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New Ruthenium-Molybdenum and -Tungsten Heterodinuclear Complexes with trans-Styryl Ligand

Atsushi FUKUOKA, Nobutoshi OHASHI, and Sanshiro KOMIYA*

Department of Applied Chemistry, Tokyo University of Agriculture and Technology,

2-24-16 Nakamachi, Koganei, Tokyo 184

New styryl ruthenium-molybdenum and -tungsten complexes $Cp(CO)_3M$-Ru(*trans*-styryl)$(CO)(PPh_3)_2$ [M = Mo (**2**), W (**3**)] have been prepared by the metathetical reactions of Ru(*trans*-styryl)$Cl(CO)(PPh_3)_2$ with Na[$MCp(CO)_3$]. The reactions of **2** with CO and with PMe_3 give $Cp(CO)_3$Mo-Ru(*trans*-styryl)$(CO)_2(PPh_3)_2$ (**4**) and $Cp(CO)_3$Mo-Ru(*trans*-styryl)$(CO)(PMe_3)_2$ (**5**), respectively. The complexes of **2**, **3**, **4**, and **5** have been characterized by IR, ^{1}H NMR, ^{31}P{^{1}H} NMR spectroscopy, and elemental analysis.

The chemistry of heterodinuclear complexes[1] has been the subject of recent study because of the potential heterometallic activation of a substrate leading to unusual products.[2] Although few examples of the heterodinuclear complexes with alkyl and alkenyl ligands are known so far,[1,3] the study on transformation of the hydrocarbon ligands is of great interest to get the products not obtained by homometallic complexes. Also, the heterodinuclear complexes are important as models of active sites in bimetallic catalysts extensively used in industry.[4] Accordingly, the chemical behavior of hydrocarbon ligands on the complexes may give us fundamental informations relevant to surface hydrocarbon species on heterogeneous bimetallic catalysts in the petroleum reforming process. We have recently discovered a series of new platinum-tungsten and -molybdenum complexes that showed unique alkyl and aryl transfer from Pt to W (or Mo) atoms on thermolysis as well as on interaction with electronegative olefins.[3] Here we report the preparation of new ruthenium-molybdenum and -tungsten heterodinuclear complexes containing a styryl ligand.

Reaction of Ru(*trans*-styryl)$Cl(CO)(PPh_3)_2$[5] (**1**) with a stoichiometric amount of Na[$MoCp(CO)_3$][6] in tetrahydrofuran (THF) at 0 °C afforded a brown solid in *ca.* 5 h. The solid was extracted with benzene, and the red solution was separated by column chromatography on silica gel by using benzene as an eluent yielding two

bands. The first band was evaporated and recrystallized from THF/hexane to give orange crystals of $Cp(CO)_3Mo$-Ru(*trans*-styryl)$(CO)(PPh_3)_2$ (**2**) in 33% yield (Eq. 1). The second band gave Ru(*trans*-styryl)Cl $(CO)_2(PPh_3)_2$ in 3% yield. The tungsten analogue $Cp(CO)_3W$-Ru(*trans*-styryl)$(CO)(PPh_3)_2$ (**3**) was also prepared by the similar reaction of **1** with Na[$WCp(CO)_3$] (yield 19%). However, reaction of **1** with Na[$CrCp(CO)_3$] resulted in the formation of Ru(*trans*-styryl)$Cp(CO)(PPh_3)_2$;[7] the heterodinuclear Ru-Cr analogue was not obtained by this metathetical reaction.

$$\underset{\mathbf{1}}{\text{Ru(}\textit{trans}\text{-styryl)Cl(CO)(PPh}_3\text{)}_2} + \text{Na[MCp(CO)}_3\text{]} \xrightarrow[\text{- NaCl}]{\text{THF, 0 °C}} \text{Cp(CO)}_3\text{M-Ru(}\textit{trans}\text{-styryl)(CO)(PPh}_3\text{)}_2 \quad (1)$$

M = Mo (**2**)
W (**3**)

Treatment of **2** with CO in benzene at 1 atm and room temperature afforded coordinatively saturated $Cp(CO)_3Mo$-Ru(*trans*-styryl)$(CO)_2(PPh_3)_2$ (**4**) in 61% yield (Eq. 2). Reaction of **2** with excess PMe_3 in benzene at room temperature gave $Cp(CO)_3Mo$-Ru(*trans*-styryl)$(CO)(PMe_3)_2$ (**5**) in 58% yield (Eq. 3).

$$\underset{\mathbf{2}}{\text{Cp(CO)}_3\text{Mo-Ru(}\textit{trans}\text{-styryl)(CO)(PPh}_3\text{)}_2} + \text{CO} \xrightarrow{\text{C}_6\text{H}_6\text{, r.t.}} \underset{\mathbf{4}}{\text{Cp(CO)}_3\text{Mo-Ru(}\textit{trans}\text{-styryl)(CO)}_2\text{(PPh}_3\text{)}_2} \quad (2)$$

$$\underset{\mathbf{2}}{\text{Cp(CO)}_3\text{Mo-Ru(}\textit{trans}\text{-styryl)(CO)(PPh}_3\text{)}_2} + 2\text{PMe}_3 \xrightarrow[\text{-2PPh}_3]{\text{C}_6\text{H}_6\text{, r.t.}} \underset{\mathbf{5}}{\text{Cp(CO)}_3\text{Mo-Ru(}\textit{trans}\text{-styryl)(CO)(PMe}_3\text{)}_2} \quad (3)$$

Reactions of **2** and **4** with dry HCl in benzene at room temperature liberated styrene in 22% and 73% yields, respectively. The resultant complexes were $RuHCl(CO)(PPh_3)_2$ and $RuHCl(CO)_2(PPh_3)_2$ in addition to $MoCpCl(CO)_3$ confirmed by IR and ^1H NMR spectroscopy.

Compounds of **2**, **3**, **4**, and **5** have been characterized by means of spectroscopic and analytical study.[8] In the IR spectrum of **2**, three terminal carbonyl bands appear at 1939, 1889, and 1806 cm^{-1}. By comparing the ν_{CO} bands of precursors **1** and Na[$MoCp(CO)_3$], the band at 1939 cm^{-1} is assigned to the terminal CO coordinated to Ru and those at 1889 and 1806 cm^{-1} to the terminal carbonyl ligands of Mo moiety. The $^{31}P\{^1H\}$ NMR spectrum of **2** in C_6D_6 at room temperature shows two singlets at 45.24 and 34.28 ppm attributed to the

magnetically inequivalent phosphorus nuclei of two PPh_3's, indicating a different coordination geometry from trigonal bipyramid of the precursor **1** where two PPh_3's are in axial positions.[5] Accordingly, the $^{31}P\{^1H\}$ NMR data for **2** suggest that one PPh_3 is in an equatrial position and the other in an axial position in the expected trigonal bipyramidal geometry of **2**. The ^1H NMR signals for the styryl group in **2-5** appear in the typical regions reported for such complexes as **1**[5] having a *trans*-styryl ligand. Figure 1 shows the proposed structure of **2**.[9] The vinyl protons in **2** are observed as two sets of resonances: a doublet of triplets at 8.43 ppm and a doublet of doublets at 3.44 ppm, which are assigned to α and β protons in the styryl group, respectively.[5] The doublet of triplets at 8.43 ppm is derived from the coupling of H_α to phosphorus nuclei of two PPh_3's and to H_β, and the doublet of doublets at 3.44 ppm from the coupling of H_β to one PPh_3 and to H_α.[10] It is notable that both H_α and H_β of the styryl group in **2**, **3**, and **5** have couplings with P nuclei, whereas no coupling between H_β and P is observed in **4**. Probably, this arises from the structural consequence of these complexes: Ru moiety in **4** is octahedral, but those in **2**, **3**, and **5** are considered to be trigonal bipyramidal with formally 16e.[10]

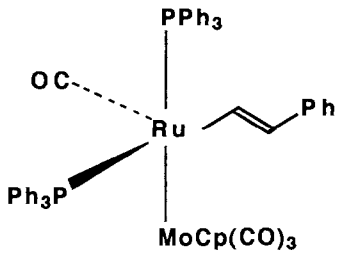

Fig.1. Proposed Structure of **2**.

The molar electric conductivity of **2-5** in THF is significantly small (Λ = 0.003-0.007 $S \cdot cm^2/mol$), implying that they are not ionic pairs but neutral complexes having Mo-Ru or W-Ru bond. From elemental analysis, it is suggested that **2-4** contain THF and/or H_2O molecules in the crystals; the chemical formula of **2** is represented by $Cp(CO)_3Mo\text{-}Ru(trans\text{-}styryl)(CO)(PPh_3)_2 \cdot THF \cdot 2H_2O$.[8] The presence of THF is further supported by the molecular-weight determination using the cryoscopic method. The apparent molecular-weight was estimated at 560, the value being approximately a half of the expected molecular weight 1110 for **2**. The result suggests the complete dissociation of an included THF molecule from **2** in solution.[11] Indeed, the THF liberated was detected in the ^1H NMR of **2** in C_6D_6. In a similar manner, the crystals of **3**, **4**, and **5** are analytically and spectroscopically determined as $Cp(CO)_3W\text{-}Ru(trans\text{-}styryl)(CO)(PPh_3)_2 \cdot THF \cdot H_2O$, $Cp(CO)_3Mo\text{-}Ru(trans\text{-}styryl)(CO)_2(PPh_3)_2 \cdot H_2O$, $Cp(CO)_3Mo\text{-}Ru(trans\text{-}styryl)(CO)(PMe_3)_2$, respectively.[8]

The chemical reactivities of styryl ligands in **2-5** are now under investigation.

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7) Ru(*trans*-styryl)Cp(CO)(PPh_3)$_2$: Yield 29%. IR(ν_{CO}, cm^{-1}; KBr): 1919, 1904. ^1H NMR(200MHz, C_6D_6) δ 8.30(dd, J_{HH} = 16.4 Hz, J_{PH} = 6.8 Hz, 1H, Ru-*H*C=CHPh), 7.5-6.9(m, 35H, PPh_3 and =CH*Ph*), 6.83(dd, J_{HH} = 16.4 Hz, 1H, Ru-HC=C*H*Ph), 4.68(s, 5H, Cp). Mp 178 °C(dec.).

8) Cp(CO)$_3$Mo-Ru(*trans*-styryl)(CO)(PPh_3)$_2$·THF·2H_2O (**2**): IR(ν_{CO}, cm^{-1}; KBr): 1939, 1889, 1806. ^1H NMR(200 MHz, C_6D_6) δ 8.43(dt, J_{HH} = 11.7 Hz, J_{PH} = 2.6 Hz, 1H, Ru-*H*C=CHPh), 7.6-7.3(m, 12H, PPh_3), 7.2-6.8(m, 23H, PPh_3 and =CH*Ph*), 4.86(s, 5H, Cp), 3.44(dd, J_{HH} = 11.7 Hz, J_{PH} = 5.9 Hz, 1H, Ru-HC=C*H*Ph). ^{31}P {^1H} NMR(160 MHz, C_6D_6, ppm from external PPh_3): δ 45.24(s), 34.28(s). Anal. Found: C, 61.68; H, 5.02%. Calcd for $C_{57}H_{54}O_7P_2MoRu$: C, 61.68; H, 4.90%. Mp 208 °C(dec.). Electric conductivity Λ(in THF at r.t.) 0.003 S·cm^2/mol. Cp(CO)$_3$W-Ru(*trans*-styryl)(CO)(PPh_3)$_2$·THF·H_2O (**3**): IR(ν_{CO}, cm^{-1}; KBr): 1939, 1886, 1801. ^1H NMR(200 MHz, C_6D_6) δ 7.85(dt, J_{HH} = 11.1 Hz, J_{PH} = 2.2 Hz, 1H, Ru-*H*C=CHPh), 7.6-7.4(m, 12H, PPh_3), 7.2-6.8(m, 23H, PPh_3 and =CH*Ph*), 4.87(s, 5H, Cp), 3.45(dd, J_{HH} = 11.1 Hz, J_{PH} = 5.9 Hz, 1H, Ru-HC=C*H*Ph). Anal. Found: C, 58.33; H, 4.34%. Calcd for $C_{57}H_{52}O_6P_2WRu$: C, 58.02; H, 4.44%. Mp 204 °C(dec.). Λ(in THF at r.t.) 0.005 S·cm^2/mol. Cp(CO)$_3$Mo-Ru(*trans*-styryl)(CO)$_2$(PPh_3)$_2$·H_2O (**4**): IR(ν_{CO}, cm^{-1}; KBr): 2061, 1985, 1888, 1821. ^1H NMR(200 MHz, C_6D_6) δ 7.72(dd, J_{HH} = 12.2 Hz, J_{PH} = 2.6 Hz, 1H, Ru-*H*C=CHPh), 7.5-7.4(m, 12H, PPh_3), 7.1-6.9(m, 23H, PPh_3 and =CH*Ph*), 4.62(s, 5H, Cp), 4.34(d, J_{HH} = 12.2 Hz, 1H, Ru-HC=C*H*Ph). Anal. Found: C, 61.41; H, 4.05%. Calcd for $C_{54}H_{44}O_6P_2MoRu$: C, 61.89; H, 4.23%. Mp 142 °C(dec.). Λ(in THF at r.t.) 0.005 S·cm^2/mol. Cp(CO)$_3$Mo-Ru(*trans*-styryl)(CO)(PMe_3)$_2$ (**5**): IR(ν_{CO}, cm^{-1}; KBr): 2002, 1913, 1858, 1775. ^1H NMR(200 MHz, C_6D_6) δ 7.71(dt, J_{HH} = 11.7 Hz, J_{PH} = 3.3 Hz, 1H, Ru-*H*C=CHPh), 7.41(d, J_{HH} = 7.5 Hz, 2H, H_{ortho} in Ph), 7.14(t, J_{HH} = 7.5 Hz, 2H, H_{meta} in Ph), 6.99(t, J_{HH} = 7.5 Hz, 1H, H_{para} in Ph), 4.87(s, 5H, Cp), 3.89(dd, J_{HH} = 11.7 Hz, J_{PH} = 6.3 Hz, 1H, Ru-HC=C*H*Ph). Anal. Found: C, 44.19; H, 5.02%. Calcd for $C_{23}H_{30}O_4P_2MoRu$: C, 43.89; H, 4.80%. Mp 178 °C(dec.). Λ(in THF at r.t.) 0.007 S·cm^2/mol

9) At present, other possible structures for **2** and **3** than trigonal bipyramid can not be completely excluded and further X-ray structural determination is desired.

10) The coupling between H_β and P was reported for Pd(*trans*-styryl)BrL_2 (L = PPh_3, PPh_2Me): M.K. Loar and J.K. Stille, *J. Am. Chem. Soc.*, **103**, 4174(1981). However, the origin of the long-range coupling ^4J in **2**, **3**, and **5** is not clear. Alternatively, a possible coupling between H_β and H_{ortho} in Ph can not be excluded.

11) Dissociation of water in benzene seems to be inconceivable; if the water in **2** was completely dissociated from **2** in benzene, the corresponding amount of water should be separated out of the benzene solution under the conditions of cryoscopic measurement. In fact, independent experiment revealed that the addition of water (24 μl) to benzene (10 ml) caused the depression of freezing temperature as small as ΔT = 0.07° because of the low solubility of water in benzene.

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