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PAPER

# Transformations of aryl isothiocyanates on tetraphosphine tungsten complexes and reactivity of the resulting dithiocarbonimidate ligand†

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Treatment of [WH$_4$(κ$^4$-**P4**)] (**3**: **P4** = *meso-o*-C$_6$H$_4$(PPhCH$_2$CH$_2$PPh$_2$)$_2$) with aryl isothiocyanate ArNCS at 50 °C afforded the dithiocarbonimidate-isocyanide complex [W(κ$^2$-S$_2$CNAr)(CNAr)(κ$^4$-**P4**)] (**4**) in moderate yields. The reaction also produced ArNHCH$_3$ and a small amount of ArNH$_2$. The yield of the hydrodesulfurization product ArNHCH$_3$ increased when the reaction was conducted under H$_2$ (up to 0.65 equiv. to **3** for Ar = *p*-MeC$_6$H$_4$ (Tol)). Complex **4** was proposed to be formed *via* reductive disproportionation of two ArNCS molecules on a zero-valent W species generated by dissociation of H$_2$ from **3**. The reaction of W(0) complex [W(dppe)(κ$^4$-**P4**)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with ArNCS also yielded **4** accompanied by free dppe, in contrast to that of [Mo(dppe)(κ$^4$-**P4**)], which had been previously reported to undergo sulfur-atom transfer to phosphine ligands. The dithiocarbonimidate ligands in **4a** (Ar = Tol) received the addition of electrophiles [PhMe$_2$NH][BF$_4$], MeI, and PhCOCl selectively at the N atom to afford the cationic dithiocarbamate complexes [W(κ$^2$-S$_2$CNHTol)(CNTol)-(κ$^4$-**P4**)][BF$_4$] (**6**), [W{κ$^2$-S$_2$CN(Me)Tol}(CNTol)(κ$^4$-**P4**)]I (**7**), and [W{κ$^2$-S$_2$CN(COPh)Tol}(CNTol)-(κ$^4$-**P4**)]Cl (**8**). Complexes **4a, 6, 7**, and **8** have been characterized by spectroscopic and crystallographic methods, and the donor strengths of their κ$^2$-dithio ligands are discussed.

## Introduction

Stereochemical control of transition metal complexes by multidentate ligands is an effective method for designing new structures, unique physical properties, and excellent catalytic functions. Synthesis and coordination chemistry of tetradentate phosphine ligands have long been studied since the 1960s.[1] A wide variety of such ligands are majorly classified into linear, tripodal, and other branched types based on structure (cyclic is also known),[2] and among the linear-type tetraphosphines, those of the general formula R$_2$P(CH$_2$)$_2$PR(CH$_2$)$_n$PR(CH$_2$)$_2$PR$_2$ (*n* = 1, 2, 3, *etc.*) are well known.[3–5] We have been investigating the group 6 metal complexes with a tetraphosphine ligand *meso-o*-C$_6$H$_4$(PPhCH$_2$CH$_2$PPh$_2$)$_2$ (abbreviated as **P4** in this report), which is easily obtained as the complex form [M(dppe)(κ$^4$-**P4**)] (M = Mo (**1**), W (**2**); dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) by heating *trans*-[M(N$_2$)$_2$(dppe)$_2$] with dppe.[6] Via an unconventional bond recombination in the coordination sphere, two dppe ligands are converted into **P4** and an equimolar benzene under excellent stereocontrol of *meso*, in spite of the possible existence of the *rac*-diastereomer. The unique structure of **P4**, in which four P atoms are linked by two flexible ethylene groups and a rigid *o*-phenylene, is distinct from those of the above representative tetraphosphines having alkyl-chain linkages only.

Although the steric bulk and donating ability seem almost comparable between **P4** and the bis-dppe system, the accumulation of chelate-ring strains in the κ$^4$-coordination of **P4** makes drastic divergences from the chemistry of bis-dppe complexes.[7] Our previous studies on Mo and W complexes have revealed structures and reactivity specific to **P4**, and recently the tetrahydride complex [WH$_4$(κ$^4$-**P4**)] (**3**) has been synthesized.[8] The structure of **3** is different from the analogous complex [WH$_4$(dppe)$_2$] in some points, and moreover, the reactivity of **3** is much higher than [WH$_4$(dppe)$_2$], probably owing to a highly strained geometry around the W centre and the ability of **P4** to change hapticity.[9] Subsequent study on the reactions of **3** with CS$_2$ and RNC (R = Bu$^t$, 2,6-Me$_2$C$_6$H$_3$) has resulted in isolation of [W(κ$^2$-S$_2$CH$_2$)(κ$^4$-**P4**)] and [W(CNR)$_2$(κ$^4$-**P4**)], proving that **3** is not only a strong hydride donor but also a good precursor of coordinatively unsaturated species. Such a dual reactivity is generally known for polyhydride complexes of transition metals,[10] and specific bond formation and cleavage has been performed on the low-valent intermediates generated by reductive elimination of H$_2$.

Now we have extended our study on **3** to reactivity toward aryl isothiocyanates[11] and discovered diverse reaction pathways. Zero-valent complex **2** and analogous W(dppe)$_2$ complexes have also been examined to compare reactivity to isothiocyanates, and the result of the former complex is unexpected from the preceding work using the Mo congener **1**.[12] In addition, further conversion of the major complex product containing a dithio ligand has

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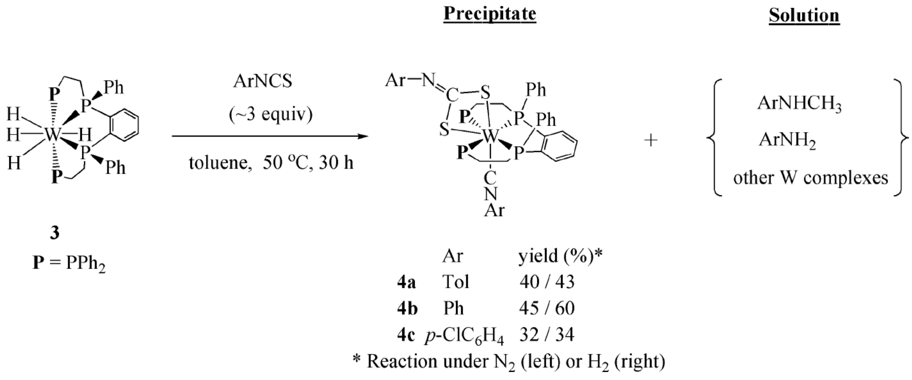


**Scheme 1**

been carried out, and structural and spectroscopic properties are discussed.

## Results and discussion

### 1. Reaction of [WH$_4$($\kappa^4$-P4)] with ArNCS

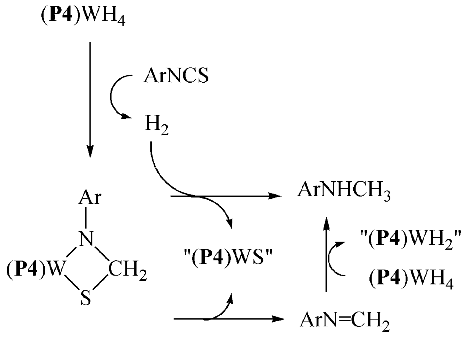
Heating a toluene solution of **3** with 3 equiv. of ArNCS (Ar = *p*-MeC$_6$H$_4$ (Tol), Ph, *p*-ClC$_6$H$_4$) at 50 °C resulted in the precipitation of a brown solid, which was identified as dithiocarbonimidate-isocyanide complex [W($\kappa^2$-S$_2$CNAr)(CNAr)($\kappa^4$-**P4**)] (**4**) (Scheme 1). Characterization of the new complex **4** is discussed in the next section. The yields of **4** were 32–45% when the reactions were carried out under N$_2$ atmosphere, and they slightly increased to 34–60% under H$_2$ atmosphere.

GLC analyses revealed that the liquid phase of these reactions contained ArNHCH$_3$, ArNH$_2$, and unreacted ArNCS as shown in Table 1. The majorly formed ArNHCH$_3$ is regarded as the hydrodesulfurization product from ArNCS, and its yield based on **3** varied from 12% for Ar = *p*-ClC$_6$H$_4$ to 45% for Ar = Tol. The yields also depended on the reaction atmosphere, and in comparison with the above results under N$_2$, they increased by about 0.5 times under H$_2$ (up to 67% on **3** for Ar = Tol). Amounts of the other product ArNH$_2$ are small, and dependence on Ar group or reaction atmosphere is of no significance for discussion. It is unclear whether ArNH$_2$ have been formed *via* hydrogenation or hydrolysis by a trace of moisture. Formation of these compounds was not catalytic, because amounts of organic products and unreacted ArNCS almost reached convergence at initial 8 h. This fact also confirms that either ArNHCH$_3$ or ArNH$_2$ is not formed *via* **4** as the intermediate.

Insertion of RNCS into a metal-H bond has been demonstrated for many transition metal complexes.[13] It has been previously revealed that double hydride insertion takes place in the reaction of **3** with a related heterocumulene CS$_2$ to give [W($\kappa^2$-S$_2$CH$_2$)($\kappa^4$-**P4**)].[8] Although the result of the reaction with ArNCS appears contrasting, a mechanism involving the corresponding complex [W($\kappa^2$-SCH$_2$NAr)($\kappa^4$-**P4**)] is postulated (Scheme 2). This intermediary complex may react directly with H$_2$ to liberate ArNHCH$_3$ or degrade into ArN=CH$_2$, which then undergoes hydrogenation. Any reaction did not take place at lower temperature, and intermediate complexes could not be observed. Attempts to identify the W species produced together with ArNHCH$_3$ and ArNH$_2$ were unsuccessful, but complexes other than **4** were detected in the liquid phase by NMR measurement. Complex **4** is probably formed *via* a different pathway, as discussed later. It has been reported that two mols of Cp$_2$ZrHCl react with RNCS (R = aryl or alkyl) to form [Cp$_2$ZrCl]$_2$($\mu$-S) concomitantly with RN=CH$_2$ and a very small amount of RNHCH$_3$.[13d] Complex **3** reacted with alkyl isothiocyanates in different ways, and the products could not be identified.

**Table 1** Amounts of organic compounds (equiv. to W) in the reactions of **3** with ArNCS; the conditions are shown in Scheme 1

| Ar | Reaction atmosphere | Consumed ArNCS | ArNHCH$_3$ | ArNH$_2$ |
|---|---|---|---|---|
| Tol | N$_2$ | 2.19 | 0.45 | 0.11 |
| | H$_2$ | 1.76 | 0.67 | 0.15 |
| Ph | N$_2$ | 2.52 | 0.23 | 0.07 |
| | H$_2$ | 2.23 | 0.33 | 0.11 |
| *p*-ClC$_6$H$_4$ | N$_2$ | 2.07 | 0.12 | 0.08 |
| | H$_2$ | 2.16 | 0.21 | 0.14 |



**Scheme 2**

### 2. Characterization of complex [W($\kappa^2$-S$_2$CNAr)(CNAr)($\kappa^4$-P4)]

The molecular structure of **4a** (Ar = Tol) has been fully determined by single-crystal X-ray crystallographic analysis. An ORTEP drawing is shown in Fig. 1 and selected bond distances and angles are collected in Table 2. The geometry of the metal centre is a highly distorted pentagonal bipyramid, in which the isocyanide ligand and one of the sulfur atoms of the dithiocarbonimidate ligand are occupying axial positions with the S–W–C angle at 173.69(8)°. The equatorial plane consists of the other S atom and four P atoms of the tetracoordinated **P4**. The acute S–W–S

**Table 2** Selected bonding parameters and IR data for **4a, 6, 7**, and **8**

| | **4a** | **6** | **7** | **8** |
|---|---|---|---|---|
| Bond distance /Å | | | | |
| W–S(1) | 2.5474(7) | 2.5282(10) | 2.5544(13) | 2.5361(10) |
| W–S(2) | 2.5553(7) | 2.5541(7) | 2.5444(16) | 2.5057(10) |
| S(1)–C(47) | 1.740(3) | 1.704(3) | 1.694(7) | 1.680(3) |
| S(2)–C(47) | 1.777(3) | 1.715(4) | 1.726(5) | 1.704(3) |
| C(47)–N(1) | 1.282(3) | 1.335(5) | 1.338(8) | 1.409(5) |
| N(1)–C(48) | 1.418(4) | 1.426(4) | 1.438(12) | 1.446(5) |
| W–C(55) | 1.947(2) | 1.975(3) | 1.943(5) | 1.967(3) |
| C(55)–N(2) | 1.231(3) | 1.196(5) | 1.229(6) | 1.198(5) |
| N(2)–C(56) | 1.394(3) | 1.404(4) | 1.403(7) | 1.396(4) |
| Bond angle/° | | | | |
| S(1)–W–S(2) | 68.68(2) | 68.22(2) | 67.79(4) | 68.12(3) |
| W–S(1)–C(47) | 91.18(9) | 89.96(14) | 90.02(19) | 89.13(13) |
| W–S(2)–C(47) | 90.08(10) | 88.85(11) | 89.6(2) | 89.60(13) |
| S(1)–C(47)–S(2) | 109.85(15) | 112.9(2) | 112.5(3) | 113.1(2) |
| S(1)–C(47)–N(1) | 121.8(2) | 120.1(2) | 123.1(4) | 128.4(2) |
| S(2)–C(47)–N(1) | 128.3(2) | 127.0(2) | 124.3(5) | 118.5(2) |
| C(47)–N(1)–C(48) | 121.7(2) | 127.2(3) | 122.2(5) | 115.5(3) |
| W–C(55)–N(2) | 174.7(2) | 177.3(3) | 174.4(4) | 175.4(3) |
| C(55)–N(2)–C(56) | 140.2(2) | 143.7(3) | 143.2(5) | 162.2(4) |
| IR (KBr)/$cm^{-1}$ | | | | |
| ν(C═N) or ν(C–N)[a] | 1512 | 1361 | 1374 | 1199, 1257[b] |
| ν(C≡N) | 1773 | 1804, 1887sh | 1887 | 1930 |

[a] Dithiocarbonimidate or dithiocarbamate ligand. [b] Discrimination from the ν(C–N) of the amide group is impossible.

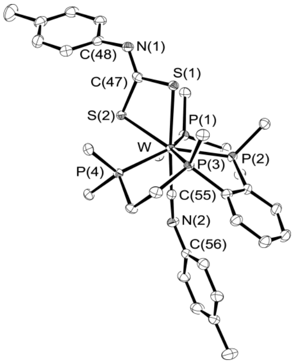
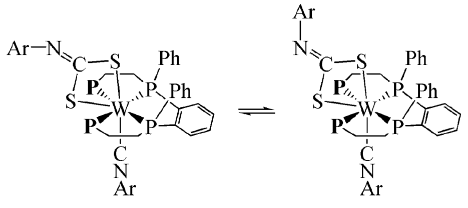


**Fig. 1** The molecular structure of **4a** showing thermal ellipsoids at 50% probability. Hydrogen atoms and the phenyl carbons except the *ipso* positions are omitted for clarity.

angle at 68.68(2)° makes the equatorial S(2) atom deviate from the pentagonal plane toward the axial S(1) atom. The P(4) atom is also out of the equatorial plane to the side of the isocyanide ligand. The two C–S distances are comparable to those of dithiocarbonimidate complexes possessing an *N*-aryl or *N*-alkyl group.[14,15] The C(47)–N(1) bond length of 1.282(3) Å is typical for a C–N double bond, while the IR absorption at 1512 $cm^{-1}$ for ν(C═N) is at a relatively low frequency among analogous complexes.[14] The C(47)–N(1)–C(48) linkage is co-planar to the $WS_2C$ ring and bent at 121.7(2)°. The Tol group is directed *cis* to S(2), and this aromatic ring and the $S_2CN$ plane are twisted with respect to each other with the dihedral angle of 64°. For the isocyanide ligand, the relatively long C(55)–N(2) bond and a large deviation from linearity of the C(55)–N(2)–C(56) linkage indicate strong back-donation from the W centre, which is also reflected in the very low frequency of ν(C≡N) in the IR spectrum (1773 $cm^{-1}$). Such bent structures are often observed for alkyl isocyanides but rarely for aryl isocyanides.[16,17]

The $^{31}P\{^1H\}$ NMR spectrum of **4a** in $CDCl_3$ solution at 20 °C showed two very broad peaks centred at δ 46 and 66, corresponding to the outer and inner P atoms, respectively. The spectrum changed at −50 °C into two pairs of signals, the major set of which was observed at δ 49.9 and 66.9, while the minor appeared at δ 47.4 and 67.3 in a intensity ratio of major/minor = 7/3. Low temperature $^1H$ NMR (−50 °C) also supported the presence of two species in the above ratio, and the spectra around 20 °C were also broadened severely. These observations are explained by the *syn*/*anti*-isomerism of the dithiocarbonimidate ligand with respect to the C═N bond (Chart 1), whose dynamic exchange causes broadening of NMR signals.[18] Structure I is found in the crystal as mentioned above, and the other conformation II is probably equilibrating with I in solution. In contrast to **4a**, the supplementary single-crystal X-ray study of **4c** (Ar = *p*-$ClC_6H_4$) has revealed the structure corresponding to II, in which the Ar group is directed to the axial S(1) atom as shown in Fig. 2. This and **4b** exhibit NMR spectra similar to **4a**.



I

II

**Chart 1**

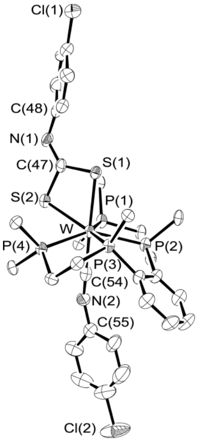
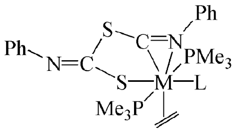


**Fig. 2** The molecular structure of **4c** showing thermal ellipsoids at 50% probability. Hydrogen atoms and the phenyl carbons except the *ipso* positions are omitted for clarity.

## 3. Mechanisms forming [W(κ²-$S_2CNAr$)(CNAr)(κ⁴-P4)]

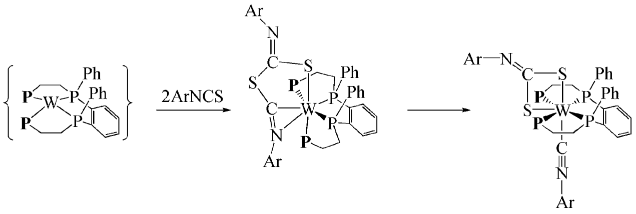
A reaction pathway different from that producing $ArNHCH_3$ is proposed for the formation of **4**. A formal W(0) species is probably generated by the liberation of $H_2$ from **3** and promotes the reductive disproportionation of two ArNCS molecules into dithiocarbonimidate and isocyanide ligands. Such bond recombinations of RNCS have been known mostly for group 8–10 metal complexes in low oxidation states. Complexes of the type [M($S_2CNR$)(CNR)$L_n$] have been obtained selectively by the reactions of Ru(0)[19] Rh(I),[19,20] and Pt(0)[21] complexes. In the cases of Pd(0), Pt(0) and their precursors, the concomitantly formed isocyanide dissociated from the metal to result in dithiocarbonimidate complexes.[14g,h,15b,21,22] These types of reactions have been reported for Mn(-I), Re(-I), and Mo(0,I), although the dithiocarbamate complexes are provided *via* the following *N*-protonation.[23] Conversion of RNCS into RNC proceeds on some complexes including W(II) and Mo(0), where the sulfur atom is accepted by the metal or its fate is unknown.[24,25]

E. Carmona and co-workers have reported that the zero-valent molybdenum and tungsten complexes *trans*-[$M(C_2H_4)_2(PMe_3)_4$] (M = Mo, W) react with PhNCS or $CS_2$ to form [$M(S_2C_2X_2)(C_2H_4)_n(PMe_3)_{4-n}$] ($n$ = 1, 2; X = NPh, S), whose structures for X = NPh have been proposed as in Chart 2 based on the single-crystal X-ray crystallography for X = S.[26] Similar metallacyclic structures are generated in the reactions of [$RhCl(PPh_3)_3$][27] and [$CpCo(PMe_3)_2$][28] with certain isothiocyanates, and postulated as the intermediate of metal-mediated disproportionation of two isothiocyanate molecules. Formation of **4** probably proceeds *via* the analogous complex that is produced by dimerization of ArNCS in the coordination sphere, and subsequent deinsertion of ArNC as illustrated in Scheme 3.



M = Mo, W;
L = $PMe_3$, $C_2H_4$

**Chart 2**



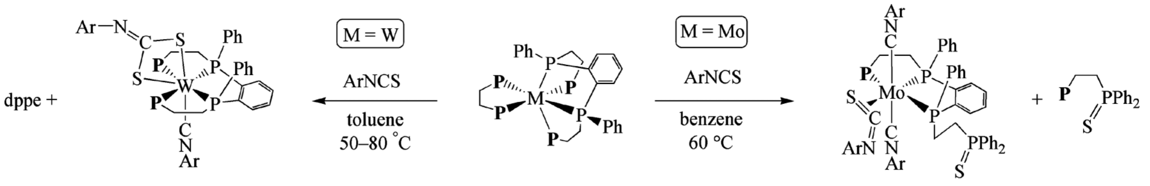
**Scheme 3**

Based on speculation that a W(0) intermediate is the key to the formation of **4**, reactivity of the zero-valent complex **2** toward aryl isothiocyanates was examined. As expected, treatment of **2** with 3 equiv. of *p*-$ClC_6H_4NCS$ in toluene at 50 °C gave **4c** accompanied by free dppe (Scheme 4). It was proved that **2** was less reactive than **3** toward ArNCS, which is not electron-deficient, and reactions with TolNCS and PhNCS to form **4a** and **4b** required a higher temperature (80 °C). Reactivity of the complexes having bis-dppe co-ligands was also tested by using *trans*-[$W(N_2)_2(dppe)_2$], which readily generates coordinatively unsaturated W(0) species. However, treatment with ArNCS at 80 °C resulted not in the formation of an analogue of **4**, but in decomposition giving sulfides of dppe.[29] Stereocontrol of coordination geometry by **P4** may play an important role in providing a wide reaction site that allows association of two ArNCS molecules and in driving a severely distorted octahedral intermediate into the relatively stable pentagonal bipyramidal structure. It is also noticeable that the reaction of the Mo complex **1** with ArNCS under similar conditions affords entirely different products, **5** and a monosulfide of dppe (Scheme 4).[12] As many as three TolNCS molecules react with **1**, two of which are converted into TolNC by desulfurization and the remaining TolNCS binds to the Mo centre in an $\eta^2$ manner at the C=S bond. With respect to the S abstraction from TolNCS, one abstracted S atom moves to the terminal P atom in **P4** to give a dangling P(=S)$Ph_2$ moiety and the other one is trapped by dppe. It is presumed that the electron-donating ability of the W(0) centre is high enough to promote the reductive disproportionation of ArNCS, while sulfur atom transfer to tertiary phosphines[28,30] proceeds on the less-donating Mo(0) centre.

## 4. Reactions of dithiocarbonimidate ligand with electrophiles

Dithiocarbonimidate ligands are commonly known to undergo addition of electrophiles such as proton and methylating agents.[14a,e,19,21,23a,31] Electrophilic attack mostly takes place at the N atom to give a dithiocarbamate ligand, while a few examples of *S*-methylation have been reported.[23a,31c] High nucleophilicity of the dithiocarbonimidate ligand in **4** is expected, but at the same time the isocyanide ligand, which is activated by extremely strong back-donation, probably has electrophilicity at its N atom.[32] In practice, **4a** reacted with various electrophiles selectively at the N atom of the dithiocarbonimidate ligand. Treatment of **4a** with [$PhMe_2NH$][$BF_4$], MeI, and PhCOCl afforded the cationic dithiocarbamate complexes [W($\kappa^2$-$S_2CNHTol$)(CNTol)($\kappa^4$-**P4**)][$BF_4$] (**6**), [W{$\kappa^2$-$S_2CN(Me)Tol$}(CNTol)($\kappa^4$-**P4**)]I (**7**), and [W{$\kappa^2$-$S_2CN(COPh)Tol$}(CNTol)($\kappa^4$-**P4**)]Cl (**8**) in 71–85% yields through *N*-protonation, *N*-methylation, and *N*-benzoylation (Scheme 5).

The structures of **6, 7,** and **8** have been fully determined by single-crystal X-ray analysis. The ORTEP drawings are shown in Fig. 3–5, and selected bond lengths and angles are listed in Table 2. The coordination geometries of **6–8** are essentially identical to that of **4a**. A number of seven-coordinate W(II) complexes having dithiocarbamate ligands have been crystallographically

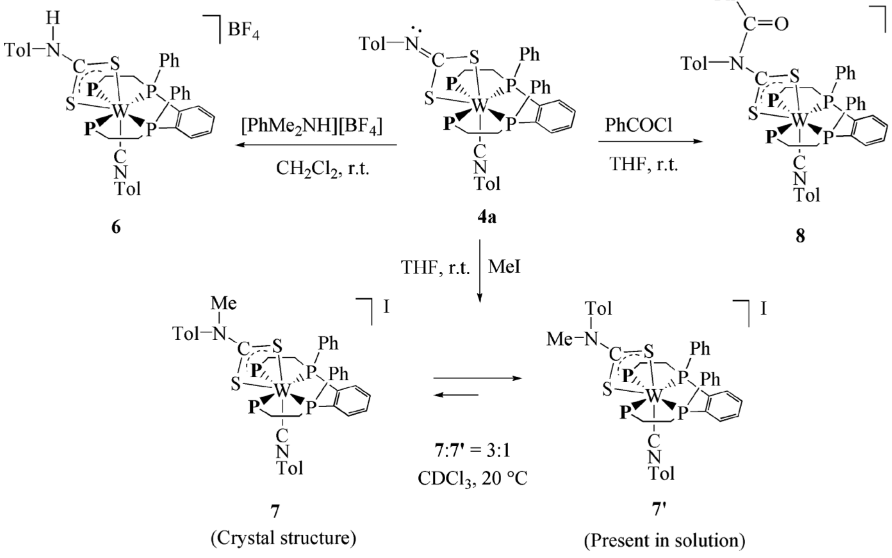


**4a**: 80 °C, 20 h, 53% yield
**4b**: 80 °C, 22 h, 58% yield
**4c**: 50 °C, 20 h, 47% yield

**1**: M = Mo
**2**: M = W

**5**

**Scheme 4**



**Scheme 5**

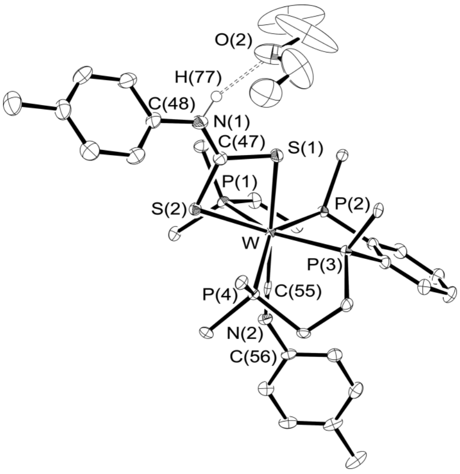


**Fig. 3** The molecular structure of the cationic part of **6** showing thermal ellipsoids at 50% probability. The $Et_2O$ molecule interacting through hydrogen bonding is also shown. Hydrogen atoms except the NH group and the phenyl carbons other than the *ipso* positions are omitted for clarity.

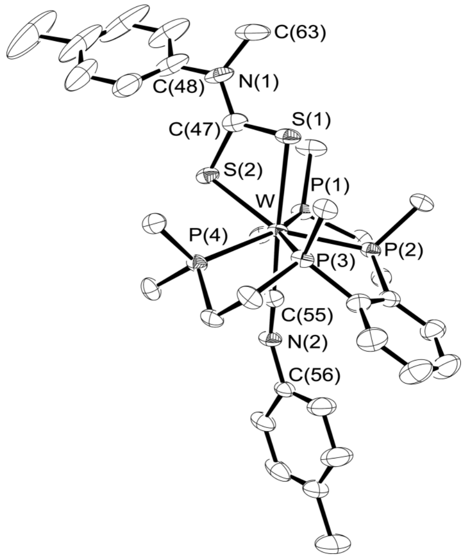


**Fig. 4** The molecular structure of the cationic part of **7** showing thermal ellipsoids at 50% probability. Hydrogen atoms and the phenyl carbons except the *ipso* positions are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(63), 1.483(9); C(47)–N(1)–C(63), 118.0(6); C(48)–N(1)–C(63), 119.8(6).

determined[33] and the bonding parameters of **6–8** are compatible with these regarding the κ$^2$-dithio ligands. For all the dithiocarbamate ligands determined here, the geometry around the C(47)–N(1) bond is essentially planar, and the Tol group is oriented *syn* to the equatorial S similarly to **4a**. Nonetheless, small distortions due to steric repulsion and packing effects are observed for **7** and **8**, where the dihedral angles between the trigonal planes around the C(47) and N(1) are 11° and 20°, respectively. For **8**, the corresponding twist along the N(1)–C(63) axis is 10°, and the tilt of the Tol and the Ph rings is much larger (69° along N(1)–C(48) and 48° along C(63)–C(64)). In accordance with the structural differences as illustrated in Chart 3, the C–S bonds are shorter and $S_2C$–N bonds are longer in dithiocarbamate complexes **6–8** than in the dithiocarbonimidate complex **4a**. The C(47)–N(1) distances in **6** and **7** are increased by > 0.05 Å in comparison with **4a** owing to the contribution of the resonance structures II. This bond elongation is reflected in the low-frequency shift (140–150 cm$^{-1}$) of the IR absorption for the C–N stretching mode. The electron-withdrawing PhCO group further elongates the C(47)–N(1) bond to 1.409(5) Å in **8**, as explained by involvement of the resonance III. For comparison, $[Mn(CO)_3(PMe_2Ph)(\kappa^2\text{-}S_2CNHCOOEt)]$ has the C–S bonds of 1.678(3) and 1.704(3) Å and the $S_2C$–N length at 1.363(4) Å.[34]

The extent of back-donation to the isocyanide ligand seems compatible to donor strength of the κ$^2$-dithio ligand, which decreases in the order **4a** > **6**, **7** > **8**. Although bond distances in the isocyanide ligands exhibit no significant differences, the bending of the C–N–C linkage is slightly reduced in **6** and **7** (36.3(3)° and 36.8(5)° from linearity) as compared with **4a** (39.8(2)°) and that

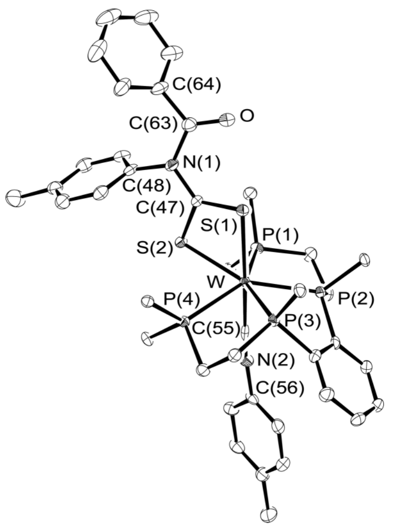
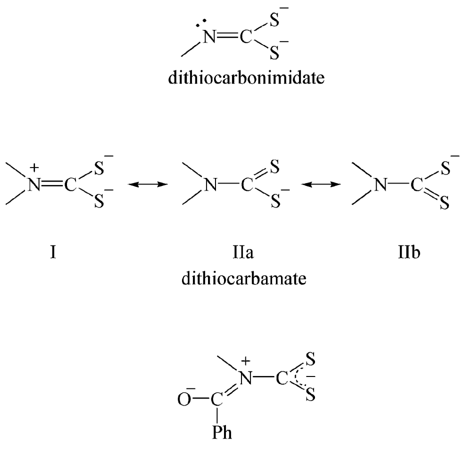


**Fig. 5** The molecular structure of the cationic part of **8** showing thermal ellipsoids at 50% probability. Hydrogen atoms and the phenyl carbons except the *ipso* positions are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(63), 1.419(5); O(1)–C(63), 1.210(5); C(63)–C(64), 1.504(6); C(47)–N(1)–C(63), 121.1(3); C(48)–N(1)–C(63), 121.9(3).


dithiocarbonimidate

I IIa IIb

dithiocarbamate

III

**Chart 3**

in **8** becomes substantially linear (17.8(4)°). The same tendency as the result of the decrease in back bonding is observed also in the high frequency shift of the $\nu(C\equiv N)$.

In the crystallographic analysis of **6**, the hydrogen atom attached to the N(1) has been found in the Fourier maps, and its existence is further evidenced by the $Et_2O$ molecule at the neighbor, which is probably acting as a hydrogen-bond acceptor (N···O = 2.956(6) Å, H···O = 2.10(8) Å). Although IR absorption due to the N–H bond could not be specified, the NH proton was clearly determined by $^1H$ NMR measurement as a singlet of 1H intensity ($\delta$ 7.79 in $CDCl_3$ at 40 °C), which disappeared after adding $D_2O$. In contrast to **4a**, the NMR spectra of **6** were well resolved, and attributed to single species. The appearance of two $^{31}P$ signals support that the cation of **6** (also **7** and **8**) possesses a mirror symmetry in NMR criteria. While the chemical shifts of the inner P atoms at lower field were almost equal between **6** and **4a**, the high-field outer P signal of **6** shifted to down field by > 6 ppm from that of **4a**. Unlike for **6**, the presence of two isomers in a 3 : 1 ratio was revealed by the NMR study of **7** in $CDCl_3$ at 20 °C. Because both $^1H$ and $^{31}P$ signals were clearly observed, exchange in solution was indicated, which was as fast as to reach equilibrium within a few minutes but much slower than the NMR time-scale. There are probably geometrical isomers **7** and **7′** present, arisen from the rotation barrier of the N–$CS_2$ bond. There were no considerable differences between the NMR signals of **7** and **7′**, and the chemical shifts were comparable to those of **6**. Only one species was observed in the NMR study of **8**, but it is unclear whether the free rotation of the N–C bond or predominance of one conformer is attributable. The chemical shift of the outer P atoms for **8** was the most down-field among the complexes here.

## Conclusion

In this study, we have revealed dual reactivity of the tetrahydride complex **3** bearing a tetraphosphine co-ligand **P4**. Conversion of aryl isothiocyanates by **3** proceeds through two different pathways. One is hydrodesulfurization to give $ArNHCH_3$, and, as far as we know, such a type of hydrogenation by a well-defined polyhydride complex is very rare albeit not catalytic. The other is the formation of a dithiocarbonimidate–isocyanide complex *via* the alternative mechanism that two ArNCS molecules undergo reductive disproportionation on a formally W(0) centre. These reactions are uniquely assisted by the **P4** co-ligand and not attainable by other W and Mo complexes with the related bis-diphosphine ligand set (*e.g.* dppe). The resulting dithiocarbonimidate ligand can be derivatized by the addition of electrophiles, which has provided a series of *N*-substituted dithiocarbamate ligands with varied electronic properties. We will continuously explore the reactivity of **3** and other **P4** complexes toward unsaturated small molecules.

## Experimental

### General considerations

All manipulations were carried out by using standard Schlenk techniques under pure $N_2$ or $H_2$. Solvents were dried by common methods and distilled under $N_2$ before use. Complexes [W(dppe)($\kappa^4$-**P4**)]·toluene (**2**·toluene)[6] and [$WH_4$($\kappa^4$-**P4**)]·0.5toluene (**3**·0.5toluene)[8] were prepared as described previously, and other reagents were commercially obtained and used without further purification. NMR spectra were measured on a JEOL alpha-400 or a JEOL ECS 400 spectrometer at 20 °C, except those indicated otherwise. Chemical shifts were referred to those of isotopic impurities for $^1H$ ($CD_2Cl_2$ at 5.32 and $CDCl_3$ at 7.26) or to external 85% $H_3PO_4$ (0 ppm) for $^{31}P$. For the $^1H$ data, the signals due to **P4** are omitted. IR spectra were recorded on a JASCO FT/IR-420. Elemental analyses were done with a Perkin–Elmer 2400 series II CHN analyzer. GLC and GC-MS analyses were performed with a Shimadzu GC-14B gas chromatograph and a GC-MS QP-5050 spectrometer equipped with a CBP1 or CBP10 fused silica capillary column (25 m length × 0.25 mm i.d.), and organic compound were quantitatively determined by using $PhCH_2CH_2Ph$ as the internal standard.

### Reaction of 3 with TolNCS

A toluene solution (5 mL) of **3**·0.5toluene (0.099 g, 0.10 mmol) and TolNCS (0.046 g, 0.31 mmol) was stirred under $N_2$ atmosphere at 50 °C for 30 h. A brown precipitate of [W($\kappa^2$-$S_2$CNTol)(CNTol)($\kappa^4$-**P4**)]·0.5toluene (**4a**·0.5toluene) was filtered off and dried under vacuum (0.052 g, 40% yield). The liquid phase was analyzed by GLC and GC-MS to determine the organic compounds. Recrystallization of **4a** from THF/hexane afforded brown prismatic crystals of **4a**·THF, which were suitable for single-crystal X-ray diffraction study. $^1$H NMR ($CD_2Cl_2$, 20 °C): $\delta$ 2.20, 2.23 (s, 3H each, $C_6H_4$*Me*), 5.26 (br d, *J* = 7.2 Hz, $NC_6H_4$), 6.37 (br, 2H, $NC_6H_4$), 6.65, 6.87 (br d, *J* = 7.6 Hz, 2H each, $NC_6H_4$), 2.34 (s, 1.5H, 0.5toluene). $^1$H NMR ($CDCl_3$, 20 °C): $\delta$ 2.27 (vbr, 6H, $C_6H_4$*Me*), 5.16 (vbr, 2H, $NC_6H_4$), other signals of $NC_6H_4$ groups appeared as very broad signals in the region of 6.0 – 7.0, 2.36 (s, 1.5H, 0.5toluene). $^1$H NMR ($CDCl_3$, −50 °C): $\delta$ 2.15, 2.19, 2.25 (br, total 6H, *ca.* 0.7 : 1 : 0.3 ratio), 5.14 (br, 2H), 6.24 (br, 1.4H), 6.52 (br, 0.6H), 6.62 (br, 2H), 6.80 (br, 1.4H). $^{31}$P{$^1$H} NMR ($CDCl_3$, 20 °C): Existence of two species was observed, although their ratio was difficult to determine due to severely broad signals; $\delta$ 42–49 (vbr, outer P), 63–69 (vbr, inner P). $^{31}$P{$^1$H} NMR ($CDCl_3$, −50 °C): $\delta$ 47.4 (br, outer P of the minor), 49.9 (br, outer P of the major), 66.9 (br, inner P of the major), 67.3 (br, inner P of the minor), major : minor = 7 : 3. IR (KBr, cm$^{-1}$): 1512 s ($\nu$(C=N)), 1773 brs ($\nu$(C≡N)). Anal. calcd for $C_{65.5}H_{60}N_2P_4S_2W$: C, 63.08; H, 4.85; N, 2.25%. Found C, 62.90; H, 4.75, N, 2.03%.

Similar reaction of **3**·0.5toluene (0.101 g, 0.106 mmol) with TolNCS (0.051 g, 0.34 mmol) under $H_2$ atmosphere gave **4a**·0.5toluene (0.057 g, 43% yield).

### Reaction of 3 with PhNCS

PhNCS (0.044 g, 0.33 mmol) was added into a 5 mL toluene solution of **3**·0.5toluene (0.098 g, 0.10 mmol). After this solution was stirred under $N_2$ atmosphere at 50 °C for 30 h, [W($\kappa^2$-$S_2$CNPh)(CNPh)($\kappa^4$-**P4**)] (**4b**) was deposited as brown precipitate, which was filtered off and dried under vacuum (0.053 g, 45% yield). $^1$H NMR ($CDCl_3$): $\delta$ 5.31 (d, *J* = 7.6 Hz, 2H, *o*-H of NPh), 6.63 (t, *J* = 7.6 Hz, 1H, *p*-H of NPh), 6.81 (t, *J* = 7.6 Hz, 2H, *m*-H of NPh), 6.3–6.85 (br, 2H, NPh), remaining 3H of NPh group is overlapping with aromatic signals of **P4**. $^{31}$P{$^1$H} NMR ($CDCl_3$): Existence of two species was observed, although their ratio was difficult to determine due to severely broad signals; $\delta$ 45 (vbr, outer P of the minor), 47 (vbr, outer P of the major), 65 (vbr, inner P of the major and minor). IR (KBr, cm$^{-1}$): 1518 m ($\nu$(C=N)), 1807 brs ($\nu$(C≡N)). Anal. calcd for $C_{60}H_{52}N_2P_4S_2W$: C, 61.44; H, 4.47; N, 2.39%. Found C, 61.56; H, 4.51, N, 2.03%.

Similar reaction of **3**·0.5toluene (0.096 g, 0.10 mmol) with PhNCS (0.039 g, 0.29 mmol) under $H_2$ atmosphere gave **4b** (0.070 g, 60% yield).

### Reaction of 3 with *p*-$ClC_6H_4NCS$

A toluene solution (5 mL) of **3**·0.5toluene (0.106 g, 0.111 mmol) and *p*-$ClC_6H_4NCS$ (0.057 g, 0.34 mmol) was stirred under $N_2$ atmosphere at 50 °C for 12 h. A brown precipitate of [W($S_2CNC_6H_4Cl$-*p*)($CNC_6H_4Cl$-*p*)($\kappa^4$-**P4**)]·0.5toluene (**4c**·0.5toluene) was filtered off and dried under vacuum (0.046 g, 32% yield). $^1$H NMR ($CDCl_3$): $\delta$ 5.19 (br d, *J* = 8.0 Hz, $C_6H_4Cl$), 6.2–6.8 (vbr, 2H, $C_6H_4Cl$), 6.72 (d, *J* = 8.0 Hz, $C_6H_4Cl$), 6.93 (br, 2H, $C_6H_4Cl$), 2.36 (s, 1.5H, 0.5toluene). $^{31}$P{$^1$H} NMR ($CDCl_3$): Existence of two species was observed, although their ratio was difficult to determine due to severely broad signals; $\delta$ 46 (vbr, outer P of the minor), 47 (vbr, outer P of the major), 65 (vbr, inner P of the major), 66 (vbr, inner P of the minor). IR (KBr, cm$^{-1}$): 1511 s ($\nu$(C=N)), 1742 brvs ($\nu$(C≡N)). Anal. calcd for $C_{63.5}H_{54}Cl_2N_2P_4S_2W$: C, 59.22; H, 4.23; N, 2.18%. Found C, 59.16; H, 4.15, N, 2.07%.

Similar reaction of **3**·0.5toluene (0.095 g, 0.10 mmol) with *p*-$ClC_6H_4NCS$ (0.051 g, 0.30 mmol) under $H_2$ atmosphere gave **4c**·0.5toluene (0.043 g, 34% yield).

### Reaction of 2 with TolNCS

A mixture of **2**·toluene (0.130 g, 0.0930 mmol) and TolNCS (0.049 g, 0.33 mmol) in toluene (5 mL) was stirred under $N_2$ atmosphere at 80 °C for 20 h. The resulting brown precipitate was filtered and dried under vacuum to give **4a**·0.5toluene as brown solid (0.062 g, 53% yield).

### Reaction of 2 with PhNCS

Similar reaction of **2**·toluene (0.137 g, 0.0983 mmol) with PhNCS (38 μL, 0.32 mmol) in toluene (5 mL) at 80 °C for 22 h gave **4b** (0.067 g, 58% yield).

### Reaction of 2 with *p*-$ClC_6H_4NCS$

Similar reaction of **2**·toluene (0.132 g, 0.0949 mmol) and *p*-$ClC_6H_4NCS$ (0.053 g, 0.31 mmol) at 50 °C for 20 h gave brown solid of **4c**·0.5toluene (0.058 g, 47% yield).

### Reaction of 4a with $[PhMe_2NH]BF_4$

A $CH_2Cl_2$ solution (4 mL) of **4a**·0.5toluene (0.098 g, 0.078 mmol) and $[PhMe_2NH]BF_4$ (0.017 g, 0.080 mmol) was stirred under $N_2$ atmosphere at room temperature for 24 h. Addition of ether (18 mL) to the concentrated solution (3 mL) formed red crystals of [W($\kappa^2$-$S_2$CNHTol)(CNTol)($\kappa^4$-**P4**)]$BF_4$·$2Et_2O$ (**6**·$2Et_2O$), from which solvating $Et_2O$ molecules were removed by drying under vacuum (0.086 g, 85% yield). $^1$H NMR ($CDCl_3$): $\delta$ 2.24, 2.28 (s, 3H each, $C_6H_4$*Me*), 5.29, 6.71, 6.85, 7.00 (d, *J* = 8.0 Hz, 2H each, $NC_6H_4$), 7.77 (br, 1H, NH, overlapping with the signals of **P4**, shifted to 7.79 at 40 °C and disappeared by addition of $D_2O$). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 56.6 (AA′XX′ pattern with $^{183}$W satellites, $J_{PW}$ = 167 Hz, outer P), 66.5 (AA′XX′ pattern with $^{183}$W satellites, $J_{PW}$ = 197 Hz, inner P), $J_{AX} + J_{AX'}$ = 22 Hz. IR (KBr, cm$^{-1}$): 1084 vs ($\nu$(B–F)), 1361 s ($\nu$(C–N)), 1804 brs, 1887 sh ($\nu$(C≡N)). Anal. calcd for $C_{62}H_{57}BF_4N_2P_4S_2W$: C, 57.78; H, 4.46; N, 2.17%. Found C, 57.43; H, 4.28, N, 2.10%.

### Reaction of 4a with MeI

Methyl iodide (8.0 μL, 0.13 mmol) was added into a THF solution (5 mL) of **4a**·0.5toluene (0.136 g, 0.109 mmol). After stirring the solution at room temperature for 18 h, brick red precipitate was formed. This was filtered off and dissolved in 3 mL of $CH_2Cl_2$ followed by addition of ether (18 mL). Red brown crystals of [W($\kappa^2$-$S_2$CN(Me)Tol)(CNTol)($\kappa^4$-**P4**)]I·$2CH_2Cl_2$ (**7**·$2CH_2Cl_2$) were formed, which lost $CH_2Cl_2$ solvate after drying under vacuum (0.104 g, 71% yield). NMR measurements showed the existence of two geometrical isomers in solution (3 : 1 in $CDCl_3$ at 20 °C). $^1$H NMR ($CDCl_3$): $\delta$ 2.23 (br s, 3H, $C_6H_4$*Me*, signals of both

**Table 3** Crystallographic data for **4a**·THF, **6**·2Et$_2$O, **7**·2CH$_2$Cl$_2$, and **8**·CH$_2$Cl$_2$

| | **4a**·THF | **6**·2Et$_2$O | **7**·2CH$_2$Cl$_2$ | **8**·CH$_2$Cl$_2$ |
|---|---|---|---|---|
| Formula | $C_{66}H_{64}N_2OP_4S_2W$ | $C_{70}H_{77}N_2O_2BF_4P_4S_2W$ | $C_{65}H_{63}Cl_4IN_2P_4S_2W$ | $C_{70}H_{63}Cl_3N_2OP_4S_2W$ |
| FW | 1273.11 | 1437.06 | 1512.81 | 1426.50 |
| Space group | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) |
| $a$/Å | 16.299(2) | 11.907(2) | 17.357(3) | 14.372(2) |
| $b$/Å | 14.918(2) | 15.051(2) | 11.468(2) | 25.725(4) |
| $c$/Å | 23.741(2) | 19.189(3) | 32.634(6) | 16.962(3) |
| $\alpha$/° | 90 | 9077.147(5) | 90 | 90 |
| $\beta$/° | 98.9410(4) | 89.331(5) | 104.0979(7) | 91.4789(9) |
| $\gamma$/° | 90 | 76.838(5) | 90 | 90 |
| $V$/Å$^3$ | 5703(10) | 3261.8(9) | 6300(2) | 6263(18) |
| $Z$ | 4 | 2 | 4 | 4 |
| $\rho_c$/g cm$^{-3}$ | 1.483 | 1.463 | 1.595 | 1.511 |
| $\mu$/mm$^{-1}$ | 2.259 | 1.993 | 2.705 | 2.187 |
| Crystal size/mm | 0.20 × 0.12 × 0.08 | 0.40 × 0.20 × 0.05 | 0.25 × 0.20 × 0.20 | 0.25 × 0.15 × 0.05 |
| transmn factor | 0.716–0.835 | 0.522–0.905 | 0.328–0.582 | 0.698–0.896 |
| unique reflns ($R_{int}$) | 13 574 (0.0295) | 15 322(0.040) | 14 995 (0.077) | 14 877 (0.047) |
| obsd reflns[a] | 11141 | 12775 | 11714 | 11092 |
| variables | 914 | 855 | 778 | 811 |
| $R_1$[b] | 0.0295 | 0.0400 | 0.0556 | 0.0372 |
| w$R_2$[c] | 0.0958 | 0.1145 | 0.1541 | 0.0816 |
| Gof[d] | 1.013 | 1.029 | 1.009 | 1.013 |

[a] $F_o^2 > 2\sigma(F_o^2)$. [b] $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ for all unique data, where $w = [\sigma(F_o^2) + a F_o^2 + b]^{-1}$. [d] gof $= [\Sigma w(F_o^2 - F_c^2)^2 / \{(\text{no. of reflns obsd}) - (\text{no. of variables})\}]^{1/2}$.

isomers are overlapping), 2.27 (s, 3H of the major, $C_6H_4Me$), 2.40 (s, 3H of the minor, $C_6H_4Me$), 2.89 (s, N*Me* of the minor), 2.96 (s, N*Me* of the major), these two signals are overlapping with the CH$_2$ signals of **P4**, 5.23, 6.25, 6.69, 6.94 (d, $J$ = 8.4 Hz, 2H of the major, $NC_6H_4$), 5.27, 6.58, 6.71 (d, $J$ = 8.4 Hz, 2H of the minor, $NC_6H_4$). $^{31}P\{^1H\}$ NMR (CDCl$_3$): $\delta$ 56.3 (AA′XX′ pattern with $^{183}$W satellites, $J_{PW}$ = 170 Hz, outer P), 66.1 (AA′XX′ pattern with $^{183}$W satellites, $J_{PW}$ = 195 Hz, inner P), $J_{AX} + J_{AX'}$ = 21 Hz, for the major isomer; 55.9 (AA′XX′ pattern, outer P), 66.4 (AA′XX′ pattern, inner P), $J_{AX} + J_{AX'}$ = 21 Hz, for the minor isomer. $^{183}$W satellites were not resolved due to low concentration and signal overlapping. IR (KBr, cm$^{-1}$): 1374 s ($\nu$(C–N)), 1887 brvs ($\nu$(C≡N)). Anal. calcd for $C_{63}H_{59}IN_2P_4S_2W$: C, 56.35; H, 4.43; N, 2.09%. Found C, 56.43; H, 4.32, N, 2.08%.

### Reaction of 4a with PhCOCl

PhCOCl (12 µL, 0.103 mmol) was added to a THF solution (5 mL) of **4a**·0.5toluene (0.102 g, 0.0819 mmol), and the mixture was stirred at room temperature for 12 h. The deposited purple solid was filtered off and recrystallized from CH$_2$Cl$_2$ (3 mL)/hexane (15 mL) to give purple crystals of [W{κ$^2$-S$_2$CN(COPh)Tol}(CNTol)(κ$^4$-**P4**)]Cl·CH$_2$Cl$_2$ (**8**·CH$_2$Cl$_2$: 0.099 g, 85% yield). $^1$H NMR (CDCl$_3$): $\delta$ 2.23, 2.27 (s, 3H each, $C_6H_4Me$), 5.27, 6.27, 6.71, 6.91 (d, $J$ = 8.4 Hz, 2H each, $NC_6H_4$), 5.30 (s, 2H, CH$_2$Cl$_2$). $^{31}P\{^1H\}$ NMR (CDCl$_3$): $\delta$ 60.0 (AA′XX′ pattern with $^{183}$W satellites, $J_{PW}$ = 170 Hz, outer P), 64.2 (AA′XX′ pattern with $^{183}$W satellites, $J_{PW}$ = 194 Hz, inner P), $J_{AX} + J_{AX'}$ = 17 Hz. IR (KBr, cm$^{-1}$): 1199 s, 1257 s ($\nu$(C–N)), 1682 s ($\nu$(C=O)), 1930 brvs ($\nu$(C≡N)). Anal. calcd for $C_{70}H_{63}Cl_3N_2OP_4S_2W$: C, 58.94; H, 4.45; N, 1.96%. Found C, 58.60; H, 4.42; N, 1.98%

### X-Ray crystallography

Single crystals were mounted on cryoloops with oil and cooled to 113 K. All diffraction studies were performed on a Rigaku Mercury-CCD diffractometer equipped with a graphite-monochromatized Mo-Kα source ($\lambda$ = 0.71070 Å). Data were processed using the CrystalClear program package[35] and corrected for absorption. Single crystals of **4c**·2.25CH$_2$Cl$_2$ were obtained by recrystallization from CH$_2$Cl$_2$/hexane. This crystal system contained three independent molecules in the asymmetric unit, one of which had considerable disorder. Therefore, the results of this structure determination are provided as supplementary information, and included in the ESI.† Details for other crystals are listed in Table 3. Structure solution and refinements were performed by using the CrystalStructure program package.[36] The positions of non-hydrogen atoms were determined by Patterson methods (PATTY[37]) and subsequent Fourier synthesis (DIRDIF99[38]). These were refined with anisotropic thermal parameters by full-matrix least-squares techniques. The NH hydrogen in **6**·2Et$_2$O and all the H atoms in the complex part of **3**·THF were found in Fourier maps and refined isotropically. Other hydrogens were placed at the calculated positions and included at the final stages of the refinements. The hydrogen atoms of the disordered moieties in **6**·2Et$_2$O and **7**·2CH$_2$Cl$_2$ were not located.

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