ORGANOMETALLICS

Disilametallacycles as a Platform for Stabilizing M(II) and M(IV) (M = Fe, Ru) Centers: Synthesis and Characterization of Half-Sandwich Complexes and Their Application to Catalytic Double Silylation of Alkenes and Alkynes

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Supporting Information

ABSTRACT: A series of group 8 half-sandwich disilametallacycles, $(\eta^{6}\text{-arene})M^{II}(Me_{2}SiC_{6}H_{4}SiMe_{2})L$ and $(\eta^{6}\text{-arene})-M^{IV}(H)_{2}(Me_{2}SiC_{6}H_{4}SiMe_{2})$ (M = Fe, Ru) in the formal oxidation states of M(II) and M(IV) were synthesized and characterized. Both the M(II) and the M(IV) oxidation states were effectively stabilized by the disilametallacycle skeleton, and facile interconversion between $(\eta^{6}\text{-arene})M^{II}\text{-dinitrogen},$ $(\eta^{6}\text{-arene})M^{II}\text{-carbonyl},$ and $(\eta^{6}\text{-arene})M^{IV}\text{-dihydride}$ complexes bearing a disilaferracycle framework was accomplished. These M(II) and M(IV) complexes can easily generate coordinatively unsaturated 16e disilametallacycles, $(\eta^{6}\text{-arene})$ -



 $M^{II}(Me_2SiC_6H_4SiMe_2)$, by dissociation of L or H_2 , and stoichiometric and/or catalytic double silvlation of alkenes and alkynes was realized thorough this 16e intermediate.

INTRODUCTION

Organosilicon compounds have attracted considerable interest as synthetic tools in organic synthesis as well as sources for materials with special properties.¹ Transition-metal-catalyzed hydrosilylation of alkenes and alkynes, in which a Si-H bond in a hydrosilane is added across a carbon-carbon multiple bond, is widely accepted as one of the most efficient methods of obtaining a variety of organosilicon compounds. It is of interest that hydrosilylation is not always the only outcome in the reaction of hydrosilanes with carbon-carbon multiple bonds. Tamao and Kumada discovered the first example of dehydrogenative double silvlation in 1975; certain nickel compounds catalyzed the reaction of HSiCl₃ or HSiMeCl₂ with alkynes (RC \equiv CR), which resulted in the evolution of H₂ and the formation of $R(Cl_3Si)C=C(SiCl_3)R$ or $R(Cl_2MeSi)$ - $C = C(SiMeCl_2)R^2$ Dehydrogenative double silvlation³⁻⁵ was recently reinvestigated by Tanaka, who reported the formation of disilacarbocycle compounds (Scheme 1) in the reaction of 1,2-bis(dimethylsilyl)benzene with RC=CR.³ Platinum compounds behave as catalysts for the formation of disilacarbocyclic products, and alkenes and dienes can be used instead of

Scheme 1. Platinum-Catalyzed Double Silylation of Alkynes



alkynes. The mechanism involved in platinum-catalyzed reactions has been studied in detail: the disilaplatina(II)cycle complex $(PPh_3)_2Pt(Me_2SiC_6H_4SiMe_2)$ was formed as the primary intermediate, followed by formation of a coordinatively unsaturated disilaplatina(II)cycle complex concomitant with the liberation of PPh₃.^{3a} This intermediate reacted with the alkyne to afford the double-silylated product. Interestingly, similar disilacarbocyclic compounds are formed by the reaction of benzodisilacyclobutenes with alkynes catalyzed by group 10 transition-metal complexes.⁴ A disilametallacycle complex with a structure similar to that of the disilaplatina(II)cycle was proposed as an intermediate. We were interested in exploring the possibility that similar reactions forming disilacarbocycles might take place using group 8 transition metals such as ruthenium and iron.

Homogeneous catalysis by ruthenium complexes has been a topic of interest over the last two decades, and a number of fundamental studies have been performed, as well as investigations of their application to catalytic organic reactions.⁶ In contrast, catalysis by complexes of iron—the most inexpensive, nontoxic, and environmentally friendly transition metal—has attracted the attention of synthetic organic chemists only recently.⁷ The design of iron catalysts and iron-catalyzed reactions is difficult, due to a lack of fundamental research on the reactions of organoiron compounds, which are

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often paramagnetic and unstable in the presence of air and moisture. The platinum-, palladium-, and nickel-promoted reactions described above suggested that coordinatively unsaturated disilametallacycle complexes of other metals may also act as intermediates for double silylation of alkenes and alkynes. In this sense, complexes with a disilaferra- or disilaruthenacycle structure, which can easily generate coordinatively unsaturated species, are an interesting target for research.

In our preliminary account,⁸ we reported the synthesis of dinuclear half-sandwich disilaferra(II)cycles containing bridging dinitrogen ligands, $[(\eta^6 \text{-} \text{arene})\text{Fe}(\text{Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2)]_2(\mu - \eta^1 \cdot \eta^1$ N_2 (1). An important point is that dinitrogen is labile enough to generate 16e " $(\eta^6$ -arene)Fe(Me₂SiC₆H₄SiMe₂)" species, which can be trapped by CO or PPh₃ to give $(\eta^6$ arene)Fe(Me₂SiC₆H₄SiMe₂)(CO) (2) and (η^{6} -arene)Fe- $(Me_2SiC_6H_4SiMe_2)(PPh_3)$ (3), subsequently undergoing oxidative addition of H₂ to form $(\eta^6$ -arene)Fe- $(H)_2(Me_2SiC_6H_4SiMe_2)$ (4). It is noteworthy that the reaction of 1 with alkenes or alkynes led to the production of disilacarbocycles, in a manner similar to the processes promoted by group 10 transition-metal complexes described above. In this paper, we describe further studies on the preparation and reactions of 1, which are particularly focused on arene exchange of 4 and interconversion among 1, 2, and 4 via the 16e " $(\eta^6$ -arene)Fe(Me₂SiC₆H₄SiMe₂)" intermediate. These new findings contribute to the progress of research in two ways: the provision of a route to $(\eta^6$ -arene)Fe- $(Me_2SiC_6H_4SiMe_2)(L')$ with a different arene ligand and the opening up of the analogous chemistry of ruthenium complexes, with the preparation and characterization of two novel complexes, $(\eta^6 \text{-arene}) \operatorname{Ru}(H)_2(\operatorname{Me}_2\operatorname{SiC}_6H_4\operatorname{SiMe}_2)$ (5) and $(\eta^6\text{-}arene)\text{Ru}(\text{Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2)(\text{CO})$ (6). The reactions of these iron and ruthenium complexes with alkenes and alkynes resulted in the formation of the desired disilacarbocycles but demonstrated a characteristic difference in reactivity between iron and ruthenium, with iron giving the corresponding disilacarbocycles in a stoichiometric manner, while ruthenium afforded the same products catalytically.

RESULTS AND DISCUSSION

Synthesis of Disilaferra(II)cycles Containing a Bridging Dinitrogen Ligand. While planning this project, we read with interest a report by Peters and co-workers suggesting an attractive method of forming Fe-Si bonds.9 Treatment of $[Fe(mesityl)_2]_2$ with tris(phosphino)silane ($[P_3Si-H] = [(2-1)^2]_2$ $R_2PC_6H_4$ [3Si-H], R = Ph, ^{*i*}Pr) gave the iron organosilyl complex $(P_3Si)Fe(mesityl)$, with the Si-H group of P_3Si -H reacting with the Fe-C(mesityl) moiety by metathesis to form the Fe-Si bond and mesitylene. Two points should be noted: the mesityl group in $[Fe(mesityl)_2]_2$ may be replaced by an organosilyl moiety and the three phosphorus moieties of the P_3 Si-H ligand also coordinate to the iron center, acting as a sixelectron donor to make a $(P_3Si)Fe(mesityl)$ complex. We examined the reaction of [Fe(mesityl)₂]₂ with several hydrosilanes (4 equiv with respect to Si-H), including EtMe₂SiH, PhMe2SiH, pentamethyldisiloxane, and tetramethyldisiloxane, in C₆H₆ at 65 °C for 16 h and observed quantitative formation of mesitylene (1 equiv with respect to Si-H). Although our attempted isolation of the corresponding iron disilyl complexes was hampered due to the instability of the products, the results clearly showed that all of the Fe–C bonds in $[Fe(mesityl)_2]_2$ can be replaced by Fe-Si moieties through treatment with the

appropriate hydrosilanes. The reaction with 1,2-bis-(dimethylsilyl)benzene in benzene or toluene at 65 °C for 16 h under a nitrogen atmosphere provided isolable disilaferra-(II)cycle complexes, $[(\eta^6-C_6H_6)Fe(Me_2SiC_6H_4SiMe_2)]_2(\mu-\eta^{1:}\eta^{1-}N_2)$ (1a) and its η^6 -toluene analogue (1b), in 26% and 28% yields, respectively (Scheme 2). As described in detail in

Scheme 2. Synthesis of Disilaferra(II)cycles Having a Bridging Dinitrogen Ligand



our former communication, these complexes contain two disilaferra(II)cycle species, $(\eta^{6}\text{-arene})\operatorname{Fe}(Si)_{2}$, connected by a bridging dinitrogen ligand. The $\eta^{6}\text{-arene}$ ligand originates from benzene or toluene used as the solvent. It should be mentioned that there are only a few examples of half-sandwich $(\eta^{6}\text{-}\operatorname{arene})\operatorname{FeX}_{2}L$ complexes,¹⁰ and complex 1 is the first example of such a complex bearing a weakly coordinated labile ligand.

Complexes **1a,b** were characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. The spectroscopic data are summarized in Table 1. As stated in our previous communication,⁸ the dinitrogen ligand in **1** can easily be replaced by two-electron-donating ligands such as CO and PPh₃ to give (η^6 -arene)Fe^{II}(Me₂SiC₆H₄SiMe₂)(L) (L = CO (**2**), PPh₃ (**3**)). In addition, **1** can react with H₂ gas (1 atm) to afford the disilaferra(IV)cycle complex **4** via oxidative addition of H₂ (Scheme 3). These experimental results suggest that the dinitrogen molecule in **1** is easily dissociated from the iron center to form 2 mol of the coordinatively unsaturated 16e intermediate "(η^6 -arene)Fe(Me₂SiC₆H₄SiMe₂)".

Interconversion among 1, 2, and 4. Facile dissociation of the coordinatively weak N₂ ligand allowed the transformation of 1 to the Fe(II)-carbonyl complexes 2 and to the Fe(IV)- dihydride complexes 4. We also found a thermal reaction pathway to the formation of 2 from 4. Upon heating a solution of 4a or 4b at 120 °C under a CO atmosphere (1 atm), two hydride ligands were eliminated as H₂, providing the Fe(II)- carbonyl complex 2a or 2b in medium yield (Scheme 4).

It is well-known that elimination of a CO ligand coordinated to a transition-metal center can be triggered by photoirradiation.¹¹ The discovery that the CO ligand of **2** dissociated easily from the iron center under photochemical conditions provided pathways to the remaining transformations, **2** to **1** and **2** to **4**, as shown in Scheme 4. Photolysis of **2a** or **2b** under a N₂ atmosphere afforded **1a** or **1b**, respectively, in high yields, whereas photoirradiation of **2a** or **2b** under a H₂ atmosphere at room temperature for 18–30 h led to quantitative formation of **4a** or **4b**. Several half-sandwich iron complexes bearing an η^6 arene ligand have been synthesized;^{10,12} however, to the best of our knowledge, there has as yet been no report suggesting that the redox process between the Fe(II) and Fe(IV) oxidation states is reversible.

Arene Exchange Reaction Associated with Interconversion Leading to Further Disilaferra(II)- and Disilaferra(IV)cycles. Arene exchange reactions in transitionmetal complexes are commonly used to synthesize a variety of

| | 'H | | -3 <u>C</u> | | | |
|---------|------------------------|-------|------------------------------|-------|--------|-----------|
| complex | η^6 -arene | M–H | η^6 -arene | М-СО | IR C≡O | Raman N≡N |
| 1a | 4.30 | | 88.1 | | | 2035 |
| 1b | 1.93, 3.77, 3.87, 5.04 | | 20.4, 86.6, 87.1, 89.3, 93.1 | | | 2022 |
| 1c | 1.78, 4.16 | | 93.2, 99.8 | | | 2012 |
| 2a | 4.74 | | 93.3 | 209.8 | 1910 | |
| 2b | 1.80, 4.47, 4.73, 4.88 | | 20.7, 90.2, 90.8, 92.2, 96.2 | 210.4 | 1907 | |
| 2c | 1.79, 4.88 | | 96.2, 101.0 | 211.3 | 1892 | |
| 4a | 4.77 | -18.0 | 87.6 | | | |
| 4b | 1.72, 4.53, 4.86-4.94 | -18.1 | 20.1, 84.9, 85.4, 87.2, 92.1 | | | |
| 4c | 1.90, 4.70 | -18.2 | 89.4, 100.7 | | | |
| 5a | 4.94 | -12.2 | 92.1 | | | |
| 5c | 1.84, 5.05 | -12.3 | 94.8, 106.7 | | | |
| 6a | 4.96 | | 94.6 | 199.4 | 1919 | |
| 6c | 1.72, 5.09 | | 99.8, 107.9 | 201.1 | 1910 | |
| | | | | | | |

Scheme 3. Reactions of 1 with CO, PPh_3 , and H_2



Scheme 4. Interconversion between Fe(II) and Fe(IV) Complexes



(4a)



half-sandwich transition-metal complexes such as $(\eta^{6}\text{-arene})$ - $\operatorname{Cr}(\operatorname{CO})_{3}^{13}$ and $(\eta^{6}\text{-arene})\operatorname{RuX}_{2}\operatorname{L}^{14,15}$ It is well-known that the electronic and steric properties of these complexes can be finely tuned by changing the η^{6} -arene ligand on the metal. However, there has been no previous report dealing with arene exchange reactions of half-sandwich $(\eta^{6}\text{-arene})$ Fe complexes. Upon considering the results of the interconversion study described above, we postulated that a series of the dinuclear Fe(II)-dinitrogen, mononuclear Fe(II)-carbonyl, and Fe(IV)-dihy-dride complexes might be accessible by a combination of arene exchange and interconversion reactions.

The η^6 -benzene ligand on the iron center of 4a was found to be replaceable by other arenes at 120 °C. As a representative example, we prepared a series of η^6 -mesitylene complexes as follows. Heating a mesitylene solution of 4a at 120 °C for 18 h under a hydrogen atmosphere gave the η^6 -mesitylene dihydride complex 4c in 52% yield (Scheme 5). According to the interconversion scheme described above (Scheme 4), the CO complex 2c was prepared by treatment of 4c with CO at 120 °C. The dinuclear dinitrogen complex 1c was synthesized from 2c by photochemical ligand exchange of CO by N₂: a mesitylene solution of 2c was irradiated by a high-pressure mercury lamp at room temperature for 30 h, after which 1c was isolated in 86% yield as red crystals. The reverse reaction from 2c to 4c was accomplished photochemically, whereas that from 1c to 2c was accomplished thermally.

R = Me (**4b**)

1,3,5-Me₃ (4c)

120 °C

under H₂ (1 atm)

The products 1c, 2c, and 4c were easily characterized by spectroscopy, similarly to the η^6 -benzene and η^6 -toluene homologues, as shown in Table 1. Two of the complexes, 1c and 4c, were subjected to X-ray structural determination; the ORTEP drawings are shown in Figure 1, and the bond distances and angles are summarized in the Supporting Information. The structural information obtained from the NMR spectra of 1c and 4c was consistent with that deduced from the molecular structures, which did not differ from those of their η^6 -benzene homologues. Despite a lack of crystallographic data, ¹H and ¹³C NMR spectra of 2c allowed reasonable consideration of its molecular structure, which was predicted on the basis of the crystal structure of the η^6 -benzene homologue 2a. It is worthwhile to point out that the ¹³C resonance due to the CO ligand was shifted downfield by 1.5 ppm compared to that of 2a. The IR spectrum of 2c was characteristic in showing a C \equiv O stretching band at 1892 cm⁻¹, which was shifted to a lower wavenumber in comparison to the equivalent signals of 2a (1910 cm⁻¹) and 2b (1907 cm⁻¹). These spectroscopic



Figure 1. Molecular structures of **1c** (left) and **4c** (right) showing 50% probability ellipsoids. Hydrogen atoms, except that on Fe, are omitted for clarity.

features indicated that the electron density around the iron center in 2a-c increased gradually in line with the introduction of methyl substituents on the η^6 -arene moiety.

Synthesis of Disilaruthenacycle Complexes. The synthesis of ruthenium homologues of the half-sandwich disilaferracycles 1, 2, and 4 was expected to be useful in contributing to our understanding of the differences in reactivity between iron and ruthenium. The preparation of half-sandwich disilaruthenacycles in a manner similar to the preparation of the iron compounds described above was problematic, because, to our knowledge, homoleptic Ru(II)dialkyls or -diaryls are unknown. Since there are several easily accessible η^6 -arene ruthenium complexes, we decided to examine the synthesis of the ruthenium complexes by different synthetic routes. Berry and co-workers reported the synthesis of $(\eta^{6}\text{-arene})\operatorname{Ru}(H)_{2}(\operatorname{SiMe}_{3})_{2}$ (arene = *p*-cymene, C₆Me₆) complexes by the reaction of $[(\eta^6 \text{-arene}) \text{RuCl}_2]_2$ with an excess of Me₃SiH; thermolysis of $(\eta^6-C_6Me_6)Ru(H)_2(SiMe_3)_2$ in benzene at 150 °C resulted in an arene exchange reaction, leading to the formation of $(\eta^6-C_6H_6)Ru(H)_2(SiMe_3)_2$.¹⁶ We found that treatment of $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ with 4.4 equiv of 1,2bis(dimethylsilyl)benzene in THF under reflux followed by purification by column chromatography using silica gel led to isolation of the disilaruthena(IV)cycle dihydride 5a in 43% yield as a white powder (Scheme 6).

Scheme 6. Synthesis of Disilaruthena(IV)cycle Complexes



Similar to the case for its iron homologue 4a, 5a is reactive toward arene exchange; heating a mesitylene solution of 5a at 140 °C under a nitrogen atmosphere resulted in displacement of the η^6 -benzene ligand to give (η^6 -mesitylene)Ru-(H)₂(Me₂SiC₆H₄SiMe₂) (5c) in 85% yield as a white powder (Scheme 6). As described above, interconversion among Fe(IV)-dihydride 4, Fe(II)-carbonyl 2, and Fe(II)-dinitrogen 1 can be achieved by thermal or photochemical processes. Attempted thermal conversion of the disilaruthena(IV)cycle dihydride complexes 5 to the disilaruthena(II)cycle carbonyl complexes 6 was not successful; no reaction took place when a benzene solution of 5a was heated to 140 °C in a sealed tube under a CO atmosphere, and complete decomposition of **5a** occurred at higher temperatures, such as 160 °C. However, photoirradiation of a benzene solution of **5a** at 50 °C under a CO atmosphere resulted in the formation of the Ru(II)– carbonyl complex **6a** in 88% yield (Scheme 7). Similarly, the η^6 -

Scheme 7. Transformation from Ru(IV) to Ru(II) Complexes



mesitylene analogue 6c was synthesized by irradiation of a mesitylene solution of 5c at 80 °C for 12 h. As in the case of the iron homologue, the $(\eta^6$ -arene)Ru(Me₂SiC₆H₂(Me)₂SiMe₂)-(CO) complex is not accessible through the reaction of $(Me_2SiC_6H_2(Me)_2SiMe_2)Ru(CO)_4$ with an arene via exchange of the carbonyl ligand at higher temperatures.¹⁷ The reverse reaction from the Ru(II)-carbonyl complexes 6 to the Ru(IV)-dihydride complexes 5 did not proceed at all, either by thermal or by photochemical processes. Attempts at synthesizing dinitrogen-bridged ruthenium dimers, which are homologues of 1, were performed both thermally and photochemically; however, trials have so far been unsuccessful. For instance, complex 5a gradually decomposed when subjected to irradiation under a dinitrogen atmosphere, whereas complex 6a was stable under photoirradiation conditions even at 80 °C under a dinitrogen or dihydrogen atmosphere.

Characterization of disilaruthena(IV)cycle dihydrides (5a,c) and disilaruthena(II)cycle carbonyl complexes (6a,c) was performed by ¹H and ¹³C NMR and IR spectroscopy, which showed features similar to those of the corresponding iron homologues. The spectroscopic features of these ruthenium compounds are shown in Table 1. ¹H NMR spectra of 5a,c consisted of signals due to the η^6 -arene ligand, two hydrides, and the disilaruthenacycle moiety; the appearance of a single Ru-H signal and a single Si-Me signal for each complex is evidence for the trans isomer. The molecular structure of 6a was determined by X-ray diffraction analysis. The ORTEP drawing is shown in Figure 2, while selected bond distances and angles are given in the Supporting Information. The molecular structure of 6a showed that the ruthenium center adopts a three-legged piano-stool coordination geometry, with the legs consisting of two silicon atoms and one CO ligand. The Ru-Si bond distances of 6a (2.3805(12) and 2.3849(11) Å) were



Figure 2. Molecular structure of 6a showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

comparable to those of a complex previously reported by Tobita ((η^6 -toluene)Ru^{II}(xantsil)(CO), 2.423(2) and 2.420(2) Å).¹⁷ The C–O bond distance in **6a** (1.153(6) Å) was also comparable to that found in Tobita's complex (1.170 (7) Å), reflecting the fact that the 1,2-bis(dimethylsilyl)benzene moiety has electron-donating properties similar to those of the xantsil ligand. The NMR data of **6a,c** are reasonable if the crystal structure is maintained in the solution state.

Double Silylation of Alkenes and Alkynes Mediated by Disilaferra- and Disilaruthenacycle Complexes. The iron and ruthenium complexes 1, 2, 4, 5, and 6 were found to be reactive with alkenes and alkynes. The iron complex 1, containing a coordinatively labile N_2 ligand, was the most reactive. Treatment of ethylene (1 atm) with 1a gave 1,2- and 1,1-double-silylated products 7a and 8a in a ratio of 2:3 with a total yield of 87% (Scheme 8). Styrene also underwent double

Scheme 8. Double Silylation of Alkenes and Alkynes Mediated by 1a



silylation mediated by 1a, from which the 1,1-double-silylated product 8b was obtained as a single product in high yield. Two alkynes, 2-butyne and phenylacetylene, were subjected to double silylation mediated by 1a at 40 °C for 14 h, giving the six-membered disilacarbocycles 9 and 10 in quantitative yield.

The Fe(II)-carbonyl complex **2a** and the Fe(IV)-dihydride complex **4a** were less reactive than **1a**, requiring either photoirradiation or heating at 120 °C. Although the reaction of **1a** with 2-butyne proceeded at 40 °C to give the sixmembered disilacarbocycle **9**, attempted reaction of **2a** with 2butyne gave the product in only 4% yield, even at 120 °C. The photochemical reaction took place efficiently; photoirradiation of **2a** in the presence of 2-butyne at room temperature gave **9** in 84% yield. Interestingly, the reaction of the Fe(IV)dihydride complex **4a** with 2-butyne gave **9** in moderate yield (34%) in a thermal process, whereas the photochemical process yielded only a trace amount of **9**. The moderate yield of **9** was attributed to concomitant thermal decomposition of **4a**.

Table 2 shows the results for reactions of the disilaferracycle complexes with 5 equiv of 1,2-bis(dimethylsilyl)benzene and 10 equiv of phenylacetylene. Excess amounts of 1,2-bis-(dimethylsilyl)benzene and phenylacetylene were used to examine whether the reaction could proceed catalytically. The results were fairly consistent with those for the reaction with 2-butyne; a stoichiometric reaction with 1a occurred at 40 °C, and a stoichiometric amount (90% yield based on Fe) of the product 10 was obtained. The reaction of 2a proceeded photochemically (entry 4), whereas that of 4a required heating to 140 °C, and the product was formed in low yield (entry 5). A difference from the reaction with 1-butyne was the thermal reaction of 2a at 140 °C, which afforded the product in 60% yield (entry 3). In all of the iron-promoted reactions, the

Table 2. Double Silylation of Phenylacetylene with 1,2-Bis(dimethylsilyl)benzene Mediated by Disilaferracycle Complexes

| , | Fe complexes (1a or 2a or 4a) | + 5 Si-H | H + 10 PhCΞCH H | 140 °C or temp, hv 18 hrs 10 |
|---|---|------------|-----------------------|---------------------------------------|
| | entry | Fe complex | conditions | yield of 10 $(\%)^a$ |
| | 1 | 1a | 40 °C | 90 |
| | 2 | 1a | 140 °C | 90 |
| | 3 | 2a | 140 °C | 60 |
| | 4 | 2a | 25 °C, hν | 80 |
| | 5 | 4a | 140 °C | 30 |

"Yields were determined on the basis of the charged iron complexes.

product 10 was formed as a single product in a stoichiometric manner.

In contrast, the three ruthenium complexes **5a** and **6a,c** catalyzed the thermal reaction of 1,2-bis(dimethylsilyl)benzene with phenylacetylene to give a mixture of **10** and **8b** at 140 °C (entries 1, 5, and 7), although the TON was not high (\sim 2.6). The results are summarized in Table 3. Complex **5c** was less

Table 3. Catalytic Double Silylation of Phenylacetylene with 1,2-Bis(dimethylsilyl)benzene Mediated by Disilaruthenacycle Complexes

| $ \underbrace{ \begin{array}{c} \begin{array}{c} \\ \\ \\ \end{array} \\ Si - H \end{array} } Si - H \\ Si - H \\ (2 \ equiv.) \end{array} } \underbrace{ \begin{array}{c} Fe \ or \ Ru \ cat. \\ (20mol\%) \\ \hline 40 \ or \ 140 \ ^{\circ}C \\ or \ temp, \ hv \\ 18 \ hrs \end{array} } \underbrace{ \begin{array}{c} \\ Si - C \\ Si - C \\ H \end{array} } \underbrace{ \begin{array}{c} \\ Si \\ Si \\ Si \\ H \end{array} } \underbrace{ \begin{array}{c} \\ Si \\ Si \\ Si \\ Si \\ Si \\ H \end{array} } \underbrace{ \begin{array}{c} \\ Si \\ H \end{array} } \underbrace{ \begin{array}{c} \\ Si \\ S$ | | | | | | | | |
|--|------|------------|------------------------|------------------------|-----|--|--|--|
| entry | cat. | conditions | yield of 10 (%) | yield of 8b (%) | TON | | | |
| 1 | 5a | 140 °C | 34 | 6 | 2.0 | | | |
| 2 | 5a | 50 °C, hv | 24 | <1 | 1.2 | | | |
| 3 | 5c | 140 °C | 12 | <1 | 0.6 | | | |
| 4 | 5c | 80 °C, hν | <1 | <1 | ~0 | | | |
| 5 | 6a | 140 °C | 42 | 10 | 2.6 | | | |
| 6 | 6a | 50 °C, hν | <1 | <1 | ~0 | | | |
| 7 | 6c | 140 °C | 35 | 15 | 2.5 | | | |
| 8 | 6c | 80 °C, hν | <1 | <1 | ~0 | | | |

reactive (entry 3). Similarly to the Fe(IV)–dihydride complex, the efficiency of the Ru(IV)–dihydride-catalyzed reactions was lower than that of the Ru(II)–carbonyl-catalyzed reactions due to decomposition of the catalyst. In contrast, the Ru(II)– carbonyl complexes were robust, and considerable amounts of them were recovered after the reaction. This suggests that efficient removal of the CO ligand from 6 increases the catalytic efficiency. It was thought that photoirradiation might be effective for this purpose; however, although it contributed to the production of 10 at 50 °C in the reaction of 5a (entry 2), it was useless for the reactions of the Ru(II)–carbonyl complexes (entries 4, 6, and 8).

Reaction Mechanisms. As explained in the Introduction, it is known that the reactions of alkenes and alkynes with 1,2bis(dimethylsilyl)benzene are catalyzed by platinum complexes; in a typical example, the reaction of phenylacetylene with 1,2bis(dimethylsilyl)benzene in the presence of 2 mol % of $(PPh_3)_2Pt(\eta^2-H_2C=CH_2)$ gave a mixture of 10 and 8b in a ratio of 7.6:1.^{3a} The TON reached 43 after 19 h at 30 °C. Although the platinum complex is more efficient as a catalyst for double silylation, the reaction is of interest from a mechanistic point of view, as the iron and ruthenium complexes promote the same double-silylation reaction. Scheme 9 shows

Scheme 9. Possible Reaction Mechanism for the Double Silylation of Alkenes (Cycle I) and Alkynes (Cycle II)



possible catalytic cycles for double-silvlation reactions, which can apply to platinum-, iron-, and ruthenium-promoted reactions. The first step is double oxidative addition of 1,2bis(dimethylsilyl)benzene to the coordinatively unsaturated metal species "M", which is followed by elimination of H₂. This generates the disilametallacycle intermediate " $M(Si)_2$ " (A) in the catalytic cycle. When $(PPh_3)_2Pt(\eta^2-H_2C=CH_2)$ is used as a catalyst, "M" denotes the 14e "(PPh₃)₂Pt" species and " $M(Si)_2$ " (A) is the disilaplatina(II)cycle (PPh₃)₂Pt- $(SiMe_2C_6H_4SiMe_2)$. Coordination of an alkene (cycle I) or an alkyne (cycle II) to the metal center of A is followed by insertion of unsaturated molecules into the M-Si bond and subsequent reductive elimination, leading to the formation of six-membered disilacarbocycles and regeneration of the lowvalent metal species "M". The mechanism of formation of the five-membered disilacarbocyclic byproduct seen in the reaction of alkenes involves an alternative pathway for cycle I; the intermediate normally furnishing reductive elimination undergoes β -hydride elimination to give a metal hydride intermediate containing a vinylsilane moiety, and reinsertion followed by reductive elimination gives the five-membered disilacarbocycle. It is noteworthy that the platinum-catalyzed reaction with phenylacetylene and 1,2-bis(dimethylsilyl)benzene also gave the five-membered disilacarbocycle 8b as a byproduct.^{3a} Another side reaction, hydrogenation of phenylacetylene to styrene, is caused by molecular hydrogen formed in the double oxidative addition of two Si-H bonds to the intermediate "M". Double silvlation of in situ formed styrene by way of the β hydrogen elimination pathway in cycle I results in the formation of 8b.

The iron- and ruthenium-mediated reactions of alkenes and alkynes presented in this paper gave products similar to those obtained in platinum-catalyzed reactions. This strongly suggests that similar reaction mechanisms, through the coordinatively unsaturated 16e disilaferra(II)- or disilaruthena(II)cycle "(η^{6} -arene)M(Me₂SiC₆H₄SiMe₂)", are involved. The way in which this 16e species is generated is dependent on the metal and the auxiliary ligands, and the interconversion reactions among the

Fe(II)-dinitrogen, M(II)-carbonyl, and M(IV)-hydride complexes shown in Scheme 10 provide the key to understanding the results.





The iron complexes 1, 2, and 4 are interconvertible, as described earlier. The reactions from 1 to 2 and 1 to 4 proceeded thermally at relatively low temperatures. The reaction from 4 to 2 also proceeded thermally, but a relatively high temperature was needed. In contrast, the other two reactions, from 2 to 1 and 2 to 4, took place photochemically. These results suggest that the weakly coordinating N₂ ligand in 1 dissociated from the iron center to form the 16e species " $(\eta^6$ arene)Fe(Me₂SiC₆H₄SiMe₂)" under mild conditions, while liberation of CO from the Fe(II)-carbonyl complexes 2 required the assistance of photoirradiation. The $Fe^{IV}(H)_2(Si)_2$ complex 4 is not a very efficient precursor of the 16e species but can generate it thermally at 120 °C. This is consistent with the results of the double-silvlation reactions of 2-butyne and phenylacetylene with these iron compounds; low-temperature thermal reactions of 1, photoassisted reactions of 2, and hightemperature thermal reactions of 4 produced the disilacarbocyclic products. It is worth noting that thermal generation of the 16e species from 2 was possible, giving the product in low to medium yields (from 2-butyne, 4% at 120 °C; from phenylacetylene, 60% at 140 °C; yields are based on the amount of 2a used). The reason interconversion from 2 to 4 only took place photochemically was that the reaction of 2 to the 16e species is reversible, but the reaction from the 16e species to 4 by oxidative addition of H₂ is not efficient as a thermal process.

Studies of interconversion of the ruthenium complexes in a fashion similar to that for their iron analogues were hampered by two factors: the lack of a dinuclear dinitrogen complex of ruthenium and the fact that although the reaction from 5 to 6 was possible under photoirradiation with heating, the reverse reaction from 6 to 5 did not occur either thermally or photochemically. The ruthenium-catalyzed reactions shown in Table 3 revealed that two ruthenium complexes, 5 and 6, were catalytically active at 140 $^{\circ}$ C, but photoirradiation did not assist the catalysis.

The catalytic cycle of ruthenium is similar to that of platinum-catalyzed double silylation (Scheme 9), where $M = (\eta^{6}$ -arene)Ru. Although the double-silylation scheme promoted by the iron complexes may be explained in a similar fashion, there is an important difference between Fe and Pt/Ru: in the final step of the catalytic cycle, dehydrogenative double oxidative addition of two Si–H bonds in 1,2-bis(dimethylsilyl)-benzene to " $(\eta^{6}$ -arene)Fe⁰" to regenerate the disilametalla(II)-cycle **A** does not work well. The lack of catalytic properties in

the disilaferracycles was presumably due to the instability of the " $(\eta^{6}\text{-arene})\text{Fe}^{0}$ " species; aggregation of this Fe(0) species to form insoluble iron species may have taken place prior to the dehydrogenative double oxidative addition. In contrast, the relatively strong coordination of the $\eta^{6}\text{-arene}$ ligand to the ruthenium(0) center may contribute to stabilization of the " $(\eta^{6}\text{-} \text{arene})\text{Ru}^{0}$ " intermediate, and subsequent dehydrogenative double oxidative addition of 1,2-bis(dimethylsilyl)benzene proceeded to regenerate the 16e intermediate " $(\eta^{6}\text{-} \text{arene})\text{Ru}(\text{Me}_{2}\text{SiC}_{6}\text{H}_{4}\text{SiMe}_{2})$ ".

Although all of the isolated iron complexes described in this paper are diamagnetic, iron complexes can adopt various spin states with relatively low spin-crossover barriers in the catalytic cycle.¹⁸ Therefore, the reaction of 14e " $(\eta^6$ -arene)Fe" species with 1,2-bis(dimethylsilyl)benzene may be a spin-forbidden step. A survey of appropriate six-electron-donating ligands other than η^6 -arene, as well as theoretical calculations to elucidate the spin state of the possible intermediate, are clearly needed to improve the efficiency of double-silylation reactions mediated by iron complexes.

CONCLUSION

We synthesized a series of group 8 half-sandwich disilametallacycles, $(\eta^6\text{-}arene)M^{II}(Me_2SiC_6H_4SiMe_2)L$ and $(\eta^6\text{-}arene)$ - $M^{IV}(H)_2(Me_2SiC_6H_4SiMe_2)$ (M = Fe, Ru). Only a few disilaferra- or disilaruthenacycle complexes are known, and many of these are coordinatively saturated and stable. For example, we confirmed that Fink's Fe(II)-carbonyl complex $(Me_2SiC_6H_4SiMe_2)Fe(CO)_4^{19}$ did not react with ethylene, 2butyne, and phenylacetylene in C₆D₆ at 120 °C for 18 h. The iron and ruthenium complexes presented in this paper are rare examples of reactive disilaferra- and disilaruthenacycle complexes and have contributed toward three novel findings in organometallic chemistry. First, the bridging dinitrogen ligand of 1 was found to be labile, and facile generation of a coordinatively unsaturated 16e species, " $(\eta^{6}$ -arene)- $M^{II}(Me_2SiC_6H_4SiMe_2)$ ", which could undergo coordination of a two-electron-donating ligand and oxidative addition of H₂, was achieved. Second, the 16e disilaferra(II)cycle species " $(\eta^{6}$ arene) $M^{II}(Me_2SiC_6H_4SiMe_2)$ " reacted reversibly with CO and H₂. The reaction with H₂ involved a redox reaction between $(\eta^{6}\text{-arene})\text{Fe}^{\text{II}}$ and $(\eta^{6}\text{-arene})\text{Fe}^{\text{IV}}$. It is noteworthy that the disilaferracycle skeleton could effectively stabilize both the Fe(II) and Fe(IV) centers and promoted interconversion between $(\eta^6\text{-}arene)\text{Fe}^{\text{II}}$ and $(\eta^6\text{-}arene)\text{Fe}^{\text{IV}}$ complexes. Third, stoichiometric reactions of 1 with alkenes and alkynes led to elimination of disilacarbocycles in high yield, and catalytic versions of these reactions were realized using the disilaruthena-(II)- or disilaruthena(IV)cycle complexes 5 and 6. Although the TON of the disilaruthenacycle-catalyzed double silvlation reaction is not high at present, it is important to note that reactions which have so far been catalyzed by group 10 transition metals, especially platinum, have now been achieved using ruthenium. The results shown here are expected to open new routes to the design and synthesis of novel reactive iron and ruthenium complexes, and active studies, including a survey of appropriate six-electron-donating ligands which can effectively stabilize the Fe(0) center and promote double oxidative addition of two Si-H groups, are under way.

EXPERIMENTAL SECTION

General Considerations. Manipulation of air- and moisturesensitive compounds was carried out under a dry nitrogen atmosphere using standard Schlenk tube techniques associated with a high-vacuum line or in the glovebox, which was filled with dry nitrogen. All solvents were distilled over appropriate drying reagents prior to use (benzene, toluene, mesitylene, ether, dioxane, THF, pentane; Ph₂CO/Na). ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature. ¹H, ¹³C, ²⁹Si, and ³¹P NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (¹H, ¹³C) or standard resonances (²⁹Si; external tetramethylsilane, ³¹P; external H₃PO₄). Elemental analyses were performed by a Perkin-Elmer 2400II/CHN analyzer. IR spectra were recorded on a JASCO FT/IR-550 spectrometer. EI-MS spectra were measured on a Shimadzu GC-MS QP5050 instrument. Photo-irradiation was carried out by an Ushio hUM-453B-A igh-pressure mercury lamp (450 W). Starting materials, 1,2-bis(dimethylsilyl)-benzene,²⁰ [Fe(mesityl)₂]₂,²¹ and disilaferracycle complexes **1a,b**, **2a,b**, **3a,b**, and **4a,b**,⁸ were synthesized by the method reported in the literature.

Preparation of $(\eta^6-C_6H_3Me_3)Fe(Me_2SiC_6H_4SiMe_2)(H)_2$ (4c). In a 20 mL Schlenk tube, complex 4a (30 mg, 0.09 mmol) was dissolved in mesitylene (3 mL), and the atmosphere was replaced with 1 atm of H₂. After this solution was mixed for 18 h at 120 °C, the solvent was evaporated in vacuo to afford the crude product. This crude product was dissolved in pentane and centrifuged to remove the small amount of insoluble materials. The supernatant was collected, and the solvent was slowly evaporated under vacuum to give 4c as a pale yellow crystalline solid (18 mg, 52%). In a similar manner, the η^6 -toluene homologue can also be prepared by heating the toluene solution of 4a at 120 °C for 18 h, from which 4b was isolated in 58% yield. ¹H NMR (600 MHz, room temperature, C_6D_6): δ –18.2 (s, 2H, Fe–H, with a satellite signal due to the coupling with ²⁹Si, $J_{Si-H} = 12.2$ Hz), 0.79 (s, 12H, SiMe₂), 1.90 (s, 9H, C₆H₃Me₃), 4.70 (s, 3H, C₆H₃Me₃), 7.27-7.29 (m, 2H, C₆H₄) 7.70-7.72 (m, 2H, C₆H₄). ¹³C NMR (150 MHz, room temperature, C₆D₆): δ 10.6 (s, SiMe₂), 21.3 (s, C₆H₃Me₃), 89.4 (s, C₆H₃Me₃), 100.7 (s, ipso-C₆H₃Me₃), 127.3, 130.8, 158.6 (s, C₆H₄). ²⁹Si NMR (119 MHz, room temperature, C_6D_6); δ 31.7 (s, SiMe₂). IR (KBr): ν_{Fe-H} 1976 cm⁻¹. Anal. Calcd for C₁₉H₃₀FeSi₂: C, 61.60; H, 8.16. Found: C, 61.48; H, 7.95.

Preparation of $(\eta^6-C_6H_3Me_3)Fe(Me_2SiC_6H_4SiMe_2)(CO)$ (2c). In a 20 mL Schlenk tube, complex 4c (30 mg, 0.08 mmol) was dissolved in mesitylene (3 mL), and the atmosphere was replaced with 1 atm of CO. After this solution was stirred for 18 h at 120 °C, the solvent was removed in vacuo. The resulting solid was dissolved in pentane (5 mL) and passed through a pad of Celite. The pentane solution was removed under vacuum, and a pale yellow powder of 2c was obtained in 41% yield (13 mg). ¹H NMR (600 MHz, room temperature, C₆D₆): δ 0.60 (s, 6H, SiMe₂), 0.84 (s, 6H, SiMe₂), 1.79 (s, 9H, C₆H₃Me₃), 4.88 (s, 3H, C₆H₃Me₃), 7.27–7.319 (m, 2H, C₆H₄) 7.72–7.73 (m, 2H, C₆H₄). ^{13}C NMR (150 MHz, room temperature, C₆D₆): δ 9.84 (s, SiMe₂), 20.7 (s, SiMe₂), 30.8 (s, C₆H₃Me₃), 96.2 (s, C₆H₃Me₃), 101.0 (s, ipso-C₆H₃Me₃), 127.9, 130.9, 157.4 (s, C₆H₄), 211.3 (s, CO). ²⁹Si NMR (119 MHz, room temperature, C₆D₆): δ 49.9 (s, SiMe₂). IR (KBr): $\nu_{C\equiv0} = 1892 \text{ cm}^{-1}$. Anal. Calcd for $C_{20}H_{28}FeOSi_2$: C, 60.59; H, 7.12. Found: C, 60.32; H, 7.00.

Preparation of $[(η^6-C_6H_3Me_3)Fe(Me_2SiC_6H_4SiMe_2)]_2(μ-η^1:η^1-N_2)$ (1c). In a 20 mL Schlenk tube, complex 2c (40 mg, 0.10 mmol) was dissolved in mesitylene (5 mL) under a nitrogen atmosphere, and the solution was irradiated by a high-pressure mercury lamp. After the resulting mixture was stirred at ambient temperature under irradiation for 30 h, the solvent was passed through a pad of Celite. After concentration of the solvent to ca. 3 mL, pentane (5 mL) was added to this solution. This solution was cooled to −35 °C to afford single crystals of 1c as red crystals in 86% yield (33 mg). ¹H NMR (600 MHz, room temperature, C₆D₆): δ 0.36 (s, 12H, SiMe₂), 1.02 (s, 12H, SiMe₂), 1.78 (s, 18H, C₆H₃Me₃), 4.16 (s, 6H, C₆H₃Me₃), 7.24−7.28 (m, 4H, C₆H₄), 7.59−7.67 (m, 4H, C₆H₄). ¹³C NMR (150 MHz, room temperature, C₆D₆): δ 6.6 (s, SiMe₂), 7.6 (s, SiMe₂), 19.2 (s, C₆H₃Me₃), 93.2, 99.8 (s, C₆H₃Me₃), 127.2, 130.3, 156.1 (s, C₆H₄). ²⁹Si NMR (119 MHz, room temperature, C₆D₆): δ 41.9 (s, SiMe₂). Raman: ν_{N≡N} 2012 cm⁻¹. Anal. Calcd for

 $\rm C_{38}H_{56}Fe_2N_2Si_4:$ C, 59.67; H, 7.38; N, 3.66. Found: C, 59.43; H, 7.08; N, 3.81.

Preparation of (η⁶-C₆H₆)Ru(H)₂(Me₂SiC₆H₄SiMe₂) (5a). In a 50 mL Schlenk tube were placed [(\eta^6-C_6H_6)RuCl_2]_2 (200 mg, 0.4 mmol) and a THF solution (10 mL) of 1,2-bis(dimethylsilyl)benzene (342 mg, 1.76 mmol). The resulting solution was stirred for 18 h under reflux condition, during which the color of the solution turned dark brown. After removal of the solvent, purification of the residue by alumina column chromatography (Hex: C₆H₆ = 4: 1) gave the complex 5a as white powder (260 mg, 43%). ¹H NMR (600 MHz, room temperature, C₆D₆): δ –12.2 (s, 2H, Ru–H, with a satellite signal due to the coupling with ²⁹Si, J_{Si–H} = 10.0 Hz), 0.77 (s, 12H, SiMe₂), 4.94 (s, 6H, C₆H₆), 7.28–7.29 (m, 2H, C₆H₄); ⁷²Si NMR (119 MHz, room temperature, C₆D₆); δ 22.7 (s, SiMe₂); IR (KBr): ν_{Ru-H} = 2025 cm⁻¹; Anal. Calcd for C₁₆H₂₄RuSi₂: C, 51.44; H, 6.47. Found: C, 51.24; H, 6.32.

Preparation of (η⁶-C₆H₃Me₃)Ru(Me₂SiC₆H₄SiMe₂)(H)₂ (5c). In a 20 mL Schlenk tube, complex **5a** (30 mg, 0.08 mmol) was dissolved in mesitylene (5 mL), and the solution was stirred for 18 h at 140 °C. The resulting solution was passed through a pad of Celite, and the solvent was evaporated in vacuo to afford the complex **5c** as a white powder (28 mg, 85%). ¹H NMR (600 MHz, room temperature, C₆D₆): δ –12.3 (s, 2H, Ru–H, with a satellite signal due to the coupling with ²⁹Si, J_{Si-H} = 8.8 Hz), 0.78 (s, 12H, SiMe₂), 1.84 (s, 9H, C₆H₃Me₃), 5.05 (s, 3H, C₆H₃Me₃), 7.34–7.35 (m, 2H, C₆H₄) 7.85– 7.86 (m, 2H, C₆H₄). ¹³C NMR (150 MHz, room temperature, C₆D₆): δ 11.2 (s, SiMe₂), 21.1 (s, C₆H₃Me₃), 94.8 (s, C₆H₃Me₃), 106.7 (s, *ipso*-C₆H₃Me₃), 127.2, 131.2, 159.7 (s, C₆H₄). ²⁹Si NMR (119 MHz, room temperature, C₆D₆); δ 22.9 (s, SiMe₂). IR (KBr): ν_{Ru-H} 2030 cm⁻¹. Anal. Calcd for C₁₉H₃₀RuSi₂: C, 54.90; H, 7.27. Found: C, 54.63; H, 6.89.

Preparation of (η⁶-C₆H₆)Ru(Me₂SiC₆H₄SiMe₂)(CO) (6a). In a 20 mL Schlenk tube, complex **5a** (30 mg, 0.08 mmol) was dissolved in benzene (5 mL), and the atmosphere was replaced with 1 atm of CO. After this solution was mixed for 12 h at 50 °C under irradiation of the high-pressure mercury lamp, the solution was passed through a pad of Celite to remove the small amount of insoluble materials. The solvent was slowly evaporated in vacuo to afford pale yellow crystals of **6a** in 88% yield (28 mg). ¹H NMR (600 MHz, room temperature, C₆D₆): *δ* 0.48 (s, 6H, SiMe₂), 0.88 (s, 6H, SiMe₂), 4.96 (s, 3H, C₆H₆), 7.28–7.30 (m, 2H, C₆H₄) 7.71–7.72 (m, 2H, C₆H₄). ¹³C NMR (150 MHz, room temperature, C₆D₆): *δ* 7.9 (s, SiMe₂), 10.5 (s, SiMe₂), 94.6 (s, C₆H₆), 127.6, 130.9, 156.1 (s, C₆H₄), 199.4 (s, CO). ²⁹Si NMR (119 MHz, room temperature, C₆D₆); *δ* 35.8 (s, SiMe₂). IR (KBr): ν_{C=O} 1919 cm⁻¹. Anal. Calcd for C₁₇H₂₂RuOSi₂: C, 51.10; H, 5.55. Found: C, 50.83; H, 5.51.

Preparation of $(\eta^6-C_6Me_3H_3)Ru(Me_2SiC_6H_4SiMe_2)(CO)$ (6c). In a 20 mL Schlenk tube, complex 5c (30 mg, 0.07 mmol) was dissolved in mesitylene (5 mL), and the atmosphere was replaced with 1 atm of CO. After this solution was mixed for 12 h at 80 °C under irradiation of the high-pressure mercury lamp, the solution was passed through a pad of Celite to remove the small amount of insoluble materials. The solvent was evaporated in vacuo to afford a pale yellow powder of 6c in 78% yield (25 mg). ¹H NMR (600 MHz, room temperature, C₆D₆): δ 0.57 (s, 6H, SiMe₂), 0.86 (s, 6H, SiMe₂), 1.72 (s, 9H, C₆H₃Me₃), 5.09 (s, 3H, C₆H₃Me₃), 7.30-7.31 (m, 2H, C₆H₄) 7.76-7.77 (m, 2H, $C_6H_4).\ ^{13}C$ NMR (150 MHz, room temperature, $C_6D_6):$ δ 7.0 (s, SiMe₂), 10.2 (s, SiMe₂), 20.6 (s, C₆H₃Me₃), 99.8 (s, C₆H₃Me₃), 107.9 (s, ipso-C₆H₃Me₃), 127.9, 131.2, 157.4 (s, C₆H₄), 201.1(s, CO). ²⁹Si NMR (119 MHz, room temperature, C₆D₆); δ 36.9 (s, SiMe₂). IR (KBr): $\nu_{C\equiv 0}$ 1910 cm⁻¹. Anal. Calcd for C₂₀H₂₈RuOSi₂: C, 54.39; H, 6.39. Found: C, 54.16; H, 6.17.

Catalytic Double Silylation of Phenylacetylene with 1,2-Bis(dimethylsilyl)benzene Catalyzd by Disilaferracycles or Disilaruthenacycles. As a typical example, 6a (25 mg, 0.063 mmol) was dissolved in benzene (0.5 mL), then phenylacetylene (68 μ L, 0.64 mmol) and 1,2-bis(dimethylsilyl)benzene (62 mg, 0.32 mmol) were added, and the reaction mixture was stirred for 18 h at 140 °C or under irradiation of the high-pressure mercury lamp at 50 or 80 °C. The obtained mixture was passed through a short pad of alumina with pentane as eluent to remove the residual metal. The yield of double-silylated products **10** and **8b** was determined by ¹H NMR analysis in benzene- d_6 with 1,4-dioxane (27 μ L, 0.32 mmol) as an internal standard.

X-ray Data Collection and Reduction. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphitemonochromated Mo K α radiation (λ = 0.71070 Å). The data were collected at 123(2) K using ω scans in the θ range $3.4 \le \theta \le 27.5^{\circ}$ (1c), $3.2 \le \theta \le 27.5^{\circ}$ (4c), and $3.8 \le \theta \le 27.5^{\circ}$ (6a). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer and were corrected for Lorentz and polarization effects. The structures were solved by direct methods²² and expanded using Fourier techniques.²³ Hydrogen atoms were refined using the riding model except for the hydride atoms in 4c. Two hydride atoms in 4c were detected from the Fourier map and refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 2190 observed reflections and 130 variable parameters for 1c, 4401 observed reflections and 235 variable parameters for 4c, and 4089 observed reflections and 212 variable parameters for 6a. Neutral atom scattering factors were taken from Cromer and Waber.²⁴ All calculations were performed using the CrystalStructure^{25,26} crystallographic software package. Details of the final refinement as well as the bond lengths and angles are summarized in the Supporting Information, and the numbering scheme employed is also shown in the Supporting Information; the structures were drawn with ORTEP as 50% probability ellipsoids. CCDC 890988 (1c), 890989 (4c), and 890990 (6a) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/ cif.

ASSOCIATED CONTENT

Supporting Information

Text giving the detailed experimental section and figures, tables, and CIF files giving the molecular structures of 1c, 4c and 6a and details of crystallographic studies (1c, 4c, 6a). This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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