Novel Bimetallic Group 9 Metal Catalysts Containing *P,S*-Chelating *o*-Carboranyl Ligand System for the Carbonylation of Methanol

Heung-Sae Lee, Jin-Young Bae,† Jaejung Ko,* Yong Soo Kang,† Hoon Sik Kim,*† and Sang Ook Kang*
Department of Chemistry, Korea University, Chochiwon, Chung-nam 339-700, Korea
†*Korea Institute of Science and Technology, P.O. Box 131, Cheongryangri, Seoul 130-650, Korea*

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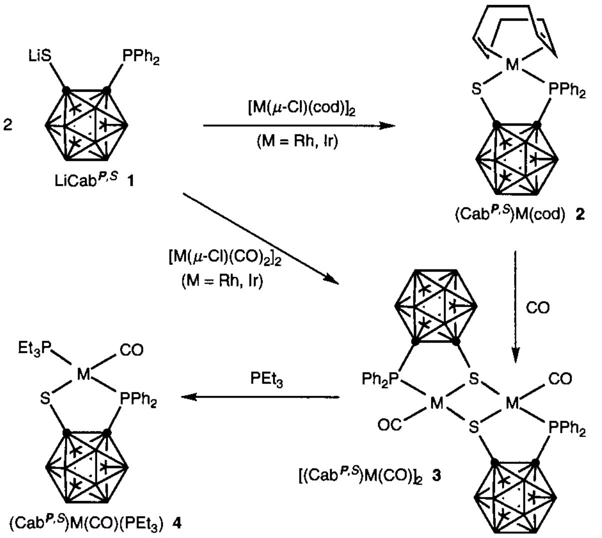
A series of novel group 9 transition metal complexes containing a *P,S*-chelating ligand have been prepared. The bimetallic rhodium carbonyl complex is much more effective in catalyzing the carbonylation of methanol to acetic acid than the previously known catalyst, $[RhI_2(CO)_2]^-$.

Bimetallic complexes using sulfur-containing bridging ligands such as thiolate,[1] aminothiolate,[2] phosphinothiolate,[3] to hold two metal atoms in close proximity have received considerable attention in recent years. One of the main reasons is the interest in the cooperative influence[4] of neighboring metal centers on catalytic reactions. The design of new bimetallic complexes involves the use of new assembling *P,S*-chelating ligand containing bulky *o*-carborane backbone. Recent reports of unusually stable *C,N*-,[5] *S,N*-,[6] and *S,S'*-chelating[7] *o*-carboranyl metal complexes appear to imply that the chelation, rigid conformation, and the *o*-carboranyl ligand backbone might be ideal for the stabilization of possible metal intermediates for organometallic reactions. In addition, the long-term thermal stability of such metal complexes can be realized by incorporating thermally robust *o*-carborane ligand backbone. Here, we describe new classes of improved methanol carbonylation catalysts containing the *o*-carboranylphosphinothiolato ligand, LiCab^{P,S} **1**, which show significant improvements in catalytic activities over those obtained with $[RhI_2(CO)_2]^-$.



The reaction of $[M(\mu\text{-Cl})(cod)]_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene) with two equiv of **1** produced the four-coordinated metallacyclic compounds (Cab^{P,S})M(cod) **2** (M = Rh **2a**, Ir **2b**). Bubbling carbon monoxide through a dichloromethane solution of **2** leads to the formation of the bimetallic *P,S*-chelate complexes $[(Cab^{P,S})M(CO)]_2$ **3** (M = Rh **3a**, Ir **3b**) as main products, which were isolated in 89-94% yields. Alternatively, such complexes **3** can be synthesized using a second route. When compounds $[M(\mu\text{-Cl})(CO)_2]_2$ (M = Rh, Ir) were reacted with two equiv of **1**, the bimetallic complexes **3a-b** were obtained in good yields (73-81%). Such complexes **3** were isolated as air-stable orange-yellow colored microcrystalline solids and were then spectroscopically characterized.[8] X-Ray structure determination of **3a** was carried out, and the resulting ORTEP plot and selected bond distances and angles of **3a** are shown in Figure 1.[9] It consists of discrete dinuclear units possessing a center of symmetry at the midpoint of the Rh(1)-Rh(1)' vector, which forms an Rh_2S_2 butterfly core with a thiolate bridge. The Rh_2S_2 ring is puckered, the dihedral angle between the planes $Rh_1S_1Rh_1'$ and $Rh_1S_1'Rh_1'$ being 71.5 (1)°. Each Rh atom is four-coordinate and displays a square-planar geometry. The average Rh-S distance of 2.370 Å is typical.[10,2a]

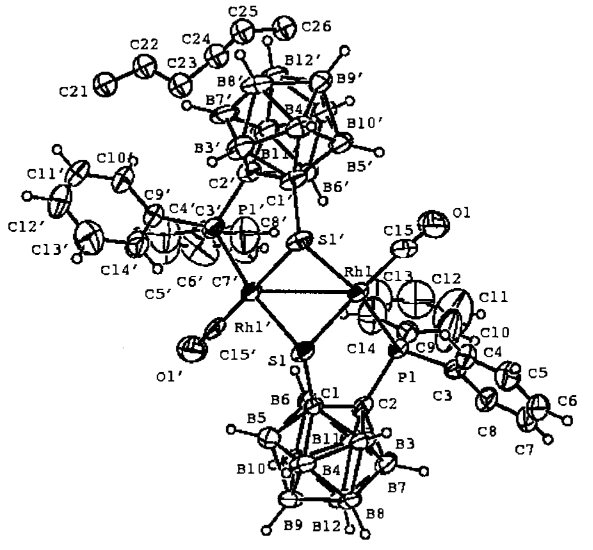


Figure 1. ORTEP drawing of **3a**. Selected bond lengths and angles: Rh(1)-Rh(1') 2.979(2), Rh(1)-S(1) 2.342(4), Rh(1)-P(1) 2.223(3), Rh(1)-S(1') 2.399(3), Rh(1)-C(15) 1.82(2), Rh(1')-S(1') 2.351(4), Rh(1')-P(1') 2.224(4), Rh(1')-S(1) 2.387(3), Rh(1')-C(15') 1.82(2) Å : P(1)-Rh(1)-S(1) 91.2(1), S(1)-Rh(1)-S(1') 78.2(1), Rh(1)-S(1)-Rh(1') 78.1(1), P(1')-Rh(1')-S(1') 91.0(1), S(1')-Rh(1')-S(1) 78.3(1), Rh(1')-S(1')-Rh(1) 77.7(1). The centres of the five atoms of the $RhPSC_2$ moiety [Rh(1), P(1), S(1), C(1), C(2)] are within 0.06 Å of a plane. The angle between planes [Rh(1), S(1), Rh(1')] and $RhPSC_2$ is 58.7(1)°. The centres of the five atoms of the $RhPSC_2$ moiety [Rh(1'), P(1'), S(1'), C(1'), C(2')] are within 0.06 Å of a plane. The angle between planes [Rh(1), Rh(1'), S(1')] and $RhPSC_2$ is 58.3(1)°.

Compounds **3a** and **3b** exhibit one ν(CO) band at 1994 and 1985 cm^{-1}, respectively. The lower frequency shift of CO stretches in **3** than those of the other carbonyl metal phosphinothiolates[3] is indicative of a higher basicity in the $Cab^{P,S}$ case. The reactivity of **3** has been explored in order to increase the nucleophilicity of the metal atoms. Such complexes **3** react with an excess PEt_3 to yield the corresponding mononuclear metal chelates **4**.[11]

The catalytic activities of the bimetallic complexes **3** were tested for the carbonylation of methanol and were compared with those of the mononuclear complexes **4** under the same conditions. Figure 2 shows the reaction profiles for the various rhodium and iridium complexes by plotting the quantity of carbon monoxide vs time, and Table 1 lists the turnover numbers. As a control experiment, the catalytic reaction was carried out with the Monsanto catalyst $[RhI_2(CO)_2]^-$, which was formed *in situ* from the added $[RhCl(CO)_2]_2$ under the stated reaction conditions.[12] As can be seen in Figure 2 and Table 1, at equivalent rhodium catalyst concentrations, the bimetallic complex **3a** exhibits significant catalytic activity over the Monsanto catalyst. The increased catalytic activity of **3a** is most likely a consequence of the formation of the thermally stable metal chelate that is imposed by bulky *o*-carborane ligand backbone. The ^{31}P NMR spectrum of the inorganic residue remaining after the carbonylation reaction by **3a** indicates that a high proportion of the phosphorus remains bound to the rhodium center and retains the original bimetallic structure as deduced from the chemical shift and coupling constant.

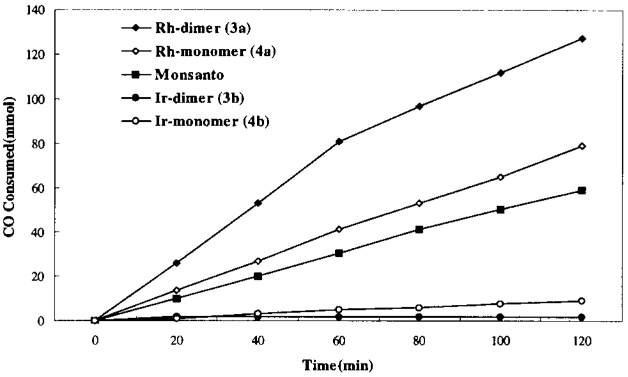


Figure 2. Carbonylation of methanol with various Rh and Ir complexes; CH_3OH (9.0 g),CH_3COOH (20.0 g), CH_3I (2.0 g), Catalyst [(1) **3a**, **3b** (0.025 mmol), (2) **4a**, **4b** (0.05 mmol)] ; P = 700 psig, T = 180℃

Table 1. Maximum turnover numbers observed during methanol carbonylation[a]

Catalyst	Max. turnover/h^{-1}
Monsanto	590
3a	1600
3b	20
4a	790
4b	90

[a] Conditions as for Figure 2

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References and Notes

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8 Data for **3a**. Anal. Calcd for $C_{30}H_{40}B_{20}O_2P_2S_2Rh_2$: C, 36.74; H, 4.11%. Found: C, 36.77; H, 4.18%. IR (KBr, cm^{-1}): ν(BH), 2577; ν(C=O), 1994.; ν(C=C), 1437. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 8.43 (br, *Ph*), 7.66 (br, *Ph*). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 185.90 (d, $^1J_{Rh\text{-}C}$ = 57 Hz, *C*O), 136.04 – 126.71 (s, 12, *Ph*), 94.00 (s, C_2B_{10}). $^{31}P\{^1H\}$ NMR (80.0 MHz, ppm, $CDCl_3$): 81.44 (d, $^1J_{Rh\text{-}P}$ = 169 Hz, *P*Ph_2). Data for **3b**. Anal. Calcd for $C_{30}H_{40}B_{20}O_2P_2S_2Ir_2$: C, 31.08; H, 3.48%. Found: C, 31.11; H, 3.52%. IR (KBr, cm^{-1}): ν(BH), 2580; ν(C=O), 1984.; ν(C=C), 1433. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 8.39 (br, *Ph*), 7.65 (br, *Ph*). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 206.10 (s, CO). $^{31}P\{^1H\}$ NMR (80.0 MHz, ppm, $CDCl_3$): 53.18 (s, *P*Ph_2).

9 Crystallographic data for **3a**: a = 10.8636(9) Å, b = 30.160(2) Å, c = 14.633(2) Å, and β = 92.414(9)° with Z = 4 in space group $P2_1/a$ (No. 14). $R_1(wR_2)$ = 0.0756 (0.1968) for 9374 data with $I > 2.0\sigma(I)$ and anisotropic refinements of the model with idealized hydrogen atoms.

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11 Data for **4a**. Anal. Calcd for $C_{21}H_{35}B_{10}OP_2SRh$: C, 41.45; H, 5.80%. Found: C, 41.50; H, 5.88%. IR (KBr, cm^{-1}): ν(BH), 2596; ν(C=O), 1975. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 8.26 (m, 5, *Ph*), 7.54 (m, 5, *Ph*), 1.85 (dq, 6, CH_2), 1.20 (dt, 9, *Me*). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 187.11 (d, $^1J_{Rh\text{-}C}$ = 58 Hz, *C*O), 16.45 (d, $^1J_{P\text{-}C}$ = 13 Hz, P(CH_2Me)$_3$), 6.93 (s, P(CH_2*Me*)$_3$). $^{31}P\{^1H\}$ NMR (80.0 MHz, ppm, $CDCl_3$): 82.21 (dd, $^1J_{Rh\text{-}P}$ = 296 Hz, $^2J_{P\text{-}P}$ = 128 Hz, *P*Ph_2), 26.22 (dd, $^1J_{Rh\text{-}P}$ = 296 Hz, $^2J_{P\text{-}P}$ = 128 Hz, *P*Et_3). Data for **4b**. Anal. Calcd for $C_{21}H_{35}B_{10}OP_2SIr$: C, 36.14; H, 5.06%. Found: C, 36.19; H, 5.10%. IR (KBr, cm^{-1}): ν(BH), 2577; ν(C=O), 1965. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 8.20 (m, 5, *Ph*), 7.55 (m, 5, *Ph*), 2.00 (dq, 6, CH_2), 1.18 (dt, 9, *Me*). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 206.10 (s, *C*O), 18.31 (d, $^1J_{P\text{-}C}$ = 34 Hz, P(CH_2Me)$_3$), 8.52 (s, P(CH_2*Me*)$_3$). $^{31}P\{^1H\}$ NMR (80.0 MHz, ppm, $CDCl_3$): 79.60 (d, $^2J_{P\text{-}P}$ = 130 Hz, *P*Ph_2), 23.12 (d, $^2J_{P\text{-}P}$ = 130 Hz, *P*Et_3).

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