170 *J. Am. Chem. Soc.* **2000,** *122,* 170−171

Regio- and Stereoselective Insertion Reactions of Thiiranes into Pt−Mn (or Re) Bond in Organoplatinum−Manganese or −Rhenium Heterodinuclear Complexes as Intermediates toward Desulfurization Reaction

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Received September 3, 1999

Introduction of direct heterotransition-metal direct bonds in cluster complexes is expected to create a new era of transition-metal chemistry in relation to multimetallic catalysis, and thus many investigations on heterotransition-metal complexes have been reported in recent years.[1] Bimetallic catalysis such as sulfurized Pt−Re oil reforming catalysts[2] and Co−Mo and Ni−Mo hydrodesulfurization (HDS) catalysts[3] shows cooperative effects of these metals, but the origin of such effect is far from understood at the molecular level. Although extensive research has been devoted to elucidate the mechanisms of the reactions of heterodinuclear transition-metal complexes and clusters with thiiranes and benzothiophenes, few examples of direct participation of both metal centers have been found in the literature.[4] Also, factors controlling selectivity in activation of thiiranes have not been well understood despite their importance as model reactions as well as their wide applications to chemical transformation of sulfur-containing compounds.[5] We previously reported model complexes of heterodinuclear organometallic complexes of group 10 and 6 (or 9) metals, where unique organic group transfer reactions along metals and enhanced CO insertion reactions have been demonstrated.[6]

Now we have found a highly regio- and stereocontrolled ring-opening reaction of thiiranes with organoplatinum−manganese (or rhenium) complexes (dppe)RPtM(CO)$_5$ (M = Mn: R = Me (**1a**), Et (**1b**), CH$_2$CMe$_3$ (**1c**); M = Re: R = Me (**2a**), Et (**2b**)), giving new heterodinuclear complexes (dppe)RPtSC^{1}R^{2}RCH$_2$M(CO)$_5$ (**3**−**9**) or *anti*- and *syn*-(dppe)RPt$\overline{\text{SCMeHCMeHCOMn}}(CO)_4$ (**10**) from which stereoselective desulfurization occurs to afford olefin and Pt−S−M type complexes.

The heterodinuclear Pt−Mn(or Re) complexes **1a**−**c** and **2a**−**b** were prepared in good yields by simple metathetical reactions of PtRCl(dppe) with the corresponding transition-metal anions Na[M(CO)$_5$] (M = Mn, Re) in THF (eq 1).[7]

$$\text{PtRCl(dppe)} + \text{NaM(CO)}_5 \xrightarrow[\text{THF}]{+\ \text{AgNO}_3} \text{(dppe)(R)Pt-M(CO)}_5 \qquad (1)$$

M = Mn	R = Me	**1a**	87%
	R = Et	**1b**	62%
	R = CH$_2$CMe$_3$	**1c**	82%
M = Re	R = Me	**2a**	60%
	R = Et	**2b**	61%

The molecular structure of **1a** was unequivocally determined by X-ray crystallography.[8] The platinum fragment has a distorted square planar geometry, and two of the carbonyl groups of the Mn(CO)$_5$ fragment are distorted away from the ideal octahedron due to the formation of semi-bridging character. The bond length of Pt1−Mn1 of 2.795 Å is typical of covalent single bond.

When **1a** was treated with thiiranes such as ethylene sulfide, propylene sulfide, and isobutylene sulfide, regioselective insertion of the Pt−M bond into the less hindered C−S bond took place to give the new dinuclear complexes (dppe)RPtSC(^{1}R)(^{2}R)C(^{3}R)(^{4}R)M(CO)$_5$, (M = Mn: R = Me, ^{1}R = ^{2}R = ^{3}R = ^{4}R = H (**3**); R = Me, ^{1}R = Me or H, ^{2}R = H or Me, ^{3}R = ^{4}R = H (**4**); R = ^{1}R = ^{2}R = Me, ^{3}R = ^{4}R = H (**5**). M = Re: R = Me, ^{1}R = ^{2}R = ^{3}R = ^{4}R = H (**6**); R = ^{1}R = Me or H, ^{2}R = H or Me, ^{3}R = ^{4}R = H (**7**); R = Et, ^{1}R = ^{2}R = ^{3}R = ^{4}R = H (**8**); R = Et, ^{1}R = Me or H, ^{2}R = H or Me, ^{3}R = ^{4}R = H (**9**)) (Scheme 1).[9] Isolation of such insertion products is still very rare to date, since further desulfurization usually takes place to liberate olefins.

Acidification of **4** with HCl in toluene liberated ^{i}PrSH exclusively in 72% yield. Similarly, **5** and **7** liberated ^{t}BuSH and ^{i}PrSH, respectively. These facts indicate that the ring-opening reactions of thiiranes take place only at the less hindered C−S bond. On the other hand, treatment of **1a** with *cis*- and *trans*-2-butene sulfides resulted in further carbonylation and S-coordination to Mn to give thiamanganacycle-coordinated platinum complexes, *anti*- and *syn*-(dppe)MePt$\overline{\text{SCHMeCHMeCOMn}}(CO)_5$ (**10**), respectively, whose structures were unequivocally determined by X-ray structure analysis (Figure 1).[10]

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(7) Physical and spectroscopic data for **1a** are as follows: Yield 87%, ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ 0.81 (dd, 3H, J_{H-P} = 6.6, 6.3 Hz, J_{H-Pt} = 61.0 Hz, Pt*Me*), 2.1−2.5 (m, 4H, PCH_2CH_2P), 7.5−7.9 (m, 20H, *Ph*); ^{31}P{^{1}H} NMR (acetone-d_6, 122 MHz) δ 49.1(s, 1P, J_{Pt-P} = 1856 Hz, dppe), 59.2 (s, 1P, J_{Pt-P} = 3394 Hz, dppe); IR (KBr, cm^{-1}) 2036, 1945, 1933, 1920, 1907. Λ (S cm^2 mol^{-1}, in THF) = 0.0346. Anal. Found: C, 40.22; H, 2.90%. Calcd for C$_{32}$H$_{27}$O$_5$P$_2$PtMn: C, 41.12; H, 2.91%. Molar electric conductivities of these complexes in THF are very small, indicating that the Pt−M bond has little ionic but covalent character. However, the observed ν(CO) bands are close to those of [M(CO)$_5$]$^{-1}$, suggesting that the actual oxidation states of Pt and M are close to +2 and −1 rather than their formal oxidation states of +1 and 0, respectively.

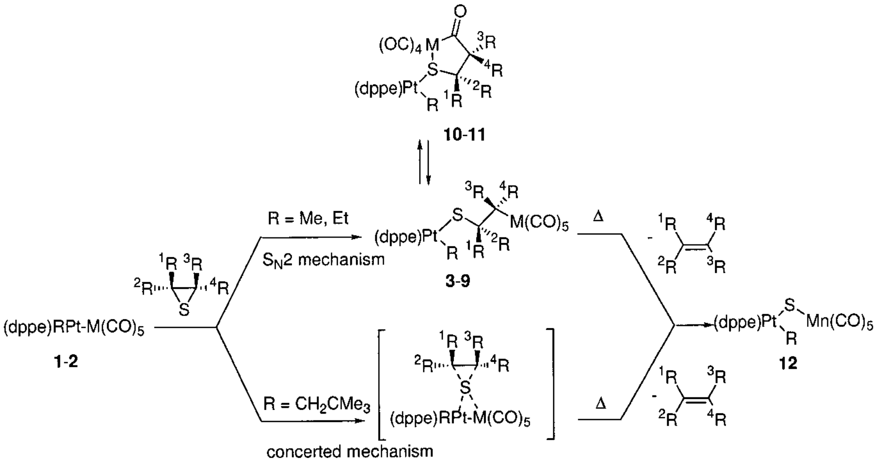
(8) X-ray data for **1a**.: triclinic, $P\bar{1}$ (No.2), $R(R_w)$ = 0.044 (0.077).

(9) Physical and spectroscopic data for **3** are as follows: Yield 81%, ^{1}H NMR (acetone-d_6, 300 MHz) δ 0.58 (dd, 3H, J_{H-P} = 6.6, 4.8 Hz, J_{H-Pt} = 58.0 Hz, Pt*Me*), 1.90 (t, 2H, J = 6.9 Hz, SCH$_2$CH_2), 2.4−2.7 (m, 4H, PCH_2CH_2P), 2.57 (m, 2H, SCH_2CH$_2$), 7.4−8.0 (m, 20H, *Ph*); ^{31}P{^{1}H} NMR (acetone-d_6, 122 MHz) δ 45.9 (s, 1P, J_{Pt-P} = 1820 Hz, dppe), 47.4 (s, 1P, J_{Pt-P} = 3289 Hz, dppe); IR (KBr, cm^{-1}) 2051, 1927, 1949, 1927, 1858. Λ (S cm^2 mol^{-1} in THF) = 0.170. Anal. Found: C, 47.46; H, 4.07; S, 3.78%. Calcd for C$_{34}$H$_{31}$O$_5$SP$_2$PtMn: C, 47.28; H, 3.62; S, 3.71%.

(10) X-ray data for *anti*- and *syn*-**10**. *anti*-**10**·Me$_2$CO from acetone: triclinic, $P1$(No. 2)$R(R_w)$ = 0.060 (0.080). *syn*-**10**·0.5C$_6$H$_6$ from benzene/hexane: triclinic, $P1$(No. 2), R (R_w) = 0.079 (0.107).

10.1021/ja993185m CCC: $19.00

Scheme 1



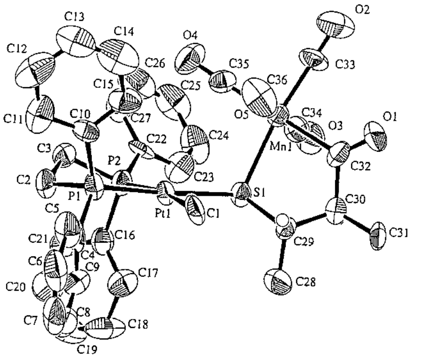


Figure 1. The molecular structure for *anti*-**10**. The hydrogen atoms except those in the thiamanganacycle are omitted for clarity. Ellipsoids represent 50% probability. Selected bond distances (Å) and angles (deg) for *anti*-**10**: Pt(1)−S(1) 2.363(3), Pt(1)−C(1) 2.11(2), Mn(1)−S(1) 2.389(4), Mn(1)−C(32) 2.08(1), S(1)−C(29) 1.81(1), C(29)−C(30) 1.54(2), C(30)−C(32) 1.54(2), S(1)−Pt(1)−C(1) 87.2(4), S(1)−Mn(1)−C(32) 83.3(5), Pt(1)−S(1)−Mn(1) 111.5(2).

The rhenium analogue **2a** with *cis*-2-butene sulfide also gave isomorphous complex (*anti*-**11**). As revealed by the ORTEP drawings, *cis*- and *trans*-2-butene sulfide gave *anti* and *syn* isomers, respectively, indicating that the stereochemistry at the carbon in the C−S bond cleavage of thiirane was complete inversion.

Thermolyses of these complexes were carried out to investigate the desulfurization process. Heating of these complexes gave the corresponding olefins and a sulfur-bridged Pt−S−M complex (dppe)MePt(μ-S)Mn(CO)$_5$ (**12a**) with retention of configuration. Namely, heating of **4**, *anti*- and *syn*-**10** at 80 °C in toluene exclusively liberated propylene, *trans*- and *cis*-2-butenes in 91, 80, and 88% yields, respectively.[11] The Pt−Re derivatives gave analogous results.

In contrast to the above results, reactions of neopentyl-Pt−Mn complex **1c** with *cis*- and *trans*-2-butene sulfides yielded analogous Pt−S−Mn complex **12b** and *cis*- and *trans*-2-butenes in 98 and 96% yields at 50 °C, respectively, without formation of intermediate. The most striking fact is that *cis*- and *trans*-2-butene sulfides released the *cis*- and *trans*-2-butenes, respectively, indicating that the total stereochemistry of the carbon in thiiranes in the reaction is retention of configuration.

To elucidate the reaction mechanism, the reactions of **1a** and **1c** with dimethyl sulfide were performed. The methyl derivative **1a** smoothly induced ionization to give a cationic methylplatinum(II) complex with $[Mn(CO)_5]^-$ anion, $[PtMe(Me_2S)(dppe)]^+[Mn(CO)_5]^-$, whereas **1c** remained unreacted under these reaction conditions. Therefore heterolytic cleavage of Pt−Mn bond in heterodinuclear complexes is most likely to take place in complexes **1a** and **1b** by addition of thiirane to give the $[PtR(dppe)]^+$ cation, which traps the thiirane by S-coordination. Such prerequisite coordination of thiiranes was postulated by Adams[4f] and Bergman[12] for these ring-opening reactions. External S_N2 attack of the $[Mn(CO)_5]^-$ anion at the less hindered carbon atom of coordinated thiirane results in the ring-opening reaction with inversion of configuration at the carbon atom in the formation of the complexes **10**. In the case of the reaction of 2-butene sulfides, a facile insertion of CO into the newly formed Mn(or Re)−C bond takes place to give a coordinatively unsaturated acylmanganese (or -rhenium) species, to which the Pt−sulfide moiety coordinates to Mn (or Re) to give final products. On the other hand, the reaction of neopentyl derivative **1c** with thiiranes did not cause heterolytic dissociation of the Pt−Mn (or Re) bond. As a result, thiiranes such as *cis*- and *trans*-2-butene sulfides are considered to interact directly with Pt−Mn (or Re) bond to liberate olefins with retention of configuration (Scheme 1).[12] A three-center concerted transition state has been proposed for the desulfurization reaction of ethylene sulfide with Ni−Zr heterodinuclear complexes leading to μ-S complex.[13]

Acknowledgment. This work was financially supported by the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Physical and spectroscopic data for **1**−**12**. Tables of crystallographic data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1a**, *anti*-**10** and *syn*-**10** (PDF). X-ray crystallographic file in CIF format. These materials are available free of charge via the Internet at http://pubs.acs.org.

JA993185M

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[11] Physical and spectroscopic data for **12a**. Yield 91%, ^{1}H NMR (acetone-d_6, 300 MHz) δ 0.27 (dd, 3H, J_{H-P} = 6.6, 5.7 Hz, J_{H-Pt} = 60.0 Hz, Pt*Me*), 2.2−2.6 (m, 4H, PC*H*$_2$C*H*$_2$P), 7.1−8.1 (m, 20H, *Ph*); $^{31}P\{^1H\}$ NMR (acetone-d_6, 122 MHz) δ 47.7 (s, 1P, J_{Pt-P} = 3234 Hz, dppe), 49.6 (s, 1P, J_{Pt-P} = 1883 Hz, dppe). Λ (S cm^2 mol^{-1} in THF) = 0.168. Anal. Found: C, 47.09; H, 3.72; S, 3.59%. Calcd for $C_{32}H_{27}MnO_5P_2PtS \cdot C_6H_6$: C, 47.04; H, 3.72; S, 2.76%.

[12] One of the reviewers commented that the concerted mechanism for the ring-opening reaction by **1c** is unlikely for steric reasons, but rather favors dissociation mechanism. However, we prefer our mechanism via unpolarized transition state, since the reaction of *trans*-2-butene sulfide with **1c** showed only slight solvent effect: the rate in benzene-d_6 is slightly faster than that in acetone-d_6.

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