

# The C=O and C=S bond cleavage in carbon dioxide and tolyl isothiocyanate by reactions with the Mo(0) tetraphosphine complex [Mo{*meso-o*-C<sub>6</sub>H<sub>4</sub>(PPhCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>}(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]

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Received 13 October 2004; accepted 11 November 2004

Available online 28 December 2004

## Abstract

A Mo(0) complex containing a new tetraphosphine ligand [Mo(P<sub>4</sub>)(dppe)] (**1**; P<sub>4</sub> = *meso-o*-C<sub>6</sub>H<sub>4</sub>(PPhCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>, dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) reacted with CO<sub>2</sub> (1 atm) at 60 °C in benzene to give a Mo(0) carbonyl complex *fac*-[Mo(CO)(η<sup>3</sup>-P<sub>4</sub>=O)(dppe)] (**2**), where the O abstraction from CO<sub>2</sub> by one terminal P atom in P<sub>4</sub> takes place to give the dangling P(=O)Ph<sub>2</sub> moiety together with the coordinated CO. On the other hand, reaction of **1** with TolNCS (Tol = *m*-MeC<sub>6</sub>H<sub>4</sub>) in benzene at 60 °C resulted in the incorporation of three TolNCS molecules to the Mo center, forming a Mo(0) isocyanide–isothiocyanate complex *trans,mer*-[Mo(TolNC)<sub>2</sub>(η<sup>2</sup>-TolNCS)(η<sup>3</sup>-P<sub>4</sub>=S)] (**4**), where the S abstraction occurs from two TolNCS molecules by P<sub>4</sub> and dppe to give the η<sup>3</sup>-P<sub>4</sub>=S ligand and free dppe=S, respectively, together with two coordinated TolNC molecules. The remaining site of the Mo center is occupied by the third TolNCS ligating at the C=S bond in an η<sup>2</sup>-manner. The X-ray analysis has been undertaken to determine the detailed structures for **2** and **4**.

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**Keywords:** Molybdenum complex; Tetraphosphine complex; Carbon dioxide; Isothiocyanate; Phosphine–phosphine oxide ligand; Phosphine–phosphine sulfide ligand

## 1. Introduction

We reported previously the facile formation of [Mo(P<sub>4</sub>)(dppe)] (**1**; P<sub>4</sub> = *meso-o*-C<sub>6</sub>H<sub>4</sub>(PPhCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>, dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) from *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] and dppe [1]. Complex **1** contains a new tetradentate phosphine P<sub>4</sub>, which is generated in the coordination sphere of Mo stereoselectively via the condensation of two dppe ligands with concomitant loss

of benzene. Subsequent study on the reactions of **1** with small molecules such as nitrile, CO, and isocyanide has resulted in the isolation of a series of substitution products including *fac*-[Mo(L)(η<sup>3</sup>-P<sub>4</sub>)(dppe)], *cis*-[Mo(L)<sub>2</sub>(η<sup>4</sup>-P<sub>4</sub>)], *trans*-[Mo(L)<sub>2</sub>(η<sup>2</sup>-P<sub>4</sub>)(dppe)], and *fac*-[Mo(L)<sub>3</sub>(η<sup>3</sup>-P<sub>4</sub>)] (L = PhCN, CO, and/or XyNC; Xy = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [2], whereby the P<sub>4</sub> ligand can readily change its coordination mode from η<sup>4</sup> to η<sup>3</sup> and then to η<sup>2</sup>, and in certain cases from η<sup>2</sup> to η<sup>3</sup> and from η<sup>3</sup> to η<sup>4</sup>, because of the substantially weaker binding of the terminal P atoms than the inner P atoms. Now we have found that in the reactions of **1** with CO<sub>2</sub> and TolNCS (Tol = *m*-MeC<sub>6</sub>H<sub>4</sub>) the C=O and C=S bond cleavage

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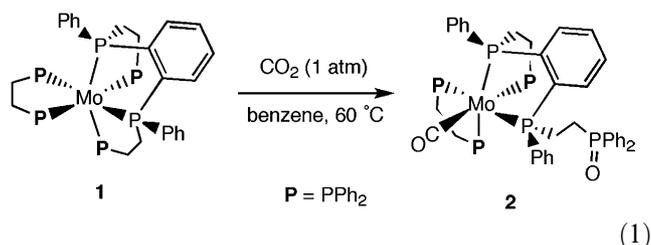
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takes place to give the coordinated CO and isocyanide accompanied by the transfer of the O and S atoms to the P atoms in the phosphine ligands. We wish to describe here the details of these interesting reactions of **1**. It is to be noted that although a significant number of tetraphosphines are known and the preparation of mono- and multi-nuclear complexes containing these phosphines as ligands has also been reported [3], studies on the reactivities of the tetraphosphine complexes are still quite rare.

## 2. Results and discussion

### 2.1. Reaction of **1** with CO<sub>2</sub>

When **1** dissolved in benzene was treated with CO<sub>2</sub> gas (1 atm) at 30 °C, reaction took place to give *fac*-[Mo(CO)( $\eta^3$ -P<sub>4</sub>=O)(dppe)] (**2**) very slowly. Even after 4 days a significant amount of unreacted **1** remained in the reaction mixture. By analogous treatment at 60 °C, the reaction completed by 6 h and **2** was isolated as red crystals in 32% yield by addition of hexane to the concentrated product solution (Eq. (1)).



In this reaction, oxygen abstraction from CO<sub>2</sub> by one terminal P atom in P<sub>4</sub> takes place to give the coordinated CO and the dangling P(=O)Ph<sub>2</sub> moiety in the  $\eta^3$ -P<sub>4</sub>=O ligand. The structure of **2** has been determined unambiguously by the X-ray analysis; the ORTEP

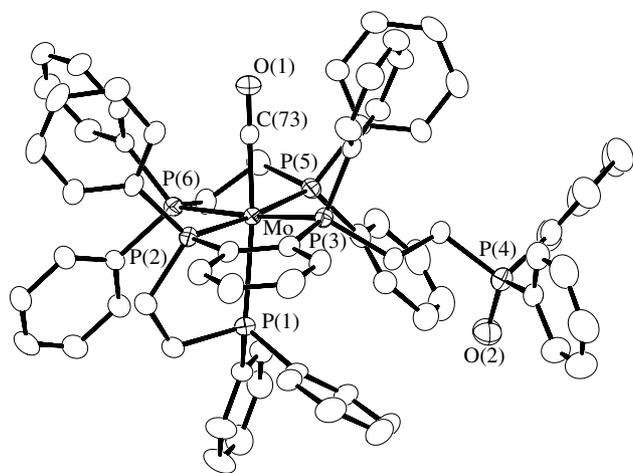


Fig. 1. An ORTEP drawing of **2** drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

drawing is depicted in Fig. 1, while the important bond distances and angles are listed in Table 1. Reactions of CS<sub>2</sub> with **1** were also carried out in benzene, toluene, and THF under various conditions. However, no characterizable Mo-containing products were isolated.

As shown in Fig. 1, **2** has an octahedral structure with the facial P<sub>4</sub>=O ligand bonded by three P atoms, the dppe ligand, and CO occupying the position *trans* to the terminal P atom in the P<sub>4</sub>=O ligand. The Mo–P(1) bond distance *trans* to the CO ligand at 2.573(2) Å is substantially longer than the other Mo–P bonds in the range 2.38–2.50 Å. The Mo–C(73) and C(73)–O(1) bond lengths are not exceptional as those of the end-on CO ligand bonded to the Mo(0) center. The P=O bond distance at 1.485(4) Å is typical as that of the tertiary phosphine oxide (e.g. mean value of 72 compounds: 1.489 Å [4]).

Table 1  
Selected bond distances (Å) and angles (°) in **2** and **4**

Compound <b>2</b>			
<i>Bond distance</i>			
Mo–P(1)	2.573(2)	Mo–P(2)	2.389(2)
Mo–P(3)	2.460(2)	Mo–P(5)	2.495(2)
Mo–P(6)	2.462(2)	Mo–C(73)	1.935(5)
P(4)–O(2)	1.485(4)	C(73)–O(1)	1.178(5)
<i>Bond angle</i>			
P(1)–Mo–P(2)	77.21(5)	P(1)–Mo–P(3)	92.85(5)
P(1)–Mo–P(5)	105.86(5)	P(1)–Mo–P(6)	91.44(5)
P(1)–Mo–C(73)	169.5(2)	P(2)–Mo–P(3)	80.49(5)
P(2)–Mo–P(5)	174.25(5)	P(2)–Mo–P(6)	94.85(5)
P(2)–Mo–C(73)	92.4(2)	P(3)–Mo–P(5)	104.02(5)
P(3)–Mo–P(6)	172.80(5)	P(3)–Mo–C(73)	84.4(1)
P(5)–Mo–P(6)	80.32(5)	P(5)–Mo–C(73)	84.6(2)
P(6)–Mo–C(73)	90.4(1)	Mo–C(73)–O(1)	176.9(4)
Compound <b>4</b>			
<i>Bond distance</i>			
Mo–P(1)	2.501(2)	Mo–P(2)	2.456(1)
Mo–P(3)	2.452(2)	Mo–C(47)	2.105(5)
Mo–C(55)	2.018(5)	Mo–C(63)	2.144(5)
Mo–S(2)	2.529(2)	C(47)–N(1)	1.155(6)
C(55)–N(2)	1.178(6)	C(63)–N(3)	1.256(6)
S(2)–C(63)	1.736(5)	P(4)–S(1)	1.954(2)
<i>Bond angle</i>			
P(1)–Mo–P(2)	76.69(6)	P(1)–Mo–P(3)	151.09(5)
P(1)–Mo–C(47)	96.1(1)	P(1)–Mo–C(55)	89.3(1)
P(1)–Mo–S(2)	83.10(6)	P(1)–Mo–C(63)	125.4(1)
P(2)–Mo–P(3)	74.48(6)	P(2)–Mo–C(47)	102.1(1)
P(2)–Mo–C(55)	86.0(2)	P(2)–Mo–S(2)	159.21(5)
P(2)–Mo–C(63)	157.9(1)	P(3)–Mo–C(47)	92.0(2)
P(3)–Mo–C(55)	86.6(2)	P(3)–Mo–S(2)	125.36(5)
P(3)–Mo–C(63)	83.5(2)	C(47)–Mo–C(55)	171.0(2)
C(47)–Mo–S(2)	84.7(1)	C(47)–Mo–C(63)	76.8(2)
C(55)–Mo–S(2)	88.9(1)	C(55)–Mo–C(63)	94.3(2)
S(2)–Mo–C(63)	42.6(1)	Mo–C(47)–N(1)	167.6(5)
C(47)–N(1)–C(48)	173.3(6)	Mo–C(55)–N(2)	178.0(5)
C(55)–N(2)–C(56)	157.7(6)	Mo–S(2)–C(63)	56.8(2)
Mo–C(63)–S(2)	80.6(2)	Mo–C(63)–N(3)	142.9(4)
S(2)–C(63)–N(3)	135.0(4)	C(63)–N(3)–C(64)	122.5(5)

The IR spectrum shows two characteristic bands at 1804 and 1186  $\text{cm}^{-1}$ , which are assignable to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{P}=\text{O})$ , respectively. The  $\nu(\text{C}=\text{O})$  value of **2** is in good agreement with those observed for the  $\text{P}_4$  analogue *fac*-[Mo(CO)( $\eta^3\text{-P}_4$ )(dppe)] (**3**; 1809  $\text{cm}^{-1}$ ) [2] and related Mo(0) complexes *fac*-[Mo(CO){PhP(CH<sub>2</sub>CH<sub>2</sub>-PPh<sub>2</sub>)<sub>2</sub>}(PMe<sub>2</sub>Ph)<sub>2</sub>] (1768  $\text{cm}^{-1}$ ) [5], while the  $\nu(\text{P}=\text{O})$  value corresponds well to those of Ph<sub>3</sub>P=O and Me<sub>3</sub>P=O at 1190 and 1176  $\text{cm}^{-1}$  [6].

The <sup>31</sup>P NMR spectrum of **2** is consistent with its X-ray structure, indicating that the solid state structure is preserved also in solution. Thus, the chemical shifts and coupling constants show clearly that the site *trans* to the terminal P atom of  $\text{P}_4=\text{O}$  is occupied by CO and those *trans* to the inner P atoms of  $\text{P}_4=\text{O}$  are by the dppe P atoms (see Section 3).

It is noteworthy that the  $\text{P}_4$  analogue **3** obtained directly from the reaction of **1** with CO gas has a slightly different geometry around Mo, in which the CO ligand occupies the position *trans* to the inner P atom adjacent to the dangling P atom in the  $\text{P}_4$  ligand (Chart 1) [2]. The structure of **3** was characterized by its <sup>31</sup>P NMR spectrum, which is apparently different from that of **2** and indicates that the P atom is absent at the site *trans* to the inner P atom next to the dangling PPh<sub>2</sub> moiety of the  $\eta^3\text{-P}_4$  ligand. This structure proposed for **3** is confirmed by comparing its <sup>31</sup>P NMR data with those of the crystallographically analyzed 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC(XyNC) analogue *fac*-[Mo(XyNC)( $\eta^3\text{-P}_4$ )(dppe)]. Apparently the geometry around Mo is dependent on the subtle factors in these complexes [Mo(L)( $\eta^3\text{-P}_4$ )(dppe)] and **2**.

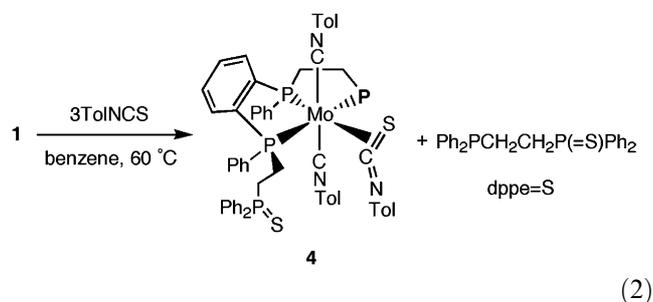
Extensive studies have been done about the reactions of CO<sub>2</sub> with transition metal complexes [7]. As for those with the related Mo(0) phosphine complexes, coordination of CO<sub>2</sub> or the disproportionation of CO<sub>2</sub> into CO and CO<sub>3</sub> ligands have been reported. Thus, formation of the substitution products [Mo(CO<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] was claimed for *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] [8], whereas not only *cis*-[Mo( $\eta^2\text{-CO}_2$ )<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] but also the Mo(II) complexes as the disproportionation products [Mo(CO)(CO<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>] and [Mo(CO)( $\mu\text{-CO}_3$ )(PMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>] were obtained from *cis*-[Mo(N<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] [9].

As the reaction quite analogous to the present work, conversion of CO<sub>2</sub> into the coordinated CO and phosphine oxide was observed in the reaction of the Mo(II)

complex [Cp\*Mo(PMe<sub>3</sub>)<sub>3</sub>H] (Cp\* =  $\eta^5\text{-C}_5\text{Me}_5$ ) with CO<sub>2</sub> to give [Cp\*Mo(PMe<sub>3</sub>)<sub>2</sub>(CO)H] and Me<sub>3</sub>P=O [10]. The proposed mechanism involves the initial displacement of PMe<sub>3</sub> by CO<sub>2</sub>, yielding [Cp\*Mo(PMe<sub>3</sub>)<sub>2</sub>( $\eta^2\text{-CO}_2$ )H], which undergoes the O atom abstraction by the free PMe<sub>3</sub>. Formation of **2** from **1** might proceed in an analogous manner, viz., an  $\eta^2\text{-CO}_2$  complex [Mo( $\eta^2\text{-CO}_2$ )( $\eta^3\text{-P}_4$ )(dppe)] generated initially is susceptible to the O atom abstraction by the dangling P atom of the  $\eta^3\text{-P}_4$  ligand to give **2**. By contrast, in the reaction of the W(II) complex [WCl<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] with CO<sub>2</sub> the C=O bond cleavage takes place to give instead the W(IV) complex as the oxidative addition product *cis,trans*-[WCl<sub>2</sub>(=O)(CO)(PPh<sub>2</sub>Me)<sub>2</sub>] [11]. Conversion of the polydentate phosphine into the mixed phosphine–phosphine oxide ligand [12] by the O atom abstraction from CO<sub>2</sub> is still quite rare but is precedent, i.e., treatment of a Ni(0) complex [Ni( $\eta^2\text{-CS}_2$ )(triphos)] (triphos = MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>) with CO<sub>2</sub> at room temperature gave a Ni(II) complex [Ni( $\eta^2\text{-CO}_3$ )( $\eta^2\text{-triphos=O}$ )] with concurrent liberation of CO [13]. In this reaction, not only the P atom in triphos but also CO<sub>2</sub> acts as the O atom acceptors.

## 2.2. Reaction of **1** with TolNCS

Treatment of **1** with 3 or more equiv of TolNCS in benzene at 60 °C afforded the bis(isocyanide)–isothiocyanate complex *trans,mer*-[Mo(TolNC)<sub>2</sub>( $\eta^2\text{-TolNCS}$ )( $\eta^3\text{-P}_4=\text{S}$ )] (**4**), which was isolated as red crystalline solid in 36 % yield (Eq. (2)).



It is quite noteworthy that 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 center 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  $\text{P}_4$  to give a dangling P(=S)Ph<sub>2</sub> moiety and the other is trapped by dppe. Formation of free dppe=S was confirmed by the <sup>31</sup>P NMR spectrum of the reaction mixture, exhibiting two doublets at 43.1 and –13.8 ppm ( $J(\text{P}-\text{P}) = 50$  Hz) assignable to dppe = S [14]. Reactions of **1** with other organic heterocumulenes such as PhNCO and Ph<sub>2</sub>CCO did not proceed cleanly and gave no characterizable products. For **4**, single crystals whose

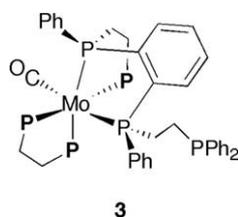


Chart 1.

asymmetric unit contains **4** and two benzene molecules were obtained in a small amount and the structure was determined in detail by the X-ray analysis. An ORTEP drawing is depicted in Fig. 2, while selected bond distances and angles are listed in Table 1.

Complex **4** has an octahedral structure with three meridional P atoms of  $P_4=S$  and TolNCS ligating in an  $\eta^2$  manner at the C=S bond in a basal plane together with two mutually *trans* TolNC ligands at the apical positions. For the Mo–P bond lengths, the distance of the terminal P(1) atom from Mo at 2.501(2) Å is longer than those of the inner P(2) and P(3) atoms from Mo at 2.456(1) and 2.452(2) Å, respectively. The TolNCS ligand coordinates to Mo in a manner that the NCS plane becomes coplanar with the basal plane. The N(3)–C(63)–S(2) linkage is bent with the angle of 135.0(4)° and the C(63)–S(2) bond length at 1.736(5) Å is significantly elongated from the typical C=S double bond length of ca. 1.66–1.68 Å [4]. The X-ray structure determination of the  $\eta^2$ -RNCS ligands has previously been carried out for [Co( $\eta^2$ -PhNCS){N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>}] (**5**) and [Ni( $\eta^2$ -PhNCS)(triphos)] (**6**), in which the N–C–S angle and the C–S bond length are 141.1(1)° and 1.72(2) Å for the former, and 141.8(2)° and 1.68(2) Å for the latter [15].

Two mutually *trans* TolNC ligands are not equivalent because of the presence of chiral P(2) and P(3) atoms. It is interesting to note that the structures of two TolNC ligands differ slightly. Thus, in the isocyanide ligating from the direction to which the *o*-phenylene group points, the C(55)–N(2)–C(56) linkage is bent considerably with the angle of 157.7(6)° and the Mo–C(55)–

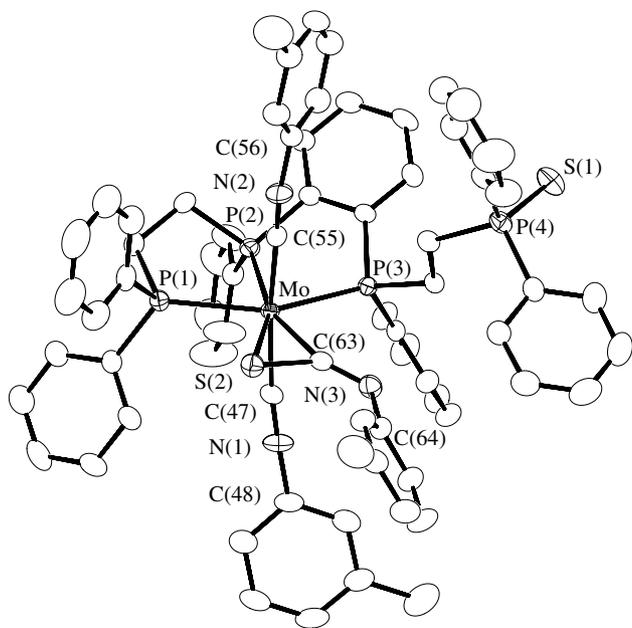


Fig. 2. An ORTEP drawing of **4** drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

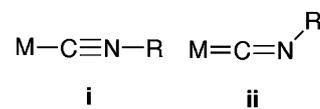


Chart 2.

N(2) is essentially linear (178.0(5)°), whereas in the other isocyanide ligand in the opposite side of the basal plane the C(47)–N(1)–C(48) angle is almost linear (173.3(6)°) and the Mo–C(47)–N(1) array (167.6(5)°) is bent slightly. Since the bending of the C–N–C angle in the end-on isocyanide ligands is accounted for by the contribution of the extreme structure **ii** to **i** shown in Chart 2, this finding can be interpreted in terms of the presence of greater contribution of the structure **ii** in the former TolNC. This correlates well with the other observation on the bond lengths in these two coordinated TolNC molecules, viz. the Mo–C(55) distance at 2.018(5) Å in the former is shorter than the Mo–C(47) distance at 2.105(5) Å in the latter and the C(55)–N(2) bond of 1.178(6) Å is elongated from the C(47)–N(1) bond of 1.155(6) Å, respectively.

In general, bent C–N–C linkage is found in the aliphatic isocyanides bound to a zero-valent metal center having no  $\pi$ -accepting ligands, in which electron density remains localized on the N atom and the C–N–C linkage tends to be bent due to the pairing effects of the electrons [16]. In the aryl isocyanide ligands, due to the ability to delocalize the charge from the N atom into the aromatic rings significant C–N–C bending is relatively rare except for, e.g. *cis*-[(CNC<sub>6</sub>H<sub>4</sub>NC)<sub>2</sub>W(dppe)<sub>2</sub>] (137(1)°, 141.4(8)°) [16], *trans*-[Mo(PhNC)(*p*-MeOC<sub>6</sub>H<sub>4</sub>CN)(dppe)<sub>2</sub>] (149.8(4)°), *trans*-[Mo(*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NC)( $\eta^2$ -H<sub>2</sub>)(dppe)<sub>2</sub>] (148.4(4)°) [17], [V(XyNC)<sub>6</sub>]<sup>*n*–</sup> (*n* = 0: av. 163(4)°, *n* = 1: av. 158(10)°) [18], and *cis*-[Mo(XyNC)<sub>2</sub>(P<sub>4</sub>)] (155.8(3) and 169.3(3)°) [2]. In **4**, it is likely that bending of the C–N–C angles is greatly affected not only by electronic effects but also by steric effects as well as crystal packing forces [18].

Formation of the phosphine sulfide moiety in the  $\eta^3$ -P<sub>4</sub>=S ligand has also been unambiguously demonstrated by the X-ray analysis, where the P=S bond length at 1.954(2) Å is in good agreement with the reported P=S bond distance of 1.954 Å as the mean value of 13 tertiary phosphine sulfides [4].

The <sup>1</sup>H NMR spectrum of **4** shows three singlets at 2.28, 1.86, and 1.77 ppm due to the Me protons of three inequivalent Tol groups, which is consistent with the results of the X-ray analysis, although these three signals were unable to be assigned. In the IR spectrum (KBr), the  $\nu(\text{N}\equiv\text{C})$  bands of two TolNC ligands are recorded as only one intense absorption at 1897 cm<sup>–1</sup>, while the characteristic  $\nu(\text{N}=\text{C})$  band due to the  $\eta^2$ -TolNCS ligand appears at 1598 cm<sup>–1</sup>. The  $\nu(\text{N}\equiv\text{C})$  value observed for **4** is not exceptional as that of the end-on aryl isocyanides. For comparison, the  $\nu(\text{N}=\text{C})$

values observed for the  $\eta^2$ -SCNPh complexes **5** [19] and **6** [20] cited above are 1620 and 1640  $\text{cm}^{-1}$ , respectively.

As described above, the reaction with  $\text{CO}_2$  is presumed to be initiated by the formation of  $[\text{Mo}(\eta^2\text{-CO}_2)(\eta^3\text{-P}_4)(\text{dppe})]$  from  $\{\text{Mo}(\eta^3\text{-P}_4)(\text{dppe})\}$  and  $\text{CO}_2$ . In contrast, since sterically much bulkier TolNCS cannot bind directly the vacant site of  $\{\text{Mo}(\eta^3\text{-P}_4)(\text{dppe})\}$ , dissociation of another P atom might be required prior to the coordination of TolNCS. The species containing both  $\eta^3\text{-P}_4$  and  $\eta^1$ -dppe ligands thus obtained  $\{\text{Mo}(\eta^2\text{-TolNCS})(\eta^3\text{-P}_4)(\eta^1\text{-dppe})\}$  is likely to undergo the S abstraction by the dangling P atom in the  $\eta^1$ -dppe ligand to give  $\{\text{Mo}(\text{TolNC})(\eta^4\text{-P}_4)\}$  and free  $\text{dppe}=\text{S}$ . This mechanism is supported by the finding that the reaction of **1** with 2 equiv of TolNCS gives  $[\text{Mo}(\text{TolNC})(\eta^2\text{-TolNCS})(\eta^4\text{-P}_4)]$  and  $\text{dppe}=\text{S}$ , although this complex could not be isolated in an analytically pure form and was characterized only spectroscopically.

Conversion of RNCS into RNC has been observed in the reaction of  $[\text{CpCo}(\text{PMe}_3)_2]$  ( $\text{Cp}=\eta^5\text{-C}_5\text{H}_5$ ) with RNCS (R = Me, Ph) to give  $[\text{CpCo}(\text{PMe}_3)(\text{RNC})]$  and  $\text{Me}_3\text{P}=\text{S}$  [21] and that of the  $\eta^2$ -SCNPh complex **5** with  $\text{NaBPh}_4$  to afford  $[\text{Co}(\text{PhNC})\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$  [19]. For the latter reaction, the fate of the abstracted sulfur is not addressed.

### 3. Experimental

#### 3.1. General considerations

All manipulations were carried out under  $\text{N}_2$  using standard Schlenk techniques. Solvents were dried by common methods and distilled under  $\text{N}_2$  before use. Complex **1** was prepared as described previously [1], while  $\text{CO}_2$  gas and all reagents were commercially obtained and used without further purification.

NMR and IR spectra were measured at room temperature on a JEOL alpha-400 or a JASCO FT/IR-420 spectrometer. For  $^{31}\text{P}$  NMR data, numbering of the P atoms in **2** and **4** are shown in Charts 3 and 4, respectively. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer.

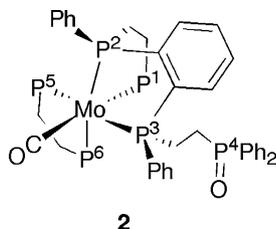


Chart 3.

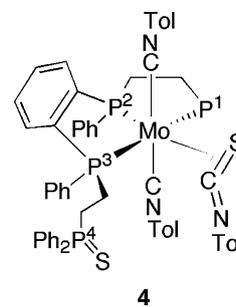


Chart 4.

#### 3.2. *fac*- $[\text{Mo}(\text{CO})(\eta^3\text{-P}_4=\text{O})(\text{dppe})]$ (**2**)

Carbon dioxide gas was bubbled through a benzene suspension (8 mL) of **1** (136 mg, 0.106 mmol) for 5 min and the mixture was continuously stirred under a  $\text{CO}_2$  atmosphere at 60 °C for 6 h. After cooling, hexane was added under  $\text{N}_2$  to the concentrated product solution, giving **2** as red crystals (41 mg, 31% yield).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 95.7 (P2), 69.2 (P3), 67.5 (P6), 65.8 (P5), 47.7 (P1), 27.7 (P4);  $J(\text{P2-P6}) = 92$ ,  $J(\text{P3-P5}) = 85$ ,  $J(\text{P3-P4}) = 23$  Hz. IR (KBr,  $\text{cm}^{-1}$ ): 1804 ( $\text{C}\equiv\text{O}$ ), 1186 ( $\text{P}=\text{O}$ ). Anal. Calc. for  $\text{C}_{73}\text{H}_{66}\text{O}_2\text{P}_6\text{Mo}$ : C, 69.75; H, 5.29. Found: C, 70.15; H, 5.47%.

#### 3.3. *trans,mer*- $[\text{Mo}(\text{TolNC})_2(\eta^2\text{-TolNCS})(\eta^3\text{-P}_4=\text{S})]$ (**4**)

To a solution of **1** (127 mg, 0.0984 mmol) in benzene (10 mL) was added TolNCS (45 mg, 0.301 mmol), and a mixture was stirred at 60 °C for 18 h. After filtration, hexane was added to the concentrated filtrate to give  $\mathbf{4} \cdot \text{C}_6\text{H}_6$  as red microcrystalline powder (46 mg, 36% yield). Single crystals obtained in a small amount were characterized to be  $\mathbf{4} \cdot 2\text{C}_6\text{H}_6$  by the X-ray crystallography.  $\mathbf{4} \cdot \text{C}_6\text{H}_6$ :  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 84.8 (P2), 73.0 (P3), 70.2 (P1), 45.9 (P4);  $J(\text{P1-P3}) = 75$ ,  $J(\text{P3-P4}) = 30$ ,  $J(\text{P1-P2}) = 23$ ,  $J(\text{P2-P3}) = 23$  Hz.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 2.28, 1.86, 1.77 (3H each, s, Me in TolNC and TolNCS). IR (KBr,  $\text{cm}^{-1}$ ): 1897 ( $\text{N}\equiv\text{C}$ ), 1598 ( $\text{N}=\text{C}$ ). Anal. Calc. for  $\text{C}_{76}\text{H}_{69}\text{N}_3\text{S}_2\text{P}_4\text{Mo}$ : C, 69.77; H, 5.32; N, 3.21. Found: C, 69.70; H, 5.65; N, 2.96%.

#### 3.4. $\text{Mo}(\text{TolNC})(\eta^2\text{-TolNCS})(\eta^4\text{-P}_4)$

A solution containing **1** (127 mg, 0.984 mmol) and 2 equiv of TolNCS (30 mg) in benzene (10 mL) was stirred at 60 °C for 18 h. After filtration, the filtrate was dried up and the residue was crystallized from benzene-hexane, yielding the title compound as a red-brown solid. The yield was not determined since the product was not available in an analytically pure form.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 97, 91, 74, 49.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,

ppm): 2.15, 1.92 (3H each, s, Me in TolNC and TolNCS). IR (KBr,  $\text{cm}^{-1}$ ): 1930 ( $\text{N}\equiv\text{C}$ ), 1587 ( $\text{N}=\text{C}$ ). The  $^{31}\text{P}$  chemical shifts are typical to the  $\eta^4\text{-P}_4$  ligand with the *fac-mer* array [1,2], although the coupling constants were unable to be determined due to the broadening of the signals.

### 3.5. X-ray crystallography

Single crystals were sealed in glass capillaries under argon and mounted on a Rigaku Mercury-CCD diffractometer for **2** or a Rigaku AFC7R four-circled diffractometer for **4** equipped with a graphite-mono-chromatized Mo  $\text{K}\alpha$  source. All diffraction studies were performed at 23 °C and intensity data were corrected for Lorentz-polarization effects and for absorption. Details are shown in Table 2.

Structure solution and refinements were carried out using the CrystalStructure program package [22]. The positions of non-hydrogen atoms were determined by Patterson methods (PATTY) [23] and subsequent Fourier synthesis (DIRDIF 99) [24]. These were refined with anisotropic thermal parameters, while hydrogen atoms were placed at the calculated positions and included at the final stages of refinements with fixed parameters.

Table 2  
Details of the X-ray crystallography

	<b>2</b>	<b>4</b> · 2C <sub>6</sub> H <sub>6</sub>
Formula	C <sub>73</sub> H <sub>66</sub> O <sub>2</sub> P <sub>6</sub> Mo	C <sub>82</sub> H <sub>75</sub> N <sub>3</sub> P <sub>4</sub> S <sub>2</sub> Mo
<i>M</i>	1257.11	1386.47
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
<i>a</i> (Å)	13.437(3)	12.232(8)
<i>b</i> (Å)	14.324(3)	25.18(1)
<i>c</i> (Å)	17.665(5)	23.507(6)
$\alpha$ (°)	76.129(10)	90
$\beta$ (°)	80.029(10)	102.47(4)
$\gamma$ (°)	70.787(9)	90
<i>V</i> (Å <sup>3</sup> )	3100(1)	7069(6)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.346	1.303
$\mu$ (Mo $\text{K}\alpha$ ) (cm <sup>-1</sup> )	4.13	3.82
Transmittance factor	0.913–0.960	0.822–0.892
Unique reflections ( <i>R</i> <sub>int</sub> )	14675 (0.049)	16523 (0.054)
Observed reflections ( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))	6831	7608
Variables	805	904
<i>R</i> <sup>a</sup>	0.050	0.045
<i>wR</i> <sup>b</sup>	0.110	0.112
GOF <sup>c</sup>	1.02	1.02
Residuals (e ; Å <sup>-3</sup> )	1.14, -0.45	0.40, -0.38

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

$$^c \text{GOF} = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\{(\text{no. observed}) - (\text{no. variables})\}} \right]^{1/2}$$

## 4. Supplementary material

Listing of atomic coordinates, anisotropic thermal parameters, and extensive interatomic distances and angles for **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 257393 and 257394, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

## Acknowledgments

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 14078206, “Reaction Control of Dynamic Complexes”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and by CREST of JST (Japan Science and Technology Agency).

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