Hydrogen Transfer in Pt-Mo Heterodinuclear Hydride Complexes Promoted by Alkynes

Toshiyuki Yasuda, Atsushi Fukuoka,† Masafumi Hirano, and Sanshiro Komiya*
Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology,
2-24-16 Nakacho, Koganei, Tokyo 184

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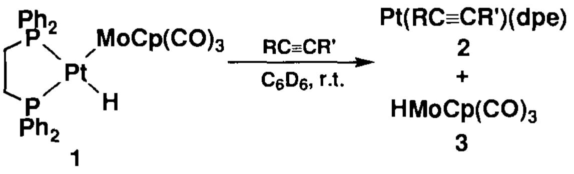
Reactions of a Pt-Mo heterodinuclear hydride complex, (dpe)HPt-MoCp$(CO)_3$ with alkynes at room temperature lead to facile reductive elimination giving HMoCp$(CO)_3$ accompanied by the formation of Pt(alkyne)(dpe). When terminal alkynes are employed, further Markovnikov addition of HMoCp$(CO)_3$ to the coordinated alkyne takes place to give new heterodinuclear alkenyl complexes (dpe)(μ-H_2C=CR)Pt-MoCp(μ-CO)(CO).

Syntheses and chemial reactivities of heterodinuclear complexes having M-R or M-H bonds are of particular interests in relation to the cooperative effects in various catalysis promoted by mixed metal systems.[1] We previously reported the synthesis of a series of platinum or palladium-containing heterodinuclear compexes L_2RM-M'L_n (L_2 = cod, dpe; R = alkyl, aryl; M = Pt, Pd; M'L_n = MoCp$(CO)_3$, WCp$(CO)_3$, Mn$(CO)_5$, FeCp$(CO)_2$, Co$(CO)_4$), where enhanced reactivities in alkyl transfer from M to M' (reductive elimination), ß-H elimination and CO insertion probably due to their cooperative effect were observed.[2] For the complexes having an ethyl group (dpe)EtPt-MoCp$(CO)_3$, facile and clean ß-H elimination reaction took place without Pt-Mo bond cleavage to give ethylene and the corresponding heterodinuclear hydride complexes (dpe)HPt-MoCp$(CO)_3$.[3] We now report alkyne assisted hydrido transfer in Pt-Mo heterodinuclear hydrido complexes from Pt to Mo. Further reaction of coordinated alkyne with the hydride is also described.

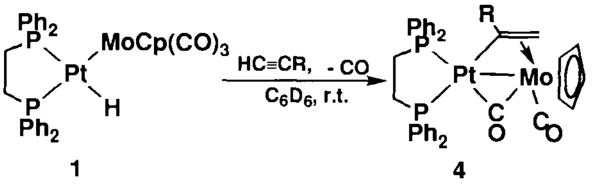
Reactions of (dpe)HPt-MoCp$(CO)_3$ (**1**) with alkyne such as $MeO_2CC{\equiv}CCO_2Me$, PhC≡CPh, $HC{\equiv}CCO_2Me$, HC≡CPh, and HC≡C(*p*-tolyl) (1 equiv.) in C_6D_6 at room temperature induced smooth hydride transfer from Pt to Mo to give HMoCp$(CO)_3$ and Pt(alkyne)(dpe) (eq. 1).



(1)

The reactions are also regarded as reductive elimination of the hydrido and Mo moieties at Pt.[4] Results are summarized in Table 1. The reactions are similar to our previous report on alkyl transfer in heterodinuclear organometallic complexes (cod)MePt-WCp$(CO)_3$.[2a, d] No reactions were observed when alkynes having electron-donating groups such as MeC≡CPh and $HC{\equiv}CC_3H_7$ were employed as reactants. The results suggest the importance of coordination of π-acidic alkyne to Pt in this process.

In the reactions of **1** with terminal alkyne such as $HC{\equiv}CCO_2Me$, HC≡CPh, and HC≡C(tolyl), further Markovnikov addition of HMoCp$(CO)_3$ to the coordinated alkyne in Pt(alkyne)(dpe) took place to give new heterodinuclear alkenyl complexes (dpe)(μ-H_2C=CR)Pt-MoCp(μ-CO)(CO) (R = CO_2Me (**4a**), Ph (**4b**), *p*-tolyl (**4c**)) in 48 h at room temperature (eq. 2).



(2)

Table 1. Reactions of **1** with alkynes[a]

alkynes	time (h)	yield (%) [b]		
		2	3	4
$MeO_2CC{\equiv}CCO_2Me$	0.75	96	83	0
PhC≡CPh	48	45	36	0
MeC≡CPh	48	0	0	0
HC≡CPh	0.5	8	8	2
	48	0	0	82
$HC{\equiv}CCO_2Me$	0.5	89	70	3
	48	0	0	63
HC≡C(*p*-tolyl)	48	0	0	96
$HC{\equiv}CC_3H_7$	48	0	0	0

[a] In C_6D_6 at r. t.. [b] Estimated by ^1H NMR.

The process is successive, since formation of HMoCp$(CO)_3$ and Pt(alkyne)(dpe) is confirmed at the initial stage of the reactions by NMR. Complexes **4a** or **4b** were purified by recrystallization from THF/hexane or benzene/hexane and were characterized by IR, NMR and elemental analysis as well as by chemical reactions.[5] The low value of molar electric conductivity (Λ = 0.0110 Scm^2mol^{-1}) in THF suggests that **4a** is not an ionic complex but a neutral one having a Pt-Mo bond. IR spectrum of **4a** shows ν(CO) bands at 1870 and 1731 cm^{-1}, suggesting the existence of both terminal and bridging carbonyls. Carbonyl stretching band due to the methoxycarbonyl group appeared at 1663 cm^{-1}. $^{31}P\{^1H\}$ NMR spectrum of **4a** shows one pair of doublets indicating the unsymmetrical geometry of the dpe ligand at the square planar Pt. In the ^1H NMR, two doublets having coupling with one of the ^{31}P nuclei with Pt satellite are observed at 2.54 and 3.24 ppm and are assigned as terminal methylene protons whose geminal coupling constant is negligible.

Molecular structure of **4a** has been determined by X-ray structure analysis and the ORTEP drawing is depicted in Figure 1.[6] Geometry at Pt is essentially square planar consisting of dpe, vinyl and bridging carbonyl ligands with an additional Pt-Mo bond (Pt-Mo = 2.806(5) Å). Pt-P1 bond distance (2.28(1) Å) is slightly longer than that of Pt-P2 (2.22(1) Å) indicating larger trans influence of the vinylic group than that of the bridging carbonyl. The vinylic C1=C2 moiety coordinates to Mo by an η^2

fashion (Mo-C1 = 2.20(5), Mo-C2 = 2.27(4) Å). One of the carbonyls acts as a bridging ligand between Pt and Mo as expected by IR.

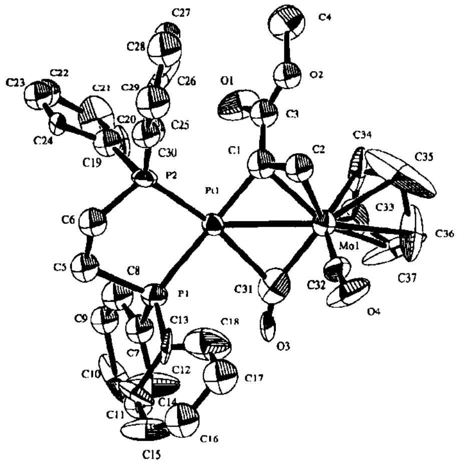
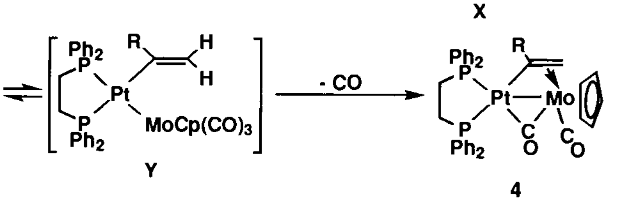


Figure 1. Molecular structure of (dpe)(μ-$H_2C{=}CCO_2Me$)Pt-MoCp(CO)(μ-CO) (**4a**). Selected bond distances (Å): Pt-Mo 2.806(5), Pt-C1 1.95(4), C1-Mo 2.20(5), C2-Mo 2.27(4).

A possible mechanism for the present hydrido transfer and hydride addition reactions has been proposed. As shown in Scheme 1, initial coordination of acetylene to Pt seems to be essential to induce hydrido transfer (reductive elimination at Pt). The acetylene having electron withdrawing substituents facilitates the reaction. Such a trend is similar to those observed in alkyl transfer at heterodinuclear complexes $L_nRPt\text{-}ML'_m$ and in reductive elimination from d^8 organotransition metal complexes.[2] Further Markovnikov addition of $HMoCp(CO)_3$ to the coordinated acetylene takes place to give an intermediate olefin complex **X**, which would further rearrange to a heterodinuclear vinylplatinum-molybdenum intermediate **Y** by oxidative addition.

Scheme 1. A plausible mechanism of formation of **4**.



1, 2, 3, X, Y, 4

The initial addition reaction must occur only to the coordinated acetylene, since no reaction of the hydride with free acetylene was confirmed by the independent experiment under the same reaction conditions. Steric congestion in acetylene may also be an important factor in this process, since disubstituted acetylenes are unreactive toward the addition. It is interesting to note that the present regioselectivity of the hydride additoin is reverse to that observed in the reaction of **3** with cyanoacetylene.[7] During the reaction one of three carbonyl ligands is removed and instead the olefinic C=C bond coordinates to Mo. The present hydride (or alkyl) migration between two different metals may reflect the mobility of hydrogen atom on the heterogeneous metal catalyst surface at the molecular level. Further mechanistic study is now in progress.

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References and Notes

† Present address: Catalysis Research Center, Hokkaido University, Sapporo, Hokkaido 060.

1 For recent reviews: D. W. Stephan, *Cood. Chem. Rev.*, **95**, 41 (1989); M.J. Chetcuti, "Comprehensive Organometallic Chemistry II," ed by R. D. Adams ed., Pergamon Press, Oxford (1995), vol 10.

2 a) S. Komiya and I. Endo, *Chem. Lett.*, **1988**, 1709; b) K. Miki, N. Kasai, I. Endo, and S. Komiya, *Bull. Chem. Soc. Jpn.*, **62**, 4033 (1989); c) A. Fukuoka, T. Sadashima, T. Sugiura, X. Wu, Y. Mizuho, and S. Komiya, *J. Organomet. Chem.*, **473**, 139 (1994); d) A. Fukuoka, T. Sadashima, I. Endo, N. Ohashi, Y. Kambara, T. Sugiura, K. Miki, N. Kasai, and S. Komiya, *Organometallics*, **13**, 4033 (1994); e) A. Fukuoka, S. Fukagawa, M. Hirano, and S. Komiya, *Chem. Lett.*, **1997**, 377.

3 A. Fukuoka, T. Sugiura, T. Yasuda, T. Taguchi, M. Hirano, and S. Komiya, *Chem. Lett.*, **1997**, 329.

4 Such reductive elimination between hydrido and transition metal has been proposed by Braunstein, but the reactions are not clean enough due to many side reactions: O. Bars, P. Braunstein, G. L. Geoffroy, and B. Metz, *Organometallics*, **5**, 2021 (1986).

5 **4a**: Orange crystals from THF/hexane; yield 43%; mp 246 °C (dec.); molar electric conductivity Λ (THF, r.t.) = 0.0110 Scm^2mol^{-1}. Anal. Found: C, 50.90; H, 3.76%. Calcd for $C_{37}H_{34}O_4P_2MoPt$: C, 49.61; H, 3.83 %. IR (KBr, cm^{-1}): 1870 (νCO(terminal)), 1731 (νCO(bridging)), 1663 (νCO(CO_2Me)). ^1H NMR (CD_2Cl_2): δ 2.2-2.5 (m, 4H, dpe CH_2), 2.54 (d, $^4J_{P\text{-}H}$ = 6.6 Hz, $^3J_{Pt\text{-}H}$ = 33 Hz, 1H, $=CH_2$), 3.06 (s, 3H, CO_2Me), 3.24 (d, $^4J_{P\text{-}H}$ = 11 Hz, $^3J_{Pt\text{-}H}$ = 117 Hz, 1H, $=CH_2$), 4.98 (s, 5H, *Cp*), 7.3-7.8 (m, 20H, dpe *Ph*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.[illegible] (d, $^2J_{P\text{-}P}$ = 2.4 Hz, $J_{Pt\text{-}P}$ = 3255 Hz), 53.3 (d, $^2J_{P\text{-}P}$ = 2.4 Hz, $J_{Pt\text{-}P}$ = 2760 Hz). **4b**: Orange powder from benzene/hexane; yield 45%; mp 234 °C (dec.); molar electric conductivity Λ (THF, r.t.) = 0.0127 Scm^2mol^{-1}. Anal. Found: C, 53.90; H, 3.97 %. Calcd for $C_{41}H_{36}O_2P_2MoPt$: C, 54.46; H, 4.03 %. IR (KBr, cm^{-1}): 1858 (νCO(terminal)), 1723 (νCO(bridging)). ^1H NMR ($CDCl_3$): δ 2.1-2.4 (m, 4H, dpe CH_2), 2.89 (d, $^4J_{P\text{-}H}$ = 6.9 Hz, $^3J_{Pt\text{-}H}$ = 25 Hz, 1H, $=CH_2$), 3.35 (d, $^4J_{P\text{-}H}$ = 13 Hz, $^3J_{Pt\text{-}H}$ = 119 Hz, 1H, $=CH_2$), 4.64 (s, 5H, *Cp*), 6.6-8.0 (m, 25H,*Ph*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 45.0 (br, $J_{Pt\text{-}P}$ = 3255 Hz), 51.6 (br, $J_{Pt\text{-}P}$ = 2708 Hz). **4c**: yield(by NMR) 96%; **4c** was characterized by IR and NMR spectroscopy. IR (KBr, cm^{-1}): 1858 (νCO(terminal)), 1724 (νCO(bridging)). ^1H NMR (C_6D_6): δ 1.8-2.1 (m, 4H, dpe CH_2), 2.14 (s, 3H, *Me*) 3.38 (d, $^4J_{P\text{-}H}$ = 6.3 Hz, $^3J_{Pt\text{-}H}$ = 24 Hz, 1H, $=CH_2$), 3.60 (d,$^4J_{P\text{-}H}$ = 14 Hz, $^3J_{Pt\text{-}H}$ = 119 Hz, 1H, $=CH_2$), 4.69 (s, 5H, *Cp*), 6.6-8.0 (m, 24H, *Ph*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 44.5 (br, $J_{Pt\text{-}P}$ = 3256 Hz), 51.2 (br, $J_{Pt\text{-}P}$ = 2701 Hz).

6 Crystal data for **4a**: $C_{37}H_{34}O_4P_2MoPt$, FW = 895.65, monoclinic, $P2_1/n$, a = 11.893(4), b = 15.350(5), c = 19.208(6) Å, β = 102.47(3)°, V = 3423(1) Å^3, Z = 4, D_{calc} = 1.737 gcm^{-3}, R = 0.073, R_w = 0.064, 1666 unique reflections with $I > 3\sigma(I)$.

7 H. Scordia, R. Kergoat, M. M. Kubicki, and J. E. Guerchais, *Organometallics*, **2**, 1681, (1983).