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Research paper

Synthesis and reactivity of [M(η^3-allyl)(η^2-amidinato)(CO)$_2$(phosphonium ylide)] (M = Mo, W): Investigation of the ligand properties of phosphonium ylides

Daichi Takaki, Kenichi Ogata, Youji Kurihara, Kazuyoshi Ueda, Toru Hashimoto, Yoshitaka Yamaguchi *

Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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ABSTRACT

Phosphonium ylide complexes of Mo and W formulated as [M(η^3-allyl){η^2-(NPh)$_2$CH}(CO)$_2$(CH$_2$PR$_3$)] (M = Mo, R = Me: **2a-Mo**; M = Mo, R = Ph: **2b-Mo**, and M = W, R = Me: **2a-W**) were prepared by the reaction of amidinato(pyridine) complex, [M(η^3-allyl){η^2-(NPh)$_2$CH}(CO)$_2$(NC$_5$H$_5$)] (M = Mo: **1-Mo** and M = W: **1-W**), with a phosphonium ylide, CH$_2$PR$_3$ (R = Me, Ph), which was generated in situ by the reaction of the corresponding phosphonium salt with ^{n}BuLi. These complexes were characterized spectroscopically, as well as by the X-ray diffraction. The phosphonium ylide ligand shows stronger electron donating ability toward the metal than *N*-heterocyclic carbene or phosphine ligands. This trend is supported by the comparison of the spectroscopic data and the DFT calculations. We also investigated the reactivity of the phosphonium ylide complexes **2-Mo** with two-electron donors such as PEt$_3$ and NHC. In the case of the PPh$_3$ ylide complex (**2b-Mo**), the substitution reaction of the ylide ligand for the two-electron donors took place cleanly to yield the corresponding complexes. On the other hand, in the PMe$_3$ ylide complex (**2a-Mo**), the substituted complexes formed but the unreacted ylide complex **2a-Mo** was also present in the reaction mixture. These results show that the bond strength of the M-C(phosphonium ylide) bond is affected by the substituents on the phosphorus atom.

1. Introduction

Electron rich metal centers in metal complexes play an important role in the control of metal-mediated processes, namely, catalysis. Therefore, the development of transition metal complexes bearing strongly electron-donating ligands has attracted much attention from academia, as well as industry. *N*-Heterocyclic carbenes (NHCs) are now fully established as an important class of ligands for organometallic chemistry because they are known to enhance the electron density at the metal center with a thermally robust metal-ligand bond [1]. NHCs are categorized as unsaturated sp^2-hybridized carbon coordinated ligands. In comparison with an NHC ligand, saturated sp^3-hybridized carbon ligands, i.e., a phosphonium ylide, which can be considered as a phosphine-stabilized carbene ligand, have been recognized as strong electron donors toward the metal because their metal complexes have a canonical zwitterionic structure. Thus, negative and positive charges are accumulated at the metal center and the phosphorus atom, respectively [2,3]. Therefore, phosphonium ylides have drawn great interest in the field of homogeneous catalysts. Recently, phosphonium ylide-based hybrid-type ligands, i.e., bidentate ylide-phosphine and -NHC ligands have been reported, and these complexes act as effective catalysts for C-C and C-N forming reactions [4] and hydrosilylation and hydrogenation reactions [5]. Furthermore, Chauvin and co-workers have reported systematic investigations on the coordinating properties of phosphonium ylide and NHC ligands on the late transition metal complexes through C-C chelating ligands containing two moieties [6]. They have concluded that phosphonium ylides act as stronger electron-donating ligands than NHCs. The electronic properties of these chelating ligands are supported by the DFT calculations [7].

We are interested in the synthesis, structure, and reactivity of group 6 transition metal complexes, especially molybdenum and tungsten. Furthermore, we have already reported the preparation and explored some of the reactivity of amidinato(pyridine) complexes formulated as [M(η^3-allyl)(η^2-amidinato)(CO)$_2$(pyridine)] (M = Mo; **1-Mo**, W; **1-W**) [8]. Complex **1** has a labile pyridine ligand, and, thus, the substitution reaction with two-electron donors such as PR$_3$ or NHC takes place smoothly to afford the corresponding complexes [8a,9]. The complexes in this series of amidinato complexes have two CO ligands and, thus, the

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* Corresponding author.
E-mail address: yamaguchi-yoshitaka-hw@ynu.ac.jp (Y. Yamaguchi).

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comparison of the CO stretching frequencies of the complexes formed is an effective probe for the electron donating ability of the coordinating ligands. We are interested in not only the electron donating ability of phosphonium ylide but also the bond strength of the M-C(phosphonium ylide) bond. In this paper, we report the preparation of phosphonium ylide complexes of Mo and W and the electronic properties of phosphonium ylides comparing to NHC and PR_3. Furthermore, we have estimated the influence of the substituents of the phosphorus moiety on the bond strength of the M-C(phosphonium ylide) bond by reaction with two-electron donors such as NHC and PR_3.

2. Experimental

2.1. General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under an atmosphere of dry nitrogen, which had been purified by SICAPENT (Merck Co., Inc.), using standard Schlenk tube or high vacuum techniques. All solvents were distilled over appropriate drying agents before use. $[PMe_4]Br$ (Tokyo Chemical Industry), $[PMePh_3]Br$ (Sigma-Aldrich), and $[PMe_4]I$ (Alfa Aesar) were purchased and used without further purification. Other reagents employed in this investigation were commercially available and used without further purification. $[M(\eta^3\text{-allyl})\{\eta^2\text{-}(NC_6H_5)_2CH\}(CO)_2(NC_5H_5)]$ (M = Mo: **1-Mo**; M = W: **1-W**) [8a] and $I^iPr{\cdot}BEt_3$ (I^iPr = 1,3-diisopropyllimidazol-2-ylidene) [10] were prepared according to literature methods.

The IR spectra were recorded on a HORIBA FT-730 spectrometer. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL EX-270 and BRUKER DRX-300 spectrometers at ambient temperature. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were recorded in ppm relative to Me_4Si as an internal standard. The $^{31}P\{^1H\}$ NMR chemical shifts were recorded in ppm relative to H_3PO_4 as an external standard. All coupling constants were recorded in hertz. The multiplicity is indicated by s (singlet), d (doublet), tt (triplet of triplets), and m (multiplet). Cyclic voltammograms were recorded on a Huso Electrochemical System, which is a combination of a potential coulometry timer (317S), potential scanning unit (321), and digital universal signal processing unit (326), in CH_3CN containing 0.1 M of $^nBu_4NBF_4$ as a supporting electrolyte and using a conventional three-electrode system. In this system, platinum was used as the working electrode, a platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The scan rate was 100 mV/s. Potentials are given vs. Fc/Fc^+. Elemental analyses were performed on a Perkin-Elmer 240C.

2.2. Preparation of phosphonium ylide complexes (**2**)

2.2.1. Preparation of $[Mo(\eta^3\text{-allyl})\{\eta^2\text{-}(NC_6H_5)_2CH\}(CO)_2(CH_2PMe_3)]$ (**2a-Mo**)

A solution of complex **1-Mo** (383 mg, 0.82 mmol) in tetrahydrofuran (THF) (5 mL) was cooled to –78 °C and then a THF solution of the CH_2PMe_3 phosphonium ylide, which was prepared by the reaction of $[PMe_4]Br$ (139 mg, 0.81 mmol) with ^nBuLi (0.51 mL of its 1.6 M hexane solution, 0.82 mmol) at –78 °C, was added. Subsequently, the reaction mixture was allowed to warm to room temperature. After 2 h, the volatiles were removed under reduced pressure. The residual solid was extracted with CH_2Cl_2 (20 mL × 1 and 10 mL × 2) and the filtrate was evaporated. The solid was washed with MeOH (5 mL × 3), and then dried in vacuo to give **2a-Mo** as a yellow powder (229 mg, 0.48 mmol, 59%). Anal. Calcd for $C_{22}H_{27}MoN_2O_2P$: C, 55.24; H, 5.69; N, 5.86. Found: C, 55.51; H, 5.48, N, 5.80%. IR (KBr): ν(CO) 1912, 1798 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.19 (d, J = 13.2 Hz, 2H, CH_2PMe_3), 1.36 (d, J = 9.9 Hz, 2H, allyl-CH*H*), 1.84 (d, J = 13.2 Hz, 9H, PMe_3), 3.47 (d, J = 6.6 Hz, 2H, allyl-CH*H*), 3.87 (tt, J = 9.9, 6.6 Hz, 1H, allyl-C*H*), 6.84–7.31 (m, 10H, Ph), 8.81 (s, 1H, amidinato-C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.2 (d, J = 55.5 Hz, PMe_3), 17.9 (d, J = 36.0 Hz, CH_2PMe_3), 57.6 (s, allyl-CH_2), 81.9 (s, allyl-*C*H), 117.5 (s, Ph), 120.8 (s, Ph), 129.1 (s, Ph), 146.6 (s, Ph), 151.8 (s, NCN), 233.3 (d, J = 3.7 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.4 (s).

2.2.2. Preparation of $[Mo(\eta^3\text{-allyl})\{\eta^2\text{-}(NC_6H_5)_2CH\}(CO)_2(CH_2PPh_3)]$ (**2b-Mo**)

Complex **2b-Mo** was prepared from **1-Mo** (57 mg, 0.12 mmol) and a THF solution of CH_2PPh_3, which was prepared by the reaction of $[PMePh_3]Br$ (49 mg, 0.14 mmol) with ^nBuLi (0.10 mL of its 1.5 M hexane solution, 0.15 mmol) at –78 °C, in the same manner as that for **2a-Mo**. **2b-Mo** was isolated as a yellow powder (48 mg, 0.072 mmol, 60%). Anal. Calcd for $C_{37}H_{33}MoN_2O_2P$: C, 66.87; H, 5.00; N, 4.22. Found: C, 66.34; H, 4.78; N, 4.27%. IR (KBr): ν (CO) 1909, 1820 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.06 (d, J = 13.8 Hz, 2H, CH_2PPh_3), 1.12 (d, J = 9.9 Hz, 2H, allyl-CH*H*), 3.49 (d, J = 6.6 Hz, 2H, allyl-CH*H*), 3.85 (tt, J = 9.9, 6.6 Hz, 1H, allyl-C*H*), 6.88–7.79 (m, 25H, Ph), 8.98 (s, 1H, amidinato-C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.1 (d, J = 30.5 Hz, CH_2PPh_3), 58.0 (s, allyl-CH_2), 81.1 (s, allyl-*C*H), 117.9 (s, Ph), 120.9 (s, Ph), 128.9 (s, Ph), 129.1 (s, Ph), 129.2 (d, J = 16.8 Hz, Ph), 132.4 (d, J = 3.1 Hz, Ph), 133.3 (d, J = 9.1 Hz, Ph), 146.9 (s, Ph), 152.5 (s, NCN), 230.7 (d, J = 3.1 Hz, CO). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 36.4 (s).

2.2.3. Preparation of $[W(\eta^3\text{-allyl})\{\eta^2\text{-}(NC_6H_5)_2CH\}(CO)_2(CH_2PMe_3)]$ (**2a-W**)

Complex **2a-W** was prepared from **1-W** (83 mg, 0.15 mmol) and a THF solution of CH_2PMe_3, which was prepared by the reaction of $[PMe_4]I$ (35 mg, 0.16 mmol) with ^nBuLi (0.12 mL of its 1.5 M hexane solution, 0.18 mmol) at −78 °C, in the same manner as that for **2a-Mo**. **2a-W** was isolated as a yellow powder (45 mg, 0.079 mmol, 53%). Anal. Calcd for $C_{22}H_{27}N_2O_2PW$: C, 46.66; H, 4.81; N, 4.95. Found: C, 46.41; H, 4.81, N, 4.78%. IR (KBr): ν (CO) 1904, 1789 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.16 (d, J = 14.5 Hz, 2H, CH_2PMe_3), 1.54 (d, J = 9.2 Hz, 2H, allyl-CH*H*), 1.87 (d, J = 12.5 Hz, 9H, PMe_3), 2.99 (tt, J = 9.9, 6.6 Hz, 1H, allyl-C*H*), 3.39 (d, J = 6.6 Hz, 2H, allyl-CH*H*), 6.87–7.33 (m, 10H, Ph), 9.47 (s, 1H, amidinato-C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.2 (d, J = 54.8 Hz, PMe_3), 23.5 (d, J = 36.9 Hz, CH_2-PMe_3), 50.3 (s, allyl-CH_2), 76.1 (s, allyl-*C*H), 117.5 (s, Ph), 121.2 (s, Ph), 129.0 (s, Ph), 145.2 (s, Ph), 151.7 (s, NCN), 226.6 (d, J = 3.4 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.4 (s).

2.3. The reaction of phosphonium ylide complex **2** with two-electron donors

2.3.1. The reaction of **2b-Mo** with $I^iPr{\cdot}BEt_3$: Isolation of complex **3**

Complex **2b-Mo** (80 mg, 0.12 mmol), $I^iPr{\cdot}BEt_3$ (31 mg, 0.12 mmol), and toluene (10 mL) were placed in a Schlenk tube. After being refluxed for 1 h, complex **3** was isolated in the same manner as reported previously (45 mg, 0.083 mmol, 69%). The product was characterized by comparison with the reported ^1H NMR data [9].

2.3.2. The reaction of **2b-Mo** with PEt_3: Isolation of complex **4**

PEt_3 (20 µL, 16 mg, 0.14 mmol) was added to a solution of complex **2b-Mo** (80 mg, 0.12 mmol) in toluene (5 mL) at room temperature. After being refluxed for 1 h, complex **4** was isolated in the same manner as reported previously (54 mg, 0.11 mmol, 92%). The product was characterized by comparison with the reported ^1H NMR data [11].

2.3.3. The reaction of **2a-Mo** with $I^iPr{\cdot}BEt_3$: Formation of complex **3**

Complex **2a-Mo** (103 mg, 0.22 mmol), $I^iPr{\cdot}BEt_3$ (55 mg, 0.22 mmol), and toluene (10 mL) were placed in a Schlenk tube. After being refluxed for 1 h, the volatiles were removed under reduced pressure. The residual solid was washed with MeOH and then dried in vacuo to give complexes **3** and **2a-Mo** as a mixture (total yield, 93 mg). The yields of each complex were determined by the proton integrations based on the ^{1}H NMR spectrum (**3**; 34 mg, 0.063 mmol, 29% and **2a-Mo**; 59 mg, 0.12 mmol, 55%).

2.3.4. The reaction of *2a-Mo* with PEt_3: Formation of complex *4*

PEt_3 (48 μL, 38 mg, 0.32 mmol) was added to a solution of complex **2a-Mo** (150 mg, 0.31 mmol) in toluene (10 mL) at room temperature. After being refluxed for 1 h, the volatiles were removed under reduced pressure. The residual solid was then subjected to ^{1}H NMR measurements. The ratio of **4**:**2a-Mo** was estimated to be ca. 1:4. After washing the residual solid with MeOH, complex **2a-Mo** was recovered as a yellow solid (83 mg, 0.17 mmol, 55%).

2.4. DFT calculations

Density functional theory (DFT) [12] calculations were performed with the Becke's hybrid three-parameter exchange functional [13] with the Lee-Yang-Parr nonlocal correlation functional [14] (B3LYP) as implemented in the Gaussian 03 program package [15]. A double-zeta valence plus polarization (DGDZVP) basis set [16] was used for all atoms. All geometries were optimized without constraints, and vibrational frequencies were computed. The molybdenum atomic charges were estimated using the Mulliken charges [17], natural population analysis (NPA) [18], and atomic polar tensor (APT) [19].

2.5. Experimental procedure for X-ray crystallography

Suitable single crystals (**2a-Mo** and **2b-Mo**) were obtained by recrystallization from CH_2Cl_2/ether and were individually mounted on glass fibers. Diffraction measurements of **2a-Mo** and **2b-Mo** were carried out on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å). The data collections were carried out at −50 ± 1 °C using the ω-2θ scan technique to a maximum 2θ value of 55.0° for **2a-Mo** and 60.0° for **2b-Mo**. Cell constants and an orientation matrix for data collection were determined from 25 reflections with 2θ angles in the range 29.54–29.99° for **2a-Mo** and 27.94–29.86° for **2b-Mo**. Three standard reflections were monitored every 150 measurements. In the data reduction, Lorentz and polarization corrections and an empirical absorption correction (ψscan) were made.

Crystallographic data and the results of measurements are summarized in Table 1. The structures were solved by direct methods (SHELXT) [20] for **2a-Mo** and **2b-Mo** and expanded using Fourier techniques. Least-square refinements were carried out using SHELXL [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at the ideal position and were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package [22].

3. Results and discussion

3.1. Synthesis and characterization of phosphonium ylide complexes of Mo and W

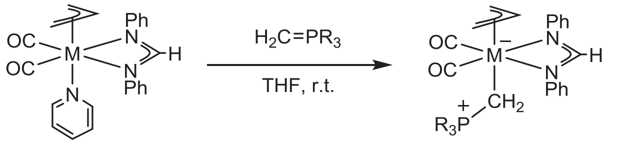
We have already reported that the pyridine ligand in the amidinato(pyridine) complex **1** is easily substituted by two-electron donors such as PR_3 and NHC to afford the corresponding complexes [8a,9]. Therefore, we examined the reaction of the complex **1** with phosphonium ylides.

Table 1
Summary of crystal data for complexes **2a-Mo** and **2b-Mo**.

	2a-Mo	**2b-Mo**
Empirical formula	$C_{22}H_{27}MoN_2O_2P$	$C_{37}H_{33}MoN_2O_2P$
Formula weight	478.38	664.59
Crystal color, habit	yellow, prismatic	yellow, needle
Crystal size/mm	0.38 × 0.25 × 0.25	0.25 × 0.13 × 0.13
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Lattice parameters		
a (Å)	16.490(10)	11.003(6)
b (Å)	9.309(7)	14.397(10)
c (Å)	16.457(10)	20.342(4)
β (°)	119.85(4)	102.12(3)
V (Å^3)	2191(3)	3151(3)
Z	4	4
D_c (g cm^{-3})	1.450	1.401
F_{000}	984.00	1368.00
μ(Mo-Kα) (cm^{-1})	6.898	5.021
Reflections measured	5211	7606
Independent reflections	5030	7239
R_{int}	0.0409	0.0453
No. variables	256	388
Reflection/parameter ratio	19.65	18.66
Residuals: R; wR2	0.0577; 0.0891	0.1073; 0.1752
Residuals: R1 [$I > 2.00\sigma(I)$]	0.0333	0.0579
Goodness-of-fit (GOF) on F^2	1.028	1.004
$\delta\rho_{max,min}$ (e$^-$ Å^{-3})	0.70, −0.54	1.87, −1.21

On treatment of molybdenum complex **1-Mo** with CH_2PMe_3, which was prepared in situ by the reaction of [PMe_4]Br with ^{n}BuLi in THF, the PMe_3 ylide complex **2a-Mo** was isolated as a yellow powder in 59% yield. The PPh_3 ylide complex of Mo (**2b-Mo**) and the tungsten analog of **2a-Mo** (**2a-W**) were also obtained in moderate yield (Scheme 1).

In the IR spectra, the molybdenum complexes showed two CO stretching bands at 1912 and 1798 cm^{-1} for **2a-Mo** and 1909 and 1820 cm^{-1} for **2b-Mo**. These results imply that the PMe_3 ylide is a better electron donor than the PPh_3 ylide. Tungsten complex **2a-W** also showed two CO stretching bands (1904 and 1789 cm^{-1}), which are at lower frequencies than those for **2a-Mo**. These observations indicate that two carbonyl ligands are in mutually *cis* positions [23]. In the ^{31}P{^{1}H} NMR spectra of complexes **2**, only one singlet was observed, and these were all found in a similar region (30.4 ppm for **2a-Mo**, 36.4 ppm for **2b-Mo**, and 30.4 ppm for **2a-W**). The ^{1}H NMR spectrum of **2a-Mo** showed symmetrical allylic signals at 1.36 (*anti*-CH_2), 3.47 (*syn*-CH_2), and 3.87 (central proton) ppm. The doublet signal assignable to the CH_2 moiety of the ylide ligand was observed at 0.19 ppm with a coupling constant of 13.2 Hz. The doublet signal assignable to the proton atoms of PMe_3 was observed at 1.84 ppm with a coupling constant of 13.2 Hz. The ^{13}C {^{1}H} NMR spectrum of **2a-Mo** also indicates that complex **2a-Mo** has a symmetrical geometry around the Mo center; that is, allylic carbon signals appeared at 57.6 ppm (terminal carbons) and 81.9 ppm (central carbon), and a doublet signal arising from two CO carbon atoms was seen at 233.3 ppm with a coupling constant of 3.7 Hz. The CH_2 carbon atom in the ylide ligand was observed at 17.9



1-Mo (M = Mo)
1-W (M = W)

2a-Mo (M = Mo, R = Me) (59%)
2b-Mo (M = Mo, R = Ph) (60%)
2a-W (M = W, R = Me) (53%)

Scheme 1. Preparation of phosphonium ylide complexes of Mo and W.

ppm as a doublet signal (J_{PC} = 36.0 Hz). These NMR data suggested that the phosphonium ylide ligand of complex **2a-Mo** was *trans* to the allyl ligand in solution. Complexes **2b-Mo** and **2a-W** showed similar spectroscopic features in their NMR spectra to those of complex **2a-Mo**.

The structure of complexes **2a-Mo** and **2b-Mo** were determined by X-ray analysis. The ORTEP drawings **2a-Mo** and **2b-Mo** are shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. These complexes show pseudo-octahedral geometry around the Mo center. The amidinato ligand is located at an equatorial position and is coplanar with two CO ligands. The phosphonium ylide ligand is at an axial position *trans* to the η^3-allyl ligand. The open face of the allyl ligand is directed toward two CO ligands, which is known to be a favorable orientation for a series of $[M(\eta^3\text{-allyl})(CO)_2]$ (M = Mo, W) complexes [24]. The geometry of these complexes revealed by X-ray analysis coincides with the solution-state geometry indicated by the ^1H and $^{13}C\{^1H\}$ NMR spectra.

The Mo1–C16 bond length for **2a-Mo** (2.277(3) Å) is slightly shorter than that for **2b-Mo** (2.305(5) Å). The P1–C16 bond length for **2a-Mo** (1.746(3) Å) is also slightly shorter than that for **2b-Mo** (1.765(5) Å). The Mo1–C16–P1 angle for **2a-Mo** (121.09(14)°) is smaller than that for **2b-Mo** (124.8(2)°). Although the electronic influence of the phosphine cannot be ruled out, these structural features might arise from the steric hindrance of the phosphine of the ylide ligand, i.e., the cone angles of these phosphines are 118° for PMe_3 and 145° for PPh_3 [25]. Additionally, in complex **2a-Mo**, the P1–C16 bond length (1.746(3) Å) is slightly shorter than those of the P1–C(Me) bond lengths (1.783(4)–1.796(4) Å), whereas the P1–C16 bond is longer than the reported P = C double bond lengths (1.640(6) Å for $Me_3P=CH_2$ [26] and 1.661(8) Å for $Ph_3P=CH_2$ [27]). A similar trend was observed in the P-C bond lengths in **2b-Mo**. The orientation of the ylide ligand is somewhat interesting. The torsion angles of C15–Mo1–C16–P1 are very small: −0.3(2) ° for **2a-Mo** and 12.3(3)° for **2b-Mo**. The Mo1–C16–P1 planes in both complexes do not bisect the C14–Mo1–C15 angle in the solid state.

Table 2
Selected bond lengths (Å) and angles (°) for **2a-Mo** and **2b-Mo**.

2a-Mo		**2b-Mo**	
Bond lengths			
Mo1-N1	2.274(3)	Mo1-N1	2.301(4)
Mo1-N2	2.253(3)	Mo1-N2	2.248(4)
N1-C1	1.322(3)	N1-C1	1.332(6)
N2-C1	1.315(5)	N2-C1	1.305(6)
Mo1-C14	1.960(4)	Mo1-C14	1.952(4)
O1-C14	1.156(5)	O1-C14	1.162(6)
Mo1-C15	1.941(3)	Mo1-C15	1.946(5)
O2-C15	1.167(3)	O2-C15	1.164(6)
Mo1-C16	2.277(3)	Mo1-C16	2.305(5)
P1-C16	1.746(3)	P1-C16	1.765(5)
P1-C17	1.783(4)	P1-C17	1.799(5)
P1-C18	1.795(5)	P1-C23	1.821(5)
P1-C19	1.796(4)	P1-C29	1.786(5)
Bond angles			
N1-Mo1-N2	58.16(11)	N1-Mo1-N2	57.93(14)
C14-Mo1-C15	78.33(14)	C14-Mo1-C15	79.76(19)
N1-Mo1-C14	164.10(9)	N1-Mo1-C14	165.98(17)
N1-Mo1-C15	113.74(14)	N1-Mo1-C15	111.22(16)
N2-Mo1-C14	108.56(12)	N2-Mo1-C14	109.91(17)
N2-Mo1-C15	169.89(14)	N2-Mo1-C15	166.93(17)
N1-Mo1-C16	80.96(12)	N1-Mo1-C16	81.71(15)
N2-Mo1-C16	78.47(10)	N2-Mo1-C16	77.68(17)
C14-Mo1-C16	87.97(14)	C14-Mo1-C16	88.99(18)
C15-Mo1-C16	94.68(12)	C15-Mo1-C16	94.12(19)
Mo1-C14-O1	177.4(3)	Mo1-C14-O1	178.1(4)
Mo1-C15-O2	176.4(3)	Mo1-C15-O2	178.2(4)
Mo1-N1-C1	93.8(2)	Mo1-N1-C1	92.7(3)
Mo1-N1-C2	142.50(16)	Mo1-N1-C2	144.8(3)
C1-N1-C2	123.7(3)	C1-N1-C2	122.5(4)
Mo1-N2-C1	94.96(16)	Mo1-N2-C1	95.9(3)
Mo1-N2-C8	140.6(2)	Mo1-N2-C8	141.2(3)
C1-N2-C8	124.3(3)	C1-N2-C8	122.8(4)
N1-C1-N2	113.1(3)	N1-C1-N2	113.3(4)
Mo1-C16-P1	121.09(14)	Mo1-C16-P1	124.8(2)

3.2. Electronic property of the phosphonium ylides as ligands: Estimation by experimental and theoretical studies

To estimate the electron donating ability of the phosphonium ylide as a ligand, we examined a comparison of CO stretching frequencies of a series of $[Mo(\eta^3\text{-allyl})\{\eta^2\text{-}(NC_6H_5)_2CH\}(CO)_2(L)]$ (L = CH_2PMe_3 (**2a-Mo**), CH_2PPh_3 (**2b-Mo**), I^iPr (I^iPr = 1,3-diisopropylimidazol-2-ylidene) (**3**), and PEt_3 (**4**)) and the oxidation potentials of these complexes by cyclic voltammetry (CV). DFT calculations were also carried out. These results are summarized in Table 3.

In the IR spectra, the mean value of two CO stretching frequencies increased in the order **2a-Mo** < **2b-Mo** < **3** < **4**. Of these complexes, phosphonium ylide complexes (**2a-Mo** and **2b-Mo**) showed lower CO stretching frequencies than those of others (**3** and **4**). This result reflects the fact that the negative charge is accumulated at the Mo center in the phosphonium ylide complexes. Furthermore, we found that, in the phosphonium ylide complexes, the substituents on the phosphorus atom have an influence on the electron donating ability toward the metal center, i.e., the PMe_3 ylide is a better electron donor than the PPh_3 ylide. To obtain further information concerning electronic influence on the Mo center, we made CV measurements of complexes **2a-Mo**, **3** and **4** in a CH_3CN solution. All complexes exhibited irreversible oxidation waves. The CV of ylide complex **2a-Mo** shows the one-oxidation wave at −0.05 V *vs.* Fc/Fc^+. This oxidation potential is lower than those of complexes **3** (0.09 V) and **4** (0.19 V). The second oxidation wave for **2a-Mo** was observed at 0.31 V, which is also lower potential than those of **3** (0.58 V) and **4** (0.69 V). Based on the oxidation potentials in those complexes, it is conceivable that the electron density accumulated at the Mo center increases in the order **4** < **3** < **2a-Mo**. We assumed that the highest occupied molecular orbital (HOMO) levels of these complexes also increase in this order. Next, we discuss the DFT calculations of the series of Mo complexes.

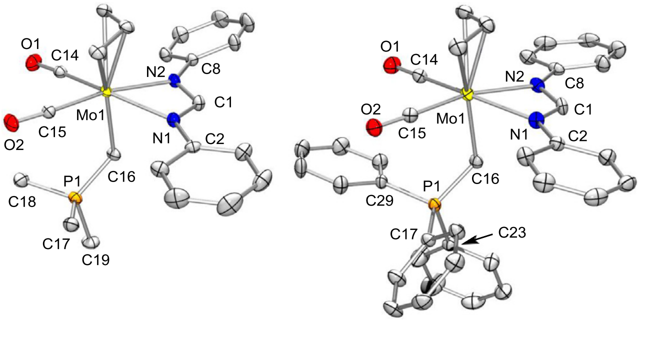


Fig. 1. ORTEP drawings of complexes **2a-Mo** (left) and **2b-Mo** (right) with thermal ellipsoids drawn at 30% probability level. All hydrogen atoms are omitted for clarity.

Geometry optimizations of Mo complexes **2a-Mo**, **2b-Mo**, **3**, and **4** were successful. The optimized molecular structures are shown in Fig. S1 (Supplementary Material). Selected geometrical parameters of these complexes are summarized in Table S1 (Supplementary Material). Geometric parameters of **2a-Mo**, **2b-Mo**, **3**, and **4** determined by DFT are in good agreement with those obtained from the X-ray analysis, although the calculations predicted slightly longer bond lengths. The calculated CO stretching frequencies for the Mo complexes are summarized in Table 3. These Mo complexes showed two CO stretching bands and these values

Table 3
Spectroscopic data of [Mo(η^3-allyl)(η^2-amidinato)(CO)$_2$L].

	2a-Mo	**2b-Mo**	**3**	**4**
	(L = CH_2PMe_3)	(L = CH_2PPh_3)	(L = I^{i}Pr)	(L = PEt_3)
CO stretching band (cm^{-1})				
ν_{CO} (found, KBr)	1912, 1798	1909, 1820	1913, 1829[f]	1921, 1836[g]
ν_{CO} (av. found)[a]	1855	1864.5	1871	1878.5
ν_{CO} (calcd)[b]	1977, 1892	1987, 1912	1999, 1922	2000, 1933
ν_{CO} (av. calcd)[a]	1934.5	1949.5	1960.5	1966.5
Cyclic voltammetry (V)[c]				
E_{p1}	−0.05	–	0.09	0.19
E_{p2}	0.31	–	0.58	0.69
HOMO (eV)[b]	−5.04	−4.95	−5.22	−5.32
Atomic charges (on Mo)[b]				
Mulliken	0.81	0.97	1.05	0.76
APT[d]	−0.41	−0.34	−0.47	−0.63
NPA[e]	−0.71	−0.69	−0.78	−0.92

[a] The mean value of two CO stretching frequencies.
[b] DFT calculations (Gaussian 03, B3LYP/DGDZVP level).
[c] Versus Fc/Fc$^+$.
[d] APT: Atomic polar tensor.
[e] NPA: Natural population analysis.
[f] Ref [9].
[g] Ref [11].

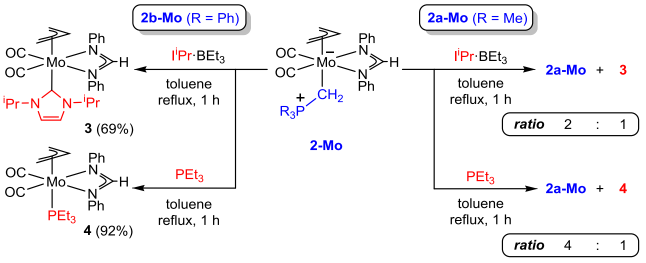
gradually increased in the order **2a-Mo** < **2b-Mo** < **3** < **4**. This trend agrees with the experimental data. The HOMO of **2a-Mo** (-5.04 eV) is slightly lower in energy than that of **2b-Mo** (−4.95 eV), whereas these energy levels are obviously higher than those of **3** (−5.22 eV) and **4** (−5.32 eV) (Table 3). For the Mo complexes, there is a good relationship between the HOMO energy and the oxidation potential. The results obtained by DFT calculations indicate that the PR_3 ylides are more electron donating than I^{i}Pr and PEt_3.

We considered that the atomic charges at the Mo center are one of the most useful properties to estimate the electron donating ability of the ligand. The properties were estimated by three different methods: Mulliken charge analysis, APT, and NPA. These results are listed in Table 3. Regarding **2a-Mo** and **2b-Mo**, the molybdenum atomic charges obtained by three methods were reasonable. On the other hand, in the cases of APT and NPA, the atomic charge at the Mo center increases in the order **2** < **3** < **4**. This result is the reverse trend to that predicted by the experimental results such as IR spectra and CV measurements. In particular, phosphine was more electron donating than the phosphonium ylide and NHC ligands. These reverse trends might originate from the different elements bonded to the metal (phosphorus or carbon) or the hybridization of the coordinating atom (sp^3 or sp^2 carbon atoms). Furthermore, in the case of complex **3**, the Mulliken charge showed the opposite trend to those of the APT and NPA charges. It is known that the Mulliken charge is very dependent on the method or basis sets [28]. Thus, further investigations of the atomic charges at the metal center as estimated by DFT calculations are needed.

3.3. The reaction of complex **2-Mo** with two-electron donors

As mentioned in Section 3.2, we have demonstrated that the phosphonium ylides act as one of the most electron-donating ligands toward transition metals. Next, we were interested in the reactivity of the phosphonium ylide complex **2-Mo** toward two-electron donors such as NHC (I^{i}Pr) and phosphine (PEt_3) to obtain the information about the robustness of the M-C(phosphorus ylide) bond. Thus, the reactions of complex **2-Mo** with I^{i}Pr or PEt_3 were investigated (Scheme 2).

On treatment of PPh_3 ylide complex **2b-Mo** with the BEt_3 adduct of I^{i}Pr (I^{i}Pr·BEt_3), which acts as an NHC transfer reagent to the metal [9,10],under toluene-refluxing conditions for 1 h, a substitution reaction took place cleanly, giving NHC complex **3** in 69% yield. In the reaction with PEt_3 under the same conditions, phosphine complex **4** was isolated in 92% yield. Next, the reactions of PMe_3 ylide complex **2a-Mo** with I^{i}Pr·BEt_3 or PEt_3 under the same conditions were examined. In the case of I^{i}Pr·BEt_3, NHC complex **3** was formed, whereas complex **2a-Mo** remained. These complexes were isolated as a mixture. The yields of each complex were determined by the proton integrations based on the ^{1}H NMR spectra (**2a-Mo**; 58%, **3**; 29%). With PEt_3, the ^{1}H NMR spectrum of the reaction mixture showed the formation of complex **4**, accompanied by **2a-Mo**. The ratio of **2a-Mo**:**4** was estimated to be ca. 4:1. From the reaction mixture, unreacted **2a-Mo** was recovered in 55% yield. These results show that the PMe_3 ylide acts as a stronger coordinating ligand to the Mo center than the PPh_3 ylide and that the M-C(phosphonium ylide) bond strength is affected by the substituents on the phosphorus atom.



Scheme 2. Reaction of complex **2-Mo** with two-electron donors.

4. Concluding remarks

This paper describes the synthesis of phosphonium ylide complexes of Mo and W and a comparison of their ligand-metal properties to those of NHC or phosphine by experimental and theoretical investigations. The phosphonium ylides are stronger electron-donating ligands than NHCs or phosphines, and the electronic features are tunable by varying the substituent on the phosphorus moiety. Furthermore, from the reactivity of complexes **2-Mo** with NHC or phosphine, the robustness of the M-C(phosphonium ylide) bond is significantly affected by the phosphorus substituents. These findings offer fundamental concepts for making an electron-rich metal center with thermally robust metal-ligand bonds and for developing an active homogeneous catalyst system for organic transformations [29].

Author contributions

D. T. and K. O. contributed equally to this work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2017.11.019.

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[29] PPh$_3$ ylide in complex **2b-Mo** acts as a stronger electron-donating ligand than NHC and PR$_3$. However the substitution reaction of PPh$_3$ ylide with NHC or PR$_3$ easily takes place. Therefore, this result suggests that a stronger electron donor ligand does not always construct the most robust metal-ligand bond in a given complex. Further investigations on the relationship between electronic and/or steric factors of the ligand and the metal-ligand bond character might be needed. We thank Reviewer #2 for the comment on this point.