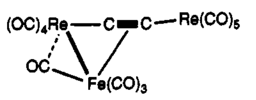
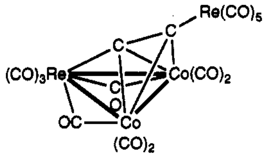
presumably through an intermediate similar to **A** or **B**. Carty and co-workers[50,51] have reported the isolation of binuclear complexes similar to the postulated intermediates **A** and **B** from the reaction of phosphinoalkynes and $[Fe_2(CO)_9]$.

The reaction of $[\{Re(CO)_5\}_2(\mu\text{-}C{\equiv}C)]$ (**6**) with a number of metal substrates[52] was reported while this manuscript was in preparation. It is noteworthy that the reaction of **6** with $[Fe_2(CO)_9]$ incorporates only one Fe atom giving $[FeRe_2(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}C{\equiv}C)(CO)_{13}]$ (**7**) in which the integrity of the Re—C≡C—Re unit in **5** is maintained. The $[Fe(CO)_4]$ unit in **7** interacts with the bicarbide ligand and one Re atom without the formation of a metal triangle, unlike the reaction of **6** with $[Co_2(CO)_8]$ which gives $[Co_2Re_2(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C{\equiv}C)(\mu\text{-}CO)_2(CO)_{12}]$ (**8**), structurally analogous to **4**.



7



8

Conclusion

The reaction of a metal ethynediyl complex with a metal carbonyl is a useful method for the synthesis of mixed-metal bicarbide complexes. Substantial skeletal rearrangement can occur during the formation of the bicarbide complexes. The positions of the metal atoms in the frameworks of the bicarbide products may reflect the relative propensities of the metal centers to form σ- or π-bonds with the C_2 ligand. In $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (**2**), the cluster ruthenium atom Ru2 has migrated from a σ-bonding position in precursor **1** to a π-bonding position, while Fe2 has moved into the σ-bonding position.

Acknowledgment. We are grateful to the U.S. Department of Energy (DE-FG05-85ER13432) and the Kentucky EPSCoR program (NSF Grant RII-8610671) for financial support, the University of Kentucky Center for Computational Science for computing time and facilities, the University of Kentucky Major Research Instrumentation Bond Program (ID No. 7E-8E48-25), and the National Science Foundation (CHE-9113581) for equipment, and to Johnson-Matthey, Inc., for a loan of ruthenium trichloride. We thank Professors W. Beck, R. M. Bullock, Y. Chi, and J. A. Davies for providing manuscripts prior to publication.

Supplementary Material Available: Tables of anisotropic displacement parameters, complete bond angles, hydrogen atom parameters, least-squares planes, and torsion angles for **2** (5 pages). Ordering information is given on any current masthead page.

OM920060G

---

(49) Fritz, P. M.; Polborn, K.; Steimann, M.; Beck, W. *Chem. Ber.* **1989**, *122*, 889.

(50) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

(51) Smith, W. F.; Yule, J.; Taylor, N. J.; Paik, H. N.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 1593.

(52) Weidmann, T.; Weinrich, V.; Wagner, B.; Robl, C.; Beck, W. *Chem. Ber.* **1991**, *124*, 1363.

Highly Selective Synthesis of Chlorosilanes from Hydrosilanes

Atsutaka Kunai, Toshihiro Kawakami, Eiji Toyoda, and Mitsuo Ishikawa*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 724, Japan

Received January 3, 1992

Summary: A highly selective synthesis of chlorosilanes from hydrosilanes is reported. The reactions of $PhMe_2SiH$, Ph_2MeSiH, and Bu_2MeSiH with 2 equiv of $CuCl_2$ and a catalytic amount of CuI in Et_2O afforded the respective triorganochlorosilanes. Similar reactions of polyhydrosilanes such as Et_2SiH_2, $PhMeSiH_2$, $PhSiH_3$, $HEt_2SiSiEt_2H$, and HMePhSiSiPhMeH with 2 equiv of the $CuCl_2(CuI)$ reagent gave the corresponding monochlorinated hydrosilanes selectively, while treatment with 4 equiv of the reagent afforded dichlorosilanes as the sole product. Similar treatment of *t*-$BuMe_2SiH$ with 2 equiv of the reagent in a mixed Et_2O and THF solvent afforded *t*-$BuMe_2SiCl$.

Chlorosilanes are useful starting materials in synthetic organosilicon chemistry. In an attempt to prepare desired silicon compounds, sometimes we have been confronted with the problem of preparing chlorosilanes from hydrosilanes. To date, several methods are available for the preparation of chlorosilanes from hydrosilanes.[1-6] These methods give the chlorosilanes in good yields. However, it is difficult to prepare selectively silicon compounds which contain both Si–Cl and Si–H bonds from polyhydrosilanes. In an effort to develop a method for the preparation of chlorohydrosilanes such as monosubstituted chlorosilanes, $RSiH_2Cl$, disubstituted chlorosilanes, R_2SiHCl, and 1-chloro-2-hydrodisilanes, ClR_2SiSiR_2H, we have found that the reaction of the H of the hydrosilanes with $CuCl_2$ in the presence of a catalytic amount of CuI is a convenient method for the synthesis of such chlorosilanes.

Results and Discussion

Triorganosilanes do not react with copper(II) chloride by themselves. For example, treatment of dimethylphenylsilane (**1a**)[7] with 2 molar equiv of $CuCl_2$ in diethyl ether or in THF afforded no chlorodimethylphenylsilane.

---

(1) Whitmore, F. C.; Pietrusza, E. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1947**, *69*, 2108.

(2) Jenkins, J. W.; Post, H. W. *J. Org. Chem.* **1950**, *15*, 556.

(3) Russel, G. A. *J. Org. Chem.* **1956**, *21*, 1190.

(4) Curtice, J.; Gilman, H.; Hammond, G. S. *J. Am. Chem. Soc.* **1957**, *79*, 4754.

(5) Nagai, Y.; Yamaszaki, K.; Shiojima, I.; Kobori, N.; Hayashi, M. *J. Organomet. Chem.* **1967**, *9*, P21.

(6) Nagai, Y.; Matsumoto, H.; Yagihara, T.; Morishita, K. *Kogyo Kagaku Zasshi* **1968**, *71*, 112.

(7) Baines, I. E.; Eaborn, C. *J. Chem. Soc.* **1956**, 1436.

0276-7333/92/2311-2708$03.00/0

The starting compound $PhMe_2SiH$ was recovered unchanged in both cases. However, when a trace of CuI was added to the mixture, the reaction proceeded very smoothly to give chlorodimethylphenylsilane (**1b**)[8] without any side reactions. Thus, treatment of $PhMe_2SiH$ with 2 molar equiv of $CuCl_2$ in the presence of a catalytic amount of CuI in diethyl ether at room temperature for 13 h produced $PhMe_2SiCl$ in 82% yield (Scheme I). A trace of tetramethyldiphenyldisiloxane from hydrolysis of the product was observed, but no other products were detected by either GLC or spectrometric analysis. Similar reaction of methyldiphenylsilane (**2a**)[9] with $CuCl_2$ in the presence of CuI in ether gave chloromethyldiphenylsilane (**2b**)[10] in 77% yield.

Scheme I

$$\underset{\textbf{1a–3a}}{R_2R'Si{-}H} + 2CuCl_2 \xrightarrow{CuI} \underset{\textbf{1b–3b}}{R_2R'Si{-}Cl} + 2CuCl{\cdot}HCl$$

1: R = Me, R′ = Ph

2: R = Ph, R′ = Me

3: R = Bu, R′ = Me

This procedure also works well with trialkylsilanes. Thus, treatment of di-*n*-butylmethylsilane (**3a**)[11] with 2 equiv of $CuCl_2(CuI)$[12] under the same conditions produced di-*n*-butylchloromethylsilane (**3b**)[11] in 87% yield.

In order to get more information for the formation of chlorosilanes in the present system, we carried out the reaction of dimethylphenylsilane with CuI alone. Thus, treatment of dimethylphenylsilane with 2 equiv of CuI in ether afforded no iodosilane, and the starting hydrosilane was recovered unchanged. However, when iodotrimethylsilane was stirred in the presence of 2 equiv of $CuCl_2$ in dibutyl ether, all of the iodosilane disappeared after 30 min and chlorotrimethylsilane was obtained in 70% yield as the sole product. The facts that a trace amount of CuI catalyzes the present reaction and 2 equiv of $CuCl_2$ is necessary for replacing one hydrogen atom by a chlorine atom suggest that a reactive species such as CuICl or CuI_2 should be formed and plays an important role in the present reaction. Although the detailed mechanism is not yet clear, it seems likely that iodosilanes are initially formed by the reaction of the hydrosilanes with such species, and the iodosilanes thus formed react with $CuCl_2$ to give the chlorosilanes.

The present method can be applicable to the synthesis of chlorodiorganosilanes (R_2SiHCl), dichlorodiorganosilanes (R_2SiCl_2), chloroorganosilanes ($RSiH_2Cl$), and dichloroorganosilanes ($RSiHCl_2$) from the corresponding organosilanes. For example, the reaction of diethylsilane (**4a**)[13] with 2 equiv of $CuCl_2(CuI)$ in ether at room temperature yielded chlorodiethylsilane (**4b**)[14] in 68% yield, while similar reaction of methylphenylsilane (**5a**)[15] afforded chloromethylphenylsilane (**5b**)[15] in 77% yield (Scheme II). In both cases, the monochloro derivatives were formed selectively. Neither the dichlorosilanes nor other products were observed.

Scheme II

$$\underset{\textbf{4a, 5a}}{RR'SiH_2} + 2CuCl_2 \xrightarrow{CuI} \underset{\textbf{4b, 5b}}{RR'SiHCl} + 2CuCl{\cdot}HCl$$

4: R = R′ = Et

5: R = Me, R′ = Ph

Chloro- and dichlorophenylsilane can readily be synthesized selectively from phenylsilane (**6a**).[16] Thus, treatment of **6a** with 2 equiv of $CuCl_2(CuI)$ in ether at room temperature afforded chlorophenylsilane (**6b**)[17] in 70% yield, in addition to a trace amount (<2%) of dichlorophenylsilane (**7b**). Similar treatment of **6a** with 4 equiv of $CuCl_2(CuI)$ under the same conditions gave only dichlorophenylsilane in 66% yield (Scheme III).

Scheme III

$$\underset{\textbf{6a}}{PhSiH_3} + 2CuCl_2 \xrightarrow{CuI} \underset{\textbf{6b}}{PhSiH_2Cl} + 2CuCl{\cdot}HCl$$

$$\textbf{6a} + 4CuCl_2 \xrightarrow{CuI} \underset{\textbf{7b}}{PhSiHCl_2} + 4CuCl{\cdot}HCl$$

1,2-Dihydrodisilanes also react with 2 equiv of $CuCl_2(CuI)$ in diethyl ether under the same conditions to give chlorodisilanes, while reaction with 4 equiv of the copper salt gave dichlorodisilanes. When 1,1,2,2-tetraethyldisilane (**8a**)[18] was treated with 2 equiv of $CuCl_2(CuI)$, 1-chloro-2-hydrotetraethyldisilane (**8b**) was obtained in 57% yield, in addition to a 16% yield of 1,2-dichlorotetraethyldisilane (**9b**)[19] and 11% of unchanged compound **8a** (Scheme IV). The product **8b** can readily be separated from **8a** and **9b** by distillation. Similar treatment of **8a** with 4 equiv of $CuCl_2(CuI)$ under the same conditions gave **9b** as sole product in 90% yield.

Scheme IV

$$\underset{\textbf{8a}}{HEt_2Si{-}SiEt_2H} + 2CuCl_2 \xrightarrow{CuI} \underset{\textbf{8b}}{ClEt_2Si{-}SiEt_2H} + 2CuCl{\cdot}HCl$$

$$\textbf{8a} + 4CuCl_2 \xrightarrow{CuI} \underset{\textbf{9b}}{ClEt_2Si{-}SiEt_2Cl} + 4CuCl{\cdot}HCl$$

$$\underset{\textbf{10a}}{HMePhSi{-}SiPhMeH} + 2CuCl_2 \xrightarrow{CuI} \underset{\textbf{10b}}{ClMePhSi{-}SiPhMeH} + 2CuCl{\cdot}HCl$$

$$\textbf{10a} + 4CuCl_2 \xrightarrow{CuI} \underset{\textbf{11b}}{ClMePhSi{-}SiPhMeCl} + 4CuCl{\cdot}HCl$$

1,2-Dimethyl-1,2-diphenyldisilane (**10a**)[20] also reacted with 2 equiv of $CuCl_2(CuI)$ under the same conditions to give 1-chloro-1,2-dimethyl-1,2-diphenyldisilane (**10b**) in 59% yield. 1,2-Dichloro-1,2-dimethyldiphenyldisilane (**11b**)[21] was also produced in 4% yield, but product **10b**

---

[8] MacMullen, R.; Helmann, C. W.; Habber, C. P.; Hymo, L. A.; Carpenter, S.; Carr, A. J. *J. Am. Chem. Soc.* **1954**, *76*, 6392.

[9] Mironv, V. F.; Petrov, A. D. *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1957**, 383; *Chem. Abstr.* **1957**, *51*, 15457.

[10] Daudt, W. H.; Hyde, J. F. *J. Am. Chem. Soc.* **1952**, *74*, 386.

[11] Chernyshev, E. A.; Petrov, A. D.; Krasnova, T. L. *Vysokomolekul. Soedin.* **1962**, 103-8.

[12] The mixture of stoichiometric $CuCl_2$ with catalytic CuI is hereafter expressed as $CuCl_2(CuI)$.

[13] Tannenbaum, S.; Kaye, S.; Lewenz, G. F. *J. Am. Chem. Soc.* **1954**, *76*, 1027.

[14] Shostakovskii, M. F.; Kochkin, D. A.; Rog, V. M. *Izvest. Akad. Nauk SSSR, Otdel. Kim. Nauk* **1955**, 953; *Chem. Abstr.* **1956**, *50*, 9320.

[15] Donald, R.; Weyenberg, D. R.; Bey, A. E.; Stewart, H. F.; Atwell, W. H. *J. Organomet. Chem.* **1966**, *6*, 583.

[16] Gilman, H.; Wittenberg, D. *J. Org. Chem.* **1958**, *23*, 500.

[17] Mawaziny, S. *J. Chem. Soc. A* **1970**, 1641.

[18] Katherine, A.; Wensley, B. *Organometallics* **1987**, *6*, 1590.

[19] Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604.

[20] Steudel, W.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 6129.

Table I. Chlorination of Hydrosilanes with Copper Salts

hydrosilane (amt, mmol)	amt of $CuCl_2$, mmol	amt of CuI, mmol	solvent (amt, mL)	reaction time, h	chlorosilane (%)	bp, °C/mmHg	mp, °C
$PhMe_2SiH$[7] (76.0)	150.2	1.60	Et_2O (300)	13	$PhMe_2SiCl$ (82)	76–77/12[a]	
Ph_2MeSiH[9] (53.8)	102.9	1.56	Et_2O (250)	21	$Ph_2MeSiCl$ (77)	85–86/0.5[b]	
Bu_2MeSiH[11] (93.7)	193.2	4.76	Et_2O (200)	70	$Bu_2MeSiCl$ (87)	92–94/16	
Et_2SiH_2[13] (159.9)	342.3	8.14	Et_2O (300)	43	Et_2SiHCl (68)	90–92[c]	
$PhMeSiH_2$[15] (125.4)	251.7	6.46	Et_2O (300)	36	$PhMeSiHCl$ (77)	76–78/21[d]	
$PhSiH_3$[16] (94.4)	187.3	4.63	Et_2O (200)	72	$PhSiH_2Cl$ (70)	154–158	
$PhSiH_3$ (97.2)	389.7	4.63	Et_2O (250)	94	$PhSiHCl_2$ (66)	77–80/16[e]	
$HEt_2SiSiEt_2H$[18] (57.2)	119.0	1.60	Et_2O (200)	18	$ClEt_2SiSiEt_2H$ (57) $ClEt_2SiSiEt_2Cl$ (16)	83/16	
$HEt_2SiSiEt_2H$ (57.9)	238.1	2.87	Et_2O (300)	8	$ClEt_2SiSiEt_2Cl$ (90)	110–112/16[f]	
$HMePhSiSiPhMeH$[20] (41.3)	82.4	1.01	Et_2O (200)	72	$ClMePhSiSiPhMeH$ (59) $ClMePhSiSiPhMeCl$ (4)	83/2	
$HMePhSiSiPhMeH$ (41.3)	174.9	1.68	Et_2O (350)	122	$ClMePhSiSiPhMeCl$ (79)	125–133/2[g]	
t-$BuMe_2SiH$[24] (213.0)	431.7	11.2	Et_2O/THF (350/150)	60	t-$BuMe_2SiCl$ (73)	124–125[h]	90–91[i]
t-$BuMe_2SiH$ (219.0)	448.9	13.3	THF (500)	70	t-$BuMe_2SiCl$ (75)	124–125	90–91

[a] Literature[10] bp 189–191 °C. [b] Literature[10] bp 295 °C. [c] Literature[25] bp 99.7 °C. [d] Literature[26] bp 176 °C/740 mmHg. [e] Literature[27] bp 184 °C. [f] Literature[19] bp 118–124 °C/27 mmHg. [g] Literature[21] bp 141–146 °C/2 mmHg. [h] Literature[24] bp 124–126 °C. [i] Literature[24] mp 91.5 °C.

Table II. Analytical Data for the Products

$PhMe_2SiCl$:[8] MS *m/e* 170 (M^+); ^1H NMR (δ in $CDCl_3$) 0.69 (s, 6 H, MeSi), 7.36–7.66 (m, 5 H, phenyl ring H); ^{13}C NMR (δ in $CDCl_3$) 2.03 (MeSi), 128.05, 130.31, 133.05, 136.19 (phenyl ring C)

$Ph_2MeSiCl$:[10] MS *m/e* 232 (M^+); ^1H NMR (δ in $CDCl_3$) 0.94 (s, 3 H, MeSi), 7.37–7.67 (m, 10 H, phenyl ring H); ^{13}C NMR (δ in $CDCl_3$) 0.88 (MeSi), 128.09, 130.51, 134.03, 134.50 (phenyl ring C)

$Bu_2MeSiCl$:[11] MS *m/e* 192 (M^+); ^1H NMR (δ in $CDCl_3$) 0.36 (s, 3 H, MeSi), 0.79 (t, 4 H, $-CH_2CH_2CH_2CH_3$), 0.90 (t, 6 H, CH_3), 1.36 (m, 8 H, $-CH_2CH_2CH_2CH_3$); ^{13}C NMR (δ in $CDCl_3$) −0.11 (MeSi), 13.68, 17.34, 25.14, 26.04 (*n*-Bu)

Et_2SiHCl:[14] MS *m/e* 122 (M^+); ^1H NMR (δ in $CDCl_3$) 0.83–0.93 (m, 4 H, $-CH_2-$), 1.06 (t, 6 H, CH_3), 4.65 (t, 1 H, HSi); ^{13}C NMR (δ in $CDCl_3$) 6.58 (CH_3), 7.39 ($-CH_2-$)

$PhMeSiHCl$:[15] MS *m/e* 156 (M^+); ^1H NMR (δ in $CDCl_3$) 0.80 (d, J = 3.3 Hz, 3 H, MeSi), 5.37 (q, J = 3.3 Hz, 1 H, HSi), 7.40–7.71 (m, 5 H, phenyl ring H); ^{13}C NMR (δ in $CDCl_3$) 0.11 (MeSi), 128.23, 130.87, 133.37, 133.62 (phenyl ring C). Anal. Calcd for C_7H_9SiCl: C, 53.66; H, 5.79. Found: C, 53.62; H, 5.96

$PhSiH_2Cl$:[17] MS *m/e* 142 (M^+); ^1H NMR (δ in $CDCl_3$) 5.26 (s, 2 H, HSi), 7.39–7.73 (m, 5 H, phenyl ring H); ^{13}C NMR (δ in $CDCl_3$) 128.41, 130.47, 131.34, 134.43 (phenyl ring C).

$PhSiHCl_2$: MS *m/e* 176 (M^+); ^1H NMR (δ in $CDCl_3$) 5.99 (s, 1 H, HSi), 7.46–7.76 (m, 5 H, phenyl ring H); ^{13}C NMR (δ in $CDCl_3$) 128.54, 131.10, 132.27, 133.33 (phenyl ring C). Anal. Calcd for $C_6H_6SiCl_2$: C, 40.69; H, 3.41. Found: C, 40.39; H, 3.30

$ClEt_2SiSiEt_2H$: MS *m/e* 208 (M^+); ^1H NMR (δ in $CDCl_3$) 0.74–1.10 (m, 20 H, EtSi), 3.65 (m, 1 H, HSi); ^{13}C NMR (δ in $CDCl_3$) 1.49, 7.01, 9.62, 9.67 (EtSi); IR 2957, 2876, 2092, 1458, 1412, 1379, 1232 cm^{-1}. Anal. Calcd for $C_8H_{21}Si_2Cl$: C, 46.00; H, 10.13. Found: C, 45.86; H, 10.08

$ClEt_2SiSiEt_2Cl$:[19] MS *m/e* 242 (M^+); ^1H NMR (δ in $CDCl_3$) 0.97–1.16 (m, 20 H, EtSi); ^{13}C NMR (δ in $CDCl_3$) 6.81 (CH_3), 8.54 (CH_2)

$ClMePhSiSiPhMeH$: MS *m/e* 276 (M^+); ^1H NMR (δ in $CDCl_3$) 0.51, 0.53 (d, 3 H, *Me*SiHPh), 0.71, 0.76 (s, 3 H, *Me*SiClPh), 7.28–7.58 (m, 10 H, phenyl ring H); ^{13}C NMR (δ in $CDCl_3$) −8.26 (*Me*SiHPh), 1.22 (*Me*SiClPh), 128.05, 128.10, 128.16, 129.45, 130.10, 130.14, 133.50, 134.95 (phenyl ring carbons); IR 3067, 3052, 3022, 2962, 2900, 2112, 1428, 1251, 1109 cm^{-1}. Anal. Calcd for $C_{14}H_{17}Si_2Cl$: C, 60.72; H, 6.19. Found: C, 60.71; H, 6.18

$ClMePhSiSiPhMeCl$:[21] MS *m/e* 310 (M^+); ^1H NMR (δ in $CDCl_3$) 0.79, 0.86 (s, 6 H, MeSi), 7.31–7.65 (m, 10 H, phenyl ring H); ^{13}C NMR (δ in $CDCl_3$) 0.06 (MeSi), 128.18, 128.27, 130.48, 130.53, 133.66, 133.71, 133.51, 134.05 (phenyl ring C)

t-$BuMe_2SiCl$:[24] MS *m/e* 150 (M^+); ^1H NMR (δ in $CDCl_3$) 0.35 (s, 6 H, MeSi), 0.97 (s, 9 H, CMe_3); ^{13}C NMR (δ in $CDCl_3$) −1.56 (MeSi), 19.05 (CMe_3)

could readily be isolated by fractional distillation. Treatment of **10a** with 4 equiv of $CuCl_2$(CuI), however, afforded the dichloride **11b** in 79% yield, as the sole volatile product.

A hydrosilane bearing a bulky substituent also can be transformed into a chlorosilane in a mixed solvent composed of Et_2O and THF at room temperature, but not in Et_2O alone. When *tert*-butyldimethylsilane (**12a**) was

$$\underset{\textbf{12a}}{tert\text{-}BuMe_2Si\text{-}H} + 2CuCl_2 \xrightarrow{CuI} \underset{\textbf{12b}}{tert\text{-}BuMe_2Si\text{-}Cl} + 2CuCl\cdot HCl$$

treated with 2 equiv of $CuCl_2$(CuI) in THF at room temperature, *tert*-butylchlorodimethylsilane (**12b**) was obtained in 75% yield.[22] In a mixed Et_2O and THF solvent in the ratio 2.3:1, t-$BuMe_2SiCl$ was obtained in 73% yield.

Experimental Section

General Procedures. Diethyl ether and tetrahydrofuran used as a solvent were dried over sodium benzophenone–ketyl and distilled just before use. All chlorination reactions were carried out at room temperature under an atmosphere of dry nitrogen. Products were separated from the reaction mixture by filtration followed by distillation of the filtrate through a short distillation column. The results of the chlorination reactions are summarized in Table I. Representative experimental procedures are described below.

Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. ^1H and ^{13}C NMR spectra were determined with a JEOL Model EX-270 spectrometer using deuteriochloroform as a solvent. Mass spectra were measured on a Simadzu Model QP-1000 instrument. Analytical data for the chlorination products are summarized in Table II.

Preparation of Chlorodimethylphenylsilane (1b). Into a 500-mL flask fitted with a condenser was placed a mixture of 10.4 g (76.0 mmol) of $PhMe_2SiH$,[7] 20.2 g (150.2 mmol) of anhydrous $CuCl_2$, and 0.305 g (1.60 mmol) of anhydrous CuI in 300 mL of ether. The mixture was stirred by magnetic stirrer at room temperature for 13 h. The resulting mixture was filtered to remove copper salts. The solution was concentrated, and the residue was fractionally distilled under reduced pressure to give 10.7 g (82%

---

(21) Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1971**, *31*, 17.

(22) The chlorosilane **12b** obtained after distillation showed light red color due to traces of iodine species, although all spectral data were identical with those obtained from Shin-Etsu Chemical Co. Ltd.

yield) of $PhMe_2SiCl$:[8] bp 76–77 °C/12 mmHg.

Preparation of Chloromethyldiphenylsilane (2b). A mixture of 10.7 g (53.8 mmol) of Ph_2MeSiH,[9] 13.8 g (102.9 mmol) of anhydrous $CuCl_2$, and 0.297 g (1.56 mmol) of anhydrous CuI in 250 mL of ether was stirred at room temperature for 21 h. The mixture was filtered, and the filtrate was concentrated. The residue was fractionally distilled under reduced pressure to give 9.7 g (77% yield) of $Ph_2MeSiCl$:[10] bp 85–86 °C/0.5 mmHg.

Preparation of Dibutylchloromethylsilane (3b). A mixture of 14.8 g (93.7 mmol) of Bu_2MeSiH,[11] 26.0 g (193.2 mmol) of anhydrous $CuCl_2$, and 0.910 g (4.76 mmol) of anhydrous CuI in 200 mL of ether was stirred at room temperature for 70 h. The mixture was fractionally distilled under reduced pressure to give 15.8 g (87% yield) of $Bu_2MeSiCl$:[11] bp 92–94 °C/16 mmHg.

Reaction of Iodotrimethylsilane with $CuCl_2$. Iodotrimethylsilane (bp 106.5 °C) was prepared by the reaction of hexamethyldisilane and iodine.[23] Into a suspension of $CuCl_2$ (23.2 g, 172.6 mmol) in di-*n*-butyl ether (200 mL), was added Me_3SiI (17.0 g, 84.8 mmol) over 10 min. The mixture was stirred at room temperature, and the progress of the reaction was monitored by GLC. After 10 min, the peak due to the iodosilane diminished to half and a new peak due to chlorotrimethylsilane appeared. All of the iodosilane completely disappeared within 30 min. The reaction mixture was filtered to remove copper salts. The filtrate was distilled through a short distillation column under atmospheric pressure to give 6.41 g (59.0 mmol, 70% yield) of Me_3SiCl:[24] bp 57 °C; ^1H NMR (δ in C_6D_6) 0.23 (SiMe); ^{13}C NMR (δ in C_6D_6) 3.00 (SiMe).

Registry No. **1a**, 766-77-8; **1b**, 768-33-2; **2a**, 776-76-1; **2b**, 144-79-6; **3a**, 999-35-9; **3b**, 996-07-6; **4a**, 542-91-6; **4b**, 1609-19-4; **5a**, 766-08-5; **5b**, 1631-82-9; **6a**, 694-53-1; **6b**, 4206-75-1; **7b**, 1631-84-1; **8a**, 7535-09-3; **8b**, 141557-03-1; **9b**, 85590-06-3; **10a**, 18410-59-8; **10b**, 141557-04-2; **11b**, 29442-41-9; **12a**, 29681-57-0; **12b**, 18162-48-6; iodotrimethylsilane, 16029-98-4; chlorotrimethylsilane, 75-77-4.

---

[23] Kumada, M.; Shiina, K.; Yamaguchi, M. *Kogyo Kagaku Zasshi* **1954**, *57*, 230.

[24] Samples were obtained from Shin-Etsu Chemical Co. Ltd.

[25] MacKenzie, C. A.; Mills, A. P.; Scott, J. M. *J. Am. Chem. Soc.* **1950**, *72*, 2032.

[26] Ponomarenko, V. A.; Odabashyan, G. V.; Petrov, A. D. *Dokl. Akad. Nauk SSSR* **1960**, *130*, 333; *Chem. Abstr.* **1960**, *54*, 10833.

[27] Lewis, R. N. *J. Am. Chem. Soc.* **1947**, *69*, 717.

Stepwise and Reversible Cleavage of the C–O Double Bond of Diaryl Ketones by Lanthanide Metals

Zhaomin Hou,[*,†] Hiroshi Yamazaki,[†] Yuzo Fujiwara,[‡] and Hiroshi Taniguchi[§]
The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama 351-01, Japan,
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 724, Japan, and Department of Chemical Science and Technology,
Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Fukuoka 812, Japan

Received February 25, 1992

Summary: Reaction of diaryl ketones with excess lanthanide (Ln = Sm, Yb) metals caused the complete cleavage of their C–O double bonds. This C–O bond-cleavage process was stepwise and reversible and was possibly mediated by a μ-oxo, μ-alkylidene complex.

It has been reported that reaction of diaryl ketones with lanthanide metals gives corresponding dianions that possess high nucleophilic reactivity.[1] We have recently isolated and structurally characterized one of these dianionic compounds,[2] and during this study we have found that further reaction of these dianionic compounds or their parent diaryl ketones with excess lanthanide metals led to complete cleavage of their C–O bonds and gave the corresponding deoxygenation products after hydrolysis.

There have been many reports on the C–O bond cleavage of ketones and aldehydes which is promoted by metals or metal complexes.[3-6] A few mechanisms have been proposed for the C–O bond-cleavage process. In the reaction of active titanium metal or some metal alkylidene

Table I. Reaction of Diaryl Ketones with Lanthanide Metals[a]

Ln[b]	ketone	Ln:ketone	reacn time	product distribn[c] (amt, %)
Yb	benzophenone	3:1	4 h	benzhydrol (100), diphenylmethane (0)
			1 day	benzhydrol (90), diphenylmethane (10)
Sm	benzophenone	3:1	4 h	benzhydrol (92), diphenylmethane (8)
			1 day	benzhydrol (85), diphenylmethane (15)
Sm	9-fluorenone	2:1	1 day	9-fluorenol (71), fluorene (29)
		5:1	1 day	9-fluorenol (66), fluorene (34)
			3 days	9-fluorenol (35), fluorene (65)

[a] Room temperature in THF/HMPA. [b] The metals were activated with 2% of ICH_2CH_2I. [c] Molar ratio determined by ^1H NMR spectroscopy. The conversion of the reactions was 100%.

[†] The Institute of Physical and Chemical Research (RIKEN).

[‡] Hiroshima University.

[§] Kyushu University.

[1] (a) Hou, Z.; Takamine, K.; Fujiwara, Y.; Taniguchi, H. *Chem. Lett.* **1987**, 2061. (b) Hou, Z.; Takamine, K.; Aoki, O.; Shiraishi, H.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1988**, 668. (c) *J. Org. Chem.* **1988**, *53*, 6077. (d) Olivier, H.; Chauvin, Y.; Saussine, L. *Tetrahedron* **1989**, *45*, 165. (e) Takaki, K.; Tanaka, S.; Beppu, S.; Tsubaki, Y.; Fujiwara, Y. *Chem. Lett.* **1990**, 1427.

[2] Hou, Z.; Yamazaki, H.; Kobayashi, K.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.*, in press.

[3] (a) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405. (b) Kahn, B. E.; Riecke, R. T. *Chem. Rev.* **1988**, *88*, 733.

[4] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 812–815. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

[5] (a) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213. (b) Chisholm, M. H.; Klang, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2324. (c) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 602, 607. (d) Chisholm, M. H.; Lucas, E. A.; Huffman, J. C.; Folting, K.; Lobkovsky, E. B.; Streib, E. *J. Chem. Soc., Chem. Commun.* **1991**, 847. (e) Fujiwara, Y.; Ishikawa, R.; Akiyama, F.; Teranishi, S. *J. Org. Chem.* **1978**, *43*, 2477.

0276-7333/92/2311-2711$03.00/0