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Incorporation of Siloxy-Substituted Diene and Dienyl Ligands into Ru(C_5Me_5) Complexes

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Reactions of $[Ru(C_5Me_5)Cl]_4$ with siloxy-substituted 1,3- or 1,4-dienes were found to lead to incorporation of the organic fragment as either a diene or dienyl ligand. From the reaction involving 3-($R_2R'SiO$)-1,4-C_5H_7 ($R = R' = CH_3$; $R = CH_3$, $R' =$ *t*-C_4H_9), a simple diene complex was isolated, Ru(C_5Me_5)[η^4-3-($R_2R'SiO$)-1,4-C_5H_7]Cl, for which spectroscopic and diffraction studies reveal an unsymmetric coordination mode for the diene ligand. Treatment of this complex with $AgPF_6$ led to an isomerization to a 1,3-diene complex. On the other hand, the use of 2,4-disiloxy-substituted 1,3-dienes was found to lead to loss of HCl, yielding η^5-dienyl complexes, e.g., Ru(C_5Me_5)[2,4-$(R_2R'SiO)_2C_5H_5$] ($R = R' = CH_3$; $R = CH_3$, $R' =$ *t*-C_4H_9). The analogous Ru(C_5Me_5)[3-$(CH_3)_2$(*t*-C_4H_9)$SiOC_5H_6$] complex could be prepared from $[Ru(C_5Me_5)Cl]_4$ and the 3-$(CH_3)_2$(*t*-C_4H_9)$SiOC_5H_6$ anion, and its structure was confirmed by X-ray diffraction. For Ru(C_5Me_5)[3-$(CH_3)_3SiOC_5H_7$]Cl, the space group is *Pbca* with $a = 15.375(3)$ Å, $b = 24.070(4)$ Å, $c = 11.010(2)$ Å, and $V = 4074.6$ Å^3 for $Z = 8$. For Ru(C_5Me_5)[3-$(CH_3)_2$(*t*-C_4H_9)$SiOC_5H_6$], the space group is $P\bar{1}$ with $a = 7.638(4)$ Å, $b = 10.468(5)$ Å, $c = 15.132(7)$ Å, $\alpha = 101.06(4)°$, $\beta = 95.33(4)°$, $\gamma = 101.40(4)°$, and $V = 1153.3$ Å^3 for $Z = 2$.

While a great number of metal pentadienyl compounds have been reported,[3] it is fairly rare for any substituents to be present, other than relatively simple alkyl or aryl groups. Since some reactions of metal pentadienyl compounds seem to offer potential for organic synthesis,[4] it would be desirable to be able to incorporate more versatile substituents into pentadienyl ligands. In particular, it is well-known that silyl and siloxy substituents are quite useful for organic transformations,[5] and we have therefore begun to utilize silyl- and siloxy-containing pentadienyl ligands. In fact, several silyl-containing species have already been reported, such as M[1,5-$(Me_3Si)_2C_5H_5$]$_2$ (M = Ti, Zr),[6] M(C_5H_5)[1,5-$(Me_3Si)_2C_5H_5$] (M = V, Cr),[7] and KMn[3-CH_3-1,5-$(Me_3Si)_2C_5H_4$]$_3$[8] species, as well as some ligand adducts of the middle species, and [Fe(1-Me-4-(Et_3Si)-C_5H_5)$(CO)_3{}^+$].[9] However, siloxy-substituted pentadienyl anions are not as stable as their silyl analogs.[10] We have therefore directed our first synthetic efforts for siloxy pentadienyl complexes at the Ru(C_5Me_5) fragment, which has been shown capable of binding to a wide variety of pentadienyl ligands, including ones with CF_3 substituents.[11] Herein we report on the resulting siloxy-substituted diene and dienyl compounds.

Experimental Section

All hydrocarbon, aromatic, and ethereal solvents were thoroughly dried and deoxygenated by distillation under nitrogen from Na/K benzophenone ketyl immediately before use. Deuterated benzene was degassed over potassium and stored in a glass bulb under nitrogen, while $CDCl_3$ was dried over P_2O_5. Infrared mulls were prepared in a glovebox with dry, degassed Nujol, and representative peaks are given for unobscured regions only. All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen using Schlenk apparatus or in a glovebox. Solvents and solutions were added by glass syringes with stainless steel needles or by a pressure-equalizing addition funnel. Spectroscopic studies were carried out as previously described.[12] Analytical data were obtained by Beller Laboratories and Atlantic Microlab Inc. $[Ru(C_5Me_5)Cl]_4$[13] and the various siloxypentadienes and their dienyl anions[10,14] were prepared by literature procedures.

(Pentamethylcyclopentadienyl)[2,4-bis(*tert*-butyldimethylsiloxy)pentadienyl]ruthenium(II), Ru(C_5Me_5){η^5-2,4-[(*t*-Bu)$(CH_3)_2SiO]_2C_5H_5$}. To a red-brown solution of 0.16 g of $[Cp^*RuCl]_4$ (0.58 mmol of Ru) in 25 mL of THF at −78 °C

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was added 0.21 g (0.64 mmol) of 2,4-bis(*tert*-butyldimethylsiloxy)-1,3-pentadiene. The mixture was warmed slowly to room temperature, and the original dark red-brown solution turned clear yellow. After 3 h of stirring, the solvent was removed in vacuo. The green-yellow solid left was extracted with 2 × 25 mL of pentane. The green-yellow extracts were filtered through a pad of Celite and concentrated to ca. 10 mL. The yellow filtrate was cooled to −20 °C, yielding air-stable yellow crystals (0.16−0.24 g, 50−76% yield; mp 78−78.5 °C). The compound can also be sublimed at ca. 65 °C under vacuum. ^{1}H NMR (benzene-d_6, ambient): δ 5.17 (s, H-3), 2.38 (d, $\mathrm{H_x}$-1,5, *J* = 4.1 Hz), 1.84 (s, 15H, $\mathrm{C}_5\mathit{Me}_5$), 1.00 (s, 18H, *t*-Bu), 0.25 (s, 6H, $\mathrm{Si(CH_3)}$), 0.21 (s, 6H, $\mathrm{Si(CH_3)}$), −0.01 (d, $\mathrm{H_n}$-1,5, *J* = 4.1 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 119.7 (s, C), 90.3 (s, $\mathit{C}_5\mathrm{Me}_5$), 81.8 (d, C-3, *J* = 163 Hz), 39.0 (t, C-1,5, *J* = 161 Hz), 26.1 (q, *t*-Bu, *J* = 125 Hz), 18.5 (s, *t*-Bu), 10.7 (q, $\mathrm{C}_5\mathit{Me}_5$, *J* = 126 Hz), −3.6 (q, $\mathrm{Si(CH_3)}$, *J* = 119 Hz), −4.6 (q, $\mathrm{Si(CH_3)}$, *J* = 119 Hz). IR (Nujol mull): 3045 (w), 1456 (s), 1363 (w), 1327 (m), 1265 (s), 1149 (s), 1022 (ms), 970 (s, br), 912 (s), 839 (s), 814 (w), 801 (ms) cm^{-1}. Mass spectrum (EI, 17 eV) [*m/z* (relative intensity)]: 567 (19), 566 (55), 565 (39), 564 (100), 563 (62), 562 (58), 561 (44), 560 (18), 311 (17). Anal. Calc for $\mathrm{C_{27}H_{50}Si_2O_2Ru}$: C, 57.50; H, 8.93. Found: C, 56.64; H, 8.89.

From a similar reaction utilizing 2,4-bis(trimethylsiloxy)-1,3-pentadiene, a similar sublimable yellow product could also be isolated. The characteristic ^{1}H and ^{13}C NMR resonances for the expected product $\mathrm{Ru(C_5Me_5)\{\eta^5\text{-}2,4\text{-}[(CH_3)_3SiO]_2C_5H_5\}}$ were observed, but the compound could not be completely separated from impurities. ^{1}H NMR (benzene-d_6, ambient): δ 5.28 (s, 1H, H-3), 2.44 (d, 2H, $\mathrm{H_x}$-1,5, *J* = 4.2 Hz), 1.86 (s, 15H, $\mathrm{C_5Me_5}$), 0.21 (s, 18H, $\mathrm{SiMe_3}$), 0.04 (d, $\mathrm{H_n}$-1,5, *J* = 4.2 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 119.4 (C-2,4), 90.2 ($\mathit{C}_5\mathrm{Me}_5$), 81.8 (C-3), 38.7 (C-1,5), 10.5 ($\mathrm{C}_5\mathit{Me}_5$), 0.5 ($\mathrm{Si(CH_3)}$). Mass spectrum (EI, 17 eV) [*m/z* (relative intensity)]: 479 (3), 449 (2), 339 (8), 313 (15), 277 (17), 239 (20), 236 (17), 199 (68), 185 (14), 129 (40), 98 (68).

(Pentamethylcyclopentadienyl)[3-(*tert*-butyldimethylsiloxy)pentadienyl]ruthenium(II), $\mathbf{Ru(C_5Me_5)\{\eta^5\text{-}3\text{-}[(\mathit{t}\text{-}Bu)(CH_3)_2SiO]C_5H_6\}}$. To a stirred solution of 0.29 g (1.4 mmol) of 3-(*tert*-butyldimethylsiloxy)-1,4-pentadiene in 20 mL of THF at −78 °C was slowly added 0.60 mL (1.5 mmol) of a 2.5 M solution of *n*-butyllithium in hexane. The solution was allowed to warm to −20 °C, during which time it turned to orange. To this anion solution was added dropwise a THF solution (20 mL) of 0.38 g of Cp*RuCl (1.4 mmol of Ru). After this, the mixture was allowed to slowly warm to room temperature and stirred for 5 h. The solvent was removed from the dark orange solution. The residue was extracted with 2 × 30 mL of pentane, and the mixture was filtered through alumina, which removed a dark red impurity. The yellow filtrate was concentrated and cooled to −20 °C, yielding yellow air-stable crystals (0.42 g, 70% yield; mp 66−67 °C). The compound can be sublimed at ca. 50 °C under vacuum. ^{1}H NMR (benzene-d_6, ambient): δ 4.16 (dd, 2H, H-2,4, *J* = 8.4 Hz), 2.20 (dd, 2H, $\mathrm{H_x}$-1,5, *J* = 8.4, 2.1 Hz), 1.78 (s, 15H, $\mathrm{C_5Me_5}$), 0.99 (s, 9H, *t*-Bu), 0.19 (s, 6H, $\mathrm{CH_3}$), 0.15 (dd, 2H, $\mathrm{H_n}$-1,5, *J* = 7.9, 2.1 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 130.7 (s, C-3), 90.5 (s, $\mathit{C}_5\mathrm{Me}_5$), 77.1 (d, C-2,4, *J* = 164 Hz), 38.8 (t, C-1,5, *J* = 150 Hz), 25.8 (q, *t*-Bu, *J* = 125 Hz), 18.3 (s, *t*-Bu), 10.4 (q, $\mathrm{C}_5\mathit{Me}_5$, *J* = 127 Hz), −4.5 (q, $\mathrm{Si(Me)_2}$, *J* = 119 Hz). IR (Nujol mull): 3041 (m), 1485 (m), 1469 (w), 1450 (s), 1379 (ms), 1259 (s), 1198 (s), 1180 (w), 1097 (s, br), 1030 (s), 891 (s), 839 (w), 806 (s), 682 (ms) cm^{-1}. Mass spectrum (EI, 17 eV) [*m/z* (relative intensity)]: 434 (73), 433 (42), 432 (61), 431 (41), 312 (30), 304 (40), 302 (34), 301 (26), 197 (41), 147 (68), 75 (35), 73 (100). Anal. Calc for $\mathrm{C_{21}H_{36}SiORu}$: C, 58.16; H, 8.37. Found: C, 58.01; H, 8.32.

(Pentamethylcyclopentadienyl)[η^4-3-(*tert*-butyldimethylsiloxy)-1,4-pentadiene]ruthenium(II) Chloride, $\mathbf{Ru(C_5Me_5)\{3\text{-}[(\mathit{t}\text{-}Bu)(CH_3)_2SiO]C_5H_7\}Cl}$. To a red-brown solution of 0.22 g of Cp*RuCl (0.81 mmol of Ru) in 25 mL of THF was added 0.17 g (0.89 mmol) of 3-(*tert*-butyldimethylsiloxy)-1,4-pentadiene. The solution immediately turned clear brown-yellow. After 4 h of stirring, the solvent was removed in vacuo. The orange-yellow solid was extracted with 2 × 25 mL of pentane, and the mixture was filtered through Celite and concentrated. The yellow solution was cooled to −20 °C, yielding flaky yellow, moderately air-stable crystals (0.34 g, 90% yield; mp 149−150 °C dec). ^{1}H NMR (benzene-d_6, ambient): δ 3.82 (dd, 1H, *J* = 10.4, 1.9 Hz), 3.67 (dd, 1H, *J* = 6.8, 10.4 Hz), 3.15 (m, 1H), 3.10 (m, 1H), 3.07 (m, 1H), 2.80 (dd, 1H, *J* = 6.8, 1.9 Hz), 1.90 (m, 1H), 1.19 (s, 15H, $\mathrm{C_5Me_5}$), 1.02 (s, 9H, *t*-Bu), 0.23 (s, 3H, $\mathrm{Si(CH_3)}$), 0.20 (s, 3H, $\mathrm{Si(CH_3)}$). ^{13}C NMR (benzene-d_6, ambient): δ 94.5 (s, $\mathit{C}_5\mathrm{Me}_5$), 84.4 (d, C-2,4 or C-3, *J* = 173 Hz), 71.1 (d, C-2,4 or C-3, *J* = 145 Hz), 63.7 (t, C-1,5, *J* = 162 Hz), 52.8 (t, C-1,5, *J* = 156 Hz), 41.0 (d, C-2,4 or C-3, *J* = 161 Hz), 26.2 (q, *t*-Bu, *J* = 125 Hz), 18.5 (s, *t*-Bu), 8.8 (q, $\mathrm{C}_5\mathit{Me}_5$, *J* = 127 Hz), −3.6 (2q, $\mathrm{Si(Me)_2}$, *J* = 118 Hz). IR (Nujol mull): 3050 (w), 3008 (w), 1506 (m), 1400 (m), 1354 (s), 1253 (ms), 1243 (s), 1198 (ms), 1064 (s), 1018 (ms), 998 (w), 965 (w), 935 (w), 917 (ms), 895 (s), 847 (s), 833 (s), 772 (s), 697 (w), 669 (ms) cm^{-1}. Anal. Calc for $\mathrm{C_{21}H_{37}SiORuCl}$: C, 53.65; H, 7.93. Found: C, 53.90; H, 7.95.

(Pentamethylcyclopentadienyl)[η^4-3-(trimethylsiloxy)-1,4-pentadiene]ruthenium(II) Chloride, $\mathbf{Ru(C_5Me_5)[\eta^4\text{-}3\text{-}(CH_3)_3SiOC_5H_7]Cl}$. This compound was made in an analogous manner as above using 3-(trimethylsiloxy)-1,4-pentadiene. Single crystals (mp 124−125 °C dec) could be obtained either by slow cooling of a saturated pentane solution to −20 °C or by slow sublimation at ca. 90 °C under vacuum. ^{1}H NMR (benzene-d_6, ambient): δ 3.86 (dd, 1H, *J* = 10.4, 1.9 Hz), 3.67 (dd, 1H, *J* = 6.8, 10.4 Hz), 3.15 (m, 1H), 3.10 (m, 1H), 3.07 (m, 1H), 2.80 (dd, 1H, *J* = 6.8, 1.9 Hz), 1.88 (m, 1H), 1.19 (s, 15H, $\mathrm{C_5Me_5}$), 0.23 (s, 9H, $\mathrm{Si(CH_3)_3}$). ^{13}C NMR (benzene-d_6, ambient): δ 94.5 (s, $\mathit{C}_5\mathrm{Me}_5$), 84.2 (d, CH, *J* = 167 Hz), 70.8 (d, CH, *J* = 139 Hz), 63.7 (t, $\mathrm{CH_2}$, *J* = 159 Hz), 53.0 (t, $\mathrm{CH_2}$, *J* = 159 Hz), 40.7 (d, CH, *J* = 161 Hz), 8.8 (q, $\mathrm{C}_5\mathit{Me}_5$, *J* = 128 Hz), 1.5 (q, $\mathrm{Si(CH_3)_3}$, *J* = 118 Hz). IR (Nujol mull): 1402 (m), 1342 (m), 1250 (s), 1200 (m), 1061 (s), 1020 (s), 969 (s), 920 (s), 902 (s), 870 (s), 847 (s), 756 (m) cm^{-1}. Mass spectrum (EI, 17 eV) [*m/z* (relative intensity)]: 544 (29), 156 (62), 155 (100), 142 (55), 141 (97), 129 (66), 127 (36), 111 (27), 99 (39), 85 (39). Anal. Calc for $\mathrm{C_{18}H_{31}SiORuCl}$: C, 50.51; H, 7.30. Found: C, 50.65; H, 7.42.

(Pentamethylcyclopentadienyl)[η^4-3-(*tert*-butyldimethylsiloxy)-1,3-pentadiene]ruthenium(II) Chloride, $\mathbf{Ru(C_5Me_5)[\eta^4\text{-}(1,3)\text{-}3\text{-}(\mathit{t}\text{-}Bu)(CH_3)_2SiOC_5H_7]Cl}$. (Pentamethylcyclopentadienyl)[η^4-3-(*tert*-butyldimethylsiloxy)-1,4-pentadiene]ruthenium(II) chloride (0.10 g, 0.21 mmol) was dissolved in 20 mL of methylene chloride. To this bright yellow solution was added 1 equiv (0.053 g) of silver hexafluorophosphate. Precipitation occurred immediately, and the solution turned yellow-brown. After 10 min of stirring, an excess amount of potassium carbonate was added and the mixture was stirred overnight. After removal of the solvent in vacuo, the brown residue was extracted with pentane and the mixture was filtered through Celite. The yellow filtrate was concentrated and cooled to −20 °C, yielding yellow air-stable crystals in nearly quantitative yield (mp 149−150 °C dec). ^{1}H NMR (benzene-d_6, ambient): δ 4.16 (dd, 1H, H-2, *J* = 9.8, 7.6 Hz), 2.84 (dd, 1H, H-1, *J* = 1.6, 7.6 Hz), 2.31 (q, 1H, H-4, *J* = 6.3 Hz), 1.54 (d, 3H, $\mathrm{CH_3}$, *J* = 6.3 Hz), 1.49 (obscd dd, 1H, H-1, *J* = 1.6, 9.8 Hz), 1.44 (s, 15H, $\mathrm{C_5Me_5}$), 0.93 (s, 9H, *t*-Bu), 0.10 (s, 3H, $\mathrm{Si(CH_3)}$), 0.06 (s, 3H, $\mathrm{Si(CH_3)}$). ^{1}H NMR ($\mathrm{CDCl_3}$, ambient): δ 4.37 (dd, 1H, H-2, *J* = 9.9, 7.7 Hz), 2.89 (dd, 1H, H-1, *J* = 1.6, 7.7 Hz), 1.95 (q, 1H, H-4, *J* = 6.6 Hz), 1.59 (s, 15H, $\mathrm{C_5Me_5}$), 1.50 (d, 3H, $\mathrm{CH_3}$, *J* = 6.6 Hz), 1.10 (obscd dd, 1H, H-1, *J* = 1.6, 9.9 Hz), 1.01 (s, 9H, *t*-Bu), 0.28 (s, 3H, $\mathrm{Si(CH_3)}$), 0.25 (s, 3H, $\mathrm{SiCH_3}$)). ^{13}C NMR ($\mathrm{CDCl_3}$, ambient): δ 134.0 (s, C), 94.5 (s, $\mathit{C}_5\mathrm{Me}_5$), 83.5 (d, C-2 or C-4, *J* = 164 Hz), 60.1 (d, C-2 or C-4, *J* = 155 Hz), 48.1 (t, C-1, *J* = 164 Hz), 25.8 (q, *t*-Bu, *J* = 125 Hz), 18.4 (s, *t*-Bu), 12.4 (q, $\mathrm{CH_3}$, *J* = 127 Hz), 9.0 (q, $\mathrm{C}_5\mathit{Me}_5$, *J* = 127 Hz), −4.2 (q, Si(Me), *J* = 119 Hz), −4.6 (q, Si(Me), *J* = 120 Hz). IR (Nujol mull): 1288 (m), 1257 (s), 1217

Table 1. Summary of Crystal Data and Details of Data Collection and Refinement Parameters for $Ru(C_5Me_5)[\eta^4\text{-}3\text{-}(CH_3)_3SiO\text{-}1,4\text{-}C_5H_7]Cl$ and $Ru(C_5Me_5)[3\text{-}(t\text{-}C_4H_9)(CH_3)_2SiOC_5H_6]$

	(a) Crystal Parameters	
formula	$C_{18}H_{31}ClORuSi$	$C_{21}H_{36}ORuSi$
fw	428.0	433.7
cryst system	orthorhombic	triclinic
space group	*Pbca*	$P\bar{1}$
a, Å	15.375(3)	7.638(4)
b, Å	24.070(4)	10.468(5)
c, Å	11.010(2)	15.132(7)
α, deg		101.06(4)
β, deg		95.33(4)
γ, deg		101.40(4)
V, Å^3	4074.6(13)	1153.3(10)
Z	8	2
cryst dimens, mm	0.22 × 0.24 × 0.43	0.30 × 0.38 × 0.38
cryst color	orange	yellow
D(calc), g cm^3	1.396	1.249
μ(Mo Kα), cm^{-1}	9.59	7.36
temp, K	296	296
T(max)/*T*(min)	1.084	1.191
	(b) Data Collection	
diffractometer	Siemens P4	
monochromator	graphite	
radiation (*λ*, Å)	Mo Kα (0.710 73)	
2*θ* scan range, deg	4−48	4−58
data collected (*h*,*k*,*l*)	+18,+23,+13	±11,±15,+22
rflns collcd	3209	4335
indpt rflns	3209	4248
indpt obsvd rflns $F_o \geq 4\sigma(F_o)$	2008	3264
std rflns	3 std/197 rflns	3 std/197 rflns
var in stds, %	<1	<1
	(c) Refinement	
R(*F*), %	4.16	4.11
$R(_wF)$, %	5.20	5.28
Δ/*σ*(max)	0.018	0.001
Δ(*ϱ*), e Å^{-3}	0.38	0.49
N_o/N_v	10.3	15.0
GOF	1.08	1.15

(s), 1039 (s), 1020 (w), 966 (m), 896 (s), 837 (s), 779 (m), 717 (m) cm^{-1}. Mass spectrum (EI, 17 eV) [*m/z* (relative intensity)]: 546 (20), 545 (19), 544 (23), 543 (23), 542 (18), 541 (16), 470 (17), 469 (15), 272 (18), 198 (42), 142 (63), 141 (97), 75 (100). Anal. Calcd for $C_{21}H_{37}SiORuCl$: C, 53.65; H, 7.93. Found: C, 53.62; H, 8.03.

Crystal Structure Determinations for $Ru(C_5Me_5)[\eta^4\text{-}3\text{-}(CH_3)_3SiOC_5H_7]Cl$ and $Ru(C_5Me_5)[\eta^5\text{-}3\text{-}(CH_3)_2(t\text{-}C_4H_9)\text{-}SiOC_5H_6]$. Crystal, data collection, and refinement parameters are collected in Table 1. Well-formed crystals of each were mounted on fine glass fibers with epoxy cement. The unit cell parameters were determined from the least squares fit of 25 reflections (20° ≤ 2*θ* ≤ 25°). Preliminary photographic characterizations showed *mmm* Laue symmetry for the former complex and $\bar{1}$ Laue symmetry for the latter. The systematic absences in the diffraction data of the first uniquely established the space group as *Pbca*. The *E*-statistics for the other suggested the centrosymmetric alternative, $P\bar{1}$, and the chemically sensible results of refinement indicated that this assignment was correct. A semi-empirical absorption correction was applied to each of the data sets (216 *ψ*-scan reflections; pseudoellipsoid model).

Structure Solution and Refinement. Both structures were solved by direct methods, which located the Ru atoms. The remaining non-hydrogen atoms were located through subsequent difference Fourier and least squares syntheses. All hydrogen atoms were included as idealized isotropic contributions (*d*(CH) = 0.960 Å, *U* is fixed at 0.080 Å^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. A secondary extinction correction was applied to each of the data sets (*χ* = 0.00018(3) and 0.0050(4), respectively).

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)^a
Ru	9930.5(3)	1523.2(2)	3997.6(5)	43.4(2)
C1	8541(1)	1655(1)	2940(2)	76(1)
Si	11563(1)	105(1)	923(2)	59(1)
O	10817(3)	273(2)	1900(5)	89(2)
C(1)	9410(4)	1861(3)	5689(6)	50(2)
C(2)	9702(4)	2323(3)	4951(6)	53(3)
C(3)	10594(5)	2275(3)	4797(7)	61(3)
C(4)	10883(4)	1786(3)	5367(6)	53(3)
C(5)	10153(4)	1543(3)	5952(6)	53(2)
C(6)	8513(4)	1784(4)	6166(8)	92(4)
C(7)	9131(5)	2800(3)	4552(8)	91(4)
C(8)	11162(6)	2705(3)	4217(8)	101(4)
C(9)	11811(5)	1619(4)	5508(9)	99(4)
C(10)	10188(5)	1064(3)	6805(7)	85(4)
C(11)	10641(6)	1775(3)	2331(7)	76(3)
C(12)	10407(6)	1247(3)	2173(7)	72(3)
C(13)	10892(5)	760(3)	2656(7)	70(2)
C(14)	10512(6)	698(3)	3882(8)	79(3)
C(15)	9611(5)	648(3)	4006(8)	71(3)
C(16)	11799(9)	667(4)	−75(9)	180(8)
C(17)	12543(6)	−64(4)	1756(10)	136(5)
C(18)	11158(6)	−513(3)	137(8)	97(4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)^a
Ru(1)	−436.8(5)	−2436.6(3)	6585.9(3)	49.2(1)
Si	2614(2)	1680(1)	8573(1)	64(1)
O(1)	1147(5)	344(3)	7989(3)	67(1)
C(1)	1798(8)	−1846(5)	5859(4)	84(2)
C(2)	1590(7)	−731(5)	6526(3)	64(2)
C(3)	1541(6)	−770(4)	7451(3)	54(2)
C(4)	1445(7)	−1912(5)	7805(4)	64(2)
C(5)	1632(7)	−3154(5)	7293(5)	77(2)
C(6)	−2999(6)	−3402(5)	6943(4)	62(2)
C(7)	−2658(7)	−4227(5)	6159(4)	70(2)
C(8)	−2599(8)	−3520(7)	5482(4)	78(2)
C(9)	−2899(8)	−2226(7)	5820(5)	79(2)
C(10)	−3147(6)	−2160(5)	6767(4)	64(2)
C(11)	−3270(10)	−3840(8)	7829(5)	108(4)
C(12)	−2545(9)	−5646(6)	6017(7)	123(4)
C(13)	−2413(10)	−4040(11)	4490(4)	164(5)
C(14)	−3094(13)	−1176(10)	5307(7)	144(5)
C(15)	−3561(8)	−1003(6)	7404(6)	110(3)
C(16)	3896(13)	1233(9)	9531(6)	137(5)
C(17)	4245(9)	2317(6)	7845(5)	110(3)
C(18)	1215(9)	2871(5)	8969(5)	80(2)
C(19)	120(13)	3121(9)	8152(8)	143(5)
C(20)	−121(11)	2250(8)	9551(6)	138(4)
C(21)	2392(10)	4196(6)	9498(6)	118(3)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Tables 2 and 3 contain positional parameters for the respective compounds, while Tables 4 and 5 contain selected bond distances and angles.

All computer programs and the sources for the scattering factors are contained in the SHELXTL PLUS program library (4.2) (G. Sheldrick; Siemens, Madison, WI).

Synthetic and Spectroscopic Results and Discussion

$[Ru(C_5Me_5)Cl]_4$ reacts readily with 3-siloxy-1,4-pentadienes (siloxy = $(CH_3)_2(t\text{-}C_4H_9)SiO$, $(CH_3)_3SiO$) to form η^4-1,4-diene complexes (eq 1, R = R′ = CH_3; R = CH_3, R′ = $t\text{-}C_4H_9$) which may be isolated as crystalline materi-

$$^1/_4[Ru(C_5Me_5)Cl]_4 + 3\text{-}R_2R'SiOC_5H_7 \rightarrow Ru(C_5Me_5)(\eta^4\text{-}3\text{-}R_2R'SiO\text{-}1,4\text{-}C_5H_7)Cl \quad (1)$$

Table 4. Selected Bond Distances and Angles for $Ru(C_5Me_5)[\eta^4\text{-}3\text{-}(CH_3)_3SiO\text{-}1,4\text{-}C_5H_7]Cl$

	Bond Distances (Å)		
Ru—Cl	2.454(2)	Ru—CNT(1)[a]	1.851(7)
Ru—C(11)	2.220(8)	Ru—C(12)	2.239(8)
Ru—C(14)	2.183(7)	Ru—C(15)	2.163(6)
Si—O	1.624(6)	O—C(13)	1.442(9)
C(11)—C(12)	1.334(11)	C(12)—C(13)	1.486(11)
C(13)—C(14)	1.479(12)	C(14)—C(15)	1.397(12)
	Bond Angles (deg)		
CNT(1)—Ru—Cl	117.8(2)	CNT(1)—Ru—C(11)	115.0(2)
CNT(1)—Ru—C(12)	146.2(2)	CNT(1)—Ru—C(14)	119.1(2)
CNT(1)—Ru—C(15)	126.0(2)	Cl—Ru—C(11)	90.0(2)
Cl—Ru—C(12)	84.1(2)	Cl—Ru—C(14)	116.6(2)
Cl—Ru—C(15)	86.0(2)	C(11)—Ru—C(12)	34.8(3)
C(11)—Ru—C(14)	89.9(3)	C(11)—Ru—C(15)	112.4(3)
C(12)—Ru—C(14)	62.8(3)	C(12)—Ru—C(15)	77.8(3)
C(14)—Ru—C(15)	37.5(3)	C(11)—C(12)—C(13)	124.7(8)
C(12)—C(13)—C(14)	102.0(6)	C(13)—C(14)—C(15)	119.3(8)
O—C(13)—C(12)	113.2(6)	O—C(13)—C(14)	114.3(6)
Si—O—C(13)	121.9(4)	O—Si—C(16)	111.4(4)
O—Si—C(17)	107.9(4)	O—Si—C(18)	106.0(3)

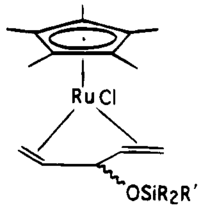
[a] CNT(1) = centroid of atoms C(1), C(2), C(3), C(4), and C(5).

Table 5. Selected Bond Distances and Angles for $Ru(C_5Me_5)[3\text{-}(t\text{-}C_4H_9)(CH_3)_2SiOC_5H_6]$

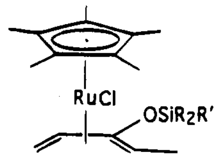
	Bond Distances (Å)		
Ru(1)—CNT(2)[a]	1.834(5)	Ru(1)—C(1)	2.168(6)
Ru(1)—C(2)	2.142(5)	Ru(1)—C(3)	2.181(4)
Ru(1)—C(4)	2.140(5)	Ru(1)—C(5)	2.160(6)
Si—O(1)	1.647(3)	O(1)—C(3)	1.390(6)
C(1)—C(2)	1.434(7)	C(2)—C(3)	1.413(7)
C(3)—C(4)	1.393(7)	C(4)—C(5)	1.420(7)
	Bond Angles (deg)		
CNT(2)—Ru(1)—C(1)	133.5(2)	CNT(2)—Ru(1)—C(2)	139.2(2)
CNT(2)—Ru(1)—C(3)	143.5(2)	CNT(2)—Ru(1)—C(4)	138.4(2)
CNT(2)—Ru(1)—C(5)	132.8(2)	C(1)—Ru(1)—C(2)	38.9(2)
C(1)—Ru(1)—C(3)	70.2(2)	C(1)—Ru(1)—C(4)	88.1(2)
C(1)—Ru(1)—C(5)	79.9(2)	C(2)—Ru(1)—C(3)	38.1(2)
C(2)—Ru(1)—C(4)	71.1(2)	C(2)—Ru(1)—C(5)	88.0(2)
C(3)—Ru(1)—C(4)	37.6(2)	C(3)—Ru(1)—C(5)	69.6(2)
C(4)—Ru(1)—C(5)	38.6(2)	Si—O(1)—C(3)	126.4(3)
O(1)—C(3)—C(2)	115.5(4)	O(1)—C(3)—C(4)	117.8(5)
O(1)—Si—C(16)	109.4(3)	O(1)—Si—C(17)	110.3(2)
O(1)—Si—C(18)	104.2(2)	C(1)—C(2)—C(3)	122.8(5)
C(2)—C(3)—C(4)	125.0(4)	C(3)—C(4)—C(5)	123.3(5)

[a] CNT(2) = centroid of atoms C(6), C(7), C(8), C(9), and C(10).

als. Their identities have been established through analytical and spectroscopic methods. ^1H and ^{13}C NMR spectroscopies reveal that the two olefins in the 1,4-dienes are coordinated to the metal center, leading to the expected 18 electron configuration. However, they are nonequivalent, suggesting that the diene is present in a sickle conformation, as in **I**. This has been con-



I



II

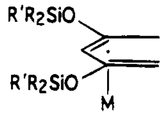
firmed by a single-crystal structural determination (*vide infra*). Treatment of the 1,4-diene complex with Ag^+ brings about an isomerization to the 1,3-diene complex, which has also been characterized analytically and spectroscopically. Presumably this complex involves *cis*-diene coordination, as in **II**, which would seem to involve less steric congestion than *trans*-diene coordination, although precedent does exist in Ru(II) complexes for both coordination modes.[15]

The mechanism for the isomerization likely involves initial abstraction of chloride ion, leading formally to a 16 electron complex. Coordination of one of the central carbon atom's C—H bonds to the metal would then lead to an 18 electron complex, analogous to the structurally characterized species resulting from protonation of $Ru(C_5Me_5)(3\text{-}C_6H_9)$,[16a] except that for the latter cationic complex the protonation transformed a terminal CH_2 group to a CH_3 group, one of whose C—H bonds was then bound to the metal center. Formal oxidative addition of the C—H bond would lead to a metal hydride, which would then transfer the hydrogen atom to a terminal CH_2 group,[12] leading to an "agostic" complex quite analogous to the protonated $3\text{-}C_6H_9$ compound mentioned above.[16b] Reincorporation of chloride ion in the coordination sphere completes the isomerization reaction.[16c]

In contrast to the results indicated by eq 1, the reaction of $[Ru(C_5Me_5)Cl]_4$ with $2,4\text{-}(R_2R'SiO)_2\text{-}1,3\text{-}C_5H_6$ ($R = R' = CH_3$; $R = CH_3$, $R' = t\text{-}C_4H_9$) leads to loss of HCl and formation of η^5-dienyl complexes (eq 2). The

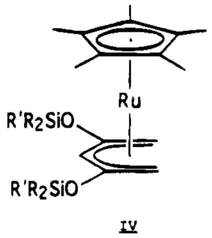
$$\tfrac{1}{4}[Ru(C_5Me_5)Cl]_4 + 2,4\text{-}(R_2R'SiO)_2\text{-}1,3\text{-}C_5H_6 \rightarrow Ru(C_5Me_5)[2,4\text{-}(R_2R'SiO)_2C_5H_5] + HCl \quad (2)$$

difference in reaction paths may readily be traced to the presence of the bulky siloxy substituent which is situated on a terminal diene carbon atom. To avoid steric interactions with the terminal CH_2 group, the siloxy group should assume an exo orientation, as in **III**. This



III

leads to an endo-oriented methyl group and to much more facile proton abstraction. Both the ^1H and ^{13}C NMR spectra of these compounds reveal mirror plane symmetry for the dienyl ligand, as would be expected for the normal η^5-U coordination (**IV**).



IV

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(15) (a) Melendez, E.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 8703. (b) Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268. (c) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Ibid.* **1990**, *9*, 1843. (d) Benyunes, S. A.; Day, J. P.; Green, M.; Al-Saadoon, A. W.; Waring, T. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1416. (e) Ernst, R. D.; Melendez, E.; Stahl, L.; Ziegler, M. L. *Organometallics* **1991**, *10*, 3635.

(16) (a) Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. Unpublished results. (b) Transfer of the hydrogen atom to the CH_2 group of the perpendicularly-orientated olefin would give, at least initially, a *cis*-η^4-diene complex, whereas transfer to the other CH_2 group would give a *trans*-η^4-diene complex. (c) Quite possibly a cationic "agostic" complex would be isolated were a chlorinated solvent not employed.

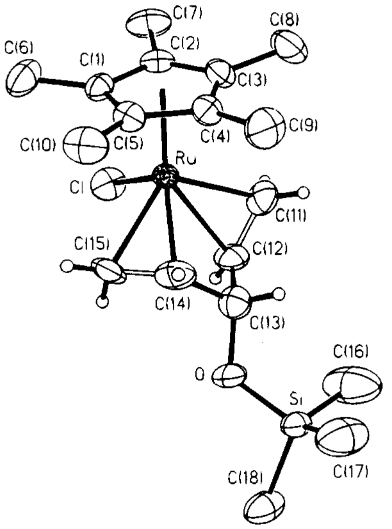
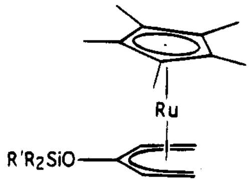


Figure 1. View and numbering scheme for the Ru(C_5Me_5)[η^4-3-$(CH_3)_3SiO$-1,4-C_5H_7]Cl compound. Thermal ellipsoids are drawn at 35% probability; hydrogens are omitted from the methyl groups for clarity.

While the η^4-3-siloxypentadiene complexes above would not undergo deprotonation readily even in the presence of K_2CO_3 in refluxing THF, it has proven possible to prepare a 3-siloxypentadienyl complex by a direct reaction involving the dienyl anion (eq 3). As the

$$^1/_4[Ru(C_5Me_5)Cl]_4 + Li[3\text{-}(CH_3)_2(t\text{-}C_4H_9)SiOC_5H_6] \rightarrow Ru(C_5Me_5)[3\text{-}(CH_3)_2(t\text{-}C_4H_9)SiOC_5H_6] \quad (3)$$

3-siloxypentadienyl anions are thermally sensitive,[14] they had to be generated at low temperatures and allowed enough time to react with the starting metal complex before the reaction mixture approached room temperature. From this procedure, however, the desired complexes could be readily isolated as bright yellow crystalline solids. As in the case of the 2,4-$(R_3SiO)_2C_5H_5$ complexes, the ^1H and ^{13}C NMR spectra reveal the mirror plane symmetry expected for a complex containing an η^5-U-bound open dienyl ligand (**V**).



V

Except for the ^{13}C resonances for the siloxy-substituted carbon atoms, which experience significant downfield shifts, the ^1H and ^{13}C NMR spectral features are quite similar to those of related half-open ruthenocenes. The expected structural pattern has been confirmed by a single-crystal structural determination (*vide infra*).

Structural Results and Discussion

The structure of Ru(C_5Me_5)[η^4-3-$(CH_3)_3SiO$-1,4-C_5H_7]Cl is depicted in Figure 1, while pertinent bonding parameters are provided in Table 4. It can be seen from the figure that the 1,4-diene ligand has adopted a sickle conformation, resulting in one coordinated olefin (C(14), C(15)) being oriented nearly parallel to the Ru—Cl vector, the other (C(11), C(12)) being nearly perpendicular. Such mixed orientations have also been seen in various other nonconjugated diene complexes.[17] For each isolated olefin unit, the end (less substituted) carbon atom lies closer than the internal carbon atom to the metal center by 0.019 and 0.020 Å, respectively. The corresponding Ru—C bond lengths for the perpendicular olefin are ca. 0.05 Å longer than those for the parallel olefin (2.220(8) vs 2.163(6) and 2.239(8) vs 2.183(7) Å), indicating that the parallel-oriented olefin is more strongly bound. As would be expected, the stronger binding to the parallel olefin leads to a longer C—C bond length compared to the perpendicular olefin, 1.397(12) vs 1.334(11) Å. It appears likely that the optimization of the Ru—diene bonding results in some internal strain for the diene, as reflected by the C(12)—C(13)—C(14) angle of 102.0(6)°. Other relatively small C—C—C angles have been observed in η^5-S-pentadienyl complexes.[18]

The bonding of the C_5Me_5 ligand to the ruthenium center is somewhat asymmetric. The average[19] Ru—C(C_5Me_5) bond length is 2.227(3) Å, roughly comparable to the bond lengths for the perpendicular olefin but significantly longer than that for the parallel olefin. Three of the diene carbon atoms (C(11,14,15)) are similarly separated from the plane defined by C(1-5), at 2.86, 2.87, and 3.05 Å, respectively, while C(12) is 3.75 Å away. The proximity of the first three atoms to the C_5Me_5 ligand appears to lead to C(3) and C(5) deviating out of the C_5Me_5 plane in a direction away from the ruthenium center (by 0.017 and 0.015 Å). In addition, C(8) and C(10) deviate from the C_5Me_5 plane by nearly twice the average of C(6,7,9) (0.186 vs 0.110 Å or ca. 7.2 vs 4.2°).[20]

The structure of Ru(C_5Me_5)[3-(t-C_4H_9)$(CH_3)_2SiOC_5H_6$] may be seen in Figure 2, while pertinent bonding parameters are provided in Table 5. At first glance the structural data seem quite similar to those of Ru(C_5Me_5)(3-C_6H_9) (C_6H_9 = methylpentadienyl), as their respective average Ru—C(C_5Me_5) (2.192(3) vs 2.193(1) Å) and Ru—C(Pdl) (2.158(3) vs 2.153(1) Å) bond lengths are identical within experimental error, and in both cases seem to reflect stronger bonding to the open dienyl ligand. Furthermore, the relative Ru—C(1,5), Ru—C(2,4), and Ru—C(3) bond lengths follow similar trends (2.164(4), 2.141(4), and 2.181(4) Å vs 2.164(2), 2.126(2), and 2.187(2) Å). The main difference—lengthening of the Ru—C(2,4) and shortening of the Ru—C(3) bonds in the siloxy ligand complex—is barely noticeable but does point to an unusual and significant facet of the former complex. One can note for the 3-C_6H_9 ligand the fact that the C(2)—C(3)—C(2)′ angle is notably smaller than

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[17] (a) Casey, C. P.; Underiner, T. L.; Vosejpka, P. C.; Gavney, J. A., Jr.; Kiprof, P. *J. Am. Chem. Soc.* **1992**, *114*, 10826. (b) Nickel, T.; Pörschke, K.-R.; Goddard, R.; Krüger, C. *Inorg. Chem.* **1992**, *31*, 4428. (c) Wright, L. L.; Wing, R. M.; Rettig, M. F.; Wiger, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 5949.

[18] (a) Hermann, W. A.; Fischer, R. A.; Herdtweck, E. *Organometallics* **1989**, *8*, 2821. (b) Waldman, T. E.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Hutchinson, J. P.; Ernst, R. D. *Organometallics* **1993**, *12*, 1543.

[19] The standard deviations accompanying average values are derived from the esd's of the individual values and therefore reflect the uncertainty in the average value, but not necessarily the range of the values which were used to obtain the averages.

[20] The sine of the tilt angle is defined as the deviation of the substituent below the ligand plane divided by the distance between the substituent and the ligand carbon atom to which it is attached.

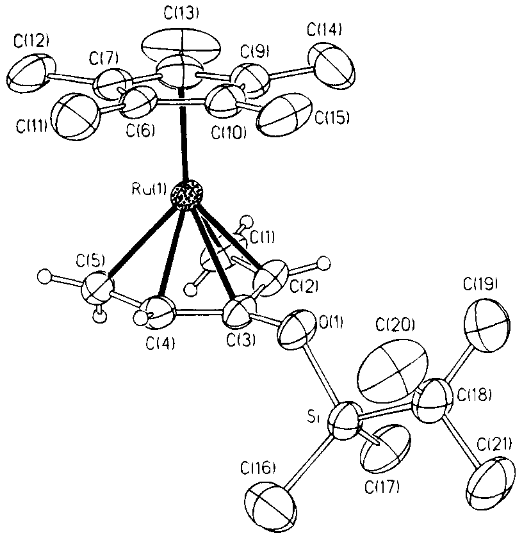
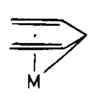


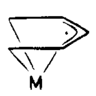
Figure 2. View and numbering scheme for the $Ru(C_5Me_5)[3-(t-C_4H_9)(CH_3)_2SiOC_5H_6]$ compound. Thermal ellipsoids are drawn at 35% probability; hydrogens are omitted from the methyl and *t*-Bu groups for clarity.

the C(1)—C(2)—C(3) angle (119.6(2) vs 125.9(2)°), as a result of the methyl group attached to C(3). Similar contractions have been seen in dozens of other pentadienyl structures.[21] However, for the siloxy complex, exactly the opposite trend is observed, with the respective average angles being 125.0(4) and 123.0(4)°. The increased angle about C(3) tends to separate the C(2) and C(4) atoms, presumably making it more difficult for them to interact simultaneously with the metal center, hence their longer bond distances. At the same time, the wider angle about C(3) causes the ligand center of mass (defined only by the five metal-bound carbon atoms) to slip closer to the C(3) position, which could therefore account for the shorter Ru—C(3) bond length. As to the question of why the siloxy group would cause an expansion, rather than a contraction, of the $C—C(OSiR_3)—C$ angle, it seems possible that the electronegativity of the oxygen atom might be playing a role. One should expect the C—O bond to be localized somewhat on the oxygen atom, thereby reducing the orbital contribution required from the carbon atom. This could make available more s orbital density for the central carbon atom's bonds to its two adjacent carbon atoms, thereby reducing the formal hybridization from sp^2 to sp^n ($n < 2$), leading to the expansion of the angle about C(3).

A second peculiarity relates to the relative pattern of delocalized C—C bond lengths in the open dienyl ligand. Almost invariably when the differences are large enough to be significant statistically, one observes a short–long–long–short pattern, which can readily be attributed to a contribution from hybrid **VI**.[21] In this case, however, it appears that the trend is just the reverse, namely, long–short–short–long (long 1.427(5) Å vs short 1.403(5) Å), which could signify a contribution from **VII**, as was in fact also observed for $Ru(C_5Me_4Et)[2,4(CF_3)_2C_5H_5]$. It is not clear why a siloxy group would have such a strong influence on the bonding,[22] however, so other alternatives might be considered. Possibly the availability of extra s character (*vide supra*) for the σ components of the C(3)—C(2,4) bonds might contribute to the shortening.

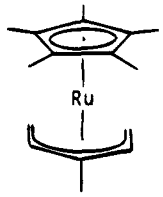


VI

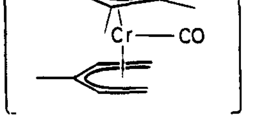


VII

Some additional insight may be obtained from the least-squares planes data. The metal-bound C_5Me_5 atoms (C(6–10)) all lie within 0.003 Å of their best plane. As is normal, their attached methyl groups are bent out of the plane in a direction away from the ruthenium center.[21] For C(11)—C(14), the tilts range 3.1–4.3° (average 3.9°), which compares well with the values for the η^4-diene complex (*vide supra*). However, the tilt for C(15) is noticeably smaller, at 1.6°, despite the fact that C(15) engages in a nearly eclipsing interaction with the siloxy group. In this regard it is important to note that there is no need for the structure to be eclipsed in the first place. In fact, $Ru(C_5Me_5)(3-CH_3C_5H_6)$ has been found to adopt the expected staggered structure, **VIII**. It would appear, then, that the eclipsed conformation for the siloxy complex actually generates a favorable interligand interaction between the C(15) methyl group and O(1) (d(O(1)--C(15)) = 3.55 Å, d(O(1)--H(15b)) = 3.26 Å, d(O(1)--H(15C)) = 3.17 Å). Further evidence for this may be seen from the least-squares plane data for the open dienyl ligand. While C(3) deviates from the C(1)—C(5) plane by 0.04 Å (away from the ruthenium center), O(1) is found on the other side of the plane, deviating by 0.15 Å toward ruthenium, corresponding to a tilt of some 6–8°.[23] This is an unusually large tilt for a pentadienyl substituent attached to the 3 position, particularly considering the presence of the eclipsing interaction with C(15). Again this points to a significant attractive interaction between O(1) and its eclipsing methyl group. A worthwhile comparison may be made to the complex $Cr(C_5Me_5)(3-CH_3C_5H_6)(CO)^+$, on which an eclipsing CH_3--CH_3 interaction is imposed due to the location of the CO ligand between two C_5Me_5 methyl groups, as in **IX**. In that situation, the open dienyl methyl group was found



VIII



IX

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[21] Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*, 1.

[22] (a) By virtue of its π-donating ability,[22b] a siloxy group should tend to destabilize anionic contributions for the pentadienyl fragment, whereas the opposite would be true for CF_3 substituents. (b) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

to tilt 6.1° *away from* the metal atom, while the corresponding C_5Me_5 methyl group was tilted significantly further (rather than less) out of the C_5Me_5 plane, away from the metal center, than the other methyl groups. Hence, it seems clear that in the siloxy structure there is an attractive interaction occurring between the siloxy group's oxygen atom and the eclipsing methyl group. Related interactions may also occur in reported siloxycyclopentadienyl complexes.[24] Given that much greater pentadienyl substituent tilting is typical for the 2 and 4 positions relative to the 3 position, it can be expected that the 2,4-disiloxypentadienyl complexes will show even more dramatic structural characteristics. Unfortunately, to date these species have not proven as amenable to crystallization, but further efforts to obtain structural data are underway.

The nature of the CH_3--O interaction may simply involve a van der Waals attraction, given that the van der Waals radii for a methyl group and an oxygen atom are 2.0 and 1.4 Å, respectively.[25] However, CH--O hydrogen bonds have been established[26] and even claimed for methyl groups.[27] Such interactions have even been proposed to occur for H_3C--heteroatom separations as large as 3.8 Å.[26b] However, the most effective O--HC interactions are observed for nearly linear O--H—C arangements, which is clearly not the case here given the fact that two of the methyl group hydrogen atoms are found in proximity to the oxygen atom (of course, the number of interactions is doubled). Hence a van der Waals description is perhaps warranted at the separations observed here, although an even closer approach would likely have been realized were it not for the strain generated by the tilting of the various substituents from their more preferred locations. Quite likely, then, even more significant interactions will be seen for 2-siloxy- or 2,4-disiloxypentadienyl ligand analogs.

The incorporation of siloxy groups into metal pentadienyl complexes clearly leads to some significant structural effects and may increase the potential for the use of such species in synthetic applications. Additional efforts in these regards are continuing.

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Supplementary Material Available: Tables of complete bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and *U* values (7 pages). Ordering information is given on any current masthead page.

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(23) A tilt of 6.1° results from the usual definition,[20] but if account is made of the deviation of the attached ligand carbon atom (C(3)) from the plane, 0.039 Å, a tilt of 7.8° is obtained.

(24) (a) Weber, L.; Kirchhoff, R.; Boese, R.; Stammler, H.-G. *J. Chem. Soc., Chem. Commun.* **1991**, 1293. (b) See also: Niecke, E.; Schmidt, D. *Ibid.* **1991**, 1659.

(25) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(26) (a) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888. (b) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1994**, 101 and references therein.

(27) Seiler, P.; Weisman, G. R.; Glendening, E. D.; Weinhold, F.; Johnson, V. B.; Dunitz, J. D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1175.