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$Me_2Si(\eta^5$-$C_5H_4)_2$-Bridged Dinuclear Ruthenium Complexes: X-ray Crystal Structures of $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(Cl)_2(CO)_4]$ and $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(\mu$-$Br)(CO)_4][BF_4]$

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The treatment of the binuclear tetracarbonyl complex $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(\mu$-$CO)_2$-$(CO)_2]$ (**1**) with HBF_4 in dichloromethane leads to the electrophilic addition of one proton to yield the bridging hydride complex $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(\mu$-$H)(CO)_4][BF_4]$ (**2**). Complex **1** also reacts with $Li[BHEt_3]$ to afford the bridging methylene complex $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}$-$(\mu$-$CH_2)(\mu$-$CO)(CO)_2]$ (**3**). Binuclear complexes $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(X)_2(CO)_4]$ (X = Cl (**4a**), Br (**4b**), and I (**4c**)) have been synthesized in good yields from the reaction of complex **1** with *N*-chlorosuccinimide (X = Cl) and X_2 (X = Br, I) in CH_2Cl_2. The structure of complex **4a** which has been determined by X-ray crystallography shows a three-legged piano-stool geometry around each ruthenium atom linked by the bridging $Me_2Si(\eta^5$-$C_5H_4)_2$ group. The cyclopentadienyl rings which are coordinated in a η^5 fashion are rotated in opposite directions around the Si−C(bridgehead) bond, leading to the trans arrrangement of the metal fragments and giving rise to a long ruthenium−ruthenium distance (6.120(6) Å). Complex **4c** has been used as a precursor in a series of halide and carbonyl substitution reactions. The reaction of **4c** with the cuprate derivative $Li[CuMe_2]$ in THF leads to the exchange of both iodide anions to give the dimethyl complex $[Ru_2(\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(CH_3)_2(CO)_4]$ (**5**). The treatment of complex **4c** with $AgBF_4$ in refluxing acetonitrile leads to halide abstraction to afford the cationic complex $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(CO)_4(NCMe)_2][BF_4]_2$ (**9**). The analogous reaction of complexes **4a**−**c** with $AgBF_4$ in CH_2Cl_2 or acetone at room temperature gives the cationic double-bridged derivatives $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2)\}(\mu$-$X)(CO)_4][BF_4]$ (**10a**−**c**). The X-ray crystal structure of **10b** shows the two ruthenium moieties bridged by a halogen atom, forcing a cisoid arrangement in the molecule. Irradiation of a solution of **4c** and PCy_3 in THF leads to carbonyl substitutions to yield the monocarbonyl complex $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}$-$(I)_2(CO)_2(PCy_3)_2]$ (**6c**). Analogous isocyanide carbonyl substituted complexes $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2$-$SiMe_2\}(I)_2(CNR)_x(CO)_{4-x}]$ (R = CH_2Ph, $x = 1$ (**7a**), $x = 2$ (**7b**), $x = 3$ (**7c**), $x = 4$ (**7d**); R = Cy, $x = 1$ (**8a**), $x = 2$ (**8b**), $x = 3$ (**8c**), $x = 4$ (**8d**)) have been obtained by UV irradiation of **4c** and the corresponding isocyanide in THF, depending on the ligand:complex ratio.

Introduction

The bridged bis(cyclopentadienyl) systems $[X(C_5H_4)_2]^{2-}$ (X = CH_2, $SiMe_2$, $SnMe_2$, $GeMe_2$, etc.) have been shown to be appropriate ligands in the formation of dinuclear compounds which are resistant to fragmentation. These derivatives are especially attractive for studying the potential interactions between two reactive sites, since the presence of the bridge places the two metal atoms in close proximity. Most of the $[X(C_5H_4)_2]$ (X = CH_2, $SiMe_2$) bridged metal complexes belong to groups 4,[1] 6,[2] and 9 (Rh and Ir),[3] but to the best of our knowledge only a few examples are known for group 8 metals.[4]

Due to the free rotation around the two silicon−cyclopentadienyl bonds, a number of different conformations may be adopted by a dimetallic fragment of the

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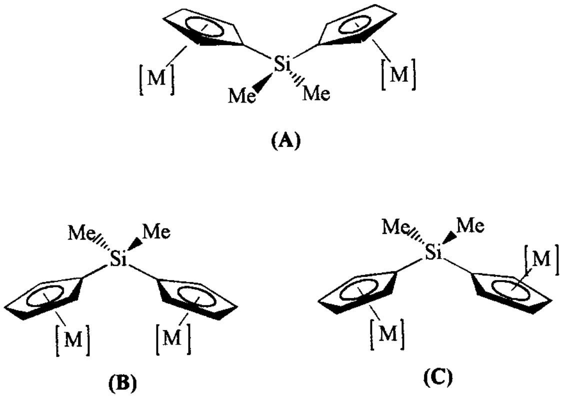
Chart 1



type $[M_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$. To date, three structural types (Chart 1) have been observed and crystallographically characterized for transition metals: (a) type **A**, in which the metal fragments are coordinated in an exo disposition with respect to the rings of the bridging group and are located in a mutually cis orientation giving rise to a formally exo-cis dimetallic arrangement;[1c,2a] (b) type **B**, in which the metal fragments are coordinated in an endo fashion with respect to the rings and in a mutually cis orientation (endo-cis dimetallic arrangement);[1b−f,2c−f,4a−d] and (c) type **C**, which results from the rotation in type **A** or **B** of one of the $(\eta^5\text{-}C_5H_4)M$ fragments around the corresponding Si−C bond leading to a formally trans dimetallic arrangement.[1a] In complexes of type **B** the metals atoms may also be linked either by an additional bridging ligand or by a metal−metal bond,[2d] which prevents the two metallic fragments from being located far away from each other, as in types **A** and **C**.

During the past few years we have described a large series of alkynyl, vinylidene, and allenylidene complexes using the half-sandwich moiety “$M(\eta^5\text{-ring})L_2$” (M = Fe, ring = C_5H_5; M = Ru, Os, ring = C_9H_7, $C_9Me_xH_{7-x}$) as metal fragments.[5] With the aim of extending this chemistry to dinuclear derivatives and in order to provide suitable precursors we have explored the synthesis of $Me_2Si(\eta^5\text{-}C_5H_4)_2$ bridged ruthenium derivatives from the known[4d,6] dinuclear complex $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CO)_2(\mu\text{-}CO)_2]$ (**1**). Herein we report the synthesis of novel derivatives (Scheme 1): (i) $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}H)(CO)_4][BF_4]$ (**2**) and $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2]$ (**3**), in which the metal atoms are also linked by a metal−metal bond; (ii) carbonyl complexes $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(X)_2(CO)_4]$ (X = Cl (**4a**); X = Br (**4b**); X = I (**4c**); X = Me (**5**)); (iii) carbonyl substituted derivatives $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(L)_x(CO)_{4-x}]$ (L = PCy_3, $x = 2$ (**6c**); L = $CNCH_2Ph$, $x = 1$ (**7a**), $x = 2$ (**7b**), $x = 3$ (**7c**), $x = 4$ (**7d**); L = CNCy, $x = 1$ (**8a**), $x = 2$ (**8b**), $x = 3$ (**8c**), $x = 4$ (**8d**)); (iv) cationic complexes $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CO)_4(NCMe)_2][BF_4]_2$ (**9**) and $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}X)(CO)_4][BF_4]$ (**10a**−**c**). The synthetic approaches of the novel compounds (Scheme 1) show the robustness of the bridging system which remains unchanged through all the transformations leading to a variety of dinuclear ruthenium(II) complexes.

Experimental Section

General Comments. The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. Methyl isobutyl ketone, I_2, Br_2, *N*-chlorosuccinimide, $Na_2S_2O_3$, anhydrous $MgSO_4$, CuI, MeLi, $AgBF_4$, $HBF_4{\cdot}OEt_2$, $Li[BHEt_3]$, benzyl isocyanide, and cyclohexyl isocyanide were used as received from Aldrich Chemical Co. $Me_2Si(C_5H_5)_2$[1c] and $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CO)_2(CO)_2]$[4d] were synthesized by a modified published method.

Photolysis experiments were performed with external irradiation using a UV lamp (400 W, Applied Photophysics). Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Unsatisfactory analyses were obtained for complex **5** (oil) and isocyanide complexes **7a**−**d** and **8a**−**d** (obtained in rather low yields). All of them have been fully characterized by IR and NMR spectroscopy (See Supporting Information). The NMR spectra were recorded on a Bruker AC300 instrument at 300 (^1H), 121.5 (^{31}P), or 75.4 MHz (^{13}C) and on an AC200 instrument at 200 (^1H), 81.0 (^{31}P), or 50.3 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards.

Synthesis of $[Me_2Si(C_5H_5)_2]$. Li^nBu (1.6 M solution in hexane) (43.75 mL, 70 mmol) was added dropwise to a solution of C_5H_6 (9 mL, 108.8 mmol) in THF at −60 °C. This mixture was stirred for 2 h, and freshly distilled $SiCl_2Me_2$ (3.9 mL, 32 mmol) was added. The temperature was allowed to reach room temperature during 2 h and stirred for an additional 1 h. The solvents were then removed in vacuo, and the product was extracted with pentane. Evaporation of the solvent in the resulting yellow solution afforded the ligand as an orange oil (5.4 mL, 89% yield).

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CO)_2(CO)_2]$ (1). A mixture of $[Ru_3(CO)_{12}]$ (4.44 g, 6.94 mmol) and $Me_2Si(C_5H_5)_2$ (1.98 mL, 10.41 mmol) in methyl isobutyl ketone (300 mL) was heated under reflux for 90 min. The solution was then concentrated under reduced pressure to give complex **1** (5.20 g, 83%) as a yellow solid. Spectroscopic data (^1H NMR and IR) are in accord with the previously reported data.[4d]

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}H)(CO)_4][BF_4]$ (2). $HBF_4{\cdot}OEt_2$ (0.03 mL, 0.2 mmol) was added to a solution of complex **1** (0.10 g, 0.2 mmol) in dicholoromethane (5 mL). The resulting mixture was stirred for 15 min and the solvent removed in vacuo. The solid was washed with diethyl ether (2 × 10 mL) and vacuum-dried to give complex **2** (0.08 g, 63%) as a yellow, air-unstable solid. ν_{max}/cm^{-1} (CH_2Cl_2) 2075, 2048, 2021. NMR data: see Tables 1 and 2.

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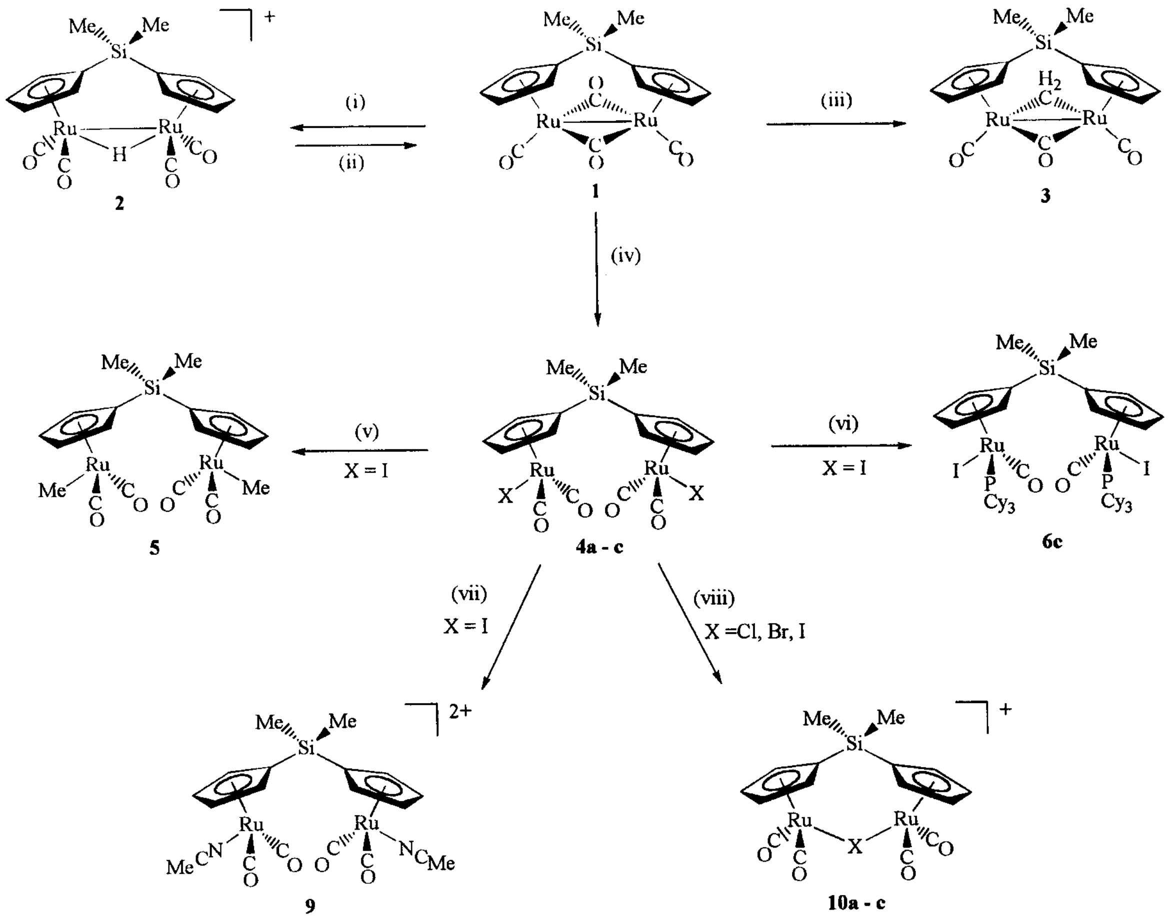
Scheme 1[a]



[a] (i) $+HBF_4$ (CH_2Cl_2, rt, 15 min), (ii) acetone, rt, (iii) +Li[$BHEt_3$] (toluene, rt, 15 min), (iv) $+X_2$ (CH_2Cl_2, rt, 30 min, X = I, Br) or +*N*-chlorosuccinimide (CH_2Cl_2, rt, 30 min, X = Cl), (v) +Li[$CuMe_2$] (thf, rt, 15 min), (vi) $+PCy_3$ (thf, *hν*, −20 °C, 9 h), (vii) + $AgBF_4$ (refluxing NCMe, 6 h), (viii) $+AgBF_4$ (CH_2Cl_2 (**10a**) or acetone (**10b**,**c**), rt, 30 min).

Table 1. ^1H NMR Data[a]

	$\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}$			
	Me	Cp	J_{HH}	others
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}H)(CO)_4][BF_4]$ (**2**)	0.58	5.76 (m), 6.00 (m)		−18.71 (H)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CH_2)(CO)_3]$ (**3**)	0.39, 0.50	5.07 (m), 5.30 (m), 5.80 (m), 5.86 (m)		7.00, 8.94 (d, CH_2, J_{HH} = 1.5 Hz)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2(Cl)_2(CO)_4]$ (**4a**)	0.63	5.44 (t), 5.61 (t)	1.9	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(Br)_2(CO)_4]$ (**4b**)	0.64	5.45 (t), 5.61 (t)	1.9	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CO)_4]$ (**4c**)	0.64	5.51 (t), 5.65 (t)	1.9	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CH_3)_2(CO)_4]$[b] (**5**)	0.49	4.62 (t), 4.77 (t)	2.2	0.24 (Me)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CO)_2(PCy_3)_2]$[c] (**6c**)	0.71	4.72 (m), 5.13 (m), 5.15 (m), 5.20 (m), 5.67 (m), 5.74 (m)		1.25, 1.83, 2.16 (m, PCy_3)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CO)_4(NCMe)_2][BF_4]_2$[d] (**9**)	0.75	6.01 (t), 6.35 (t)	1.9	2.61 (s, NCMe)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}Cl)(CO)_4][BF_4]$ (**10a**)	0.69	5.38 (t), 6.07 (t)	1.7	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}Br)(CO)_4][BF_4]$ (**10b**)	0.67	5.45 (t), 6.06 (t)	2.0	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}I)(CO)_4][BF_4]$ (**10c**)	0.63	5.62 (t), 6.07 (t)	1.8	

[a] δ in parts per million and *J* in hertz. Spectra recorded in $CDCl_3$. [b] Spectra recorded in C_6D_6. [c] Two isomers. [d] Spectra recorded in CD_3COCD_3.

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2]$ (3). Li[$BHEt_3$] (4.80 mL, 4.8 mmol) was added to a solution of complex **1** (0.50 g, 1 mmol) in toluene (48 mL). The resulting mixture was stirred for 15 min and the solvent removed in vacuo. Chromatography on silica, with hexane−dichloromethane (4:1) as eluent, afforded a yellow band, which after evaporation gave the complex **3** (0.11 g, 22%) as a yellow solid. Found: C, 39.5; H, 3.3. $C_{16}H_{16}O_3Ru_2Si$ requires C, 39.5; H, 3.3. ν_{max}/cm^{-1} (CH_2Cl_2): 1982, 1944, 1784. ν_{max}/cm^{-1} (KBr): 1959, 1923, 1900, 1795 (CO), 1255, 1162, 1056, 886, 824, 673 (Cp_2SiMe_2).

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(Cl)_2(CO)_4]$ (4a). A mixture of complex **1** (0.25 g, 0.5 mmol) and *N*-chlorosuccinimide (0.14 g, 1 mmol) in dichloromethane (70 mL) was stirred for 30 min. The solution was then concentrated at reduced pressure, and diethyl ether was added to give complex **4a** (0.22 g, 75%) as a yellow solid. ν_{max}/cm^{-1} (CH_2Cl_2): 2054, 2002. ν_{max}/cm^{-1} (KBr): 2047,1989 (CO), 1250, 1167, 1064, 892, 837, 671 (Cp_2SiMe_2).

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(Br)_2(CO)_4]$ (4b). A solution of Br_2 (0.4 mmol) in dichloromethane (0.4 mL) was added to a solution of complex **1** (0.20 g, 0.4 mmol) in dichloromethane (35 mL). After stirring for 30 min, the resulting mixture was washed with a saturated solution of $Na_2S_2O_3$ in water, the organic layer was dried with anhydrous $MgSO_4$ and filtered, and the solvent was removed in vacuo.

Table 2. $^{13}C\{^1H\}$ NMR Data[a]

	$\{\mu\text{-}(\eta^5\text{-}C_5H_{4)2}SiMe_2\}$				
	Me	Cp	Cp$_q$[c]	CO	others
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}H)(CO)_4][BF_4]$ **(2)**	−2.4	91.6, 92.2	89.1	195.6	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CH_2)(CO)_3]$ **(3)**	−2.1, −1.6	87.6, 89.9, 98.2, 100.7	83.0	201.3	105.1 (CH_2)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(Cl)_2(CO)_4]$ **(4a)**	−0.9	86.4, 100.2	88.9	196.8	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(Br)_2(CO)_4]$ **(4b)**	−0.6	86.9, 99.7	88.1	196.4	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CO)_4]$ **(4c)**	−0.4	87.7, 98.3		196.1	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CH_3)_2(CO)_4]$ **(5)**	−0.4	90.7, 97.2	91.2	202.6	−32.1(Me)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CO)_2(PCy_3)_2]$[b] **(6)**	−0.4, 0.1 0.7, 1.1	84.2−86.2, 106.4	97.8, 98.1	206.8 (d), $J_{CP} = 19.7$ Hz 206.5 (d), $J_{CP} = 19.7$ Hz	26.8−39.3 (Cy)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CO)_4(NCMe)_2]$-$[BF_4]_2$ **(9)**	−2.2	87.6, 99.8	87.0	192.8	4.1 (NC*Me*), 131.8 (N*C*Me)
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}Cl)(CO)_4][BF_4]$ **(10a)**	−3.0	83.9, 99.8	105.8	194.4	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}Br)(CO)_4][BF_4]$ **(10b)**	−2.7	84.7, 99.7	99.9	194.2	
$[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}I)(CO)_4][BF_4]$**(10c)**	−2.2	86.4, 99.3	97.3	194.5	

[a] δ in ppm. Spectra recorded in CD_2Cl_2. [b] Two isomers. [c] Quaternary carbon of the cyclopentadienyl rings.

The residue was then dissolved in diethyl ether, and hexane was added to give complex **4b** (0.21 g, 77%) as a yellow solid. Found: C, 29.3; H, 2.2. $C_{16}H_{14}Br_2O_4Ru_2Si$ requires C, 29.1; H, 2.1. ν_{max}/cm^{-1} (CH_2Cl_2): 2052, 2003. ν_{max}/cm^{-1} (KBr): 2045, 2011, 1985 (CO), 1254, 1164, 1056, 891, 836, 674 (Cp_2SiMe_2).

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CO)_4]$ (4c). A solution of I_2 (0.61 g, 2.4 mmol) in dichloromethane (30 mL) was added to a solution of complex **1** (1.20 g, 2.4 mmol) in dichloromethane (60 mL), and the resulting mixture was stirred for 30 min. The solution was then concentrated at reduced pressure, and hexane was added to give complex **4c** (1.79 g, 99%) as a yellow solid. Found: C, 25.5; H, 1.9. $C_{16}H_{14}I_2O_4Ru_2Si$ requires C, 25.5; H, 1.9. ν_{max}/cm^{-1} (CH_2Cl_2): 2048, 1999. ν_{max}/cm^{-1} (KBr): 2043, 2034, 1992, 1980 (CO), 1253, 1170, 1067, 893, 834, 680 (Cp_2SiMe_2).

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CH_3)_2(CO)_4]$ (5). A solution of LiMe in hexane (6.3 mL, 9.4 mmol) was added to a solution of CuI (0.9 g, 4.7 mmol) in THF (30 mL) until the complete dissolution of the precipitate formed initially was achieved. The resulting solution was added to a solution of complex **4c** (1.03 g, 1.36 mmol) in THF (200 mL), and the mixture was stirred for 15 min. After evaporation to dryness at reduced pressure, the residue was extracted with diethyl ether. The solvent was then removed in vacuo to give complex **5** (0.59, 82%) as a brown oil. ν_{max}/cm^{-1} (THF): 2012, 1951. ν_{max}/cm^{-1} (KBr): 2962, 2904, 2819, (CH_3), 2015, 1941 (CO), 1260, 1163, 1060, 891, 829, 674 (Cp_2SiMe_2). (The ^1H NMR spectrum is provided as Supporting Information.)

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CO)_2(PCy_3)_2]$ (6c). A mixture of complex **4c** (0.30 g, 0.4 mmol) and PCy_3 (0.34 g, 1.2 mmol) in THF (60 mL) was irradiated with a UV lamp at −20 °C for 9 h and the solvent removed in vacuo. Chromatography on silica, with hexane−dichloromethane (3:1) as eluent, gave the complex **6c** (0.26 g, 50%) as a yellow solid. Found: C, 47.5; H, 6.5. $C_{50}H_{44}I_2O_2P_2Ru_2Si$ requires C, 47.7; H, 6.4. ν_{max}/cm^{-1} (CH_2Cl_2): 1942. ν_{max}/cm^{-1} (KBr): 2964, 2920, 2851, (CH_2), 1938 (CO), 1262, 1175, 881, 844, 684 (Cp_2SiMe_2). $^{31}P\{^1H\}$ (δ, ppm): 57.0, 57.1.

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CNCH_2Ph)_x(CO)_{4-x}]$, $x = 1$ (7a), 2 (7b), 3 (7c). A mixture of complex **4c** (0.25 g, 0.3 mmol) and benzyl isocyanide (0.10 mL, 0.8 mmol) in THF (60 mL) was irradiated with a UV lamp at −20 °C for 5 h and the solvent removed in vacuo. Chromatography on silica at 0 °C, with hexane−dichloromethane as eluent, gave different yellow bands, from which the complexes **7a**−**c** were isolated after removing the solvents. **7a**: eluent 3:4 hexane−CH_2Cl_2. Yield: 0.01 g, 4%. ν_{max}/cm^{-1} (CH_2Cl_2): 2172 (CN), 2046, 1996, 1984 (sh) (CO). ^1H NMR ($CDCl_3$) (δ, ppm): 7.42 (m, 5H, Ph), 5.61 (m, 2H, C_5H_4), 5.46 (m, 3H, C_5H_4), 5.33 (m, 1H, C_5H_4), 5.27 (m, 2H, C_5H_4), 5.03 (s, 2H, CH_2), 0.56 (s, 3H, CH_3), 0.54 (s, 3H, CH_3). **7b**: eluent 1:2 hexane−CH_2Cl_2. Yield: 0.028 g, 10.3%. ν_{max}/cm^{-1} (CH_2Cl_2): 2171 (CN), 1982 (CO). ^1H NMR ($CDCl_3$) (δ,ppm): 7.46−7.32 (m, 10H, Ph), 5.37 (s, br, 2H, C_5H_4), 5.30 (s, br, 2H, C_5H_4), 5.20 (s, br, 4H, C_5H_4), 5.00 (s, 4H, CH_2), 0.46 (virtual triplet $J_{HH} = 3.0$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2) (δ, ppm): 200.5 (CO), 147.2 (CN), 133.4, 129.4, 128.9, 127.1 (Ph), 96.3, 94.9, 85.5, 84.1 (C_5H_4), 49.0 (CH_2), −0.1 (CH_3). **7c**: eluent 1:4 hexane−CH_2Cl_2. Yield: 0.02 g, 6.5%. ν_{max}/cm^{-1} (CH_2Cl_2) 2160, 2119 (CN), 1980 (CO). ^1H NMR ($CDCl_3$) (δ, ppm): 7.51−7.20 (m, 15H, Ph), 5.30 (m, 6H, C_5H_4), 5.16 (m, 1H, C_5H_4), 5.09 (m, 1H, C_5H_4), 4.96 (m, 6H, CH_2), 0.41 (s, 6H, CH_3). (The ^1H NMR spectra are provided as Supporting Information for complexes **7a**−**c**.)

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CNCH_2Ph)_4]$ (7d). A mixture of complex **4c** (0.25 g, 0.3 mmol) and benzyl isocyanide (0.37 mL, 3 mmol) in THF (60 mL) was irradiated with a UV lamp at 0 °C for 6.5 h and the solvent removed in vacuo. Chromatography on silica at 0 °C, with hexane−CH_2Cl_2 (1:10) as eluent, gave a major band identified as the complex **7d** (0.08 g, 24%). ν_{max}/cm^{-1} (CH_2Cl_2): 2156, 2117 (CN). ^1H NMR ($CDCl_3$) (δ, ppm): 7.51−7.20 (m, 20H, Ph), 5.07 (m, 8H, C_5H_4), 4.93 (m, 8H, CH_2), 0.37 (s, 6H, CH_3). (The ^1H NMR spectrum is provided as Supporting Information.)

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(I)_2(CNCy)_x(CO)_{4-x}]$, $x = 1$ (8a), 2 (8b), 3 (8c), 4 (8d). A mixture of complex **4c** (0.15 g, 0.2 mmol) and cyclohexyl isocyanide (0.05 mL, 0.4 mmol) in THF (50 mL) was irradiated with a UV lamp for 3 h at −20 °C and the solvent removed in vacuo. Chromatography on silica, with hexane−dichloromethane as eluent, permits the separation of five bands from which, after removal of the solvents, complexes **8a**−**d** were isolated as follows. Unreacted starting material was recovered using hexane as eluent. Using as eluent a 10:3 mixture of hexane−CH_2Cl_2, a yellow band was collected, from which complex **8a** was obtained. With a 2:1 hexane−CH_2Cl_2 ratio a yellow band was obtained, from which a yellow solid identified as complex **8b** was isolated. A solvent ratio of 1:5 leads to the separation of a fourth band, from which complex **8c** was isolated, and a final band was collected using dichloromethane as solvent (complex **8d**). **8a**: eluent hexane−CH_2Cl_2 (10:3). ν_{max}/cm^{-1} (CH_2Cl_2): 2168 (CN), 2046, 1996, 1979 (CO). ^1H NMR ($CDCl_3$) (δ, ppm): 5.64 (m, 1H, C_5H_4), 5.61 (m, 1H, C_5H_4), 5.49 (m, 2H, C_5H_4), 5.41 (m, 1H, C_5H_4), 5.29 (m, 1H, C_5H_4), 5.22 (m, 2H, C_5H_4), 3.97 (m, 1H, CH), 1.93−1.65 (m, 6H, CH_2), 1.52−1.30 (m, 4H, CH_2), 0.88 (s, 3H, CH_3), 0.85 (s, 3H, CH_3). **8b**: eluent hexane−CH_2Cl_2 (2:1). ν_{max}/cm^{-1} (CH_2Cl_2): 2167 (CN), 1978 (CO). ^1H NMR ($CDCl_3$) (δ, ppm) 5.37 (s, br, 2H, C_5H_4), 5.29 (s, br, 2H, C_5H_4), 5.21 (m, 4H, C_5H_4), 3.97 (m, 2H, CH), 2.00−1.65 (m, 11H, CH_2), 1.60−1.30 (m, 9H, CH_2), 0.54 (s, 6H, CH_3). **8c**: eluent hexane−CH_2Cl_2 (1:5). ν_{max}/cm^{-1} (CH_2Cl_2): 2153, 2114 (CN), 1976 (CO). ^1H NMR ($CDCl_3$) (δ, ppm): 5.34 (m, 1H, C_5H_4), 5.32 (m, 1H, C_5H_4), 5.23 (m, 2H, C_5H_4), 5.05 (m, 2H, C_5H_4), 4.95 (m, 2H, C_5H_4), 3.94 (m, 3H, CH), 2.0−1.6 (m, 19H, CH_2), 1.6−1.3 (m, 11H, CH_2), 0.54 (s, 3H, CH_3), 0.53 (s, 3H, CH_3). **8d**: eluent CH_2Cl_2. ν_{max}/cm^{-1} (CH_2Cl_2): 2153, 2120 (CN). ^1H NMR ($CDCl_3$) (δ, ppm): 5.20 (m, 4H, C_5H_4), 4.89 (m, 4H, C_5H_4), 4.01 (m, 4H, CH), 2.0−1.6

(m, 20H, CH_2), 1.6−1.3 (m, 20H, CH_2), 0.43 (s, 6H, CH_3). (The ^1H NMR spectra of **8a**−**d** are provided as Supporting Information.)

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(CO)_4(NCMe)_2][BF_4]_2$ (9). A mixture of complex **4c** (0.10 g, 0.14 mmol) and $AgBF_4$ (0.11 g, 0.53 mmol) in acetonitrile (10 mL) was heated under reflux for 6 h. The solution was filtered and concentrated at reduced pressure, and diethyl ether (2 × 10 mL) was then added to give complex **9** (0.042 g, 42%) as a yellow solid. Found: C, 31.6; H, 2.7; N, 3.6. $C_{20}H_{20}B_2F_8N_2O_4Ru_2Si$ requires C, 31.8; H, 2.7; N, 3.7. ν_{max}/cm^{-1} (NCMe): 2081, 2035. ν_{max}/cm^{-1} (KBr): 2300 (CN), 2074, 2045, 1992 (CO), 1260 (Cp_2SiMe_2), 1069 (BF_4), 1031, 891, 836, 677 (Cp_2SiMe_2).

Synthesis of $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}X)(CO)_4][BF_4]$, X = Cl (10a), Br (10b), I (10c). A mixture of complex **4a**−**c** (0.13 mmol) and $AgBF_4$ (0.06 g, 0.26 mmol) in dichloromethane (20 mL) (**10a**) or acetone (20 mL) (**10b**−**c**) was stirred for 30 min. The solution was filtered and concentrated at reduced pressure, and diethyl ether (2 × 10 mL) was then added to give complexes **10a**−**c** as yellow solids. **10a**: yield 35%. ν_{max}/cm^{-1} (CH_2Cl_2): 2075, 2064, 2025. **10b**: yield 63%. Found: C, 28.7; H, 2.1. $C_{16}H_{14}BBrF_4O_4Ru_2Si$ requires C, 28.8; H, 2.1. ν_{max}/cm^{-1} (CH_2Cl_2): 2074, 2064, 2025. ν_{max}/cm^{-1} (KBr): 2046, 1992 (CO), 1258, 1163, 890, 833, 675 (Cp_2SiMe_2), 1063 (BF_4). Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 129.6. **10c**: yield 82%. ν_{max}/cm^{-1} (CH_2Cl_2): 2070, 2059, 2022; ν_{max}/cm^{-1} (KBr) 2046, 1996 (CO), 1264, 1163, 885, 836, 678 (Cp_2SiMe_2), 1059 (BF_4). Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 129.9.

X-ray Diffraction Studies of 4a and 10b. Crystals suitable for X-ray diffraction analyses were obtained by slow diffusion of hexane (**4a**) or diethyl ether (**10b**) into a concentrated solution of the complexes in dichloromethane. Both diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Data were collected with the $\omega-2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. On all reflections, profile analysis[7,8] was performed. Lorentz and polarization corrections were applied, and the data were reduced to F_o^2 values. The structures were solved by DIRDIF-96[9] (Patterson methods and phase expansion). Full-matrix least-squares refinement on F_o^2 using SHELXL97[10] was performed. All hydrogen atoms were geometrically placed. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography* (1974).[11] Geometrical calculations were made with PARST97.[12] The crystallographic plots were made with EUCLID.[13] All calculations were made at the University of Oviedo on the X-Ray group ALPHA-AXP computers.

Crystal data for **4a**: $[C_{16}H_{14}Cl_2O_4Ru_2Si]$; M_r = 571.40; monoclinic; space group $P2_1/n$; a = 7.731(2) Å, b = 24.627(6) Å, c = 10.378(4) Å; β = 90.89(3)°; V = 1975(1) Å^3; ρ_{calcd} = 1.921 g cm^{-3}; $F(000)$ = 1112; μ = 1.877 mm^{-1}; red crystal (0.20 × 0.20 × 0.16 mm); T = 293(2) K; λ(Mo Kα) = 0.710 73 Å; 4051 reflections measured. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 15° and 20°). The final drift correction factors were between 1.00 and 1.02. A semiempirical absorption correction was applied using ψ scans[14] resulting in maximum and minimum correction factors of 1.00 and 0.58, respectively. Isotropic full-matrix least-squares refinement on F_o^2 converged to R = 0.086. At this stage an empirical absorption correction was applied using XABS2.[15] Maximum and minimum transmission factors were 1.00 and 0.52, respectively. The geometrically placed hydrogen atoms were isotropically refined, riding on their parent atoms, with two common thermal parameters; one for the hydrogen atoms bonded to aromatic rings, and the other for the hydrogen atoms bonded to the methyl groups. The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 1.44P]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. Final R_1 = 0.0398 and $R_w(F^2)$ = 0.1030 (both for $I > 2\sigma(I)$). The maximum shift to esd ratio in the last full-matrix least-squares cycle was 0.005. The final difference Fourier map showed no peaks higher than 1.04 e Å^{-3} (near the Ru atoms), nor deeper than −0.75 e Å^{-3}.

Crystal data for **10b**: $[C_{33}H_{30}B_2Br_2Cl_2F_8O_8Ru_4Si_2]$; M_r = 1419.37; orthorhombic; space group $Pbca$; a = 15.7155(10) Å, b = 32.155(8) Å, c = 18.6302(18) Å; V = 9415(3) Å^3; ρ_{calcd} = 2.003 g cm^{-3}; $F(000)$ = 5456; μ = 3.197 mm^{-1}; red crystal (0.26 × 0.20 × 0.13 mm); T = 293 K; λ(Mo Kα) = 0.710 73 Å; 8818 reflections measured. Two different molecules have been found in the asymmetric unit as well as a dichloromethane solvent molecule of crystallization. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 15° and 17°). The final drift correction factors were between 0.98 and 1.03. The geometrically placed hydrogen atoms were isotropically refined, riding on their parent atoms, with three common thermal parameters: the first one for the hydrogen atoms bonded to aromatic rings, the second one for the hydrogen atoms bonded to the methyl groups, and the third one for those belonging to the CH_2Cl_2 solvent molecule. The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 28.27P]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. Final R_1 = 0.0473 and $R_w(F^2)$ = 0.1095 (both for $I > 2\sigma(I)$). The maximum shift to esd ratio in the last full-matrix least-squares cycle was 0.013. The final difference Fourier map showed no peaks higher than 1.86 e Å^{-3} (near the Ru atoms), nor deeper than −0.85 e Å^{-3}.

Results and Discussion

Reactivity of Complex $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CO)_2(CO)_2]$ (1). The starting material is the complex $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}CO)_2(CO)_2]$ (**1**) which has been synthesized (83% yield) by heating under reflux a solution of $[Ru_3(CO)_{12}]$ and $Me_2Si(C_5H_5)_2$ in methyl isobutyl ketone. This complex, which has been previously prepared in much lower yield (8%),[4d] proves to be a good precursor for the synthesis of a variety of dinuclear derivatives (Scheme 1).

Treatment of a solution of **1** in dichloromethane with a stoichiometric amount of $HBF_4{\cdot}OEt_2$ proceeds rapidly with electrophilic addition of one proton to yield the hydride complex **2** (63% yield). No evidence has been found for C−Si bond cleavage. Complex **1** also undergoes nucleophilic addition of hydride to give the bridging methylene complex **3** which is formed (22% yield after workup and chromatography) by the treatment of a solution of **1** in toluene with an excess of $Li[BHEt_3]$. Formation of **3** probably proceeds through the initial nucleophilic attack of the hydride to one of the carbonyl

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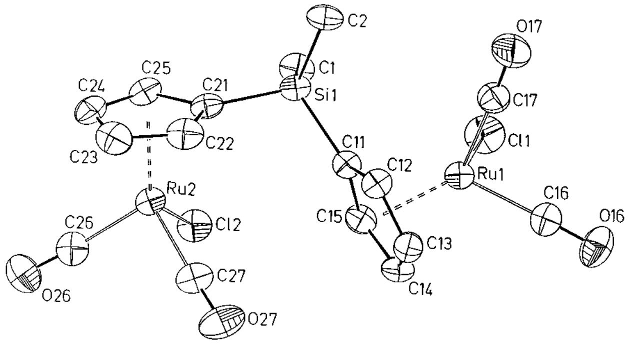

Figure 1. ORTEP drawing of complex **4a** with the atom-numbering scheme.

groups as it has been reported for the formation of the analogous $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2CH_2\}(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2]$.[4c]

^1H and $^{13}C\{^1H\}$ NMR data of **2** and **3** (Tables 1 and 2) are consistent with the presence of the hydride and methylene bridging groups. In particular the ^1H NMR spectrum of **2** shows a high-field singlet at $\delta = -18.71$ ppm due to the bridging hydride, while the resonances of the methylene group in complex **3** appear as two doublets at $\delta = 7.00$ and 8.94 ppm ($^2J_{HH} = 1.5$ Hz). The proton resonances of the cyclopentadienyl rings appear as two sets of multiplets for complex **2** and four sets of multiplets for complex **3** (Table 1) consistent with the presence of the unsymmetrical double bridging system μ-CH_2, μ-CO.

Attempts to study the reactivity of complex **2** in insertion reactions of alkynes such as $MeO_2CC{\equiv}CCO_2Me$ and $PhC{\equiv}CPh$ were unsuccessful, leading instead to decomposition products or to the parent complex **1**, respectively. In fact, complex **2** is transformed reversibly to complex **1** by stirring a solution of the former in acetone at room temperature or at the temperature of refluxing toluene.

It is well-known that the dimeric $[M(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)(CO)]_2$ (M = Fe, Ru, Os) carbonyl derivatives readily undergo oxidative additions of halogens to give metal(II) halide carbonyl complexes. Similarly, complex **1** is readily oxidized to give ruthenium(II) halide derivatives. An equimolecular mixture of **1** and *N*-chlorosuccinimide or X_2 (X = Br, I) in CH_2Cl_2 reacts at room temperature to give complexes **4a**−**c** (Scheme 1) (75−99% yield) isolated as yellow air-stable solids. IR spectra (CH_2Cl_2 solutions) show the expected two ν(CO) strong absorptions in the range 2052−2048 and 2005−1999 cm^{-1} due to the formally cis dicarbonyl arrangement in a pseudo-octahedral geometry. ^1H NMR and $^{13}C\{^1H\}$ NMR show resonances (Tables 1 and 2) in agreement with the presence of the bridging $Me_2Si(\eta^5\text{-}C_5H_4)_2$ group. In particular the proton spectra at room temperature show two sets of pseudotriplets at $\delta = 5.44-5.65$ ppm ($^3J_{HH} = 1.9$ Hz) for the protons of each cyclopentadienyl ring, consistent with an AA′BB′ spin system. This pattern remains unchanged at low temperature (213 K). Since the spectroscopic data does not provide information on the relative orientation of both metal moieties, a single X-ray crystal structural determination of **4a** was carried out.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(Cl)_2(CO)_4]$ (4a)[a]

Distances			
Ru(1)−C(16)	1.904(8)	Ru(2)−C(26)	1.881(9)
Ru(1)−C(17)	1.879(8)	Ru(2)−C(27)	1.891(7)
Ru(1)−Cl(1)	2.406(2)	Ru(2)−Cl(2)	2.402(2)
C(16)−O(16)	1.122(8)	C(26)−O(26)	1.141(9)
C(17)−O(17)	1.137(8)	C(27)−O(27)	1.117(8)
C(11)−Si	1.876(6)	C(21)−Si	1.868(7)
Ru(1)−C^{*1}	1.860(6)	Ru(2)−C^{*2}	1.863(7)
Angles			
C(17)−Ru(1)−C(16)	92.4(3)	Cl(1)−Ru(1)−C^{*1}	123.6(2)
C(17)−Ru(1)−Cl(1)	91.6(2)	C(16)−Ru(1)−C^{*1}	124.7(3)
C(16)−Ru(1)−Cl(1)	88.7(2)	C(17)−Ru(1)−C^{*1}	125.4(3)
C(26)−Ru(2)−C(27)	93.2(3)	Cl(2)−Ru(2)−C^{*2}	123.6(2)
C(26)−Ru(2)−Cl(2)	89.0(2)	C(26)−Ru(2)−C^{*2}	122.8(3)
C(27)−Ru(2)−Cl(2)	89.7(2)	C(27)−Ru(2)−C^{*2}	127.8(3)
C(21)−Si−C(11)	106.7(3)		

[a] C^{*1} = centroid of C(11), C(12), C(13), C(14), C(15). C^{*2} = centroid of C(21), C(22), C(23), C(24), C(25).

A view of the molecular structure is shown in Figure 1. Selected bond distances and angles are listed in Table 3. The crystal structure shows a three-legged piano-stool geometry around each of the two ruthenium atoms, which are linked by the bridging $Me_2Si(\eta^5\text{-}C_5H_4)_2$ group. The ruthenium atoms are also bonded to two carbonyl groups and one chloride group, showing typical Ru−C (1.879(8)−1.904(8) Å) and Ru−Cl (2.402(2)−2.406(2) Å) bonding distances. The most remarkable feature of the molecular structure is the trans arrrangement of the metal fragments leading to a long ruthenium−ruthenium distance of 6.120(6) Å. The cyclopentadienyl rings of the bridging ligand are rotated in opposite directions around the Si−C(bridgehead) bond. This rotation can be evaluated by the torsion angles Ru(1)C*(1)SiC*(2) θ_1 and Ru(2)C*(2)SiC*(1) θ_2 (C* is the centroid of the cyclopentadienyl ring), which are used[2a] to rationalize the arrangement of the metal centers in the structures of bimetallic $Me_2Si(\eta^5\text{-}C_5H_4)_2$ bridged complexes. The values of $\theta_1 = 173.4°$ and $\theta_2 = 42.5°$ in complex **4a** are in accordance with a transoid arrangement for the ruthenium atoms. Such distortion can be also evaluated by comparing the distances from the carbon atoms adjacent to the bridgehead carbon C(12), C(15), C(22), and C(25) (proximal carbons) to the plane defined by Si−C(1)−C(2). These distances would be equal in a symmetric situation but in complex **4a** are as follows: C(12), 2.075(6) Å; C(15), 2.158(6) Å; C(22), 1.806(7) Å; C(25), 2.73(7) Å. The molecular structure of **4a** is similar to that found for the complex $[\{TiCl_2(\eta^5\text{-}C_5Me_5)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)\}]$,[1a] with distances from proximal carbons to the plane Si−C−C being 1.65, 2.74, 2.17, and 1.75 Å, which seems to reflect that the transoid form is the lower energy rotamer in which the metal atoms are located as far as possible.

The structure of complex **4a** is fully consistent with the proton NMR data although a fluxional process involving a rapid rotation around the Me_2Si−C bonds even at 213 K cannot be discarded.

Reactivity of Complexes $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(X)_2(CO)_4]$ (4a−c). Complexes **4a**−**c** have been shown to be good precursors for the preparation of novel dinuclear ruthenium(II) derivatives through carbonyl and halide substitution reactions.

(a) Synthesis of Complex $[Ru_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)\}(CH_3)_2(CO)_4]$ (5). Complex **4c** reacts in THF with lithium dimethylcuprate (prepared in situ) at room temperature to give the methyl complex **5** isolated as a brown oil (yield 82%). IR and ^1H NMR spectroscopic data support this formulation. Thus, the IR spectrum shows ν(CO) absorptions at 2012 and 1951 cm^{-1} and the ^{1}H NMR spectrum shows the methyl group resonance at $\delta = 0.24$ ppm and the signals for the cyclopentadienyl rings as two doublets at $\delta = 4.62$ and 4.77 ($^3J_{HH} = 2.2$ Hz). Attempts to promote the formation of acyl derivatives through migratory CO insertion by refluxing **5** in the presence of excess PMe$_3$ were unsuccessful.

(b) Carbonyl Substituted Complexes [Ru$_2${μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$}(I)$_2$(L)$_x$ (CO)$_{4-x}$], L = PCy$_3$, *x* = 2 (6c); L = CNCH$_2$Ph, *x* = 1 (7a), *x* = 2 (7b), *x* = 3 (7c), *x* = 4 (7d); L = CNCy, *x* = 1 (8a), *x* = 2 (8b), *x* = 3 (8c), *x* = 4 (8d). Photolysis of complex **4c** in the presence of monodentate ligands leads to the substitution of carbonyl groups.

Thus, the irradiation of **4c** with PCy$_3$ in THF (3:1 molar ratio) for 9 h at −20 °C affords the complex [Ru$_2${μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$}(I)$_2$(CO)$_2$(PCy$_3$)$_2$] (**6c**) (50% yield). The IR spectrum (CH$_2$Cl$_2$) shows the expected ν(CO) absorption at 1951 cm^{-1}. However, NMR spectroscopy indicates the formation of two isomers (in ca. 1:1 ratio) (i.e., ^{31}P{^{1}H}: $\delta = 57.0$, 57.1 ppm; for ^{1}H NMR spectrum see Table 1). Although these species could not be separated, they are identified as the complexes containing the phosphines in mutually cis and trans positions.

Similarly, complex **4c** readily undergoes carbonyl substitutions by π-acceptor isocyanide ligands. The reactions, however, are not selective, leading instead to a mixture of different carbonyl−isocyanide derivatives whose nature depends on the ligand:complex ratio. The reactions can be monitored by IR in the ν(CO) region, and the irradiation is discontinued when the ν(CO) absorptions of the starting complex disappear. Thus, the irradiation of **4c** with CNCH$_2$Ph (1:2.5 molar ratio) in THF for 5 h at −20 °C leads to a colored solution, from which the substituted complexes **7a**−**c** are obtained after chromatographic workup (yields 4−10%). Similarly complex **7d** is obtained by using a complex:ligand molar ratio of 1:10 (24% yield). Analogous complexes **8a**−**d** are isolated after chromatography from the irradiation of complex **4c** with CNCy (molar ratio 1:2). All of these complexes were characterized by ^{1}H NMR and IR spectroscopy (See Experimental Section and Supporting Information). IR spectra show the expected ν(CO) and ν(CN) absorptions. (i) Monosubstituted complexes: ν(CN) 2172 (**7a**), 2168 (**8a**) cm^{-1}; ν(CO) 2046, 1996, 1984 (**7a**), 2046, 1996, 1979 (**8a**) cm^{-1}. (ii) Disubstituted complexes: ν(CN) 2171 (**7b**), 2167 (**8b**) cm^{-1}; ν(CO) 1982 (**7b**), 1978 (**8b**) cm^{-1}. (iii) Trisubstituted complexes: ν(CN) 2160, 2119 (**7c**), 2153, 2114 (**8c**) cm^{-1}; ν(CO) 1980 (**7c**), 1976 (**8c**) cm^{-1}. (iv) Tetrasubstituted complexes: ν(CN) 2156, 2117 (**7d**), 2153, 2120 (**8d**) cm^{-1}.

(c) Cationic Complexes [Ru$_2${μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$}(CO)$_4$(NCMe)$_2$][BF$_4$]$_2$ (9) and [Ru$_2${μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$}(μ-X)(CO)$_4$][BF$_4$] (X = Cl (10a); X = Br (10b); X = I (10c)). Cationic complexes were readily accessible through halide abstraction when a large excess of AgBF$_4$ was added to solutions of complexes **4a**−**c**.

Thus, when acetonitrile was used as the solvent, the dicationic complex **9** was isolated as the tetrafluoroborate salt from the reaction mixture, after the evaporation of the solvent (42% yield). In contrast, the reactions in acetone or dichloromethane lead to the double-bridged dinuclear complexes [Ru$_2${μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$}(μ-X)(CO)$_4$][BF$_4$] (X = Cl (**10a**); X = Br (**10b**); X = I (**10c**)) isolated as air-stable solids (35−82% yield). It is worth mentioning that the formation of complexes **10a**−**c** occurs even in the presence of a large excess of AgBF$_4$, the second halide anion being inert toward the silver salt. Elemental analyses, conductivity measurements, and IR and NMR spectroscopy support the proposed formulations. Thus, ^{1}H NMR spectra show only two triplets for the cyclopentadienyl protons (AA′BB′ spin system) and a singlet for the methyl group of the ligand, as expected for a symmetrical arrangement (See Tables 1 and 2).

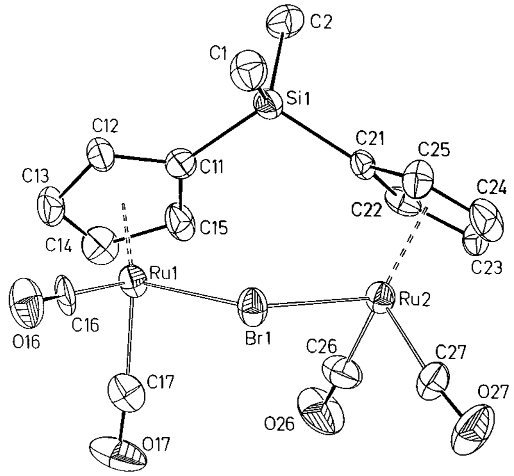

Figure 2. ORTEP view of the structure of the cationic complex **10b** with the atom-numbering scheme.

The structure of complex **10b** has been confirmed by X-ray diffraction. A view of the cation is shown in Figure 2, and the main bonding distances and angles are listed in Table 4. Two different molecules have been found in the asymmetric unit as well as a dichloromethane solvent molecule of crystallization. The crystal structure, as for complex **4a**, shows the typical three-legged piano-stool coordination around each of the ruthenium atoms in a pseudooctahedral structure. Besides the presence of the bridging Me$_2$Si(η^5-C$_5$H$_4$)$_2$ group bonded in a η^5 fashion, the coordination around each ruthenium atom is completed by two carbonyl groups and the bromide anion acting as a bridging ligand between the metal atoms. Typical Ru−CO (1.84(1)−1.92(2) Å), Ru−C* (1.85(1)−1.87(1) Å), and Ru−Br (2.529(1)−2.554(1)) bond lengths and angles (Ru2−Br1−Ru1 = 108.21(5)°) are observed. The structure also shows that the C$_5$H$_4$ rings of the ligand Me$_2$Si(η^5-C$_5$H$_4$)$_2$ are not eclipsed, leading instead to a staggered conformation of the two three-legged piano-stool ruthenium moieties. The angles θ_1 and θ_2 which are smaller than the corresponding ones of the complex **4a** show a different sign ($\theta_1 = 56.6(6)$, $\theta_2 = -33.5(6)$), indicating a cisoid arrangement leading to a Ru−Ru distance of 4.114(1) Å, much smaller than that in the complex **4a**. The distances of the ring carbon atoms C22, C25 and C15, C12 (proximal carbons) to the SiC(1)C(2) plane also confirm the staggered conformation (cf. C(22), 2.01(1) Å; C(25), 2.67(1) Å; C(12), 2.75(1) Å; C(15), 1.71(1) Å) and agree with the published data for analogous endo-cis complexes.[1b−f, 2c−f, 4a−d]

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(\mu$-$Br)(CO)_4][BF_4]$ (10b)[a]

	molecule 1	molecule 2
Distances		
Ru(1)−C(16)	1.89(1)	1.91(1)
Ru(1)−C(17)	1.92(2)	1.84(1)
Ru(1)−Br(1)	2.549(1)	2.538(1)
C(16)−O(16)	1.13(1)	1.11(1)
C(17)−O(17)	1.10(1)	1.15(1)
C(11)−Si(1)	1.88(1)	1.88(1)
Ru(1)−C*^{1}	1.86(1)	1.86(1)
Ru(2)−C(26)	1.88(1)	1.91(1)
Ru(2)−C(27)	1.89(1)	1.87(1)
Ru(2)−Br(1)	2.529(1)	2.554(1)
C(26)−O(26)	1.13(1)	1.12(1)
C(27)−O(27)	1.16(1)	1.13(1)
C(21)−Si(1)	1.86(1)	1.87(1)
Ru(2)−C*^{2}	1.85(1)	1.87(1)
Angles		
C(16)−Ru(1)−C(17)	91.2(6)	90.7(6)
C(16)−Ru(1)−Br(1)	87.9(4)	92.3(4)
C(17)−Ru(1)−Br(1)	91.4(4)	92.2(4)
C(26)−Ru(2)−C(27)	90.7(6)	91.8(5)
C(26)−Ru(2)−Br(1)	91.6(4)	90.7(4)
C(27)−Ru(2)−Br(1)	93.1(4)	91.2(4)
C(21)−Si(1)−C(11)	111.2(5)	111.0(5)
Br(1)−Ru(1)−C*^{1}	126.5(4)	122.6(3)
C(16)−Ru(1)−C*^{1}	123.8(6)	124.9(5)
C(17)−Ru(1)−C*^{1}	125.1(6)	124.7(6)
Br(1)−Ru(2)−C*^{2}	122.4(4)	125.1(4)
C(26)−Ru(2)−C*^{2}	126.7(5)	123.9(6)
C(27)−Ru(2)−C*^{2}	122.9(6)	124.1(6)
Ru(2)−Br(1)−Ru(1)	108.21(5)	108.16(5)

[a] C*^{1} = centroid of C(11), C(12), C(13), C(14), C(15). C*^{2} = centroid of C(21), C(22), C(23), C(24), C(25).

Conclusions

In summary, $Me_2Si(\eta^5$-$C_5H_4)_2$-bridged ruthenium(II) halide complexes $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(X)_2(CO)_4]$ (X = Cl (**4a**), Br (**4b**), and I (**4c**)) are suitable precursors for the synthesis of new dinuclear ruthenium(II) derivatives. Thus, carbonyl substitutions by the two-electron ligands PCy_3 and CNR take place in **4c** under UV irradiation to give neutral derivatives $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2$-$SiMe_2\}(I)_2(CO)_2(PCy_3)_2]$ (**6c**) and $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2$-$SiMe_2\}(I)_2(CNR)_x(CO)_{4-x}]$ (R = CH_2Ph, $x = 1$(**7a**), $x = 2$(**7b**), $x = 3$ (**7c**), $x = 4$ (**7d**); R = Cy, $x = 1$ (**8a**), $x = 2$ (**8b**), $x = 3$ (**8c**), $x = 4$ (**8d**)), the number of substituted carbonyl groups being dependent on the molar ratio ligand:complex **4c**. The halide complexes **4** have been also used for the synthesis of novel cationic dinuclear derivatives of the type $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(CO)_4$-$(NCMe)_2][BF_4]_2$ (**9**) and $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(\mu$-X)-$(CO)_4][BF_4]$ (**10a**−**c**) in which the ruthenium atoms are linked both by the bridging $Me_2Si(\eta^5$-$C_5H_4)_2$ group and by one halide group. The cationic complexes are readily formed from acetonitrile or dichloromethane solutions, respectively, after treatment with $AgBF_4$ as the halide abstractor. It is interesting to note that we have found no evidence of the breaking of the C−Si bond even when photochemical conditions are used. In contrast, the photolysis of the complex $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(\mu$-$CO)_2(CO)_2]$ (**1**) for 2 h leads[4e] to the cleavage of one of the C−Si bonds in the bridging ligand. The resulting fragments, namely, $Me_2SiC_5H_4$ and C_5H_4, are stabilized through the coordination to the ruthenium atoms acting as bridging systems to form the complex $[\{Ru(CO)_2\}_2$-$(\mu$-η^5: $\eta^1\kappa$-(Si)-$C_5H_4SiMe_2)(\mu$-η^5: η^1-$C_5H_4)]$.

The structures of complexes $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}$-$(Cl)_2(CO)_4]$ (**4a**) and $[Ru_2\{\mu$-$(\eta^5$-$C_5H_4)_2SiMe_2\}(\mu$-$Br)(CO)_4]$-$[BF_4]$ (**10b**) which have been determined by X-ray diffraction provide evidence, like other $Me_2Si(\eta^5$-$C_5H_4)_2$-bridged dinuclear complexes,[1a,c] of the tendency to locate the ruthenium atoms mutually apart (transoid arrangement) (**4a**). It is apparent that only when a second bridging halide group is present are the ruthenium atoms located at a closer proximity (cisoid arrangement) (**10b**). Further studies involving the reactivity of these systems with unsaturated organic molecules are in progress.

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Supporting Information Available: Text and tables giving details of the X-ray diffraction studies of **4a** and **10b** and ^1H NMR spectra for complexes **5**, **7a**−**d**, and **8a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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