CHEMISTRY LETTERS, pp. 471-474, 1989.

Novel Halogen Exchange Reactions between Halosilanes and Rh(I) or Ir(I) Complexes

Hiroshi YAMASHITA, Toshi-aki KOBAYASHI, Teruyuki HAYASHI, and Masato TANAKA*
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

Vaska-type complexes such as $MCl(CO)L_2$ (M = Rh or Ir, L = tertiary phosphine) or the Wilkinson complex $RhCl(PPh_3)_3$ underwent halogen exchange reactions with halosilanes Me_3SiX (X = Br, I) to give $MX(CO)L_2$ or $RhX(PPh_3)_3$ respectively with the formation of Me_3SiCl. The reaction of $RhH(CO)(PPh_3)_3$ with $MeSiCl_3$ also afforded $RhCl(CO)(PPh_3)_2$.

Oxidative addition of organic halides to transition metal complexes is a versatile reaction which allows numerous applications in organic syntheses.1) On the other hand, examples of the reaction of halosilanes are still few. Hence, we have been interested in the reactivities of low-valent transition metal complexes toward halosilanes. In the previous paper, we have disclosed the oxidative addition of halosilanes to Pt(0) complexes to give Si-Pt complexes.2) Further investigation along this line has revealed a novel class of halogen exchange reactions between Rh(I) or Ir(I) halide complexes and halosilanes. Very recently, Churchill and coworkers have found a similar alkoxy-Cl exchange reaction between $Ir(OR)(CO)[P(p\text{-}CH_3C_6H_4)_3]_2$ and Me_3SiCl.3) The paper prompted us to report our preliminary results.4)

When $RhCl(CO)(PMe_3)_2$ was treated with 3 equiv. of Me_3SiI in benzene-d_6 at room temperature, a new ^{1}H-NMR signal arising from methyl protons of Me_3SiCl immediately emerged at 0.28 ppm with reference to Me_4Si. In addition, the reaction mixture showed an IR absorption band at 468 cm^{-1} assignable to ν_{Si-Cl} of Me_3SiCl. The intensity of the ^{1}H-NMR signal of methyl protons of Me_3SiCl formed in the reaction mixture was about half of that of PMe_3 bound to the Rh complex, suggesting that the reaction proceeded nearly quantitatively. After volatiles were removed, yellow powder of $RhI(CO)(PMe_3)_2$ was obtained; mp 110 °C (dec.); IR ($CHCl_3$) 1974 cm^{-1} (ν_{CO}). Anal. Found: C, 20.53; H, 4.42%. Calcd for $C_7H_{18}IOP_2Rh$: C, 20.51; H, 4.43%. These observations clearly indicate that halogen exchange reaction between the Rh-Cl complex and the iodosilane occurs under very mild conditions, Eq. 1.

$$RhCl(CO)(PMe_3)_2 + Me_3SiI \longrightarrow RhI(CO)(PMe_3)_2 + Me_3SiCl \qquad (1)$$

In a separate experiment, the reaction mixture was heated up to 120 °C. But monitoring by means of ^{1}H-NMR did not indicate any further reactions such as oxidative addition of Me_3SiI to $RhI(CO)(PPh_3)_2$.

Similar results of other combinations of Rh(I) or Ir(I) halide complexes with halosilanes are summarized in Table 1. When Me_3SiBr was used in place of Me_3SiI, $RhBr(CO)(PMe_3)_2$ and Me_3SiCl were formed. $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ also underwent similar reactions at room temperature. However, $IrCl(CO)(PPh_3)_2$ did not react with Me_3SiI at room temperature, and the occurrence of halogen exchange required heating at 60 °C. Dissociation energy of the Si-X bond in Me_3SiX increases in the order of $X = I < Br < Cl$ (238, 318, and 410 kJ mol^{-1} respectively).[5)] Hence, the driving force of the halogen exchange is presumably associated with the formation of thermodynamically more stable Si-Cl bond.

$RhH(CO)(PPh_3)_3$ did not react with Me_3SiI at room temperature. However, when

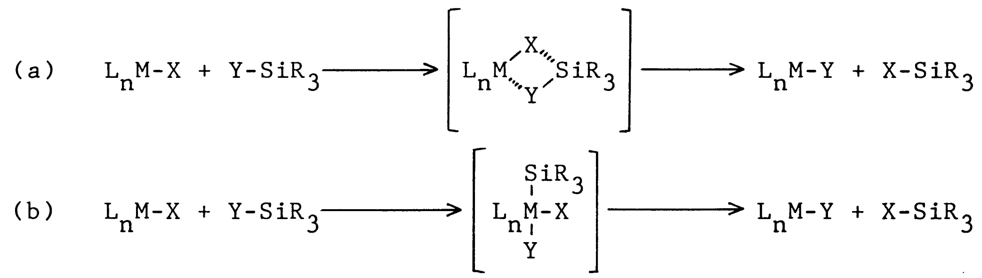
Table 1. Reactions of Rh(I) or Ir(I) complexes with halosilanes[a)]

M(I) complex	Halosilane	Temp/°C	Time/h	Product	Yield[b)]/%
$RhCl(CO)(PPh_3)_2$	Me_3SiI	r.t.	0.5	$RhI(CO)(PPh_3)_2$	84
	Me_3SiBr	r.t.	0.5	$RhBr(CO)(PPh_3)_2$	63
$RhCl(CO)(PMe_3)_2$	Me_3SiI	r.t.	0.25	$RhI(CO)(PMe_3)_2$	58
	Me_3SiBr	r.t.	0.25	$RhBr(CO)(PMe_3)_2$	55
	$MeSiCl_3$	120	20	N.R.[c)]	-
$IrCl(CO)(PPh_3)_2$	Me_3SiI	r.t.	0.5	N.R.[c)]	-
	Me_3SiI	60	1	$IrI(CO)(PPh_3)_2$	80
$IrCl(CO)(PEt_3)_2$	$MeSiCl_3$	120	7	N.R.[c)]	-
$RhCl(PPh_3)_3$	Me_3SiI	r.t.	0.5	$RhI(PPh_3)_3$	83[d)]

a) Rh or Ir complex 0.05-0.2 mmol, halosilane 0.15-0.5 mmol, benzene 0.2-1 ml. b) Isolated yield after recrystalization. In most cases, the reactions proceeded cleanly, as judged from the observation of ^{1}H-NMR. c) No reaction. d) Recrystalization was not made.

the reaction was carried out at 90 °C, ^{1}H-NMR signals of Me_3SiH was observed. Hydride-iodide exchange seemed to take place, though the formation of $RhI(CO)(PPh_3)_2$ could not be confirmed probably because of its unstability in solution.$^{6)}$ In the reaction of $RhH(CO)(PPh_3)_3$ with $MeSiCl_3$, a Rh complex resulted from hydride-chloride exchange could be isolated. Thus, when $RhH(CO)(PPh_3)_3$ was treated with $MeSiCl_3$ at 90 °C for 9.5 h, $RhCl(CO)(PPh_3)_2$ was isolated in 48% yield after recrystalization.$^{7)}$ On the other hand, $IrH(CO)(PPh_3)_3$ did not react with $MeSiCl_3$ even at 120 °C.

As to the mechanism of the halogen exchange reaction, either (a) four center interaction mechanism or (b) oxidative addition-reductive elimination mechanism is envisaged.



$$\text{(a)}\quad L_nM{-}X + Y{-}SiR_3 \longrightarrow \left[L_nM\begin{smallmatrix}X\\ \\ Y\end{smallmatrix}SiR_3 \right] \longrightarrow L_nM{-}Y + X{-}SiR_3$$

$$\text{(b)}\quad L_nM{-}X + Y{-}SiR_3 \longrightarrow \left[\begin{array}{c} SiR_3 \\ | \\ L_nM{-}X \\ | \\ Y \end{array} \right] \longrightarrow L_nM{-}Y + X{-}SiR_3$$

(X = Cl, H; Y = Cl, Br, I)

The only new ^{1}H-NMR signal observed upon the treatment of $RhCl(CO)(PMe_3)_2$ with Me_3SiI in toluene-d_8 at low temperature down to -40 °C was assignable to Me_3SiCl, and any signals which were supposed to arise from possible intermediates could not be observed. Ir(I) complexes are normally more reactive than corresponding Rh(I) complexes in oxidative addition reactions.$^{8)}$ However, in the present halogen exchange reactions, the reactivity was the reverse. This appears against the mechanism (b). In addition, chloro complexes more readily reacted with halosilanes than hydorido complexes; $RhCl(CO)(PPh_3)_2$ reacted with Me_3SiI at room temperature, while $RhH(CO)(PPh_3)_3$ did not react under the same conditions. This does not appear consistent with the mechanism (b) either, since the hydrido ligand being a stronger donor than the chloro ligand.$^{9)}$ On the other hand, the mechanism (b) receives a support from the result that $IrH(PPr^i{}_3)_2$, in situ generated from $IrH_5(PPr^i{}_3)_2$ by the treatment with 2 equiv. neohexene,$^{10)}$ reacted with $MeSiCl_3$ to give $IrHCl(SiMeCl_2)(PPr^i{}_3)_2$.$^{11)}$ According to the papers by Uson and coworkers, oxidative addition of chlorosilanes also seems to take place with $Ir(Oq)(CO)(PAr_3)$

(Oq = 8-oxyquinolate) or $[Ir(cod)(PAr_3)_2]ClO_4$, though the products were not well characterized.[12,13] In addition, there are precedents of the reductive elimination of Si-Cl species from chloro(silyl)metal complexes.[14] Thus, the mechanism (b) can not be denied. At the moment, we cannot unequivocally decide which mechanism is valid.

In conclusion, this paper discloses novel halogen exchange reactions of Rh(I) or Ir(I) complexes with halosilanes. Further studies on the reactivities of halosilanes toward low-valent transition metal complexes are in progress.

References

1) J. P. Collmann, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley (1987), p. 681.
2) H. Yamashita, T. Hayashi, T. -a. Kobayashi, M. Tanaka, and M. Goto, J. Am. Chem. Soc., 110, 4417 (1988).
3) B. J. Rappoli, T. S. Janik, M. R. Churchill, J. S. Thompson, and J. D. Atwood, Organometallics, 7, 1939 (1988).
4) Presented at the 35th Symposium on Organometallic Chemistry, Osaka, November 1988, Abstr., No. PA112.
5) D. A. Armitage, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford (1982), Vol. 2, p. 6.
6) L. Vallarino, J. Chem. Soc., 1957, 2287.
7) Chlorination of transition metal hydride complexes with chlorosilanes have been reported; see N. J. Archer, R. N. Haszeldine, and R. V. Parish, J. Organomet. Chem., 81, 335 (1974), and R. N. Haszeldine, L. S. Malkin, and R. V. Parish, J. Organomet. Chem., 182, 323 (1979).
8) J. Halpern, Acc. Chem. Res., 3, 386 (1970).
9) For example, $IrH(CO)(PPh_3)_3$ was reported to react more readily with R_3SiH to give the adduct than $IrCl(CO)(PPh_3)_2$; see J. F. Harrod, D. F. R. Gilson, and R. Charles, Can. J. Chem., 47, 2205 (1969).
10) J. W. Faller and H. Felkin, Organometallics, 4, 1488 (1985).
11) H. Yamashita, T. Hayashi, M. Tanaka, and M. Goto, J. Organomet. Chem., manuscripts involving the X-ray analysis data are in preparation.
12) R. Uson, L. A. Oro, M. A. Ciriano, and R. Gonzalez, J. Organomet. Chem., 205, 259 (1981).
13) R. Uson, L. A. Oro, and M. J. Fernandez, J. Organomet. Chem., 193, 127 (1980).
14) C. S. Cundy, B. M. Kingstone, and M. F. Lappert, Adv. Organomet. Chem., 11, 253 (1973).

(Received January 10, 1989)