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Metal Effects on the Asymmetric Synthesis of a New Heterobidentate As/P=S Ligand

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Keywords: As ligands / P ligands / S ligands / Palladium / Platinum / Asymmetric synthesis / Cycloaddition

The cycloaddition reaction between 3,4-dimethyl-1-phenylarsole and diphenylvinylphosphane sulfide was promoted by chiral palladium and platinum complexes containing *ortho*-metalated (*S*)-[1-(dimethylamino)ethyl]naphthalene. They exhibited similar stereoselectivity; the palladium cycloadducts could not be separated via column chromatography and fractional crystallization, however, the corresponding platinum complexes could be successfully converted into their enantiomerically pure counterpart. A formal arsanylidene elimination reaction was observed on the liberated free As/P=S bidentate ligand.

Introduction

Heterobidentate ligands have very important applications in transition metal-catalyzed asymmetric reactions due to the fact that they contain both substitutionally labile and substitutionally inert groups in the same molecule.[1–5] These heterobidentate ligands containing one soft and one hard donor atom often offer some unique advantages over traditional symmetrical bidentate ligands in potential applications such as catalysis using transition metals. In such scenarios their hemilabile nature readily vacates a coordination position thus allowing the incoming reactant to bind on the metal and thus be activated during the catalytic cycle. Amongst such ligands, phosphorus–sulfur-based ligands make up a popular class of heterobidentate ligands and have been successfully applied in many asymmetric reactions.[6–8] For example recently Faller et al. reported the enantioselective allylic alkylation and amination of acyclic carbonates catalyzed by the axially chiral (*S*)-BINAP(S) ligand with up to 97% *ee* and 99% conversion.[9–12]

However, compared to the relatively extensive application of phosphorus–sulfur-based heterobidentate ligands in many fields, reports on such ligands incorporating inert arsenic and labile sulfur centers, especially those that are optically pure, are very rare. Herein we report the successful resolution of a new chiral As/P=S heterobidentate ligand via the asymmetric cycloaddition reaction between 3,4-dimethyl-1-phenylarsole (DMPA) and diphenylvinylphosphane sulfide promoted by a chiral platinum complex. This work is part of our ongoing exploration into the chemistry of such chiral systems incorporating As and P moieties with a view to understanding the subtle but significant variations in the chemistry of arsenic (vs. phosphorus) exhibited in such reaction scenarios.[13–18]

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Results and Discussion

Asymmetric Diels–Alder Reaction between DMPA and Diphenylvinylphosphane Sulfide Promoted by a Chiral Palladium Complex

Our group has successfully employed a series of cyclometallated complexes, mainly based on benzyl and naphthylamine systems, as efficient promoters and chiral auxiliaries for a wide variety of asymmetric synthetic protocols.[19] In the present study a palladium complex containing an *ortho*-metalated (*S*)-[1-(dimethylamino)ethyl]naphthalene auxiliary was allowed to coordinate to DMPA thus yielding the complex (+)-**1**. Subsequently the complex (+)-**1** was treated with aqueous silver perchlorate in dichloromethane, the resulting perchlorate complex could be used directly for subsequent reaction with diphenylvinylphosphane sulfide without isolation. The reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. When the reaction mixture was stirred for 13 d at 40 °C, the $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited two singlets at δ 50.2 and 51.5 ppm in the ratio of 1:2 (Scheme 1). Attempts to isolate the two diastereomers (S_c,S_{As})- and (S_c,R_{As})-**2** via column chromatography or fractional crystallization, however, were not successful.

In order to confirm the identities of the two diastereomers, the chiral naphthylamine auxiliary in the diastereomeric mixture was removed chemoselectively from (S_c,S_{As})- and (S_c,R_{As})-**2** by stirring a dichloromethane solution of the complexes with concentrated hydrochloric acid

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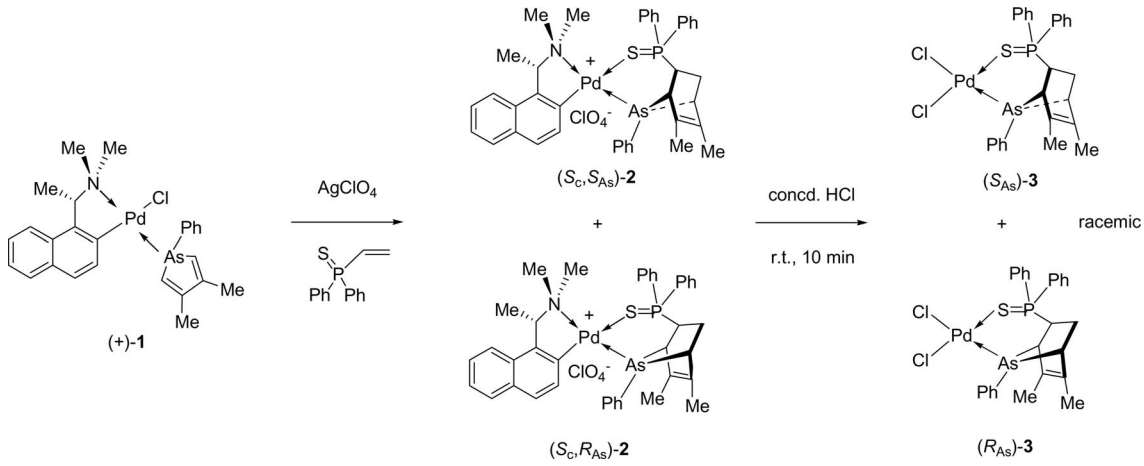


Scheme 1.

for 10 min at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of the crude neutral dichloro complex **3** in $CDCl_3$ showed only one singlet at δ 50.7 ppm. Brown-yellow crystals suitable for single-crystal X-ray diffraction analysis were obtained from acetonitrile in 70% yield. However, the X-ray structural analysis of dichloro complex **3** revealed the presence of both enantiomers in the unit cell. The molecular structure of complex **3** is shown in Figure 1 and is taken as the representative molecule in order to study the coordination aspects for the cycloadducts which were formed as a racemic mixture. Selected bond lengths and angles are listed in the caption of Figure 1. The cycloadduct coordinated to the palladium center as a bidentate ligand via arsenic and sulfur donor atoms. It also confirmed that the desired cycloadduct had formed exclusively via the *exo*-cycloaddition reaction pathway. The geometry at the palladium is distorted square planar with angles at palladium in the range of 83.7(1)–95.9(1) and 172.6(1)–179.4(1)°. The bond angle at the bridgehead arsenic (C12–As1–C7) is 77.1(3)°, which is indicative of higher strain usually seen in such norbornene chelates.

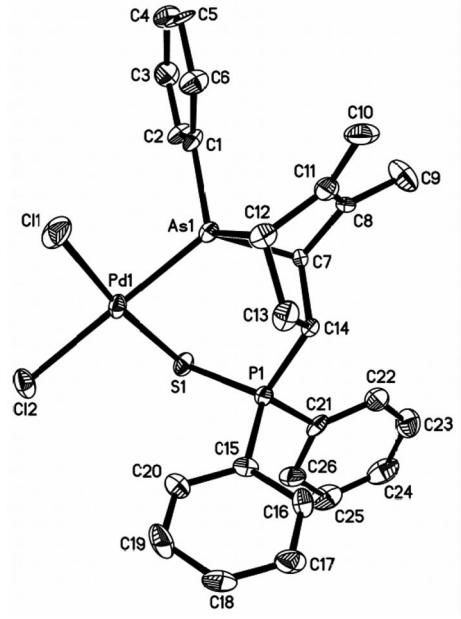
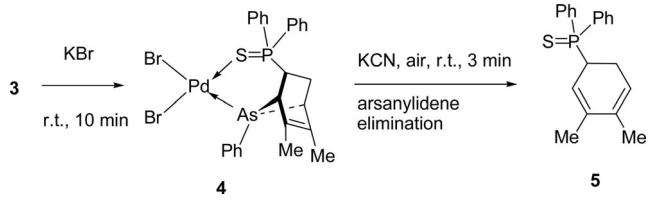


Figure 1. Molecular structure of dichloro complex **3**. Selected bond lengths [Å] and angles [°]: Pd1–S1 2.301(2), Pd1–As1 2.305(1), Pd1–Cl1 2.323(2), Pd1–Cl2 2.389(2), As1–C7 1.976(7), As1–C12 1.961(8), S1–Pd1–As1 89.0(1), S1–Pd1–Cl1 172.6(1), As1–Pd1–Cl1 83.7(1), S1–Pd1–Cl2 91.4(1), As1–Pd1–Cl2 179.4(1), Cl1–Pd1–Cl2 95.9(1), C12–As1–C7 77.1(3).

Arsinidene–Elimination Reaction

In order to better understand the influence of the *trans* ligand in determining the stability of the As bridgehead as seen from our previous studies, the dichloro complex **3** was treated with potassium bromide for 10 min at room temperature and the dibromo complex **4** was obtained as a yellow solid in 96% yield (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum exhibited only one singlet at δ 51.4 ppm indicating the absence of any side reaction. Complex **4** was subsequently recrystallized with dichloromethane/acetonitrile to give the product as orange yellow crystals (Figure 2). The structural analysis of dibromo complex **4** reveals the presence of both enantiomers in the unit cell which is similar to the analogous dichloro complex **3**.



Scheme 2.

The dichloro complex **3** is stable in the solid state, but it decomposes completely after 3 weeks in CD_2Cl_2 at room temperature. However, contrastingly the dibromo complex **4** is stable both in the solid state and in solution. This could be proven by its $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 where the chemical shift remained unchanged even after the sample was kept in solution for more than two months. But when complex **4** was treated with potassium cyanide for

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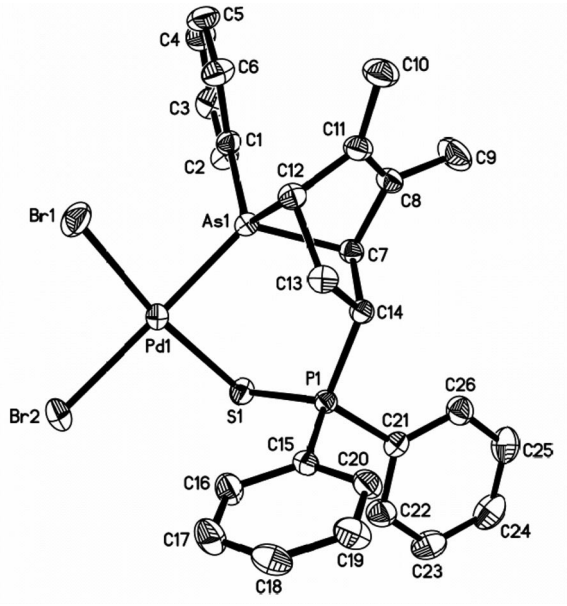
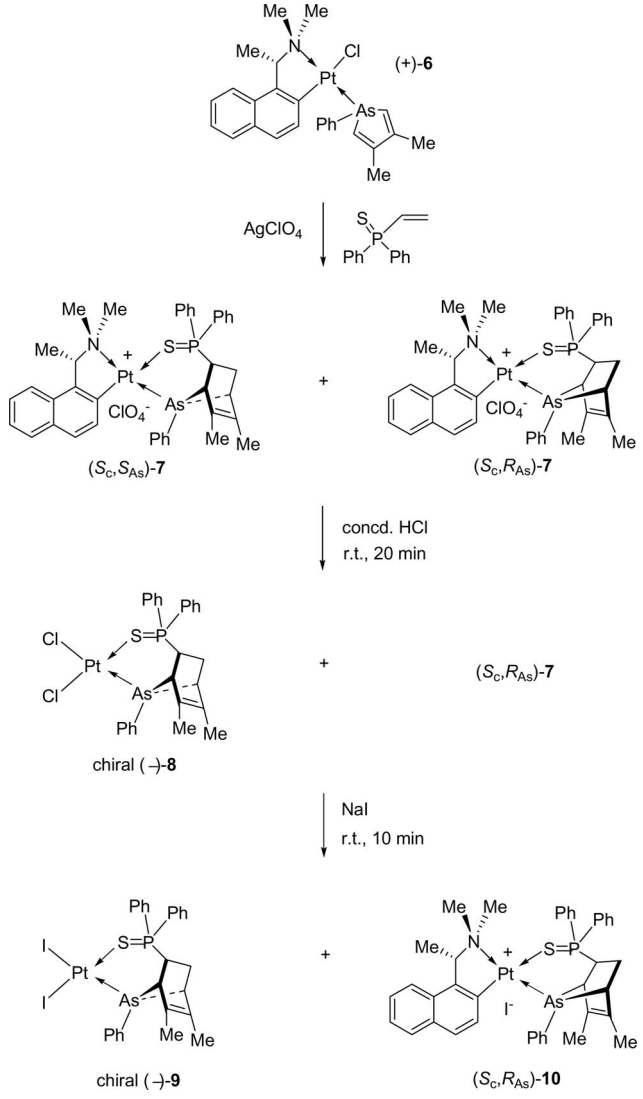


Figure 2. Molecular structure of dibromo complex **4**. Selected bond lengths [Å] and angles [°]: Pd1–S1 2.312(1), Pd1–As1 2.315(1), Pd1–Br1 2.441(1), Pd1–Br2 2.510(1), As1–C7 1.986(2), As1–C12 1.969(2), S1–Pd1–As1 89.4(1), S1–Pd1–Br1 172.5(1), As1–Pd1–Br1 83.1(1), S1–Pd1–Br2 92.1(1), As1–Pd1–Br2 178.4(1), Br1–Pd1–Br2 95.4(1), C12–As1–C7 77.3(1).

3 min at room temperature, the solution rapidly changed from red to colorless. The uncoordinated ligand is very unstable and the arsanylidene elimination reaction occurred instantly to give the new compound **5** and phenylarsonic acid as seen in our previous studies.[14] The organic compound **5** could be isolated and purified by column chromatography on a silica column with dichloromethane/*n*-hexane. It is also not very stable and changed to numerous unknown compounds after being kept for one week even in the solid state.

Metal Effects: Asymmetric Diels–Alder Reaction between DMPA and Diphenylvinylphosphane Sulfide Promoted by the Analogous Platinum Complex

Similar to the analogous palladium complex, upon removal of the chloro ligand in (+)-**6** with $AgClO_4$, the resulting perchlorate complex was treated with diphenylvinylphosphane sulfide for 5 d at room temperature (Scheme 3). Two diastereomers (S_c,S_{As})-**7** and (S_c,R_{As})-**7** were obtained in much shorter reaction time in the ratio of 1:2 (as indicated by two singlets at δ 49.6 and 47.7 ppm, respectively, in the $^{31}P(^1H)$ NMR spectrum). Unfortunately these diastereomeric cycloadducts also could not be separated by column chromatography or fractional crystallization. However, when they were treated with concentrated hydrochloric acid for 20 min at room temperature, the minor isomer (S_c,S_{As})-7 was converted into the corresponding neutral dichloro platinum complex (–)-**8**, while the major isomer (S_c,R_{As})-**7** remained unchanged. The mixture was recrystallized with dichloromethane/diethyl ether to produce the yellow crystals of the optically pure (–)-**8** in 83% yield, $[a]_D$ = –57.7 (c = 0.3, CH_2Cl_2). The unreacted (S_c,R_{As})-**7** was then readily isolated from the mother liquid by column chromatography. Because of the fact that the dichloro complex (–)-**8** crystallized very slowly (several weeks), for separation purposes it was more efficient to treat the resultant mixture at the onset with NaI for 10 min at room temperature. The resulting diiodo complex (–)-**9** and (S_c,R_{As})-**10** were separated more easily and faster via column chromatography (a few hours).



Scheme 3.

The X-ray analysis of dichloro platinum complex (–)-**8** showed that it indeed was chiral [Flack parameter: –0.001(4)]. Selected bond lengths and angles are listed in the caption of Figure 3. The geometry at the platinum in (–)-**8** is distorted square planar with angles at the platinum in the range of 88.2(1)–92.2(1) and 176.0(1)–176.4(1)°. The cycloadduct coordinated to the platinum center as a bidentate ligand via arsenic and sulfur donor atoms. The As–Pt–S bond angle [89.4(1)°] in complex (–)-**8** is the same as the As–Pd–S bond angle of complex **4** and a little bigger than

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that of complex **3** [89.0(1)°], however, the Cl1–Pt–Cl2 bond angle [92.2(1)°] in complex (–)-**8** is smaller than similar bond angles in complexes **3** and **4** [95.9(1) and 95.4(1)°, respectively]. Complex (S_c,R_{As})-**10** could be recrystallized with dichloromethane/diethyl ether to produce yellow crystals. As expected, the structural analysis of (S_c,R_{As})-**10** also revealed that the perchlorate was replaced by an iodide. Selected bond lengths and angles are listed in the caption of Figure 4. The geometry at the platinum in (S_c,R_{As})-**10** is distorted square planar with angles at the platinum in the range of 80.0(2)–93.8(2) and 172.6(2)–173.4(1)°. The cycloadduct coordinated to the platinum center as an As/P=S bidentate ligand where the sulfur is *trans* to the carbon and arsenic is *trans* to the nitrogen.

The enantiomer of (–)-**8**, dichloro complex (+)-**8**, could be obtained by treatment of optically active (S_c,R_{As})-**7** or (S_c,R_{As})-**10** with concentrated hydrochloric acid for 4 h at room temperature (Scheme 4). Further treatment of enantiomerically pure diiodo complex (–)-**9** with aqueous potassium cyanide liberated the desired optically pure As/P=S ligand (+)-**11** in quantitative yield, $[a]_D$ = +44.3 (c = 0.43, CH_2Cl_2). The liberated ligand was unstable and readily produced the optically active compound (+)-**5**, $[a]_D$ = +60.7 (c = 0.40, CH_2Cl_2) (Scheme 5).

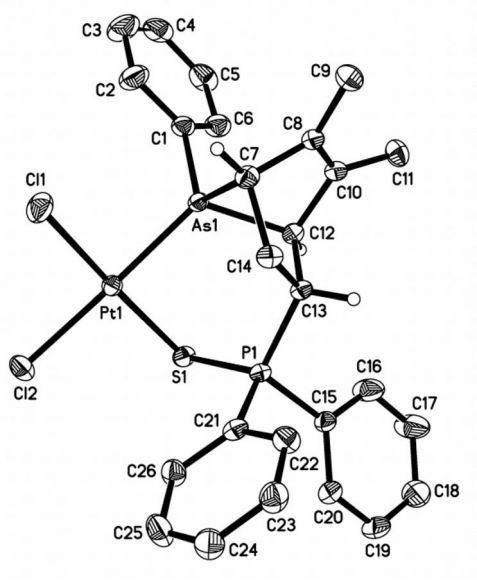
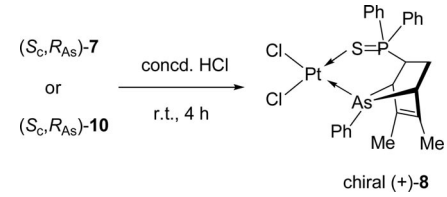
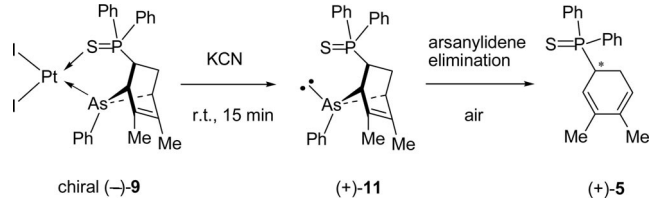


Figure 3. Molecular structure of dichloro complex (–)-**8**. Selected bond lengths [Å] and angles [°]: Pt1–S1 2.301(1), Pt1–As1 2.312(1), Pt1–Cl1 2.329(1), Pt1–Cl2 2.355(1), As1–C7 1.967(3), As1–C12 1.968(3), S1–Pt1–Cl1 176.4(1), S1–Pt1–As1 89.4(1), Cl1–Pt1–As1 88.2(1), S1–Pt1–Cl2 90.4(1), Cl1–Pt1–Cl2 92.2(1), As1–Pt1–Cl2 176.0(1), C7–As1–C12 77.8(1).



Scheme 4.



Scheme 5.

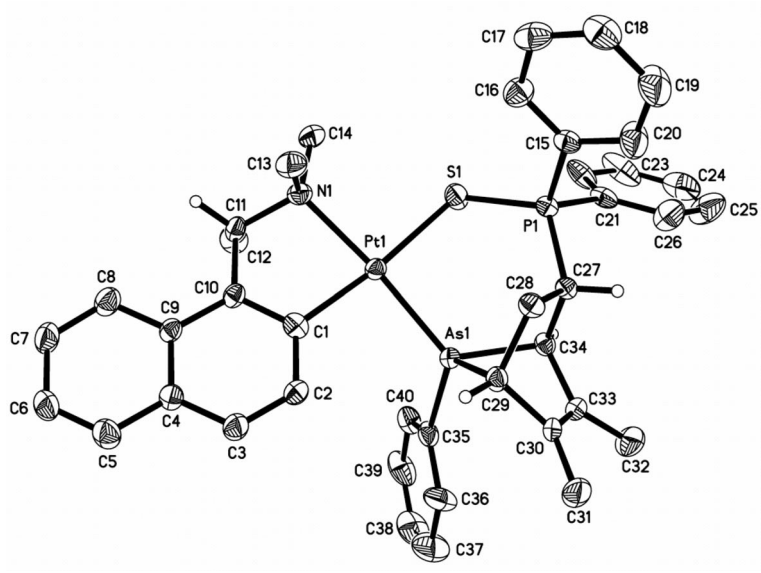


Figure 4. Molecular structure of complex (S_c,R_{As})-**10**. Selected bond lengths [Å] and angles [°]: Pt1–C1 2.024(7), Pt1–N1 2.136(5), Pt1–As1 2.321(1), Pt1–S1 2.406(2), As1–C29 1.964(6), As1–C34 1.980(6), C1–Pt1–N1 80.0(2), C1–Pt1–As1 93.8(2), N1–Pt1–As1 173.4(1), C1–Pt1–S1 172.6(2), N1–Pt1–S1 93.7(1), As1–Pt1–S1 92.6(1), C29–As1–C34 77.1(3).

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Conclusions

The cycloaddition reaction between DMPA and diphenylvinylphosphane sulfide was promoted by a chiral palladium complex, however, both the resulting diastereomers **2** and the corresponding dihalogen complexes **3** and **4** could not be separated into their enantiomeric counterparts via column chromatography or fractional crystallization. When the chiral metal promoter was changed from palladium to platinum, the reaction selectivity is similar although the rate improved drastically. However, the major isomer (S_c,R_{As})-**7** and the dichloro complex (–)-**8** could be separated via fractional crystallization and column chromatography. Alternatively they could be converted into the corresponding iodo complexes (S_c,R_{As})-**9** and (–)-**10**. The two iodo complexes were readily separated by means of column chromatography. The optically pure As/P=S ligand (+)-**11** could be liberated by treatment of (–)-**9** with KCN. The arsanylidene elimination reaction was observed on the racemic or chiral free ligand **9**.

Experimental Section

General Methods: Reactions involving air-sensitive compounds were performed under inert argon using standard Schlenk techniques. Solvents were dried and freshly distilled according to standard procedures and degassed prior to use when necessary. NMR spectra were recorded at 25 °C on Bruker Avance 300, 400, and 500 spectrometers. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a Perkin–Elmer 341 polarimeter. Elemental analysis was performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. Melting points were measured with a Stanford Research Systems OptiMelt MPA 100 instrument and are uncorrected. Diphenylvinylphosphane sulfide,[20] (+)-**1**[15] and (+)-**6**[16] were prepared following literature procedures.

Caution! *Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.*

Preparation of Dichloro Complex 3: A solution of (+)-**1** (0.47 g, 0.82 mmol) in dichloromethane (50 mL) was stirred for 2 h in the presence of a solution of silver perchlorate (1.0 g) in water (1 mL). The organic layer, after the removal of AgCl, was then washed with water (3 × 50 mL), dried ($MgSO_4$), and subsequently treated with diphenylvinylphosphane sulfide (0.20 g, 0.82 mmol) for 13 d at 40 °C. The crude diastereomeric mixture was treated with excess concentrated hydrochloric acid (2 mL) for 10 min at room temperature. The mixture was then washed with water (3 × 50 mL), dried ($MgSO_4$), and subsequently recrystallized from acetonitrile to give **3** as brown yellow crystals (0.40 g, 70%); m.p. 126–127 °C. $C_{26}H_{26}AsCl_2PPdS$ (653.77): calcd. C 48.4, H 4.2, N 2.0, S 4.6; found C 48.0, H 3.9, N 1.7, S 4.5. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 51.3 ppm. ^1H NMR (CD_2Cl_2): δ = 1.63 (s, 3 H, =CCH_3), 1.64 (s, 3 H, =CCH_3), 2.15 (dd, $^3J_{HH}$ = 10.6, $^2J_{PH}$ = 25.4 Hz, 1 H, P*CH*), 2.95 (m, 1 H, CHCH_2), 3.40 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, As*CH*), 3.45 (m, 1 H, CHCH_2), 3.55 (s, 1 H, As*CH*), 7.42–8.29 (m, 15 H, arom.) ppm.

Preparation of Dibromo Complex 4: The solution of **3** (0.07 g, 0.10 mmol) in dichloromethane (50 mL) was treated with excess potassium bromide (0.20 g) in acetone (50 mL) and water (10 mL) and stirred vigorously for 10 min at room temperature. The solvents were removed and the residue was extracted with dichloromethane and water and the organic layer was dried with $MgSO_4$. Removal of the solvent gave **4** as a solid, which was then recrystallized from dichloromethane/acetonitrile to give the product as orange yellow crystals (0.075 g, 96%); m.p. 131–132 °C. $C_{28}H_{29}AsBr_2NPPdS$ (783.69): calcd. C 42.9, H 3.7, N 1.8, S 4.1; found C 42.7, H 3.4, N 1.7, S 4.3. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 51.4 ppm. ^1H NMR (CD_2Cl_2): δ = 1.59 (s, 3 H, =CCH_3), 1.67 (s, 3 H, =CCH_3), 2.12 (dd, $^3J_{HH}$ = 11.0, $^2J_{PH}$ = 25.8 Hz, 1 H, P*CH*), 2.85 (m, 1 H, CHCH_2), 3.39 (d, $^3J_{HH}$ = 4.8 Hz, 1 H, As*CH*), 3.41 (m, 1 H, CHCH_2), 3.55 (s, 1 H, As*CH*), 7.43–8.28 (m, 15 H, arom.) ppm.

Preparation of Compound 5: Dibromo complex **4** (0.16 g, 0.22 mmol) in dichloromethane (30 mL) was treated with potassium cyanide (0.2 g) in water (30 mL) for 3 min at room temperature in air. The solution changed from red to colorless. The organic layer was washed with water (3 × 30 mL), dried ($MgSO_4$), and the solvent was removed. The residue was purified by column chromatography with dichloromethane to give compound **5** as a white solid (0.06 g, 84%); m.p. 94–95 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 49.0 ppm. ^1H NMR ($CDCl_3$): δ = 1.54 (s, 3 H, =CCH_3), 1.70 (s, 3 H, =CCH_3), 2.15 (m, 1 H, P*CH*), 2.78 (dd, $^3J_{HH}$ = 16.2, $^3J_{PH}$ = 32.3 Hz, 1 H, CHCH_2), 3.58 (dd, $^3J_{HH}$ = 10.0, $^3J_{PH}$ = 15.2 Hz, 1 H, CHCH_2), 5.37 (s, 1 H, =*CH*), 5.39 (s, 1 H, =*CH*), 7.42–7.95 (m, 10 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.0 (CH_3), 19.9 (d, $^4J_{PC}$ = 7.3 Hz, CH_3), 22.6 (d, $^2J_{PC}$ = 6.7 Hz, CH_2), 37.1 (d, $^1J_{PC}$ = 220.7 Hz, P*CH*), 116.1 (d, $^3J_{PC}$ = 20.4 Hz, =*CH*), 120.6 (d, $^2J_{PC}$ = 53.7 Hz, =*CH*), 128.0, 128.1, 128.4, 128.6, 129.9, 130.9, 131.1, 131.19, 131.2, 131.3, 131.4, 131.9, 132.3, 132.4, 132.9 (arom.), 133.4 (d, $^4J_{PC}$ = 14.8 Hz, =*C*CH_3), 137.8 (d, $^3J_{PC}$ = 47.5 Hz, =*C*CH_3) ppm. EI-MS: *m*/*z* (%)= 325.1 $[M]^+$.

Preparation of Complexes (S_c,R_{As})-7, (–)-8, (–)-9, and (S_c,R_{As})-10: A solution of (+)-**6** (0.26 g, 0.39 mmol) in dichloromethane (30 mL) was stirred for 2 h in the presence of a solution of silver perchlorate (0.15 g) in water (1 mL). The organic layer, after the removal of AgCl, was then washed with water (3 × 30 mL), dried ($MgSO_4$), and subsequently treated with diphenylvinylphosphane sulfide (0.10 g, 0.39 mmol) for 5 d at room temperature. The crude diastereomeric mixture was treated with excess concentrated hydrochloric acid (2 mL) for 20 min at room temperature.

Method A: The mixture was washed with water (3 × 30 mL), dried ($MgSO_4$), and subsequently recrystallized from dichloromethane/diethyl ether to give (–)-**8** as pale yellow crystals (0.08 g, 83%). $[\alpha]_D$ = –57.7 (c = 0.3, CH_2Cl_2); m.p. >300 °C. $C_{26}H_{26}AsCl_2PPtS$ (742.43): calcd. C 42.1, H 3.5, S 4.3; found C 42.2, H 3.9, S 4.1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 43.9 (s, J_{PtP} = 147 Hz, 1 P) ppm. ^1H NMR (CD_2Cl_2): δ = 1.46 (s, 3 H, =CCH_3), 1.59 (s, 3 H, =CCH_3), 1.92 (dd, $^3J_{HH}$ = 1.5, $^3J_{HH}$ = 12.2 Hz, 1 H, CHCH_2), 2.94 (m, 1 H, P*CH*), 3.16 (d, $^3J_{HH}$ = 10.6 Hz, 1 H, CHCH_2), 3.38 (s, 1 H, As*CH*), 3.42 (d, $^3J_{HH}$ = 5.2 Hz, 1 H, As*CH*), 7.32–8.18 (m, 15 H, arom.) ppm.

The solvents from the remaining solution were removed and the residue was isolated by column chromatography with dichloromethane/diethyl ether as elute to give (S_c,R_{As})-**7** as a yellow solid (0.18 g, 71%). $[\alpha]_D$ = +196.4 (c = 0.3, CH_2Cl_2); m.p. 160–161 °C. $C_{40}H_{42}AsClNO_4PPtS$ (969.26): calcd. C 49.6, H 4.4, N 1.5, S 3.3; found C 49.4, H 4.6, N 1.4, S 3.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 47.7 (s, J_{PtP} = 63 Hz, 1 P) ppm. ^1H NMR ($CDCl_3$): δ = 1.61 (s, 3 H, =CCH_3), 1.86 (d, $^3J_{HH}$ = 6.2 Hz, 3 H, CHCH_3), 2.00 (s, 3 H, =CCH_3), 2.63 (m, 1 H, CHCH_2), 2.71 (s, 3 H, NCH_3), 2.84 (m, 1 H, CHCH_2), 3.20 (d, $^3J_{HH}$ = 6.5 Hz, 1 H, As*CH*), 3.37 (s, 3 H, NCH_3), 3.70 (s, 1 H, As*CH*), 3.86 (broad s, 1 H, P*CH*), 4.65 (q, $^3J_{HH}$ = 6.2 Hz, 1 H, *CH*CH_3), 6.61–7.97 (m, 21 H, arom.) ppm.

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Table 1. Crystallographic data for complexes **3**, **4**, (–)-**8**, and (S_c,R_{As})-**10**.

	3	**4**	(–)-**8**	(S_c,R_{As})-**10**
*F*ormula	$C_{28}H_{29}AsCl_2NPPdS$	$C_{28}H_{29}AsBr_2NPPdS$	$C_{26}H_{26}AsCl_2PPtS$	$C_{40}H_{42}AsINPPtS$
Fw	694.77	783.69	742.41	996.69
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
a [Å]	12.5118(9)	12.4925(5)	9.4457(2)	13.4708(3)
b [Å]	18.4493(14)	18.7724(8)	12.4631(3)	16.2313(4)
c [Å]	13.1877(9)	13.3221(6)	21.4517(5)	17.7194(4)
α [°]	90	90	90	90
β [°]	110.221(4)	109.532(2)	90	90
γ [°]	90	90	90	90
V [Å^3]	2856.5(4)	2944.4(2)	2525.35(10)	3874.32(16)
Z	4	4	4	4
T [K]	173(2)	173(2)	173(2)	173(2)
$D_{calcd.}$ [g cm^{-3}]	1.616	1.768	1.953	1.709
λ [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm]$^{-1}$	2.134	4.603	7.228	5.389
F(000)	1392	1536	1432	1936
R_1 [obsd. data][a]	0.0619	0.0238	0.0232	0.0305
wR_2 [obsd. data][b]	0.1546	0.0505	0.0454	0.0706
Flack parameter	–	–	–0.001(4)	–0.003(6)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \sqrt{\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}}$, $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

Method B: The mixture was washed with water (3 × 30 mL), excess sodium iodide (0.2 g) in acetone (20 mL) was added and stirred for 10 min at room temperature. The solvents were removed and the diiodo complex (–)-**9** and (S_c,R_{As})-**10** were easily isolated by column chromatography with dichloromethane/diethyl ether as elute. Complex (–)-**9** was recrystallized with dichloromethane/diethyl ether to produce yellow crystals (0.09 g, 75%). $[\alpha]_D$ = –48.8 (*c* = 0.1, CH_2Cl_2); m.p. 186–187 °C. $C_{26}H_{26}AsI_2PPtS$ (925.33): calcd. C 33.8, H 2.8, S 3.5; found C 34.0, H 2.9, S 3.3. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* = 44.4 (s, J_{PtP} = 132 Hz, 1 P) ppm. ^1H NMR (CD_2Cl_2): *δ* = 1.57 (d, $^5J_{HH}$ = 0.8 Hz, 3 H, =C*CH*$_3$), 1.75 (s, 3 H, =C*CH*$_3$), 1.97 (dt, $^3J_{HH}$ = 11.9, $^2J_{PH}$ = 12.1 Hz, 1 H, P*CH*), 2.83 (m, 1 H, CH*CH*$_2$), 3.28 (m, 1 H, CH*CH*$_2$), 3.46 (s, 1 H, As*CH*), 3.47 (d, $^3J_{HH}$ = 5.2 Hz, 1 H, As*CH*), 7.42–8.27 (m, 15 H, arom.) ppm. Complex (S_c,R_{As})-**10** was recrystallized with dichloromethane/diethyl ether to produce yellow crystals (0.19 g, 73%). $[\alpha]_D$ = +171.4 (*c* = 0.35, CH_2Cl_2); m.p. 180–181 °C. $C_{40}H_{42}AsINPPtS$ (996.71): calcd. C 48.2, H 4.3, N 1.4, S 3.2; found C 48.4, H 4.1, N 1.2, S 3.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ* = 47.2 ppm. ^1H NMR ($CDCl_3$): *δ* = 1.65 (s, 3 H, =C*CH*$_3$), 1.87 (d, $^3J_{HH}$ = 6.1 Hz, 3 H, CH*CH*$_3$), 2.04 (s, 3 H, =C*CH*$_3$), 2.73 (s, 3 H, N*CH*$_3$), 2.78 (m, 1 H, CH*CH*$_2$), 2.89 (q, $^3J_{HH}$ = $^2J_{PH}$ = 11.5 Hz, 1 H, P*CH*), 3.19 (d, $^3J_{PH}$ = 6.4 Hz, 1 H, As*CH*), 3.39 (s, 3 H, N*CH*$_3$), 3.70 (s, 1 H, As*CH*), 4.60 (broad s, 1 H, CH*CH*$_2$), 4.68 (q, $^3J_{HH}$ = 6.2 Hz, 1 H, *CH*CH$_3$), 7.10–8.41 (m, 21 H, arom.) ppm.

Removal of Chiral Auxiliary: Synthesis of Dichloro Complex (+)-8: The optically pure (S_c,R_{As})-**7** (0.14 g, 0.14 mmol) [or (S_c,R_{As})-10] was dissolved in dichloromethane (30 mL) and treated with excess concentrated hydrochloric acid (2 mL) for 4 h at room temperature. The solution was washed with water (3 × 30 mL) and dried ($MgSO_4$). The solvent was removed and the residue was subsequently recrystallized from dichloromethane/diethyl ether to give (+)-**8** as yellow crystals (0.09 g, 84%); $[\alpha]_D$ = +80.5 (*c* = 0.2, CH_2Cl_2). Other data were the same as complex (–)-**8**.

Liberation of the As/P=S Ligand (+)-11: A solution of (–)-**9** (0.06 g, 0.06 mmol) in dichloromethane (10 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.0 g) for 15 min. The organic layer was separated, then washed with water (3 × 10 mL), and dried ($MgSO_4$). Upon removal of the solvent, the free ligand (+)-**11** was obtained as an air-sensitive solid in quantitative yield. $[\alpha]_D$ = +44.3 (*c* = 0.43, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ* = 48.0 ppm.

X-ray Crystal Structure Determination: Crystallographic data for complexes **3**, **4**, (–)-**8**, and (S_c,R_{As})-**10** are given in Table 1. Diffraction data were collected with a Bruker X8 CCD diffractometer with Mo-K_α radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The absolute configuration of the chiral complex was determined unambiguously by using the Flack parameter.

CCDC-757121 (for **3**), -757122 (for **4**), -757123 [for (–)-**8**], and -757120 [for (S_c,R_{As})-**10**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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