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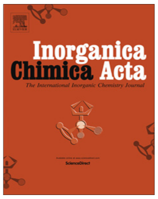

Research paper

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

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ABSTRACT

Phosphonium ylide complexes of Mo and W formulated as [M(η^3-allyl){η^2-$(NPh)_2CH$}$(CO)_2(CH_2PR_3)$] (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-$(NPh)_2CH$}$(CO)_2(NC_5H_5)$] (M = Mo: **1-Mo** and M = W: **1-W**), with a phosphonium ylide, CH_2PR_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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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-CH), 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-CH), 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_2PMe_3), 50.3 (s, allyl-CH_2), 76.1 (s, allyl-CH), 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