $\tilde{\nu}$ = 3028 (m), 2999 (m), 2922 (s), 2877 (s), 1601 (m), 1495 (s), 1455 (s), 1404 (s), 1266 (m), 1117 (m), 1088 (m), 1074 (m), 1023 (w), 888 (m), 708 (s), 571 (w), 487 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.48 (m, 4H), 7.39 (m, 6H), 4.24 (d, 4H, J_{HP} = 15.6), 2.86 (m, 4H), 2.42 (m, 8H), 1.93 (m, 4H), 1.70 (m, 4H), 1.58 ppm (m, 10H). $^{13}C\{^{1}H\}$ NMR (CD_3OD): δ = 131.2 (d, J_{CP} = 5.1), 130.6 (d, J_{CP} = 2.1), 130.2 (d, J_{CP} = 9.1), 129.5 (d, J_{CP} = 3.5), 31.1 (d, J_{CP} = 15.9), 28.8 (s), 28.7 (d, J_{CP} = 40.9), 27.0 (d, J_{CP} = 4.9), 22.7 (d, J_{CP} = 4.4), 21.6 (d, J_{CP} = 43.0), 21.0 (d, J_{CP} = 50.3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ = 54.0 ppm (s). MS (ESI(+), CH_3OH): m/z = 533 $[M - Br]^+$, 227 $[M - 2Br]^{2+}$.

1,9-Bis(benzylphospholanium)nonane dibromide (2c). Yield: 2.4 g (93%). Mp = 215 °C. Found C, 57.90; H, 7.53. Calc. for $C_{31}H_{48}Br_2P_2$: C, 57.95; H, 7.53. IR $\tilde{\nu}$ = 3029 (m), 2924 (s), 2909 (s), 2858 (m), 1631 (w), 1602 (w), 1495 (m), 1456 (m), 1406 (m), 1265 (m), 1114 (s), 1077 (m), 831 (m), 707 (s), 489 (m) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 7.51 (m, 4H), 7.39 (m, 6H), 4.32 (d, 4H, J_{HP} = 15.6), 2.77 (m, 4H), 2.41 (m, 8H), 1.87 (m, 4H), 1.65 (m, 8H), 1.43 ppm (m, 10H). $^{13}C\{^{1}H\}$ NMR (CD_3OD): δ = 131.2 (d, J_{CP} = 5.1), 130.6 (d, J_{CP} = 3.1), 130.2 (d, J_{CP} = 9.0), 129.5 (d, J_{CP} = 3.6), 31.6 (d, J_{CP} = 15.7), 29.9 (s), 29.7 (s), 28.7 (d, J_{CP} = 41.0), 27.0 (d, J_{CP} = 4.9), 22.9 (d, J_{CP} = 4.7), 22.1 (d, J_{CP} = 42.9), 21.0 (d, J_{CP} = 50.3). $^{31}P\{^{1}H\}$ NMR (CD_3CN): δ = 53.7 (s). MS (ESI(+), CH_3OH): m/z = 561 $[M - Br]^+$, 241 $[M - 2Br]^{2+}$.

Preparation of bis-phospholanes 3a–c

2.0 mmol of the respective bis-phosphonium salt (**2a–c**) were added to a suspension of 0.12 g (3.0 mmol) $LiAlH_4$ in THF (40 mL). The reaction mixture was stirred at rt overnight and then quenched carefully with 10 mL of degassed methanol.

The solvent was removed under reduced pressure and the residue extracted with hexanes (3 × 10 mL). The solvent was removed under reduced pressure and pure bis-phospholanes were obtained by bulb-to-bulb distillation at 10^{-3} mbar as colorless oils. The spectroscopic data of **3a–c** are in agreement with those reported previously.[11]

1,5-Bis(phospholano)pentane (3a). Yield: 0.40 g (82%). ^{1}H NMR ($CHCl_3$): δ = 1.85–1.56 (m, 12H), 1.51–1.18 ppm (m, 14H). ^{13}C NMR ($CHCl_3$): δ = 32.8 (t, J_{CP} = 11.6), 28.8 (d, J_{CP} = 15.5), 27.8 (d, J_{CP} = 3.8), 26.6 (d, J_{CP} = 11.4), 25.9 ppm (d, J_{CP} = 11.4 Hz). ^{31}P{^{1}H} NMR ($CHCl_3$): δ = −26.7 ppm (s).

1,7-Bis(phospholano)heptane (3b). Yield: 0.48 g (89%). ^{1}H NMR ($CHCl_3$): δ = 1.76–1.52 (m, 12H), 1.39–1.14 ppm (m, 18H). ^{13}C NMR ($CHCl_3$): δ = 31.1 (d, J_{CP} = 11.5), 29.1 (s), 28.9 (d, J_{CP} = 15.6), 27.7 (d, J_{CP} = 3.7), 26.8 (d, J_{CP} = 15.4), 25.9 ppm (d, J_{CP} = 11.5). ^{31}P{^{1}H} NMR ($CHCl_3$): δ = −26.9 ppm (s).

1,9-Bis(phospholano)nonane (3c). Yield: 0.50 g (83%). ^{1}H NMR ($CHCl_3$): δ = 1.82–1.52 (m, 12H), 1.46–1.11 ppm (m, 22H). ^{13}C NMR ($CHCl_3$): δ = 31.2 (d, J_{CP} = 11.6), 29.3 (s), 28.8 (d, J_{CP} = 14.9), 27.7 (d, J_{CP} = 3.7), 26.8 (d, J_{CP} = 15.1), 25.8 ppm (d, J_{CP} = 11.2). ^{31}P{^{1}H} NMR ($CHCl_3$): δ = −26.8 ppm (s).

Preparation of compounds 4, 5, 6, 7

$AgBF_4$ (97 mg; 0.50 mmol) was added to a stirred solution of the bis-phospholane (**3a–d**) (0.50 mmol) in CH_2Cl_2 (10 mL). After stirring for 3 h at rt, the solution was filtered and volatile compounds were removed *in vacuo*. The white solid obtained was washed with *n*-pentane (3 × 10 mL). Suitable crystals for X-ray diffraction studies could be obtained from saturated dichloromethane/toluene solutions at rt as colorless prisms (**4–6**) or needles (**7**). All compounds were dried *in vacuo* prior to elemental analysis.

Bis[μ-1,5-bis(phospholano)pentane-κ^{2}P,P′]disilver(I) bis(tetrafluoridoborate) (4). Yield: 209 mg (95%). Mp = 214 °C. Found C, 35.21; H, 5.98. Calc. for $C_{26}H_{52}Ag_2B_2F_8P_4$: C, 35.57; H, 5.97. IR $\tilde{\nu}$ = 2936 (s), 2858 (m), 1637 (w), 1447 (w), 1411 (w), 1055 (s), 854 (w), 718 (w), 519 (w), 487 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 2.12 (m, 8H), 1.86 (m, 24H), 1.66 (m, 8H), 1.55 ppm (m, 12H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 32.7 (br s), 27.6 (br s), 27.1 (br d, J_{CP} = 16.1), 26.9 (br s), 25.1 ppm (br d, J_{CP} = 19.1). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = −1.2 ppm (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = −0.3 ppm (s). MS (ESI(+), CH_2Cl_2, CH_3CN): *m*/*z* = 791 $[M - BF_4]^+$, 351 $[Ag(\mathbf{3a})]^+$.

Bis[μ-1,7-bis(phospholano)heptane-κ^{2}P,P′]disilver(I) bis(tetrafluoridoborate) (5). Yield: 222 mg (95%). Mp = 199 °C. Found C, 38.90; H, 6.49. Calc. for $C_{30}H_{60}Ag_2B_2F_8P_4$: C, 38.58; H, 6.47. IR $\tilde{\nu}$ = 2925 (s), 2851 (s), 2100 (w), 1810 (w), 1466 (s), 1448 (m), 1410 (s), 1306 (m), 1282 (m), 1183 (m), 1067 (s), 950 (m), 870 (m), 852 (m), 719 (m), 688 (m), 518 (s), 493 (m), 454 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 2.12 (m, 8H), 1.86 (m, 28H), 1.63 (m, 8H), 1.47 (m, 12H), 1.34 ppm (m, 4H). ^{13}C NMR (CD_2Cl_2): δ = 30.6 (br d, J_{CP} = 12.0), 29.2 (br s), 27.4 (br s), 27.1 (br d, J_{CP} = 16.2 Hz), 26.9 (br s), 25.1 ppm (br d, J_{CP} = 19.6). ^{11}B NMR (CD_2Cl_2): δ = −1.2 ppm (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = −0.8 ppm (s). MS (ESI(+), CH_2Cl_2, CH_3CN): *m*/*z* = 847 $[M - BF_4]^+$, 379 $[Ag(\mathbf{3b})]^+$.

Bis[μ-1,9-bis(phospholano)nonane-κ^{2}P,P′]disilver(I) bis(tetrafluoridoborate) (6). Yield: 235 mg (95%). Mp = 87 °C. Found C, 41.28; H, 6.79. Calc. for $C_{34}H_{68}Ag_2B_2F_8P_4$: C, 41.24; H, 6.92. IR $\tilde{\nu}$ = 2924 (s), 2848 (s), 1466 (m), 1449 (m), 1413 (m), 1304 (w), 1054 (s), 918 (w), 855 (m), 741 (w), 721 (w), 698 (m), 519 (m), 471 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 2.11 (m, 8H), 1.88 (m, 24H), 1.64 (m, 8H), 1.51 (m, 16H), 1.32 ppm (m, 12H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 32.8 (s), 30.3 (br s), 29.4 (br s), 28.7 (s), 27.0 (s), 26.9 (s), 25.2 ppm (br s). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = −1.2 ppm (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = −2.4 ppm (s). MS (ESI(+), CH_2Cl_2, CH_3CN): *m*/*z* = 903 $[M - BF_4]^+$, 407 $[Ag(\mathbf{3c})]^+$.

Bis[μ-1,11-bis(phospholano)undecane-κ^{2}P,P′]disilver(I) bis(tetrafluoridoborate) (7). Yield: 251 mg (96%). Mp = 109 °C. Found C, 43.36; H, 7.31. Calc. for $C_{38}H_{76}Ag_2B_2F_8P_4$: C, 43.62; H 7.32. IR $\tilde{\nu}$ = 2924 (s), 2850 (s), 1467 (s), 1449 (m), 1412 (s), 1304 (m), 1282 (m), 1262 (m), 1052 (s), 950 (m), 897 (w), 855 (m), 803 (m), 722 (m), 689 (m), 518 (s), 487 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 2.21–1.76 (m, 32H), 1.75–1.18 ppm (m, 44H). ^{13}C NMR (CD_2Cl_2): δ = 30.7 (d, J_{CP} = 14.6), 30.7 (s), 29.2 (s), 29.0 (d, J_{CP} = 12.3), 27.1 (d, J_{CP} = 18.6), 26.8 (s), 26.6 (s), 25.3 ppm (d, J_{CP} = 22.2). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = −1.2 ppm (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = −1.4 ppm (s). MS (ESI(+), CH_2Cl_2, CH_3CN): *m*/*z* = 959 $[M - BF_4]^+$, 435 $[Ag(\mathbf{3d})]^+$.

Acknowledgements

We gratefully acknowledge financial support from the Fonds der Chemischen Industrie (FCI, doctoral grant to A. S.), the European Union and the Free State of Saxony (ESF, project no. 100148808; R. H.), the Graduate School Leipzig School of Natural Sciences – Building with Molecules and Nano-objects (BuildMoNa), and the COST Action CM1302 Smart Inorganic Polymers (SIPs). We thank M. Böhlmann, F. Seifert, S. Märcker, and R. Zäbe for measurements of IR and NMR spectra and Dr P. Lönnecke, Dr K. Zeckert, and Dr R. Frank for help with structure solutions.

References

1 (*a*) D. Perreault, M. Drouin, A. Michel, V. M. Miskowski, W. P. Schaefer and P. D. Harvey, *Inorg. Chem.*, 1992, **31**, 695–702; (*b*) Effendy, C. di Nicola, M. Nitiatmodjo, C. Pettinari, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2005, **358**, 735–747; (*c*) Effendy, J. V. Hanna, F. Marchetti, D. Martini, C. Pettinari, R. Pettinari, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2004, **357**, 1523–1537; (*d*) D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **22**, 4073–4079; (*e*) S. P. Neo, Z.-Y. Zhou, T. C. W. Mak and T. S. A. Hor, *Inorg. Chem.*, 1995, **34**, 520–523.

2 P. Di Bernardo, G. Dolcetti, R. Portanova, M. Tolazzi, G. Tomat and P. Zanonato, *Inorg. Chem.*, 1990, **29**, 2859–2862.

3 Effendy, C. di Nicola, M. Fianchini, C. Pettinari, B. W. Skelton, N. Somers and A. H. White, *Inorg. Chim. Acta*, 2005, **358**, 763–795.
4 E. R. T. Tiekink, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 1933–1934.
5 A. Cassel, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1976, **32**, 2521–2523.
6 M. L. Smith, P. M. Almond, T. E. Albrecht-Schmitt and W. E. Hill, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, m1013–m1014.
7 S. P. Crabtree, A. S. Batsanov, J. A. Howard and M. Kilner, *Polyhedron*, 1998, **17**, 367–372.
8 (*a*) M.-C. Brandys and R. J. Puddephatt, *Chem. Commun.*, 2001, 1280–1281; (*b*) M.-C. Brandys, M. C. Jennings and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 2000, 4601–4606.
9 S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1995, **34**, 1455–1465.
10 M.-C. Brandys and R. J. Puddephatt, *Chem. Commun.*, 2001, 1508–1509.
11 M. Streitberger, A. Schmied and E. Hey-Hawkins, *Inorg. Chem.*, 2014, **53**, 6794–6804.
12 (*a*) C. Y. Chen, J. Y. Zeng and H. M. Lee, *Inorg. Chim. Acta*, 2007, **360**, 21–30; (*b*) L. Ray, M. M. Shaikh and P. Ghosh, *Inorg. Chem.*, 2008, **47**, 230–240; (*c*) X. Liu, G.-C. Guo, M.-L. Fu, X.-H. Liu, M.-S. Wang and J.-S. Huang, *Inorg. Chem.*, 2006, **45**, 3679–3685; (*d*) L. Dobrzanska, H. G. Raubenheimer and L. J. Barbour, *Chem. Commun.*, 2005, 5050–5052; (*e*) H. Schmidbaur and A. Schier, *Angew. Chem., Int. Ed.*, 2015, **127**, 756–797; (*f*) H. Schmidbaur and A. Schier, *Angew. Chem., Int. Ed.*, 2015, **54**, 746–784.
13 A. Bayler, A. Schier, G. A. Bowmaker and H. Schmidbaur, *J. Am. Chem. Soc.*, 1996, **118**, 7006–7007.
14 M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonser, O. Elbjeirami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage and H. V. R. Dias, *Inorg. Chem.*, 2005, **44**, 8200–8210.
15 (*a*) M. Fianchini, C. F. Campana, B. Chilukuri, T. R. Cundari, V. Petricek and H. V. R. Dias, *Organometallics*, 2013, **32**, 3034–3041; (*b*) H. V. R. Dias, M. Fianchini, T. R. Cundari and C. F. Campana, *Angew. Chem., Int. Ed.*, 2008, **120**, 566–569; (*c*) H. V. R. Dias, M. Fianchini, T. R. Cundari and C. F. Campana, *Angew. Chem., Int. Ed.*, 2008, **47**, 556–559; (*d*) A. Das, C. Dash, M. A. Celik, M. Yousufuddin, G. Frenking and H. V. R. Dias, *Organometallics*, 2013, **32**, 3135–3144; (*e*) A. Das, C. Dash, M. Yousufuddin, M. A. Celik, G. Frenking and H. V. R. Dias, *Angew. Chem., Int. Ed.*, 2012, **51**, 3940–3943; (*f*) A. Das, C. Dash, M. Yousufuddin, M. A. Celik, G. Frenking and H. V. R. Dias, *Angew. Chem., Int. Ed.*, 2012, **124**, 4006–4009.
16 (*a*) J.-C. Wang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **52**, 611–613; (*b*) R. E. Bachman and D. F. Andretta, *Inorg. Chem.*, 1998, **37**, 5657–5663.
17 (*a*) P. Schwerdtfeger, P. D. W. Boyd, A. K. Burrell, W. T. Robinson and M. J. Taylor, *Inorg. Chem.*, 1990, **29**, 3593–3607; (*b*) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker and P. D. W. Boyd, *J. Chem. Phys.*, 1989, **91**, 1762–1774; (*c*) P. Pyykko, *Chem. Rev.*, 1988, **88**, 563–594; (*d*) P. Jerabek, H. W. Roesky, G. Bertrand and G. Frenking, *J. Am. Chem. Soc.*, 2014, **136**, 17123–17135.
18 M. F. Haddow, A. J. Middleton, A. G. Orpen, P. G. Pringle and R. Papp, *Dalton Trans.*, 2009, 202–209.
19 (*a*) L. Horner, P. Walach and H. Kunz, *Phosphorus*, 1975, **6**, 63; (*b*) L. Horner, P. Walach and H. Kunz, *Phosphorus Sulfur Relat. Elem.*, 1978, **5**, 171–184.
20 E. M. López-Vidal, V. Blanco, M. D. García, C. Peinador and J. M. Quintela, *Org. Lett.*, 2012, **14**, 580–583.
21 C.-X. Wang, Y. Gao, Y.-X. Deng, Y.-J. Lin, Y.-F. Han and G.-X. Jin, *Organometallics*, 2015, **34**, 5801–5806.
22 R. Lin and J. H. K. Yip, *Inorg. Chem.*, 2006, **45**, 4423–4430.
23 J.-C. Wang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **52**, 611–613.
24 E. C. Alyea, S. Kannan and P. R. Meehan, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2002, **58**, m365–m367.
25 E. C. Alyea, G. Ferguson and A. Somogyvari, *Inorg. Chem.*, 1982, **21**, 1369–1371.
26 L. Horner, H. Hoffmann and P. Beck, *Chem. Ber.*, 1958, **91**, 1583–1588.
27 I. Bonnaventure and A. B. Charette, *J. Org. Chem.*, 2008, **73**, 6330–6340.
28 *CrysAlis Pro*, Oxford Diffraction Ltd, Oxfordshire, UK, 2010.
29 *SCALE3 ABSPACK*, Oxford Diffraction Ltd, Oxfordshire, UK, 2010.
30 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343–350.
31 G. M. Sheldrick, *SHELX97: Programs for Crystal Structure Analysis (Release 97-2)*, Universität Göttingen, Göttingen, 1997.
32 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.