

論文の内容の要旨

論文題目 A study on Unique Transformation of Organic Molecules on Group 6 Metal Tetraphosphine Complexes

(6族金属-四座ホスフィン錯体上での特異な有機分子変換に関する研究)

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Introduction

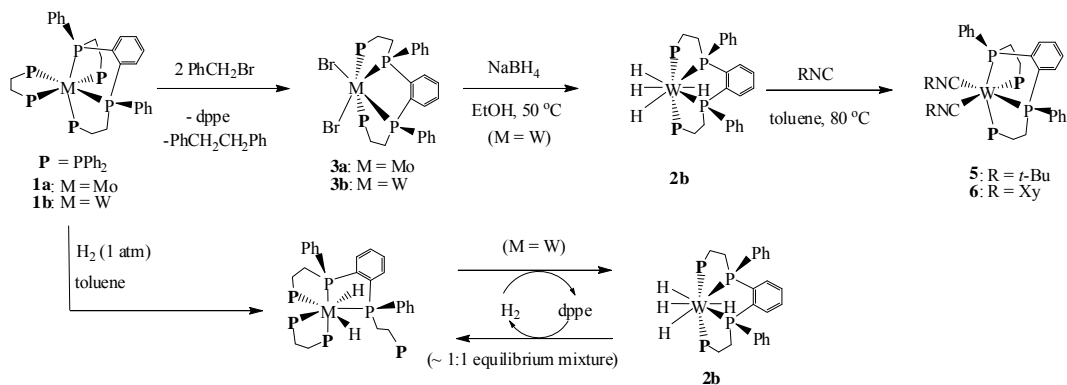
Low-valent group 6 metal centers surrounded by tertiary phosphine coligands have remarkable ability to activate the coordinated small molecules. Typical example is the $[M(dppe)_2]$ ($M = Mo, W$; $dppe = Ph_2PCH_2CH_2PPh_2$) site, which readily transforms numerous substrate molecules including N_2 , CO_2 , alkenes, alkynes, nitriles, isocyanides, etc. into a variety of attractive ligands or compounds under mild conditions. The linear tetraphosphine ligand *meso-o*- $C_6H_4(PPhCH_2CH_2PPh_2)_2$ (**P4**) has been discovered in the course of these studies by Mizobe's group. Formation of **P4** is recognized as an example of unique bond rearrangement in the coordination sphere of low-valent Mo and W complexes, by which **P4** and benzene are produced via the condensation of two *dppe* ligands. Tetradentate coordination of **P4** to a metal center accumulates strain of three consecutive chelates, in which the P-M-P angles of five-membered rings are fairly smaller than 90° . This induces unusual structures that are distorted extremely from regular octahedron or facile change of the coordination mode from κ^4 to κ^3 and κ^2 . The most easily prepared starting compounds for the Mo and W tetraphosphine complexes are $[M(dppe)(\kappa^4-P4)]$ (**1**) but their metal centers are obstructed by steric bulk and strong M-P bonds of **P4** and *dppe*. Therefore new precursor complexes that can effectively provide the reaction sites are anticipated. Polyhydride complexes are dependable candidates, since the reactivity types of polyhydride complexes are not limited to those of common hydride complexes but are also featured by their ability to generate coordinatively unsaturated intermediates via reductive elimination of H_2 .

Results and Discussion

1. Synthesis and properties of tetrahydride complexes containing P4 ligand

The tetrahydride complex $[WH_4(\kappa^4-P4)]$ (**2b**) was prepared in 77% yield by treatment of the W(II) complex $[WBr_2(\kappa^4-P4)]$ (**3b**) with excess $NaBH_4$ in ethanol at $50^\circ C$ (Scheme 1). Formation of **2b** was also observed by the reaction of **1b** with 1 atm H_2 at $80^\circ C$, but equilibrium with the dihydride complex $[WH_2(\kappa^2-dppe)(\kappa^3-P4)]$

Scheme 1



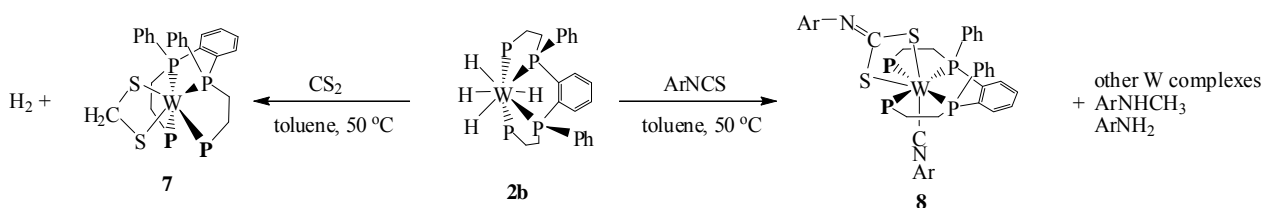
(**4b**) and free dppe in the ratio of **2b**:**4b** = 1:1 hampered selective formation. The Mo analogue [MoH₄(κ⁴-**P4**)] (**2a**) was not formed at all by any routes shown in Scheme 1. The molecular structure of **2b** was determined by X-ray crystallography, which revealed a distorted dodecahedral geometry of the W center. The κ⁴-**P4** ligand asymmetrically divided the coordination sphere into two. Three hydrido ligands were found at the wider part, and the other one existed at the opposite narrow side. The ¹H NMR spectrum of **2b** at 20 °C showed two hydrido signals at δ -3.06 and -5.46 with 3H and 1H intensities, indicating that one hydrido ligand is separated from the others also in solution.

The reaction of **2b** with 3 equiv of RNC in toluene at 80 °C produced [W(CNR)₂(κ⁴-**P4**)] (R = *t*-Bu (**5**), Xy (**6**); Xy = 2,6-Me₂C₆H₃) after 7 h (Scheme 1). Formation of the intermediates speculated as [WH₂(CNR)(κ⁴-**P4**)] was observed during this conversion. It is important to note that the related [WH₄(dppe)₂] shows no reactivity towards RNC under the same conditions. A highly distorted octahedral structure, in which two isocyanide ligands are oriented mutually cis, has been confirmed crystallographically for **5**, and NMR spectra of both **5** and **6** are consistent with this structure. One of the isocyanide ligands in **5** (trans to the internal P atom) has a considerably bent C–N–C linkage (139.3(4)°) in solid state as a result of strong back-donation from the W(0) center, which is also indicated by low frequency shift of ν(N≡C) in the IR spectra. From the lower ν(N≡C) values for **6** (1837 and 1943 cm⁻¹) than those for its Mo analogue (1851, 1879 and 1957 cm⁻¹), electron-donating ability of the W(**P4**) moiety is estimated to be somewhat superior to that of the Mo(**P4**).

2. Transformations of heterocumulenes

Although the reaction of **2b** with CO₂ resulted in complicated mixture, from which no products could be fully characterized. Isoelectronic CS₂ and RNCS molecules were found to be converted in the coordination sphere derived from **2b** (Scheme 2). Treatment of **2b** with 3 equiv of CS₂ at 50 °C in toluene cleanly formed [W(κ²-S₂CH₂)(κ⁴-**P4**)] (**7**), which was obtained as green prismatic crystals in 76% yield. GC analysis of gas phase confirmed the concomitant formation of H₂ in 0.73 equiv to W atom. In the ¹H NMR spectrum of **7**, no hydride signals were observed, and a singlet signal integrated to 2H appeared at δ 6.56, which was assigned to the CH₂S₂ moiety. The W center in **7** has a trigonal prismatic geometry, in which one of the three side rectangles is capped by the κ⁴-**P4** ligand. Although there have been many examples of CS₂ insertion into a M–H bond to give dithioformate complexes, formation of a methanedithiolate ligand from a CS₂ molecule and two hydride ligands are still rare. The reaction of **2b** with 3 equiv of aryl isothiocyanate ArNCS (Ar = Ph, *p*-CH₃C₆H₄ (Tol), *p*-ClC₆H₄) in toluene proceeded at 50 °C to form majorly two W complexes, and the less soluble [W(S₂CNAr)(CNAr)(κ⁴-**P4**)] (**8**) was separated out from the mixture as a brown precipitate (Scheme 2). X-ray crystallography of **8** (Ar = Tol) has revealed a distorted pentagonal bipyramidal structure, in which the isocyanide ligand and one of the sulfur atom of the dithiocarbonimidato ligand are occupying apical positions. The ³¹P{¹H}

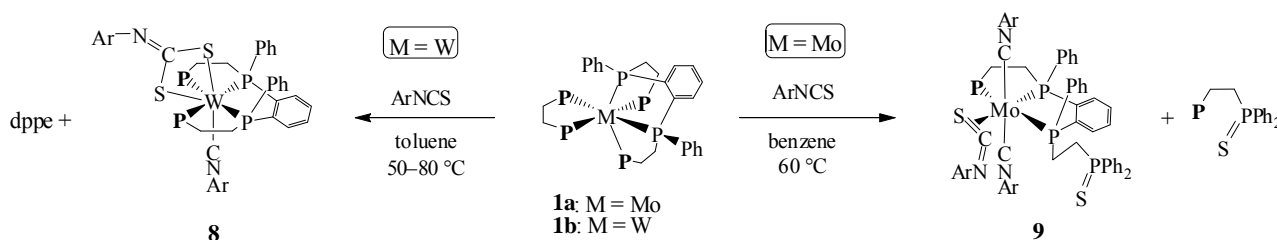
Scheme 2



NMR spectrum of **8** (Ar = Tol) in CDCl₃ solution at 20 °C showed two very broad peaks at δ 46 and 66, and these changed at -50 °C to two pairs of signals at (δ 49.9 and 66.9 vs δ 47.4 and 67.3 in a 2.5:1 ratio) probably corresponding to the *syn*- and *anti*-conformations around the C=N bond in the dithiocarbonimidato ligand. On the other hand, the liquid phase of the reaction mixture contained ArNHCH₃, ArNH₂, and unreacted ArNCS in addition to other W complexes. Yields of the hydrodesulfurization product ArNHCH₃ were dependent on the Ar groups (0.45, 0.23, and 0.12 equiv to W for Ar = Tol, Ph, *p*-ClC₆H₄, respectively) and increased to about 1.5 times large (up to 0.65 equiv to W for Ar = Tol) when the reactions were carried out under H₂ atmosphere.

Since the formation of **8** is recognized as disproportionation of two RNCS molecules on a W(0) center, the reactions of zero-valent complex **1b** with aryl isothiocyanates were examined, and these proceeded at 50–80 °C to give **8** (Scheme 3). In contrast, the reactions of Mo complex **1a** with 3 equiv of ArNCS in benzene at 60 °C have been found to afford [Mo(ArNC)₂(η²-ArNCS)(κ³-P₄S)] (**9**) and monosulfide of dppe. The formal oxidation states of the products, viz, W(II) for **8** and Mo(0) for **9**, reflect higher electron-donating ability of W than Mo. The N atom of the dithiocarbonimidato ligand in **8** had a nucleophilic character, and it smoothly reacted with H⁺, MeI, and PhCOCl.

Scheme 3

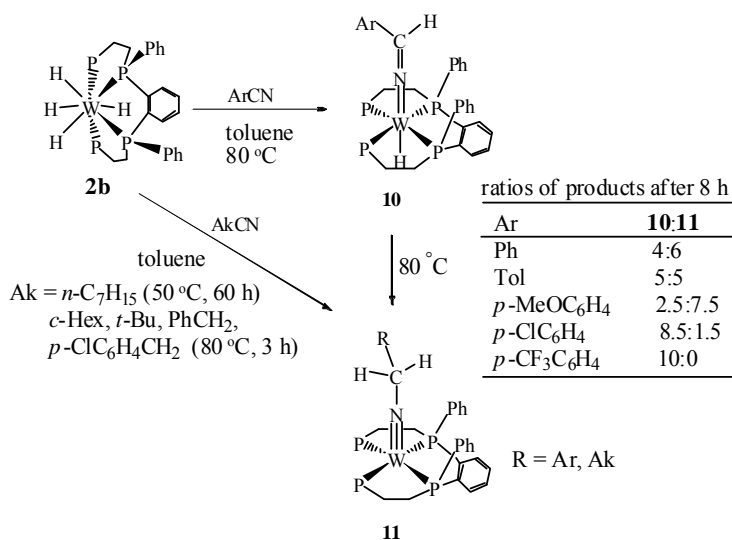


3. Transformations of nitriles

When **2b** was heated with 3 equiv of TolCN in toluene at 80 °C for 3 h, the hydrido-alkylideneamido complex [W(H=N=CHTol)(κ⁴-P₄)] (**10_{Tol}**) was obtained as almost sole complex product (Scheme 4). X-ray crystallography has revealed that **10_{Tol}** has a highly distorted octahedral geometry with the hydrido and the alkylideneamido ligands at mutually trans positions. The N–C distance at 1.305(6) Å and the N–C–C angle at 126.7(4)° are usual for an N=C(sp²) system.

Scheme 4

The short W–N bond length of 1.863(3) Å suggests multiple bond character that the alkylideneamido ligand acts as a 2σ2π-electron donor. Existence of the hydrido ligand was confirmed by the ¹H NMR spectrum, which showed a broad quintet signal at δ -3.42. Prolonged heating of the above reaction mixture gradually produced another new complex, which became the sole product after 20 h and was identified as the imido complex [W(NCH₂Tol)(κ⁴-P₄)] (**11_{Tol}**). The conversion from **10_{Tol}** to **11_{Tol}** was unambiguously

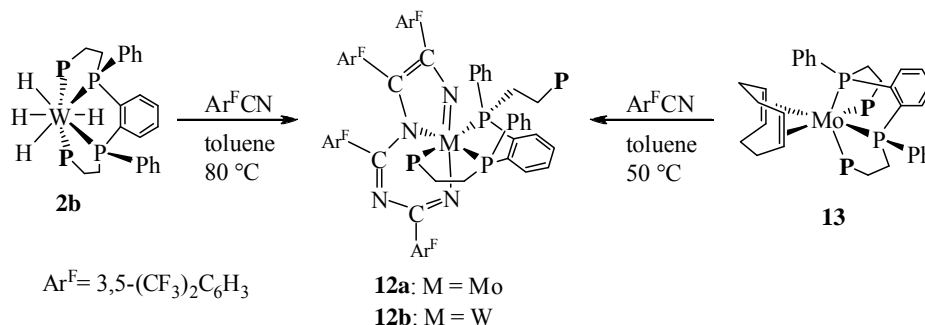


confirmed by heating isolated sample of **10**_{Tol}. The metal center in **11**_{Tol} has a distorted square pyramidal geometry with the imido ligand at the apical position. The W–N bond length at 1.794(2) Å is considerably shorter than that of **10**_{Tol} and typical of triple bond, that allows 18 electron counts around the W center.

Reactions of **2b** with a variety of aromatic nitriles formed **10** similarly, while the isomerization from **10** to **11** proceeded fast with electron-rich Ar groups. Complexes **10** with considerably electron-deficient *p*-CF₃C₆H₄ group as Ar did not convert to **11** at all. In contrast, **10** were never detected in the reactions of **2b** with aliphatic nitriles AkCN (Ak = *n*-C₇H₁₅, *c*-Hex, *t*-Bu, PhCH₂, *p*-ClC₆H₄CH₂), and **11** were directly obtained.

Remarkably, highly electron-deficient nitriles Ar^FCN (Ar^F = 3,5-(CF₃)₂C₆H₃) reacted with **2b** in a quite different way. Stirring **2b** and 3–9 equiv of this nitrile in toluene at 80 °C for 20 h gave [W{NC(Ar^F)C(Ar^F)NC(Ar^F)NC(Ar^F)N}(κ³-**P4**)] (**12b**) as the major product, but neither **10** nor **11** were observed at all (Scheme 5). The complex **12b** was isolated as black prismatic crystals in 41% yield, and the X-ray crystallography has revealed that four nitrile molecules are linked linearly and that the resulting chain binds to the W center with three N atoms in a meridional fashion, forming the fused five- and six-membered chelate rings. By tridentate coordination of **P4**, the W center forms a distorted octahedral structure. The ³¹P{¹H} NMR spectrum showed four signals at δ –10.3 (non-coordinated), 40.2, 46.8, and 73.8. Although **12b** is considered to be produced via reductive bond forming reaction on a formally W(0) center, it could not be obtained from the reaction of **1b** with Ar^FCN. Instead, the Mo analogue **12a** was successfully obtained by the reaction of [Mo(cod)(κ⁴-**P4**)] (**13**: cod = η⁴-1,5-cyclooctadiene) with Ar^FCN at 50 °C.

Scheme 5



Conclusion

The tetrahydride complex of W containing the linear tetraphosphine ligand **P4** has been synthesized, and its reactions with organic molecules have been investigated. Highly strained geometry around the W center and ability of **P4** to readily change hapticity probably increase the activity of [WH₄(κ⁴-**P4**)] so much higher than the related complex with diphosphine ligands [WH₄(dppe)₂]. It has been proved that [WH₄(κ⁴-**P4**)] is not only a strong hydride donor but also a good precursor of coordinatively unsaturated active species that facilitate specific bond formation and cleavage. Reactions involving zero-valent intermediates proceed more smoothly and cleanly with [WH₄(κ⁴-**P4**)] than [W(dppe)(κ⁴-**P4**)], which may have a difficulty in dissociating dppe ligand. Transformation of organic molecules in this study are based on strong reducing power of W–H or W(0) species and quite unique in comparison with other transition metal complexes. Usability of recently prepared [Mo(cod)(κ⁴-**P4**)] in related reactions has been also demonstrated, and albeit lower electron-donating ability than W, it may be a key precursor for extending above stoichiometric reactions to catalysis.