

Communications

Palladium-Assisted Regioselective Olefin Insertion into and β -Hydrogen Elimination of Hydrogen–Molybdenum and –Tungsten Bonds. Synthesis and Reactions of Heterodinuclear Hydrido Complexes of Palladium and Platinum with Molybdenum and Tungsten

Ayako Kuramoto, Kouhei Nakanishi, Tatsuya Kawabata, Nobuyuki Komine, Masafumi Hirano, and Sanshiro Komiya*

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan

Received August 9, 2005

Summary: Smooth reversible olefin insertion of ethyl acrylate, acrylonitrile, ethylene, dimethyl fumarate, and dimethyl maleate into $\text{MHCp}(\text{CO})_3$ ($M = \text{Mo}$ (**1a**), W (**1b**)) has been catalyzed by $\text{Pd}(\text{PPh}_3)_4$ (**4**) or $\text{Pd}(\text{ethyl acrylate})(\text{dppe})$ (**8**) at room temperature.

Transition metal–hydride addition to olefins (so-called olefin insertion) is one of the most well-established, important, fundamental reactions in organometallic catalysis.¹ Such a process is frequently facile and reversible, as observed in transition-metal-catalyzed olefin isomerization² as well as in disproportionation of the alkyl ligands in dialkylplatinum(II) complexes.³ However, for some transition-metal hydrides such as the molybdenum and tungsten hydrides $\text{MHCp}(\text{CO})_3$ ($M = \text{Mo}$ (**1a**), W (**1b**)), olefin insertion did not take place, though

alkynes with a strong electron-withdrawing group can insert.⁴ Insertion and its reverse, β -hydrogen elimination processes, generally require a coplanar transition state or intermediate consisting of a metal hydride and a $\text{C}=\text{C}$ double bond.⁵ We recently reported enhanced β -hydrogen elimination in a heterodinuclear ethylplatinum–molybdenum complex, $(\text{dppe})\text{EtPt}-\text{MoCp}(\text{CO})_3$ (**2**), giving the corresponding hydridoplatinum–molybdenum complex $(\text{dppe})\text{HPt}-\text{MoCp}(\text{CO})_3$ (**3a**), which further reacts with alkynes having an electron-withdrawing group to cause facile reductive elimination to give $\text{MoHCp}(\text{CO})_3$ and $\text{Pt}(\text{alkyne})(\text{dppe})$.⁶ When a terminal alkyne is employed, the succeeding Markovnikov addition of $\text{MoHCp}(\text{CO})_3$ to the coordinated alkyne takes place to give the new heterodinuclear μ -alkenyl complexes $(\text{dppe})(\mu\text{-CH}_2=\text{CR})\text{Pt}-\text{MoCp}(\mu\text{-CO})(\text{CO})$. These facts prompted us to investigate the

* To whom correspondence should be addressed. E-mail: komiya@cc.tuat.ac.jp.

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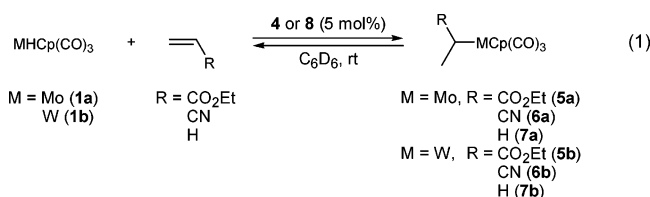
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enhancement effect of platinum-group metal complexes toward olefin insertion of the stable molybdenum- or tungsten-hydrogen bond. In this paper, we wish to report palladium-catalyzed olefin insertion into molybdenum- and tungsten-hydrogen bonds, giving the corresponding organomolybdenum and -tungsten complexes. Synthesis and related reactions of these heterodinuclear hydrido complexes of palladium and platinum with molybdenum and tungsten complexes are also described.

When the hydridomolybdenum complex **1a** (0.064 M) in benzene was treated with an approximately equimolar amount of ethyl acrylate (0.071 M) in the presence of 5 mol % of the zerovalent palladium complex Pd(PPh₃)₄ (**4**) at room temperature, instant olefin insertion took place to give Mo[CH(CO₂Et)Me]Cp(CO)₃ (**5a**) in 82% yield (based on **1a**) in 10 min (eq 1).



Acrylonitrile and ethylene also instantly gave the corresponding insertion products in 100 and 91% yields under similar conditions, respectively. However, insertion of 1,2-disubstituted olefins such as dimethyl fumarate and dimethyl maleate was relatively slow and took a few hours to complete, giving 59 and 79% yields, respectively. No insertion took place for substituted alkenes such as styrene, propylene, and 1-butene, where extensive isomerization of the unreacted 1-butene to a mixture of *cis*- and *trans*-2-butene was observed,⁷ suggesting that rapid and reversible insertion of 1-butene into the Mo-H bond is actually taking place. The olefin-coordinated complex Pd(ethyl acrylate)(dppe) (**8**) also catalyzed the insertion, but the catalytic activity of **8** was lower than that of **4**. In fact, **8** did not catalyze insertion of dimethyl fumarate and dimethyl maleate. Olefin insertion into the tungsten-hydrogen bond in **1b** was also achieved under similar reaction conditions, though the apparent insertion of **1b** was much slower than that of molybdenum hydride **1a**. For example, after treatment of **1b** with acrylonitrile and ethyl acrylate in the presence of **4** (5 mol %) for 10 min at room temperature, the corresponding insertion products were obtained only in ca. 20% yields, respectively, but the reactions were complete in 5 h.⁸ It should be noted that no insertion took place in the reaction of these hydrides with these olefins in the absence of Pd complexes as well as in the presence of only ligands such as PPh₃ and dppe.

Another important fact is that the reactions are reversible, since the alkylmolybdenum product **5a**, which was independently prepared by the metathetical reaction of MeSO₃CH(CO₂Et)Me with Na[MoCp(CO)₃],⁹ smoothly gave **1a** and CH₂=CHCO₂Et in 39 and 44% yields, respectively, in 12 min in the presence of 5 mol % of **4** under the same reaction conditions with a low concentration of **5a** (0.031 M). The

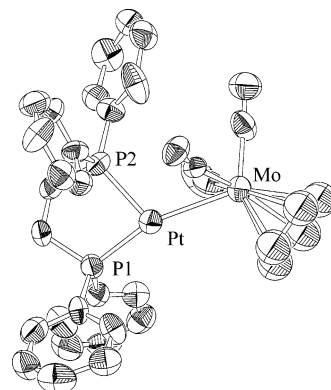
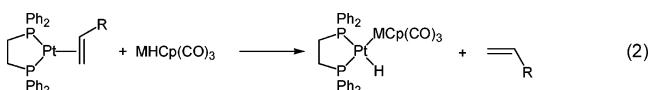


Figure 1. Molecular structure of (dppe)HPt-MoCp(CO)₃ (**3a**). All hydrogen atoms and the incorporated C₆H₆ molecule are omitted for clarity. Ellipsoids represent 50% probability.

equilibrium constants ($K_{\text{eq}} = [\text{5a}]/[\text{1a}][\text{ethyl acrylate}]$) estimated from the NMR spectra of the reaction mixture of **1a** and ethyl acrylate in C₆D₆ at 20 °C was $2.0 \times 10^2 \text{ M}^{-1}$, which was approximately the same as the K_{eq} value of $1.9 \times 10^2 \text{ M}^{-1}$ obtained from the solution of **5a** in the presence of **4**.

To shed some light on the reaction mechanism, deuterium labeling experiments were carried out. When WDCp(CO)₃ (**1b-d**) was employed in this reaction, an extensive regioselective H-D exchange reaction of the deuterium in **1b-d** with only geminal methylene protons of free ethyl acrylate took place immediately, indicating that facile and reversible Markovnikov addition of W-D to ethyl acrylate takes place before the formation of product **5b** before the rate-determining step.¹⁰ A dinuclear alkylpalladium-tungsten intermediate may be smoothly formed in equilibrium, and slow reductive elimination from this intermediate would give **5b** (vide infra).

Stoichiometric reactions of the zerovalent platinum complexes Pt(CH₂=CHR)(dppe) (R = Ph (**9**), CO₂Et (**10**)) with the hydridomolybdenum complex MoHCp(CO)₃ (**1a**) were carried out in benzene at room temperature. They smoothly gave the heterodinuclear hydridoplatinum complex (dppe)HPt-MoCp(CO)₃ (**3a**)^{6a} in high yields with liberation of the corresponding olefin (eq 2). Similar reactions with the hydridotungsten complex



R = Ph (**9**) or CO₂Et (**10**)

M = Mo (**1a**) or W (**1b**)

M = Mo (**3a**), 84% from **9**, 100% from **10**

M = W (**3b**), 88% from **9**

1b also gave the corresponding heterodinuclear hydridoplatinum complex (dppe)HPt-WCp(CO)₃ (**3b**).^{6a}

Complexes **3a** and **3b** were characterized by ¹H and ³¹P{¹H} NMR and IR spectroscopy as well as by X-ray structure analysis.¹¹ Figure 1 gives an ORTEP drawing of **3a**, showing

(10) Reaction of WDCp(CO)₃ (90% D, 0.023 mmol, 0.034 M) with ethyl acrylate (0.023 mmol, 0.034 M) in C₆D₆ at room temperature immediately caused H-D exchange between W-D and geminal methylene protons of ethyl acrylate, giving WDCp(CO)₃ (17% D, 0.017 mmol, 74%, 6 min), and the alkyltungsten complex **5b-d** was formed in 21% yield. The D content in free ethyl acrylate (0.017 mmol, 77%) could not be estimated, due to extensive broadening of these signals. However, the final alkyltungsten complex **5b-d** contained 30% D (79% yield) in the α-methyl group but no deuterium in the methine proton, which is confirmed by both ¹H and ²D NMR. The result indicates that only the geminal two protons in ethyl acrylate were rapidly exchanged, but not the vicinal proton. The smaller deuterium content in tungsten hydride **1b** as compared to the statistical value (30%) may be due to the equilibrium isotope effect of these species: Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403.

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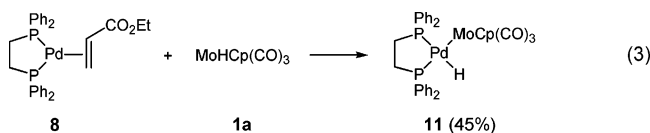
(7) 1-Butene was catalytically isomerized to 2-butenes in C₆D₆ for 6 h at 20 °C to give a butene mixture with the ratio 1-butene:*cis*-2-butene:*trans*-2-butene = 1:5:18.

(8) Reactions of **1b** with acrylonitrile and ethyl acrylate (10 min, 20 °C, C₆D₆) gave 18 and 24% yields of the corresponding insertion products, respectively. After 5 h, the yields reached 100 and 72%.

(9) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

formation of a Pt–Mo single bond. The geometry around Pt in **3a** is essentially square planar, though the hydride was not clearly found in the differential Fourier map, and the Mo has a four-legged piano-stool configuration.¹² The Pt–Mo bond distance (2.786(1) Å) is significantly shorter than those for (Ph₃P)₂HPT–MoCp(CO)₃ (2.839(1) Å)¹³ and (dppe)EtPt–MoCp(CO)₃ (2) (2.912(3) and 2.934(3) Å),¹⁴ suggesting weaker steric repulsion between the small hydride and the Mo moiety.

Analogous treatment of the olefin-coordinated zerovalent palladium complex **8** with 1 equiv of **1a** in C₆D₆ for 1 h also gave a heterodinuclear hydridopalladium complex, (dppe)HPd–MoCp(CO)₃ (**11**),¹⁵ in 44% yield (NMR), but in this reaction the insertion product **5a** was always a contaminant (9%). **11** can be isolated in 45% yield from a similar reaction mixture in THF by adding a large excess amount of hexane at –40 °C (eq 3).



The variable-temperature ³¹P{¹H} and ¹H NMR studies of **11** showed dynamic behavior due to characteristic cis site exchange of the hydride and Mo moiety,¹⁶ in contrast to the case for the stereochemically rigid platinum analogue **3a**.

When (dppe)HPt–MoCp(CO)₃ (**3a**) was treated with 2 equiv of ethyl acrylate at room temperature, hydride migration took place to give the starting hydridomolybdenum complex **1a** and zerovalent platinum complex **10** in ca. 10% yields. On the other hand, reaction of the heterodinuclear palladium analogue **11** with 2 equiv of ethyl acrylate caused immediate reductive elimination of the hydridomolybdenum complex **1a** in 67% yield. These data indicate the reversibility of this addition–elimination process of the Mo–H bond to Pt or Pd. It should also be

(11) Crystallographic data of **3a**·C₆H₆: C₄₀H₃₆MoO₃P₂Pt, FW = 917.70, monoclinic, *P*2₁/*n* (No. 14), *a* = 15.403(6) Å, *b* = 10.846(5) Å, *c* = 22.757(5) Å, β = 105.33(2)°, *V* = 3666(2) Å³, *Z* = 4, *D*_{calcd} = 1.662 g cm^{–3}, 4435 unique reflections with *I* > 3σ(*I*). *R* (*R*_w) = 0.099 (0.147).

(12) Unfortunately, the hydride was not clearly found in the X-ray analysis of **3a**, but Pt, Mo, P1, and P2 are in the plane and deviated from their least-squares plane within 0.17 Å, and the P1–Pt–P2 and P2–Pt–Mo bond angles are 84.9(2) and 112.0(1)°, suggesting that the Pt has essentially square-planar geometry with a putative hydride ligand. The dihedral angle of the two Pt–C(O)–Mo planes is 53.5°, suggesting a four-legged piano-stool structure at Mo.

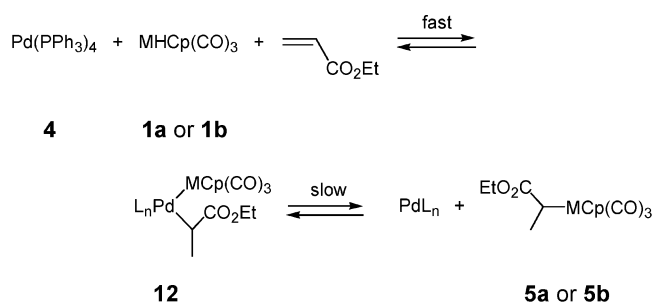
(13) Bars, O.; Braunstein, P.; Geoffroy, G. L.; Metz, B. *Organometallics* **1986**, 5, 2021.

(14) Single crystals of **2**, which was prepared by the metathetical reaction of PtEt(NO₃)(dppe) with Na[MoCp(CO)₃] according to our previous method,^{6a} were obtained from cold benzene/hexane solution. Crystallographic data of **2**: C₃₅H₃₄MoO₃P₂Pt, FW = 855.63, monoclinic, *P*2₁/*n* (No. 14), *a* = 14.755(9) Å, *b* = 26.58(1) Å, *c* = 20.482(7) Å, β = 99.16(4)°, *V* = 7930(6) Å³, *Z* = 8, *D*_{calcd} = 1.433 g cm^{–3}, 5647 unique reflections with *I* > 3σ(*I*). *R* (*R*_w) = 0.073 (0.114). The unit cell contained two crystallographically independent molecules.

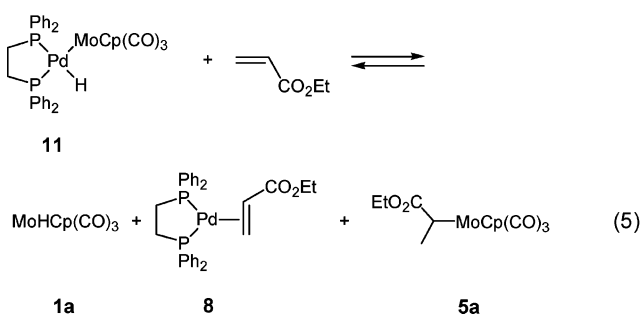
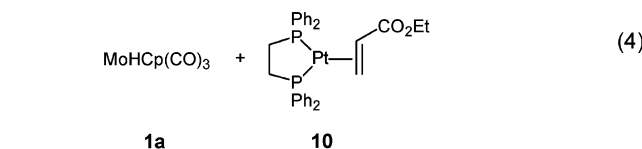
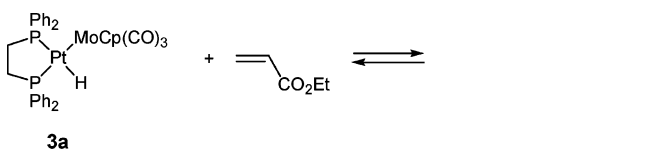
(15) Physical and spectroscopic data for **11**·0.5THF are as follows. Mp: 125–128 °C dec. Molar electric conductivity Λ (THF, –21 °C) = 0.49 S cm² mol^{–1}. Anal. Found: C, 55.77; H, 5.13. Calcd for C₃₉H₄₀MoO_{3.5}P₂Pd: C, 56.50; H, 4.86. IR (KBr): ν(CO) 1722, 1856, 1928 cm^{–1}. ³¹P{¹H} NMR (toluene-*d*₈, –50 °C, 121.6 Hz): δ 25.1 (d, ²*J*_{PP} = 28 Hz), 26.5 (d, ²*J*_{PP} = 28 Hz). ¹H NMR (toluene-*d*₈, –70 °C, 300.4 Hz): δ –4.64 (dd, ²*J*_{PH} = 80.5, 9.0 Hz, 1H, PdH), 2.3–2.4 (m, 4H, dppe CH₂), 5.25 (s, 5H, Cp), 7.40–7.65 (m, 12H, *m*, *p*-Ph), 7.70–7.95 (m, 8H, *o*-Ph).

(16) When the temperature was lowered to –70 °C, the center signal of the triplet at δ –5.00 (²*J*_{PH} = 36.3 Hz) assignable to the hydride gradually broadened and collapsed, and then new signals appeared at the outsides of the remaining two sharp signals to give a doublet of doublets.¹⁵ The present feature is interpreted by the facile site exchange process of the hydrido and Mo moieties at Pd, as is known for the hydrido(silyl)platinum complexes: Danny, C.; Simon, B. D.; Sarah, L. H.; Iman, G. K.; Robin, N. P.; Sylviane, S.-E.; Philippa, L. T. *Organometallics* **2004**, 23, 5744.

Scheme 1



noted that, in the reaction of the Pd complex, a succeeding Markovnikov addition of the metal hydride to ethyl acrylate also took place to give the insertion product **5a** (60%), whereas no such reaction is observed for the Pt case (eqs 4 and 5).



To confirm the reversibility of the stoichiometric reactions, the following three reactions were performed at room temperature: (a) the reaction of the dinuclear hydridopalladium complex **11** with ethyl acrylate, (b) the reaction of the zerovalent palladium complex **8** with molybdenum hydride **1a**, and (c) the reaction of the zerovalent palladium complex Pd(styrene)(dppe), having a weakly coordinated styrene ligand, with the (1-(ethoxycarbonyl)ethyl)molybdenum complex **5a**. These reactions all gave essentially mixtures containing all these species in the same ratio at room temperature in a few hours. Though an accurate ratio of the products was difficult to estimate, due to line broadening of the signals by fast olefin exchange at room temperature, the ratio **1a**:**5a**:**8**:**11** was roughly 2:2:4:3 by NMR. The result clearly indicates the equilibration of all these complexes under these conditions.

A tentative reaction mechanism for this palladium complex catalyzed insertion is considered. At first, **4** and Pd(ethyl acrylate)(PPh₃)₂¹⁷ are in facile equilibrium in the presence of ethyl acrylate. Addition of the hydridomolybdenum or -tungsten complex **1a** or **1b** to this solution also joins in this facile equilibrium via a putative alkylpalladium–molybdenum complex, (1-(ethoxycarbonyl)ethyl)palladium–molybdenum or -tungsten (**12**) (Scheme 1). Such an intermediate is likely formed by (1) nucleophilic addition of the hydride to the coordinated ethyl

acrylate, (2) oxidative addition of the hydride to the olefin complex followed by insertion, or (3) initial oxidative addition of the hydride to **4**, giving a hydridopalladium complex followed by olefin insertion. These fast and reversible processes are suggested by deuterium scrambling between free ethyl acrylate

(17) Takahashi, S.; Hagiwara, N. *Nippon Kagaku Kaishi* **1967**, 88, 1306; *Chem. Abstr.* **1968**, 69, 27514g.

(18) A brief kinetic study showed that the initial rate increased on increasing the concentrations of the tungsten hydride **1b** (0.038–0.19 M) and catalyst **4** (0.000 38–0.0019 M, 1–5 mol %) but was independent of the ethyl acrylate concentration (0.038–0.18 M). Although slow reductive elimination of the alkylpalladium–tungsten intermediate associated with **1b** after facile and reversible insertion of olefin into the Pd–H bond is one of the possible processes, the reaction seems to be actually more complicated, since the added triphenylphosphine significantly retarded the reaction but the enhancement effect (up to 30%) of the added olefin (0.036–0.79 M) on the rate was not significant even under the reaction conditions in the presence of triphenylphosphine (0.019 M). In addition, unfortunately, major palladium active species under these catalytic conditions could not be characterized by NMR due to extensive broadening. Further detailed kinetic studies to clarify the mechanism are in progress.

and tungsten deuteride. The following rate-limiting step should involve slow but reversible reductive elimination of **12** to give the insertion products, slowly reaching the total equilibration, though the mechanism is not clear at present.¹⁸

A detailed investigation including kinetics is required to clarify the mechanism. Despite this consideration, the present communication provides a new route for olefin insertion into stable transition-metal hydrides.

Acknowledgment. This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: CIF files and text and tables giving crystallographic data for **3a** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0506872