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Coordination chemistry, reactivities, and stereoelectronic properties of chelating phosphine ligands containing thioamide substituents

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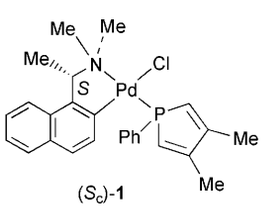
The intramolecular *exo*-cycloaddition reaction between *N*,*N*-dimethylthioacrylamide and 3,4-dimethyl-1-phenylphosphole in the presence of a perchloratopalladium template containing *ortho*-metallated (*S*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary gave the corresponding thioamide-substituted P-chiral phosphanorbornene stereospecifically in 6 d. The *exo*-cycloadduct coordinated to the palladium template as a bidentate chelate *via* its phosphorus and thioamide-sulfur donor atoms. The corresponding intermolecular *endo*-cycloaddition reaction using the analogous chloropalladium template containing the same *ortho*-metallated naphthylamine auxiliary produced a pair of separable diastereomeric *endo*-cycloadducts in 60 d. Both the *endo*-cycloadducts coordinated to the palladium template as monodentates *via* their phosphorus donor atoms and their thioamide functions were not involved in the metal complexation. The faster rate observed in the *exo*-cycloaddition reaction is attributed to the electronic polarization and hence the activation of *N*,*N*-dimethylthioacrylamide *via* thioamide-*S* coordination. Optically active thioamide-substituted phosphanorbornenes could be liberated from these product complexes by treatment with aqueous cyanide. For comparison purposes, the novel ligand $Ph_2PC(S)NMe_2$ was prepared. This short-chain ligand displaced acetonitrile and monodentate phosphine ligands on Pd^{II} to form stable 4-membered P–S chelates. The C=S bond in these sterically hindered chelates are unreactive toward cycloaddition reaction with the phosphole cyclic diene. The thioamido (S)C–N bonds in this series of P–S palladium(II) chelates were found to be significantly shorter than those reported for organic thioamides and their non-chelating counterparts in the *endo*-cycloadducts, thus indicating that nitrogen in the thioamide function contributed electronically to the stability of the Pd→S bonds.

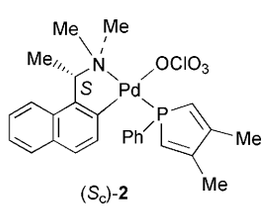
Introduction

Ever since the discovery of the Grignard reaction much attention has been focused on the application of metals and metal ions in organic synthesis.[1] The importance of these classic inorganic materials in synthetic chemistry has been well recognized. Numerous excellent achievements in the field of metals and metal complex promoted and catalysed reactions have indeed changed profoundly the strategic thinking of synthetic chemists. Recently, we have been interested in the palladium template syntheses of a series of functionalized chiral phosphanorbornenes *via* [4 + 2] cycloaddition reactions.[2,3] These asymmetric syntheses involve both the metal activation of 3,4-dimethyl-1-phenylphosphole (DMPP) as the cyclic diene and the subsequent stereochemically controlled formation of carbon–carbon bonds with various dienophiles in the presence of a highly efficient chiral *ortho*-palladated naphthylamine template. In most of these syntheses the *endo*- and the *exo*-cycloaddition reaction pathways can effectively be controlled by manipulating the number of template sites available for these intra- and inter-molecular Diels–Alder reactions. In this paper we report the template synthesis and coordination chemistry of the first optically active thioamide-substituted phosphanorbornenes. Unlike most documented P–S heterobidentates which contain thiolato or thioether sulfur donors, examples of neutral phosphine ligands containing thiocarbonyl C=S sulfur donors are rare.[4] This is somewhat surprising as thiocarbonyl compounds are well developed by organic chemists and transition metal complexes containing simple thiocarbonyl–S donor atoms have long been reported.[5,6]

We have recently reported that the coordinated DMPP in the chiral chloro complex (S_c)-**1** reacts as a typical cyclic diene towards the intermolecular [4 + 2] *endo*-cycloaddition.[2,3] For example, when (S_c)-**1** was treated with *N*,*N*-dimethylacrylamide at room temperature for 32 d the corresponding intermolecular cycloaddition reaction occurred and the two possible *endo*-cycloadducts were obtained as a separable 1 : 3 diastereomeric mixture. The slow reaction rate has been attributed to the inherent low dienophilicities of *N*,*N*-dimethylacrylamide.[3] On the other hand, when the kinetically and thermodynamically stable chloro ligand in (S_c)-**1** was replaced by a kinetically labile



(S_c)-**1**



(S_c)-**2**

perchlorate the potential donor atoms in the dienophiles were able to interact with the palladium template and adopt the alternative intra-molecular *exo*-cycloaddition pathway. Thus when *N*,*N*-dimethylacrylamide was treated with (S_c)-**2** for 3 d under similar conditions to those employed in the *endo*-cycloaddition process the corresponding optically pure P–O chelating *exo*-cycloadduct was obtained quantitatively. The dramatic acceleration observed in the *exo*-cycloaddition process had been attributed to electronic activation of the dienophile *via* amido-O coordination to the readily available template site on (S_c)-**2**. In view of these drastic stereoelectronic template effects associated with *N*,*N*-dimethylacrylamide, we were interested to analyse the analogous *exo*- and *endo*-cycloaddition reactions involving *N*,*N*-dimethylthioacrylamide

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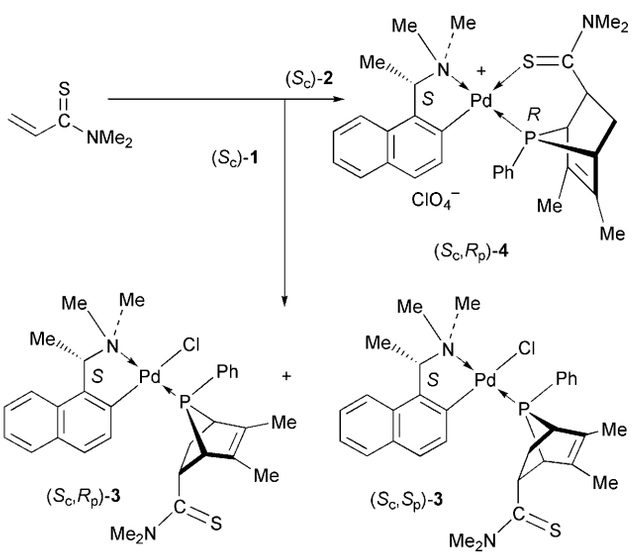
where the amido-oxygen is replaced by a sulfur atom. It is well known that sulfur exhibits a lower electronegativity than oxygen in organic chemistry. Therefore, *N*,*N*-dimethylthioacrylamide itself is expected to be a weaker dienophile than *N*,*N*-dimethylacrylamide. Compared with oxygen, however, sulfur generally shows higher affinities to the soft palladium(II) ion. Thus it is possible that the stronger sulfur–palladium coordination would further activate the reactivity of the thioamide-substituted dienophile in the metal-template promoted *exo*-cycloaddition reaction.

Results and discussion

Metal template promoted cycloaddition of DMPP with *N*,*N*-dimethylthioacrylamide

N,*N*-Dimethylthioacrylamide was prepared from the corresponding *N*,*N*-dimethylacrylamide using the standard Lawesson's Reagent as the thionation reagent.[5] As expected, the thioamide-substituted dienophile is clearly less reactive than *N*,*N*-dimethylacrylamide in the intermolecular *endo*-cycloaddition reaction with DMPP. The reaction between the thioamide substituted dienophile and (S_c)-**1** at room temperature in dichloromethane was found to be complete in 60 d (Scheme 1).



Scheme 1

However, under similar conditions the corresponding cycloaddition reaction with acrylamide required only 30 d for completion. Interestingly, the stereoselectivities observed with the two dienophiles in these *endo*-cycloaddition processes were similar. The ^{31}P NMR spectra of the crude thio-substituted cycloadducts in $CDCl_3$ exhibited two sharp singlets at δ 121.6 and 123.1 in the ratio of 3:1. No other ^{31}P NMR signals were recorded in the low field region thus indicating that only two diastereomeric phosphanorbornenes were formed in the cycloaddition reaction. The major diastereomer (S_c,S_p)-**3** could be isolated from the product mixture by silica-gel column chromatography in 39% yield. The pale yellow complex crystallized from dichloromethane–diethyl ether as bright yellow prisms with α −60° (589 nm, *d*-chloroform). The diastereomer crystallizes as a pair of crystallographically independent molecules [**I** and **II**] in the asymmetric unit cell. However, the two molecules have the same absolute stereochemistry and molecular connectivity and differ only in the rotational angles along the P–Pd bonds. For clarity, only one molecule of (S_c,S_p)-**3** [**I**] is depicted in Fig. 1. Selected bond lengths and bond angles of both molecules are give in Table 1. The X-ray analysis confirms that the chiral phosphanorbornene coordinates to the palladium template as a monodentate ligand solely *via* its phosphorus. Both the sulfur and the nitrogen atoms in the thioamide function are not involved in metal complexation. The absolute configurations of the four newly generated stereogenic centres at P(1), C(15), C(18) and C(20) are *S*, *R*, *S* and *S*, respectively, with the thioamide functional group orientated in the *endo* position at C(20). The minor diastereomer (S_c,R_p)-**3** could not be induced to crystallize.

Table 1 Selected bond lengths (Å) and angles (°) for complex (S_c,S_p)-**3**

Molecule **I**		Molecule **II**	
Pd(1)–P(1)	2.224(1)	Pd(2)–P(2)	2.227(1)
Pd(1)–Cl(1)	2.401(1)	Pd(2)–Cl(2)	2.395(1)
Pd(1)–Cl(1)	2.014(3)	Pd(2)–C(41)	2.008(4)
Pd(1)–N(1)	2.152(3)	Pd(2)–N(2)	2.149(3)
P(1)–C(15)	1.842(4)	P(2)–C(55)	1.853(4)
P(1)–C(18)	1.845(4)	P(2)–C(58)	1.853(3)
C(16)–C(17)	1.331(5)	C(56)–C(57)	1.332(5)
C(19)–C(20)	1.537(5)	C(59)–C(60)	1.552(5)
C(20)–C(21)	1.528(6)	C(60)–C(61)	1.520(6)
S(1)–C(21)	1.687(4)	S(2)–C(61)	1.671(4)
N(3)–C(21)	1.326(5)	N(4)–C(61)	1.344(6)
N(1)–Pd(1)–Cl(1)	95.5(1)	N(2)–Pd(2)–Cl(2)	95.4(1)
N(1)–Pd(1)–C(1)	80.9(1)	N(2)–Pd(2)–C(41)	81.0(1)
N(1)–Pd(1)–P(1)	173.4(1)	N(2)–Pd(2)–P(2)	171.5(1)
Cl(1)–Pd(1)–C(1)	176.1(1)	Cl(2)–Pd(2)–C(41)	175.4(1)
Cl(1)–Pd(1)–P(1)	91.1(1)	Cl(2)–Pd(2)–P(2)	89.5(1)
C(1)–Pd(1)–P(1)	92.5(1)	C(41)–Pd(2)–P(2)	94.5(1)
C(15)–P(1)–C(18)	81.4(2)	C(55)–P(2)–C(58)	80.7(2)
C(20)–C(21)–N(3)	117.4(4)	C(60)–C(61)–N(4)	116.5(4)
C(20)–C(21)–S(1)	121.5(3)	C(60)–C(61)–S(2)	122.1(3)
N(3)–C(21)–S(1)	121.0(3)	N(4)–C(61)–S(2)	121.4(3)

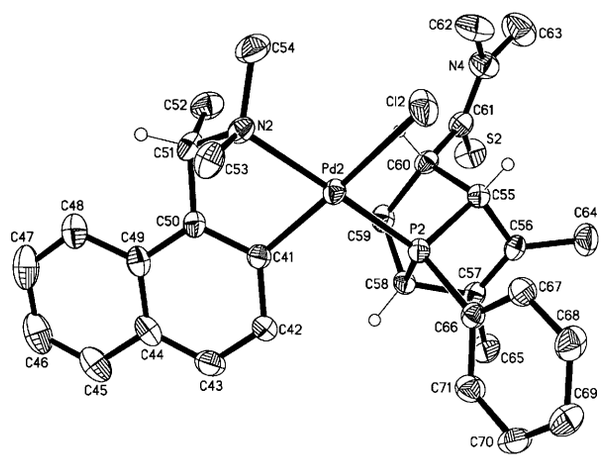


Fig. 1 The molecular structure and the absolute stereochemistry of complex (S_c,S_p)-**3**.

Relative to the rate observed in the *endo*-cycloaddition reaction, the *exo*-cycloaddition reaction between complex (S_c)-**2** and *N*,*N*-dimethylthioacrylamide under similar conditions may be regarded as a fast process. The chiral template promoted intramolecular cycloaddition was monitored by ^{31}P NMR spectrscopy and found to be complete in 6 d. Furthermore, a high stereoselectivity was observed as, prior to purification, the ^{31}P NMR spectrum of the crude cycloadducts in $CDCl_3$ recorded only one sharp singlet at δ 109.7 with no other signals in this low field region. The spectrum thus indicated that only one cycloadduct was formed stereospecifically in this cycloaddition reaction. The cationic complex **4** was subsequently crystallized from acetone as pale yellow prisms in 58% yield, α +221.5° (589 nm, dichloromethane). The X-ray structural analysis confirmed that this sole cycloadduct is (S_c,R_p)-**4** as depicted in Scheme 1 and the *exo*-thioamide substituted phosphanorbornene is coordinated to the chiral palladium as a bidentate chelate *via* the bridgehead phosphorus and the

Table 2 Selected bond lengths (Å) and angles (°) for the cationic complex (S_c,R_p)-**4**

Pd–P(16)	2.203(1)	C(24)–C(25)	1.333(6)
Pd–C(1)	2.017(4)	C(26)–C(27)	1.552(5)
Pd–S(35)	2.382(1)	C(27)–C(28)	1.571(6)
Pd–N(12)	2.172(3)	C(27)–C(31)	1.517(5)
P(16)–C(23)	1.854(4)	C(31)–S(35)	1.711(4)
P(16)–C(26)	1.840(4)	C(31)–N(32)	1.309(6)
N(12)–Pd–S(35)	93.8(1)	C(1)–Pd–P(16)	93.4(1)
N(12)–Pd–C(1)	80.6(1)	C(23)–P(16)–C(26)	81.3(2)
N(12)–Pd–P(16)	166.8(1)	C(27)–C(31)–N(32)	117.9(4)
S(35)–Pd–C(1)	172.3(1)	C(27)–C(31)–S(35)	122.9(3)
S(35)–Pd–P(16)	93.2(1)	N(32)–C(31)–S(35)	119.2(3)
C(31)–S(35)–Pd	107.5(1)	C(27)–C(26)–P(16)	101.0(2)

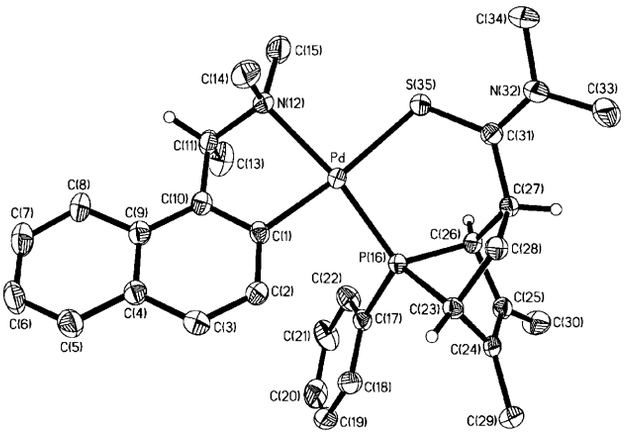
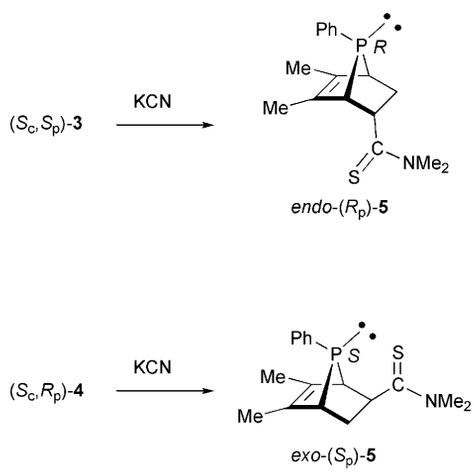


Fig. 2 The molecular structure and absolute stereochemistry of the cation in complex (S_c,R_p)-**4**.

thioamide-sulfur donor atoms (Fig. 2). The absolute configurations of the four new chiral centres at P(16), C(23), C(26) and C(27) are *R*, *R*, *S* and *S*, respectively, with the thioamide functional group orientated in the *exo* position at C(27). It is noteworthy that the C=S bond in (S_c,R_p)-**4** [1.711(4) Å, Table 2] is notably longer than that observed in monodentate complex (S_c,S_p)-**3** [1.687(4) Å in molecule **I** and 1.671(4) Å in **II**]. The lengthening of the C=S bond in the *S*-bonded complex is an indication of the weakening of the double bond character *via* coordination. Interestingly, however, the thioamido C(31)–N(32) distance [1.309(6) Å] in the bidentate complex (S_c,R_p)-**4** is clearly shorter than those observed in the *endo* complex (S_c,S_p)-**3** [1.326(5) Å in molecule **I** and 1.344(6) Å in **II**]. The shortening of the thioamido (S)C–N bond together with the lengthening of the C=S bond in (S_c,R_p)-**4** suggests that the all three S=C–N atoms of the thioamide group contribute electronically to the S→Pd coordination. It is noted that the previously reported oxygen-substituted amidophosphanorbornene palladium complexes exhibit similar, but less dramatic, coordination effects on the amido group.[3] For example, the C=O distance in the *exo*-bidentate-*P,O* complex is 1.252(7) Å, which is slightly longer than that recorded for the two monodentate-*P endo*-diastereomers [1.220(5) and 1.237(8) Å, respectively].[3] Consistent with the thioamide analogues, the amido (O)C–N distance in the reported P–O chelate is 1.321(7) Å which is somewhat shorter than that recorded for the two diastereomeric non-chelating *endo*-counterparts [1.335(6) and 1.353(9) Å, respectively].[3] In analysing the changes in the bond distances, it appears that the nitrogen atom in the thioamide chelate is significantly more sensitive to coordination effects than its counterpart in the previously reported amido-*P,O* complex.

As with the accelerated *exo*-cycloaddition reaction observed with *N*,*N*-dimethylacrylamide, the thioamide-substituted dienophile evidently can be activated *via* metal complexation. With both dienophiles, the intramolecular *exo*-cycloaddition processes involving (S_c)-**2** occurred *ca*. 10 times faster than the corresponding intermolecular *endo*-Diels–Alder reaction. However, it was expected that the strong sulfur–palladium bond would produce a more dramatic electronic polarizing effect on the thioamide-substituted dienophile. Apparently, this electronic polarization effect was transmitted predominantly to the amido-nitrogen atom rather than to the reacting vinylic C=C bond. This interesting electronic divergence made the *exo*-cycloaddition with *N*,*N*-dimethylthioacrylamide proceed at a slower rate than that involving *N*,*N*-dimethylacrylamide, despite the fact that the S→Pd bond is more stable than the O→Pd bond.

It is noteworthy that optically active phosphanorbornenes *endo*-(R_p)-**5** and *exo*-(S_p)-**5** could be liberated by treatment of (S_c,S_p)-**3** and (S_c,R_p)-**4**, respectively, with aqueous potassium cyanide (Scheme 2). The apparent inversion of configuration



Scheme 2

that takes place at the phosphorus stereogenic centres when the phosphanorbornenes are liberated from the metal is merely the consequence of the Cahn–Ingold–Prelog (CIP) sequence rules.[7] These liberated ligands are highly air-sensitive and configurationally unstable. Hence they must be recomplexed to selected metal ions within 30 min.

Coordination chemistry and reactivity of diphenylphosphino-*N*,*N*-dimethylthioamide

The isolation and the structural investigation of complex (S_c,R_p)-**4** suggest that, due to the electronic properties of the thioamide function, chelating agents containing phosphorus and amido-sulfur donor atoms are powerful sequesterers for palladium(II). To investigate further the full potential of this class of P–S metal complexation and the reactivities of the amido C=S bonding, the thioamide-substituted phosphine **6** was prepared (Scheme 3). This ligand was designed with the intention of examining the electronic contribution of the amido group towards metal complexation and the reactivity of the C=S towards the cycloaddition reaction. It has been established that C=S bonds in thioamides are able to undergo a hetero Diels–Alder reaction.[8] Furthermore, the thiocarbonyl function in **6** is located at the vinylic position with respect to the phosphorus donor atom. We have reported that the C=C bonds in coordinated vinylphosphines are able to function as dienophiles toward cycloaddition reaction with DMPP.[9] In reactivity considerations, however, the formation of a stable P–S chelation may deter the dienophilicity of **6** as the C=S bond becomes part of a chelate ring. In steric considerations, on the other hand, the sterically unfavorable 4-membered ring may be kinetically labile and thus allow the C=S bond to undergo the coupling reaction. We have previously reported a series of kinetically labile palladium(II) complexes containing thiophosphine chelates.[10]

Table 3 Selected bond lengths (Å) and angles (°) for complex **7**

Pd(1)–P(1)	2.209(1)	C(1)–S(1)	1.705(3)
Pd(1)–S(1)	2.290(1)	C(1)–P(1)	1.838(2)
Pd(1)–Cl(1)	2.329(1)	C(1)–N(1)	1.298(3)
Pd(1)–Cl(2)	2.376(1)	C(2)–N(1)	1.466(3)
S(1)–Pd(1)–Cl(1)	169.7(1)	C(1)–P(1)–Pd(1)	91.1(1)
S(1)–Pd(1)–Cl(2)	95.0(1)	C(1)–S(1)–Pd(1)	91.9(1)
S(1)–Pd(1)–P(1)	75.2(1)	S(1)–C(1)–N(1)	126.1(2)
Cl(1)–Pd(1)–P(1)	94.6(1)	S(1)–C(1)–P(1)	101.5(1)
Cl(2)–Pd(1)–P(1)	170.1(1)	N(1)–C(1)–P(1)	132.3(2)
Cl(2)–Pd(1)–Cl(1)	95.3(1)	C(1)–N(1)–C(2)	120.2(2)

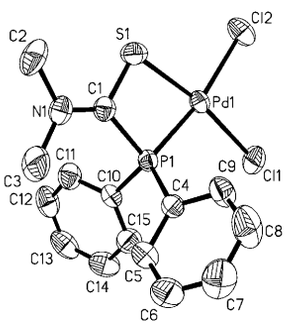
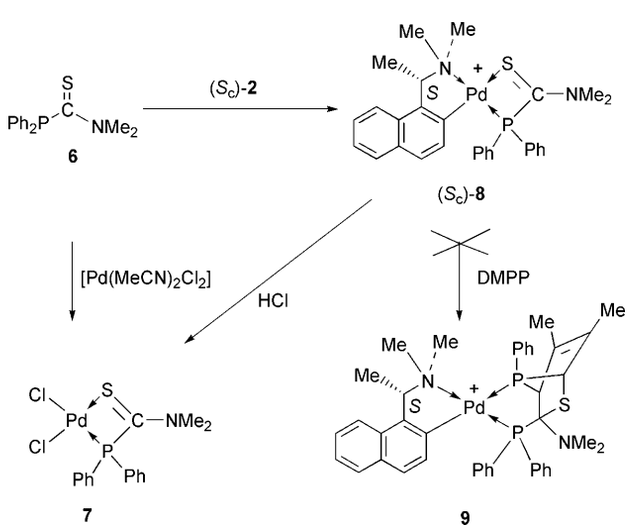


Fig. 3 The molecular structure of the dichloro complex **7**.



Scheme 3

The phosphine ligand **6** was obtained as a stable yellow solid from the reaction between sodium diphenylphosphide and dimethylthiocarbamoyl chloride in THF. The ^{31}P NMR spectrum of **6** in $CDCl_3$ exhibited a sharp singlet at δ 18.4. In the absence of other strong donor atoms, the thioamide-substituted ligand is able to form a P–S chelate with Pd^{II}. Thus when **6** was treated with $[Pd(MeCN)_2Cl_2]$ in dichloromethane the dichloro complex **7** was formed immediately. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited only one sharp singlet at δ −29.6. The neutral complex was subsequently crystallized from dichloromethane–diethyl ether as yellow prisms. The molecular structure and the coordination chemistry of **7** were studied by X-ray structural analysis (Fig. 3). Selected bond lengths and bond angles are given in Table 3. The X-ray analysis revealed that the short-chain thioamido-phosphine ligand was indeed coordinated to palladium(II) as a bidentate chelate *via* its phosphorus and sulfur donor atoms to form a 4-membered ring. The geometry at palladium is distorted square planar with angles at palladium in the range 75.2(1)–95.3(1)°. The C(1)–S(1)–Pd(1) and C(1)–P(1)–Pd(1) angles [91.9(1) and 91.1(1)°, respectively] within the 4-member chelate ring are acute. The N(1)–C(1)–P(1) angle [132.3(2)°] is enlarged, presumably due to the steric repulsion between the projecting NMe group and the PPh rings. The C=S bond distance [1.705(3) Å] is comparable with that recorded for (S_c,R_p)-**4**. However, the N–C distance [1.298(3) Å] in the amido function of **7** is clearly shorter than those observed in organic thioamides[6] and in both (S_c,S_p)-**3** and (S_c,R_p)-**4**. The short N(1)–C(1) distance once again reaffirmed clearly that the amido-nitrogen atom, although not directly attached to palladium, is electronically involved in the metal–thioamide sulfur coordination. Furthermore, the S→Pd bond in the 4-membered chelate was found to be kinetically stable as no cycloaddition reaction occurred between **7** and DMPP, despite the strong reaction conditions that were used.

Interestingly, the thioamido-substituted phosphine **6** was found to displace DMPP from (S_c)-**2** to give the cationic complex (S_c)-**8** regiospecifically in quantitative yield, α −60.0° (589 nm, dichloromethane). The ^{31}P NMR spectrum of (S_c)-**8** in $CDCl_3$ showed a singlet at δ 8.4. Once again, the 4-member ring and the C=S bond in this cationic complex were found to be stable and unreactive. Attempts to prepare complex **9** from the cycloaddition reaction between DMPP and (S_c)-**8** were unsuccessful. In all these attempts, (S_c)-**8** remained unchanged even though strong reaction conditions were used. The P–S chelate was also found to be stable under strong acidic conditions. Thus, when (S_c)-**8** was treated with concentrated HCl only the *ortho*-metallated naphthylamine auxiliary was removed chemoselectively to give the dichloro complex **7** in quantitative yield.

In this work the formation of the non-chelating *endo*-cycloadduct (S_c,S_p)-**3** indicates that the thioamide functional group in *N*,*N*-dimethylthioacrylamide may not be a sufficiently strong donor system to form stable monodentate complexes with palladium(II). The solid state structural features and the reactivities of (S_c,R_p)-**4** and **7**, however, clearly illustrate that with the assistance of a phosphorus donor the nitrogen atom in the thioamide function plays an important role to the kinetic and thermodynamic stabilities of the thioamido P–S bidentate chelates.

Experimental

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. For NMR, proton spectra were recorded at 500.14 MHz and ^{31}P spectra at 202.46 MHz on Bruker ACF 300 and AMX500 NMR spectrometers. Molar conductivities were measured with a Horiba ES-12 conductivity meter for 10^{-3} M solutions of the complexes at 25 °C. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

N,*N*-Dimethylthioacrylamide[5] and the chiral complexes (S_c)-**1** and (S_c)-**2**[2,3] were obtained as previously described.

endo-Cycloaddition reaction: isolation of chloro{(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*^{2},*N*}{(1α,4α,5β,7*S*)-5-(*N*,*N*-dimethylthiocarbamoyl)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{7}}palladium(II) (S_c,S_p)-3

A mixture of complex (S_c)-**2** (0.20 g, 0.38 mmol) and *N*,*N*-dimethylthioacrylamide (0.21 g, 1.9 mmol) in dichloroethane (30 cm^3) was stirred for 60 d at room temperature. The solvent was removed under reduced pressure to give a black residue. This material was chromatographed on a silica column (50 g, Merck, 40–63 μm) giving the diastereomeric neutral complexes (S_c,R_p)-**3** and (S_c,S_p)-**3** in 22 and 39% yield, respectively. Complex (S_c,S_p)-**3** could be crystallized from dichloromethane–diethyl ether as pale yellow prisms, mp 209–210 °C (decomp.) (Found: C, 57.7; H, 5.8; N, 4.4; S, 4.8. Calc. for $C_{31}H_{38}ClN_2PPdS$: C, 57.9; H, 5.9; N, 4.4; S, 5.0%). α −60.0° (589 nm, *c* 0.1 g per 100 cm^3, $CDCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 3 H, C=CMe), 1.83 (s, 3 H, C=CMe), 1.92 (d, 3 H, $^3J_{HH}$ = 6.0,

Table 4 Crystallographic data for complexes (S_c,S_p)-**3**, (S_c,R_p)-**4** and **7**

	(S_c,S_p)-**3**	(S_c,R_p)-**4**	**7**
Formula	$C_{31}H_{38}ClN_2PPdS{\cdot}0.5Et_2O$	$C_{31}H_{38}ClN_2O_4PPdS$	$C_{15}H_{16}Cl_2NPPdS$
M	680.57	707.51	450.62
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
a/Å	12.5862(4)	10.7346(2)	10.1583(2)
b/Å	22.6849(7)	14.3998(3)	12.3121
c/Å	23.3035(7)	20.3434(2)	14.4431
β/°			98.122(1)
V/Å^3	6653.5(4)	3144.60(9)	1788.28(5)
Z	8	4	4
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
μ/cm^{-1}	7.75	8.31	15.34
$R1$ (obs. data)	0.0362	0.0379	0.0291
$wR2$ (obs. data)	0.0716	0.0891	0.0618

CH*Me*), 2.36–2.43 (m, 1 H, $CH_{(exo)}H_{(endo)}$), 2.56 (s, 3 H, NMe), 2.86 (d, 3 H, $^4J_{PH}$ = 2.8, N*Me*), 3.00–3.16 (m, 2 H, $CH_{(exo)}$-$H_{(endo)}$ + PCH), 3.47 (s, 3H, C(S)NMe), 3.67 (bs, 1 H, PCH), 3.76 (s, 3H, C(S)NMe), 4.28 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2, C*H*Me), 4.80–4.84 (m, 1 H, C(S)CH), 7.08 (dd, 1 H, $^3J_{HH}$ = 8.4, $^4J_{PH}$ = 6.4 Hz, naphthyl H_γ) and 7.33–7.96 (m, 10 H, aromatics). ^{31}P-{H} NMR ($CDCl_3$): δ 121.6 (s, 1P). Complex (S_c,R_p)-**3** could not be induced to crystallize in all solvent systems attempted.

exo-Cycloaddition reaction: isolation of {(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*^{2},*N*}{(1α,4α,5α,7*R*)-5-(*N*,*N*-dimethylthiocarbamoyl)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{7},*S*}palladium(II) perchlorate, (S_c,R_p)-4

A mixture of the perchlorato complex (S_c)-**2** (0.66 g, 1.1 mmol) and *N*,*N*-dimethylthioacrylamide (0.64 g, 5.58 mmol) in dichloroethane (50 cm^3) was stirred for 6 d at room temperature. The solvent was removed under reduced pressure to give a yellow residue. This material was crystallized from acetone as pale yellow prisms (0.39 g, 58%), mp 219–223 °C (decomp.) (Found: C, 52.3; H, 5.4; N, 4.1; S, 4.2. Calc. for $C_{31}H_{38}ClN_2O_4PPdS$: C, 52.6; H, 5.4; N, 4.0; S, 4.5%). α +221.5° (589 nm, c 0.5 g per 100 cm^3, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 3 H, C=CMe), 1.78 (d, 3 H, $^3J_{HH}$ = 6.0, CH*Me*), 1.96 (s, 3 H, C=CMe), 2.44–2.66 (m, 1 H, $CH_{(exo)}H_{(endo)}$), 2.56 (s, 3 H, NMe), 2.70–2.79 (m, 2 H, $CH_{(exo)}H_{(endo)}$) 2.87 (d, 3 H, $^4J_{PH}$ = 3.3, NMe), 3.05 (s, 1 H, PCH), 3.56–3,69 (m, 2H, C(S)CH + PCH), 3.71 (s, 3H, C(S)NMe), 3.74 (s, 3H, C(S)NMe), 4.31 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me) and 7.07–7.67 (m, 11 H, aromatics). ^{31}P-{H} NMR ($CDCl_3$): δ 109.7 (s, 1P).

Liberation of (1α,4α,5β,7*S*)-5-(*N*,*N*-dimethylthiocarbamoyl)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene, *endo*-(R_p)-5

A solution of complex (S_c,S_p)-**3** (0.41 g, 0.06 mmol) in dichloromethane (10 cm^3) was stirred for 2 h with an excess of potassium cyanide (0.42 g, 6.4 mmol) in water (1 cm^3). The organic layer was separated, washed consecutively with water and dilute sulfuric acid (to remove the naphthylamine auxiliary) and finally dried over $MgSO_4$. Removal of the solvent left a viscous oil (0.01 g, 51%). α −15.0° (589 nm, c 0.5 g per 100 cm^3, CH_2Cl_2). ^{31}P-{H} NMR ($CDCl_3$): δ 120.2 (s, 1P). The bidentate ligand *exo*-(S_p)-**5** was similarly liberated from (S_c,R_p)-**4**. α +114.0° (589 nm, c 0.5 g per 100 cm^3, CH_2Cl_2). ^{31}P-{H} NMR ($CDCl_3$): δ 98.8 (s, 1P).

Syntheses

***N*,*N*-Dimethyl(diphenylphosphino)thioformamide, 6.** A solution of *N*,*N*-dimethylthiocarbamoyl chloride (0.73 g, 5.9 mmol) in THF (30 cm^3) was added over a period of 10 min to a solution of sodium diphenylphosphide, that had previously been prepared from diphenylphosphine (1.1 g, 5.9 mmol) and sodium foil (0.14 g, 5.9 mmol) in the same solvent. After the addition the reaction mixture was stirred at room temperature for 8 h. At this stage the solvent was removed under reduced pressure and the residue treated with water (3 × 30 cm^3). The product was extracted with dichloromethane and subsequently chromatographed on a silica column with dichloromethane–hexane (7 : 3). Pure ligand **6** was thus obtained as yellow crystals (0.88 g, 55%), mp 108–110 °C (decomp.) (Found: C, 65.7; H, 6.1; N, 4.8; S, 12.1. Calc. for $C_{15}H_{16}NPS$: C, 65.9; H, 5.9; N, 5.1; S, 11.7%). ^{1}H NMR ($CDCl_3$): δ 3.39 (d, 3 H, $^4J_{PH}$ = 1.2 Hz, NMe), 3.54 (s, 3 H, NMe) and 7.03–7.69 (m, 10 H, aromatics). ^{31}P-{H} NMR ($CDCl_3$): δ 18.4 (s, 1P). ^{13}C-{H} NMR ($CDCl_3$): δ 43.6 (d, $^3J_{PC}$ = 22.7, NMe), 44.8 (s, NMe), 128.4–134.8 (m, aromatics) and 208.5 (d, $^1J_{PC}$ = 30.3 Hz, S=C).

Dichloro{*N*,*N*-dimethyl(diphenylphosphino)thioformamide-*S*,*P*}palladium(II), 7. A solution of [$Pd(MeCN)_2Cl_2$] (0.08 g, 0.2 mmol) in dichloromethane (30 cm^3) was treated with the thioamide ligand **6** (0.06 g, 0.2 mmol) in the same solvent for 30 min. The dichloro complex **7** was filtered off and washed with diethyl ether. It was subsequently crystallized from acetone–diethyl ether as pale yellow prisms (0.07 g, 71%), mp 220–221 °C (decomp.) (Found: C, 39.7; H, 3.4; N, 3.4; S, 6.7. Calc. for $C_{15}H_{16}Cl_2NPPdS$: C, 40.0; H, 3.6; N, 3.1; S, 7.1%). ^{1}H NMR (CD_2Cl_2): δ 3.20 (s, 3 H, NMe), 3.45 (s, 3 H, NMe) and 7.62–7.96 (m, 10 H, aromatics). ^{31}P-{H} NMR (CD_2Cl_2): δ −29.6 (s, 1P).

{(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*^{2},*N*}{*N*,*N*-dimethyl(diphenylphosphino)thioformamide-*S*,*P*}palladium(II), (S_c)-8. A mixture of the perchlorato complex (S_c)-**2** (0.31 g, 0.52 mmol) and **6** (0.05 g, 0.17 mmol) in dichloroethane (20 cm^3) was stirred for 4 d at room temperature. The mother liquor was concentrated under reduced pressure to give a yellow solid (0.03 g, 20%), mp 168–169 °C (decomp.). α −60° (589 nm, c 0.5 g per 100 cm^3, CH_2Cl_2). Λ_M = 22 Ω^{-1} cm^2 mol^{-1} (CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.83 (d, 3 H, $^3J_{HH}$ = 6.4, CH*Me*), 2.96 (d, 3 H, $^4J_{PH}$ = 2.0 Hz, NMe), 2.96 (s, 3 H, NMe), 3.06 (d, 3 H, $^4J_{PH}$ = 4.8, NMe), 3.33 (s, 3H C(S)NMe), 3.60 (s, 3H C(S)NMe), 4.47 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ 6.0, C*H*Me), 6.65 (dd, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 8.4 Hz, naphthyl H_γ) and 7.15–7.98 (m, 15 H, aromatics). ^{31}P-{H} NMR ($CDCl_3$): δ 8.4 (s, 1P).

Crystal structure determinations of complexes (S_c,S_p)-3, (S_c,R_p)-4 and 7

Crystal data for complexes (S_c,S_p)-**3**, (S_c,R_p)-**4** and **7** and a summary of the crystallographic analyses are given in Table 4. Diffraction data were collected on a Siemens CCD diffractometer using graphite monochromated Mo-Kα radiation.

SADABS[11] absorption corrections were applied and all non-hydrogen atoms refined anisotropically, except for those of the solvent molecule. Hydrogen atoms were introduced at fixed distances from carbon atoms and assigned fixed thermal parameters. All calculations were performed on a Silicon Graphics workstation using programs provided by Siemens.

CCDC reference number 186/2289.

See http://www.rsc.org/suppdata/dt/b0/b007970g/ for crystallographic files in .cif format.

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