Enhancement of β-Hydrogen Elimination Reaction on Platinum-containing Heterodinuclear Complexes

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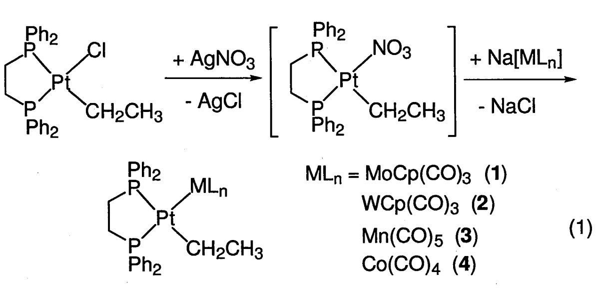
Novel heterodinuclear ethylplatinum complexes with a 1,2-bis(diphenylphosphino)ethane (dpe) ligand (dpe)EtPt-ML$_n$ (ML$_n$ = MoCp(CO)$_3$, WCp(CO)$_3$, Mn(CO)$_5$, Co(CO)$_4$) have been synthesized and characterized. The dinuclear complexes show higher activity for ß-H elimination reaction than a mononuclear PtEtCl(dpe), and in the case of Pt-Mo and Pt-W complexes the reaction proceeds with retention of the dinuclear structure.

The chemistry of organoheterodinuclear complexes has been a topic of recent interest, since they may show cooperative effect of different metal centers on the reactivity of organic ligands such as alkyl and aryl groups.[1,2] We previously reported synthesis and structure of a series of platinum-containing heterodinuclear complexes L$_2$RPt-ML$_n$ (L$_2$ = cycloocta-1,5-diene, dpe; R = methyl, aryl; ML$_n$ = MoCp(CO)$_3$, WCp(CO)$_3$, Mn(CO)$_5$, FeCp(CO)$_2$, Co(CO)$_4$).[3] Under thermolysis conditions, methyl and aryl groups migrated to the other metal M to give RML$_n$ in good yields, i.e., reductive elimination took place selectively. In the present study, heterodinuclear ethylplatinum complexes with a dpe ligand have been synthesized, and their reactivity toward ß-H elimination has been investigated.

New heterodinuclear complexes **1**-**4** having an ethyl group were synthesized by the metathetical reactions of PtEt(NO$_3$)(dpe), which was prepared in situ from PtEtCl(dpe) and AgNO$_3$, with a slight excess amounts of Na[ML$_n$] in THF at -30 °C under N$_2$ [Eq. (1)]. **1**-**4** were obtained as orange crystals by recrystallization from toluene/hexane, and they were characterized by analytical and spectroscopic methods.[4] Molar electric conductivities (Λ) of **1**-**4** were low, suggesting that they are not ionic but neutral complexes. ^{1}H and ^{31}P{^{1}H} NMR data of **1**-**4** indicate that the geometry at Pt is square planar.



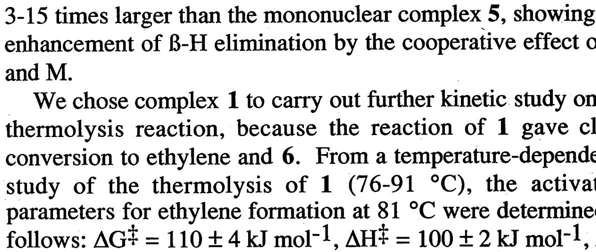
(1)

Thermolysis reactions of **1**-**4** and a mononuclear complex PtEtCl(dpe) (**5**) were investigated. The reactions were performed in diphenylmethane or toluene at 80 °C and were followed by GLC or ^{1}H NMR [Eq. (2)]. Yields of the products when the reactions no longer proceeded (3-8 h later) are summarized in Table 1. Ethylene was formed in high yields,[5] and for complexes **1** and **2** the corresponding dinuclear hydride complexes (dpe)HPt-ML$_n$ (ML$_n$ = MoCp(CO)$_3$ (**6**), WCp(CO)$_3$ (**7**)) were also formed in good yields.[6,7] It is noteworthy that ß-H elimination reaction proceeded with retention of Pt-Mo or Pt-W bonds, and to our knowledge this is one of rare examples of ß-H elimination reaction on dinuclear complexes.[3d,8] The reactions of **3** and **4** gave complicated mixtures of dark precipitates and solutions involving several metal species, so that the fate of metal complexes is not clearly determined.[9] Products of reductive elimination EtML$_n$ were not observed in the thermolysis reactions.

Table 1. Thermolysis reactions of heterodinuclear complexes

Complex	Reaction time /h	Yield /%	
		C$_2$H$_4$[a]	(dpe)HPt-ML$_n$[b]
(dpe)EtPt-MoCp(CO)$_3$ (**1**)	4	96	71
(dpe)EtPt-WCp(CO)$_3$ (**2**)	5	91	73
(dpe)EtPt-Mn(CO)$_5$ (**3**)	6	58	-
(dpe)EtPt-Co(CO)$_4$ (**4**)	3	74	-
PtEtCl(dpe) (**5**)	8	79	-

[a] Analyzed by GLC. Conditions: in CH$_2$Ph$_2$ at 80 °C.
[b] Analyzed by ^{1}H NMR. Conditions: in C$_6$D$_5$CD$_3$ at 80 °C.



(2)

First-order plots yielded straight lines for the formation of ethylene from **1**, **2**, **4**, and **5** (Table 2). Interestingly, the heterodinuclear complexes gave first-order rate constants (k_{obs}) 3-15 times larger than the mononuclear complex **5**, showing the enhancement of ß-H elimination by the cooperative effect of Pt and M.

We chose complex **1** to carry out further kinetic study on the thermolysis reaction, because the reaction of **1** gave clean conversion to ethylene and **6**. From a temperature-dependence study of the thermolysis of **1** (76-91 °C), the activation parameters for ethylene formation at 81 °C were determined as follows: $\Delta G^\ddagger = 110 \pm 4$ kJ mol^{-1}, $\Delta H^\ddagger = 100 \pm 2$ kJ mol^{-1}, $\Delta S^\ddagger = -26 \pm 4$ J mol^{-1} K^{-1}. The negative value of $\Delta S^\ddagger$ suggests that the rate determining step involves a non-dissociative path, in which the ß-H in Et is eliminated using the fifth coordination site on Pt center.[10]

Effect of additives has been studied in the thermolysis of **1** under the same conditions of Table 2. In the presence of excess

Table 2. First-order rate constants for the formation of ethylene in the thermolysis reactions of heterodinuclear complexes[a]

Complex	k_{obs} (x 10^{-4} s^{-1})
(dpe)EtPt-MoCp(CO)$_3$ (**1**)	4.0 (± 0.1)
(dpe)EtPt-WCp(CO)$_3$ (**2**)	2.8 (± 0.1)
(dpe)EtPt-Co(CO)$_4$ (**4**)	12 (± 2)
PtEtCl(dpe) (**5**)	0.78 (± 0.03)

[a] In CH_2Ph_2 at 80 °C. [Complex]$_0$ = 5.5 mM.

Na[MoCp(CO)$_3$] (11 equiv.), no effect was observed on the reaction rate (k_{obs} = 4.2 x 10^{-4} s^{-1}). This result excludes the dissociation of [MoCp(CO)$_3$]$^-$ from **1** to give an unstable cationic species, from which facile ß-H elimination would take place.[11] Another possibility is partial dissociation of dpe to be monodentate, which makes an vacant site in the square planar geometry. Thus, excess dpe (10 equiv.) was added to **1**, but the reaction gave a complicated mixture containing the products of ß-H elimination and ionization. When excess PPh$_3$ (10 equiv.) was added to the benzene solution of **1**, ionization preferentially occurred to give [PtEt(PPh$_3$)(dpe)]$^+$[MoCp(CO)$_3$]$^-$ (**7**).[12] Although we cannot completely exclude the dissociative path involving a mondentate dpe in the ß-H elimination, the non-dissociative mechanism seems to be plausible by considering above results and the activation entropy.

In order to clarify the effect of second metal species ML$_n$ on the rate enhancement of ß-H elimination, electronegativities (χ) of Pt were determined from chemical shifts of Et groups in ^{1}H NMR.[13] The χ values for **1**-**5** are in the range of Pt(II), and **1**-**4** (χ = 2.6-2.7) are more electron-deficient than **5** (χ = 2.3). From this result, one possible explanation for the rate enhancement by ML$_n$ is that the ML$_n$ moiety reduces the electron-density of Pt to facilitate abstraction of a ß-H with hydride character.[14]

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4 **1**: Yield 57%; mp 141 °C(dec.); molar electric conductivity Λ (in THF at r.t.) 0.027 S cm^2 mol^{-1}. Anal. Found: C, 50.09; H, 4.44%. Calcd for $C_{36}H_{34}O_3P_2MoPt$: C, 49.84; H, 3.95%. IR (KBr, cm^{-1}) 1902, 1788 (ν_{CO}). ^{1}H NMR (C_6D_6): δ 1.32 (dt, $^4J_{PH}$ = 11 Hz, $^3J_{HH}$ = 11 Hz, 3H, CH_2CH_3), 1.5-1.9 (m, 4H, dpe CH_2), 2.23 (sextet, $^3J_{PH}$ = 11 Hz, $^3J_{HH}$ = 11 Hz, $^3J_{PtH}$ = 69 Hz, 2H, CH_2CH_3), 4.67 (s, 5H, Cp), 6.9-7.5 (m, 20H, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 39.59 (s, $^1J_{PtP}$ = 1487 Hz), 59.01 (s, $^1J_{PtP}$ = 3662 Hz).
2: Yield 37%; mp 157 °C(dec.); Λ (in THF at r.t.) 0.039 S cm^2 mol^{-1}. This complex was identified by the spectroscopic methods. IR (KBr, cm^{-1}) 1899, 1789 (ν_{CO}). ^{1}H NMR (C_6D_6): δ 1.35 (dt, $^4J_{PH}$ = 9 Hz, $^3J_{HH}$ = 8 Hz, 3H, CH_2CH_3), 1.5-1.8 (m, 4H, dpe CH_2), 2.41 (sextet, $^3J_{PH}$ = 8 Hz, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 71 Hz, 2H, CH_2CH_3), 4.61 (s, 5H, Cp), 6.9-7.9 (m, 20H, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 40.32 (s, $^1J_{PtP}$ = 1485 Hz), 60.47 (s, $^1J_{PtP}$ = 3633 Hz).
3: Yield 31%; mp 146 °C(dec.); Λ (in THF at r.t.) 0.15 S cm^2 mol^{-1}. Anal. Found: C, 48.41; H, 3.80%. Calcd for $C_{33}H_{29}O_5P_2MnPt$: C, 48.48; H, 3.58%. IR (KBr, cm^{-1}) 2034, 1936, 1908 (ν_{CO}). ^{1}H NMR (C_6D_6): δ 1.17 (dt, $^4J_{PH}$ = 10 Hz, $^3J_{HH}$ = 7 Hz, 3H, CH_2CH_3), 1.5-1.9 (m, 4H, dpe CH_2), 2.22 (sextet, $^3J_{PH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, $^3J_{PtH}$ = 68 Hz, 2H, CH_2CH_3), 6.9-7.8 (m, 20H, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 47.03 (s, $^1J_{PtP}$ = 1607 Hz), 57.08 (s, $^1J_{PtP}$ = 3570 Hz).
4: Yield 61%; mp 154 °C(dec.); Λ (in THF at r.t.) 0.13 S cm^2 mol^{-1}. This complex was identified by the spectroscopic methods. IR (KBr, cm^{-1}) 2024, 1957, 1924, 1883 (ν_{CO}). ^{1}H NMR (C_6D_6): δ 1.22 (dt, $^4J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 3H, CH_2CH_3), 1.5-2.0 (m, 4H, dpe CH_2), 2.01 (sextet, $^3J_{PH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, $^3J_{PtH}$ = 61 Hz, 2H, CH_2CH_3), 6.9-7.7 (m, 20H, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 46.85 (s, $^1J_{PtP}$ = 4055 Hz), 48.06 (s, $^1J_{PtP}$ = 1535 Hz).

5 Formation of a small amount of ethane was also observed for the thermolysis of **2**-**5**. Yields of ethane: **2**, 3%; **3**, 5%; **4**, 14%; **5**, 5%. One of the reasons for the formation of ethane may be the intermolecular reaction of (dpe)EtPt-ML$_n$ and (dpe)HPt-ML$_n$, the latter being formed from ß-H elimination of (dpe)EtPt-ML$_n$.

6 **6**: Yellow needles from toluene/hexane; yield 49%; mp 188 °C(dec.); Λ (in THF at r.t.) 0.080 S cm^2 mol^{-1}. Anal. Found: C, 48.99; H, 3.67%. Calcd for $C_{34}H_{30}O_3P_2MoPt$: C, 48.64; H, 3.60%. IR (KBr, cm^{-1}): 2042 (ν_{PtH}), 1926 (ν_{CO}), 1819 (ν_{CO}). ^{1}H NMR (C_6D_6):-2.37 (d, $^2J_{PH}$ = 192 Hz, $^1J_{Pt-H}$ = 885 Hz, 1H, Pt-*H*), 1.8-2.1 (m, 4H, dpe CH_2), 5.25 (s, 5H, Cp), 6.9-7.8 (m, 20H, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 49.78 (d, $^2J_{PP}$ = 4 Hz, $^1J_{PtP}$ = 3313 Hz), 51.60 (d, $^2J_{PP}$ = 4 Hz, $^1J_{PtP}$ = 2113 Hz).
7: Yellow needles from toluene/hexane; yield 54%. This complex was identified by the spectroscopic methods. IR (KBr, cm^{-1}): 2041 (ν_{PtH}), 1925 (ν_{CO}), 1817 (ν_{CO}). ^{1}H NMR (C_6D_6): -2.92 (d, $^2J_{P-H}$ = 210 Hz, $^1J_{Pt-H}$ = 970 Hz, 1H, Pt-*H*), 1.8-2.1 (m, 4H, dpe CH_2), 5.26 (s, 5H, Cp), 6.9-7.8 (m, 20H, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51.33 (d, $^2J_{PP}$ = 4 Hz, $^1J_{PtP}$ = 3313 Hz), 52.76 (d, $^2J_{PP}$ = 4 Hz, $^1J_{PtP}$ = 2093 Hz).

7 Analogous (PPh$_3$)$_2$HPt-MoCp(CO)$_3$ was reported in Ref. 2a.

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12 **7**: Pale yellow crystals from CH_2Cl_2/ether; yield 77%; mp 112 °C(dec.); Λ (in THF at r.t.) 1.99 S cm^2 mol^{-1}. This complex was identified by the spectroscopic methods. IR (KBr, cm^{-1}): 1893, 1774, 1767 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 0.12 (dt, $^4J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, 3H, CH_2CH_3), 1.0-1.4 (m, 2H, CH_2CH_3), 2.2-2.5 (m, 4H, dpe CH_2), 5.19 (s, 5H, Cp), 7.2-7.7 (m, 35H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.82 (dd, $^2J_{PP}$ = 373, 19 Hz, $^1J_{PtP}$ = 2949 Hz, PPh$_3$), 46.48 (dd, $^2J_{PP}$ = 19, 5 Hz, $^1J_{PtP}$ = 1566 Hz, dpe P cis to PPh$_3$), 52.08 (dd, $^2J_{PP}$ = 373, 5 Hz, $^1J_{PtP}$ = 2942 Hz, dpe P trans to PPh$_3$).

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14 Greater enhancement of ß-H elimination for **4** than for **1** and **2** may be due to other effects such as steric factors and dissociation of the Pt-Co bond in **4**.