Metallo-selective Substitution Reactions by Amines or Phosphines in HRuCo$_3$(CO)$_{12}$. ^{1}H and ^{59}Co N.M.R. Studies of HRuCo$_3$(CO)$_{12-x}$L$_x$ (L = Amines or Phosphines, $x = 0$ to 2)[1]

Masanobu Hidai,*[a] Hiroyuki Matsuzaka,[a] Yukio Koyasu,[b] and Yasuzo Uchida[b]

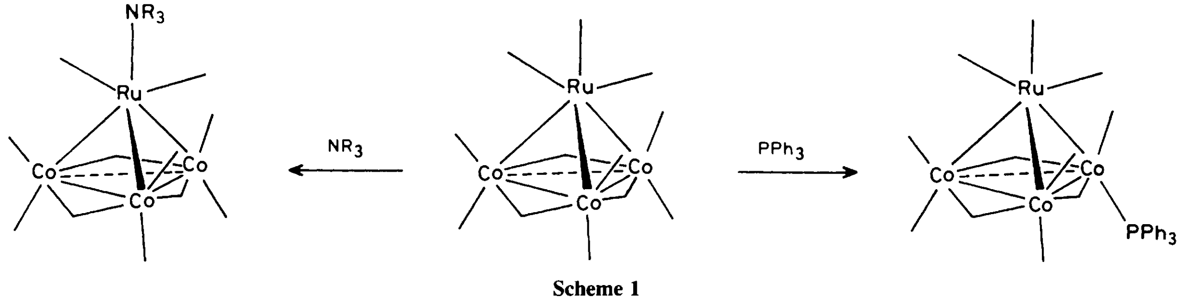
[a] *Department of Synthetic Chemistry and* [b] *Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*

The substitution of amines for the CO ligand of HRuCo$_3$(CO)$_{12}$ takes place preferentially at the ruthenium atom whereas the substitution of phosphines occurs exclusively at the cobalt atoms.

Mixed-metal clusters are currently under intensive investigation because unique catalysis is expected owing to the possible different site reactivities. We previously reported the synthesis and crystal structure of the tetrahedral mixed-metal clusters M[RuCo$_3$(CO)$_{12}$] [M = Na, Et$_4$N, (Ph$_3$P)$_2$N, Ph$_4$P, and H][2] and their catalytic activity for homologation of methanol[2] and hydroformylation of olefins.[1] Herein we report the metallo-selective substitution reaction of amines and phosphines in HRuCo$_3$(CO)$_{12}$ (**1**). To our knowledge, this is one of a few examples in which reactions of mixed-metal clusters with similar substrates occur at different specific locations.[3]

Reactions (Scheme 1) of (**1**) with trimethylamine *N*-oxide (1 mol equiv.) give an amine substituted cluster HRuCo$_3$(CO)$_{11}$(NMe$_3$) (**2**) in moderate yield concurrent with evolution of CO$_2$. Treatment of (**1**) with triethylamine or *N,N,N',N'*-tetramethylethylenediamine (TMEDA) also produces amine-substituted clusters HRuCo$_3$(CO)$_{11}$(NEt$_3$) (**3**) or HRuCo$_3$(CO)$_{10}$(TMEDA) (**4**), respectively. Spectroscopic data for (**1**)—(**4**) are given in Tables 1 and 2. Substitution of electron-donating amines for the carbonyl ligands results in lower shift of ν(CO) in the i.r. spectra. ^{1}H N.m.r. spectra of (**2**)—(**4**) show a broad singlet at δ −17.2 to −17.4 characteristic of a metal hydride. The line-width becomes narrower as the temperature is lowered. The ^{1}H n.m.r. spectrum of (**2**) in the presence of free triethylamine exhibits two sets of distinct peaks assigned to the co-ordinated amine (δ 3.31 triplet; δ 1.46 quartet) and free amine (δ 2.95 triplet; δ 1.26 quartet). This indicates that exchange between the co-ordinated amine and free amine does not occur on the n.m.r. time scale at ambient temperature. In the ^{59}Co n.m.r. spectra of (**2**)—(**4**), only one resonance appears at δ −2630 to −2649 which is similar to the spectrum of the parent cluster. Although we could not obtain crystals of (**2**)—(**4**) suitable for the *X*-ray structural analysis, the above findings lead to the conclusion that amine substitution takes place at the ruthenium atom and the hydride ligand is probably μ$_3$-bound to the Co$_3$ face as in HFeCo$_3$(CO)$_{12}$ and (**1**).[4] Interestingly, analogous treatment of HFeCo$_3$(CO)$_{12}$ with amines gives ammonium salts [HNR$_3$][FeCo$_3$(CO)$_{12}$] and the i.r. spectra in the ν(CO) region are essentially the same as [NEt$_4$][RuCo$_3$(CO)$_{12}$].

The reaction of (**1**) with PPh$_3$ (1 mol equiv.) in dichloromethane gives a mono-substituted cluster HRuCO$_3$(CO)$_{11}$(PPh$_3$) (**5**) in 90% yield. The ^{1}H n.m.r. spectrum exhibits a broad singlet at δ −19.4 assigned to the metal hydride. In the ^{59}Co n.m.r. spectrum two strong peaks at −2574 and −2648 p.p.m. appear with intensity ratio 1 : 2, indicating that the phosphine substitution reaction takes place at the cobalt atom. The existence of a small amount of isomers in solution is supposed by observation of weak peaks at −2461 and −2712 p.p.m. in addition to the above strong peaks. As shown in Table 2, the i.r. spectrum in the ν(CO) region is completely different from that of (**2**) in which the amine ligand is attached to the ruthenium atom. Complex (**5**) shows two medium peaks at 1861 and 1846 cm^{-1} characteristic of bridging carbonyl groups, whereas (**2**) exhibits one medium peak at 1811 cm^{-1}



Scheme 1

Table 1. Chemical shifts of ^{1}H and ^{59}Co n.m.r. spectra of amine- or phosphine-substituted clusters.

Compounds		δH[a]	δCo[b]				
HRuCo$_3$(CO)$_{12}$	(**1**)	−19.4	−2648		[−2464	−2514	−2768][c]
HRuCo$_3$(CO)$_{11}$(NMe$_3$)	(**2**)	−17.2	−2649				
HRuCo$_3$(CO)$_{11}$(NEt$_3$)	(**3**)	−17.2	−2630				
HRuCo$_3$(CO)$_{10}$(TMEDA)	(**4**)	−17.4	−2649				
HRuCo$_3$(CO)$_{11}$(PPh$_3$)	(**5**)	−19.4	−2574(1)[d]	−2648(2)[d]	[−2461	−2712][c]	
HRuCo$_3$(CO)$_{10}$(PPh$_3$)$_2$	(**6**)	−19.7	−2575(1)[d]	−2715(2)[d]	[−2530][c]		

[a] Chemical shifts of metal hydride peaks in CD$_2$Cl$_2$ at 27 °C. [b] In [^{2}H$_6$]acetone at 27 °C. Measured from an aqueous solution of K$_3$[Co(CN)$_6$] as external standard. [c] The peaks in brackets are quite minor. [d] Intensity ratio in parenthesis.

Table 2. I.r. spectra of amine- or phosphine-substituted clusters in the ν(CO) region.

Compounds	ν(CO) (cm^{-1}; in acetone)				
(1)	2062s	2021m	1877m		
(2)	2060w	2018s	2004s	1971m	1811m
(3)	2067w	2020s	2006s	1973m	1815m
(4)	2065w	2019s	2003s	1970m	1812m
(5)	2081m	2045s	2008s	1861m	1846m
(6)	2081m	2045s	2008s	1861m	1846m

assigned to bridging carbonyl groups. Treatment of (**1**) with PPh_3 (2 mol equiv.) gives a disubstituted cluster $HRuCo_3(CO)_{10}(PPh_3)_2$ (**6**). The ^{59}Co n.m.r. spectrum shows two strong peaks with intensity ratio 1:2 at −2575 and −2715 p.p.m. Pursiainen *et al.* have recently disclosed the crystal structure of (**6**) where each phosphine ligand is axially co-ordinated to two different cobalt atoms.[5] A similar substitution reaction of $HFeCo_3(CO)_{12}$ with phosphorus donor ligands was previously reported by Mays *et al.*[6] The substitution takes place preferentially at cobalt and the complexes $HFeCo_3(CO)_{12-x}(PPh_3)_x$ ($x = 1, 2$) are formed by successive substitution of one CO group at each cobalt atom.

We thank the Ministry of Education, Japan, for financial support by a Grant-in-Aid for Scientific Research.

Received, 26th June 1986; Com. 885

References

1 For part 6 in the series 'Homogeneous Multimetallic Catalysts' see, M. Hidai, A. Fukuoka, Y. Koyasu, and Y. Uchida, *J. Mol. Catal.*, 1986, **35**, 29.

2 M. Hidai, M. Orisaku, M. Ue, Y. Koyasu, T. Kodama, and Y. Uchida, *Organometallics*, 1983, **2**, 292.

3 J. R. Fox, W. L. Gladfelter, T. G. Wood, J. A. Smegal, T. K. Foreman, G. L. Geoffroy, I. Tavanaiepour, V. W. Day, and C. S. Day, *Inorg. Chem.*, 1981, **20**, 3214.

4 T. Saito and S. Sawada, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 159.

5 J. Pursiainen and T. A. Pakkanen, *J. Organomet. Chem.*, 1985, **290**, 85.

6 C. G. Cooke and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1975, 455.