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Reactions of tetraphosphine complex $[Mo\{meso\text{-}o\text{-}C_6H_4(PPhCH_2CH_2PPh_2)_2\}(Ph_2PCH_2CH_2PPh_2)]$ with nitrile, CO, and isocyanide

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Abstract

When treated with three equivalents of PhCN in benzene at room temperature, $[Mo(\eta^4\text{-}\mathbf{P_4})(dppe)]$ (**1**) containing a linear tetraphosphine *meso*-*o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ (**P₄**) as well as a diphosphine $Ph_2PCH_2CH_2PPh_2$ (dppe) afforded a nitrile complex $[Mo(PhCN)(fac\text{-}\eta^3\text{-}\mathbf{P_4})(dppe)]$ (**2**), whereas treatment of **1** with CO (1 atm) in benzene at room temperature resulted in the formation of a 1:1 mixture of the CO analogue of **2** $[Mo(CO)(fac\text{-}\eta^3\text{-}\mathbf{P_4})(dppe)]$ and a bis(carbonyl) complex *cis*-$[Mo(CO)_2(\eta^4\text{-}\mathbf{P_4})]$. In contrast, reactions of **1** with XyNC ($Xy = 2,6\text{-}Me_2C_6H_3$) gave more diversified products varying from mono(isocyanide) to tris(isocyanide) complexes. Thus, reaction of **1** with an equimolar amount of XyNC gave a mixture of two isomers of mono(isocyanide) complex $[Mo(XyNC)(fac\text{-}\eta^3\text{-}\mathbf{P_4})(dppe)]$ (**5** and **6**) along with a bis(isocyanide) complex *cis*-$[Mo(XyNC)_2(\eta^4\text{-}\mathbf{P_4})]$ (**7**). It has also been found that mono(isocyanide) complexes **5** and **6** are treated further with one equivalent of XyNC at elevated temperatures to form the expected bis(isocyanide) complex **7** as well as the other bis(isocyanide) complex *trans*-$[Mo(XyNC)_2(\eta^2\text{-}\mathbf{P_4})(dppe)]$ (**8**). By heating in solution, the latter was converted into the former. From the reaction of **7** with excess XyNC, a tris(isocyanide) complex $[Mo(XyNC)_3(fac\text{-}\eta^3\text{-}\mathbf{P_4})]$ was obtained. The X-ray analyses have disclosed the detailed structures for **2**, **5**, **7**, and **8**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mo complex; Tetraphosphine; Carbon monoxide; Isocyanide; X-Ray structure

1. Introduction

In the previous paper [1], we have reported the synthesis of a zero-valent Mo complex $[Mo(\mathbf{P_4})(dppe)]$ (**1**; $\mathbf{P_4} = meso\text{-}o\text{-}C_6H_4(PPhCH_2CH_2PPh_2)_2$ (Chart I); dppe $= Ph_2PCH_2CH_2PPh_2$) from a dinitrogen complex *trans*-$[Mo(N_2)_2(dppe)_2]$, which contains a new tetraphosphine ligand **P₄** formed through the condensation of two dppe ligands in the coordination sphere of Mo (Eq. (1)) [2]. It is to be noted that this reaction proceeds stereoselectively with respect to the two inner P atoms in this linear tetraphosphine to give a *meso* diastereomer exclusively. Since **1** has a severely distorted octahedral structure owing to the coordination of six sterically encumbered, tertiary phosphorous atoms involved in the linear tetradentate phosphine **P₄** and the diphosphine dppe, coordinatively unsaturated species might readily be generated by dissociating either the dppe ligand or the terminal P atom(s) in **P₄**. This presumably leads to the formation of a series of new **P₄** complexes incorporating various substrate molecules. It is noteworthy that in spite of the extensive studies on the polydentate phoshines as well as the metal complexes containing such ligands [3], those associated with linear tetraphosphines are quite limited [4]. Since the Mo(0) centers surrounded by the tertiary phosphine coligands are known to bind and highly activate N_2 as well as certain molecules isoelectonic with N_2, we have investigated the reactivities of **1** towards the substrate molecules such as nitrile, CO, and isocyanide. In this paper, we wish to summarize the results of these studies, which have

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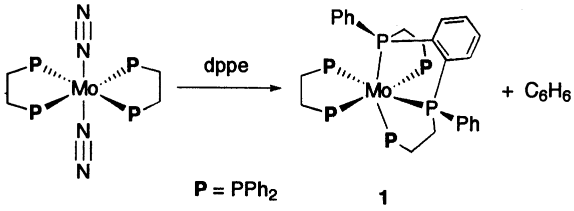
revealed the interesting feature of $\mathbf{P_4}$ containing both the inner P atoms that can bind tightly to the metal center and the outer P atoms that have relatively weaker coordinating ability, resulting in the facile change in its coordination mode from η^4 to η^3 and η^2 in particular complexes.



(1)

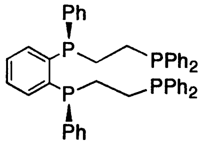
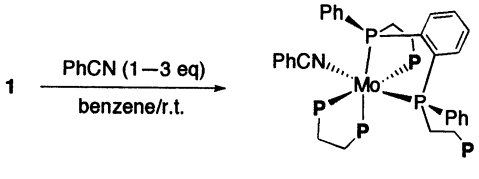


Chart I

2. Results and discussion

2.1. Reaction of **1** with benzonitrile

When **1** was treated with three equivalents of PhCN at room temperature in benzene, [Mo(PhCN)(*fac*-η^3-$\mathbf{P_4}$)(dppe)] (**2**) was obtained as dark green crystals (Eq. (2)). Coordination of PhCN has been substantiated by the characteristic ν(C≡N) band at 2103 cm^{-1} observed in its IR spectrum, which is much lower than that of the free PhCN (2231 cm^{-1}). This ν(C≡N) for **2** is considerably lower than those in the other zero-valent $Mo(dppe)_2$ complexes such as *trans*-[Mo(PhCN)(N_2)$(dppe)_2$] (2134 cm^{-1}) [5] and *trans*-[Mo(PhCN)(CO)$(dppe)_2$] (2174 cm^{-1}) [6], indicating that the π-back donating abilities of the Mo centers towards the PhCN ligand are in the order {Mo(*fac*-η^3-$\mathbf{P_4}$)(dppe)} > {Mo(N_2)$(dppe)_2$} > {Mo(CO)$(dppe)_2$}. The *p*-$MeOC_6H_4CN$ analogue of **2** was able to be prepared analogously, which shows the ν(C≡N) band at 2124 cm^{-1}.



2 (87%)

(2)

Reactions of **1** with PhCN at higher temperatures were also undertaken, which resulted in the formations of other products containing PhCN in addition to **2**. However, we could not characterize these products in a well-defined manner. It shoud be noteworthy that any reaction mixtures obtained under the diversified reaction conditions did not contain a bis(nitrile) complex *cis*-[Mo$(PhCN)_2$(η^4-$\mathbf{P_4}$)]. In contrast, it has been found as described below that the reactions of **1** with CO and XyNC (Xy = 2,6-$Me_2C_6H_3$) readily afford the corresponding *cis*-[Mo$(L)_2$(η^4-$\mathbf{P_4}$)] (L = CO, XyNC). This finding might be consistent with the previous observations that *trans*-[Mo$(N_2)_2$$(dppe)_2$] readily reacts with CO and isocyanides to give *cis*-[Mo$(CO)_2$$(dppe)_2$] [7] and *trans*-[Mo$(RNC)_2$$(dppe)_2$] [8], respectively, whereas treatment of **1** with nitriles affords only the monosubstituted products *trans*-[Mo(RCN)(N_2)$(dppe)_2$] [5].

The structure of **2** has been determined in detail by the single crystal X-ray analysis. An ORTEP drawing is shown in Fig. 1, while the important bond distances and angles are listed in Table 1. Complex **2** has a distorted octahedral geometry with a $\mathbf{P_4}$ ligand bonded to Mo in a facial manner by only the P(1)–P(3) atoms. The remaining sites are occupied by the chelating dppe and an η^1-PhCN ligand. In the nitrile ligand located *trans* to P(3) with the P(3)–Mo–N angle of 167.26(10)°, both the C(74)–C(73)–N and C(73)–N–Mo linkages are essentially linear, whose angles are 176.7(5) and 176.3(4)°, respectively. As expected from the IR data, the C(73)–N bond distance at 1.155(5) Å is elongated from the typical C ≡ N bond lengths of the aryl nitriles (1.133–1.143 Å) [9] but only slightly. This C≡N bond distance in **2** is almost comparable to those of the nitrile

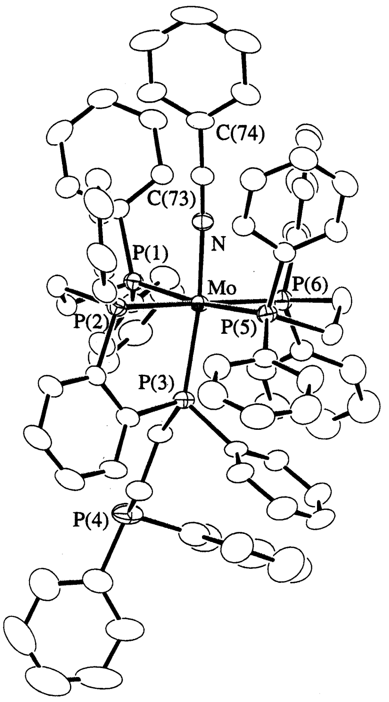


Fig. 1. An ORTEP drawing of **2**. For clarity, all hydrogen atoms are omitted.

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

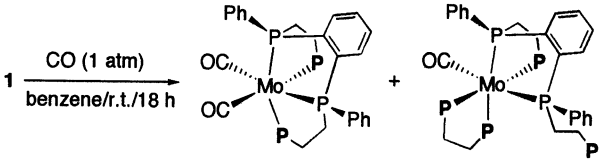
Bond lengths			
Mo–P(1)	2.471(1)	Mo–P(2)	2.391(1)
Mo–P(3)	2.446(1)	Mo–P(5)	2.456(1)
Mo–P(6)	2.463(1)	Mo–N	2.080(4)
N–C(73)	1.155(5)	C(73)–C(74)	1.423(6)
Bond angles			
P(l)–Mo–P(2)	79.10(4)	P(l)–Mo–P(3)	96.19(4)
P(l)–Mo–P(5)	173.19(4)	P(l)–Mo–P(6)	99.28(4)
P(l)–Mo–N	87.4(1)	P(2)–Mo–P(3)	79.34(4)
P(2)–Mo–P(5)	102.29(4)	P(2)–Mo–P(6)	178.27(5)
P(2)–Mo–N	89.4(1)	P(3)–Mo–P(5)	90.62(4)
P(3)–Mo–P(6)	100.29(4)	P(3)–Mo–N	167.26(10)
P(5)–Mo–P(6)	79.39(4)	P(5)–Mo–N	86.0(1)
P(6)–Mo–N	91.2(1)	Mo–N–C(73)	176.3(4)
N–C(73)–C(74)	176.7(5)		

ligand in the recently analyzed Mo(0) complexes *trans*-[Mo(L)(*p*-MeOC$_6$H$_4$CN)(dppe)$_2$] (L = PhNC: 1.153(4) Å [10], CO: 1.131(6); N$_2$: 1.127(4) Å [11]), each of which shows the ν(C≡N) band due to the nitrile ligand at 2171, 2184, and 2142 cm^{-1} (free *p*-MeOC$_6$H$_4$CN: 2217 cm^{-1}).

In accordance with this solid state structure, the ^{31}P-NMR spectrum of **2** shows six signals, although two of them are overlapping and unable to be resolved in a well-defined manner. The data are summarized in the Section 3. The most significant difference observed in the spectrum of **2** from that of **1** is the appearance of one resonance in very high field (δ -14.9), which is unambiguously assignable to the dangling P atom in the **P$_4$** ligand (P4 in Chart II in Section 3). It is commonly observed that the ^{31}P-NMR signal of the phosphine shifts to the higher field upon dissociation from the metal center. As described in the previous paper [1b], resonances due to the inner P atom in **P$_4$** tend to appear in relatively low field, when their two adjacent P atoms are both bound to the Mo center. Hence, the signal resonating at δ 93.8 can be attributed to P2. However, the other resonances cannot be assigned unequivocally.

2.2. *Reaction of **1** with CO*

When **1** was reacted with CO (1 atm) in benzene at room temperature for 18 h, the ^{31}P-NMR spectrum of the reaction mixture revealed the formation of two products in a ratio of ca. 1:1. One product isolated in an analytically pure form after fractional crystallization was characterized as *cis*-[Mo(CO)$_2$(η^4-**P$_4$**)] (**3**), whereas the other was unable to be purified satisfactorily and tentatively formulated as [Mo(CO)(*fac*-η^3-**P$_4$**)(dppe)] (**4**) on the basis of its spectroscopic data obtained for the mixture with **3** (Eq. (3)). Even after stirring this reaction mixture under CO (1 atm) for an additional period, the ratio of **3**:**4** did not change at this temperature, indicating that the conversion of **4** into **3** does not proceed under these conditions and the transformation of **1** into the bis(CO) complex **3** at room temperature probably proceeds via the mono(CO) intermediate other than **4**. It is to be noted that the presence of the isomer of **4** is possible as substantiated for the XyNC analogues (vide infra), although we could not detect it in the reactions with CO. Meanwhile, treatment of this mixture of **3** and **4** with CO at higher temperatures, e.g. 80 °C, the ratio of **3/4** apparently increased, e.g. from 1:1 to 4:1. However, the reaction did not proceed cleanly because of the presence of other intractable product in addition to **3** and **4**. This is also the case when **1** was treated directly with CO at elevated temperatures.



3 **4**

(3 : 4 = ca. 1 : 1)

(3)

Complex **3** shows two intense ν(C ≡ O) bands at 1864 and 1810 cm^{-1} in its IR spectrum, which are slightly higher than those of *cis*-[Mo(CO)$_2$(dppe)$_2$] (1852 and 1786 cm^{-1}) [12] and related diphosphine complexes *cis*-[Mo(CO)$_2${Ph$_2$P(CH$_2$)$_n$PPh$_2$}$_2$] (n = 1: 1850 and 1780; n = 3: 1860 and 1785 cm^{-1}) [13]. This finding indicates that the {Mo(η^4-**P$_4$**)} chromophore is a poorer π-donor than the {Mo{Ph$_2$P(CH$_2$)$_n$PPh$_2$}$_2$ (n = 1–3) moiety towards the CO ligands occupying the remaining two mutually *cis* sites. For **4**, which is available only as a mixture with **3**, the ν(C ≡ O) band was not assignable unambiguously, since the IR spectrum of the mixture of **3** and **4** also showed only two ν(C ≡ O) bands with nearly the same frequencies as those of **3**. However, the band of the lower frequency (1809 cm^{-1}) is much more intense than that of the higher frequency. This presumably indicates that the ν(C ≡ O) band for **4** is overlapping the former. Monocarbonyl complexes containing five tertiary phosphine ligands such as *fac*-[Mo(CO){PhP(CH$_2$CH$_2$PPh$_2$)$_2$}(PMe$_2$Ph)$_2$] [14], *fac*-[Mo(CO){PhP(CH$_2$CH$_2$PPh$_2$)$_2$}(Ph$_2$PCH$_2$PPh$_2$)] [15], and [Mo(CO)(PMe$_3$)$_5$] [16] were reported to exhibit the ν(C ≡ O) bands at 1760, 1782, and 1773 cm^{-1}, respectively.

The ^{31}P-NMR spectrum of **3** shows four signals, two of which in the low field (δ 99.7 and 97.2) are due to the inner P atoms, while the remaining two in the higher region (δ 70.0 and 56.5) are attributable to the outer P atoms. In consideration of a large coupling constant observed only between the mutually *trans* P2 and P4 atoms, the four signals are all assignable unequivocally to the P atoms P1–P4 shown in Chart III of Section 3. On the other hand, since the spectrum of **4** is in good agreement with that of the fully characterized [Mo(XyNC)(*fac*-η^3-$\mathbf{P_4}$)(dppe)] (**5**) described below, its structure is inferred to be same as that of **5**. Assignment of the ^{31}P-NMR resonances for **4** is also shown in Chart III, which still includes ambiguity for identifying the P1 and P5 signals.

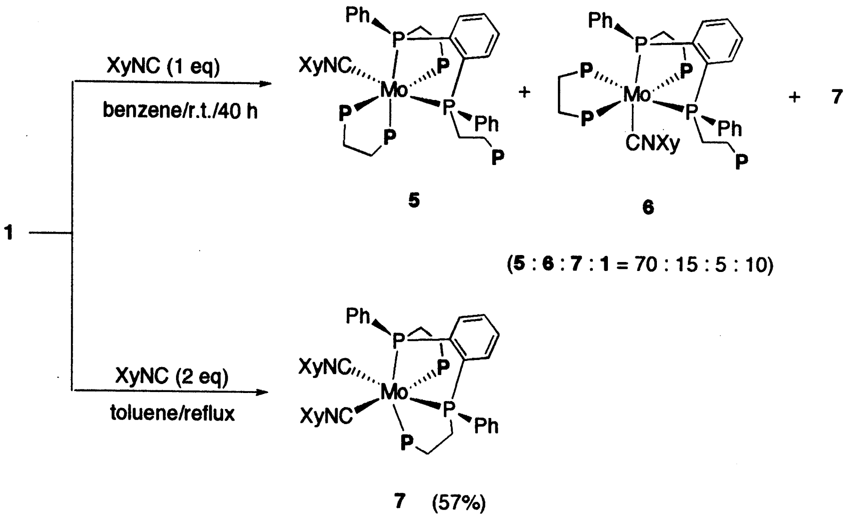
2.3. Reactions of parent complex *1* with XyNC

Treatment of **1** with an equimolar amount of XyNC in benzene at room temperature for 40 h afforded a mixture of three products, which are the expected mono(isocyanide) complex **5**, and its isomer **6**, together with a bis(isocyanide) complex *cis*-[Mo(XyNC)$_2$(η^4-$\mathbf{P_4}$)] (**7**) in low yield (Scheme 1). The molar ratio of these three products and unreacted **1**, viz. **5**:**6**:**7**:**1**, in the reaction mixture can be calculated to be ca. 70:15:5:10 by NMR spectroscopy, from which **5** and **6** were isolated in 58 and 10% yields, respectively. These were characterized spectroscopically and by elemental analyses. For **5**, X-ray analysis was also undertaken. Complex **7** in the product mixture was identified by comparing its ^{31}P-NMR spectrum with that of authenticated **7** prepared independently (vide infra).

It is noteworthy that the two isomers of the mono-substituted complexes **5** and **6** are isolable in the reaction with XyNC. Interconversion between these two in solutions does not occur at room temperature. Complex **6** is presumed to be the kinetically favored product since it forms through the direct binding of XyNC to the vacant site generated by dissociation of one terminal P atom in $\mathbf{P_4}$. However, neither mono(PhCN) nor mono(CO) complexes of this type could be isolated as described above. Stabilities of mono-substituted complexers with dppe and η^3-$\mathbf{P_4}$ coligands might be determined by a subtle balance of the electronic and steric factors associated with the ligating substrate molecule.

The X-ray analysis of **5** has disclosed that the asymmetric unit contains two crystallographycally independent molecules of **5**. Table 2 summarizes the selected bond distances and angles in **5**, while an ORTEP drawing of one of the two essentially isostructural molecules is depicted in Fig. 2. Complex **5** has an octahedral structure with an η^3-$\mathbf{P_4}$ ligand as well as a chelating dppe and a XyNC ligand. The XyNC ligand occupies the *trans* site of one of the inner P atoms in $\mathbf{P_4}$ (P(3)), which is adjacent to the dangling outer P atom (P(4)). As for the XyNC ligand, the N ≡ C bond lengths at 1.18(2) and 1.21(2) Å as well as the Mo–C distances of 2.00(1) and 1.99(1) Å are consistent with those in the XyNC ligands functioning as a good π-acceptor [17,18]. These values are in good agreement with those in *trans*-[Mo(PhNC)(N$_2$)(dppe)$_2$] (Mo–C: 1.992(3), N ≡ C: 1.179(4) Å) and *trans*-[Mo(PhNC)$_2$(dppe)$_2$] (Mo–C: 2.031(6), N ≡ C: 1.171(6) Å), whereas the Mo–C bonds are shorter and the N ≡ C bonds are longer considerably than those in *trans*-[Mo(PhNC)(CO)(dppe)$_2$] (Mo–C: 2.072(4), N ≡ C: 1.099(4) Å) having a strongly π-accepting CO ligand [10]. The Mo–C–N linkages with the angles of 176(1) and 177(1)° are essentially linear, while the C–N–C angles of 168(1) and 165(1)° indicate that these arrays are bent slightly.

In the IR spectrum of **5**, an intense ν(N ≡ C) band appeared at 1848 cm^{-1}, which is much lower than the value observed for free XyNC (2121 cm^{-1}). This clearly supports the results of the X-ray analysis indicating the presence of strong π-back donation from Mo. It has been shown that the ν(N ≡ C) frequency for a series of mono-PhNC complexes *trans*-[Mo(PhNC)(L)(dppe)$_2$] varies significantly, depending on the nature of L: the observed values in cm^{-1} are 1991 and 2017 for L = CO,



Scheme 1.

Table 2
Selected bond lengths (Å) and angles (°) in **5**

Bond lengths			
Molecule 1			
Mo(1)–P(1)	2.485(4)	Mo(1)–P(2)	2.388(3)
Mo(1)–P(3)	2.520(4)	Mo(l)–P(5)	2.480(4)
Mo(1)–P(6)	2.481(4)	Mo(1)–C(73)	2.00(1)
C(73)–N(1)	1.18(2)	N(1)–C(74)	1.38(2)
Molecule 2			
Mo(2)–P(7)	2.480(4)	Mo(2)–P(8)	2.394(3)
Mo(2)–P(9)	2.511(4)	Mo(2)–P(11)	2.466(4)
Mo(2)–P(12)	2.477(3)	Mo(2)–C(l54)	1.99(1)
C(154)–N(2)	1.21(2)	N(2)–C(155)	1.38(1)
Bond angles			
Molecule 1			
P(1)–Mo(1)–P(2)	79.9(1)	P(1)–Mo(1)–P(3)	93.7(1)
P(1)–Mo(1)–P(5)	177.2(1)	P(1)–Mo(1)–P(6)	99.2(1)
P(1)–Mo(1)–C(73)	87.9(4)	P(2)–Mo(1)–P(3)	79.5(1)
P(2)–Mo(2)–P(5)	100.7(1)	P(2)–Mo(1)–P(6)	179.1(2)
P(2)–Mo(1)–C(73)	89.1(4)	P(3)–Mo(1)–P(5)	89.1(1)
P(3)–Mo(1)–P(6)	100.4(1)	P(3)–Mo(1)–C(73)	168.0(4)
P(5)–Mo(1)–P(6)	80.2(1)	P(5)–Mo(1)–C(73)	893.0(4)
P(6)–Mo(1)–C(73)	91.0(4)	Mo(l)–C(73)–N(1)	176.0(1)
C(73)–N(1)–C(74)	168.0(1)		
Molecule 2			
P(7)–Mo(2)–P(8)	80.0(1)	P(7)–Mo(2)–P(9)	91.6(1)
P(7)–Mo(2)–P(11)	178.43(10)	P(7)–Mo(2)–P(12)	100.0(1)
P(7)–Mo(2)–C(l54)	89.9(4)	P(8)–Mo(2)–P(9)	79.5(1)
P(8)–Mo(2)–P(11)	99.4(1)	P(8)–Mo(2)–P(12)	179.0(1)
P(8)–Mo(2)–C(154)	89.8(4)	P(9)–Mo(2)–P(11)	89.8(1)
P(9)–Mo(2)–P(12)	101.5(1)	P(9)–Mo(2)–C(l54)	168.8(4)
P(11)–Mo(2)–P(12)	80.6(1)	P(11)–Mo(2)–C(l54)	88.6(4)
P(12)–Mo(2)–C(154)	89.2(4)	Mo(2)–C(154)–N(2)	177.0(1)
C(154)–N(2)–C(155)	165.0(1)		

1910 for L = N_2, 1875 and 1817 for L = H_2, and 1821 and 1715 for L = p-$MeOC_6H_4CN$ [10]. The ^{31}P-NMR spectrum exhibited well-separated six signals, whose possible assignment is shown in Chart IV in Section 3. As described already, one resonance observed in a high field (δ −15.5) is attributable to the uncoordinated P4, while one signal with quite a large, positive chemical shift (δ 94.2) is presumed to result from the inner P atom between two coordinating P atoms in $\mathbf{P_4}$ (P2). Two peaks among the other four signals are assignable unambiguously to P3 and P6 on the basis of their coupling mode with other P atoms, but the assignment for the remaining two is uncertain.

The IR spectrum of **6** also shows a strong band characteristic of $\nu(N\equiv C)$. The observed frequency of 1830 cm^{-1} is almost comparable to that of **5**. The ^{31}P-NMR spectrum also suggests that **6** has an analogous coordination environment to that of **5**. However, the ^{31}P signal observed in the unusually low field for the other complexes containing η^3-$\mathbf{P_4}$ ligand such as **4** and **5** shifts considerably to the higher field; viz. the signal assignable to P(2) with the largest chemical shift appears at δ 77.6. This is presumed to arise from the electronic effect of XyNC occupying the position *trans* to P2 in this complex in place of one P atom in the dppe ligand for **5**. Based on this finding as well as the coupling constants observed between the six P atoms, the structure of **6** can be described as that shown in Scheme 1.

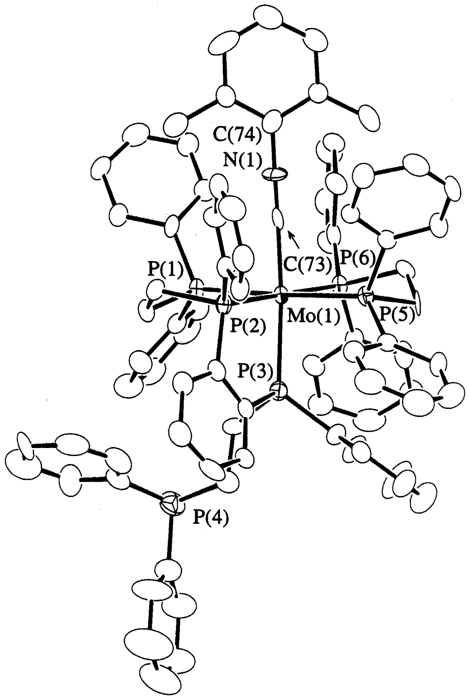


Fig. 2. An ORTEP drawing for molecule **1** of **5**. For clarity, all hydrogen atoms are omitted.

In contrast, when **1** was treated with two equivalents of XyNC in toluene at reflux for 4 h, reaction proceeded cleanly and bis(isocyanide) complex **7** was obtained exclusively (Scheme 1). Complex **7** was able to be isolated in 57% yield and characterized by X-ray crystallography. An ORTEP drawing is shown in Fig. 3 and selected bond distances and angles are listed in Table 3.

Complex **7** has a distorted octahedral structure with the η^4-$\mathbf{P_4}$ ligand. Metric parameters associated with the $\mathbf{P_4}$ ligand in **7** are essentially analogous to those in **1** [1]. Two XyNC ligands are mutually *cis*, one of which occupies the position *trans* to the outer P atom (P(1)) and the other is located *trans* to the inner P atom (P(3)). The Mo–C and C–N bond lengths for the former XyNC ligand are 1.998(3) and 1.200(3) Å, while those for the latter are 2.035(3) and 1.180(3) Å. These almost comparable values indicate that both are functioning as good π-acceptors. However, the C–N–C angles for each ligands differ considerably by 155.8(3) and 169.3(3)°, respectively. This is presumably because the stronger π-back donation occurs towards the XyNC ligand *trans* to the outer P atom, P(1), than that *trans* to the inner P atom, P(3). Consistent with this trend is our previous finding that, in $[Mo(N_2)(PR_3)(\eta^4$-$\mathbf{P_4})]$ (R = Et, ^nBu), not

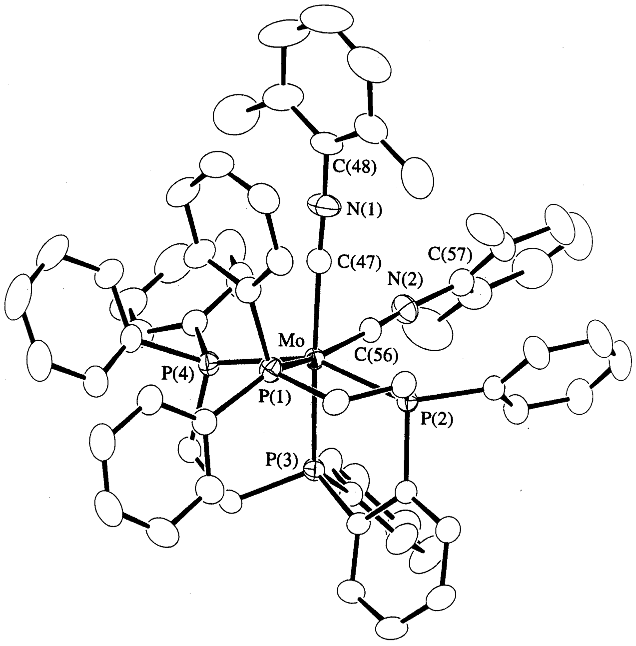
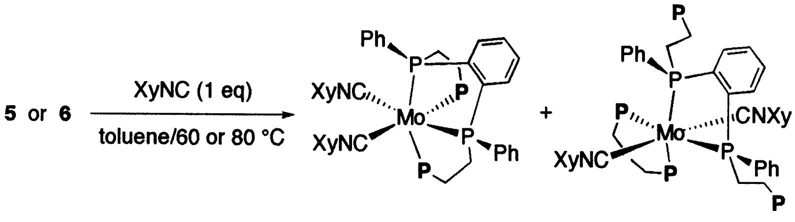


Fig. 3. An ORTEP drawing of **7**. For clarity, hydrogen atoms are omitted.

the PR_3 but the more π-accepting N_2 occupies the site *trans* to the outer P [1b]. The difference in the steric hinderance around these ligands might also be taken into account to some extent, since it is well known that the C–N–C angles in the isocyanide ligand tend to be affected considerably by the steric factors [17]. The $\nu(N\equiv C)$ frequencies observed in the IR spectrum of **7** (1957, 1879, and 1851 cm^{-1}) also indicate the presence of π-back donation from Mo to these XyNC ligands. A series of bis(isocyanide) complexes $[Mo(RNC)_2(dppe)_2]$ (R = aryl) has a *trans* structure, whose $\nu(N\equiv C)$ values vary in the range 1810–1920 cm^{-1} [8].



7 8 (4)

2.4. Reactions of mono(isocyanide) complexes 5 and 6 with XyNC

Upon treatment with one equivalent of XyNC in toluene at 60 °C for 24 h, the mono(isocyanide) complex **5** gives a mixture of the two products. The ^{31}P-NMR spectrum indicates that the major product is the expected bis(isocyanide) complex **7**, while the minor component has been characterized to be an another bis(isocyanide) complex *trans*-$[Mo(XyNC)_2(\eta^2$-$\mathbf{P_4})(dppe)]$ (**8**), the ratio of **7** and **8** being 3:1 (Eq. (4)). From this reaction mixture, only **7** was isolable in a pure form in 47% yield through fractional crystallization.

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

Bond lengths			
Mo–P(1)	2.5206(7)	Mo–P(2)	2.3933(7)
Mo–P(3)	2.3806(7)	Mo–P(4)	2.4539(7)
Mo–C(47)	2.035(3)	Mo–C(56)	1.998(3)
C(47)–N(1)	1.180(3)	C(56)–N(2)	1.200(3)
N(1)–C(48)	1.379(4)	N(2)–C(57)	1.392(3)
Bond angles			
P(1)–Mo–P(2)	77.78(2)	P(1)–Mo–P(3)	100.51(2)
P(1)–Mo–P(4)	96.84(3)	P(1)–Mo–C(47)	84.29(8)
P(l)–Mo–C(56)	160.38(7)	P(2)–Mo–P(3)	79.24(2)
P(2)–Mo–P(4)	156.27(3)	P(2)–Mo–C(47)	101.23(8)
P(2)–Mo–C(56)	91.53(8)	P(3)–Mo–P(4)	79.08(2)
P(3)–Mo–C(47)	175.15(8)	P(3)–Mo–C(56)	93.46(8)
P(4)–Mo–C(47)	101.20(8)	P(4)–Mo–C(56)	99.30(7)
C(47)–Mo–C(56)	81.7(1)		
Mo–C(47)–N(1)	175.8(2)	Mo–C(56)–N(2)	175.5(2)
C(47)–N(1)–C(48)	169.3(3)	C(56)–N(2)–C(57)	155.8(3)

Reaction of **6** with one equivalent of XyNC in toluene also afforded a mixture containing **7** and **8** together with other product(s). Since **6** was somewhat less reactive towards XyNC than **5**, more forcing conditions were employed (80 °C). The ratio of **7** and **8** in the reaction mixture was estimated to be ca. 1:2 from the ^{31}P-NMR criteria (Eq. (4)). From this reaction mixture, **8**·$C_6H_5CH_3$ was isolated in 42% yield as the first crop by fractional crystallization of the reaction mixture using toluene–hexane, and its structure was determined by an X-ray analysis. It has also been found that in toluene at reflux quantitative conversion of **8** into **7** takes place by liberation of the dppe ligand with concurrent change of the coordination mode of the $\mathbf{P_4}$ ligand from η^2 to η^4.

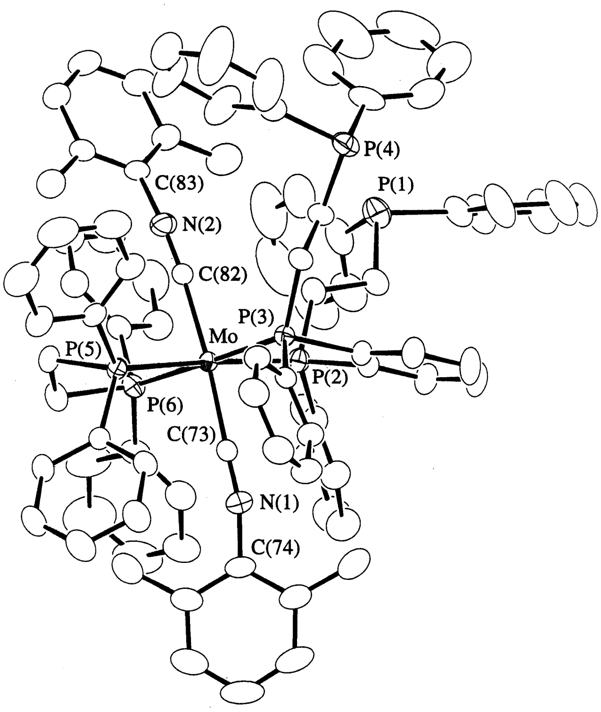


Fig. 4. An ORTEP drawing of **8**. For clarity, all hydrogen atoms are omitted.

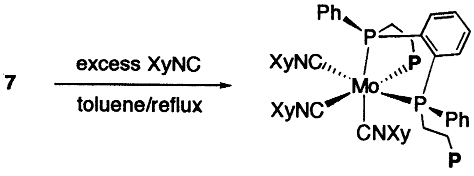
Table 4
Selected bond lengths (Å) and angles (°) in **8**

Bond lengths			
Mo–P(2)	2.428(1)	Mo–P(3)	2.427(1)
Mo–P(5)	2.441(1)	Mo–P(6)	2.444(1)
Mo–C(73)	2.046(4)	Mo–C(82)	2.057(4)
C(73)–N(1)	1.189(5)	C(82)–N(2)	1.192(5)
N(1)–C(74)	1.395(5)	N(2)–C(83)	1.403(5)
Bond angles			
P(2)–Mo–P(3)	79.08(2)	P(2)–Mo–P(5)	176.92(4)
P(2)–Mo–P(6)	98.52(4)	P(2)–Mo–C(73)	87.0(1)
P(2)–Mo–C(82)	96.0(1)	P(3)–Mo–P(5)	100.97(4)
P(3)–Mo–P(6)	178.05(4)	P(3)–Mo–C(73)	88.9(1)
P(3)–Mo–C(82)	94.7(1)	P(5)–Mo–P(6)	80.86(4)
P(5)–Mo–C(73)	90.0(1)	P(5)–Mo–C(82)	87.0(1)
P(6)–Mo–C(73)	91.9(1)	P(6)–Mo–C(82)	84.7(1)
C(73)–Mo–C(82)	175.7(2)		
Mo–C(73)–N(1)	178.6(4)	Mo–C(82)–N(2)	175.3(4)
C(73)–N(1)–C(74)	166.5(5)	C(82)–N(2)–C(83)	171.8(4)

As shown in Fig. 4, **8** has an octahedral structure whose basal plane consists of two inner P atoms of the η^2-$\mathbf{P_4}$ ligand and two dppe P atoms ligating to Mo. Two apical sites are occupied by XyNC ligands, whose important bonding parameters are summarized in Table 4 in addition to those associated with the η^2-$\mathbf{P_4}$ and dppe ligand. In mutually *trans* XyNC ligands, the Mo–C distances at 2.046(4) and 2.057(4) Å are longer than those in **5** and **7** but only slightly, while the N ≡ C bond lengths at 1.189(5) and 1.192(5) Å are analogous to those in **5** and **7**. The C–N–C angles are 166.5(5) and 171.8(4)°. The IR spectrum shows one intense ν(N ≡ C) band at 1871 cm^{-1}, indicating that two XyNC ligands are mutually *trans* and both in **8** are also functioning as a good π-acceptor.

2.5. Reaction of bis(isocyanide) complex 7 with excess XyNC

When bis(isocyanide) complex **7** with the η^4-$\mathbf{P_4}$ ligand is treated with excess XyNC in toluene at reflux, tris(isocyanide) complex *fac*-[Mo(XyNC)$_3$(*fac*-η^3-$\mathbf{P_4}$)] (**9**) forms as the only detectable product at least from the NMR criteria (Eq. (5)). However, **9** could be isolated in only 28% yield, because of its high solubility into common organic solvents. Complex **9** was characterized spectroscopically and by elemental analyses; the ^{31}P-NMR spectrum of **9** exhibited the pattern characteristic of the η^3-$\mathbf{P_4}$ ligand coordinating in a facial manner, while three singlets assignable to the Xy methyl protons appeared with the same intensities in the ^{1}H-NMR spectrum. The IR spectrum showed the ν(N ≡ C) bands at 1985, 1892, and 1851 cm^{-1}.



9 (28%)

(5)

2.6. Summary of the reactions with XyNC

It has been disclosed that the reaction of **1** with XyNC proceeds in a stepwise manner. By reacting with one equivalent of XyNC, the outer P atom of $\mathbf{P_4}$ *trans* to the inner P atom readily dissociates and **1** is converted into the mono(isocyanide) complex with the η^3-$\mathbf{P_4}$ and dppe ligands, **5** or **6**, in which XyNC occupies the position *trans* to one of the inner P atoms. Complexes **5** and **6** are treated with additional XyNC to be transformed into the bis(isocyanide) complexes **8** containing the η^2-$\mathbf{P_4}$ and dppe ligands and **7** with only the η^4-$\mathbf{P_4}$ ligand, among which the former is less stable and thermally convertible to the latter. In **5** and **6**, mutually *trans* P atoms that are both terminal are probably most labile. Dissociation of the remaining outer P atom in $\mathbf{P_4}$ might lead ultimately to **8**, while that of one P atom in dppe gives **7** as a final product. When treated with excess XyNC under forcing conditions, **7** is further transformed into the tris(isocyanide) complex with the η^3-$\mathbf{P_4}$ ligand **9**. It is noteworthy that the coordination mode of the $\mathbf{P_4}$ ligand can interconvert readily between η^4, η^3, and η^2, as the environment around the Mo center changes by stepwise binding of one to three XyNC molecules.

3. Experimental

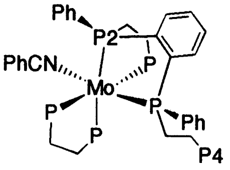
3.1. General considerations

All manipulations were carried out under an atmosphere of N_2. IR and NMR spectra were recorded on a JASCO FTIR-420 or a JEOL LA-400 spectrometer, respectively. The signals due to the aromatic protons and the methylene protons in phosphine ligands are omitted from the ^{1}H-NMR data below. Elemental analyses were conducted by the use of a Perkin–Elmer 2400 series II CHN analyzer. Complex **1** was prepared as reported previously [1], while other chemicals were used as received.

3.2. Preparation of 2

A mixture of **1**·C_6H_6 (130 mg, 0.101 mmol) and PhCN (31 μl, 0.30 mmol) in benzene (5 ml) was stirred at room temperature (r.t.) for 12 h. By addition of hexane to the filtered solution, dark green prisms of **2** were obtained (115 mg, 87% yield). Anal. Calc. for $C_{79}H_{71}NP_6Mo$: C, 72.09; H, 5.44; N, 1.06. Found: C, 72.24; H, 5.73; N, 1.25%. $^{31}P\{^{1}H\}$-NMR (C_6D_6, ppm): −14.9 (d, *J* = 21 Hz, 1P, P4), 64–66 (m, 2P), 66.9 (dt, *J* = 112 and 21 Hz, 1P), 80.5 (dt, *J* = 112 and 16 Hz, 1P), 93.8 (dd, *J* = 112 and 19 Hz, 1P, P2). IR (KBr, cm^{-1}): 2103 [ν(C≡N)]. Assignment of P2 and P4 is shown in Chart II.

Chart II



2

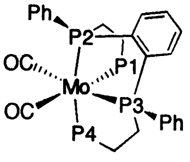
3.3. Preparation of [Mo(p-MeOC$_6$H$_4$CN)(fac-η^3-P$_4$)(dppe)]

This complex was obtained similarly from **1**·C_6H_6 and *p*-$MeOC_6H_4CN$ in 77% yield as dark green crystals. Anal. Calc. for $C_{80}H_{73}NOP_6Mo$: C, 71.37; H, 5.47; N, 1.04. Found: C, 71.09; H, 5.61; N, 1.30%. IR (KBr, cm^{-1}): 2124 [ν(C≡N)].

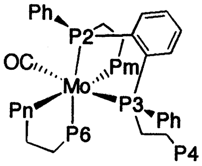
3.4. Reaction of 1 with CO to give 3 and 4

A suspension of **1**·C_6H_6 (129 mg, 0.100 mmol) in benzene (5 ml) was stirred under CO atmosphere (1 atm) for 25 h. NMR measurement of the resulting orange–red solution revealed the formation of **3** and **4** in a ratio of 1:1. Addition of hexane to the concentrated product solution gave pale orange crystals of **3**·C_6H_6 (30 mg, 32% yield). Amount of solvating benzene was determined by a GLC analysis of the toluene solution of **3**·C_6H_6. **3**. Anal. Calc. for $C_{54}H_{48}O_2P_4Mo$: C, 68.36; H, 5.10. Found: C, 68.53; H, 5.18%. $^{31}P\{^{1}H\}$-NMR (C_6D_6, ppm): 56.5 (P1), 70.0 (P4), 97.2 (P2), 99.7 (P3); *J*(P1–P2) = 0, *J*(P1–P3) = 20, *J*(P1–P4) = 24, *J*(P2–P3) = 15, *J*(P2–P4) = 75, *J*(P3–P4) = 0 Hz. IR (KBr, cm^{-1}): 1864, 1810 [ν(C≡O)]. **4**. $^{31}P\{^{1}H\}$-NMR (C_6D_6, ppm): −15.1 (P4), 51.0 (P3), 60.7 (P1), 64.6 (P6), 70.7 (P5), 98.5 (P2); *J*(P1–P2) = 0, *J*(P1–P3) = 19, *J*(P1–P4) = 0, *J*(P1–P5) = 85, *J*(P1–P6) = 24, *J*(P2–P3) = 11, *J*(P2–P4) = 0, *J*(P2–P5) = 19, *J*(P2–P6) = 92, *J*(P3–P4) = 21, *J*(P3–P5) = 20, *J*(P3–P6) = 24, *J*(P4–P5) = *J*(P4–P6) = *J*(P5–P6) = 0 Hz. IR (KBr, cm^{-1}): 1809 [ν(C≡O)]. Assignment of the P atoms in **3** and **4** is shown in Chart III.

Chart III



3



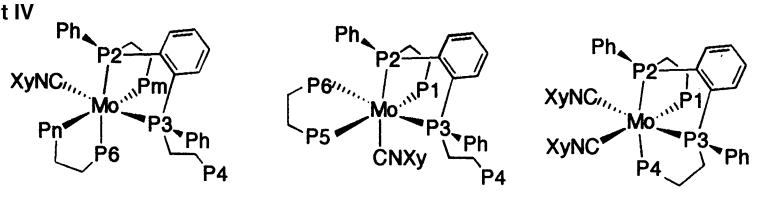
m = 1, n = 5 or m = 5, n = 1

4

3.5. Reaction of 1 with one equivalent of XyNC

A mixture of **1**·C_6H_6 (260 mg, 0.201 mmol) and XyNC (27 mg, 0.20 mmol) in benzene (10 ml) was stirred at r.t. for 40 h. The NMR spectrum of the resulting red solution showed the presence of three products, **5**, **6**, and **7**, together with unreacted **1** in a ratio of 70:15:5:10, The product solution was filtered and concentrated in vacuo, to which was added hexane to give **5** as red plates (157 mg after thorough drying under vacuum, 58% yield) and reddish orange microcrystals of **6**·1/2C_6H_{14} (29 mg, 10% yield). A single crystal of **5** collected from the product mixture before drying for the X-ray analysis has the formula **5**·17/8C_6H_6·3/16C_6H_{14}. **5**. Anal. Calc. for $C_{81}H_{75}NP_6Mo$: C, 72.37; H, 5.62; N, 1.04. Found: C, 72.04; H, 5.98; N, 1.33%. ^{1}H-NMR (C_6D_6, ppm): 1.45 (s, 6H, C_6Me_2), $^{31}P\{^{1}H\}$-NMR (C_6D_6) δ −15.5 (P4), 51.9 (P3), 59.7 (P6), 61.1 (P1), 67.9 (P5), 94.2 (P2); *J*(P1–P2) = 3, *J*(P1–P3) = 13, *J*(P1–P4) = 0, *J*(P1–P5) = 92, *J*(P1–P6) = 23, *J*(P2–P3) = 8, *J*(P2–P4) = 0, *J*(P2–P5) = 19, *J*(P2–P6) = 97, *J* (P3–P4) = 22, *J*(P3–P5) = 16, *J*(P3–P6) = 21, *J*(P4–P5) = J(P4–P6) = *J*(P5–P6) = 0 Hz. IR(KBr, cm^{-1}): 1880 (br, s), 1848 (br, s) [ν(N≡C)]. **6**·1/2C_6H_{14}. Anal. Calc. for $C_{84}H_{82}NP_6Mo$: C, 72.72; H, 5.96; N, 1.01. Found: C, 73.21; H, 5.84; N, 1.04%. ^{1}H-NMR (C_6D_6, ppm): 2.20 (s, 6H, C_6Me_2). $^{31}P\{^1H\}$-NMR (C_6D_6, ppm): −13.6 (P4), 66.3 (P6), 67.1 (P5), 69.4 (P3), 72.8 (P1), 77.6 (P2); *J*(P1–P2) = 7, *J*(P1–P3) = 9, *J*(P1–P4) = 0, *J*(P1–P5) = 90, *J*(P1–P6) = 23, J(P2–P3) = 9, *J*(P2–P4) = 0, J(P2–P5) = 17, *J*(P2–P6) = 14, *J*(P3–P4) = 26, *J*(P3–P5) = 20, *J*(P3–P6) = 89, *J*(P4–P5) = *J*(P4–P6) = *J*(P5–P6) = 0 Hz. IR (KBr, cm^{-1}): 1863 (sh), 1830 (vs) [ν(N≡C)]. Amount of the solvating hexane was estimated from the ^{1}H-NMR spectrum. Assignment of P atoms is shown in Chart IV.

Chart IV



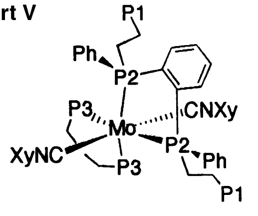
m = 1, n = 5 or m = 5, n = 1

5 **6** **7**

3.6. Reaction of **1** with two equivalents of XyNC—direct synthesis of **7** from **1**

A toluene solution (6 ml) of **1**·C_6H_6 (130 mg, 0.101 mmol) and XyNC (27 mg, 0.20 mmol) was refluxed for 4 h. After cooling, the reaction mixture was filtered and hexane was added to the concentrated filtrate, affording **7** as red prisms (62 mg, 57% yield). Anal. Calc. for $C_{64}H_{60}N_2P_4Mo$: C, 71.37; H, 5.62; N, 2.60. Found: C, 71.59; H, 5.64; N, 2.39%. ^{1}H-NMR (C_6D_6, ppm): 1.53, 2.27 (s, 6H each, C_6Me_2). $^{31}P\{^1H\}$-NMR (C_6D_6, ppm): 60.8 (P1), 70.0 (P4), 97.6 (P2), 101.8 (P3); *J*(P1–P2) = 0, *J*(P1–P3) = 16, *J*(P1–P4) = 23, *J*(P2–P3) = 17, *J*(P2–P4) = 81, *J*(P3–P4) = 0 Hz. Refer Chart IV for assignment of P atoms, IR (KBr, cm^{-1}): 1957 (vs), 1879 (s), 1851 (s) [ν(N≡C)].

Chart V



8

3.7. Reaction of **5** with XyNC

A toluene solution (10 ml) containing **5** (131 mg, 0.097 mmol) and XyNC (13 mg, 0.10 mmol) was stirred at 60 °C for 24 h. The ^{31}P-NMR measurement of the resulting solution disclosed the presence of **7** and **8** in a ratio of 3:1. Addition of hexane to the concentrated product solution deposited only **7** as red prisms (49 mg, 47% yield).

3.8. Reaction of **6** with XyNC

A suspension of **6**·1/2C_6H_{14} (120 mg, 0.086 mmol) and XyNC (12 mg, 0.092 mmol) in toluene (1.0 ml) was stirred at 80 °C for 6 h. The resultant red solution containing **7** and **8** in a molar ratio of ca. 1:2 was concentrated to 1 ml and hexane (10 ml) was added, affording only **8**·C_7H_8 as red prisms (57 mg, 42% yield). By subsequent crystallization of the products remained in the mother liquor, **7** was deposited as red prisms (26 mg, 28% yield) together with red powder of the byproduct(s) (10 mg). **8**·C_7H_8. Anal. Calc. for $C_{97}H_{92}N_2P_6Mo$: C, 74.32; H, 5.92; N, 1.79. Found: C, 74.03; H, 5.85; N, 1.54%. ^{1}H-NMR (C_6D_6, ppm): 1.26, 1.93 (s, 6H each, C_6Me_2), 2.10 (C_6H_5Me). $^{31}P\{^1H\}$-NMR (C_6D_6, ppm): −12.6 (P1), 67.5–70.0 (P2 and P3); *J*(P1–P2) = 21 Hz (See Chart V). Other *J* values could not be determined. IR(KBr, cm^{-1}): 1871 (vs), 1844 (sh) [ν(N≡C)].

3.9. Conversion of **8** into 7

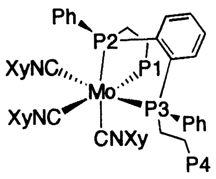
A toluene solution (5 ml) of **8**·C_7H_8 (90 mg, 0.058 mmol) was refluxed for 4 h. Quantitative formation of **7** was confirmed by the ^{31}P NMR measurement. Addition of hexane to the concentrated product solution gave **7** (50 mg, 80% yield).

3.10. Reaction of 7 with excess XyNC

A toluene solution (5 ml) of **7** (118 mg, 0.110 mmol) and XyNC (43 mg, 0.33 mmol) was refluxed for 12 h.

The ^{31}P-NMR spectrum of the product solution showed the exclusive formation of **9** in addition to the presence of only a trace amount of unreacted **7**. The filtered reaction mixture was evaporated under reduced pressure and the resulting orange oil was disolved in benzene(1 ml)- hexane (10 ml). Upon storage at −20 °C, an orange solid precipitated, which was filtered off and dried in vacuo (37 mg, 28%). High solubility of **9** hampered the isolation of this complex in better yield. Anal. Calc. for $C_{73}H_{69}N_3P_4Mo$: C, 72.57; H, 5.76; N, 3.48. Found: C, 72.76; H, 5.90; N, 3.47%. ^{1}H-NMR (C_6D_6, ppm): 1.87, 1.90, 2.63 (s, 6H each, C_6Me_2), $^{31}P\{^1H\}$-NMR (C_6D_6, ppm): −12.7 (P4), 57.1 (P1), 60.3 (P3), 84.5 (P2); *J*(P1–P2) = 0, *J*(P1–P3) = 12, *J*(P1–P4) = 0, *J*(P2–P3) = 8, *J*(P2–P4) = 0, *J*(P3–P4) = 34 Hz. See Chart VI for assignment. IR (KBr, cm^{-1}): 1985(vs), 1892 (vs), 1851 (vs) [ν(N≡C)].

Chart VI



9

3.11. X-ray diffraction studies

Single crystals were sealed in glass capillaries under Ar and mounted on a Rigaku AFC7R diffractometer equipped with a graphite-monochromatized Mo–K_α source. All diffraction studies were done at r.t. The intensities of three check reflections were monitored every 150 reflections during data collection, which revealed no significant decay for $\mathbf{5}\cdot 17/8C_6H_6\cdot 3/16C_6H_{14}$ **7**, and $\mathbf{8}\cdot C_6H_5CH_3$ but an essentially linear decay for **2** with an average 26.8% loss at the end of data collection. Intensity data were corrected for Lorentz and polarization effects and for absorption (ψ scans), and for **2** decay correction was also applied. Details of crystal and data collection parameters are summarized in Table 5.

Structure solution and refinements were carried out by using the TEXSAN program package [19], The positions of the non-hydrogen atoms were determined by direct methods (**2**: SAPI91 [20]; **5**: SIR92 [21]) or Patterson methods (**7** and **8**: PATTY [22]) followed by Fourier synthesis (DIRDIF 94 [23]). These atoms were refined anisotropically. A unit cell of the crystal of complex **5** contained two independent molecules of **5**, 7/2 molecules of benzene with 100% occupancy, and one molecule of benzene and 1/2 molecule of hexane each

Table 5
Crystallographic data for **2**, $\mathbf{5}\cdot 17/8C_6H_6\cdot 3/16C_6H_{14}$, **7** and $\mathbf{8}\cdot C_6H_5CH_3$

	2	$\mathbf{5}\cdot 17/8C_6H_6\cdot 3/16C_6H_{14}$	**7**	$\mathbf{8}\cdot C_6H_5CH_3$
Formula	$C_{79}H_{71}NP_6Mo$	$C_{94.88}H_{90.38}NP_6Mo$	$C_{64}H_{60}N_2P_4Mo$	$C_{97}H_{92}N_2P_6Mo$
Formula weight	1316.22	1526.42	1077.03	1567.59
Space group	$P\bar{1}$ (Number 2)	$P\bar{1}$ (Number 2)	$P\bar{1}$ (Number 2)	$P\bar{1}$ (Number 2)
a (Å)	13.564(4)	18.916(4)	12.434(1)	13.742(2)
b (Å)	14.068(3)	20.194(4)	12.593(1)	18.052(2)
c (Å)	18.608(2)	25.241(9)	19.952(2)	18.739(4)
α (°)	74.97(1)	68.23(2)	72.128(8)	102.24(1)
β (°)	86.92(2)	68.02(2)	73.443(8)	106.66(1)
γ (°)	74.24(2)	87.81(2)	68.814(8)	98.76(1)
V (Å^3)	3299(1)	8246(4)	2718.5(5)	4238(1)
Z	2	4	2	2
ρ_{calc} (g cm^{-3})	1.325	1.229	1.316	1.228
μ_{calc} (cm^{-1})	3.89	3.21	4.01	3.14
Crystal size (mm^3)	0.6 × 0.5 × 0.2	0.7 × 0.5 × 0.3	0.5 × 0.4 × 0.1	0.6 × 0.4 × 0.3
Number of data [$I > 3\sigma(I)$]	9318	11 802	8795	11 464
Number of variables	784	1749	640	1018
Transmn factor	0.9282–0.9997	0.7842–0.9994	0.9168–0.9999	0.9674–0.9998
R [a]	0.051	0.069	0.035	0.048
R_w [b]	0.068	0.084	0.035	0.060
Goodness-of-fit [c]	1.92	2.98	1.44	1.85
Residual peaks (e Å^{-3})	0.92 and −0.91	0.92 and −0.51	0.51 and −0.80	0.28 and −0.27

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma\ w(|F_o| - |F_c|)^2/\Sigma\ wF_o^2]^{1/2}$ ($w = [\{\sigma(F_o)\}^2 + (p^2/4)F_o^2]^{-1}$).

[c] Goodness-of-fit = $[\Sigma\ w(|F_o| - |F_c|)^2/\{(\text{number observed}) - (\text{number of variables})\}]^{1/2}$.

with 75% occupancy. For **8**·$C_6H_5CH_3$, one Ph group in the dppe ligand is found at two disordered positions with the same occupancies, and the solvating toluene is also shown to be disordered over two positions with the occupancies of 70 and 30%.

Hydrogen atoms were placed at the calculated positions and included in the final stages of the refinements with fixed parameters except for those of the solvating toluene in **8**·$C_6H_5CH_3$.

4. Supplementary material

Listings of atomic coordinates, anisotropic thermal parameters, and extensive bond lengths and angles for **2**, **5**·17/8C_6H_6·3/16C_6H_{14}, **7**, and **8**·$C_6H_5CH_3$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 189003, 189004, 189005 and 189006, 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 www: http://www.ccdc.cam.ac.uk).

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