Preparation and Reactions of Molybdenum and Tungsten Hydride Complexes Containing the Tetraphosphane Ligand *meso-o*-C₆H₄(PPhCH₂CH₂PPh₂)₂

Qi Xiu Dai,^[a] Hidetake Seino,^{*[a]} and Yasushi Mizobe^{*[a]}

Keywords: Molybdenum / Tungsten / Phosphane ligands / Hydride ligands

The reaction of $[Mo(\kappa^2-dppe)(\kappa^4-P4)]$ (1a) {dppe = PPh₂CH₂CH₂PPh₂, P4 = meso-o-C₆H₄(PPhCH₂CH₂PPh₂)₂} with 1 atm of H₂ at room temperature selectively gave $[MoH_2(\kappa^2-dppe)(\kappa^3-P4)]$ (3a). The W analogue of 1a reacted with 1 atm of H₂ at 80 °C to form a mixture of $[WH_2(\kappa^2-dppe)-(\kappa^3-P4)]$ and $[WH_4(\kappa^4-P4)]$ (5b), the latter of which could be cleanly prepared by the reduction of $[WBr_2(\kappa^4-P4)]$ with NaBH₄ in ethanol at 50 °C. The molecular structure of complex 5b differed from that of the related complex $[WH_4-(dppe)_2]$ and showed much higher reactivity. Insertion into

the W–H bonds took place in the reaction of **5b** with CS₂ at 50 °C to give the methylenedithiolate complex [W(κ^2 -S₂CH₂)(κ^4 -P4)] (6) as the sole product, and the hydride ligands in **5b** were replaced by isocyanides at 80 °C to form [W(CNR)₂(κ^4 -P4)] {R = *t*Bu (7), 2,6-Me₂C₆H₃ (8)} in moderate yields. The detailed structures were determined by X-ray crystallography for **3a**, **5b**, **6**, and **7**, while the fluxional behavior of **3a** in solution was clarified by variable-temperature NMR (VT NMR) spectroscopic studies.

Introduction

Transition-metal polyhydride complexes have been attracting much attention because of their intriguing structures and unusual reactions.^[1,2] The reactivity types of the polyhydride complexes are not limited to those of the common hydride complexes because of their ability to generate coordinatively unsaturated intermediates by the reductive elimination of H₂. Polyhydride complexes containing tertiary phosphanes as stabilizing ligands have been extensively studied. Although a large number of polyhydride complexes of monodentate and bidentate phosphane ligands are known, examples of polyhydride complexes having a tri- or tetraphosphane ancillary ligand are still limited. However, some of the advantages of chelating polyphosphanes have been discussed. For instance, $[WH_6(triphos)]$ {triphos = $PhP(CH_2CH_2PPh_2)_2$ ^[3] exhibits catalytic activity for the dehydrogenation of cyclooctane, which cannot be attained by the W monophosphane hexahydride complexes such as [WH₆(PMe₂Ph)₃]. The complexes [ReH₆{PhP(CH₂CH₂- $CH_2PcHex_2_2$ ^{+[4]} and $[ReH_6(triphos)]^{+[5]}$ are remarkably resistant to the loss of H₂ in sharp contrast to their monophosphane analogues.

The chemistry of molybdenum and tungsten polyhydride complexes containing phosphane ligands has been developed over four decades. Among these complexes, the tetrahydride complex with diphosphane ligands, $[MoH_4(dppe)_2]$ (dppe = PPh₂CH₂CH₂PPh₂), is a well studied example because it generates highly reactive 16e or 14e species by liberating one or two mol of H₂ either thermally or on irradiation.^[6,7] The ability to liberate two H_2 and, presumably, the role of the dppe ligand in protecting the coordinatively unsaturated intermediates from decomposition, enable the diverse chemistry. Although it is expected that polydentate phosphanes bring about higher stabilization or a different kind of steric effect, molybdenum and tungsten polyhydride complexes containing polyphosphanes are quite rare. As far as we know, there are some precedents with tridentate phosphanes.^[8] but none of the tetrahydride complexes containing tetradentate phosphanes are known. Only a class of molybdenum trihydride complexes with the pentadentate ligand comprised of a P-P-E-P-P framework (E = Si, Ge)^[9] and the isoelectronic complex [ReH₄(meso-Ph₂PCH₂CH₂PPhCH₂CH₂PPhCH₂CH₂PPh₂)]⁺ have been reported.[10]

We have previously discovered that when the dinitrogen complexes *trans*- $[M(N_2)_2(dppe)_2]$ (M = Mo, W) are heated in the presence of tertiary phosphanes under an argon tetraphosphane atmosphere the ligand meso-o- $C_6H_4(PPhCH_2CH_2PPh_2)_2$ (P4) is readily formed by the condensation of two dppe ligands in the coordination sphere of the low-valent Mo and W complexes.^[11] These reactions with dppe give $[M(\kappa^2-dppe)(\kappa^4-P4)]$ {M = Mo (1a), W (1b)} in moderate yield. These complexes serve as good precursors to various P4 complexes of Mo and W. The P4 ligand in these complexes shows characteristic binding modes arising from the unique structure of P4. Because each five-membered chelate ring is strained by the P-M-P angle, which is much smaller than 90°, κ^4 -coordination of P4 accumulatively causes severe deviation from a regular

 [[]a] Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan Fax: +81-3-5452-6361
 E-mail: seino@iis.u-tokyo.ac.jp

FULL PAPER

octahedron. An uncommon trigonal prismatic structure has been found for $[MX_2(\kappa^4 - P4)]$ {X = Cl, M = Mo; X = Br, M = Mo (2a), W (2b), which is in sharp contrast to the octahedral geometry of *trans*-[MX₂(tertiary phosphane)₄].^[12] This structural distortion also facilitates dissociation of one or two terminal P atoms of P4 to take a κ^3 or κ^2 -coordination mode, and various donor molecules can be incorporated into the resulting open sites.^[13] Therefore, although it is speculated that the electron-donating properties and the steric bulk of the ligands in the [M(P4)] and the $[M(dppe)_2]$ chromophores will be almost similar, the P4 complexes are expected to present unique structures and reactivity that are distinct from those of the dppe complexes. We aimed to prepare Mo and W polyhydride complexes containing P4 as the co-ligand. A synthetic method for the W tetrahydride complex has been successfully developed and its reactivity towards some small molecules has been examined.

Results and Discussion

Reaction of 1a with H₂

A stirred suspension of 1a in thf or an aromatic hydrocarbon solvent under a H₂ atmosphere (1 atm) at room temperature gave the dihydride complex $[MoH_2(\kappa^2-dppe)(\kappa^3-$ P4)] (3a) (Scheme 1). Complex 3a was stable up to 80 °C in solution even under a N₂ atmosphere. In contrast, it has been reported that the κ^3 -triphosphane complex [MoH₂(triphos)(PMe₂Ph)₂] loses H₂ from its solid state at room temperature under 1 atm of N₂ to give [Mo(N₂)(triphos)- $(PMe_2Ph)_2$].^[8a] Complex **3a** was converted into $[Mo\{(\eta^6 -$ Ph)PPhCH₂CH₂PPh₂ $(\kappa^3$ -P4)] (4a) by heating under reflux in toluene. Complex 4a was obtained as a mixture of two diastereomers (5:4 ratio based on ³¹P NMR spectroscopy) that arises from the chirality of the Mo center and of the phosphorus atom bonded to the η^6 -Ph group. The same mixture was obtained by heating 1a under reflux in toluene under a N₂ atmosphere.



Scheme 1.

The X-ray diffraction study of **3a** confirmed that the tetraphosphane **P4** coordinated to the molybdenum center in a κ^3 -fashion with one of the terminal phosphorus atoms dissociated from the metal (Figure 1). The geometry around the Mo is a distorted pentagonal bipyramid, like that of the related complex $[MoH_2(PMe_3)_5]$.^[14] The axial sites are occupied by one of the internal phosphorus atoms in **P4** and one in the dppe [P(2)-Mo-P(5) is 174.56(8)°], and the other coordinated phosphorus atoms P(1), P(3), and P(6) comprise three corners of the pentagonal plane. In comparison to the P(1)-Mo-P(6) angle of 89.82(9)°, the P(1)-Mo-P(3) angle of 124.00(9)° and the P(3)-Mo-P(6) angle of 144.66(8)° are considerably larger, and the peaks of electron density assigned to the two hydride ligands H(67) and H(68) are found almost at the middle of these two sites, respectively.



Figure 1. The molecular structure of 3a showing the thermal ellipsoids at a 30% probability. The hydrogen atoms are omitted for clarity except for the hydride ligands.

The fluxional behavior of 3a was revealed by the VT NMR measurement in the [D₈]toluene solution. At 80 °C, the hydride ligands were observed as one well resolved signal at $\delta = -4.83$ ppm, which coupled with five ³¹P nuclei bound to the molybdenum center. That signal separated into two broad signals centered at $\delta = -6.50$ and -2.65 ppm on cooling to -60 °C, corresponding to two nonequivalent hydrides as found in the solid-state structure. In the ${}^{31}P{}^{1}H$ spectra at -60 °C, five signals for the coordinating P atoms appeared in the region of $\delta = 69-107$ ppm, and one signal for the noncoordinating P atom was observed at $\delta = -17.8$ ppm. The two resonance signals in the low field assigned to the dppe ligand merged into one at 80 °C, while the signals of the P4 ligands remained separate. These indicate that the site exchanges of both the hydride ligands and the coordinated phosphorus atoms take place at high temperature. This fluxional motion is attributed to the nonrigidity of the seven-coordinate geometry, but the free terminal PPh₂ group in P4 does not participate. Such dynamic behavior is slower than that of [MoH₂(PMe₃)₅] and $[MoH_2{P(OMe)_3}_5]$,^[14,15] which are nonrigid down to -83 °C or lower. The highly chelated and sterically hindered structure of 3a presumably restrains the fluxionality.

Reaction of 1b with H₂

Although the W complex 1b did not react with H_2 at room temperature, the reaction proceeded by heating the

Eurjic European Journal of Inorganic Chemistry



complex in toluene at 80 °C under a H₂ atmosphere. Complex 1b was consumed after 4 h and the resulting red solution contained two kinds of hydride complexes in a nearly 1:1 ratio and free dppe as shown by NMR spectroscopy [Equation (1)]. Attempts to isolate any product from this reaction mixture were not successful. One product was identified as $[WH_2(\kappa^2-dppe)(\kappa^3-P4)]$ (3b) from the NMR spectra, which resembled those of **3a**. The ³¹P signals of the coordinating P atoms in 3b were shifted to a higher field than those in 3a, but the chemical shifts of the hydride signals were almost comparable to those of **3a**. The other W species was the tetrahydride complex without the dppe ligand $[WH_4(\kappa^4-P4)]$ (5b), whose characterization was done by preparing the complex by a different route (vide infra). It should be noted that the Mo complex analogous to 5b was not formed by reacting 1a with 1 atm of H₂. Because the ratio of the tungsten complexes formed in this reaction was almost the same, even after a long reaction time or at a high temperature, the existence of an equilibrium between 3b, 5b, dppe, and H₂ was postulated. This was confirmed by the reaction of isolated **5b** and dppe at 80 $^{\circ}$ C under a N₂ atmosphere for 4 h to form a mixture of 3b and 5b.

Some hydride complexes of Mo and W containing phosphane ligands have been synthesized by the reaction of zero-valent complexes with H₂.^[16] The dinitrogen complex *trans*- $[Mo(N_2)_2(dppe)_2]$ reacts smoothly with 1 atm of H₂ at room temperature to give $[MoH_4(dppe)_2]$, and the analogous reaction of the tungsten congener takes place at 55 °C.^[17] Treatment of the monophosphane complex [Mo(PMe₃)₆] with H₂ is also a route to synthesize [MoH₄(PMe₃)₄].^[18] The W analogue [WH₄(PMe₃)₄], as well as $[WH_2(PMe_3)_5]$, have been prepared from $[WH(\eta^2 CH_2PMe_2)(PMe_3)_4$ in a similar way except that a higher temperature (60-65 °C) is required for the W complexes than that required for the Mo complexes (room temperature).^[19] The electron-donating ability of the metal center is higher for the PMe₃ complexes than for the P4 complexes and for W than for Mo. The tetrahydride complexes with the P4 ligand are difficult to form, especially for Mo, probably because the oxidative addition of H₂ to electron-donating complexes is more advantageous. Another general method for synthesizing the tetrahydride complexes of Mo and W containing four P-donors is the reduction of the high-valent metal species with NaBH₄ or LiEt₃BH in the presence of the free phosphane ligands.^[20] Since the presence of dppe seemed to interfere with the selective formation of 5b, reaction of 2b with NaBH₄ was examined.

Reaction of 2b with NaBH₄

Treatment of the W^{II} complex **2b** with excess NaBH₄ in ethanol at 50 °C for 4 h formed the tetrahydride complex **5b** as the sole complex product, which was obtained as red crystals in 77% yield [Equation (2)].



A single-crystal X-ray diffraction study was carried out to determine the solid-state structure of **5b** (Figure 2, Table 1). All the hydride atoms were found in difference Fourier maps and refined isotropically. The eight-coordinate W atom has an approximately dodecahedral geometry.^[21] All the crystallographically determined complexes of the type [MH₄(tertiary phosphane)₄] (M = Mo, W) have dodecahedral structures in which all four P atoms occupy the less-hindered B sites (Scheme 2).^[20c,22] In **5b** two trapezoids defining this geometry are formed as P(1)–H(54)– P(3)–H(53) and P(2)–H(51)–H(52)–P(4), and these planes intersect almost orthogonally (87°). Although both the P atoms in the latter plane occupy the B sites, one P atom in



Figure 2. The molecular structure of **5b** showing the thermal ellipsoids at a 50% probability. The hydrogen atoms are omitted for clarity except for the hydride ligands.

the former plane interchanges with one of the H atoms to be located at an A site. This characteristic can be attributed to the steric restriction due to the triply-linked chelate rings.

Table 1. Selected bond lengths [Å] and angles [°] in 5b.

Bond lengths			
W-P(1)	2.4463(10)	W-H(51)	1.68(3)
W-P(2)	2.3827(11)	W-H(52)	1.44(5)
W-P(3)	2.4026(11)	W-H(53)	1.70(4)
W–P(4)	2.4179(9)	W-H(54)	1.61(3)
Bond angles			
P(1)-W-H(53)	152.9(14)	P(1)-W-P(2)	81.26(3)
H(53) - W - P(3)	72.4(15)	P(1) - W - P(3)	132.25(3)
P(3) - W - H(54)	65.1(14)	P(1) - W - P(4)	96.70(3)
H(54) - W - P(1)	68.2(14)	P(2) - W - P(3)	78.67(3)
P(2) - W - P(4)	148.28(3)	P(3) - W - P(4)	79.69(3)
P(4) - W - H(52)	74.1(16)		
H(52)-W-H(51)	67(2)		
H(51) - W - P(2)	70.1(15)		



Scheme 2.

The molecular structure of **5b** can also be viewed as four P atoms constituting a pseudoplane that divides the coordination sphere asymmetrically. This results in the location of only one hydride ligand [H(54)] at the narrow side and the others at the opposite wide region. Similar ligand locations have been observed in the X-ray structures of [MoH₂(κ^1 -OCOMe)(P-P-Si-P-P)] {P-P-Si-P-P = Si(Ph)[Ph₂PCH₂-CH₂P(Ph)C₆H₄-o-]₂-P,P,P,P,S,i} and [MoH₃(P-P-Si)(dppe)] (P-P-Si = {Ph₂PCH₂CH₂P(Ph)C₆H₄-o-}SiPh₂-P,P,S,i, in which the equatorial P₄-plane separates one acetate or hydride ligand from the Si atom and two hydride ligands at the opposite side.^[9c,23] The ¹H NMR spectra of **5b** in C₆D₆ at 20 °C showed two hydride signals at δ = -3.05 and -5.46 ppm, whose intensities were 3 H and 1 H, respectively. This clearly indicates that the three hydride ligands at the

wide side are equivalently observed in solution, and the site exchange among these is very rapid even at -70 °C in [D₈]-toluene. The hydride ligand at the opposite narrow side is almost segregated from the other hydrides, as these hydride signals barely broadened at 80 °C. Nonrigidity of the eight-coordinate geometry is reflected by the symmetric ³¹P{¹H} NMR spectroscopic peaks at δ = 89.8 and 60.8 ppm for the inner and the outer P atoms, respectively. The IR spectrum gives a broad and weak absorption at 1775 cm⁻¹ corresponding to the W–H bonds.

Preparation of the Mo congener $[MoH_4(\kappa^4-P4)]$ (5a) by the reaction of $[MoBr_2(\kappa^4-P4)]$ (2a) with NaBH₄ was not successful under a N₂ or a H₂ atmosphere. A different kind of product was observed by NMR spectroscopy in the reaction conducted under a H₂ atmosphere, but it could not be isolated.^[24]

Reaction of 5b with CS₂

The reactivity of the Mo and W polyhydride-phosphane complexes towards CO_2 has often been investigated.^[1,25] The typical reaction is the insertion of CO₂ into the M-H bond to form the formato ligand (HCO_2^{-}) .^[14b,26] Disproportionation of CO_2 into the carbonato (CO_3^{2-}) and the CO ligands,^[27] and the cleavage of a C=O bond to give a CO ligand and a phosphane oxide,^[28] have also been known. These reactions, in which no hydride is involved, probably proceed in the low-valent complexes generated by the reductive elimination of H₂ from the metal center. Reaction of 3a with 1 atm of CO₂ only resulted in the formation of $[Mo(CO)(\kappa^3-P4=O)(\kappa^2-dppe)]$ {P4=O = meso-o- $C_6H_4(PPhCH_2CH_2PPh_2)[PPhCH_2CH_2P(O)Ph_2]$ which was previously prepared from 1a and CO2.^[29] The reaction of **5b** with CO_2 was also examined, but the products were complicated and difficult to characterize.

On the other hand, treatment of **5b** with 3 equiv. of CS₂ at 50 °C in toluene cleanly formed [W(κ^2 -S₂CH₂)(κ^4 -P4)] (6), which was obtained as green prismatic crystals in 76% yield [Equation (3)]. GC analysis confirmed the concomitant formation of H₂. In the ¹H NMR spectrum no hydride signals were observed and a singlet signal integrated to 2 H appeared at $\delta = 6.56$ ppm, which could be assigned to the CH₂S₂ moiety. The ³¹P{¹H} NMR spectrum showed two peaks with ¹⁸³W satellites at $\delta = 61.0$ and 105.9 ppm corresponding to the outer and inner P atoms, which indicated C_s molecular symmetry. There have been many examples of



(3)



 CS_2 insertion into M–H bonds to give dithioformate complexes,^[25,30] but the formation of a methanedithiolate ligand from a CS_2 molecule and two hydride ligands is still rare.^[31]

The structure of **6** has been determined by single-crystal X-ray crystallography (Figure 3). The W center in **6** has a trigonal prismatic geometry in which one of the three side rectangles is capped by the κ^4 -**P4** ligand. The three edges of the prism are defined by one SCH₂S and two PCH₂CH₂P chelates. The analogous structure has been found previously for the bis(hydrosulfide) complex [Mo(SH)₂(κ^4 -**P4**)].^[32] The solid-state structure of [MoCl₂(κ^4 -**P4**)] has the same coordination geometry, except for the orientation of the **P4** ligand, in which each base of the prism comprises a Cl, an inner P, and an outer P atom.^[12]



Figure 3. The molecular structure of **6** showing the thermal ellipsoids at a 50% probability. The hydrogen atoms are omitted for clarity except for those in the S_2CH_2 ligand.

The bonding parameters of the methanedithiolate ligand in **6** [C–S: 1.81(1)–1.83(1) Å; S–C–S: 103.0(5)°] are comparable to those reported for other transition metal complexes (C–S: 1.81–1.85 Å; S–C–S: 103–105°)^[31c,31e,33] and are noticeably different from those of the dithioformate ligand (C–S: 1.64–1.69 Å; S–C–S: 112–117°).^[34]

Reaction of 5b with Isocyanides

Polyhydride complexes often undergo reactions with donor molecules where hydride ligands are replaced as H₂. For instance, the molybdenum hydride complexes with a polychelate ligand, [MoH₃(P-P-Si)(dppe)] and [MoH₃(P-P-Si-P-P)], react with various isocyanides RNC to give [MoH(CNR)(P-P-Si)(dppe)] and [MoH(CNR)(P-P-Si-P-P)], respectively.^[35] Treatment of **5a** with 3 equiv. of RNC in toluene at 80 °C cleanly formed [W(CNR)₂(κ^4 -**P4**)] {R = *t*Bu (7), Xy (8) where Xy = 2,6-Me₂C₆H₃} after 7 h [Equation (4)]. Complex **8** was identified spectroscopically by comparison to the previously known Mo analogue [Mo(CNXy)₂(κ^4 -**P4**)],^[13] while **7** was obtained as red needle crystals in 54% yield and crystallographically analyzed (Figure 4, Table 2). The W center exhibits a highly distorted octahedral structure in which the two isocyanide ligands are mutually oriented cis. While the isocyanide ligand trans to P(1) has an essentially linear C–N–C linkage, the other isocyanide [trans to P(3)] deviates considerably [40.7(4)°] from linearity. Such a bending at the N atom has often been observed in low-valent isocyanide complexes,^[36] and can be explained from the accumulation of electron density at the N atom by the strong back-donation from the metal center. The solid-state FTIR spectrum of 7 showed two intense absorptions at 1804 and 2002 cm⁻¹ that can be assigned to v(N=C). These low frequency shifts indicate the presence of strong π -back donation from the W center. NMR spectroscopic measurement in C₆D₆ confirmed the rigidity of the molecular structure. The ³¹P{¹H} NMR spectrum exhibits four resolved signals, and the two singlets in the ¹H NMR spectrum correspond to two nonequivalent tBu groups.





Figure 4. The molecular structure of 7 showing the thermal ellipsoids at a 50% probability. The hydrogen atoms are omitted for clarity.

While the reaction of Equation (4) was complete in 7 h, a shorter reaction time (1.5 h) allowed observation of the intermediary species. These were tentatively formulated as $[WH_2(CNR)(\kappa^4-P4)]$ from the NMR spectroscopic data,^[37] although isolation and full characterization of the complexes has not been successful as yet. The analogous Mo complex, $[MoCl_2(CNXy)(\kappa^4-P4)]$, has been reported previously.^[38] The Mo complex analogous to **8** has been obtained before from the reaction of **1a** with XyNC, but this

FULL PAPER

Bond lengths			
W-P(1)	2.4542(11)	W-C(47)	2.040(4)
W-P(2)	2.3696(8)	W-C(52)	2.016(3)
W-P(3)	2.3943(8)	C(47) - N(1)	1.172(6)
W–P(4)	2.4255(9)	C(52)–N(2)	1.214(5)
Bond angles			
P(1)-W-P(2)	78.00(3)	P(1)-W-C(47)	161.95(10)
P(1) - W - P(3)	101.48(3)	P(1)-W-C(52)	92.02(12)
P(1) - W - P(4)	92.68(3)	P(2)-W-C(47)	89.14(9)
P(2) - W - P(3)	79.50(2)	P(2)-W-C(52)	102.88(10)
P(2) - W - P(4)	153.05(3)	P(3)-W-C(47)	88.36(10)
P(3) - W - P(4)	77.67(2)	P(3)-W-C(52)	166.48(13)
W-C(47)-N(1)	172.9(3)	P(4) - W - C(47)	104.27(10)
W-C(52)-N(2)	169.2(3)	P(4) - W - C(52)	102.67(10)
C(47)–N(1)–C(48)	176.1(3)	C(47) - W - C(52)	78.43(16)
C(52)-N(2)-C(53)	139.9(3)		

Table 2. Selected bond lengths [Å] and angles [°] in 7.

reaction system is highly complicated and gives multiple products depending on the stoichiometry and the reaction conditions.^[13]

Conclusion

The tetrahydride complex of tungsten containing a tetraphosphane co-ligand, 5b, was synthesized for the first time by the reaction of the dibromide complex **2b** with NaBH₄. The highly strained structure of the P4 ligand makes complex 5b highly reactive towards CS₂ and RNC. It has been confirmed that the tetrahydride complex with the diphosphane ligands, $[WH_4(dppe)_2]$, is completely inert towards these molecules under the same or more severe reaction conditions. It is worth mentioning that complex 5b has the potential to open a coordination site not only by the loss of H₂ but also by dissociation of one or two terminal P atoms, as proposed for the mechanism of catalysis by $[{P(CH_2CH_2PPh_2)_3}FeH(H_2)]^+$.^[39] Finally, **5b** has been shown to be a versatile precursor to complexes with a κ^4 tetraphosphane ligand, which are still rarely explored for the Group 6 metals.^[40]

Experimental Section

General: All preparations were carried out by using the standard Schlenk technique under a pure H₂ or N₂ atmosphere. The solvents were dried by standard methods and distilled under a N₂ atmosphere before use. Complexes $[M(\kappa^2-dppe)(\kappa^4-P4)]^{[11]}$ and $[MBr_2(\kappa^4-P4)]^{[12]}$ were prepared as described previously, and other reagents were commercially obtained and used without further purification.

NMR spectra were measured with JEOL alpha-400 or JEOL ECS 400 NMR spectrometers at 20 °C, except for those indicated otherwise. Chemical shifts were referenced to the isotopic impurities (C₆D₆ at 7.15 ppm and [D₈]toluene at 2.09 ppm) for ¹H or the external 85% H₃PO₄ ($\delta = 0$ ppm) for ³¹P. For the ¹H data, the signals due to **P4** are omitted. IR spectra were recorded with a JASCO FTIR-420. Elemental analyses were performed with a Perkin–Elmer 2400 series II CHN analyzer or a Thermol Fisher Scientific FLASH 2000 organic elemental analyzer. Gas phase analysis was

performed with a Shimadzu GC-14B gas chromatograph equipped with a molecular sieves 13X column.

Reaction of [Mo(κ^2 -dppe)(κ^4 -P4)] with 1 atm of H₂: A suspension of $[Mo(\kappa^2-dppe)(\kappa^4-P4)] \cdot C_6H_6$ (0.129 g, 0.100 mmol) in toluene (6 mL) was stirred under a H₂ atmosphere (1 atm) at 25 °C for 5 h. Concentration of the resulting orange solution to 3 mL followed by the addition of ether (12 mL) afforded the orange needles of $[MoH_2(\kappa^2-dppe)(\kappa^3-P4)]$ (3a) (0.102 g, 84% yield). ¹H NMR (400 MHz, [D₈]toluene, 80 °C): $\delta = -4.83$ (tddd, $J_{\rm HP} = 49$, 32, 30, 15 Hz, 2 H, Mo-H) ppm. ¹H NMR (400 MHz, [D₈]toluene, -60 °C): $\delta = -6.8$ to -6.2 (br., 1 H, Mo-H), -3.0 to -2.3 (br., 1 H, Mo-H) ppm. For the ³¹P spectra, the positions of the P atoms correspond to those indicated in Scheme 1. ³¹P{¹H} NMR ([D₈]toluene, 80 °C): $\delta = -11.2$ (P_d), 77.0 (P_e and P_f), 86.1 (P_c), 91.4 (P_a), 108.5 (P_b) ppm, $J_{ab} = 18$ Hz, $J_{ac} = 7$ Hz, $J_{ae} = 3$ Hz, $J_{af} = 3$ Hz, $J_{\rm bc} = 24$ Hz, $J_{\rm be} = 42$ Hz, $J_{\rm bf} = 42$ Hz, $J_{\rm cd} = 33$ Hz, $J_{\rm ce} = 16$ Hz, $J_{cf} = 16$ Hz. ³¹P{¹H} NMR ([D₈]toluene, -60 °C): $\delta = -17.8$ (P_d), 69.8, 76.2 (1P each, P_e and P_f), 82.4 (P_c), 98.0 (P_a), 106.2 (P_b) ppm, signals were not resolved. IR (KBr): $\tilde{v} = 1868$, 1779 [w, v(Mo-H)] cm⁻¹. C₇₂H₆₈MoP₆ (1215.11): calcd. C 71.17, H 5.64; found C 71.22, H 5.73.

[Mo{(η^6 -Ph)PPhCH₂CH₂PPh₂}(κ^3 -P4)] (4a): Complex [MoH₂(κ^2 dppe)(κ^3 -P4)] (0.121 g, 0.099 mmol) was heated under reflux in toluene (5 mL) under a H₂ atmosphere (1 atm) for 5 h. NMR measurement of the resulting orange solution revealed that it contained two diastereomers of $[Mo{(\eta^6-Ph)PPhCH_2CH_2PPh_2}(\kappa^3-P4)]$ in a 5:4 ratio. Concentration of the solution to 2 mL followed by addition of hexane (15 mL) afforded orange crystals of the major isomer (0.035 g, 29% yield). Although this sample remained intact in solution at room temperature, a mixture of diastereomers was formed once again by heating under reflux in toluene. ¹H NMR $(400 \text{ MHz}, C_6D_6): \delta = 3.31 (t, 1 \text{ H}), 3.4-3.5 (m, 2 \text{ H}), 3.51 (t, 1 \text{ H}),$ 3.82 (q, 1 H) ppm for η^6 -Ph. ³¹P{¹H} NMR (C₆D₆): $\delta = -13.3$ (P_f), -12.1 (P_d), -11.4 (P_e), 75.8 (P_c), 86.6 (P_a), 115.9 (P_b) ppm, $J_{ab} =$ 7 Hz, $J_{ac} = 22$ Hz, $J_{bc} = 24$ Hz, $J_{be} = 3$ Hz, $J_{cd} = 31$ Hz, $J_{ef} =$ 34 Hz. C72H66MoP6 (1213.10): calcd. C 71.29, H 5.48; found C 71.51, H 5.63. ³¹P{¹H} NMR (C₆D₆) of the minor isomer: δ = -13.0 (P_f), -11.4 (P_d), -11.3 (P_e), 77.1 (P_c), 86.2 (P_a), 114.4 (P_b) ppm, $J_{ab} = 9$ Hz, $J_{ac} = 23$ Hz, $J_{bc} = 24$ Hz, $J_{be} = 4$ Hz, $J_{cd} = 32$ Hz, $J_{\rm ef}$ = 32 Hz. See Scheme 1 for notation of the ³¹P signals.

Reaction of $[W(\kappa^2-dppe)(\kappa^4-P4)]$ with 1 atm of H₂: A suspension of $[W(\kappa^2-dppe)(\kappa^4-P4)]$ -toluene (0.130 g, 0.0934 mmol) in toluene (6 mL) was stirred under a H₂ atmosphere (1 atm) at 80 °C for 4 h. NMR measurement of the resulting red solution revealed that it contained two complexes $[WH_2(\kappa^2-dppe)(\kappa^3-P4)]$ (3b) and $[WH_4(\kappa^4-P4)]$ (5b) in a ratio of 1:1. The ratio of these two complexes was same after the reaction was continued for further 20 h. The NMR spectroscopic data of $[WH_2(\kappa^2-dppe)(\kappa^3-P4)]$ are as follows: ¹H NMR (400 MHz, C₆D₆): $\delta = -4.6$ to -4.2 (m, 2 H, W-H) ppm. ³¹P{¹H} NMR (C₆D₆): $\delta = -12.9$ (P_d), 57.0 (P_e and P_f), 61.8 (P_c), 65.3 (P_a) and 89.2 (P_b) ppm, assignment of the coupling constants was not possible due to the low S/N ratio. The notation for the P atoms is same as that for the Mo analogue **3a** in Scheme 1.

[WH₄(\kappa^4-P4)] (5b): A mixture of [WBr₂(κ^4 -P4)]·0.5C₆H₆ (0.682 g, 0.619 mmol) and NaBH₄ (0.234 g, 6.19 mmol) in ethanol (30 mL) was stirred under a N₂ atmosphere at 50 °C for 4 h and resulted in an orange-red suspension. After the suspension was concentrated in vacuo, the residual solid was extracted with toluene (20 mL). Red crystals of [WH₄(κ^4 -P4)]·0.5toluene (0.459 g, 77% yield) were obtained by adding ethanol (5 mL) to the extract after concentration to 3 mL. ¹H NMR (400 MHz, C₆D₆): $\delta = -5.46$ (m, 1 H, W-H), -3.05 (m, 3 H, W-H) ppm. ³¹P{¹H} NMR (C₆D₆): $\delta = 60.8$

 $(J_{PW} = 177 \text{ Hz}, \text{ outer P}), 89.8 (J_{PW} = 151 \text{ Hz}, \text{ inner P}) \text{ ppm}, AA'XX' \text{ pattern with }^{183}W \text{ satellites}, J_{AX} + J_{AX'} = 8 \text{ Hz}. \text{ IR (KBr):}$ $\tilde{v} = 1762 [v(W-H)] \text{ cm}^{-1}. \text{ C}_{49.5}\text{H}_{50}\text{P}_4\text{W} (952.68): \text{ calcd. C } 62.41, \text{ H} 5.29; \text{ found C } 62.94, \text{ H } 5.37.$

Reaction of [WH₄(\kappa^4-P4)] with CS₂: Carbon disulfide (18 µL, 0.30 mmol) was added to a solution of [WH₄(κ^4 -P4)]·0.5toluene (0.091 g, 0.10 mmol) in toluene and the mixture was stirred at 50 °C under a N₂ atmosphere for 18 h. The resulting green solution was filtered and diethyl ether (18 mL) was added to the concentrated filtrate (3 mL) to afford green cubic crystals of [W(κ^2 -S₂CH₂)(κ^4 -P4)] (6) (0.071 g, 76% yield). In order to determine the concomitantly formed H₂ another reaction was carried out under vacuum and the gas phase was analyzed by GC after dilution with pure argon gas. ¹H NMR (400 MHz, C₆D₆): $\delta = 6.56$ (s, 2 H, CH₂S₂) ppm. ³¹P{¹H} NMR (C₆D₆): $\delta = 61.0$ (br s with ¹⁸³W satellites, $J_{PW} = 218$ Hz, outer P), 105.9 (br s with ¹⁸³W satellites, $J_{PW} = 214$ Hz, inner P) ppm. C₄₇H₄₄P₄S₂W (980.73): calcd. C 57.56, H 4.52; found C 57.35, H 4.52.

Reaction of [WH₄(κ^4 -P4)] with tBuNC: A solution of [WH₄(κ^4 -P4)]·0.5toluene (0.082 g, 0.086 mmol) and tBuNC (30 μL, 0.27 mmol) in toluene was stirred at 80 °C under a N2 atmosphere for 7 h. The resulting red solution was filtered, and hexane (18 mL) was added to the concentrated filtrate (3 mL) to afford red needle crystals of $[W(tBuNC)_2(\kappa^4-P4)]$ (7). The X-ray crystallographic study revealed that the crystals contained 0.75 equiv. hexane as the solvate, which was removed by drying under vacuum (0.050 g, 54%)yield). ¹H NMR (400 MHz, C₆D₆): $\delta = 0.78$ [s, 9 H, C(CH₃)₃], 1.27 [s, 9 H, C(CH₃)₃] ppm. ³¹P{¹H} NMR (C₆D₆): δ = 42.4 (J_{PW} = 222 Hz, P_a), 54.8 (J_{PW} = 328 Hz, P_d), 81.1 (J_{PW} = 307 Hz, P_b), 90.1 $(J_{PW} = 216 \text{ Hz}, P_c) \text{ ppm}, J_{ab} = 11 \text{ Hz}, J_{ac} = 9 \text{ Hz}, J_{ad} = 13 \text{ Hz}, J_{bc}$ = 5 Hz, J_{bd} = 79 Hz, J_{cd} = 14 Hz. See Equation (4) for the notation of the P atoms. IR (KBr): $\tilde{v} = 1804$ (s), 2002 (s) $[v(N \equiv C)]$ cm⁻¹. C₅₆H₆₀N₂P₄W (1068.85): calcd. C 62.93, H 5.66, N 2.62; found C 62.49, H 5.69, N 2.55.

Reaction of [WH₄(\kappa^4-P4)] with XyNC: A solution of [WH₄(κ^4 -P4)][•] 0.5toluene (0.096 g, 0.10 mmol) and XyNC (0.040 g, 0.30 mmol) in



toluene was stirred at 80 °C under a N₂ atmosphere for 7 h. Compound [W(XyNC)₂(κ^4 -P4)] was obtained as an orange-red solid by crystallization from toluene and hexane at -20 °C (0.076 g, 64%). ¹H NMR (400 MHz, C₆D₆): δ = 1.54 (s, 6 H, CH₃), 2.28 (s, 6 H, CH₃) ppm. ³¹P{¹H} NMR (C₆D₆): δ = 41.4 (J_{PW} = 202 Hz, P_a), 49.3 (J_{PW} = 320 Hz, P_d), 79.4 (J_{PW} = 304 Hz, P_b), 85.2 (J_{PW} = 215 Hz, P_c) ppm, J_{ab} = 11 Hz, J_{ac} = 13 Hz, J_{ad} = 15 Hz, J_{bc} = 4 Hz, J_{bd} = 80 Hz, J_{cd} = 12 Hz. IR (KBr): $\tilde{\nu}$ = 1837 (s), 1943 (s) [ν (N=C)] cm⁻¹.

X-ray Crystallography: A single crystal of 3a was sealed in a glass capillary tube under an Ar atmosphere and measured at 293 K. Crystals of 5b, 6, and 7 were mounted on loops with oil and cooled to 113 K. All diffraction studies were performed with a Rigaku Mercury-CCD diffractometer equipped with a graphite-monochromatized Mo- K_{α} source. Data were processed using the CrystalClear program package^[41] and corrected for absorption. Among several trials, crystallization from toluene/diethyl ether gave the largest single crystals of 3a. However, the crystal volumes were still not enough to obtain intense data, and only 29% of the reflections in the range of $2\theta < 50.5^{\circ}$ met the criteria of $I > 2\sigma(I)$. Since crystals of 6 showed severe twinning, diffraction data were collected with a non-merohedral twin crystal and processed using the TwinSolve program package.^[42] The reflections were assigned to two crystal domains of different orientations, and the intensity data integrated for each domain were combined together. The resulting data set, which included 93% of the unique reflections in the range of $2\theta <$ 50°, was used in the structure solution and refinement. Details are listed in Table 3.

The structure solutions and refinements were performed by using the CrystalStructure program package.^[43] The positions of the nonhydrogen atoms were determined by the Patterson methods (PATTY^[44] for **3a** and **5b** or SHELXS97^[45] for **6** and **7**) and subsequent Fourier synthesis (DIRDIF99^[46]). These were refined with anisotropic thermal parameters by full-matrix least-squares techniques. The hydride ligands in **3a** and **5b** were found in the Fourier maps and refined isotropically (**5b**) or with fixed thermal param-

Table 3. Crystallographic data.

	3a	5b·0.5 toluene	6	7 •0.75 hexane
Formula	C ₇₂ H ₆₈ P ₆ Mo	$C_{495}H_{50}P_4W$	C47H44 P4S2W	$C_{60} {}_{5}H_{70} {}_{5}N_{2}P_{4}W$
Formula weight	1215.11	952.68	980.73	1133.48
Space group	<i>P</i> 1 (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	C2/c (no. 15)
a [Å]	10.228(5)	12.0415(9)	17.815(1)	45.447(9)
b [Å]	12.307(5)	24.746(1)	11.7463(9)	10.479(2)
c [Å]	24.35(1)	14.691(1)	19.319(2)	25.852(5)
a [°]	84.43 (1)	90	90	90
β ^[°]	88.51(1)	108.354(1)	96.850(5)	118.236(2)
γ [°]	88.71(1)	90	90	90
V[Å ³]	3049(2)	4154.9(5)	4013.9(6)	10846(3)
Z	2	4	4	8
$\rho_{\rm calcd} [\rm g cm^{-3}]$	1.324	1.523	1.623	1.388
$\mu [{\rm mm}^{-1}]$	0.415	2.972	3.179	2.290
Crystal size [mm ³]	$0.10 \times 0.06 \times 0.02$	$0.10 \times 0.08 \times 0.04$	$0.25 \times 0.10 \times 0.02$	$0.40 \times 0.15 \times 0.03$
Transmission factor	0.565-0.992	0.715-0.888	0.787-0.939	0.646-0.934
Unique reflections (R_{int})	10696 (0.106)	9882 (0.042)	13148 (0.081)	12806 (0.041)
Observed reflections ^[a]	3088	7683	10379	9906
Variables	784	589	485	601
<i>R</i> ₁ ^[b]	0.0697	0.0355	0.0713	0.0364
$wR_2^{[c]}$	0.1502	0.0712	0.1977	0.0776
Gof ^[d]	1.015	1.024	1.137	1.114

eters (**3a**). Other hydrogen atoms were placed at the calculated positions and included in the final stages of the refinements. The structure refinement of **6** with twin data was performed using the SHELXL97^[45] program. The disorder was observed for one of the Ph groups and these carbon atoms, except for the *ipso* position, were split to 0.5/0.5 occupancies for two orientations and refined with isotropic parameters. The solvating hexane molecules in **7** were also disordered and these were refined isotropically with some restraints. The hydrogen atoms of the disordered moieties in **6** and **7** were not located.

CCDC-787876 (for **3a**), -787877 (for **5b**), -787878 (for **6**), and -787879 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Acknowledgments

We thank Ms. Yukiko Tanzawa and Mr. Chirima Arita for their experimental assistance. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan: i. Grant-in-Aid for Scientific Research on Priority Areas, grant number 18065005, "Chemistry of Concerto Catalysis", to Y. M.), ii. Grant-in-Aid for Scientific Research (B), grant number 21350033, to H. S.). H. S. gratefully acknowledges the special funding from the Institute of Industrial Science, The University of Tokyo (GCOE program, "Chemistry Innovation through Cooperation of Science and Engineering").

- [1] G. G. Hlatky, R. H. Crabtree, Coord. Chem. Rev. 1985, 65, 1– 48.
- [2] M. Peruzzini, R. Poli (Eds.), *Recent Advances in Hydride Chemistry*, Elsevier, Amsterdam, 2001.
- [3] D. Michos, X. L. Luo, J. W. Faller, R. H. Crabtree, *Inorg. Chem.* 1993, 32, 1370–1375.
- [4] Y. Kim, H. Deng, D. W. Meek, A. Wojcicki, J. Am. Chem. Soc. 1990, 112, 2798–2800.
- [5] X. L. Luo, R. H. Crabtree, J. Chem. Soc., Dalton Trans. 1991, 587–590.
- [6] T. Ito, Bull. Chem. Soc. Jpn. 1999, 72, 2365-2377.
- [7] C. G. Young, in: Comprehensive Coordination Chemistry II (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Pergamon, Amsterdam, 2004, vol. 4, pp. 474–475.
- [8] a) T. A. George, R. C. Tisdale, *Inorg. Chem.* 1988, 27, 2909–2912; b) L. Dahlenburg, B. Pietsch, *J. Organomet. Chem.* 1989, 378, 199–210.
- [9] a) D. Y. Zhou, M. Minato, T. Ito, M. Yamasaki, *Chem. Lett.* 1997, 1017–1018; b) M. Minato, R. Hirabayashi, T. Matsumoto, Y. Yamaguchi, T. Ito, *Chem. Lett.* 2001, 30, 960–961; c) M. Minato, D. Y. Zhou, L. B. Zhang, R. Hirabayashi, M. Kakeya, T. Matsumoto, A. Harakawa, G. Kikutsuji, T. Ito, *Organometallics* 2005, 24, 3434–3441.
- [10] G. Jia, A. J. Lough, R. H. Morris, J. Organomet. Chem. 1993, 461, 147–156.
- [11] a) C. Arita, H. Seino, Y. Mizobe, M. Hidai, *Chem. Lett.* 1999, 28, 611–612; b) C. Arita, H. Seino, Y. Mizobe, M. Hidai, *Bull. Chem. Soc. Jpn.* 2001, 74, 561–567.
- [12] H. Seino, D. Watanabe, T. Ohnishi, C. Arita, Y. Mizobe, *Inorg. Chem.* 2007, 46, 4784–4786.
- [13] H. Seino, C. Arita, M. Hidai, Y. Mizobe, J. Organomet. Chem. 2002, 658, 106–116.
- [14] a) M. B. Hursthouse, D. Lyons, M. Thornton-Pett, G. Wilkinson, J. Chem. Soc., Chem. Commun. 1983, 476–477; b) D. Lyons, G. Wilkinson, M. Thornton-Pett, M. B. Hursthouse, J. Chem. Soc., Dalton Trans. 1984, 695–700.

[15] H. W. Choi, E. L. Muetterties, J. Am. Chem. Soc. 1982, 104,

Q. X. Dai, H. Seino, Y. Mizobe

- 153–161. [16] L. J. Archer, T. A. George, M. E. Noble, J. Chem. Educ. 1981,
- 58, 727–728.
- [17] J. L. Graff, T. J. Sobieralski, M. S. Wrighton, G. L. Geoffroy, J. Am. Chem. Soc. 1982, 104, 7526–7533.
- [18] a) F. G. N. Cloke, K. P. Cox, M. L. H. Green, J. Bashkin, K. Prout, *J. Chem. Soc., Chem. Commun.* **1982**, 393–394; b) M. Brookhart, K. Cox, F. G. N. Cloke, J. C. Green, M. L. H. Green, P. M. Hare, J. Bashkin, A. E. Derome, P. D. Grebenik, *J. Chem. Soc., Dalton Trans.* **1985**, 423–433.
- [19] a) M. L. H. Green, G. Parkin, C. Mingqin, K. Prout, J. Chem. Soc., Chem. Commun. 1984, 1400–1402; b) M. L. H. Green, G. Parkin, M. Chen, K. Prout, J. Chem. Soc., Dalton Trans. 1986, 2227–2236.
- [20] a) F. Pennella, J. Chem. Soc., Chem. Commun. 1971, 158–159;
 b) B. Bell, J. Chatt, G. J. Leigh, T. Ito, J. Chem. Soc., Chem. Commun. 1972, 34–35;
 c) P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, J. P. Jesson, J. Am. Chem. Soc. 1973, 95, 1467–1474;
 d) F. Pennella, Inorg. Synth. 1974, 15, 42–44;
 e) R. H. Crabtree, G. Hlatky, Inorg. Chem. 1982, 21, 1273–1275.
- [21] B. J. L. Hoard, J. V. Silverton, Inorg. Chem. 1963, 2, 235-242.
- [22] a) L. J. Guggenberger, *Inorg. Chem.* 1973, *12*, 2295–2304; b)
 E. B. Lobkovskii, A. P. Borisov, V. D. Makhaev, K. N. Semenenko, *J. Struct. Chem.* 1980, *21*, 100–104; c) A. J. L. Pombeiro, A. Hills, D. L. Hughes, R. L. Richards, *Acta Crystallogr, Sect. C* 1995, *51*, 23–26.
- [23] M. Minato, D. Y. Zhou, K. Sumiura, R. Hirabayashi, Y. Yamaguchi, T. Ito, *Chem. Commun.* 2001, 2654–2655.
- [24] Selected spectroscopic data: ³¹P{¹H} NMR (C₆D₆): δ = 43.8 and 73.8 ppm (AA'XX' pattern, $J_{AX} + J_{AX'} = 211$ Hz). ¹H NMR (C₆D₆): no hydride signals in the high-field region.
- [25] K. K. Pandey, Coord. Chem. Rev. 1995, 140, 37-114.
- [26] a) D. Lyons, G. Wilkinson, J. Chem. Soc., Dalton Trans. 1985, 587–590; b) R. Ellis, R. A. Henderson, A. Hills, D. L. Hughes, J. Organomet. Chem. 1987, 333, C6–C10; c) L. K. Fong, J. R. Fox, N. J. Cooper, Organometallics 1987, 6, 223–231; d) T. Ito, T. Matsubara, J. Chem. Soc., Dalton Trans. 1988, 2241–2242; e) D. Dawson, R. A. Henderson, A. Hills, D. L. Hughes, Polyhedron 1989, 8, 1870–1871.
- [27] D. L. Allen, M. L. H. Green, J. A. Bandy, J. Chem. Soc., Dalton Trans. 1990, 541–549.
- [28] a) A. P. Borisov, V. D. Makhaev, K. N. Semenenko, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 1914; b) A. P. Borisov, V. D. Makhaev, K. N. Semenenko, *Koord. Khim.* **1983**, *9*, 536–539.
- [29] T. Ohnishi, H. Seino, M. Hidai, Y. Mizobe, J. Organomet. Chem. 2005, 690, 1140–1146.
- [30] a) I. S. Butler, A. E. Fenster, J. Organomet. Chem. 1974, 66, 161–194; b) P. V. Yaneff, Coord. Chem. Rev. 1977, 23, 183–220.
- [31] a) J. Okuda, Z. Naturforsch., Teil B 1990, 45, 753–754; b) G. Jia, D. W. Meek, Inorg. Chem. 1991, 30, 1953–1955; c) W. D. Jones, A. D. Selmeczy, Organometallics 1992, 11, 889–893; d) M. L. Christ, S. Sabo-Etienne, G. Chung, B. Chaudret, Inorg. Chem. 1994, 33, 5316–5319; e) T. Gandhi, M. Nethaji, B. R. Jagirdar, Inorg. Chem. 2003, 42, 667–669; f) T. Gandhi, B. R. Jagirdar, Inorg. Chem. 2005, 44, 1118–1124.
- [32] K. Iwasa, H. Seino, F. Niikura, Y. Mizobe, *Dalton Trans.* 2009, 31, 6134–6140.
- [33] a) V. W. W. Yam, P. K. Y. Yeung, K. K. Cheung, *J. Chem. Soc., Chem. Commun.* **1995**, 267–269; b) R. Mas-Balleste, M. Capdevila, P. A. Champkin, W. Clegg, R. A. Coxall, A. Lledos, C. Megret, P. Gonzalez-Duarte, *Inorg. Chem.* **2002**, *41*, 3218–3229.
- [34] a) V. G. Albano, P. L. Bellon, G. Ciani, J. Organomet. Chem.
 1971, 31, 75–87; b) Y. Gao, D. G. Holah, A. N. Hughes, G. J. Spivak, M. D. Havighurst, V. R. Magnuson, V. Polyakov, Polyhedron 1997, 16, 2797–2807; c) H. V. Nanishankar, S. Dutta, M. Nethaji, B. R. Jagirdar, Inorg. Chem. 2005, 44, 6203–6210.
- [35] a) M. Minato, J. Nishiuchi, M. Kakeya, T. Matsumoto, Y. Yamaguchi, T. Ito, *Dalton Trans.* 2003, 483–487; b) M. Minato,



G. Kikutsuji, M. Kakeya, K. Osakada, M. Yamasaki, *Dalton Trans.* 2009, 7684–7687.

- [36] a) J. Chatt, A. J. L. Pombeiro, R. L. Richards, G. H. D. Royston, K. W. Muir, R. Walker, J. Chem. Soc., Chem. Commun. 1975, 708–709; b) G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, P. Woodward, J. Chem. Soc., Chem. Commun. 1977, 256–258; c) J. M. Basset, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard, F. G. A. Stone, J. Chem. Soc., Dalton Trans. 1979, 1003–1011; d) C. Hu, W. C. Hodgeman, D. W. Bennett, Inorg. Chem. 1996, 35, 1621–1626; e) H. Seino, C. Arita, D. Nonokawa, G. Nakamura, Y. Harada, Y. Mizobe, M. Hidai, Organometallics 1999, 18, 4165–4173; f) N. L. Wagner, F. E. Laib, D. W. Bennett, J. Am. Chem. Soc. 2000, 122, 10856–10867.
- [37] Selected spectroscopic data (for R = *t*Bu): ¹H NMR (C₆D₆): δ = -3.7 (br., 2 H, WH), 1.27 [s, 9 H, C(CH₃)₃] ppm. ³¹P{¹H} NMR (C₆D₆): δ = 52.9 (J_{PW} = 241 Hz, P_w), 75.0 (J_{PW} = 194 Hz, P_z), 98.1 (J_{PW} = 167 Hz, P_x), 102.4 (J_{PW} = 235 Hz, P_y) ppm, J_{wz} = 8 Hz, J_{wz} = 16 Hz, J_{xy} = 41 Hz, J_{xz} = 14 Hz, J_{yz} = 24 Hz.
- [38] T. Ohnishi, H. Tsuboi, H. Seino, Y. Mizobe, J. Organomet. Chem. 2008, 693, 269–277.
- [39] C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M. A. Esteruelas, L. A. Oro, *Organometallics* 1992, 11, 138– 145.

- [40] a) R. B. King, R. N. Kapoor, M. S. Saran, P. N. Kapoor, *Inorg. Chem.* 1971, 10, 1851–1860; b) R. Romer, G. Stephan, C. Habeck, C. Hoberg, G. Peters, C. Nather, F. Tuczek, *Eur. J. Inorg. Chem.* 2008, 3258–3263.
- [41] CrystalClear 1.3.6: Rigaku/MSC, The Woodlands, TX, USA, 2006.
- [42] TwinSolve: Rigaku/MSC, The Woodlands, TX, USA, 2002.
- [43] CrystalStructure 3.8.2: Rigaku/MSC, The Woodlands, TX, USA, 2007.
- [44] PATTY P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykall, *The DIRDIF program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, **1992**.
- [45] SHELX97: G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112.
- [46] DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF-*99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, **1999**.

Received: August 9, 2010 Published Online: November 17, 2010