Synthesis of hydridoplatinum–molybdenum (or tungsten) heterodinuclear complexes by β-hydrogen elimination of (dppe)EtPt–MCp(CO)₃. Selective hydride transfer from Pt to Mo (or W)

Sanshiro Komiya[*], Toshiyuki Yasuda, Atsushi Fukuoka, Masafumi Hirano

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

Abstract

Hydridoplatinum–molybdenum (or tungsten) heterodinuclear complexes (dppe)HPt–MCp(CO)₃ [M = Mo (**1**), W (**2**); dppe = 1,2-bis(diphenylphosphino)ethane] have been prepared by selective β-hydrogen elimination of corresponding ethylplatinum–molybdenum (or tungsten) complexes (dppe)EtPt–MCp(CO)₃ [M = Mo (**3**), W (**4**)]. The β-hydrogen elimination process is significantly facilitated by electron-withdrawing transition metal ligand at platinum such as Co(CO)₄ (**5**). Acetylenes having electron withdrawing groups induce selective hydride transfer reaction in these heterodunuclear complex **1**–**2** to give hydridomolybdenum (or tungsten) and zero-valent (acetylene)platinum complexes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heterodinuclear complexes; β-hydrogen elimination; Hydride transfer; Kinetics; Platinum
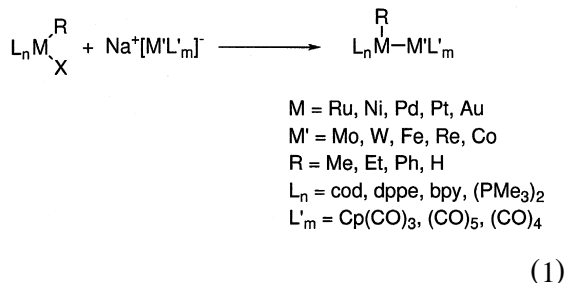
1. Introduction

Cooperative effect in multimetallic catalysis is one of the most intriguing and interesting unsolved problems at the molecular level both in homo- and heterogeneous catalyses [1–11].

Combination of two or more different metals in catalysis is especially interesting, since industrially important catalyses such as Pt–Re naphtha reforming catalyst and Co–Mo or Ni–Mo hydrodesulfurization catalysts are achieved by the bimetallic catalysts, probably for the sake of cooperative effects of two metals. In order to obtain fundamental insight concerning such effects, we have prepared a series of heterodinuclear organometallic complexes having both direct M–R and M–M′ σ-bonds, $L_nRM–M'L_m$ (M = Pt, Pd, Ni, Au; M′ = Mo, W, Co, Fe, Re;

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[*] Corresponding author. Tel.: +81-42-387-7500; fax: +81-42-387-7500.
   E-mail address: komiya@cc.tuat.ac.jp (S. Komiya).

L = cod, dppe, bpy, PPh$_3$; L' = Cp, CO) as possible models in bimetallic catalyses [12–18].

$$L_nM\overset{R}{\underset{X}{{\Big\backslash}}} + Na^+[M'L'_m]^- \longrightarrow L_nM\overset{R}{-}M'L'_m$$

M = Ru, Ni, Pd, Pt, Au
M' = Mo, W, Fe, Re, Co
R = Me, Et, Ph, H
L$_n$ = cod, dppe, bpy, (PMe$_3$)$_2$
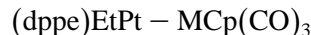L'$_m$ = Cp(CO)$_3$, (CO)$_5$, (CO)$_4$

(1)

In this paper we report preparation of hydridoplatinum–tungsten and –molybdenum heterodinuclear complexes (dppe)HPt–MCp(CO)$_3$ by thermal β-hydrogen elimination of (dppe)-Et–MCp(CO)$_3$ and hydride transfer from Pt to group 6 metals induced by acetylene compounds. A part of the results has been reported as a preliminary form [16].

2. Results and discussion

2.1. Preparation of hydridoplatinum–molybdenum and –tungsten heterodinuclear complexes

Hydridoplatinum–molybdenum and –tungsten heterodinuclear complexes (dppe)HPt–MCp(CO)$_3$ [dppe = 1,2-bis(diphenylphoshpino)ethane: M = Mo (1), W (2)] have been prepared by thermolysis of ethylplatinum–metal com-

plexes (dppe)EtPt–MCp(CO)$_3$ [M = Mo (3), W (4)] at 80°C for 6 h. In these reactions, equimolar amounts of ethylene along with small amounts of ethane were liberated by β-hydrogen elimination. The total yields of ethane for (dppe)EtPt–WCp(CO)$_3$ (2), (dppe)EtPt–Co(CO)$_4$ (5), and PtEtCl(dppe) were 3%, 14% and 5% yields, respectively, which would be formed by the bimolecular reaction of ethylplatinum with hydridoplatinum complexes. These dinuclear complexes were characterized by IR and NMR spectroscopies and elemental analyses as well as by chemical reactions. On the other hand, thermolysis of (dppe)EtPt–Co(CO)$_4$ also liberated ethylene as a major gaseous product, though the platinum products were not isolated in pure form. Table 1 summarizes yields, melting points, molar electric conductivities in THF, and analytical data for these hydridoplatinum–Mo (or W) complexes with bidentate phosphine ligand. IR and ^{1}H and ^{31}P{^{1}H} NMR data for these complexes are summarized in Table 2.

$$(dppe)EtPt - MCp(CO)_3$$
$$\underset{CH_2Ph_2}{\overset{80°C}{\rightarrow}} (dppe)HPt - MCp(CO)_3 + C_2H_4$$

M = Mo(1) W(2)	(2)

IR spectra of these complexes display v(Pt–H) bands at ca. 2020–2050 cm^{-1} and v(CO) bands at 1788–1924 cm^{-1}. ^{1}H NMR spectrum of 1 and 2 show a doublet of doublets with ^{195}Pt

Table 1
Yields, melting points, molar electric conductivities, and analytical data for 1–5

Complex	Yield, %	M.p.,[a] °C ·	Λ,[b] S cm^2 mol^{-1}	Anal., %			
				C		H	
				Calcd.	Found	Calcd.	Found
(dppe)HPt–MoCp(CO)$_3$ (1)	49	188 (dec.)	0.080	48.64	48.99	3.60	3.67
(dppe)HPt–WCp(CO)$_3$ (2)	12	211 (dec.)	–	43.89	44.03	3.15	3.26
(dppe)EtPt–MoCp(CO)$_3$ (3)	57	141 (dec.)	0.027	49.84	50.09	3.95	4.44
(dppe)EtPt–WCp(CO)$_3$ (4)	37	157 (dec.)	0.039	45.25	43.97	3.59	4.37
(dppe)EtPt–Co(CO)$_4$ (5)	61	154 (dec.)	0.13	48.43	47.49	3.68	3.73

[a] Melting points were uncorrected.
[b] In THF at 20°C.

Table 2
IR-, ^{1}H-, ^{31}P{^{1}H}-NMR data for **1**–**5**

Complex	IR[a] (cm^{-1})	^{1}H NMR[b] (δ)	^{31}P{^{1}H} NMR[c] (δ)
(dppe)HPt–Mo Cp(CO)$_3$ (**1**)	2050	−2.37 (d, 1H, J_{H-P} = 194 Hz, J_{H-Pt} = 868 Hz, PtH)	49.76 (d, J_{P-Pt} = 3.7 Hz, J_{P-Pt} = 3313 Hz)
	1926	1.7–2.0 (m, 4H, PCH_2CH_2P)	51.58 (d, J_{P-Pt} = 3.7 Hz, J_{P-Pt} = 2113 Hz)
	1831	5.27 (s, 5H, Cp)	
	1818	6.9–7.2 (m, 12H, *m*-, *p*-Ph) 7.6–7.8 (m, 8H, *o*-Ph)	
(dppe)HPt–W-Cp(CO)$_3$ (**2**)	2042	−2.92 (d, 1H, J_{H-P} = 193 Hz, J_{H-Pt} = 892 Hz, PtH)	51.29 (d, J_{P-Pt} = 4.9 Hz, J_{P-Pt} = 3226 Hz)
	1923	1.8–1.9 (m, 4H, PCH_2CH_2P)	51.58 (d, J_{P-Pt} = 4.9 Hz, J_{P-Pt} = 2090 Hz)
	1831	5.21 (s, 5H, Cp)	
	1812	6.9–7.2 (m, 12H, *m*-, *p*-Ph) 7.6–7.8 (m, 8H, *o*-Ph)	
(dppe)EtPt–Mo-Cp(CO)$_3$ (**3**)	1902	0.72 (dtd, 3H, J_{H-P} = 11, J_{H-H} = 7.5, J_{H-P} = 1.8 Hz, J_{H-Pt} = 40 Hz, PtCH$_2$CH_3)	39.58 (s, J_{P-Pt} = 1508 Hz)
	1788	1.51 (dqd, 2H, J_{H-P} = 7.5, J_{H-H} = 7.5, J_{H-P} = 7.5 Hz, J_{H-Pt} = 63 Hz, PtCH_2CH$_3$)	59.47 (s, J_{P-Pt} = 3711 Hz)
		2.0–2.3 (m, 4H, PCH_2CH_2P)	
		4.65 (s, 5H, Cp)	
		7.5–7.6 (m, 12H, *m*-, *p*-Ph)	
		7.7–8.0 (m, 8H, *o*-Ph)	
(dppe)EtPt–W-Cp(CO)$_3$ (**4**)	1899	0.71 (dtd, 3H, J_{H-P} = 11, J_{H-H} = 7.2, J_{H-P} = 1.5 Hz, J_{H-Pt} = 42 Hz, PtCH$_2$CH_3)	40.14 (s, J_{P-Pt} = 1502 Hz)
	1789	1.66 (dqd, 2H, J_{H-P} = 7.2, J_{H-H} = 7.2, J_{H-P} = 7.2 Hz, J_{H-Pt} = 77 Hz, PtCH_2CH$_3$)	61.11 (s, J_{P-Pt} = 3677 Hz)
		2.0–2.3 (m, 4H, PCH_2CH_2P)	
		4.70 (s, 5H, Cp)	
		7.4–7.6 (m, 12H, *m*-, *p*-Ph)	
		7.7–8.0 (m, 8H, *o*-Ph)	
(dppe)EtPt–Co-(CO)$_4$ (**5**)	2024	0.74 (dt, 3H, J_{H-P} = 9.4 Hz, J_{H-H} = 8.1 Hz, J_{H-Pt} = 35 Hz, PtCH$_2$CH_3)	47.76 (s, J_{P-Pt} = 2797 Hz)
	1957	1.48 (dqd, 2H, J_{H-P} = 8.1, J_{H-H} = 8.1, J_{H-P} = 8.1Hz, J_{H-Pt} = 45 Hz, PtCH_2CH$_3$)	47.95 (s, J_{P-Pt} = 4096 Hz)
	1924	2.1–2.5 (m, 4H, PCH_2CH_2P)	
	1883	7.4–7.6 (m, 12H, *m*-, *p*-Ph) 7.6–7.9 (m, 8H, *o*-Ph)	

[a] KBr disk.
[b] 300 MHz, in C$_6$D$_6$ for **1**–**4**, in CD$_2$Cl$_2$ for **5**.
[c] 122 MHz, in C$_6$D$_6$ for **1**–**4**, in CD$_2$Cl$_2$ for **5**.

satellite for the hydride. While the hydride has a large coupling constant to *trans*-P nucleus (194 Hz for **1**, 193 Hz for **2**), negligible coupling constant to *cis*-P is observed, suggesting distinct difference of trans influence in the square planar configuration. ^{31}P{^{1}H} NMR displays two doublets with Pt satellites (J_{P-P} = 3.7–4.9 Hz, J_{P-Pt} = 2090–3313 Hz), the small J_{P-P} values also being consistent with the square planar *cis* structure of these complexes.

2.2. Thermal β-hydrogen elimination of ethylplatinum–molybdenum and –tungsten heterodinuclear complexes

Time-courses of thermal β-hydrogen elimination reactions of these heterodinuclear complexes were followed in diphenylmethane at 80°C by monitoring the evolved ethylene by GLC. Fig. 1 shows the linear relationship between ([ethylene]$_t$/{[ethylene]$_\infty$ − [ethylene]$_t$})
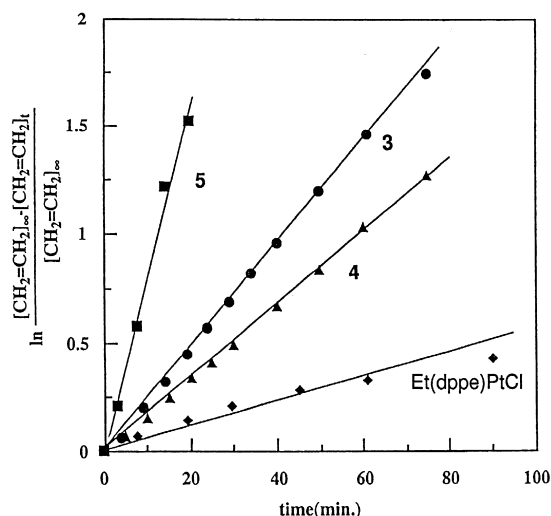
Fig. 1. First order rate plots for the thermolysis of (dppe)EtPt–MoCp(CO)$_3$ (3), (dppe)EtPt–WCp(CO)$_3$ (4), (dppe)EtPt–Co(CO)$_4$ (5), and PtEtCl(dppe) at 80°C in diphenylmethane.

and time, indicating that the reactions are first order in the concentration of heterodinuclear complexes under these conditions. The reactions can also be followed by monitoring the formation of the dinuclear hydride complexes in toluene-d$_8$ to give approximately the same rate constants. These results indicate that the thermolysis of these complexes gave concomitant formation of ethylene and dinuclear hydride complex. Estimated first order rate constants for these reactions are summarized in Table 3.

$$-\frac{d\left[(dppe)EtPt - MCp(CO)_3\right]}{dt}$$
$$= \frac{d\left[(dppe)HPt - MCp(CO)_3\right]}{dt} \qquad (3)$$
$$= \frac{d[CH_2 = CH_2]}{dt}$$
$$= k_{obsd}\left[(dppe)EtPt - MCp(CO)_3\right]$$

For comparison, the first order plots for the thermolysis of monomeric platinum complex PtEtCl(dppe) are also shown in Fig. 1. Although the fate of the platinum moiety by thermolysis of PtEtCl(dppe) is not clear, PtHCl(dppe) is the most likely product because the related complex

trans-PtEtCl(PPh$_3$)$_2$ is reported to form trans-PtHCl(PPh$_3$)$_2$ by thermolysis [19]. The β-hydrogen elimination reaction in EtPt–Co complex 5 was the fastest, followed by EtPt–Mo (3), EtPt–W (4) and the monomeric EtPt–Cl complexes. This trend may be interpreted by enhanced electrophilicity at Pt metal center due to more electronegative transition metal such as tetracarbonylcobalt ligand, giving rise to a facile hydrogen elimination. Eyling plot (76–91°C) of the first order rate constants for the thermolysis of 3 gave kinetic parameters $\Delta H^{\neq} = 100 \pm 2$ kJ/mol, $\Delta S^{\neq} = -26 \pm 4$ kJ/mol/K and $\Delta G^{\neq}$ (81°C) $= 110 \pm 4$ kJ/mol (Fig. 2). The negative value of entropy of activation suggests that the reaction does not involve dissociative processes such as prior dissociation of dppe or Mo anion ligands, as frequently observed in thermolysis of such organotransition metal complexes. Probably the β-hydrogen elimination has a relatively restricted environment where the β-hydrogen has an interaction with Pt by using the fifth coordination site of square planar geometry at Pt (Scheme 1) [20–23].

Hoffmann et al. proposed that the reaction of ethylene with PtHCl(PH$_3$)$_2$, the reverse reaction of β-hydrogen elimination, undergoes via a cationic 3-centered intermediate by the prior dissociation of chloride anion [24]. However, possible prior heterolytic dissociation of Mo anion is excluded, because no additive effect of

Table 3
First order rate constants for β-hydride elimination of (dppe)EtPt–ML$_n$

Complex	$k_{obs} \times 10^4$, s^{-1}	
(dppe)EtPt–MoCp(CO)$_3$ (3)	4.0[a,b]	3.7[c]
(dppe)EtPt–WCp(CO)$_3$ (4)	2.8[a,b]	2.7[c]
(dppe)EtPt–Co(CO)$_4$ (5)	12[a,b]	–
PtEtCl(dppe)	0.78[a,b]	–

[a]Estimated from formation of ethylene by GLC in CH$_2$Ph$_2$ at 80°C.

[b]Standard deviations are as follows: 0.1 for 3, 0.1 for 4, 2 for 5 and 0.03 for PtEtCl(dppe).

[c]Estimated from formation of (dppe)HPt–ML$_n$ by NMR in C$_6$D$_5$CD$_3$ at 80°C.
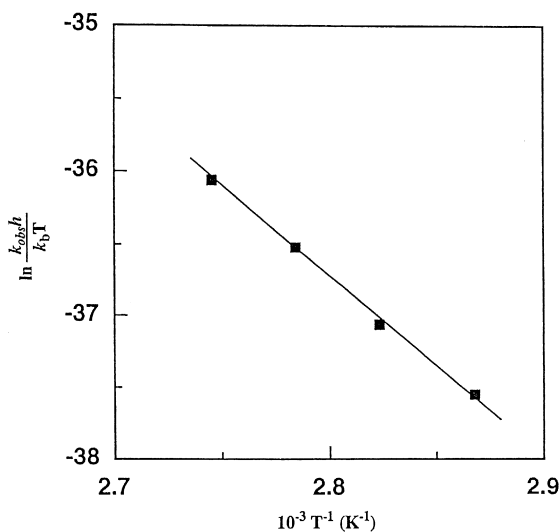
Fig. 2. Eyring plot of the first order rate constants for the thermolysis of (dppe)EtPt–MoCp(CO)$_3$ (**3**).

Na[MoCp(CO)$_3$] (11 equiv) on the rate was observed ($k_{obsd} = 4.2 \times 10^{-4}$ s^{-1}) under the same conditions. Another possible pathway includes prior phosphine-dissociation giving a 3-coordinate intermediate. However, exclusive formation of the cationic complexes [PtEt-(dppe)(PR$_3$)]$^+$[MoCp(CO)$_3$]$^-$ (Eq. (4)) in the presence of excess amount of tertiary phosphine ligands such as PMe$_3$ and PPh$_3$ prevents to study such possibility experimentally (see Experimental).

$$(dppe)EtPt - MoCp(CO)_3 + PR_3$$

$$\rightarrow [(dppe)PtEt(PR_3)^+ [MoCp(CO)_3]^-$$

$$(R = Me, Ph) \tag{4}$$
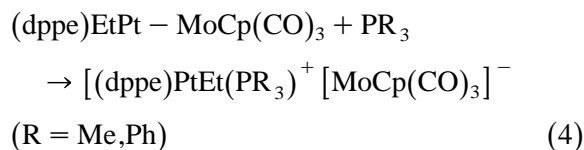
It is well established that β-hydrogen elimination from PtR$_2$L$_2$ proceeds by a dissociative mechanism giving a coordinatively unsaturated reactive species from which a facile β-elimination takes place [25]. However, direct β-hydrogen elimination process from 4-coordinated Pt(II) complex is also known to proceed, if the dissociation process of the tertiary phosphine ligand is blocked [23]. In the present case, strong coordiantion of the bidentate ligands is considered to prevent the phosphine dissociation process, and therefore electron withdrawing transition metal consequently enhances the direct β-hydrogen elimination process at Pt.
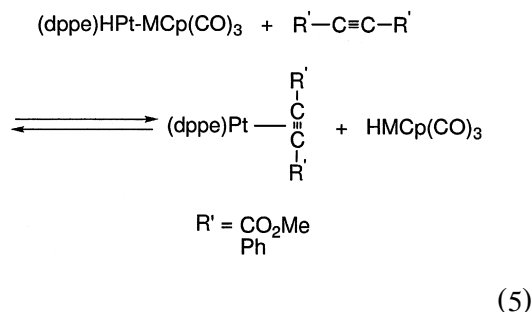
2.3. Hydride transfer in heterodinuclear organometallic complexes

Selective hydride transfer in (dppe)HPt–MCp(CO)$_3$ (M = Mo, W) was induced quantitatively on interaction with dimethyl acetylene-dicarboxylate MeO$_2$CC≡CCO$_2$Me to give MHCp(CO)$_3$ and Pt(MeO$_2$CC≡CCO$_2$-Me)(dppe). However, in the reaction of **1** with diphenylacetylene, only 58% conversion was observed at room temperature, suggesting that the reaciton is reversible. Accordingly, the independent reaction of Pt(PhC≡CPh)(dppe) with MoHCp(CO)$_3$ afforded (dppe)HPt–MoCp(CO)$_3$ in ca. 40% conversion. A similar reaction of W analogue **2** gave higher yields of the (acetylene)platinum(0) (95%) and hydridotungsten(II) complexes (61%). Thus, the acetylene induced β-hydrogen elimination reaction is considered to be a reversible process. Acetylene having electron donating substituents such as 1-methyl-2-phenylacetylene and 1-pentyne did not react at all with these heterodinuclear complexes. Although detail mechanistic investigations were not carried out for this reversible reaction, the reactions probably proceed by an associative mechanism, since analogous associative route is known for alkyl transfer reactions in (dppe)MePt–MCp(CO)$_3$ which are also enhanced by electron deficient olefins. Coordination of electron deficient acetylene is considered
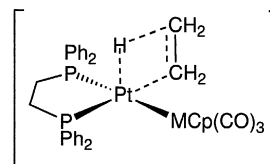
Scheme 1.

not only to enhance the hydride transfer reaction, but also to stabilize the zero-valent (acetylene)platinum(0) product.

$$(dppe)HPt\text{-}MCp(CO)_3 \ + \ R'\text{—}C\!\equiv\!C\text{—}R'$$

$$\xrightarrow{\qquad\qquad} (dppe)Pt \begin{array}{c} R' \\ | \\ C \\ ||| \\ C \\ | \\ R' \end{array} \ + \ HMCp(CO)_3$$

$$R' = \begin{array}{c} CO_2Me \\ Ph \end{array}$$

$$(5)$$

3. Concluding remarks

Selective β-hydrogen elimination from ethylplatinum complexes having transition metal as a ligand gave new heterodinuclear hydridoplatinum–metal complexes by a non-dissociative mechanism [20–23]. The hydrido ligand in the heterodinuclear complexes moves from Pt to Mo (or W) on interaction with acetylene. These reactions are similar to the alkyl transfer reaction of alkylplatinum-transition metal heterodinuclear complexes [13–18] and regarded as preferential reductive elimination of the hydride and transition metal at Pt. Such reactions may reflect the high mobility of hydride or organic moieties on the heterogeneous metal catalyst surface, where such hydride or organic group would meet a possible site suitable for a next catalytic reaction.

4. Experimental

4.1. General

All manipulations were carried out using standard Schlenk and vacuum techniques. PtEtCl(dppe) [26,27], NaMoCp(CO)$_3$ [28], NaWCp(CO)$_3$ [28] and NaCo(CO)$_4$ [29] were prepared by literature methods. Pt(PhC≡ CPh)(dppe) was prepared by the literature method using PhC≡CPh [30]. Solvents such as THF, benzene, toluene, Et$_2$O and hexane were distilled over benzophenone ketyl and stored under nitrogen or argon. Reagents were purchased and used as received. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}-NMR spectra were measured on a JEOL LA-300 NMR (300.4 MHz for ^{1}H) apparatus and the chemical shifts were given in ppm relative to TMS for ^{1}H and ^{13}C, and to external 85% H$_3$PO$_4$ for ^{31}P. Infrared spectra were measured using KBr disk on JASCO FT/IR-410 spectrometer. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. GLC analyses were performed on a Shimadzu GC-8 or a Shimadzu GC-14 B gas liquid chromatography. Molar electric conductivities were measured on a TOA model CM-7 B instrument. Melting points were estimated under nitrogen with a Yazawa capillary melting apparatus and are uncorrected.

4.2. Synthesis of (dppe)EtPt–MCp(CO)$_3$

Preparation of (dppe)EtPt–MoCp(CO)$_3$ (**3**) was shown as a typical experiment: the mixture of PtEtCl(dppe) (150.0 mg, 0.2279 mmol) and silver nitrate (38.7 mg, 0.2279 mmol) was stirred at room temperature for 30 min in THF (15 ml) in the dark to give brown solid of silver chloride. The silver chloride was removed by filtration and the solution was added NaMoCp(CO)$_3$ (240.8 mg, 0.9025 mmol) at −20°C. The reaction mixture was stirred for 2 h at −20°C. The orange solution was evaporated to dryness under reduced pressure to remove all volatile matters. The resulting orange solid was extracted with toluene and the extract was concentrated. Addition of hexane to the toluene solution and then cooling at −30°C gave orange crystals of **3** (112.4 mg, 0.1286 mmol, 57%). Complexes **4** and **5** were prepared analogously. The yields, analytical data, spectroscopic and physical data for these complexes are summarized in Tables 1 and 2.

4.3. Synthesis of (dppe)HPT–MCp(CO)$_3$

Preparation of (dppe)HPt–MoCp(CO)$_3$ (**1**) is shown as a typical example: **3** (0.1254 g, 0.1445 mmol) was dissolved in toluene and was heated at 80°C for 6 h, during which the color of the solution turned from orange to deep green yellow. The solution was filtrated and all volatile matters were removed under reduced pressure. Crystallization of the resulted oily material from a benzene/hexane mixture gave yellow plates of **1** (0.0594 g, 0.708 mmol, 49%). (dppe)EtPt–WCp(CO)$_3$ (**4**) was prepared by the similar method. The yields and physical and spectroscopic data of **1** and **2** involving elemental analyses were shown in Tables 1 and 2.

4.4. Synthesis of (dppe)EtPt–Co(CO)$_4$ (**5**)

Mixing of PtEtCl(dppe) (354.8 mg, 0.539 mmol) with silver nitrate (91.5 mg, 0.539 mmol) in THF (15 ml) at room temperature for 30 min gave brown precipitate of silver chloride. The precipitate was filtered off and the resulting solution was added into NaCo(CO)$_4$ (220.8 mg, 1.13 mmol). The solution was stirred at −20°C for 2 h. The yellow solution was evaporated to dryness under reduced pressure to remove all volatile matters. The resulting orange solid was extracted with toluene and the extract was concentrated. Addition of hexane into the toluene solution and then cooling at −30°C gave orange crystals of **5** (246.8 mg, 0.329 mmol, 61%).

4.5. Kinetic measurement of β-hydrogen elimination of 3–5 and PtEtCl(dppe)

As a typical example, kinetic measurement of **3** was described. Diphenylmethane (2.00 ml) was added into a Schlenk tube containing **3** (10.0 mg, 0.0113 mmol) by using a pipet. The Schlenk tube was capped with a rubber septum and degassed for three times by freeze–pump–thaw cycles. Then, a settled amount of methane

gas (1.10 ml) was introduced into the Schlenk tube by using a hypodermic syringe as an internal standard for GLC analysis. The reaction mixture was placed in a thermostatted oil bath (80 ± 1°C). A small gas sample (20 μl) was periodically obtained by a gas-tight syringe and the generated gases were quantitatively analyzed by GLC. On the other hand, the time-course of the formation of hydride complexes was also followed by ^{1}H NMR. **3** (8.7 mg, 0.010 mmol) was placed into a NMR tube and toluene-d$_8$ (600 μl) was introduced into the NMR tube by a trap-to-trap method. 1,4-Dioxane (0.0064 mmol) was added by a hypodermic microsyringe as an internal standard. Then the reaction mixture was heated at 80°C as above and the ^{1}H NMR spectrum was periodically measured.

The estimated rate constants by GLC are as follows: $k_{obs} \times 10^4$ (s^{-1}) = 4.0(1) (**3**), 2.8(1) (**4**), 12(2) (**5**) and 0.78(3) (PtEtCl(dppe)). The estimated rate constants by NMR are as follows: $k_{obs} \times 10^4$ (s^{-1}) = 3.7 (**3**) and 2.7 (**4**).

4.6. Synthesis of [PtEt(dppe)(PPh$_3$)]$^+$ [MoCp(CO)$_3$]$^-$

[PtEt(dppe)(PPh$_3$)]$^+$[MoCp(CO)$_3$]$^-$ was prepared as follows: **3** (79.6 mg, 0.123 mmol) was dissolved into benzene (2 ml) and then triphenylphosphine (26.5 mg, 0.101 mmol) was added into the solution. The reaction mixture was stirred for 2 days at room temperature. The removal of all volatile matters from the light yellow solution gave brown oil. Crystallization of the oil from CH$_2$Cl$_2$/Et$_2$O gave yellow crystals of [(dppe)EtPt(PPh$_3$)]$^+$[MoCp(CO)$_3$]$^-$ (79.8 mg, 77% yield). Molar electric conductivity Λ = 1.99 S cm^{-2} mol^{-1}. m.p. 112°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.12 (dt, 3H, J_{H-P} = 14.4 Hz, J_{H-H} = 7.2 Hz, PtCH$_2$CH_3), 1.0–1.4 (br, 2H, PtCH_2CH$_3$), 2.2–2.5 (m, 4H, PCH_2CH_2P), 5.19 (s, 5H, Cp), 7.2–7.5 (br, 35H, Ph). ^{31}P{^{1}H} NMR (121.6 MHz, CDCl$_3$): δ 25.8 (dd, 1P, J_{P-P} = 373.2, 19.4 Hz, J_{Pt-P} = 2948.8 Hz,

PPh$_3$), 46.5 (dd, 1P, J_{P-P} = 19.4, 4.9 Hz, J_{P-Pt} = 1565.6 Hz, dppe), 52.1 (dd, 1P, J_{P-P} = 373.2, 4.9 Hz, J_{P-Pt} = 2941.5 Hz, dppe). IR (KBr, cm^{-1}): 1893, 1774, 1767.

[PtEt(dppe)(PMe$_3$)]$^+$[MoCp(CO)$_3$]$^{-1}$ was prepared similarly and characterized spectroscopically. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.58 (q, 3H, $J_{H-P} = J_{H-H}$ = 7.2 Hz, J_{H-Pt} = 95 Hz, PtCH$_2$CH_3), 1.31 (d, 9 H, J_{H-P} = 13.5 Hz, J_{H-Pt} = 22.5 Hz, PMe_3), 1.25–1.37 (overlapped with the peak at δ 1.31, 2H, PtCH_2CH$_3$), 2.34–2.45 (m, 4 H, PCH_2CH_2P), 5.14 (s, 5 H, Cp), 7.5–7.6 (br, 35 H, Ph). ^{31}P{^{1}H} NMR (121.6 MHz, CDCl$_3$): δ −16.3 (dd, 1P, J_{P-P} = 379.2, 18.2 Hz, J_{P-Pt} = 2802.9 Hz, PMe$_3$), 46.6 (dd, 1P, J_{P-P} = 18.2, 3.6 Hz, J_{P-Pt} = 1535.2 Hz, dppe), 52.6 (dd, 1P, J_{P-P} = 379.2, 3.6 Hz, J_{P-Pt} = 2696.0 Hz, dppe).

4.7. Reaction of (dppe)HPt–MCp(CO)$_3$ with alkynes

As a typical example, reaction of **1** is described: into a 5 mmϕ NMR tube, **1** (11.6 mg, 0.0138 mmol) and ferrocene (1.0 mg, 0.0049 mmol) as an internal standard were added, and then benzene-d$_6$ (600 μl) was introduced by vacuum distillation. The NMR tube was capped with a rubber septum under nitrogen and dimethyl acetylenedicarboxylate (1.7 μl, 0.014 mmol) was added by a microsyringe. The NMR tube was rotated mechanically for 2 days at room temperature. The NMR spectrum of the reaction mixture showed the formation of Pt(MeO$_2$CC≡CCO$_2$Me)(dppe) (100%) and MoHCp(CO)$_3$ (100%) [31]. The treatment of **1** with diphenylacetylene was also carried out in the similar way.

4.8. Reaction of Pt(PhC≡CPh)(dppe) with Mo-HCp(CO)$_3$

Pt(PhC≡CPh)(dppe) (16.6 mg, 0.0215 mmol), MoHCp(CO)$_3$ (6.3 mg, 0.023 mmol) and ferocenene (1.0 mg, 0.0049 mmol) as an internal standard were added into a 5 mmϕ NMR tube. Benzene-d$_6$ (600 μl) was intro-

duced into the NMR tube by vacuum distillation. The NMR tube was rotated at room temperature for 2 days to give **1** in 40% yield with 40% conversion.

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