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Synthesis and Reactivity of the Osmate(0) Complexes $M[Os(CO)_2(\eta\text{-}C_5R_5)]$ ($M = Li, Na; R = H, Me$): Versatile Synthons for Synthesis of Organoosmium Complexes

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The anionic osmium complex $Li[Os(CO)_2(\eta\text{-}C_5Me_5)]$ (**2a**) was synthesized by the reaction of the hydrido complex $(\eta\text{-}C_5Me_5)Os(CO)_2H$ (**3a**) with *n*-BuLi. The unsubstituted cyclopentadienyl derivatives $M[Os(CO)_2(\eta\text{-}C_5H_5)]$ (**2b**, M = Li; **2c**, M = Na) were also prepared by an identical method or by two-electron reduction of $(\eta\text{-}C_5H_5)Os(CO)_2I$ with sodium naphthalenide. Reactions of **2a** with various electrophiles (CH_3I, D_2O, Me_3SiCl, $^tBuSiH_2Cl$, $Me_3SiSiMe_2Cl$, Me_2SiCl_2, and Me_3GeCl) afforded the nucleophilic substitution products $(\eta\text{-}C_5Me_5)Os(CO)_2R$ (R = CH_3, D, $SiMe_3$, $SiH_2{}^tBu$, $SiMe_2SiMe_3$, $SiClMe_2$, and $GeMe_3$) in good to excellent yields. Analogous products were also obtained by the reaction of **2b** with $^tBuSiH_2Cl$ and by the reactions of **2c** with $^tBuSiH_2Cl$ and $^tBuSiHCl_2$.

Introduction

Iron and ruthenium complexes having cyclopentadienyl and carbonyl ligands, $(\eta\text{-}C_5R_5)M(CO)_2R'$ (M = Fe, Ru; R′ = alkyl, acyl, silyl, germyl, etc.), have been studied extensively. In sharp contrast, we can find only a few reports on analogous organoosmium complexes,[1,2] apparently due to the lack of good preparative methods for such compounds. The synthesis of the methyl complex $(\eta\text{-}C_5Me_5)Os(CO)_2CH_3$ (**1**) was achieved by the reaction of the iodo complex $(\eta\text{-}C_5Me_5)Os(CO)_2I$ with methyllithium by Geoffroy and co-workers.[2] However, this method is not straightforwardly applicable for the synthesis of silyl or germyl complexes, since their lithium reagents are not always available, particularly in the case of functionalized silyl or germyl derivatives.[3]

In organoiron and organoruthenium chemistry, the anionic complexes $[Fe(CO)_2(\eta\text{-}C_5R_5)]^-$ (R = H, Me)[4−7] and $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$ [8] have been used as useful synthons, but the corresponding osmate complexes $[Os(CO)_2(\eta\text{-}C_5R_5)]^-$ (R = H, Me) have been elusive. The reactions of the anions with various electrophiles should give a variety of organoosmium complexes. Here we report the synthesis of the osmate complexes $M[Os(CO)_2(\eta\text{-}C_5R_5)]$ (**2a**, R = Me, M = Li; **2b**, R = H, M = Li; **2c**, R = H, M = Na) and their derivation to novel silyl and germyl complexes.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade hexane, benzene, and THF were distilled from sodium−benzophenone ketyl immediately before use. Benzene-d_6 was dried over a potassium mirror and transferred into NMR tubes under vacuum before use. $(\eta\text{-}C_5Me_5)Os(CO)_2H$ (**3a**),[1] $(\eta\text{-}C_5H_5)Os(CO)_2H$ (**3b**),[1] $^tBuSiH_2Cl$,[9] $^tBuSiHCl_2$,[10] and Me_3GeCl[11] were prepared according to literature methods. CH_3I (Wako Pure Chemical Industries, Ltd.) was freshly distilled from P_2O_5 before use. Me_3SiCl, Me_2SiCl_2, and $Me_3SiSiMe_2Cl$ (Shin-Etsu Chemical Co., Ltd.) were distilled from CaH_2. Butyllithium was standardized by titration before use.[12] Cyclopentadiene was obtained by cracking of its dimer and used immediately. Other chemicals were purchased from Wako Pure Chemical Industries, Ltd., and used as received. IR spectra were recorded on Horiba FT-200 and Bruker IFS66v spectrophotometers. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX-300 spectrometer at ambient temperature. ^{29}Si NMR spectra were obtained on the same spectrometer using the DEPT pulse sequence. Mass spectra were recorded on a JEOL JMS HX-110 spectrometer. Spectral and analytical data for the new complexes are listed in Tables 1−3.

Synthesis of $(\eta\text{-}C_5Me_5)Os(CO)_2CH_3$ (1). To a cold solution (−45 °C) of the hydrido complex $(\eta\text{-}C_5Me_5)Os(CO)_2H$ (**3a**; 36 mg, 9.0×10^{-2} mmol) in THF (4 mL) was added a hexane solution of butyllithium (1.59 M, 0.065 mL, 0.10 mmol) with stirring. During the addition, a yellow color developed. The solution was stirred for 5 min at −45 °C. Methyl iodide (0.1 mL) was then added to the solution, and the mixture was stirred for 30 min at this temperature and then for 4 h at room temperature. Volatiles were removed under reduced pressure, and the residue was extracted with hexane. Hexane was evaporated from the extract to give a pale yellow solid. Sublimation of the solid (70 °C/0.01 Torr) afforded **1** (21 mg, 5.3×10^{-2} mmol, 59%) as a colorless crystalline solid.

Synthesis of $(\eta\text{-}C_5Me_5)Os(CO)_2D$ (3a-*d*). To a THF solution of **3a** (52 mg, 0.14 mmol) was added butyllithium in hexane (1.48 M, 0.10 mL, 0.15 mmol) at −45 °C. After the

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Table 1. IR and Analytical Data for Osmium Complexes

	IR[a] $\tilde{\nu}$, cm^{-1}		anal. found (calcd), %	
compd	ν_{CO}	other	C	H
$(\eta\text{-}C_5Me_5)Os(CO)_2Me$ (**1**)	1994, 1934 (lit.[b] 1995, 1935)			
$(\eta\text{-}C_5Me_5)Os(CO)_2D$ (**3a**-*d*)	2001, 1941	1481 (ν_{OsD})	37.88 (37.59)	3.95 (4.21)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_3$ (**4**)	1993, 1935		39.88 (39.63)	5.10 (5.32)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiH_2{}^tBu$ (**5a**)	1995, 1940	2046 (ν_{SiH})	40.85 (41.01)	5.68 (5.59)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_2SiMe_3$ (**6**)	1992, 1936		39.16 (39.82)	5.77 (5.90)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiClMe_2$ (**7**)[c]	2004, 1946			
$(\eta\text{-}C_5Me_5)Os(CO)_2GeMe_3$ (**8**)	1992, 1936		36.33 (36.09)	4.56 (4.85)
$(\eta\text{-}C_5H_5)Os(CO)_2SiH_2{}^tBu$ (**5b**)	2014, 1960	2082 (ν_{SiH})	34.32 (33.15)	4.08 (4.05)
$(\eta\text{-}C_5H_5)Os(CO)_2SiHCl{}^tBu$ (**10**)	2023, 1968	2100 (ν_{SiH})	30.52 (30.51)	3.38 (3.49)

[a] IR spectra were measured in hexane. [b] Reference 2. [c] Contaminated by $(\eta\text{-}C_5Me_5)Os(CO)_2Cl$ (the purity was ca. 95%).

Table 2. NMR Spectral Data for Osmium Complexes[a]

compd	^{1}H NMR δ, ppm	^{13}C NMR δ, ppm	^{29}Si NMR δ, ppm
1	0.66 (s, 3H, OsMe), 1.55 (s, 15H, C_5Me_5) (lit.[b] 0.65 (s, 3H, OsMe), 1.56 (s, 15H, C_5Me_5))	−38.1 (OsMe), 9.3 ($C_5\mathit{Me}_5$), 96.7 (C_5Me_5), 186.3 (CO)	
3a-*d*	1.76 (s, 15H, C_5Me_5)		
4	0.68 (s, 9H, $SiMe_3$), 1.67 (s, 15H, C_5Me_5)	6.0 (SiMe), 10.0 ($C_5\mathit{Me}_5$), 97.0 (C_5Me_5), 187.2 (CO)	−5.0
5a	1.47 (s, 9H, ^{t}Bu), 1.61 (s, 15H, C_5Me_5), 3.97 (s, 2H, Si—H)	9.2 ($C_5\mathit{Me}_5$), 20.3 ($\mathit{C}Me_3$), 30.8 ($C\mathit{Me}_3$), 96.4 (C_5Me_5), 186.7 (CO)	−6.9
6	0.38 (s, 9H, $SiMe_3$), 0.71 (s, 6H, $SiMe_2$), 1.68 (s, 15H, C_5Me_5)	0.0 ($Si\mathit{Me}_3$), 1.4 ($Si\mathit{Me}_2$), 10.1 ($C_5\mathit{Me}_5$), 97.1 (C_5Me_5), 186.8 (CO)	−34.3 (Si_β), −13.9 (Si_α)
7	1.03 (s, 6H, SiMe), 1.67 (s, 15H, C_5Me_5)	9.7 ($C_5\mathit{Me}_5$), 11.7 (SiMe), 98.0 (C_5Me_5), 184.9 (CO)	33.4
8	0.75 (s, 9H, $GeMe_3$), 1.68 (s, 15H, C_5Me_5)	3.9 (GeMe), 10.1 ($C_5\mathit{Me}_5$), 96.4 (C_5Me_5), 186.7 (CO)	
5b	1.29 (s, 9H, ^{t}Bu), 4.43 (s, 5H, C_5H_5), 4.55 (s, 2H, Si—H)	27.6 ($\mathit{C}Me_3$), 30.3 ($C\mathit{Me}_3$), 83.9 (C_5H_5), 182.2 (CO)	−25.9
10	1.25 (s, 9H, ^{t}Bu), 4.47 (s, 5H, C_5H_5), 6.02 (s, 1H, Si—H)	24.8 ($\mathit{C}Me_3$), 27.6 ($C\mathit{Me}_3$), 84.9 (C_5H_5), 180.8, 181.1 (CO)	28.4

[a] NMR spectra were taken in benzene-d_6. [b] Reference 2.

Table 3. Mass Spectral Data for New Complexes[a]

compd	molecular and fragment ions, *m/z* (rel intensity, assignt)
$(\eta\text{-}C_5Me_5)Os(CO)_2D$ (**3a**-*d*)	385 (61, M^+), 352 (100)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_3$ (**4**)	456 (20, M^+), 441 (100, $(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_2{}^+$)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiH_2{}^tBu$ (**5a**)	470 (10, M^+), 413 (100, $(\eta\text{-}C_5Me_5)Os(CO)_2SiH_2{}^+$), 383 (24, $(\eta\text{-}C_5Me_5)Os(CO)_2{}^+$)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_2SiMe_3$ (**6**)	514 (3, M^+), 499 (3, $(\eta\text{-}C_5Me_5)Os(CO)_2SiMe(SiMe_3)^+$), 441 (100, $(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_2{}^+$)
$(\eta\text{-}C_5Me_5)Os(CO)_2SiClMe_2$ (**7**)	476 (19, M^+), 461 (100, $(\eta\text{-}C_5Me_5)Os(CO)_2SiMeCl^+$)
$(\eta\text{-}C_5Me_5)Os(CO)_2GeMe_3$ (**8**)	502 (8, M^+), 487 (100, $(\eta\text{-}C_5Me_5)Os(CO)_2GeMe_2{}^+$)
$(\eta\text{-}C_5H_5)Os(CO)_2SiH_2{}^tBu$ (**5b**)	400 (13, M^+), 343 (100, $(\eta\text{-}C_5H_5)Os(CO)_2SiH_2{}^+$), 313 (40, $(\eta\text{-}C_5H_5)Os(CO)_2{}^+$), 285 (22, $(\eta\text{-}C_5H_5)Os(CO)^+$), 257 (9, $(\eta\text{-}C_5H_5)Os^+$)
$(\eta\text{-}C_5H_5)Os(CO)_2SiHCl{}^tBu$ (**10**)	434 (7, M^+), 377 (100, $(\eta\text{-}C_5H_5)Os(CO)_2SiHCl^+$), 348 (22, $(\eta\text{-}C_5H_5)Os(CO)_2Cl^+$), 313 (23, $(\eta\text{-}C_5H_5)Os(CO)_2{}^+$)

[a] Mass spectra were measured by the EI method.

mixture was stirred for 5 min, D_2O (25 mg, 1.3 mmol) was added to the solution. The mixture was stirred at this temperature for 5 min and then slowly warmed to room temperature over a period of 15 min. Volatiles were removed at −48 °C, and the residue was extracted with hexane. After evaporation of hexane at −48 °C from the extract, the residue was sublimed (65 °C/0.1 Torr) to afford **3a-*d*** (40 mg, 0.10 mmol, 77%) as a colorless crystalline solid.

Synthesis of $(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_3$ (4). To a THF (3 mL) solution of **3a** (36 mg, 9.4×10^{-2} mmol) was added butyllithium in hexane (1.48 M, 0.066 mL, 9.8×10^{-2} mmol) at −45 °C, and the mixture was stirred for 5 min. Me_3SiCl (100 mg, 0.92 mmol) was then added to the solution. After it was stirred for 90 min, the solution was warmed to room temperature and stirred for 18 h. After removal of volatiles under vacuum, the residue was extracted with hexane. The extract was then filtered through a silica gel short column (6 mm i.d. × 1 cm). From the filtrate, hexane was evaporated to give a colorless solid. Sublimation of the solid (80 °C/0.03 Torr) afforded **4** (26 mg, 5.7×10^{-2} mmol, 61%) as a colorless crystalline solid.

Synthesis of $(\eta\text{-}C_5Me_5)Os(CO)_2SiH_2{}^tBu$ (5a). The compound **5a** was synthesized by a method almost identical with that for **4**, using **3a** (133 mg, 0.35 mmol) and $^tBuSiH_2Cl$ (98 mg, 0.80 mmol). The colorless crystalline solid of **5a** was isolated in 94% yield (152 mg, 0.33 mmol).

Synthesis of $(\eta\text{-}C_5Me_5)Os(CO)_2SiMe_2SiMe_3$ (6). The synthetic procedure for **6** is analogous to that for **4**, except for the use of $Me_3SiSiMe_2Cl$ instead of Me_3SiCl. The yield of **6**, a colorless crystalline solid, was 60% (64 mg, 0.13 mmol).

Synthesis of $(\eta\text{-}C_5Me_5)Os(CO)_2SiClMe_2$ (7). Compound **7** was synthesized from **3a** (17 mg, 4.5×10^{-2} mmol) and Me_2SiCl_2 (20 mg, 0.16 mmol) by almost the same method as that for **4**. After the reaction, volatiles were evaporated from the reaction mixture and the residue was extracted with hexane. The extract was filtered through a Celite pad. After removal of hexane, sublimation of the residue gave **7** (21 mg, 0.44 mmol, 98%) as a colorless crystalline solid.

Synthesis of $(\eta\text{-}C_5Me_5)Os(CO)_2GeMe_3$ (8). The synthesis of compound **8** was achieved by use of **3a** (45 mg, 0.12 mmol) and Me_3GeCl (50 mg, 0.33 mmol) with a method similar to that for **4**. The complex **8** was obtained as a colorless crystalline solid in 78% yield (46 mg, 9.2×10^{-2} mmol).

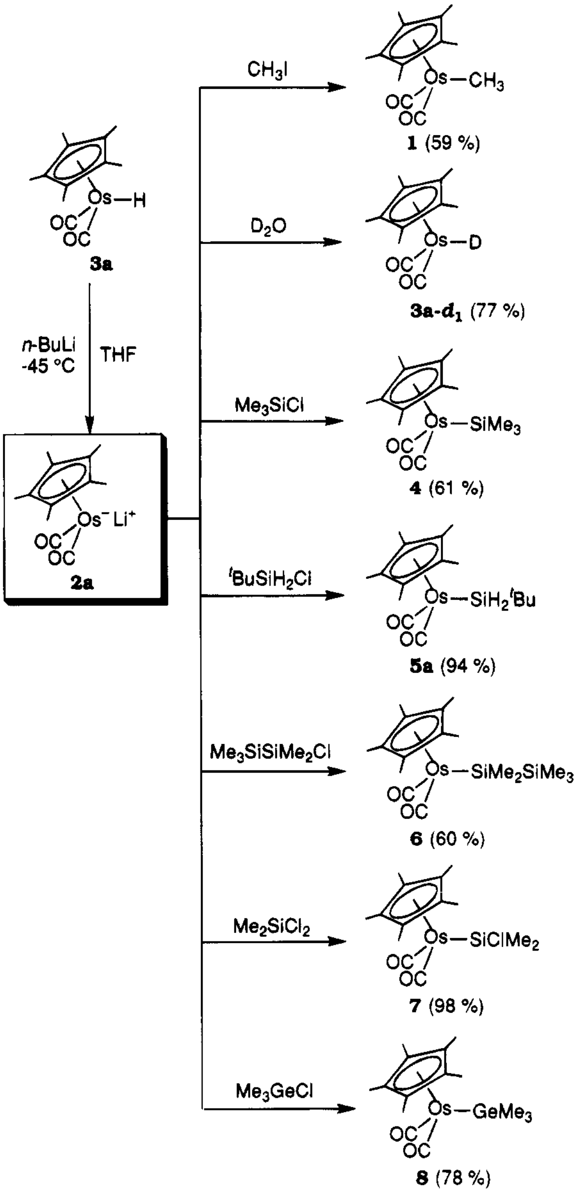
Synthesis of $(\eta\text{-}C_5H_5)Os(CO)_2SiH_2{}^tBu$ (5b) from $(\eta\text{-}C_5H_5)Os(CO)_2H$ (3b). To a THF (5 mL) solution of **3b** (148 mg, 0.47 mmol) was added butyllithium in hexane (1.56 M, 0.30 mL, 0.47 mmol) at −20 °C. After the mixture was stirred for 30 min, $^tBuSiH_2Cl$ (100 mg, 0.82 mmol) was added to the resulting yellow solution. The mixture was warmed to room temperature and stirred for 12 h. Volatiles were removed under vacuum, and the residue was extracted with hexane. After evaporation of hexane, the oily residue was purified by molecular distillation (90 °C, 0.01 Torr) to afford **5b** (82 mg, 0.21 mmol, 44%) as colorless crystals which melt around room temperature.

Synthesis of (η-C_5H_5)Os$(CO)_2$I (9). This compound was prepared by a modified method of that for (η-C_5Me_5)Os$(CO)_2$I reported by Geoffroy:[2] A 50 mL autoclave was charged with $Os_3(CO)_{12}$ (1.36 g, 1.51 mmol), I_2 (574 mg, 2.26 mmol), and benzene (30 mL). The suspension was heated with stirring at 170 °C for 24 h. After this suspension was cooled, cyclopentadiene (2 mL) was added and the mixture was heated at 170 °C for 24 h. To the resulting yellow solution was added cyclopentadiene (1 mL), and it was heated again at 170 °C for 24 h. The solution was placed on a silica gel column (2.5 cm i.d. × 30 cm), and a lemon yellow band was eluted with dichloromethane. Evaporation of solvent from the eluate followed by washing of the residue with hexane afforded **9** (1.402 g, 3.20 mmol, 71%). The IR and ^{1}H NMR data were consistent with the literature values.[1]

Synthesis of (η-C_5H_5)Os$(CO)_2$Si$H_2{}^t$Bu (5b) from 9. A THF solution of sodium naphthalenide (0.3 M, 6.2 mL, 1.88 mmol) was added dropwise to a cold (−64 °C) solution of **9** (375 mg, 0.86 mmol) in THF (7 mL) with stirring over a period of 15 min. During the addition, an orange-yellow color developed. To the solution was added ^{t}BuSiH_2Cl (300 mg, 2.45 mmol) with stirring. The mixture was stirred for 1 h at −64 °C and then for 12 h at room temperature. After evaporation of volatiles under vacuum, the residue was extracted with hexane. From the extract, hexane was removed under vacuum to give a pale yellow oil. Molecular distillation of the oil afforded **5b** (229 mg, 0.58 mmol, 67%).

Synthesis of (η-C_5H_5)Os$(CO)_2$SiHCl^{t}Bu (10). The synthetic method for **10** is almost identical with that for **5b** from **9**, except for use of ^{t}BuSiHCl_2 instead of ^{t}BuSiH_2Cl. Molecular distillation (90 °C/0.03 Torr) afforded **10** (162 mg, 0.395 mmol, 48%) as a colorless oil.

Scheme 1. Synthesis and Reactions of Li[Os$(CO)_2$(η-C_5Me_5)] (2a)



Results and Discussion

Synthesis and Characterization of Li[Os$(CO)_2$(η-C_5Me_5)] (2a). Treatment of a colorless solution of the hydrido complex (η-C_5Me_5)Os$(CO)_2$H (**3a**)[1] in THF with 1.1 equiv of butyllithium at −45 °C gave a deep yellow solution. Subsequent addition of excess CH_3I gave a pale yellow mixture from which the methyl complex **1** was isolated in 59% yield (Scheme 1). The ^{1}H NMR and IR spectral data for **1** agreed well with the literature values.[1] The ^{13}C NMR data for the complex, which have not been reported in the literature, also support the formation of the methyl complex **1**. Treatment of **3a** with butyllithium followed by addition of D_2O gave the deuterated complex **3a-*d*** in 77% yield (Scheme 1). The ^{1}H NMR spectrum of **3a-*d*** reveals a C_5Me_5 signal at the same position as that of **3a** (1.76 ppm) and no signal in the Os—H region. In the IR spectrum, the Os—H stretching band of **3a** appears at 2059 cm^{-1}, while the Os—D stretching band of **3a-*d*** is at 1481 cm^{-1}. The ratio of the stretching frequencies is reasonably close to $\sqrt{2}$. These results indicate that the anionic complex **2a** is generated in high yield by the deprotonation from **3a**.

Although **2a** is thermally unstable, we found that the anion is stabilized by addition of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to the system. Figure 1 shows the differential IR spectrum between **3a** and **2a**. Before the reaction with butyllithium, the ν_{CO} bands of **3a** appear at 1990 and 1929 cm^{-1} along with the ν_{OsH} band at 2054 cm^{-1}. After the deprotonation, these bands disappear completely and three pairs of new bands all assignable to the ν_{CO} of **2a** appear at 1880 and 1805 (s), 1870 and 1741 (m), and 1778 and 1720 cm^{-1} (w). As expected, frequencies of the ν_{CO} bands of **2a** are much lower than those of the precursor **3a**. Moreover, the appearance of three pairs of ν_{CO} bands with three different intensities suggests that **2a** exists as the mixture of three types of ion pairs. In the case of analogous iron complexes, M[Fe$(CO)_2$(η-C_5H_5)] (M = Li, Na), it has been proposed that each complex exists as a mixture containing three kinds of ion pairs, an Fe···M contact ion pair, an Fe—CO···M ion pair with a metal—carbonyl oxygen interaction, and a solvent-separated ion pair.[6,7] Therefore, the three ion pairs of osmium complex **2a** would be **A**—**C** (Chart 1) as considered for the iron complexes. The most abundant ion pair, giving the ν_{CO} bands at 1880 and 1805 cm^{-1}, can be regarded as the Os···Li contact ion pair (**A**) since the frequencies are the highest. The ν_{CO} bands at 1778 and 1720 cm^{-1} can be assigned to the Os—CO···Li ion pair (**B**) for their low frequencies. The ν_{CO} bands with intermediate frequencies (1840, 1741 cm^{-1}) are assignable to the solvent-separated ion pair (**C**). Nitay and Rosenblum reported that a THF solution of Li[Fe$(CO)_2$(η-C_5H_5)] contains roughly equal amounts of type **A** and type **B** ion pairs.[7] The higher abundance of ion pair **A** in **2a** is apparently due to the higher basicity of the

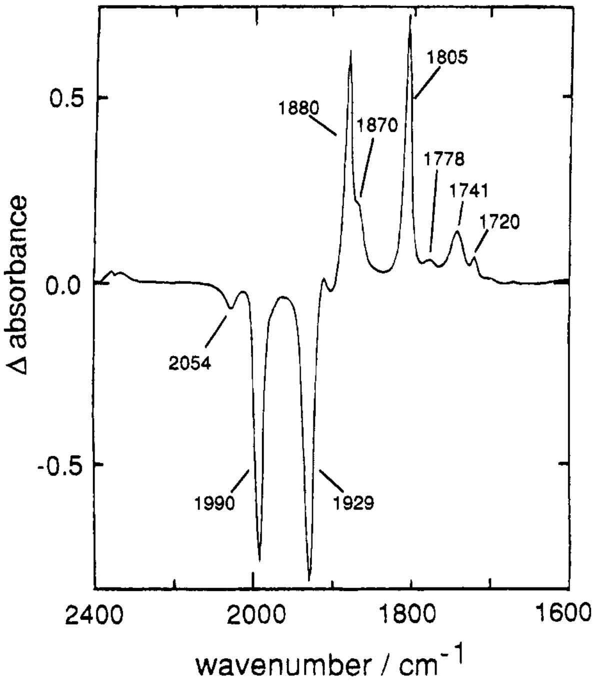
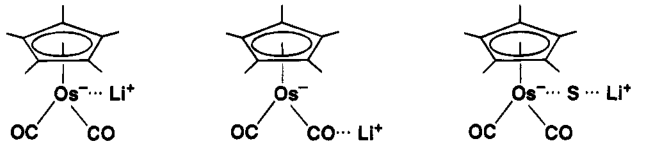


Figure 1. Differential IR spectrum between the THF solution of (η-C_5Me_5)Os$(CO)_2$H (**3a**) in the presence of TMEDA and the solution obtained after butyllithium was added to it at room temperature.

Chart 1



A B C

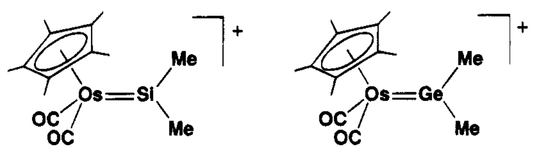
metal center in the osmium complex **2a** than in the corresponding iron complex.

It is noteworthy that the hydridic character of the "hydrido" ligand in **3a** has been reported by Graham et al.[1] Thus, hydride abstraction from **3a** by trityl cation in the presence of ligands affords cationic complexes. The occurrence of deprotonation from **3a** in the present work demonstrates the amphoteric character of the Os*H* in **3a**.

Reactions of 2a with Silicon and Germanium Electrophiles. In order to elucidate the reactivity of **2a**, reactions with silicon and germanium electrophiles were examined. Addition of Me_3SiCl to a cold solution (−45 °C) of **2a** and subsequent workup gave the trimethylsilyl complex **4** in 61% yield. Similarly, the reactions with ^{t}BuSiH_2Cl, $Me_3SiSiMe_2Cl$, Me_2SiCl_2, and Me_3GeCl afforded the corresponding silyl and germyl complexes **5a** and **6**–**8**, respectively, in good to excellent yields (Scheme 1). The products were colorless crystalline solids and were characterized by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR (for **4**–**7**), IR, and mass spectroscopy as well as elemental analyses (Tables 1–3).

The ^{29}Si NMR signals for the silyl derivatives **4**–**7** appear at higher fields than those of the corresponding iron and ruthenium complexes. For example, trimethylsilyl complex **4** shows the ^{29}Si NMR signal at −5.0 ppm while the iron analogue (η-C_5Me_5)Fe$(CO)_2SiMe_3$[13] gives it at 40.6 ppm. In the silyl complexes of other transition metals, it has been shown that the ^{29}Si NMR signals for 5d metal complexes appear at higher fields than those of the corresponding 3d or 4d metal complexes.[14,15]

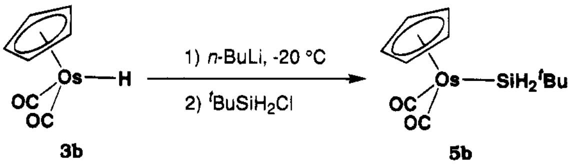
Chart 2



D E

The mass spectra of the complexes prepared in this work (Table 3) show that every silyl complex loses the largest substituent from the silyl ligand to give the base peak, which is assignable to the cationic silylene complex. For example, the *m/z* value of the base peak for **6** (*m/z* 441) corresponds to $M^+ - SiMe_3$ and is assignable to the cationic (dimethylsilylene)osmium complex **D** (Chart 2). Similarly, in the case of the germyl derivative **8**, the base peak appears at *m/z* 487, which is assignable to the dimethylgermylene complex **E** (Chart 2). In the mass spectra of analogous iron complexes, a relatively strong peak for the fragment ion $[LFe(CO)_2{=}SiMe_2]^+$ (L = cyclopentadienyl, indenyl) is observed when the complex has a weak Si—Si or Si—Ge bond, but in most cases, the dominant process is the stepwise loss of carbonyl ligands.[16] These results indicate that the electron-deficient silylene or germylene moiety in the fragment ion is stabilized more strongly by the electron-rich osmium center than by the iron center.

Synthesis and Reactions of M[Os$(CO)_2$(η-C_5H_5)] (2b, M = Li; 2c, M = Na). The osmate complexes with a nonsubstituted cyclopentadienyl ligand were also synthesized. Treatment of (η-C_5H_5)Os$(CO)_2$H (**3b**) in THF with 1.1 equiv of butyllithium at −20 °C afforded a yellow solution which suggested the formation of the anionic complex Li[Os$(CO)_2$(η-C_5H_5)] (**2b**). The addition of excess ^{t}BuSiH_2Cl to the solution and subsequent workup afforded the *tert*-butylsilyl complex **5b** in 44% yield (eq 1). The rather low yield of **5b** indicates that a part of the butyllithium might be exhausted for the lithiation of the cyclopentadienyl ligand in **3b**. Indeed, Gladysz et al. reported that deprotonation from (η-C_5H_5)Re(NO)(PPh_3)H by butyllithium at low temperature initially gives the lithiocyclopentadienyl derivative (η-LiC_5H_4)Re(NO)(PPh_3)H, which then rearranges to Li[(η-C_5H_5)Re(NO)(PPh_3)] on warming.[17]



3b **5b** (1)

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[14] Pannell, K. H.; Rozell, J. M.; Tsai, W.-M. *Organometallics* **1987**, *6*, 2085.

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[16] (a) Guerrero, A.; Cervantes, J.; Velasco, L.; Gómez-Lara, J.; Sharma, S.; Delgado, E.; Pannell, K. *J. Organomet. Chem.* **1994**, *464*, 47. (b) Guerrero, A.; Gómez-Lara, J.; Cervantes, J.; Velasco, L.; Sharma, H.; Pannell, K. *J. Organomet. Chem.* **1994**, *464*, 47.

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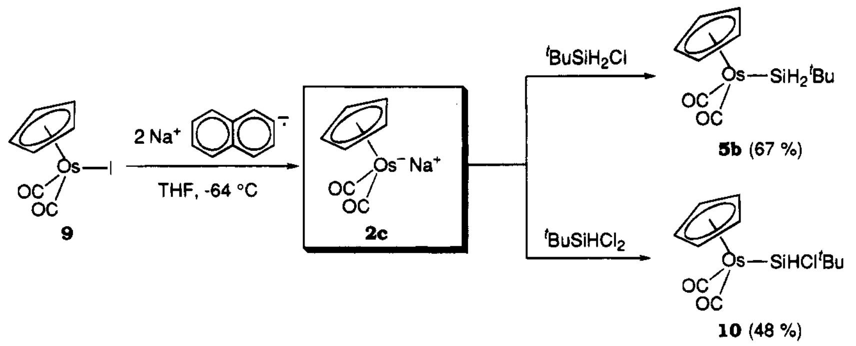
Scheme 2



Alternatively, the sodium salt **2c** can be generated by the reduction of the iodo complex (η-C_5H_5)Os(CO)$_2$I (**9**) with 2 equiv of sodium naphthalenide at −64 °C. Treatment of the yellow solution of **2c** thus obtained with ^{t}BuSiH$_2$Cl afforded **5b** in 67% yield (Scheme 2). The chlorosilyl derivative **10** was also prepared by the reaction of **2c** with ^{t}BuSiHCl$_2$ in 48% yield (Scheme 2). The ^{13}C NMR spectrum of **10** shows two carbonyl signals, because the chiral silyl group in **10** makes the two carbonyl ligands mutually diastereotopic (Table 2).

Conclusions

We have prepared the new anionic osmium reagents **2a–c** by the simple metalation of Os—H or Os—I. Reactions of these reagents with carbon, silicon, and germanium electrophiles gave organoosmium complexes with Os—C, Os—Si, and Os—Ge bonds, respectively. These results clearly demonstrate that they are versatile synthons for organoosmium complexes which have not been easily available by other methods.

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