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Synthesis of heterodinuclear hydride complexes by oxidative addition of a transition-metal hydride to Pt(0) and Pd(0) complexes^{\ddagger}



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ABSTRACT

Heterodinuclear hydridoplatinum and -palladium complexes, (dppe)HPt–ML_n (ML_n = MoCp(CO)₃ (**3a**), WCp(CO)₃ (**3b**)), (dppe)Pt(μ -H)(μ -CO)Mn(CO)₄ (**3c**), (dppe)Pt(μ -H)(μ -CO)FeCp(CO) (**3d**), *cis*-L'₂HPt–ML_n (**5aa**: L' = PPh₃; ML_n = MoCp(CO)₃, **5ba**: L' = PPh₃; ML_n = WCp(CO)₃, **5ab**: L' = PMePh₂; ML_n = MoCp(CO)₃, **5ac**: L' = PMe₂Ph; ML_n = MoCp(CO)₃), (dppe)Pd(μ -H)(μ -CO)ML_n (ML_n = MoCp(CO)₂ (**7a**), WCp(CO)₂ (**7b**)), (dppe)Pd(μ -H)(μ -CO)Mn(CO)₄ (**7c**) are prepared by the oxidative addition of mononuclear transition-metal hydride complexes to zero-valent platinum or palladium complexes. The reactions of the heterodinuclear hydride complexes **3a**, **3d** and **7a** with electron deficient alkenes and alkynes such as dimethyl fumarate or DMAD cause reductive elimination at the Pt or Pd center to give the Pt(alkene or alkyne)(dppe) and MHL_n, suggesting reversibility of this process. The DFT calculations suggest that these reactions are controlled by the thermodynamic stability and the electron rich alkene complexe of Pt(0) (or Pd(0)) are preferable to prepare these heterodinuclear hydride complexes by the oxidative addition.

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Introduction

Cooperative effect among different transition-metal elements is a well-known phenomenon both in homo- and heterogeneous catalyses but the intrinsic insight into this nature is still one of the most intriguing and interesting unsolved problems [1–10]. Nevertheless, the combination of two or more different metal elements is widely used for industrially important catalysts such as Pt–Re in naphtha reforming and Co–Mo or Ni–Mo in hydrodesulfurization processes. One of the leading approaches for understanding of the cooperative effect at the molecular level is the study of heterodinuclear transition-metal complexes. Among these approaches, studies of heterodinuclear hydrides promise to reveal the cooperative effect on the reactivity of the metal–hydride bond. In fact, a transition metal–hydride species closely engages in many fundamental reactions such as hydrogenations, hydrosilylations, isomerizations, polymerizations, etc. These backgrounds have stimulated the studies on heterodinuclear hydrides. The synthetic pathways for heterodinuclear hydride complexes are therefore of great interest for these studies. One of the solid synthetic approaches is a metathetical reaction (Scheme 1).

Braunstein and coworkers have reported the synthesis of the heterodinuclear hydridoplatinum complexes cis-(Ph₃P)₂HPt- $MCp(CO)_3$ (M = Mo, W) and $cis(R_3P)_2Pt(\mu-H)(\mu-CO)Mn(CO)_4$ (R = Ph, Et) by the metathetical reaction of *trans*-PtH(Cl)(PR₃)₂ with the corresponding carbonylmetalates [11]. A β-hydride elimination from heterodinuclear ethyl complex is also a great method to prepare the hydride complex. We have documented the preparation of $(dppe)HPt-MoCp(CO)_3$ by β -hydride elimination from (dppe)EtPt-MoCp(CO)₃ [12]. The last but not least methodology shown in Scheme 1 is the oxidative addition of mono-nuclear hydride complex to a zero-valent metal compound [13]. We previously communicated the oxidative addition of MHCp(CO)3 (M = Mo, W) to Pt(alkene)(dppe) (alkene = styrene, ethyl acrylate) giving the corresponding heterodinuclear platinum hydride complex (dppe)HPt-MCp(CO)₃ (M = Mo, W) [14]. At the same time, Adams and coworkers also reported the preparation of (^tBu₃P)Pt(µ-



^{*} This paper is dedicated to Prof. Mingos for his outstanding contribution to organometallic chemistry.

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Scheme 1. Possible pathways for the preparation of heterodinuclear hydride complexes.

H)(μ -CO)Os(CO)₃(SnPh₃) by the oxidative addition of OsH(-CO)₄(SnPh₃) to Pt(PBu^t₃)₂ [15]. Not only for the importance as a synthetic method for the heterodinuclear hydrides, this reaction potentially changes the nature and reactivity of the hydride ligand because the hydride migrates between different metal elements. In this paper, we report a full account for the synthesis of hetero-dinuclear hydridoplatinum and -palladium complexes by the oxidative addition of the corresponding mononuclear hydride complexes. The reactions of the heterodinuclear hydride complexes are also described.

Results and discussion

Preparations of heterodinuclear hydridoplatinum and -palladium complexes by oxidative addition

Oxidative addition of transition-metal hydride to Pt(0) complex having a dppe ligand

Oxidative addition of $MoHCp(CO)_3$ (2a) to a zero-valent platinum complex, $Pt(CH_2 = CHPh)(dppe)$ (1) smoothly gave a heterodinuclear hydridoplatinum complex, (dppe)HPt–MoCp(CO)₃ (**3a**) at room temperature in 92% yield with liberation of styrene in 78% yield (Scheme 2). Similar treatment of 1 with WHCp(CO)₃ (2b) also gave the corresponding heterodinuclear hydridoplatinum complex, (dppe)HPt-WCp(CO)₃ (3b) in 88% with concomitant formation of styrene in 75%. On the other hand, other transition-metal hydrides having tertiary phosphine ligand(s) **2e-h** did not react with **1** at all. Notably, WHCp(CO)₂(PPh₃) (2f) did not react with 1 at all, while 2b readily produced **3b** in high yield, suggesting the importance of the acidity of the hydride used [16]. In the case of ruthenium dihydrides **2i,j**, **1** reacted with these dihydridoruthenium(II) to give a complex mixture, which was difficult to be characterized. In these reactions using dihydride complexes, a considerable amount of ethylbenzene was formed (56% for 2i, 56% for 2j), suggesting styrene was hydrogenated during the reaction.

These complexes **3a-b** were characterized by ¹H and ³¹P{¹H} NMR and IR spectroscopies, as well as by X-ray structure analysis of **3a**. The single crystals of **3a** suitable for the X-ray analysis were obtained by recrystallization from a benzene and hexane mixed solvent. Fig. 1 depicts an ORTEP drawing of **3a**, showing the formation of a Pt–Mo single bond. Unfortunately, the hydride was not clearly found in the differential Fourier map of **3a**, but Pt, Mo, P1, and P2 were placed in the same plane and their deviation from their least-squares plane is within 0.17 Å. The P1–Pt–P2 and P2–Pt–Mo bond angles are 84.9(2)° and 112.0(1)°, respectively. These data suggest the Pt having a distorted square-planar geometry with a putative hydride ligand. On the other hand, the Mo fragment can be regarded as a distorted four-legged piano-stool structure. The Pt–Mo bond distance (2.786(1) Å) is significantly shorter than those for $(Ph_3P)_2HPt-MoCp(CO)_3(2.839(1) \text{ Å})$ [11] and (dppe)EtPt-MoCp(CO)₃ (2.912(3) and 2.934(3) Å) [14]. The IR spectra of **3a** and **3b** showed absorption bands at 2042 cm⁻¹ and 2041 cm⁻¹, respectively, which were assigned to the v(Pt-H) vibrations for terminal hydride ligands. The v(CO) frequencies in KBr pellets of 3a, at 1926 and 1819 cm⁻¹, and of 3b, at 1925 and 1828 cm⁻¹, correspond to a typical pattern for a MXCp(CO)₃ "fourlegged piano-stool" structure [17]. The ¹H and ³¹P{¹H} NMR data for **3a** and **3b** are consistent with the structure drawing in Scheme 2. Unlike the triethylphosphine derivatives, (Ph₃P)₂HPt-MoCp(CO)₃ (M = Mo, W) [11], the NMR spectra of **3a** and **3b** do not show any fluxional behavior below room temperature. It is worthwhile to note that the ${}^{31}P{}^{1}H$ NMR in C₆D₆ showed two doublets with ${}^{195}Pt$ satellites at δ 49.0 (d, ${}^{2}J_{PP} = 3$ Hz, ${}^{1}J_{PtP} = 3312$ Hz) and 50.8 (d, ${}^{2}J_{PP} = 3 \text{ Hz}, {}^{1}J_{PtP} = 2118 \text{ Hz}$ for **3a**, and δ 51.3 (d, ${}^{2}J_{PP} = 4 \text{ Hz}, {}^{1}J_{PtP} = 3313 \text{ Hz}$) and 52.8 (d, ${}^{2}J_{PP} = 4 \text{ Hz}, {}^{1}J_{PtP} = 2093 \text{ Hz}$) for **3b**. Without ¹H decoupling, a large P–H coupling (${}^{2}J_{PH} = 194 \text{ Hz}$) for the downfield resonance was observed in the ³¹P NMR of **3a**, while upfield resonance has no P-H coupling. Therefore, the downfield resonance is assigned to the phosphorus nucleus trans to the hydride. In both cases, the upfield resonances have larger ${}^{1}I_{PtP}$ coupling than the other. This perturbation comes from the smaller trans influence of the ML_n fragment than the hydride [18].

The reaction of **1** with hydridomanganese complex MnH(CO)₅ (2c) is noteworthy. This reaction also proceeded in benzene at room temperature but the product obtained was a u-hydrido-u-carbonyl platinum-manganese complex. $(dppe)Pt(u-H)(u-CO)Mn(CO)_{4}$ (3c) in 93% vield. Single crystals of **3c** suitable for the X-ray analysis involve two quite similar but crystallographically independent molecules in a unit cell and one of them is depicted in Fig. 2. Unlike the Mo analogs, **3c** has a bridging carbonyl and hydride ligands between the Pt and Mn atoms. The Pt geometry is regarded as a square-planar by the bridging hydride and carbonyl carbon, and two phosphorus atoms of dppe, whereas the Mn has a near-perfect octahedral geometry generated from the µ-H and the five CO's ligands. The Pt–Mn distance for **3c** is 2.686(2) Å, which is shorter than those for $(Et_3P)_2Pt(\mu-H)(\mu-CO)Mn(CO)_4$ (2.730(2) Å) [11] and (dppe)MePt-Mn(CO)₅ (2.795(2) Å) [20]. The Pt-P1 and Pt-P2 distances are 2.292(1) and 2.230(2) Å, respectively. These distances are slightly shorter than these in $(Et_3P)_2Pt(\mu-H)(\mu-CO)Mn(CO)_4$ (2.353 (3), 2.283(3) Å). The bridging carbonyl C1–O1 is symmetrically bound to Pt and Mn with Pt(or Mn)-C1 distances of 2.03 and 2.02 Å, respectively. These values are close to 2.02(1) and 2.03(1) Å found for $(Et_3P)_2Pt(\mu-H)(\mu-CO)Mn(CO)_4$. The IR spectrum of the dinuclear hydrideplatinum-manganese complex shows v(CO)bands for terminal carbonyl ligands at 1949, 1930 and 1836 cm⁻¹ and a typical lower band for a bridging carbonyl at 1707 cm⁻¹. Therefore, this intense and lower shifted band can be used as a criterion for the presence of u-carbonyl group [17].

The NMR spectrum of **3c** showed fluxional behavior, which is described in the following section, but the fluxionality is almost frozen at -80 °C. The ¹H NMR in CD₂Cl₂ at -80 °C showed a double doublet at δ -4.39 (dd, ²*J*_{PH} = 99.8, 13.2 Hz, ¹*J*_{PtH} = 547 Hz, 1H) which is assigned as the hydride. The ¹*J*_{PtH} value for **3c** in CD₂Cl₂ is smaller than one for **3a**. The ³¹P{¹H} NMR spectrum at -80 °C showed an AB pattern with ¹⁹⁵Pt satellites at δ 44.6 (¹*J*_{PtP} = 2303 Hz) and 46.1 (¹*J*_{PtP} = 4057 Hz). The doublet resonance at δ 46.1 in the ³¹P{¹H} NMR changed to a double doublet in non-decoupling ³¹P NMR by a large coupling with the hydride (²*J*_{PH} = 87 Hz). Therefore, this resonance was assigned to the phosphorus trans to the hydride. The small ¹*J*_{PtP} coupling constant (¹*J*_{PtP} = 2303 Hz) at δ 44.6 arises from the stronger trans influence, suggesting the presence of a carbon fragment, but it does not have a Mn in the trans position. This fact is considered to have the bridged



Scheme 2. Reactions of Pt(styrene)(dppe) (1) with transition-metal hydride complexes.

hydride and carbonyl structure, even in the CD₂Cl₂ solution. These ¹⁹⁵Pt–P coupling constants in **3c** reflect smaller trans influence from the bridging hydride than carbonyl ligand. These NMR data in CD₂Cl₂ are close to these of PPh₃ derivative reported by Braunstein and coworkers [11c]. These are consistent with the molecular structure shown in Fig. 2. However, the NMR spectrum of **3c** measured in toluene-*d*₈ was remarkably different from those in CD₂Cl₂. Namely, the ³¹P{¹H} NMR of **3c** in toluene-*d*₈ at –80 °C showed two signals with ¹⁹⁵Pt satellites at δ 49.7 (¹*J*_{PtP} = 2803 Hz) and 52.8 (¹*J*_{PtP} = 2856 Hz). The hydride resonance appeared as a double doublet at δ –2.24 (²*J*_{PH} = 154, 6.6 Hz, ¹*J*_{PtH} = 719 Hz). The

larger ${}^{1}J_{PtH}$ and smaller ${}^{1}J_{PtP}$ values indicate stronger bonding of the hydride ligand with Pt in toluene- d_8 solution.

Similarly, the treatment of FeHCp(CO)₂ (**2d**) with **1** produced (dppe)Pt(μ -H)(μ -CO)Fe(CO) (**3d**) in 52% yield. This compound was also characterized by ¹H and ³¹P{¹H} NMR and IR spectroscopies. As the most characteristic feature of **3d**, the IR spectrum showed intense ν (CO) bands at 1950 cm⁻¹ and 1695 cm⁻¹. The latter ν (CO) band indicates the presence of a μ -carbonyl group in **3d**. The NMR spectra suggest the involvement of some dynamic processes in a solution of **3d** (*vide infra*).



Fig. 1. ORTEP drawing of $(dppe)HPt-MoCp(CO)_3$ (**3a**) [19]. All hydrogen atoms and incorporated solvent molecule are omitted for clarity. Ellipsoids represent 50% probability.



Fig. 2. An ORTEP drawing of one of the two crystallographically independent molecules of $(dppe)Pt(\mu-H)(\mu-CO)Mn(CO)_4$ (**3c**) obtained from the benzene/hexane solution [21]. All hydrogen atoms except the hydride and incorporated solvent molecule are omitted for clarity. Ellipsoids represent 50% probability.

Oxidative addition of transition-metal hydrides to Pt(0) complex having monodentate phosphine ligands

A series of reactions of monodentate phosphine complex $Pt(alkene)L_2'(4)$ with **2a** or **2b** were achieved to give corresponding cis-dinuclear hydridoplatinum complex 5 (Table 1). Without exception, these products have the *cis* geometry regardless of the cone angle of phosphines used ($\theta = 145^{\circ}$ for PPh₃, 136° for PMePh₂, 122° for PMe₂Ph) [22]. The molvbdenum hydride **2a** was found to be more reactive than the tungsten hydride 2b (entries 4 and 5). No reaction occurred when dimethyl fumarate (e value = 1.490) complex was used (entries 6 and 7), while the ethylene (e value = -0.200), (*E*)-stilbene (*e* value = -0.080), and methyl acrylate (e value = 0.600) complexes readily reacted with **2a** and **2b** (entries 1–5). The π -acidic character of the coordinating alkene seems to discourage the reaction. Probably this reaction may be controlled by the electron density of the Pt center in the oxidative addition reaction of MHL_n or facile dissociation of the alkene ligand in **4** to give a reactive coordinatively unsaturated species.

Oxidative addition of transition-metal hydride complexes to Pd(0) ethyl acrylate complex

The same method can be applied to the Pd(0) complex. The reaction of Pd(ethyl acrylate)(dppe) (**6**) [23] with 1 equiv of **2a** in C₆D₆ produced a heterodinuclear hydridopalladium complex **7a** in 45% yield [Eq. (1)].



Complex **7a** showed a fluxional behavior in solution, but this behavior could be frozen below -80 °C in toluene- d_8 . The IR spectrum of **7a** shows the stretching vibration assignable to the *v*CO at 1936, 1852 and 1703 cm⁻¹. According to the IR spectrum, compared with the Pt analog, the last band suggests the presence of a μ -carbonyl group. Thus, we tentatively assigned this compound as (dppe)Pd(μ -H)(μ -CO)MoCp(CO)₂ (**7a**). Similarly, treatment of **6** with hydridotungsten **2b** and -manganese complexes **2c** in THF also gave corresponding bridged heterodinuclear complexes, (dppe) Pd(μ -H)(μ -CO)WCp(CO)₂ (**7b**) and (dppe)Pd(μ -H)(μ -CO)Mn(CO)₄ (**7c**). In the IR spectrum of **7b** and **7c**, bridging ν CO bands were

Table 1

Reactions of Pt(alkene)L₂' with transition-metal hydride complexes.^a



Fig. 3. Variable temperature ¹H NMR spectra of $(dppe)Pt(\mu-H)(\mu-CO)Mn(CO)_4$ (**3c**) in toluene-*d*₈.

observed at 1710 and 1749 cm⁻¹, respectively, suggesting the analogous bridging structure.

Dynamic behavior of heterodinuclear hydride complexes

As described above, all μ -hydrido- μ -carbonyl heterodinuclear complexes showed fluxional behavior in a solution. Figs. 3 and 4 show variable-temperature ¹H and ³¹P{¹H} NMR spectra of (dppe) Pt(μ -H)(μ -CO)Mn(CO)₄ (**3c**) in toluene- d_8 [24]. In the ³¹P{¹H} NMR, a couple of AB patterns at -80 °C gradually broadened and collapsed, and a singlet is eventually appeared at 100 °C. A double

Pt(alkene)L'2	+ MHL _n	r.t., C ₆ D ₆ ►	L' ML _n Pt L' H	+ alkene	
4			5		

Entry	L'	Alkene	MHLn	Product	Yield/%
1	PPh ₃	(E)-stilbene	2a	<i>cis</i> -(Ph ₃ P) ₂ HPt-MoCp(CO) ₃ (5aa)	90
2	PPh ₃	(E)-stilbene	2b	cis-(Ph ₃ P) ₂ HPt-WCp(CO) ₃ (5ba)	96
3	PPh_3	Ethylene	2a	cis-(Ph ₃ P) ₂ HPt-MoCp(CO) ₃ (5aa)	88
4	PPh_3	Methyl acrylate	2a	cis-(Ph ₃ P) ₂ HPt-MoCp(CO) ₃ (5aa)	90
5	PPh_3	Methyl acrylate	2b	cis-(Ph ₃ P) ₂ HPt-WCp(CO) ₃ (5ba)	23
6	PPh_3	Dimethyl fumarate	2a	NR ^b	
7	PPh_3	Dimethyl fumarate	2b	NR ^b	
8	PMePh ₂	Methyl acrylate	2a	cis-(Ph ₂ MeP) ₂ HPt-MoCp(CO) ₃ (5ab)	92
9	PMe ₂ Ph	Methyl acrylate	2a	<i>cis</i> -(PhMe ₂ P) ₂ HPt-MoCp(CO) ₃ (5ac)	95

^a Conditions: temp = r.t., solvent = C_6D_6 time = 20 min.

^b NR = no reaction.



Fig. 4. Variable temperature ${}^{31}P{}^{1}H$ NMR spectra of (dppe)Pt(μ -H)(μ -CO)Mn(CO)₄ (**3c**) in toluene- d_8 .

doublet in ¹H NMR, which is assigned to hydride ligand also broadened *simultaneously* and finally gave a triplet. These spectral changes are consistent with the exchange of two phosphorus nuclei without dissociation (nor half-dissociation) of the phosphorus, hydride and manganese fragments [25]. It is interesting to note that only the outer two signals of the double doublet in ¹H NMR was broadened and coalesced, but the inner two signals remained sharp (separation = $\{|^2 J_{P(1)H}| - |^2 J_{P(2)H}|$)). The coalescence of the outer resonance indicates the opposite sign of the two P–H coupling constants in **3c**. Similar dynamics is also observed in analogous complexes such as *cis*-(R₃P)₂Pt(μ -H)(μ -CO)Mn(CO)₄ (R = Ph, Et) [11].

The activation parameters for these dynamic processes of the ¹H NMR are estimated by gNMR simulation [26]: $\Delta H^{\neq} = 37.2 \text{ kJ mol}^{-1}$, $\Delta G^{\neq}{}_{298} = 55.8 \text{ kJ mol}^{-1}$, and $\Delta S^{\neq} = -62.5 \text{ J mol}^{-1} \text{ K}^{-1}$ in toluene- d_6 and $\Delta H^{\neq} = 34.3 \text{ kJ mol}^{-1}$, $\Delta G^{\neq}{}_{298} = 56.8 \text{ kJ mol}^{-1}$, mol⁻¹, $\Delta S^{\neq} = -75.3 \text{ J mol}^{-1} \text{ K}^{-1}$ in CD₂Cl₂. The solvent did not significantly affect these activation parameters, suggesting this dynamic process to proceed in the same mechanism in toluene- d_8 and CD_2Cl_2 . The large negative entropy of activation supports the non-dissociative process. The following mechanisms shown in Scheme 3 are consistent with all these experimental results. Process A is a twistrotation at Pt center via a pseudotetrahedral transition state. A similar mechanism is suggested for fluxional behavior of cisbis(stannyl)- and bis(silyl)bis(phosphine)platinum and palladium complexes [27]. The activation parameters for the twist-rotation at Pt in *cis*-Pt(SnMe₃)₂(PMePh₂)₂ have been reported as $\Delta H^{\neq} = 60 \pm 1 \text{ kJ mol}^{-1}$ and $\Delta S^{\neq} = 32 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$. The most significant difference between the dynamic processes in 3c and cis-Pt(SnMe₃)₂(PMePh₂)₂ is the ΔS^{\neq} value. An alternative mechanism involves rotation of the σ -bonded H–Mn(CO)₅ intermediate

(process B). In this process, **3c** converts into (dppe)Pt-MnH(CO)₅ intermediate, where the σ -bonded H–Mn(CO)₅ fragment can freely rotate, and get back to the μ -hydrido- μ -carbonyl species via nonbridged structure, (dppe)HPt-Mn(CO)₅. Although we do not have conclusive data to differentiate the present mechanism, we believe that process B seems to be likely because (i) the entropy of activation for the twist-rotation in cis-Pt(SnMe₃)₂(PMePh₂)₂ is quite different from the present results, (ii) we have observed similar rotation for $(dppe)[\mu - \eta^1, \eta^2 - (E) - cinnamyl]$ non-dissociative $Pt-Co(CO)_4$ through the process alike process B [28], and (iii) the activation parameters for the rotation of $(dppe)[\mu-\eta^1,\eta^2-(E)-cin$ namyl]Pt–Co(CO)₄ in toluene- d_8 [$\Delta H^{\neq} = 46$ kJ mol⁻¹, $\Delta G^{\neq}_{303} = 57$ kJ mol⁻¹, and $\Delta S^{\neq} = -37$ J mol⁻¹ K⁻¹] are very close to that for 3c. Braunstein and coworkers already suggested the same intermolecular mechanism for the dynamic process in analogous complexes with monodentate phosphine ligands [11c]. The NMR spectra of the iron analog 3d suggest the involvement of similar dynamic processes. The activation parameters for the dynamic behavior of **3d** are also estimated as follows: $\Delta H^{\neq} = 25.7 \text{ kJ mol}^{-1}$, $\Delta G^{\neq}_{298} = 58.5 \text{ kJ mol}^{-1}, \Delta S^{\neq} = -109.8 \text{ J mol}^{-1} \text{ K}^{-1} \text{ in CD}_2 \text{Cl}_2$. The larger negative entropy of activation probably results from sterical balkiness of the $FeCp(CO)_2$ fragment.

Reaction of heterodinuclear hydridoplatinum and -palladium complexes with unsaturated compounds

Reactions with alkenes

Of particular interest to hydride complexes is the reaction with unsaturated compounds. Reactions of the heterodinuclear hydridoplatinum complexes with alkenes were studied, and the results are summarized in Table 2. When a hydridoplatinum-molybdenum complex (dppe)HPt-MoCp(CO)₃ (**3a**) was treated with dimethyl fumarate at room temperature, the hydridomolybdenum complex 2a and a zero-valent platinum complex Pt(dimethyl fumarate)(dppe) were produced in 100% and 74% yields, respectively (entry 1). From the platinum's point of view, this reaction is regarded as the reductive elimination between the MoCp(CO)₃ and H ligands at the Pt center. This is, therefore, the reverse reaction of the oxidative addition of 2a to the Pt(0) complex. Similar treatments of 3a with dimethyl maleate, acrylonitrile, and ethyl acrylate gave 2a and corresponding Pt(alkene)(dppe) in low yields at small conversions (entries 2-4). When ethylene was employed in this reaction, a heterodinuclear ethyl complexes (dppe)EtPt-MoCp(CO)₃ was obtained in 88% yield. Similar treatment of 3d with ethyl acrylate at room temperature also resulted in the reductive elimination to give 2d and Pt(ethyl acrylate)(dppe) in 80% and 100% yields, respectively [29].

Reactions of the palladium derivative $(dppe)Pd(\mu-H)(\mu-CO)$ MoCp(CO)₂ (**7a**) with alkenes were also studied, and the results are summarized in Table 3.

Treatment of **7a** with electron-deficient alkenes such as dimethyl fumarate caused facile reductive elimination to give $MoHCp(CO)_3$ (**2a**) in 55% yield (entry 1). Similar treatment of **7a** with ethylene gave a new heterodinuclear ethyl complex (dppe) EtPt- $MoCp(CO)_3$ (entry 7). However, when terminal alkenes such as methyl acrylate or acrylonitrile were employed, mononuclear branched alkylmolybdenum complexes **10** were observed (entries 3 and 4). We consider that these branched alkylmolybdenum complexes **10** are produced by a Markovnikov insertion of the alkene into the Pd-H bond in **7a** followed by the subsequent reductive elimination at Pd [14,30].

Reactions with alkynes

The reactions of $(dppe)HPt-MoCp(CO)_3$ (**3a**) with electrondeficient alkynes such as MeO₂CC \equiv CCO₂Me, PhC \equiv CPh, HC \equiv CCO₂Me, and HC \equiv CPh resulted in the facile reductive



Scheme 3. Possible mechanisms for the dynamic process of (dppe)Pt(µ-H)(µ-CO)Mn(CO)₄ (3c).

elimination to give hydridomolybdenum complex, $MoHCp(CO)_3$ (**2a**) and the corresponding zero-valent platinum(0) complexes, Pt(alkyne)(dppe) (**11**) (Table 4, entries 1,2,4,6) [31].

In contrast, **3a** did not react with electron-rich alkyne such as propyne. This is a similar to the reactivity of **3a** for electron rich alkenes. It should also be noted that, in the reaction with terminal alkynes having an electron-withdrawing group, further Markovnikov addition of $MoHCp(CO)_3$ (2a) to the coordinating alkyne in Pt(alkyne)(dppe) took place to give new heterodinuclear alkenyl complexes $(dppe)Pt(\mu-CR=CH_2)(\mu-CO)MoCp(CO)_2$ $(R = CO_2Me$ (12a), Ph (12b), $C_6H_4Me-p(12c)$) in 48 h at room temperature (enties 5,7,8). These complexes **12a-c** were characterized by ${}^{1}H$ and ${}^{31}P{}^{1}H$ NMR and IR spectroscopies, as well as by X-ray structure analysis of 12a. Single crystals of 12a suitable for the X-ray analysis were obtained by recrystallization from THF with hexane. Fig. 5 shows an ORTEP drawing of 12a. The geometry at Pt is essentially square planar consisting of dppe, alkenyl and bridging carbonyl ligands. The alkenyl C1=C2 moiety coordinates to Mo by an η^2 fashion, and one of the carbonyl ligands is bridging between the Pt and Mo centers. The IR spectra of **12a** showed ν (CO) bands at 1870 cm⁻¹ and 1731 cm⁻¹ assignable to a terminal and bridging carbonyl groups,

Table 2

Reaction of heterodinuclear hydrideplatinum complexes with alkenes.^a

respectively. A ν (CO) band at 1663 cm⁻¹ is assignable to the methoxycarbonyl group. ³¹Pt{¹H} NMR spectrum of **12a** showed a couple of doublets with ¹⁹⁵Pt satellites at 2.54 and 3.24 ppm.

Similar to the platinum derivative, the reactions of $(dppe)Pd(\mu-H)(\mu-CO)MoCp(CO)_2$ (**7a**) with electron-deficient alkynes such as $MeO_2CC \equiv CCO_2Me$, $PhC \equiv CPh$, and $HC \equiv CPh$ in C_6D_6 at room temperature induced smooth hydride transfer from Pd to Mo to give $MoHCp(CO)_3$ (**2a**) and Pd(alkyne)(dppe) (Table 5, entries 1,3,5). Further Markovnikov addition of resulting **2a** to the coordinating alkyne in Pd(alkyne)(dppe) took place to give new heterodinuclear alkenyl complexes (dppe)Pd(μ -CR $=CH_2$)(μ -CO)MoCp(CO) (R = Ph (**14b**), C_6H_4Me-p (**14c**)) in 24 h at room temperature. Contrary to the platinum derivative, the corresponding alkenyl complexes (dppe)Pd(μ -CR=CHR)(μ -CO)MoCp(CO) (R = CO_2Me (**14d**), Ph (**14e**)) were formed even when 1,2-disubstituted electron deficient alkynes were used in the reaction with **7a**.

DFT calculations of heterodinuclear hydridoplatinum complexes

In order to understand the thermodynamic property and the energy diagram of heterodinuclear hydridoplatinum complexes,

	$\begin{array}{c} Ph_2 \\ P \\ P \\ P \\ Ph_2 \end{array} P \\ Ph_2 \end{array} or \qquad \begin{array}{c} Ph_2 \\ P \\ P \\ P \\ P \\ Ph_2 \end{array} P \\ Ph_2 \end{array} P \\ Ph_2 \\ P$						
	3a	a 3d		8	2		
Entry	Complex	Alkene	Time/h	Conv./%	Yield/%		
					8	2	
1	3a	Dimethyl fumarate	00.25	82	74	100	
2	3a	Dimethyl maleate	00.25	30	36	28	
3	3a	Acrylonitrile	00.25	23	23	17	
4	3a	Ethyl acrylate	06	2	2	4	
5	3a	Styrene	43	0	0	0	
6	3a	1-Butene	24	0	0	0	
7 ^b	3a	Ethylene	42	80	0	0	
8	3d	Dimethyl fumarate	00.25	100	100	85	
9	3d	Ethyl acrylate	00.25	100	100	80	

^a Conditions: $[\mathbf{3}] = 0.02$ M, [alkene] = 0.03 M. temp = 30 °C, solvent = C_6D_6 .

^b Ethylene insertion product (dppe)EtPt-MoCp(CO)₃ was formed in 88%.

Table 3

Reactions of $(dppe)Pd(\mu-H)(\mu-CO)MoCp(CO)_2$ (7a) with alkenes.^a



Entry	Alkene	Time/h	Conv./%	Yield/%		
				9	2a	10
1	Dimethyl fumarate	00.5	100	ND ^d	55	0
2	Dimethyl maleate	00.1	100	ND ^d	60	0
3	Acrylonitrile	00.1	100	ND ^d	33	19 (R = CN)
4	Ethyl acrylate	00.5	80	ND ^d	35	$12 (R = CO_2Me)$
5	Styrene	43	0	0	0	0
6 ^b	1-Butene	26	92	0	0	0
7 ^c	Ethylene	42	80	0	0	0

^a Conditions: [7a] = 0.02 M, [alkene] = 0.03 M. temp = 30 °C, solvent = C_6D_6 .

^b Isomerization of 1-butene to cis-2-butene and trans-2-butene (1:4) was observed.

^c Ethylene insertion product (dppe)EtPd–MoCp(CO)₃ was formed in 88%.

^d Not determined.

the density functional theory (DFT) calculations were performed. In these calculations, 1,2-bis(dihydrophoshino)ethane (dhpe) was used instead of dppe, and the effect of solvent was not included. Thermodynamic analyses for the oxidative addition of Pt(alkene)(dhpe) with MoHCp(CO)₃ (**2a**) and FeHCp(CO)₂ (**2d**) were shown in Scheme 4. In both cases, the oxidative addition of MHL_n to Pt(styrene)(dhpe) is an exothermic reaction and the reaction spontaneously proceeds to the heterodinuclear hydridoplatinum side. On the other hand, the oxidative addition of MoHCp(CO)₃ to Pt(methyl acrylate)(dhpe) is considered to be slightly more favorable process, but FeHCp(CO)₂ is unlikely to add oxidatively to Pt(methyl acrylate)(dhpe). This is consistent with the experimental results described above.

The relative free energies for $(dhpe)Pt(\mu-H)(\mu-CO)ML_n'$ $(ML_n' = MoCp(CO)_2, Mn(CO)_4, FeCp(CO))$ compared to (dhpe) $HPt-ML_n (ML_n = MoCp(CO)_3, Mn(CO)_5, FeCp(CO)_2)$ are summarized in Scheme 5. The non-bridged structure is found to be more stable than the bridged one for the Pt-Mo complex. On the other

Table 4

Reactions of $(dppe)HPt-MoCp(CO)_3$ (3a) with alkynes.^a

hand, only little energy difference between them was observed for the Pt–Mn and Pt–Fe complexes. This is consistent with the fact that the Pt–Mo complex **3a** has a robust non-bridged structure, while facile interconversion between the bridged and non-bridged structures is observed for the Pt–Mn complex **3c** and the Pt–Fe complex **3d**.

Conclusion

A series of heterodinuclear hydridoplatinum and -palladium complexes were synthesized by the oxidative addition of corresponding mononuclear hydride complex with zero-valent platinum and palladium complexes. The backward reductive elimination of the metal fragment and hydride ligand at the Pt and Pd center also proceeded smoothly, especially when electron deficient alkenes were introduced. The trends are similar to the reductive elimination of diorganotransition metal complexes. The product ratios are controlled by the relative thermodynamic

	Pt Ph ₂ Pt Ph ₂ Ph ₂	$\xrightarrow{Ph_2} R \xrightarrow{Ph_2} Pt \xrightarrow{R} \overset{Ph_2}{\underset{Ph_2}{\overset{R}{\underset{Ph_2}}} R'}$	+ MHCp(CO)3	$\xrightarrow{Ph_2} \\ \xrightarrow{Ph_2} \\ \xrightarrow{Pt} \\ \xrightarrow{Pt} \\ \xrightarrow{Pt} \\ \xrightarrow{Ph_2} \\ O \\ \xrightarrow{Ph_2} \\ O \\ \xrightarrow{Pt} \\ Pt$:O)	
	3a	11	2a	12		
Entry	Alkyne	Time/h	Conv./%	Yield/%		
				11	2a	1:
1	DMAD	1	100	96	83	
2	Diphenylacetylene	48	50	45	36	
3	Phenylpropyne	48	0	0	0	
4	Methyl 2-propynate	0.5	98	89	70	:
5		48	100	0	0	6
6	Phenylacetylene	0.5	54	8	8	:
7		48	100	0	0	83
8	4-ethynyltoluene	48	100	0	0	9
9	Propargyl alcohol	48	100	0	0	
10	Propyne	48	0	0	0	
11	Acetylene	48	100	0	0	

^a Conditions: [3a] = 0.02 M, [alkyne] = 0.03 M. temp = 30 °C, solvent = C_6D_6 .



Fig. 5. ORTEP drawing of $(dppe)Pt{\mu-C(CO_2Me)=CH_2}(\mu-CO)MoCp(CO)$ (**12a**) [32]. All hydrogen atoms and incorporated solvent molecule are omitted for clarity. Ellipsoids represent 50% probability.

stability of the starting compounds and products. Thus the Pt(0) or Pd(0) complexes having an electron-rich alkene are favorable starting complex for preparation of the heterodinuclear hydride complexes by this oxidative addition method.

Experimental section

General procedures

All manipulations were carried out under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were dried over and distilled from appropriate drying agents under N₂: hexane, benzene, toluene, diethyl ether and THF from Na/ benzophenone ketyl; CH₂Cl₂ from P₂O₅; acetone from Drierite; MeOH from magnesium methoxide. The deuterated solvent for NMR were commercially obtained and dried with appropriate drying agents before use (C₆D₆ from Na; CD₂Cl₂ from P₂O₅; acetone-*d*₆ from Drierite). NMR spectra were recorded on a JEOL LA-300 (300.4 MHz for ¹H, 121.6 MHz for ³¹P, 75.3 Hz for ¹³C) and a JEOL ECX400P (399.8 MHz for ¹H, 161.8 MHz for ³¹P) spectrometers.

Table 5

Reactions of heterodinuclear hydridepalladium complexes with alkynes.^a

Chemical shifts were reported in ppm downfield from TMS for ¹H and ¹³C and 85% H₃PO₄ in D₂O for ³¹P. IR spectra were recorded on a JASCO FT/IR-410 and JASCO FT/IR-4100 spectrometers using KBr disks. Elemental analyses were carried out with a Perkin–Elmer 2400 series II CHN analyzer. PtI₂(dppe) [33], MoHCp(CO)₃ [34], WHCp(CO)₃ [35], MnH(CO)₅ [36], and FeHCp(CO)₂ [37] were prepared according to literature procedures.

Synthesis of platinum(0) and palladium(0) complex having a dppe ligand

Synthesis of Pt(styrene)(dppe) (1)

This new compound was prepared according to the modified literature method [21]. To a solution of Ptl₂(dppe) (105.1 mg, 0.124 mmol) in THF (5 mL) was added a solution of NaBH₄ (25.3 mg, 0.668 mmol) in EtOH (10 mL) and THF (3 mL) at -40 °C and the solution was stirred for 30 min at this temperature. Styrene (0.5 mL, 4.4 mmol) was added dropwise to this reaction solution under -40 °C. The mixture was warmed up to room temperature gradually for 3 h. Then, the solution was concentrated under reduced pressure, and excess MeOH was added to give analytically pure pale yellow powder, which was filtered, washed with MeOH, and dried under vacuum at room temperature. Yield 90% (77.7 mg, 0.114 mmol). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 51.3 (d, ²J_{PP} = 81.8 Hz, ¹J_{PtP} = 3305 Hz), 51.7 (d, ²J_{PP} = 81.8 Hz, ¹J_{PtP} = 3305 Hz), 51.7 (d, ²J_{PP} = 81.8 Hz, ¹J_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 31.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_P = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_{PtP} = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_{PtP} = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_{PtP} = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_{PtP} = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_{PtP} = 81.8 Hz, ¹H_{PtP} = 3305 Hz), 51.7 (d, ²H_{PtP} = 7.5 Hz, Ph), 7.6 – 7.8 (m, 6H, o-Ph).

Synthesis of Pd(ethyl acrylate)(dppe) (6)

This new compound was prepared according to the modified literature method [21]. To a suspension of PdCl₂(dppe) (241.0 mg, 0.418 mmol) in THF (8 mL) was added a solution of NaBH₄ (77.7 mg, 2.05 mmol) in MeOH (5 mL) and THF (5 mL) at -70 °C and this reaction mixture was stirred until the color solution formed at this temperature. Ethyl acrylate (2 mL, 18 mmol) was added dropwise to this reaction solution under -40 °C. The mixture was warmed to room temperature for 6 h. Then, the solution was concentrated under reduced pressure, and excess MeOH was added to give analytically pure white powder, which was filtered, washed with MeOH, and dried under vacuum at room temperature. Yield 71% (179.0 mg, 0.2958 mol). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 33.5 (d,



Entry	Alkyne	Time/h	Yield/%	Yield/%		
			13	2a	14	
1	DMAD	0.1	87	76	0	
2		24	0	0	100	
3	Diphenylacetylene	0.2	16	11	0	
4		24	0	0	25	
5	Phenylacetylene	0.1	ND ^b	39	0	
6		24	0	0	45	
7	4-ethynyltoluene	24	0	0	32	

 a Conditions: [7a]=0.02 M, [alkyne] = 0.03 M. temp = 30 $^\circ\text{C}$, solvent = $C_6\text{D}_6.$

^b Not determined.



 $\Delta G = 17.7 \text{ kJmol}^{-1} (R = CO_2 Me)$ = -2.5 kJmol⁻¹ (R = Ph)

Scheme 4. DFT calculations for reaction of Pt(alkene)(dhpe) with MoHCp(CO)₃ or FeHCp(CO)₂.

²*J*_{PP} = 42.5 Hz), 39.9 (d, ²*J*_{PP} = 42.5 Hz). ¹H NMR (C₆D₆, rt, 300.4 Hz): δ 1.0 (t, ³*J*_{HH} = 8 Hz, 1H, OCH₂CH₃), 1.9–2.1 (m, 4H, PCH₂CH₂P), 3.4 (br, 1H, *cis*-CH₂=CHCO₂Et), 4.0 (br, 1H, CH₂=CHCO₂Et), 4.2 (br, 2H, OCH₂CH₃), 4.6 (1H, br, *trans*-CH₂=CHCO₂Et), 6.9–7.1 (m, 12H, *m*,*p*-*Ph*), 7.5–7.8 (m, 8H, *o*-*Ph*).

Synthesis of heterodinucler hydrideplatinum and -palladium complexes

$(dppe)HPt-MoCp(CO)_3$ (**3a**)

To a solution of Pt(styrene)(dppe) (1) (97.5 mg, 0.139 mmol) in benzene (12 mL) was added a solution of MoHCp(CO)₃ (1a) (17.8 mg, 0.0723 mmol) in benzene (3 mL) at room temperature and the solution was stirred for 30 min at this temperature. Then, the solution was concentrated under reduced pressure, and excess hexane was added to give analytically pure pale yellow powder, which was filtered, washed with hexane, and dried under vacuum at room temperature (yield 84%, 99.7 mg, 0.118 mmol). Recrystallization from benzene/hexane gave yellow cubes of **3a**. Yield 45% (52.4 mg, 0.0624 mmol). Mp 188 °C (dec.). Anal. Found: C, 48.99; H, 3.67%. Calcd for C₃₄H₃₀O₃P₂MoPt: C, 48.64; H, 3.60%. IR (KBr, cm⁻¹): 1817 (vCO), 1925 (vCO), 2041 (vPtH). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 49.0 (d, ²J_{PP} = 3 Hz, ¹J_{PtP} = 3112 Hz 1P, trans to Mo), 50.8 (d, ²J_{PP} = 3 Hz, ²J_{PH} = 201 Hz, ¹J_{PtP} = 2118 Hz, 1P, trans to H). ¹H NMR (C₆D₆, rt, 300.4 Hz): δ δ –2.39 (d, ²J_{PH} = 194 Hz, ¹J_{PtH} = 869 Hz, PtH), 1.8–2.1 (m, 4H, PCH₂CH₂P), 5.25 (s, 5H, Cp), 6.9–7.8 (m, 20H, Ph).

(*dppe*)*HPt*–*WCp*(*CO*)₃ (**3b**)

To a solution of Pt(styrene)(dppe) (1) (97.5 mg, 0.139 mmol) in benzene (12 mL) was added a solution of WHCp(CO)₃ (17.8 mg, 0.0723 mmol) in benzene (3 mL) at room temperature and the solution was stirred for 30 min at this temperature. Then, the solution was concentrated under reduced pressure, and excess hexane was added to give an analytically pure pale yellow powder, which was filtered, washed with hexane, and dried under vacuum at room temperature (yield 84%, 99.7 mg, 0.118 mmol). Recrystalization from benzene/hexane gave orange powder of **3b**. Yield 45% (52.4 mg, 0.0624 mmol). IR (KBr, cm⁻¹): 1817 (vCO), 1925 (vCO), 2041 (vPtH). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 51.33 (d, ²*J*_{PP} = 4 Hz, ¹*J*_{PtP} = 3313 Hz). 52.76 (d, ²*J*_{PP} = 4 Hz, ¹*J*_{PtP} = 2093 Hz). ¹H NMR (C₆D₆, rt, 300.4 Hz): δ -2.92 (d, ²*J*_{PH} = 210 Hz, ¹*J*_{PtH} = 970 Hz, PtH), 1.8–2.1 (m, 4H, PCH₂CH₂P), 5.26 (s, 5H, Cp), 6.9–7.8 (m, 20H, Ph).

$(dppe)Pt(\mu-H)(\mu-CO)Mn(CO)_4$ (**3c**)

To a solution of Pt(styrene)(dppe) (1) (143.8 mg, 0.2061 mmol) in benzene (3 mL) was added a solution of $MnH(CO)_5$ (2c) (90.4 mg, 0.461 mmol) in benzene (1.5 mL) at room temperature and the solution was stirred for 30 min at this temperature. Then, the solution was concentrated under reduced pressure, and excess hexane was added to give analytically pure red powder, which was filtered, washed with hexane, and dried under vacuum at room temperature (yield 93%, 151.4 mg, 0.192 mmol). Recrystallization from benzene/hexane gave red cubes of **3c**. Yield 21% (77.0 mg,



Scheme 5. Relative free energies of $(dhpe)Pt(\mu-H)(\mu-CO)ML_n'$ compared to $(dhpe)HPt-ML_n$.

0.0975 mmol). Anal. Found: C, 48.55; H, 3.67%. Calcd for C₃₁H₂₅MnO₅P₂Pt: C, 47.16; H, 3.19%. IR (KBr, cm⁻¹): 1707 (vCO), 1836 (vCO), 1930 (vCO), 1949 (vCO), 2045 (vPtH). ³¹P{¹H} MMR (toluene-d₈, -80 °C, 161.8 Hz): δ 49.7 (d, ²J_{PP} = 13.2 Hz, ¹J_{PtP} = 2803 Hz), 52.8 (m, ¹J_{PtP} = 2856 Hz). ¹H NMR (toluene-d₈, -80 °C, 399.8 Hz): δ -2.15 (d, ²J_{PH} = 158 Hz, ¹J_{PtH} = 726 Hz, PtH), 1.68 (m, 4H, PCH₂CH₂P), 6.8–7.0 (m, 12H, *m*,*p*-*P*h), 7.51 (m, 2H, *o*-*P*h), 7.62 (m, 2H, *o*-*P*h). ³¹P{¹H} NMR (CD₂Cl₂, -80 °C, 161.8 Hz): δ 44.6 (d, ²J_{PP} = 33 Hz, ¹J_{PtP} = 2303 Hz), 46.1 (d, ²J_{PP} = 33 Hz, ²J_{PH} = 87 Hz, ¹J_{PtP} = 4057 Hz). ¹H NMR (CD₂Cl₂, -80 °C, 399.8 Hz): δ -4.39 (dd, ²J_{PH} = 99.8, 13.2 Hz, ¹J_{PtH} = 547 Hz, PtH), 2.43 (m, 4H, PCH₂CH₂P), 7.3–7.5 (m, 12H, *m*,*p*-*P*h), 7.55 (m, *o*-*P*h), 7.74 (m, *o*-*P*h). ³¹P{¹H</sup> NMR (acetone-d₆, -80 °C, 121.6 Hz): δ 46.6 (d, ²J_{PP} = 30.6 Hz, ¹J_{PtP} = 3846 Hz), 47.1 (d, ²J_{PP} = 30.6 Hz, ¹J_{PtP} = 2404 Hz). ¹H NMR (acetone-d₆, -80 °C, 399.8 Hz): δ -4.13 (dd, ²J_{PH} = 104, 12.5 Hz, ¹J_{PtH} = 555 Hz, PtH), 2.73 (m, 4H, PCH₂CH₂P), 7.4–7.6 (m, 12H, *Ph*). 7.70 (m, 4H, *o*-*Ph*), 7.92 (m, 4H, *o*-*Ph*).

$(dppe)Pt(\mu-H)(\mu-CO)FeCp(CO)$ (3d)

To a solution of Pt(styrene)(dppe) (1) (100.27 mg, 0.14372 mmol) in THF (3 mL) was added a THF solution of FeHCp(CO)₂ (2d) [35], prepared from NaFeCp(CO)₂ and AcOH at -30 °C and the solution was stirred for 1 h at this temperature. Then, the solution was concentrated under reduced pressure, and excess hexane was added to give dark-purple powder, which was filtered, washed with hexane, and dried under vacuum at room temperature. Recrystallization from THF/hexane gave purple powder of 3d. Yield 52% (57.9 mg, 0.0751 mmol). Anal. Found: C. 51.79; H, 4.07%. Calcd for C₃₃H₃₀FeO₂P₂Pt: C, 51.38; H, 3.92%. IR (KBr. cm⁻¹): 1695 (vCO), 1904 (vCO). ³¹P{¹H} NMR (toluene-*d*₈, -80 °C, 161.8 Hz): δ 44.2 (d, ${}^{2}J_{PP} =$ 48 Hz, ${}^{1}J_{PtP} =$ 2238 Hz), 45.7 (d, ${}^{2}J_{PP} =$ 48 Hz, ${}^{1}J_{PtP} =$ 4245 Hz). ${}^{1}H$ NMR (toluene- d_{8} , -80 °C, 399.8 Hz): $\delta - 7.27$ (dd, ²*J*_{PH} = 83.9, 26.8 Hz, ¹*J*_{PtH} = 564 Hz, Pt*H*), 1.83 (m, 4H, PCH₂CH₂P), 4.58 (s, 5H, Cp), 6.93 (m, 12H, m,p-Ph), 7.7 (m, 8H, o-Ph). ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, -80 °C, 161.8 Hz): δ 44.3 (d, ${}^{2}J_{PP} = 44$ Hz, ${}^{1}J_{PtP} = 2243$ Hz), 48.0 (d, ${}^{2}J_{PP} = 44$ Hz, ${}^{1}J_{PtP} = 4193$ Hz). 1 H NMR (CD₂Cl₂, -80 °C, 399.8 Hz): δ -7.93 (dd, $^{2}J_{PH}$ = 83.5, 23.7 Hz, ${}^{1}J_{PtH} = 553$ Hz, PtH), 2.43 (m, 4H, PCH₂CH₂P), 4.63 (s, 5H, *Cp*), 7.41 (m, 12H, *m*,*p*-*Ph*), 7.56 (m, 4H, *o*-*Ph*), 7.73 (m, 4H, *o*-*Ph*).

$(Ph_3P)_2HPt-MoCp(CO)_3$ (**5aa**)

To a solution of $Pt(trans-stilbene)(PPh_3)_2$ (0.0690 g, 0.0621 mmol) in benzene was added MoHCp(CO)_3 (0.0246 g (0.100 mmol)) at room temperature and the solution was stirred for 20 min at this temperature. After removal of the solvent, the residue was washed with hexane and dried under vacuum. Recrystallization from benzene and hexane gave yellow powder of **5aa** in 73% (22.0 mg, 0.0286 mmol). Spectroscopic data of the product was compared with literature [11].

(*Ph*₃*P*)₂*HPt*-*WCp*(*CO*)₃ (**5ba**)

To a solution of Pt(*trans*-stilbene)(PPh₃)₂ (0.0105 g, 0.012 mmol) in benzene was added WHCp(CO)₃ (0.0040 g, 0.012 mmol) at room temperature and the solution was stirred for 30 min at this temperature. After addition of hexane to the reaction mixture, this solution was stored at $-30 \degree$ C overnight to give yellow needles. This needles were dried under vacuum. Yield 91% (0.0118 g, 0.011 mmol). ³¹P{¹H} NMR (121.6 MHz, rt, toluene-*d*₈): δ 27.6 (s, ¹*J*_{PtP} = 3615 Hz), 32.5 (s, ¹*J*_{PtP} = 2625 Hz). ¹H NMR (300.4 MHz, rt, toluene-*d*₆): δ -6.75 (d, 1H, ¹*J*_{PH} = 166 Hz, ¹*J*_{PtH} = 681 Hz, PtH), 5.18 (s, 5H, *Cp*), 6.88–7.65 (m, 30H, *Ph*).

(Ph₂MeP)₂HPt-MoCp(CO)₃ (**5ab**)

To a solution of $Pt(trans-stilbene)(PPh_2Me)_2$ (0.0267 g, 0.0479 mmol) in benzene was added $MoHCp(CO)_3$ (0.0190 g,

0.0772 mmol) at room temperature and the solution was stirred for 10 min at this temperature. After removal of the solvent, the residue was washed with hexane and dried under vacuum. Recrystallization from benzene and hexane gave yellow powder of **5ab** in 59% (20.4 mg, 0.0284 mmol). IR (KBr, cm⁻¹): 1811 (vCO), 1915 (vCO), 2110 (vPtH). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 10.6 (d, ²*J*_{PP} = 11.0 Hz, ¹*J*_{PtP} = 3564 Hz), 13.8 (d, ²*J*_{PP} = 11.0 Hz, ¹*J*_{PtP} = 2451 Hz). ¹H NMR (C₆D₆, rt, 300.4 Hz): δ -5.99 (d, ²*J*_{PH} = 176 Hz, ¹*J*_{PtH} = 714 Hz, 1H, PtH), 1.49 (m, 3H, PMe), 1.97 (m, 3H, PMe), 5.26 (s, 5H, Cp), 6.98–7.60 (m, 20H, Ph).

(PhMe₂P)₂HPt-MoCp(CO)₃ (**5ac**)

To a solution of Pt(methyl acrylate)(PPhMe₂)₂ (0.0333 g, 0.0597 mmol) in benzene was added MoHCp(CO)₃ (0.0170 g, 0.0691 mmol) at room temperature and the solution was stirred for 15 min at this temperature. After removal of the solvent, the residue was washed with hexane and dried under vacuum. Recrystallization from benzene and hexane gave yellow powder of **5ac** in 95% yield. IR (KBr, cm⁻¹): 1811 (vCO), 1915 (vCO), 2110 (vPtH). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ -1.15 (d, ²J_{PP} = 11.0 Hz, ¹J_{PtP} = 2260 Hz), -5.66 (s, ²J_{PP} = 36.0 Hz, ¹J_{PtP} = 3531 Hz) ¹H NMR (C₆D₆, rt, 300.4 Hz): δ -6.12 (dd, ²J_{PH} = 186, 6.3 Hz, ¹J_{PtH} = 748 Hz, 1H, PtH), 1.18 (d, ²J_{PH} = 9.9 Hz, ³J_{PtH} = 42.0 Hz, 6H, *Me*), 1.50 (d, ²J_{PH} = 8.1 Hz, 6H, *Me*), 5.32 (s, 5H, *Cp*), 6.96-7.52 (m, 10H, *Ph*).

$(dppe)Pd(\mu-H)(\mu-CO)MoCp(CO)_2$ (7a)

To a solution of Pd(ethyl acrylate)(dppe) (6) (38.5 mg, 0.0636 mmol) in THF (ca. 1 mL) was added MoHCp(CO)₃ (17.8 mg, 0.0723 mmol) at -30 °C and the solution was stirred for 30 min at this temperature. Then hexane (ca. 20 mL) was added to precipitate analytically pure yellow powder of $(dppe)Pd(\mu-H)(\mu-CO)$ $MoCp(CO)_2$ (7a), which was filtered, washed with hexane, and dried under vacuum at room temperature (yield 94%, 46.1 mg, 0.0601 mmol). Recrystallization from toluene gave orange powder of 7a. Yield 45% (22.0 mg, 0.0286 mmol). Anal. Calcd for C₃₆H₃₄MoO_{3.5}P₂Pd: C, 56.50; H, 4.86. Found: C, 55.77, H, 5.13. Mp 125-128 °C (dec.). Molar electric conductivity Λ $(THF, -21 \circ C) = 0.49 \text{ S cm}^2 \text{ mol}^{-1}$. IR (KBr, cm⁻¹): 1703 (vCO), 1852 (vCO), 1936 (vCO). ${}^{31}P{}^{1}H{}$ NMR (toluene- d_{8} , -80 °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} , -80 °C, 300.4 Hz): δ -4.64 (dd, ${}^{2}J_{PH}$ = 80.5, 9.0 Hz, 1H, PdH), 2.3-2.4 (m, 4H, PCH₂CH₂P), 5.25 (s, 5H, Cp), 7.40-7.65 (m, 12H, m,p-Ph), 7.70-7.95 (m, 8H, o-Ph).

$(dppe)Pd(\mu-H)(\mu-CO)WCp(CO)_2$ (7b)

To a solution of Pd(styrene)(dppe) (**6**) (73.4 mg, 0.121 mmol) in THF (6 mL) was added WHCp(CO)₃ (60.4 mg, 0.181 mmol) at -30 °C and the solution was stirred for 1 h at this temperature. Then, the solution was concentrated under reduced pressure at -30 °C, and excess hexane was added to give analytically pure yellow powder of **7b**. Yield 90% (95.6 mg, 0.109 mmol). IR (KBr, cm⁻¹): 1710 (vCO), 1851 (vCO), 1926 (vCO), 1731 (vPdH). ³¹P{¹H} NMR (toluene- d_8 , -80 °C, 121.6 Hz): δ 25.8 (br), 27.8 (br). ¹H NMR (toluene- d_8 , -80 °C, 300.4 Hz): δ -5.4 (d, ² $J_{PH} = 63.4$ Hz, 1H, PdH), 2.0–2.1 (m, 4H, PCH₂CH₂P), 4.7 (s, 5H, Cp), 6.7–7.1 (m, 12H, *m,p-Ph*), 7.4–7.6 (m, 8H, *o-Ph*).

$(dppe)Pd(\mu-H)(\mu-CO)Mn(CO)_4$ (**7c**)

To a solution of Pd(styrene)(dppe) (**6**) (45.0 mg, 0.0739 mmol) in THF (3 mL) was added MnH(CO)₅ (42.2 mg, 0.215 mmol) at -30 °C and the solution was stirred for 1 h at this temperature. Then, the solution was concentrated under reduced pressure at -30 °C, and excess hexane was added to give analytically pure orange powder of **7c**. Yield 90% (46.6 mg, 0.0665 mmol). Anal. Calcd for C₃₁H₂₅MnO₅P₂Pd: C, 53.13; H, 3.60. Found: C, 52.72, H, 3.75. IR (KBr,

cm⁻¹): 1749 (vCO), 1919 (vCO), 1940 (vCO), 1956 (vCO), 2054 (vCO). ³¹P{¹H} NMR (toluene- d_8 , -80 °C, 121.6 Hz): δ 25.1 (br). ¹H NMR (toluene- d_8 , -80 °C, 300.4 Hz): δ -6.05 (vt, ² J_{PH} = 23.7 Hz, 1H, PdH), 1.68–1.72 (m, 4H, PCH₂CH₂P), 6.9–7.1 (m, 12H, *m*, *p*-*Ph*), 7.3–7.6 (br, 8H, *o*-*Ph*).

Reactions of heterodinucler hydrideplatinum and -palladium complexes with alkynes and alkenes

Reaction of heterodinucler hydrideplatinum—molybdenum complex (**3a**) *with methyl propiolate*

A typical procedure for reaction of **3a** with methyl propiolate is given. (a) NMR reaction: C_6D_6 (0.5 mL) was vacuum-transferred to an NMR tube (5 mm $\phi \times$ 180 mm) containing **3a** (11.6 mg, 0.0138 mmol) and ferrocene. After addition of methyl propiolate (17 µL, 0.014 mmol), the sample tube was placed in NMR probe, and ¹H and ³¹P{¹H} NMR spectra were periodically measured to follow the reaction. (b) Reaction in Schlenk tube: To a solution of (dppe) HPt-MoCp(CO)₃ (**3a**) (83.3 mg, 0.0992 mmol) in benzene (10 mL) was added a solution of methyl propiolate (18.3 µL, 0.198 mmol) at room temperature and the solution was stirred for 48 h at this temperature. After removal of the solvent, recrystallization from benzene/hexane gave orange crystal of (dppe)Pt{µ-C(CO₂Me)= CH₂}(µ-CO)MoCp(CO) (12a). Yield 69% (61.2 mg, 0.0683 mmol). Mp 246 °C (dec.). Molar electric conductivity Λ (in THF at rt): 0.0110 S cm² mol⁻¹. Anal. Found: C, 50.90; H, 3.76%. Calcd for C₃₇H₃₄MoO₄P₂Pt: C, 49.62; H, 3.83%. IR (KBr, cm⁻¹): 1663 (vCO), 1731 (νCO), 1870 (νCO). ³¹P{¹H} NMR (CD₂Cl₂, rt, 121.6 Hz): δ 46.54 $(d, {}^{2}J_{PP} = 36 \text{ Hz}, {}^{1}J_{PtP} = 3258 \text{ Hz}), 53.86 (d, {}^{2}J_{PP} = 3.6 \text{ Hz})$ (d, $J_{PP} = 2772 \text{ Hz}$). ¹H NMR (CDCl₃, rt, 300.4 Hz): δ 2.2–2.5 (m, 4H, PCH₂CH₂P), 2.58 (d, ⁴J_{PH} = 6.0 Hz, ³J_{PtH} = 34 Hz, 1H, =CH (Pt *cis*)), 3.03 (s, 3H, CH₃), 3.29 (dd, ⁴J_{PH} = 10, 1.5 Hz, ³J_{PtH} = 116 Hz, 1H, =CH (Pt trans)), 5.04 (s, 5H, Cp), 7.3-7.8 (m, 20H, Ph). ¹³C{¹H} NMR $(CD_2Cl_2, rt, 75.3 Hz)$: δ 139.20 (d, $J_{PC} = 80 Hz, C=CPt$), 38.57 (s, $J_{PtC} = 16$ Hz, C=CPt), 50.57 (s, CO₂Me), 179.22 (s, CO₂Me), 28.71 (d, ${}^{J}_{JPC} = 35$ Hz, ${}^{2}_{JPC} = 13$ Hz, PCH₂CH₂P), 31.39 (d, ${}^{1}_{JPC} = 36$, ${}^{2}_{JPC} = 14$ Hz, PCH₂CH₂P), 127–135 (m, *Ph*), 236.32 (m, CO(terminal)), 245.88 (d, ${}^{2}J_{PC} = 23$ Hz, CO(bridging)).

(*dppe*)Pt{µ–CPh=CH₂}(µ-CO)MoCp(CO) (**12b**)

Yield 45%. Mp 234 °C (dec.). Molar electric conductivity Λ (in THF at rt): 0.0127 S cm² mol⁻¹. Anal. Found: C, 54.46; H, 4.03%. Calcd for C₄₁H₃₆MoO₂P₂Pt: C, 53.89; H, 3.97%. IR (KBr, cm⁻¹): 1723 (vCO), 1858 (vCO). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 49.78 (d, ²*J*_{PP} = 4 Hz, ¹*J*_{PtP} = 3313 Hz), 51.60 (d, ²*J*_{PP} = 4 Hz, ¹*J*_{PtP} = 2113 Hz). ¹H NMR (CDCl₃, rt, 300.4 Hz): δ 2.1–2.4 (m, 4H, PCH₂CH₂P), 2.89 (d, ⁴*J*_{PH} = 6.9 Hz, ³*J*_{PtH} = 25 Hz, 1H, =CH (Pt *cis*)), 3.35 (d, ⁴*J*_{PH} = 13 Hz, ³*J*_{PtH} = 119 Hz, 1H, =CH (Pt *trans*)), 4.64 (s, 5H, *Cp*), 6.6–8.0 (m, 25H, *Ph*).

 $(dppe)Pt{\mu-C(C_{6}H_{4}Me-p)=CH_{2}(\mu-CO)MoCp(CO) (12c)}$

IR (KBr, cm⁻¹): 1724 (vCO), 1858 (vCO). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 44.53 (s, ¹J_{PtP} = 3256 Hz), 51.15 (s ¹J_{PtP} = 2701 Hz). ¹H NMR (C₆D₆, rt, 300.4 Hz): δ 1.8–2.1 (m, 4H, PCH₂CH₂P), 2.14 (s, 3H), 3.38 (d, ⁴J_{PH} = 6.3 Hz, ³J_{PtH} = 24 Hz, 1H, =CH (Pt *cis*)), 3.60 (d, ⁴J_{PH} = 14 Hz, ³J_{PtH} = 119 Hz, 1H, =CH (Pt *trans*)), 4.69 (s, 5H, *Cp*), 6.6–8.0 (m, 24H, *Ph*).

$(dppe)Pd\{\mu-CPh=CH_2\}(\mu-CO)MoCp(CO)$ (**14b**)

³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 35.2 (d, ²*J*_{PP} = 29.8 Hz), 36.7 (d, ²*J*_{PP} = 29.8 Hz). ¹H NMR (C₆D₆, rt, 300.4 Hz): δ 1.6–2.2 (m, 4H, PCH₂CH₂P), 2.73 (dd, ⁴*J*_{PH} = 11.7 Hz, ²*J*_{HH} = 1.8 Hz, 1H, =CHH), 3.12 (ddd, ⁴*J*_{PH} = 8.1 Hz, 1.8 Hz, ²*J*_{HH} = 2.7 Hz, 1H, =CHH), 5.45 (s, 5H, Cp), 7.3–7.7 (m, 25H, Ph).

$(dppe)Pd\{\mu-(MeO_2C)C=C(CO_2Me)\}(\mu-CO)MoCp(CO)$ (14e)

Anal. Found: C, 54.39, H, 4.37%. Calcd for $C_{39}H_{36}MoO_6P_2Pd$: C, 54.15; H, 4.19%. IR (KBr, cm⁻¹): 1692 (vCO), 1748 (vCO), 1905 (vCO). ³¹P{¹H} NMR (C₆D₆, rt, 121.6 Hz): δ 38.17 (d, ²J_{PP} = 41.3 Hz), 45.79 (d, ²J_{PP} = 41.3 Hz). ¹H NMR (C₆D₆, rt, 300.4 Hz): δ 1.71–1.78 (m, 4H, PCH₂CH₂P), 3.06 (s, 3H, CO₂Me), 3.51 (s, 3H, CO₂Me), 3.40 (s, 1H, = CHCO₂Me), 5.44 (s, 5H, *Cp*), 7.0–7.2 (m, 12H, *m,p-Ph*), 7.5–7.8 (m, 8H, *o-Ph*). ³¹P{¹H} NMR (CD₂Cl₂, rt, 121.6 Hz): δ 39.75 (d, ²J_{PP} = 42 Hz), 47.25 (d, ²J_{PP} = 42 Hz). ¹H NMR (CD₂Cl₂, rt, 300.4 Hz): δ 2.06–2.41 (m, 4H, PCH₂CH₂P), 2.67 (d, *J_{PH}* = 7.8 Hz, 1H, = CHCO₂Me), 2.88 (s, 3H, CO₂Me), 3.45 (s, 3H, CO₂Me), 5.19 (s, 5H, *Cp*), 7.3–7.5 (m, 12H, *m,p-Ph*), 7.6–7.7 (m, 8H, *o-Ph*).

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Appendix A. Supplementary data

CCDC No. 1041348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.04.048.

References

- (a) P. Braunstein, L.A. Oro, P.R. Raith (Eds.), Metal Clusters in Chemistry, WileyVCH, 1999 and references cited therein;
 (b) D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster
 - Complexes, VCH, 1990 and references cited therein; (c) R.D. Adams, F.A. Cotton (Eds.), Catalysis by Polynuclear Metal Cluster
 - Complexes, Wiley-VCH, 1998 and references cited therein;
- (d) M. Shibasaki, Y. Yamamoto (Eds.), Multimetallic Catalysts in Organic Synthesis, Wiley-VCH, 2004 and references cited therein.
- [2] R.A. Sanchez-Delgado, Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrigenation Reactions, Kluwer Academic Publishers, 2002 and references cited therein.
- [3] (a) J.H. Jinfelt, in: J.R. Anderson, M. Boudard (Eds.), Catalysis-science and Technology, Springer-Verlag, Berlin, 1981;
 (b) J. Biswas, G.M. Bickle, P.G. Gray, D. Do, J. Barbier, J. Catal. Rev. Sci. Eng. 30
- (b) J. Biswas, G.M. Bickle, P.G. Gray, D. Do, J. Barbier, J. Catal. Rev. Sci. Eng. 30 (1988) 161;
- (c) V.K. Shum, J.B. Butt, W.M.H. Sachtler, J. Catal. 96 (1985) 371;
- (d) C. Kim, G.A. Somorjai, J. Catal. 134 (1992) 179.
- 4] Y. Ishii, K. Miyashita, K. Kamita, M. Hidai, J. Am. Chem. Soc. 119 (1997) 6448.
- [5] M.A. Rida, A.K. Smith, J. Mol. Catal. 202 (2003) 87.
 [6] N. Yoshikai, M. Yamanaka, I. Ojima, K. Morokuma, E. Nakamura, Organome-
- tallics 25 (2006) 3867.
- [7] L. Li, M.V. Metz, H. Li, M.-C. Chen, T. Marks, L. Liable-Sands, A. Rheingold, J. Am. Chem. Soc. 124 (2002) 12725.
- [8] S.K. Mandal, H.W. Roesky, Acc. Chem. Res. 43 (2010) 248.
- [9] M.L. Man, K.C. Lam, W.N. Sit, S.M. Ng, Z. Zhou, Z. Lin, C.P. Lau, Chem. Eur. J. 12 (2006) 1004.
- [10] R.D. Adams, Chapter 8, in: R.D. Adams, F.A. Cotton (Eds.), Catalysis by Di- and Polynuclear Metal Cluster Complexes, Wiley-VCH, 1998, p. 283. and references cited therein.
- [11] (a) O. Bars, P. Braunstein, Angew. Chem. 94 (1982) 319;
 - (b) P. Braunstein, G.L. Geoffroy, B. Metz, Nouv. J. Chimo. 9 (1986) 221;
 (c) O. Bars, P. Braunstein, G.L. Geoffroy, B. Metz, Organometallics 5 (1986) 2021.
- [12] (a) S. Komiya, T. Yasuda, A. Fukuoka, M. Hirano, J. Mol. Catal. A Chem. 159 (2000) 63;
 - (b) T. Yasuda, A. Fukuoka, M. Hirano, S. Komiya, Chem. Lett. (1998) 29.
- [13] This concept of oxidative-addition of a M-H bond to a zero-valent Pt fragment was already described in the reference 11.

- [14] A. Kuramoto, K. Nakanishi, T. Kawabata, N. Komine, M. Hirano, S. Komiya, Organometallics 25 (2006) 311.
- [15] (a) R.D. Adams, B. Captain, L. Zhu, J. Am. Chem. Soc. 128 (2006) 13672; (b) R.D. Adams, B. Captain, E. Trufan, L. Zhu, J. Am. Chem. Soc. 129 (2007) 7545.
- [16] The pKa value for 2b is reported to be 16.1 in acetonitrile. Although pKa of the **2f** is not reported to our best knowledge, that for the PMe₃ analogue of **2f** is reported to 26.6. (a) A.F. Hill, in: Organotransition Metal Chemistry, The Royal Society of Chemistry, Cambridge, 2002. The pKa values for some hydride complexes: (b) H.W. Walker, R.G. Pearson, P.C. Ford, J. Am. Chem. Soc. 105 (1983) 1179:
 - (c) X.-J. Qi, L. Liu, Y. Fu, Q.-X. Guo, Organometallics 25 (2006) 5879.
- [17] K. Nakamoto, in: Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bio-inorganic Chemistry, fifth ed., Wiley, New York, 1997, p. 291.
 [18] T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335.
- [19] The crystallographic details are deposited in the Supporting Information of the previous communication (ref. 13).
- [20] S. Komiya, S. Muroi, M. Furuya, M. Hirano, J. Am. Chem. Soc. 122 (2000) 170.
 [21] The X-ray analysis shows the Pt and Mn centers in 3c having a near-perfect
- square plane and octahedral geometries, respectively. This means the Pt and Mn have the dsp^2 and d^2sp^3 hybridizations. We, therefore, prefer not to draw the Pt-Mn bond despite the close Pt-Mn distance.
- [22] C. Tolman, Chem. Rev. 77 (1977) 313.
- [23] (a) A. Jutand, K. Hii, M. Thornton-Pett, J.M. Brown, Organometallics 18 (1999) 5367·
 - (b) N. Komine, H. Hoh, M. Hirano, S. Komiya, Organometallics 19 (2000) 5251.

- [24] The variable temperature NMR spectra of 3c in CD₂Cl₂ are illustrated in the supporting information.
- [25] These dynamic behaviors in both of the ¹H and ³¹P{¹H} NMR spectra indicate the inequivalent two phosphorus nuclei becoming equivalent to each other upon heating. Therefore, this dynamic process has no relation to the equilibrium between the bridged and non-bridged complexes.
- [26] gNMR for Windows (5.0.6.0).
- [27] (a) Y. Obora, Y. Tsuji, Y. Nishiyama, M. Ebihara, T. Kawamura, J. Am. Chem. Soc. 118 (1996) 10922:
 - (b) Y.K. Tsuji, K. Nishiyama, S. Hori, M. Ebihara, T. Kawamura, Organometallics 17 (1998) 507:
 - (c) F. Ozawa, J. Kamite, Organometallics 17 (1998) 5630.
- N. Komine, T. Hirota, M. Hirano, S. Komiya, Organometallics 27 (2008) 2145. [28] [29] Such higher reactivity of 3d than 3a toward ethyl acrylate is probably due to
- the intrinsic thermodynamic stability of the hydridoiron(II) 2d because this is a reversible reaction.
- [30] N. Komine, A. Kuramoto, K. Nakanishi, M. Hirano, S. Komiya, Top. Catal. 57 (2014) 960.
- T. Yasuda, A. Fukuoka, M. Hirano, S. Komiya, Chem. Lett. 27 (1998) 29. [31] The crystallographic details are deposited in the Supporting Information of [32]
- the previous communication (ref. 29). [33] N.P. Rath, V.S.S. Kumar, M. Janka, G.K. Anderson, Inorg. Chim. Acta 360 (2007) 2997.
- T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 104 (1956) 1956. [34]
- [35] E.O. Fischer, Inorg. Synth. 7 (1963) 136.
 [36] R.B. King, F.G.A. Stone, Inorg. Synth. 7 (1963) 198.
- [37] T.A. Shackleton, M.C. Baird, Organometallics 8 (1989) 225.