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Preparation of Mo and W Complexes Containing a New Linear Tetradentate Phosphine Ligand *meso-o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ from Dinitrogen Complexes *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo, W)[1]

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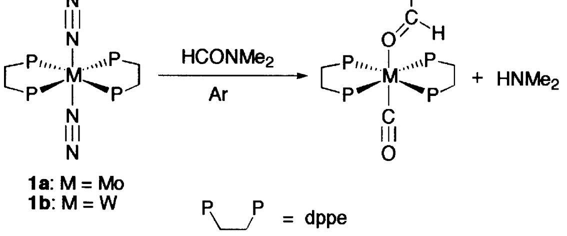
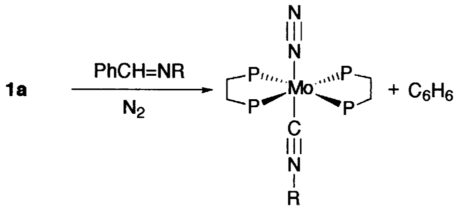
A benzene solution of *trans*-$[Mo(N_2)_2(dppe)_2]$ (**1a**; dppe = $Ph_2PCH_2CH_2PPh_2$) and an equimolar amount of dppe was heated at reflux for 2 h under Ar to give $[Mo(\mathbf{P_4})(dppe)]$ (**2a**; $\mathbf{P_4}$ = *meso-o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$), where the new linear tetraphosphine $\mathbf{P_4}$ is presumed to form through condensation of two dppe ligands in the coordination sphere of Mo. The W complex $[W(\mathbf{P_4})(dppe)]$ (**2b**) and its dppm analogue $[W(\mathbf{P_4})(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) were also prepared from the reactions of *trans*-$[W(N_2)_2(dppe)_2]$ with one equiv of dppe or dppm in toluene at reflux for 2 h under Ar. Detailed structures of **2a** and **2b** were determined by X-ray crystallography. In contrast, when the reaction mixtures obtained by treatment of **1a** with excess PR_3 (R = Bu^n, Et) in place of dppe were cooled down to room temperature under N_2, novel dinitrogen complexes containing the $\mathbf{P_4}$ ligand $[Mo(N_2)(\mathbf{P_4})(PR_3)]$ formed; these were characterized spectroscopically and by elemental analyses.

Molybdenum and tungsten N_2 complexes *trans*-$[M(N_2)_2(dppe)_2]$ (**1a**: M = Mo, **1b**: M = W; dppe = $Ph_2PCH_2CH_2PPh_2$) are quite noteworthy in that the coordinated N_2 in these complexes are susceptible to the attack by numerous electrophilic reagents including acidic ruthenium dihydrogen complexes[1,2] to give a variety of nitrogen-containing inorganic and organic ligands or compounds.[3] These findings have been attracting much attention owing to their possible relevance to the biological and industrial N_2 fixing systems. Furthermore, complexes **1** exhibit interesting reactivities which are owing to highly reactive species generated through dissociation of the coordinated N_2 ligand(s) under forcing conditions. Thus, the low-valent, coordinatively unsaturated Mo or W complexes generated in situ promote the interesting transformations of certain substrate molecules.[4–6] As depicted, these include the conversion of DMF into a CO ligand (Eq. 1)[4] and the transformation of a series of benzaldehyde imines PhCH=NR into the coordinated isocyanides RNC (Eq. 2).[5]



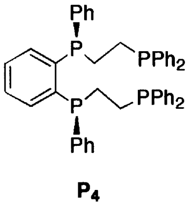
(1)



(2)

In the former reaction the amide C–N and aldehydic C–H bonds are cleaved on the "$M(dppe)_2$" site (M = Mo, W), while the latter proceeds through the scission of the benzylidene C–C and C–H bonds by the "$Mo(dppe)_2$" species.

In the course of the studies in this laboratory on the reactions of **1a** with various benzaldehyde imines, it has turned out recently that when a benzene solution dissolving **1a** alone is heated at reflux, a complex containing a novel linear tetradentate phosphine *meso-o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ ($\mathbf{P_4}$; Chart 1) is produced in low yield, which has subsequently been characterized to be $[Mo(\mathbf{P_4})(dppe)]$ (**2a**) by the X-ray analysis. This paper describes the synthesis and characterization of **2a** and its



$\mathbf{P_4}$

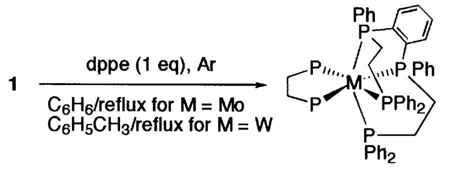
Chart 1.

W analogue **2b**. The results of the attempts to synthesize dinitrogen complexes containing $\mathbf{P_4}$ are also reported. The preparation of **2** has already been communicated briefly.[7]

Results and Discussion

Preparation of [M($\mathbf{P_4}$)(dppe)] (2). When **1a** dissolved in benzene was heated at reflux for 2 h, the color of the solution changed from orange to dark red. By adding hexane to the reaction mixture, **2a** was obtained in 18% yield as red crystals. The structure of **2a** was determined unambiguously by the single-crystal X-ray diffraction (vide infra). Complex **2a** contains a new linear tetradentate phosphine $\mathbf{P_4}$, which appears to form through condensation of two dppe ligands with concurrent liberation of benzene in the coordination sphere of Mo. Importantly, the condensation proceeds stereoselectively to afford only a *meso* diastereomer, which was confirmed by the ^{31}P NMR spectrum of the reaction mixture, including only one set of resonances arising from the tetraphosphine. Formation of **2a** is probably completed by abstracting one dppe ligand from the other "Mo(dppe)$_2$" species, although the other product(s) after the loss of one dppe ligand were not isolable or detectable.

To improve the yield of **2a**, a benzene solution of **1a** was heated in the presence of an equimolar amount of dppe under Ar, which, as expected, resulted in the isolation of **2a** in much higher yield (56%) after a similar workup of the reaction mixture (Eq. 3).



(3)

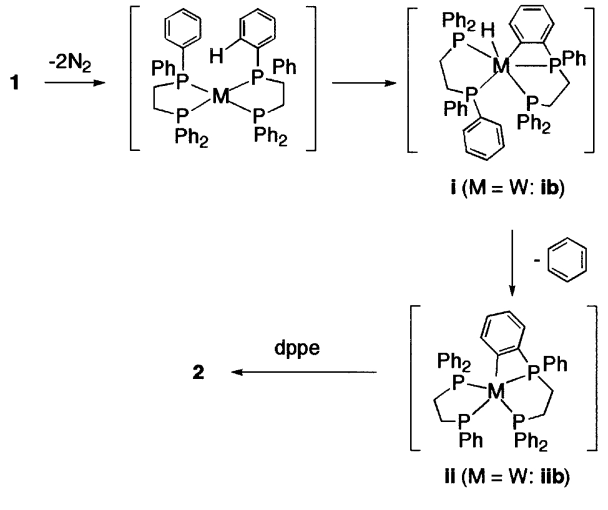
2a: M = Mo
2b: M = W

It is to be noted that the reaction carried out under analogous conditions appeared previously in the literature, where the product was tentatively formulated as [Mo(dppe)$_3$], based principally on the elemental analysis data.[8]

Attempts were made to prepare the W analogue **2b** (Eq. 3), which also disclosed the conversion of **1b** into **2b** but under more forcing reaction conditions. Thus, **1b** was dissolved in toluene containing an equimolar amount of dppe and then heated at reflux for 2 h under Ar. Similar workup of the reaction mixture afforded **2b**, whose yield of 23% was, however, significantly lower than that of **2a**. When Ph$_2$PCH$_2$PPh$_2$ (dppm) was added in place of dppe, **1b** was converted into [W($\mathbf{P_4}$)(dppm)] (**3**), which was isolated in 12% yield and characterized spectroscopically and by elemental analysis. Although the spectral data of the reaction mixture of **1a** and dppm also showed the formation of the Mo analogue of **3**, this complex was unable to be isolated in a pure form because of the concurrent formation of **2a** in an almost identical amount.

From the reaction of **1b** alone carried out under these conditions without adding dppe, **2b** was not obtained and the products were not isolable for full characterization. However, when the reaction mixture was monitored by NMR spectroscopy, it was suggested that in this reaction the *o*-metallated species [WH{Ph(C$_6$H$_4$)PCH$_2$CH$_2$PPh$_2$}(dppe)] (**ib**) formed initially, which was then converted into [W{Ph(C$_6$H$_4$)PCH$_2$CH$_2$PPh$_2$}(PhPCH$_2$CH$_2$PPh$_2$)] (**iib**). Thus, the hydrido signal appeared first as a broad multiplet at −2.7 ppm in the ^{1}H NMR spectrum. In accordance with this observation, the ^{31}P NMR spectrum showed that the one resonance initially observed at δ 45.4 for **1b** separated into four signals after heating at refluxing temperature in benzene, only one of which shifted to a much higher field (δ −13.5) than the other three (δ 58.9–47.4), indicating that the *o*-metallation occurred in one P–Ph moiety in a dppe ligand.[9] It is likely that these signals are attributable to the intermediate species **ib**. Then, accompanied by the disappearance of the hydride as confirmed by the ^{1}H NMR spectrum, a new set of four signals appeared in the ^{31}P NMR spectrum, one of which exhibits a shift to the unusually low field (160.1 ppm) with quite a large W–P coupling constant (411 Hz), presumably assignable to the P atom of the phosphide ligand[10] resulting from the P–Ph bond cleavage. The observed ^{31}P NMR parameters are not inconsistent with **iib**. When this solution containing **iib** as the major component was heated after addition of dppe, **2b** was obtained in moderate yield. These spectral data are summarized in the Experimental Section, although the detailed coordination geometry around W is uncertain for **ib** and **iib**. In contrast to these observations, no intermediates were detectable with respect to the thermal reaction of **1a**. This difference in reactivity between Mo and W is reminiscent of the reactions of **1** with DMF shown in Eq. 1. Although no intermediate stages were isolated or detected for the reaction of the Mo complex **1a**, careful workup of the reaction mixture from the W complex **1b** resulted in the isolation of the fully characterizable intermediate [WH(η^2-CONMe$_2$)(dppe)$_2$].[4c]

Based on the present findings, a plausible mechanism for the formation of **2** from **1** is shown in Scheme 1; a coordinatively unsaturated species generated by the loss of N$_2$ ligands is first converted into **i** through the *o*-C–H bond scission of one dppe ligand. This conversion is followed by the P–Ph bond cleavage in the other dppe ligand and subsequent reductive elimination



Sheme 1.

of benzene from the M–H and M–Ph moieties to form **ii**. Formation of a new C–P bond in **ii** gives the **P$_4$** ligand and the binding of the added dppe results in the formation of **2**.

Not only the *o*-C–H bond cleavage but also the scission of the P–C bond in the tertiary phosphine ligand[11] involved in Scheme 1 is well demonstrated to be promoted by various transition metal centers. However, the latter reaction tends to afford phosphido-bridged polynuclear complexes[11,12] and subsequent regeneration of a new P–C bond to give a polydentate phosphine ligand is rarely reported.

Structures of 2. Complexes **2** were fully characterized by the X-ray analysis. The structures of **2a** and **2b** are quite analogous and the ORTEP drawing is shown in Fig. 1 for only **2a**. As listed in Table 1, the bond angles in these two are in good agreement, whereas the M–P bonds are slightly longer for M = Mo than those for M = W. Longer M–P bonds in the Mo complexes than those in the isomorphous W species were also observed in certain zero-valent complexes such as [M(N$_2$)(PMe$_3$)$_5$] (Mo–P$_{\text{apical}}$: 2.483(7), Mo–P$_{\text{basal plane}}$: 2.457(6) (av);[13] W–P$_{\text{apical}}$: 2.473(4), W–P$_{\text{basal plane}}$: 2.446(4) (av) Å)[14] and *trans*-[M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$] (Mo–P: 2.492(2) (av),[15] W–P: 2.481(3) (av) Å),[14] although in **1** the averaged M–P bond distances are identical (M = Mo: 2.454(1),[16] M = W: 2.454(3) Å).[17]

Complexes **2** have a severely distorted octahedral geometry, which apparently arises from the coordination of **P$_4$** in an η^4 fashion with the three chelating angles all considerably smaller than 90° along with the steric crowding due to the presence of eleven Ph rings. Thus, the P–M–P angles with respect to the two mutually trans P atoms are 152.63(9), 173.57(10), and 161.92(9)° for P(1)–Mo–P(3), P(2)–Mo–P(5), and P(4)–Mo–P(6) in **2a**, and 152.55(7), 173.74(7), and 161.63(7)°, for P(1)–W–P(3), P(2)–W–P(5), and P(4)–W–P(6) in **2b**, respectively. Among the P atoms of three types, those attached to the phenylene group are bound to the metal center with significantly shorter M–P distances (M = Mo 2.409(3) and 2.397(3), M = W 2.395(2) and 2.389(2) Å) if compared with the P atoms of the other two types (M = Mo 2.505(3)–2.551(3), M = W 2.476(2)–2.516(2) Å).

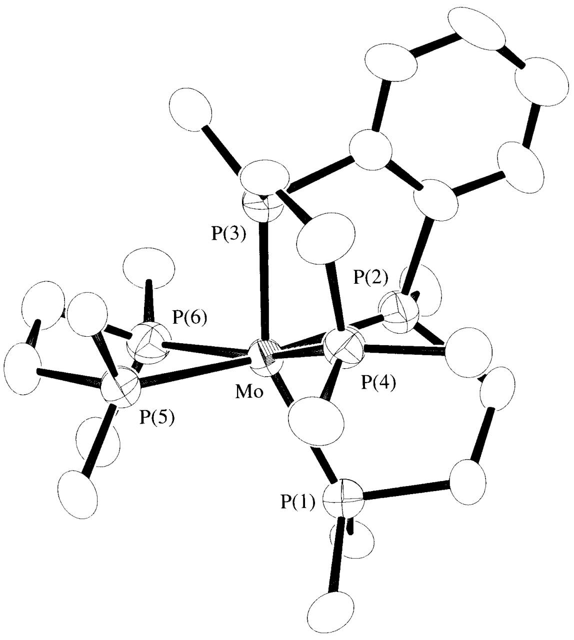


Fig. 1. ORTEP drawing of **2a**. For clarity, only the ipso carbons are shown for the phenyl groups and all hydrogen atoms are omitted.

As a related tetradentate phosphine, Ph$_2$PCH$_2$CH$_2$PPhCH$_2$CH$_2$PPhCH$_2$CH$_2$PPh$_2$ (**L**) is precedented and several complexes containing **L** are known. In the complexes containing a planar η^4-**L** ligand, the same trend is observed; the averaged M–P$_{\text{inner}}$ and M–P$_{\text{terminal}}$ distances are, for example, 2.274(5) and 2.327(5) Å for [Pt(**L**)][BPh$_4$]$_2$,[18] 2.207(5) and 2.239(5) Å for [FeH(N$_2$)(**L**)]Br (**4**),[19] and 2.295 and 2.392 Å for *trans*-[RuCl$_2$(**L**)],[20] respectively. However, this is not necessarily the case for the complexes with the η^4-**L** ligand in a different chelating fashion, e.g. trigonal bypyramidal [FeBr(**L**)][BPh$_4$][21] and highly distorted tetrahedral [Cu(**L**)][PF$_6$].[22] For comparison, the Mo–P bond lengths in zero-valent complexes of the type [Mo(PR$_3$)$_6$] were reported to be 2.467(2) Å for [Mo(PMe$_3$)$_6$][23] and 2.421(3) Å for [Mo(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_3$].[24]

In accordance with this solid state structure, six multiplet resonances appeared in the ^{31}P{^{1}H} NMR spectra for **2**. It is noteworthy that the signals of the Mo complex **2a** are observed in a lower field than those of the W analogue **2b**, which is consistent with the previous findings that the ^{31}P resonances of **1a** and **1b** appear at δ 65.1 and 45.4, respectively.[25] A similar trend is also seen for *trans*-[Mo(CO)(L)(dppe)$_2$], which show the signals at δ 69 for L = N$_2$[4b] and 69.8 for L = DMF,[4c] whereas their W analogues exhibit the corresponding signals at δ 50.0 and 57.8.[4c] Among the six signals for each of **2**, two were observed in quite a low field, which are presumably assignable to the inner P atoms in the η^4-**P$_4$** ligand. Also for an η^4-**L** ligand, the inner P atoms were shown to resonate in a much lower field than the terminal P atoms.[26] However, at present further assignment of the six signals is unsuccessful. Thus, on the basis of the chemical shifts and the observed large coupling constants, each spectrum might be interpreted in four ways as described in the Experimental Section (Chart 2). On the other hand, with respect to the ^{31}P{^{1}H} spectrum of **3**, assignment of six signals is straightforward (Chart 3) since the resonances characteristic of the dppm ligand appear in the much higher field.

Preparation of Dinitrogen Complexes Containing P$_4$ Ligand. As mentioned already,[3] Mo and W dinitrogen complexes with tertiary phosphine coligands have been extensively prepared and the unique reactivities of the coordinated N$_2$ ligand in complexes of this type have been disclosed in detail. However, these Mo and W complexes generally contain monophosphines and/or diphosphines. Triphosphine-N$_2$ complexes of Mo and W are still rare,[27] while those with a tetraphosphine coligand are unprecedented. To our knowledge, Fe complex **4** is the sole example of the well-defined tetraphosphine-N$_2$ compound reported to date.[19] In our preliminary studies on the reactions of **2a** with a series of small molecules, we have observed that **P$_4$** ligand can bind to Mo not only in an η^4 fashion but also in η^2 and η^3 manners.[28] For the N$_2$ complexes contain-

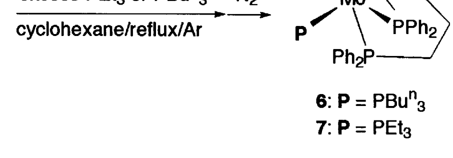
Table 1. Selected Bond Distances and Angles in **2a** (M = Mo) and **2b** (M = W)

	2a	**2b**		**2a**	**2b**
Bond distances (Å)					
M–P(1)	2.515(3)	2.481(2)	M–P(2)	2.409(3)	2.395(2)
M–P(3)	2.397(3)	2.389(2)	M–P(4)	2.505(3)	2.476(2)
M–P(5)	2.551(3)	2.516(2)	M–P(6)	2.507(3)	2.477(2)
Bond angles (°)					
P(1)–M–P(2)	74.62(9)	74.61(7)	P(1)–M–P(3)	152.63(9)	152.55(7)
P(1)–M–P(4)	92.59(9)	92.58(7)	P(1)–M–P(5)	111.81(9)	111.65(7)
P(1)–M–P(6)	102.90(9)	103.15(7)	P(2)–M–P(3)	80.24(9)	80.19(7)
P(2)–M–P(4)	90.93(9)	91.21(7)	P(2)–M–P(5)	173.57(9)	173.74(7)
P(2)–M–P(6)	102.02(9)	101.96(7)	P(3)–M–P(4)	77.01(9)	77.06(7)
P(3)–M–P(5)	93.41(9)	93.66(7)	P(3)–M–P(6)	92.66(9)	92.47(7)
P(4)–M–P(5)	88.64(9)	88.54(6)	P(4)–M–P(6)	161.92(9)	161.63(7)
P(5)–M–P(6)	77.06(9)	76.96(6)			

ing such a flexible polydentate ligand, some intriguing reactivities might be expected. Syntheses of the N_2 complexes containing $\mathbf{P_4}$ were attempted in this context.

Direct replacement of the dppe ligand in **2** by N_2 ligands took place only with great difficulty. Alternatively, according to one of the typical procedures to prepare the complexes of the type $[M(N_2)_2(\text{tertiary phosphine})_4]$ (M = Mo, W),[29] halide complexes $[MX_2(\mathbf{P_4})]$ (**5**; M = Mo: X = Cl, Br; M = W: X = Br), readily obtained from **2** in a pure form, were reduced with Mg or Na–Hg in THF under N_2. However, isolation of the desired N_2 complexes from these reaction mixtures was also unsuccessful. Syntheses and characterization of **5** will be reported elsewhere.

Now, in place of the attempts to prepare $[M(N_2)_2(\mathbf{P_4})]$, reactions have been undertaken, aiming at the syntheses of N_2 complexes of the type $[M(N_2)(\mathbf{P_4})(\mathbf{P})]$, which might be attained by heating the solution of **1** in the presence not of diphosphines such as dppe and dppm but of monophosphines **P** with a suitable size. These studies showed that when a mixture containing **1a** as well as an excess of PBu^n_3 or PEt_3 in cyclohexane was refluxed for 2 or 3 h under Ar and, after cooling to room temperature under N_2, 2-propanol was added to the resultant solution to precipitate the product, the complexes formulated as $[Mo(N_2)(\mathbf{P_4})(\mathbf{P})]$ (**6**: **P** = PBu^n_3; **7**: **P** = PEt_3) were isolated in moderate yields (Eq. 4).



(4)

6: **P** = PBu^n_3
7: **P** = PEt_3

An analogous reaction carried out in benzene in place of cyclohexane afforded the product tentatively characterized as $[Mo(\eta^3\text{-}\mathbf{P_4})(\eta^6\text{-}C_6H_6)]$ along with **6** or **7**, which hampered the isolation of these products in a pure form. The reaction of **1a** with PMe_2Ph in benzene resulted in the preferential formation of a complex assignable as $[Mo(\eta^3\text{-}P_4)(\eta^6\text{-}PhPMe_2)]$, for which the ^{31}P NMR spectrum clearly indicated not only the dissociation of one P atom in P_4 from the Mo center but also the absence of a bonding interaction between the P atom in PMe_2Ph and the Mo atom.

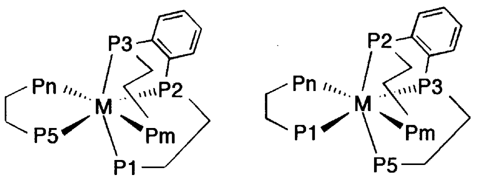
Complexes **6** and **7** were characterized by IR, NMR, and microanalytical data. Thus, the IR spectra show the characteristic $\nu(N{\equiv}N)$ bands at 2010 and 2005 cm^{-1} for **6** and **7**, which are somewhat higher than those in mono-N_2 complexes with five phosphine ligands such as $[Mo(N_2)(PMe_3)_5]$ (1942 cm^{-1})[23] and $[Mo(N_2)(\textit{fac}\text{-}\mathbf{P_3})(PMe_2Ph)_2]$ (1978 cm^{-1}; $\mathbf{P_3}$ = $PhP(CH_2CH_2PPh_2)_2$) as well as the one isomer of $[Mo(N_2)(\textit{fac}\text{-}\mathbf{P_3})(dppe)]$ (1955 cm^{-1}) but comparable to the $\nu(N{\equiv}N)$ value of its other isomer (2008 cm^{-1}).[27] At present, single crystals are not available for **6** or **7** despite the repeated trials and we are unable to disclose their structures in detail. Attempts to determine their structures as well as the syntheses and characterization of the related N_2 complexes containing $\mathbf{P_4}$ are still continuing and the results of these studies will be reported in due course together with the reactivities of the coordinated N_2 in these complexes.

Experimental

General. All manipulations were carried out under an atmosphere of Ar or N_2. IR spectra were recorded on a JASCO FT/IR-420 spectrometer, while the NMR spectra were obtained by a JEOL EX270 or LA400 spectrometer. Elemental analyses were carried out by a Perkin–Elmer 2400 series II CHN analyzer. Complexes **1** were prepared according to the published methods.[29]

Preparation of 2a. (1) Complex **1a** (166 mg, 0.175 mmol) dissolved in benzene was heated to reflux for 2 h under N_2. After cooling to room temperature, the product solution was concentrated and hexane was layered on it. After a few days, $\mathbf{2a}{\cdot}C_6H_6$ deposited as red crystals, which were collected by filtration and dried in vacuo (18% yield). Found: C, 72.16; H, 5.96%. Calcd for: C, 72.56; H, 5.62%. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 109.2 (P3), 102.5 (P2), 83.9 (P6), 68.0 (P4), 66.0 (P5), 58.7 (P1); $J_{P1-P2} = 12$, $J_{P1-P3} = 90$, $J_{P1-P4} = 0$, $J_{P1-P5} = 16$, $J_{P1-P6} = 27$, $J_{P2-P3} = 17$, $J_{P2-P4} = 6$, $J_{P2-P5} = 79$, $J_{P2-P6} = 12$, $J_{P3-P4} = 12$, $J_{P3-P5} = 17$, $J_{P3-P6} = 13$, $J_{P4-P5} = 20$, $J_{P4-P6} = 87$, $J_{P5-P6} = 18$ Hz. Four possible assignments of P1–P6 are shown in Chart 2.

(2) A benzene solution containing **1a** (1.00 g, 1.05 mmol) and dppe (418 mg, 1.05 mmol) was heated to reflux for 2 h under Ar.



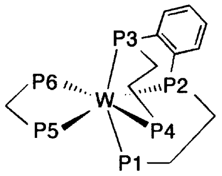
M = Mo, W
m = 4, n = 6 or m = 6, n = 4

Chart 2.

Crystallization of the product from benzene-hexane as above gave **2a**•C_6H_6 in 56% yield.

Preparation of 2b. A toluene solution of **1b** (181 mg, 0.175 mmol) and dppe (70 mg, 0.18 mmol) was heated to reflux for 2 h under argon. After cooling down to room temperature, hexane was added to the concentrated reaction mixture, affording **2b**•$C_6H_5CH_3$ as red crystals (23% yield). Found: C, 67.54; H, 5.62%. Calcd for: C, 68.11; H, 5.35%. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 85.9 (P2), 81.0 (P3), 58.6 (P6), 43.9 (P4), 40.7 (P1), 36.2 (P5); $J_{P1-P2} = 36$, $J_{P1-P3} = 83$, $J_{P1-P4} = 15$, $J_{P1-P5} = 12$, $J_{P1-P6} = 9$, $J_{P2-P3} = 0$, $J_{P2-P4} = 0$, $J_{P2-P5} = 94$, $J_{P2-P6} = 5$, $J_{P3-P4} = 4$, $J_{P3-P5} = 5$, $J_{P3-P6} = 29$, $J_{P4-P5} = 12$, $J_{P4-P6} = 91$, $J_{P5-P6} = 19$, $J_{P3-W} = 293$, $J_{P5-W} = 293$, $J_{P1-W} = 328$, $J_{P4-W} = 287$, $J_{P2-W} = 263$, $J_{P6-W} = 300$ Hz.

Preparation of 3. This complex was obtained as a dark red solid of the composition **3**•$1/2C_6H_{14}$ from **1b** and dppm by the analogous procedure to that for preparing **2b** (12% yield). Found: C, 67.44; H, 5.58%. Calcd for: C, 66.82; H, 5.38%. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 88.6 (P2), 84.5 (P3), 55.1 (P4), 49.1 (P1), –22.3 (P6), –27.5 (P5); $J_{P1-P2} = 26$, $J_{P1-P3} = 79$, $J_{P1-P4} = 10$, $J_{P1-P5} = 12$, $J_{P2-P3} = 5$, $J_{P2-P4} = 0$, $J_{P2-P5} = 92$, $J_{P2-P6} = 13$, $J_{P3-P4} = 21$, $J_{P3-P5} = 2$, $J_{P3-P6} = 2$, $J_{P4-P5} = 29$, $J_{P4-P6} = 80$, $J_{P5-P6} = 16$, $J_{P1-W} = 302$, $J_{P2-W} = 305$, $J_{P3-W} = 320$, $J_{P4-W} = 286$, $J_{P5-W} = 236$, $J_{P6-W} = 258$ Hz. Chart 3 depicts the assignment of P1–P6.

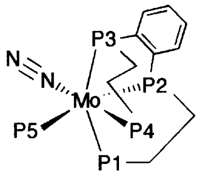


3

Chart 3.

NMR Study on the Conversion of 1b into 2b via Intermediates ib and iib. Complex **1b** (212 mg) in benzene (5 ml) was heated at reflux for 30 min under Ar to give a dark brown solution. The NMR spectrum showed the presence of **1b**, **ib**, **iib**, and $[WH(PPh_2)(dppe)_2]$ (**8**)[30] in a molar ratio of 7:4:4:1. Continuous refluxing of this solution for a further 6 h resulted in the formation of a mixture containing these complexes in the ratio of 0:5:25:2. The mixture was evaporated to dryness under reduced pressure and dppe (83 mg) and toluene (3 ml) were added. By refluxing this mixture for 7 h, complexes **iib**, **8**, and **2b** were obtained in the ratio of 10:2:9. **ib.** $^{31}P\{^1H\}$ NMR (C_6D_6) δ 58.9 (P4), 54.8 (P3), 47.4 (P2), –13.5 (P1); $J_{P1-P2} = 8$, $J_{P1-P3} = 21$, $J_{P1-P4} = 0$, $J_{P2-P3} = 77$, $J_{P2-P4} = 14$, $J_{P3-P4} = 8$, $J_{P1-W} = 124$, $J_{P2-W} = 182$, $J_{P3-W} = 183$, $J_{P4-W} = 138$ Hz. The P1 corresponds to the P atom bearing the o-metallated phenyl group. ^1H NMR (C_6D_6) δ –2.7 (m, WH). **iib.** $^{31}P\{^1H\}$ NMR (C_6D_6) δ 160.1 (P4), 64.7 (P3), 54.6 (P2), –10.0 (P1); $J_{P1-P2} = 25$, $J_{P1-P3} = 17$, $J_{P1-P4} = 216$, $J_{P2-P3} = 62$, $J_{P2-P4} = 26$, $J_{P3-P4} = 9$, $J_{P1-W} = 152$, $J_{P2-W} = 187$, $J_{P3-W} = 188$, $J_{P4-W} = 411$ Hz. The P1 corresponds to the P atom bearing the *o*-metallated phenyl group, while the P4 is assignable to that subjected to the P–Ph bond cleavage. ^1H NMR (C_6D_6): no hydride resonances.

Preparation of 6. A mixture of **1a** (489 mg, 0.515 mmol) and PBu^n_3 (0.64 ml, 2.6 mmol) in cyclohexane (30 ml) was refluxed under Ar for 4 h. The resultant dark red solution was cooled to room temperature under N_2 and filtered. Addition of 2-propanol (30 ml) to the concentrated filtrate afforded red crystals of **6** (262 mg, 49% yield). Found: C, 66.85; H, 6.71; N, 2.25%. Calcd for $C_{58}H_{69}N_2P_5Mo$: C, 66.66; H, 6.66; N, 2.68. IR (KBr) $\nu(N{\equiv}N) = 2010\ cm^{-1}$. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 128.6 (P2), 89.6 (P3), 69.3 (P4), 66.2 (P1), 9.3 (P5); $J_{P1-P2} = 9$, $J_{P1-P3} = 95$, $J_{P1-P4} = 19$, $J_{P1-P5} = 20$, $J_{P2-P3} = 16$, $J_{P2-P4} = 12$, $J_{P2-P5} = 97$, $J_{P3-P4} = 0$, $J_{P3-P5} = 7$, $J_{P4-P5} = 26$ Hz. The P1–P5 atoms are assigned as shown in Chart 4.

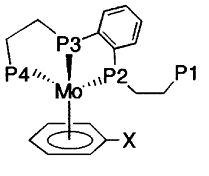


6: P5 = PBu^n_3
7: P5 = PEt_3

Chart 4.

Preparation of 7. This complex was obtained in 43% yield by the same method as that for preparing **6**. However, attempted purification to isolate the analytically pure **7** was unsuccessful. Found: C, 65.65; H, 6.29; N, 2.19%. Calcd for: C, 65.00; H, 5.98; N, 2.92%. IR (KBr) $\nu(N{\equiv}N) = 2005\ cm^{-1}$. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 128.5 (P2), 90.1 (P3), 68.1 (P4), 66.1 (P1), 16.5 (P5); $J_{P1-P2} = 9$, $J_{P1-P3} = 94$, $J_{P1-P4} = 20$, $J_{P1-P5} = 19$, $J_{P2-P3} = 17$, $J_{P2-P4} = 12$, $J_{P2-P5} = 96$, $J_{P3-P4} = 0$, $J_{P3-P5} = 7$, $J_{P4-P5} = 26$ Hz.

Reaction of 1a with PEt_3 in Benzene. To a suspension of **1a** (164 mg, 0.173 mmol) in benzene (4 ml) was added PEt_3 (20% toluene solution, 270 mg, 0.35 mmol PEt_3). The mixture was refluxed for 2 h under Ar and the resulting solution was cooled to room temperature under N_2. The NMR spectrum of the evaporated reaction mixture residue revealed the formation of about 1:1 mixture of **7** and $[Mo(\eta^3\text{-}\mathbf{P_4})(\eta^6\text{-}C_6H_6)]$. $^{31}P\{^1H\}$ NMR of the latter (C_6D_6) δ 112.1 (P3), 86.4 (P4), 79.7 (P2), –12.8 (P1); $J_{P1-P2} = 31$, $J_{P1-P3} = 0$, $J_{P1-P4} = 0$, $J_{P2-P3} = 25$, $J_{P2-P4} = 23$, $J_{P3-P4} = 10$ Hz. Chart 5 depicts the assignment of P1–P4.



X = H or PMe_2

Chart 5.

Reaction of 1a with PMe_2Ph in Benzene. Complex **1a** (152 mg, 0.160 mmol) and PMe_2Ph (45.5 µl, 0.320 mmol) in benzene

Table 2. Crystallographic Data for $\mathbf{2a}\cdot C_6H_6$ and $\mathbf{2b}\cdot C_6H_5CH_3$

	$\mathbf{2a}\cdot C_6H_6$	$\mathbf{2a}\cdot C_6H_5CH_3$
Formula	$C_{78}H_{72}MoP_6$	$C_{79}H_{74}WP_6$
Formula weight	1291.21	1393.15
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	13.730(2)	13.725(5)
b/Å	20.173(2)	20.10(1)
c/Å	23.953(2)	23.796(8)
β/deg	100.334(8)	100.05(4)
V/Å^3	6527(1)	6465(4)
Z	4	4
ρ_{calc}/g cm^{-3}	1.314	1.431
F(000)	2688	2848
μ_{calc}/cm^{-1}	3.92	19.83
Transmn factor	0.9521–0.9998	0.8617–0.9985
Cryst size/mm^3	0.5×0.4×0.3	0.35×0.35×0.25
2θ range/deg	5–50	5–50
No. unique	11858	11311
No. obsd ($I > 3.0\sigma(I)$)	5298	7099
No. variables	719	719
R	0.062	0.040
R_{W}	0.064	0.038
GOF	1.86	1.62
Residuals (e$^-$Å^{-3})	+0.67, −0.43	+1.91, −0.79

were heated at reflux for 4 h under N_2. The NMR spectrum of the reaction mixture showed the predominant formation of $[\mathrm{Mo}(\eta^3\text{-}\mathbf{P_4})(\eta^6\text{-PhPMe}_2)]$. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 114.5 (P3), 84.9 (P4), 77.0 (P2), −12.5 (P1), −43.0 (s, PMe_2Ph); $J_{\mathrm{P1-P2}} = 29$, $J_{\mathrm{P1-P3}} = 0$, $J_{\mathrm{P1-P4}} = 0$, $J_{\mathrm{P2-P3}} = 25$, $J_{\mathrm{P2-P4}} = 22$, $J_{\mathrm{P3-P4}} = 8$ Hz.

X-Ray Crystallographic Studies. Single crystal X-ray analyses of $\mathbf{2a}\cdot C_6H_6$ and $\mathbf{2b}\cdot C_6H_5CH_3$ were carried out by a Rigaku AFC7R diffractometer equipped with a Mo $K\alpha$ source at room temperature. Details of crystal and data collection parameters are summarized in Table 2. Structure solution and refinements were done by the use of teXsan program package.[31] The positions of the non-hydrogen atoms were determined by DIRDIF PATTY[32] and refined anisotropically, while the hydrogen atoms were placed at the ideal positions and included in the final stages of refinements with fixed parameters. Solvating C_6H_6 and $C_6H_5CH_3$ were both treated as rigid groups. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 153725 and 153726. The data are also deposited as Document No. 74019 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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