Protonation of Cr(CO)₃ Complexes of Triphenylsilanol and Triphenylcarbinol: Synthetic, X-ray Crystallographic, and NMR Study of (Ph₃SiOH)[Cr(CO)₃]ₙ (n = 1-3) and of (Ph₃COH)Cr(CO)₃

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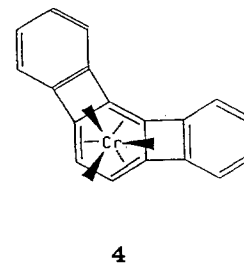Ecole Nationale Supérieure de Chimie de Paris, UA CNRS 403, 11, rue Pierre et Marie Curie,
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The mono-, bis- and tris-Cr(CO)₃ complexes of triphenylsilanol have been prepared and characterized by ¹H and ¹³C NMR spectroscopy and by X-ray crystallography. (Ph₃SiOH)-Cr(CO)₃ (9) crystallizes in the monoclinic space group C2/c with a = 29.061(3) Å, b = 7.136(2) Å, c = 21.331(3) Å, β = 115.85(2)°, and Z = 8. (Ph₃SiOH)[Cr(CO)₃]₂ (10) crystallizes in the triclinic space group P1̄ with a = 7.731(2) Å, b = 12.013(2) Å, c = 13.929(3) Å, α = 102.89(2)°, β = 102.34(2)°, γ = 105.17(2)°, and Z = 2. The tris complex (Ph₃SiOH)[Cr(CO)₃]₃ (11) crystallizes in the rhombohedral space group R3̄ with a = 19.251(2) Å, c = 12.449(2) Å, and Z = 6. The phenyl rings of all three complexes adopt propeller conformations such that the Cr(CO)₃ groups are oriented toward the OH group of the silanol. These molecules exhibit unrestricted rotation of the phenyl rings on the NMR time scale. In contrast, slowed phenyl ring rotation is observed for (Ph₃COH)[Cr(CO)₃] (12), which also adopts a propeller-type conformation and crystallizes in the monoclinic space group C2/c with a = 23.520(7) Å, b = 8.231(2) Å, c = 21.608(6) Å, β = 117.84(0)°, and Z = 8. The conformations of the triphenylsilyl and triphenylmethyl moieties in these systems, and also those for a series of related molecules, are analyzed in terms of the Bürgi-Dunitz trajectory approach. Protonation of the silanol complexes 9-11 does not lead to formation of silicenium ions; however, treatment of the carbinol 12 with triflic acid yields the stable cation [(Ph₃C)Cr(CO)₃]⁺ (13), which was readily characterized by ¹H and ¹³C NMR spectroscopy.

Introduction

The detection of hindered rotation of molecular fragments in sterically crowded molecules has attracted much attention in recent years.[1] In a now-classic series of publications, Mislow et al. have elucidated the mechanistic pathways for many such processes. Typically, these studies have focused on such systems as triarylboranes, triarylamines, or polyarylbenzenes in which the incorporation of bulky substituents in the *ortho* or *meta* positions raises the aryl rotation barriers into the NMR-detectable range.[2] In many of these cases, it has been shown that the motions of these aryl rings are coupled in such a way that no ring moves independently of the others; such processes are termed *correlated rotations*. Moreover, in an elegant extension of this concept, it has been demonstrated that molecules containing a closed cyclic array of securely meshed gears have parity constraints entirely analogous to mechanical systems.[3]

Our own contributions have been aimed not at differentiating the *edges* of aryl rings but rather on "painting the *faces* different colors" via the attachment of π-bonded organometallic moieties. Using this approach, it has been shown that one can measure the rotational barriers for substituents attached to the central ring since they can adopt conformations in which they are *proximal* or *distal* with respect to the metal, as in 1 or 2.[4,5] It is also possible, when the molecular symmetry is judiciously broken, to determine the steric or electronic barriers to tripodal rotation, as in 3 or 4, respectively.[6,7]

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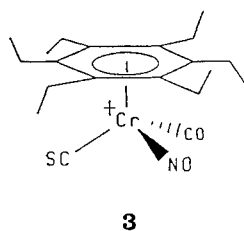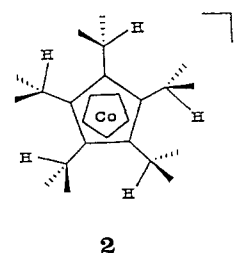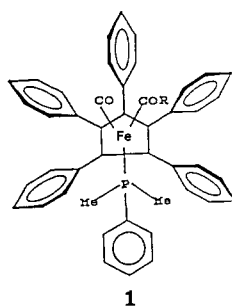
† McMaster University.
‡ Ecole Nationale Supérieure de Chimie de Paris.
(1) Mislow, K. *Chemtracts: Org. Chem.* 1989, 2, 151.
(2) (a) Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Top. Curr. Chem.* 1973, 47, 1. (b) Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. In *Advances in Dynamic Stereochemistry*; Gielen, M., Ed.; Freund Publishing House: London, 1985; p 207. (c) Mislow, K. *Acc. Chem. Res.* 1976, 9, 26. (d) Glaser, R.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* 1980, 102, 2777.
(3) (a) Iwamura, H.; Mislow, K. *Acc. Chem. Res.* 1988, 21, 175. (b) Chance, J. M.; Geiger, J. H.; Mislow, K. *J. Am. Chem. Soc.* 1989, 111, 2326. (c) Avent, A. G.; Bott, S. G.; Ladd, J. A.; Lickiss, P. D.; Pidcock, A. J. *Organomet. Chem.* 1992, 427, 9 and references therein.

We here describe the syntheses, X-ray structures, and variable-temperature NMR behavior of a series of tricarbonylchromium complexes of triphenylsilanol and triphenylcarbinol and also of the triphenylmethyl cation.

Results and Discussion

We have previously reported synthetic and variable-temperature NMR data on the mono-, bis- and tris-Cr-(CO)₃ derivatives of 1,3,5-triphenylbenzene (5–7, respectively)[8] and also on (C₆Ph₆)Cr(CO)₃ (8).[9] We were unable

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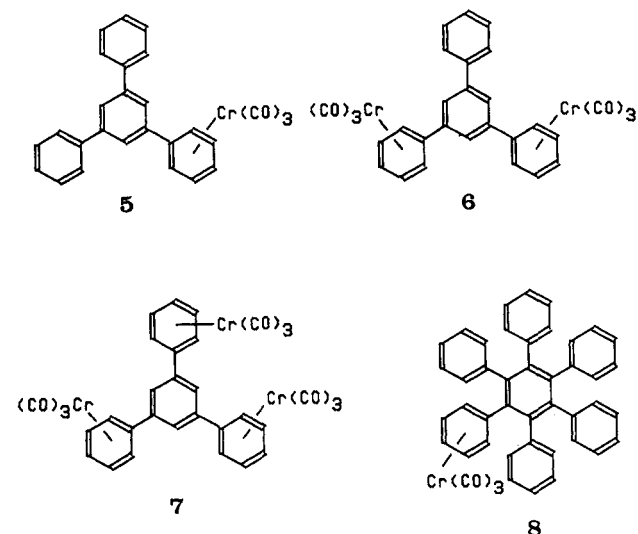
to detect slowed rotation of the peripheral phenyl rings in 5–7 even at –90 °C on a 500-MHz NMR spectrometer. Moreover, X-ray crystallographic data on 7 reveal[8] that no insurmountable barriers should arise so long as the molecules avoid conformations in which the metal tripods would clash. In contrast, slowed rotation of the (π-Cr-(CO)₃C₆H₅) ring of 8 is readily detectable by variable-temperature ^{13}C NMR spectroscopy and yields an activation energy of 12.2 kcal mol⁻¹.[9] This value may be compared to the approximately 33 kcal mol⁻¹ barrier previously reported for hexaarylbenzenes bearing methyl or methoxy substituents in *ortho* positions; the corresponding *meta*-substituted hexaphenylbenzenes yield aryl rotational barriers of ~17 kcal mol⁻¹.[10] Apparently, π-bonded addenda such as Cr(CO)₃ groups impose much smaller steric constraints than do *o*-alkyl substituents.

The molecular dynamics of triarylsilanes Ar₃SiX have been investigated, and in those molecules in which the aryl rings possess *o*-methyl groups, the rotations of the phenyls may be slowed on the NMR time scale.[11] The

(4) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* 1981, *103*, 6073.

(5) (a) Brégaint, P.; Hamon, J.-R.; Lapinte, C. *Organometallics* 1992, *11*, 1417. (b) Li, L.; Decken, A.; Sayer, B. G.; McGlinchey, M. J.; Brégaint, P.; Hamon, J.-R.; Lapinte, C.; Toupet, L., submitted for publication. (c) Gloaguen, B.; Astruc, D. *J. Am. Chem. Soc.* 1990, *112*, 4607.

(6) Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; Top, S.; McGlinchey, M. J. *J. Am. Chem. Soc.* 1991, *113*, 1177.

(7) (a) Nambu, M.; Siegel, J. S. *J. Am. Chem. Soc.* 1988, *110*, 3675. (b) Nambu, M.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* 1992, *114*, 369. (c) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* 1990, *111*, 27. (d) Kilway, K. V.; Siegel, J. S. *J. Am. Chem. Soc.* 1992, *114*, 255. (e) Kilway, K. V.; Siegel, J. S. *Organometallics* 1992, *11*, 1426.

(8) Mailvaganam, B.; McCarry, B. E.; Sayer, B. G.; Perrier, R. E.; Faggiani, R.; McGlinchey, M. J. *J. Organomet. Chem.* 1987, *335*, 213.

(9) Mailvaganam, B.; Sayer, B. G.; McGlinchey, M. J. *J. Organomet. Chem.* 1990, *395*, 177.

(10) Gust, D.; Patton, A. *J. Am. Chem. Soc.* 1978, *100*, 8175.

ΔG^* values for enantiomerization of such molecules, where X is H or Cl, lie in the range 11–12 kcal mol⁻¹. To study the effects of π-bonded addenda, we have prepared the mono-, bis-, and tris-Cr(CO)₃ derivatives of triphenylsilanol (9–11, respectively).

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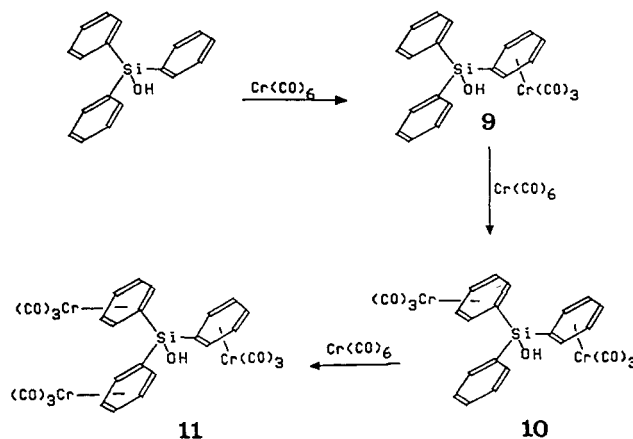
The mono complex (9) is prepared in straightforward fashion by the reaction of Ph₃SiOH with chromium hexacarbonyl in refluxing di-*n*-butyl ether and tetrahydrofuran. The bis (10) and tris (11) derivatives are prepared by further treatment of the mono-complexed material with excess Cr(CO)₆. All three (Ph₃SiOH)[Cr-(CO)₃]ₙ complexes yield yellow crystals suitable for structural characterization by X-ray diffraction techniques. Numbers related to data collection appear in Table I, and the atomic positional parameters for the molecules 9–11 are collected in Tables II–IV, respectively.

(Ph₃SiOH)[Cr(CO)₃] (9) crystallizes in the monoclinic space group C2/c with eight molecules per unit cell. As expected, the phenyls are arranged in a propeller fashion. The dihedral angles O–Si–C_{ipso}–C_{ortho} are 45, 23, and 73° for the complexed ring and the two noncomplexed rings, respectively. The phenyl–silicon–phenyl angles between the complexed and noncomplexed rings average 108.7°, while the C_{ipso}–Si–C_{ipso} angle between the two phenyls is 109.9°; the average O–Si–C_{ipso} angle is 109.8°. Overall, the deviations from a regular tetrahedral environment around silicon are rather small. The π-complexed ring is rotated such that the tricarbonylchromium fragment is oriented toward the silanol moiety. The Cr(CO)₃ tripod adopts a position almost exactly intermediate between a perfectly eclipsed rotamer and the ideally staggered conformation. If the Cr—C≡O linkages were to lie directly beneath the *para* and the two *ortho* carbons of the complexed ring, they would make dihedral angles of +60, +180, and –60° with the ring-centroid-to-*ipso*-carbon vector. In contrast, the staggered conformer would give dihedral angles of +30, +150, and –90°. The crystallographically observed torsion angles, *i.e.* the values C_{ipso}–ring centroid–Cr–C(O), are +45, +164, –77° and almost exactly bisect the two sets of idealized values. It is the phenyl positioned closest to the Cr(CO)₃ tripod which adopts the smallest dihedral angle (23°), while the third phenyl ring is able to lie almost orthogonal to the silicon–oxygen bond axis. Figure 1 shows a view of the molecule, and relevant bond length and angle data are collected in Table S2 of the supplementary material.

(11) Boettcher, R. J.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* 1973, *95*, 7157.

Table I. Structure Determination Summary

	9	10	11	12
empirical formula	$C_{21}H_{16}CrO_4Si$	$Cr_{24}H_{16}Cr_2O_7Si$	$Cr_{27}H_{16}Cr_3O_{10}Si$	$Cr_{22}H_{16}CrO_4$
color; habit	yellow; parallelpiped	yellow; plate	yellow; needle	yellow; plate
cryst size (mm)	$0.22 \times 0.25 \times 0.28$	$0.3 \times 0.15 \times 0.08$	$0.15 \times 0.05 \times 0.05$	$0.3 \times 0.1 \times 0.04$
cryst syst	monoclinic	triclinic	rhombohedral	monoclinic
space group	$C2/c$	$P\bar{1}$	$R\bar{3}$	$C2/c$
unit cell dimens				
a (Å)	29.061(3)	7.731(2)	19.251(2)	23.520(7)
b (Å)	7.136(2)	12.013(2)		8.231(2)
c (Å)	21.331(3)	13.929(3)	12.449(2)	21.608(6)
α (deg)		102.89(2)		
β (deg)	115.85(2)	102.34(2)		117.84(2)
γ (deg)		105.17(2)		
V (Å^3)	3980.9(8)	1165.1(3)	3997(3)	3699(3)
Z	8	2	6	8
fw	412.4	548.5	684.5	396.3
density (calc) (Mg/m^3)	1.376	1.563	1.705	1.423
abs coeff (cm^{-1})	6.57	10.27	13.1	6.43
$F(000)$	1696	556	2064	1632
temp (K)	302	302	302	302
2θ range (deg)	3.0–45.0	3.0–45.0	7.0–45.0	7.0–45.0
scan type	θ–2θ	θ–2θ	ω	θ–2θ
scan speed (deg/min)	variable; 1.50–14.65 in ω	variable; 1.50–14.65 in ω	variable; 1.50–15.00 in ω	variable; 3.00–60.00 in ω
scan range (ω) (deg)	1.20 plus Kα separation	0.60 plus Kα separation	0.60	0.60
index ranges	$-1 \le h \le 26, 0 \le k \le 7,$ $-22 \le l \le 20$	$-1 \le h \le 8, -12 \le k \le 12,$ $-15 \le l \le 14$	$-20 \le h \le 2, -1 \le k \le 20,$ $-1 \le l \le 13$	$-1 \le h \le 25, -1 \le k \le 10,$ $-24 \le l \le 24$
no. of rflns collected	2808	3422	1634	3514
no. of indep rflns	2505	3058	1157	3363
no. of obs rflns	1811 ($F \ge 4.0\sigma(F)$)	2513 ($F \ge 4.0\sigma(F)$)	716 ($F \ge 4.0\sigma(F)$)	1820 ($F \ge 4.0\sigma(F)$)
abs cor	N/A	semiempirical	N/A	N/A
min/max transmissn		0.0207/0.0385		
quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
extinction cor	N/A	N/A	N/A	$\chi = 0.000\ 20(6)$, where $F^* = F[1 + 0.002\chi F^2/$ $(\sin 2\theta)]^{-1/4}$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$	$w^{-1} = \sigma^2(F) + 0.0002F^2$	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0003F^2$
no. of params refined	260	323	130	245
final R indices (obs data) (%)	$R = 3.65, R_w = 4.30$	$R = 3.73, R_w = 5.12$	$R = 3.94, R_w = 3.49$	$R = 6.06, R_w = 6.38$
R indices (all data) (%)	$R = 5.88, R_w = 10.60$	$R = 4.91, R_w = 9.15$	$R = 8.10, R_w = 4.20$	$R = 11.16, R_w = 7.13$
goodness of fit	1.25	2.15	1.19	1.99
largest and mean Δ/σ	0.012, 0.001	0.004, 0.000	0.051, 0.010	0.001, 0.000
data-to-param ratio	7.0:1	7.8:1	5.5:1	7.4:1
largest diff peak (Å^{-3})	0.25	0.32	0.26	0.32
largest diff hole (Å^{-3})	-0.19	-0.25	-0.27	-0.38

(Ph$_3$SiOH)[Cr(CO)$_3$]$_2$ (10) crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. As with 9, the phenyls are again arranged in a propeller fashion. The dihedral angles O–Si–C$_{ipso}$–C$_{ortho}$ are 26, 36, and 46° for the two complexed rings and the single noncomplexed ring, respectively. The phenyl–silicon–phenyl angle between the two Cr-complexed rings is 107.2° but opens up to 109.9° for the other two C$_{ipso}$–Si–C$_{ipso}$ angles; the O–Si–C$_{ipso}$ angle to the phenyl ring is 112.9° but is reduced to 108.4° (average) for the chromium-complexed rings. In this case, as for the monochromium system 9, both π-complexed rings are rotated such that the tricarbonylchromium fragments are oriented toward the silanol moiety. Again, the Cr(CO)$_3$ tripods adopt positions such that they are almost precisely intermediate between the eclipsed and staggered rotamers. The measured dihedral angles C$_{ipso}$–ring centroid–Cr–C(O) are +43, +164, -77° for one (C$_6$H$_5$)Cr(CO)$_3$ moiety and +49, +168, and -72° for the other. Figure 2 shows a view of the molecule, and relevant bond length and angle data are collected in Table S7 of the supplementary material.

(Ph$_3$SiOH)[Cr(CO)$_3$]$_3$ (11) crystallizes in the rhombohedral space group $R\bar{3}$ with six molecules per unit cell. The phenyls are again arranged in a propeller fashion, but in this case, the molecule possesses a 3-fold axis. The dihedral angles O–Si–C$_{ipso}$–C$_{ortho}$ are 39.8° for all three complexed rings, the phenyl–silicon–phenyl angles are

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for (Ph$_3$SiOH)Cr(CO)$_3$ (9)

	x	y	z	U(eq)^a
Cr(1)	6843(1)	8129(1)	8233(1)	43(1)
Si	5764(1)	7203(2)	8689(1)	45(1)
O(1)	7514(2)	8388(6)	7504(2)	113(2)
O(2)	6239(1)	5152(5)	7222(2)	78(2)
O(3)	7546(2)	5207(6)	9153(2)	114(2)
O(10)	5507(1)	5787(4)	8017(1)	62(1)
C(1)	7249(2)	8284(7)	7783(2)	69(2)
C(2)	6475(2)	6292(6)	7614(2)	50(2)
C(3)	7274(2)	6342(7)	8796(2)	66(2)
C(11)	6241(1)	8778(5)	8578(2)	43(2)
C(12)	6128(2)	9685(6)	7938(2)	53(2)
C(13)	6474(2)	10859(6)	7850(3)	64(2)
C(14)	6955(2)	11163(6)	8412(3)	68(3)
C(15)	7082(2)	10318(6)	9049(2)	58(2)
C(16)	6726(2)	9121(6)	9123(2)	50(2)
C(21)	5260(2)	8697(6)	8755(2)	53(2)
C(22)	4919(2)	7956(10)	8976(3)	82(3)
C(23)	4556(2)	9097(14)	9058(3)	109(4)
C(24)	4536(3)	10971(13)	8906(3)	104(4)
C(25)	4855(2)	11721(10)	8670(4)	105(4)
C(26)	5215(2)	10595(8)	8599(3)	77(3)
C(31)	6093(2)	5814(6)	9496(2)	48(2)
C(32)	6264(2)	4009(7)	9495(2)	63(2)
C(33)	6508(2)	3012(8)	10099(3)	81(3)
C(34)	6589(2)	3753(9)	10718(3)	82(3)
C(35)	6443(2)	5571(10)	10754(3)	89(3)
C(36)	6199(2)	6582(7)	10148(2)	78(3)

^{a} Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for (Ph₃SiOH)[Cr(CO)₃]₂ (10)

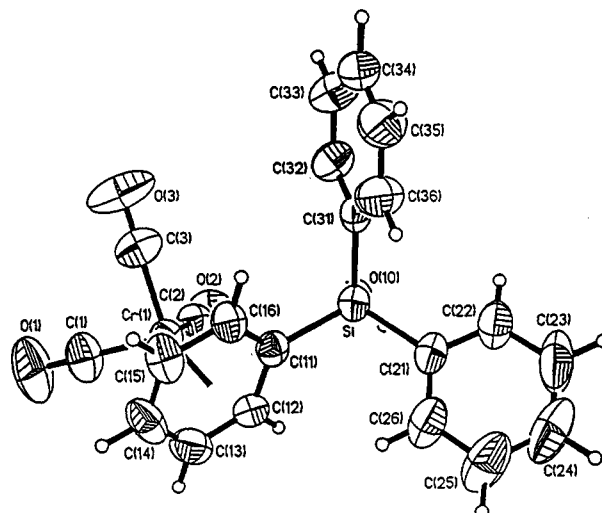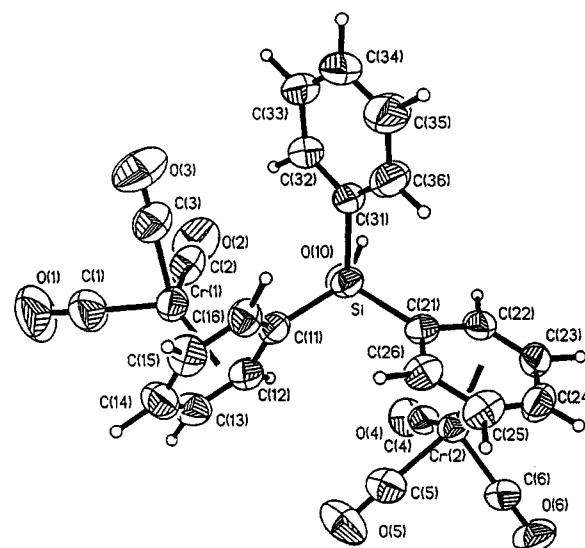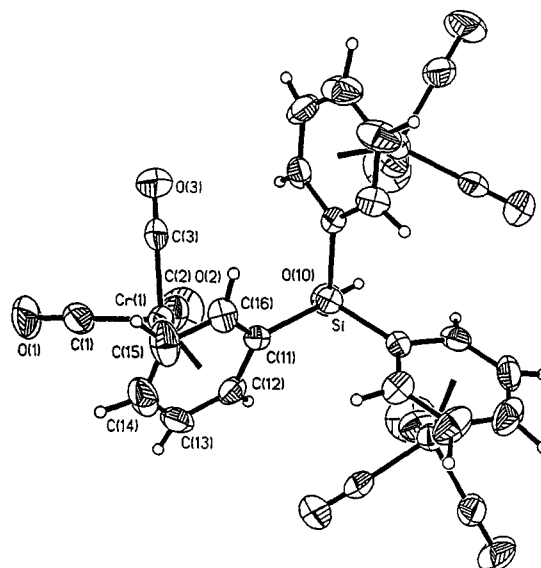|	x	y	z	$U(eq)^a$
Cr(1)	-3570(1)	-185(1)	7928(1)	52(1)
Cr(2)	660(1)	3144(1)	5582(1)	43(1)
Si	-564(2)	2797(1)	7968(1)	47(1)
O(1)	-6814(8)	-2228(5)	7860(5)	139(3)
O(2)	-5747(7)	1467(5)	8463(4)	100(3)
O(3)	-2192(8)	123(5)	10174(4)	113(3)
O(4)	-3088(5)	3490(3)	5147(3)	66(2)
O(5)	-1356(6)	545(4)	4370(3)	91(2)
O(6)	995(6)	3682(3)	3617(3)	77(2)
O(10)	-2290(5)	3328(3)	7708(3)	63(2)
C(1)	-5586(10)	-1449(6)	7874(5)	89(3)
C(2)	-4888(8)	829(6)	8256(4)	68(3)
C(3)	-2706(8)	-1(5)	9310(5)	67(3)
C(4)	-1649(7)	3361(4)	5332(3)	48(2)
C(5)	-561(7)	1534(5)	4842(4)	58(2)
C(6)	827(7)	3462(4)	4363(4)	54(2)
C(11)	-1545(6)	1118(4)	7463(3)	46(2)
C(12)	-3232(7)	531(5)	6625(3)	55(2)
C(13)	-3940(7)	-723(5)	6247(4)	65(2)
C(14)	-3042(8)	-1444(5)	6690(4)	66(3)
C(15)	-1385(8)	-891(5)	7493(4)	64(3)
C(16)	-628(6)	388(4)	7893(4)	51(2)
C(21)	1139(6)	3307(4)	7252(3)	45(2)
C(22)	1490(7)	4481(4)	7097(3)	49(2)
C(23)	2779(7)	4883(5)	6577(4)	57(2)
C(24)	3685(7)	4121(6)	6165(4)	65(3)
C(25)	3388(7)	2967(5)	6298(4)	59(2)
C(26)	2112(7)	2570(4)	6835(3)	52(2)
C(31)	663(7)	3262(4)	9367(3)	49(2)
C(32)	-356(7)	3182(5)	10078(4)	59(2)
C(33)	522(9)	3411(5)	11118(4)	71(3)
C(34)	2436(10)	3763(5)	11462(4)	77(3)
C(35)	3483(8)	3873(6)	10787(5)	87(3)
C(36)	2585(8)	3622(6)	9743(4)	71(3)

^{a} Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for (Ph₃SiOH)[Cr(CO)₃]₃ (11)

	x	y	z	$U(eq)^a$
Cr(1)	4817(1)	3453(1)	836(1)	38(1)
Si	6667	3333	744(2)	31(1)
C(1)	3826(4)	3373(4)	720(6)	57(4)
C(2)	4868(4)	3406(5)	-631(6)	60(4)
C(3)	4266(4)	2332(4)	867(6)	53(4)
C(11)	6052(3)	3757(3)	1271(4)	29(3)
C(12)	5543(4)	3429(4)	2160(5)	42(3)
C(13)	5063(4)	3727(5)	2560(5)	59(4)
C(14)	5099(5)	4384(5)	2055(7)	65(5)
C(15)	5592(4)	4742(4)	1179(7)	59(4)
C(16)	6066(3)	4433(3)	782(5)	41(3)
O(1)	3210(3)	3325(3)	649(5)	93(3)
O(2)	4913(4)	3403(4)	-1553(4)	109(4)
O(3)	3938(3)	1658(3)	873(5)	88(3)
O(10)	6667	3333	-555(5)	46(2)

^{a} Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Figure 1. Molecular structure of (Ph₃SiOH)Cr(CO)₃ (9).

Figure 2. Molecular structure of (Ph₃SiOH)[Cr(CO)₃]₂ (10).

Figure 3. Molecular structure of (Ph₃SiOH)[Cr(CO)₃]₃ (11).

108.3°, and the phenyl–silicon–oxygen angles are 110.6°. As with 9 and 10, the π-complexed rings are rotated such that the tricarbonylchromium fragments are oriented toward the silanol moiety. However, in this case, the tripods almost perfectly eclipse the *ortho* and *para* ring carbons; the observed dihedral angles C_{ipso}–ring centroid–Cr–C(O) are +62, +179, and -59°. Inevitably, the hydrogen of the Si–OH unit is disordered over three sites, and only one has been selected for Figure 3, which shows the atom-numbering scheme. Figure 4 provides a space-filling view of the molecule which shows clearly that the tripod eclipses the *para* and the two *ortho* ring carbon positions. Figure 5 illustrates the contents of the unit cell, and relevant

bond length and angle data are collected in Table S12 of the supplementary material.

It is interesting to speculate as to why the tripods are in all cases oriented *proximal* to the silanol functionality.
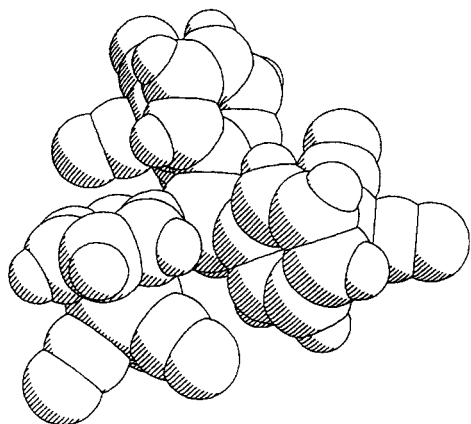
Figure 4. Space-filling model of (Ph₃SiOH)[Cr(CO)₃]₃ (11).
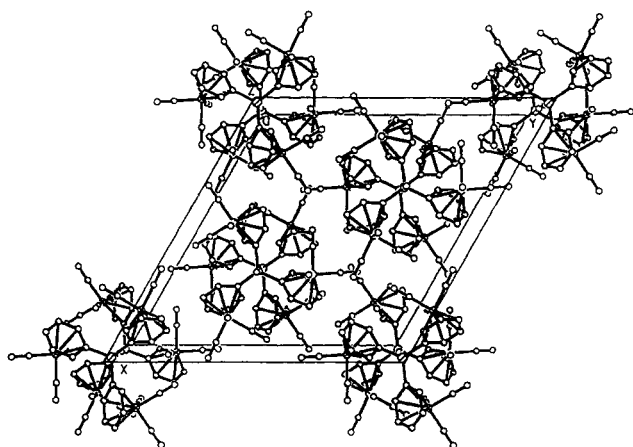
Figure 5. Rhombohedral unit cell of (Ph₃SiOH)[Cr(CO)₃]₃ (11).

Figure 6. 500-MHz ¹H NMR spectra of 9–11, in CD₂Cl₂ solution.

Since the siloxy hydrogen cannot be precisely located, one might hypothesize that there is an interaction with a Cr-(CO)₃ unit. However, the shortest (Si)O···Cr separation is over 4 Å, and even the shortest siloxy to carbonyl oxygen distance is 3.2 Å; this latter distance is perhaps appropriate to support a weak hydrogen-bonding interaction. Interestingly, a very recent Russian report presents infrared spectroscopic evidence for O–H···O(C) interactions in (C₅H₄CPh₂OH)Mn(CO)₃ and related systems.[12]

The ¹H and ¹³C NMR spectra of 9–11 are shown in Figures 6 and 7; the shifts are collected in Table V. They are unchanged over the range +30 to –110 °C and show no evidence of slowed rotation about the *ipso*-carbon-silicon bonds. Thus, in (Ph₃SiOH)[Cr(CO)₃] (9) the ¹H NMR spectrum exhibits a doublet for the *ortho* hydrogens and triplets for the *meta* and *para* protons in the noncomplexed rings; similar patterns of half the intensity are given by the chromium-complexed ring. In accord with this picture, the ¹³C NMR spectrum exhibits single peaks for the *ipso*, *ortho*, *meta*, and *para* carbons of the two noncomplexed rings at δ 132.3, 134.6, 127.8, and 130.5, respectively; corresponding resonances for the single π-complexed ring appear at δ 93.8, 100.8, 90.6, and 96.9, respectively. The differentiation of *ortho* and *meta* ¹³C environments are made by standard two-dimensional shift-correlated techniques. If aryl rotation were to become slow on the NMR time scale, and if the spectrum were to reflect the lack of molecular symmetry found in the solid
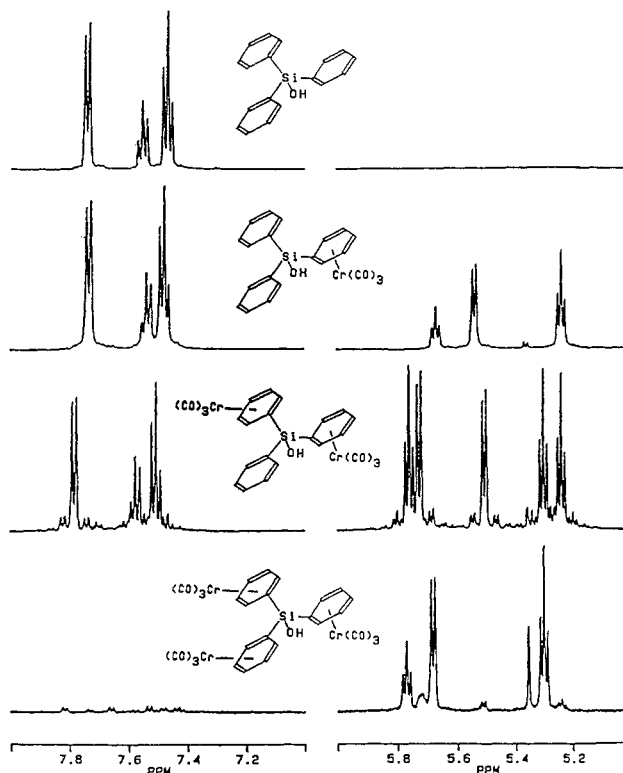
state, the *ortho* and *meta* carbons and hydrogens of the phenyl rings should be split.

The NMR spectra of (Ph₃SiOH)[Cr(CO)₃]₂ (10) bear careful examination, since it is apparent that the ¹H absorptions attributable to the two complexed rings give rise to a pair of *ortho* and a pair of *meta* resonances. At first sight, one might suspect that rotation of the (π-Cr-(CO)₃-C₆H₅) rings has been slowed even at room temperature. Upon further reflection, however, one comes to the realization that the highest symmetry available to 10 is Cₛ, a single mirror plane. As shown in Figure 8, the "inner" and "outer" edges of the (π-Cr(CO)₃C₆H₅) rings can never be equilibrated by a simple bond rotation process. Thus, each π-complexed phenyl ring will give rise to six carbon resonances even under conditions of rapid ring rotation. If rotation about the *ipso*-carbon–silicon bonds were to become slow on the NMR time scale, we would expect to see 12 resonances, 6 for each complexed ring. The alert reader will have already noted that (Ph₃SiOH)[Cr(CO)₃] (9) also possesses Cₛ symmetry at best, yet we see only four peaks for the (π-Cr(CO)₃C₆H₅) ring. The explanation is simple: in 9, the complexed ring straddles the molecular mirror plane, whereas in 10 the two rings bearing Cr(CO)₃ substituents are related by reflection in this mirror plane. Clearly, as we have all been cautioned by Sanders and Hunter,[13] one must take careful account of molecular symmetry before making claims about restricted rotations.

The above interpretation of the behavior of 10 is corroborated by the variable-temperature spectra of (Ph₃-SiOH)[Cr(CO)₃]₃ (11), which show only three proton environments and four ¹³C resonances for the three complexed aryl rings. The molecule can adopt time-average C₃ᵥ symmetry, and the three vertical mirror planes render equivalent the edges of the phenyl rings. Clearly,

(12) Shubina, E. S.; Krylov, A. N.; Timofeeva, T. V.; Struchov, Yu. T.; Ginzburg, A. G.; Loim, N. M.; Epstein, L. M. *J. Organomet. Chem.* **1992**, *434*, 329.

(13) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, U.K., 1987; pp 299–302.
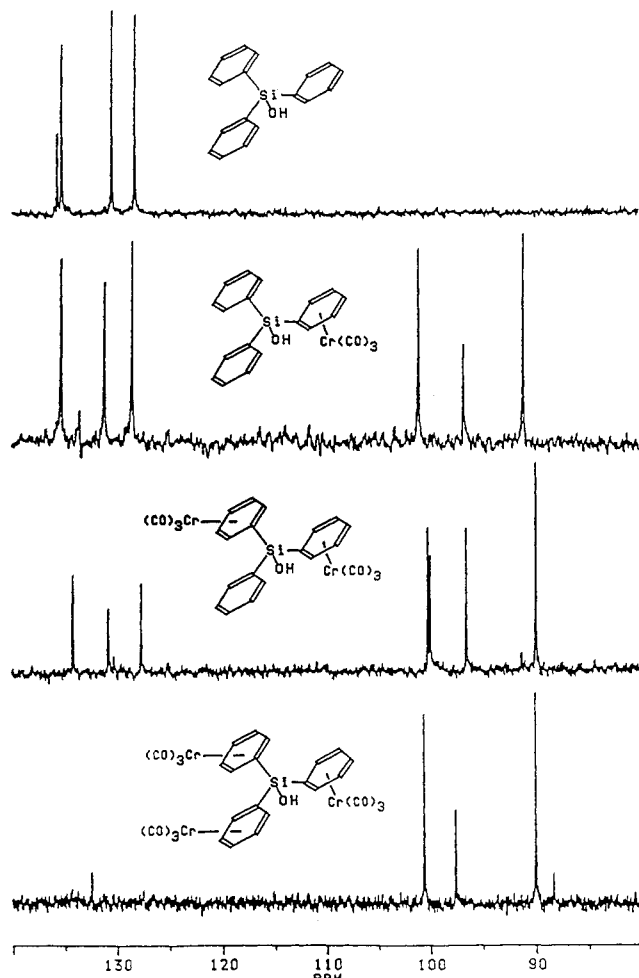
Figure 7. 125.7-MHz ^{13}C NMR spectra of 9–11, in CD$_2$Cl$_2$ solution.

Table V. ^{1}H and ^{13}C NMR Data for Ph₃SiOH and for the Cr(CO)$_3$ Complexes 9–11

	Ph₃SiOH[a]	(Ph₃SiOH)-Cr(CO)$_3$ (9)[b]	(Ph₃SiOH)-[Cr(CO)$_3$]$_2$ (10)	(Ph₃SiOH)-[Cr(CO)$_3$]$_3$ (11)
H-*ortho*	7.64 (d)	7.64 (d)	7.60 (d)	
H-*meta*	7.42 (t)	7.43 (t)	7.35 (t)	
H-*para*	7.51 (t)	7.50 (t)	7.43 (t)	
C-*ipso*	135.1	132.33	130.48	
C-*ortho*	135.0	134.63[c]	134.53	
C-*meta*	127.9	127.77[c]	127.82	
C-*para*	130.2	130.52[c]	131.07	
H-*ortho*		5.51 (d)	5.50 (d) H2	5.64 (d)
			5.72 (d) H6	
H-*meta*		5.20 (t)	5.23(d,t) H3[d]	5.29 (t)
			5.29(d,t) H5[d]	
H-*para*		5.64 (t)	5.75 (t)	5.76 (t)
C-*ipso*		93.76	92.69	87.92
C-*ortho*		100.80[e]	100.63	100.60
			100.84	
C-*meta*		90.58[e]	90.27	90.02
			90.33	
C-*para*		96.88[e]	97.07	97.61
Cr–CO		233.2	232.7	232.0

[a] ^{29}Si –12.45 ppm. [b] ^{29}Si –12.96 ppm. [c] J(C–H) = 159 Hz. [d] Doublet (0.9 Hz) of triplets (6.5 Hz). [e] J(C–H) = 174 Hz.

since there is no evidence for slowed aryl rotation on the NMR time scale in the crowded tris complex 11, there is no reason to invoke it for the bis-Cr(CO)$_3$ system 10.

Molecular modeling of the tris complex, by starting from the X-ray structure and using the programs ALCHEMY[14] or PC-MODEL,[15] shows that it is possible to spin the rings
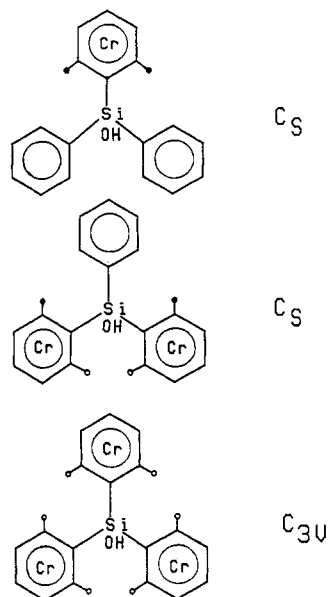

Figure 8. Highest possible symmetries of the complexes 9–11.

without invoking correlated rotations. The *ipso*-carbon–silicon bonds (average length 1.86 Å) are sufficiently long to allow considerable molecular flexibility; however, these modeling studies suggested that the analogous carbinol complexes should show evidence of restricted aryl rotation.[16]

(Triphenylcarbinol)chromium tricarbonyl (12) has been synthesized previously via the reaction of a phenyl Grignard reagent with (benzophenone)Cr(CO)$_3$.[17] We


12   **13**
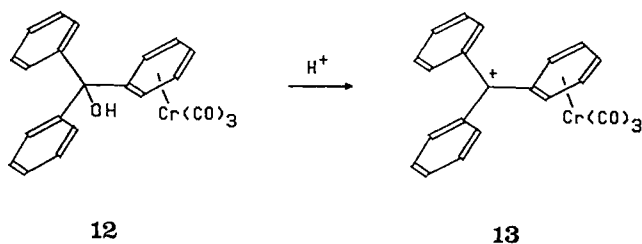
selected the more direct route from Ph₃COH and Cr(CO)$_6$; this procedure gave excellent yields of 12, which was examined by variable-temperature ^{1}H and ^{13}C NMR spectroscopy. Portions of these spectra are shown in Figure 9. One sees that, at –80 °C, the *ortho* protons of the noncomplexed phenyl rings have clearly split into a central peak (of intensity 2 H's) and two broader peaks each representing a single hydrogen. Continued cooling reveals that these two outer resonances each become 8-Hz doublets at –90 °C; these are clearly *ortho* hydrogens. Below this temperature, the central absorption begins to broaden and it is apparent that, if the low-temperature limiting spectrum were attainable, one would see four different *ortho* proton environments.

This fluxional behavior is rationalizable in terms of slowed rotation of the aryl rings about the central C–*ipso*-C

(14) ALCHEMY: available from Tripos Associates, St. Louis, MO.

(15) PCMODEL: available from Dr. K. Gilbert, Serena Software, Bloomington, IN.

(16) We must, however, remind ourselves that steric barriers derived from rigid models (be they plastic, metallic, or merely computer images) can seriously overestimate the energy requirements associated with a particular conformation. Molecules are capable of surprising flexibility; they are much more versatile than we give them credit for!

(17) (a) Holmes, J. D.; Jones, D. A. K.; Pettit, R. *J. Organomet. Chem.* **1965,** *4,* 324. (b) Card, A.; Besançon, J.; Gautheron, B. *Bull. Soc. Chim. Fr.* 1981, 43 (Part 2).
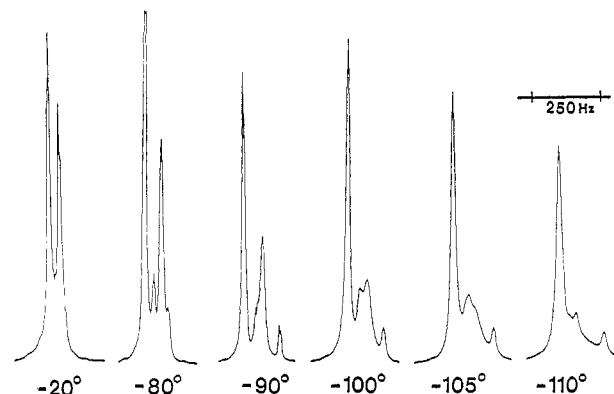
Figure 9. Sections (δ 7.6–7.3) of the variable-temperature 500-MHz ^{1}H NMR spectra of the noncomplexed phenyl rings of (Ph$_3$COH)Cr(CO)$_3$ (12). Peaks attributable to the *ortho* protons coalesce at higher temperatures (see text).

axes. Prior to the availability of crystallographic data on 12, we chose to model the system simply by taking the X-ray structure of the analogous silanol complex 9 and shortening the Si–C$_{ipso}$ bonds from 1.86 to 1.52 Å. As was pointed out above for 9, one of the noncomplexed phenyl rings is in a noticeably more crowded environment than is its partner. Initially, one can invoke slowed rotation of the relatively bulky chromium-complexed phenyl ring. (Such a scenario is in accord with the known behavior of (C$_6$Ph$_6$)Cr(CO)$_3$ (8), in which rotation of the chromium-complexed ring is slowed but the other peripheral rings continue to spin rapidly on the NMR time scale.[9]) Thus, even though the two remaining phenyl groups in 12 may continue to spin rapidly, one of them is oriented *proximally* with respect to the chromium atom while the other is *distal*. Thus, one might expect to see two different *ortho* environments. Moreover, the noncomplexed phenyl ring positioned *proximal* to the Cr(CO)$_3$ moiety will be more sterically hindered than will its partner. Slowed rotation of this more crowded phenyl ring should render non-equivalent its two *ortho* hydrogens. Subsequently, at lower temperatures, the smaller rotational barrier associated with the less hindered phenyl ring will eventually cause the ring edges to become nonequivalent. The Gutowsky–Holm approximation yields a $\Delta G^{\ddagger}$ value of ~11 ± 0.5 kcal mol^{-1} for the barrier to rotation of the more hindered phenyl ring. It is difficult to offer a $\Delta G^{\ddagger}$ value for the less crowded phenyl ring since the temperature required to see the limiting spectrum is not accessible. Finally, we note that in these molecules there is no evidence for cessation of rotation of the Cr(CO)$_3$ tripod as has been noted in other sterically hindered systems.[18]

Subsequently, X-ray-quality crystals of 12 were obtained and the structure was solved in the monoclinic space group *C*2/*c* with eight molecules per unit cell. As with the analogous mono-complexed silanol 9, the phenyls are arranged in a propeller fashion. The dihedral angles O–C–C$_{ipso}$–C$_{ortho}$ are 32, 36, and 65° for the complexed ring and the two noncomplexed rings, respectively. The phenyl-carbon–phenyl angles between the complexed and non-complexed rings average 110.4°, while the C$_{ipso}$–C–C$_{ipso}$ angle between the two phenyls is 112.3°; the average C$_{ipso}$–C–O angle is 108°. As is the case for the silanol complexes 9–11, the π-complexed ring in the carbinol system 12 is rotated such that the tricarbonylchromium fragment is bonded to the face oriented toward the hydroxyl moiety.

(18) McGlinchey, M. J. *Adv. Organomet. Chem.* **1992**, *34*, 285.
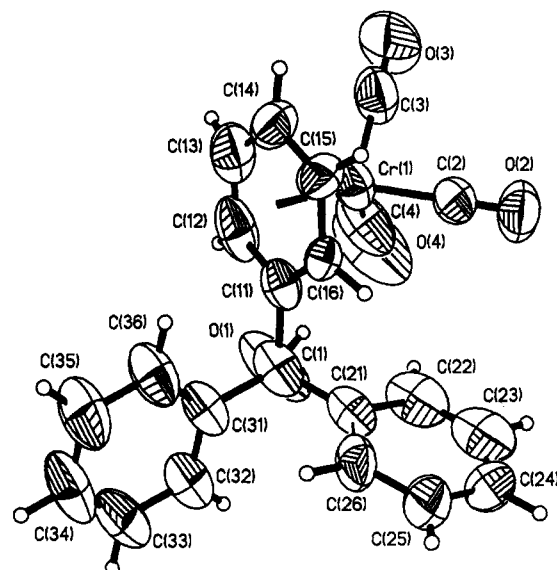
Figure 10. Molecular structure of (Ph$_3$COH)Cr(CO)$_3$ (12).

Table VI. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for (Ph$_3$COH)Cr(CO)$_3$ (12)

	x	y	z	$U(\text{eq})^a$
Cr(1)	6828(1)	7129(1)	1040(1)	67(1)
C(1)	5519(3)	7649(9)	–607(3)	71(3)
O(1)	5162(2)	8323(7)	–276(2)	125(3)
C(2)	7354(3)	8790(9)	1072(3)	72(3)
O(2)	7683(2)	9849(6)	1087(2)	100(3)
C(3)	7295(3)	6924(9)	1990(3)	96(4)
O(3)	7579(3)	6822(8)	2594(2)	158(4)
C(4)	6347(3)	8590(12)	1219(4)	113(4)
O(4)	6047(3)	9517(10)	1341(3)	184(5)
C(11)	6063(2)	6650(7)	–47(3)	59(3)
C(12)	5960(3)	5693(10)	443(3)	90(4)
C(13)	6420(4)	4669(10)	910(3)	105(5)
C(14)	7016(4)	4560(8)	918(3)	87(4)
C(15)	7132(3)	5454(7)	452(3)	65(3)
C(16)	6657(2)	6497(6)	–28(2)	49(2)
C(21)	5790(3)	9021(8)	–858(3)	69(3)
C(22)	6043(4)	10392(10)	–452(4)	113(4)
C(23)	6316(5)	11587(11)	–656(6)	161(7)
C(24)	6327(5)	11491(11)	–1262(6)	145(6)
C(25)	6094(3)	10169(11)	–1675(4)	105(4)
C(26)	5828(3)	8920(8)	–1471(4)	76(3)
C(31)	5065(3)	6563(9)	–1205(3)	67(3)
C(32)	4500(3)	7210(10)	–1711(3)	84(3)
C(33)	4069(3)	6250(13)	–2239(3)	99(4)
C(34)	4197(4)	4681(14)	–2289(4)	112(5)
C(35)	4754(4)	4012(11)	–1797(4)	113(5)
C(36)	5186(3)	4973(10)	–1258(3)	88(4)

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

Again, as with the silanol analogues, the Cr(CO)$_3$ tripod adopts the conformation which places the carbonyls midway between the idealized eclipsed and staggered rotamers. The angles C$_{ipso}$–ring centroid–Cr–C(O) are +42, +158, and –79°. It is the phenyl positioned closest to the Cr(CO)$_3$ tripod which adopts the smaller dihedral angle (36°), while the third phenyl ring is able to lie at a much larger angle (65°) to the carbon–oxygen bond axis. Figure 10 shows a view of the molecule, and atomic positional parameters, together with relevant bond length and angle data, are collected in Tables VI and S16 of the supplementary material. The similarities between the structures of the silanol 9 and the carbinol 12 are evident and provide support for the hypothesis advanced to account for the fluxional behavior of 12.

Table VII. Phenyl Torsion Angles (deg) in Ph₃EO–Z Systems (E = Si, C)

ring A	ring B	ring C	molecule	ref
90	28	35	Ph₃SiO–ClO₃	19a
90	28	39	Ph₃SiO–ClO₃	19a
70	70	70	Ph₃SiO–C(vinyl)₃	19f
63	37	18	(Ph₃Si)₂CrO₄	19e
56	29	50	Ph₃SiO–U(C₅H₅)₃	19d
56	45	36	Ph₃Si–O–SiPh₃	19c
31	31	31	Ph₃Si–O–SiPh₃ benzene clathrate	19b
29	29	29	Ph₃Si–O–SiPh₃ piperidine clanthrate	19b
73	45[a]	23	(Ph₃SiOH)–[Cr(CO)₃]	this work
46	36[a]	26[a]	(Ph₃SiOH)–[Cr(CO)₃]₂	this work
40[a]	40[a]	40[a]	(Ph₃SiOH)–[Cr(CO)₃]₃	this work
65	36	32[a]	(Ph₃COH)–[Cr(CO)₃]	this work
93	28	–15	Ph₃C–OCHMeC₆H₅	24a
92	28	–19	Ph₃C–OCHMeC₆H₄Cl	24a
89	32	23	Ph₃C–OEt	24c
66	30	–11	Ph₃C–OCHMeC₆H₄NO₂	24a
76	33	–1	(Ph₃C)₂O	24b
61	39	–17	(Ph₃C)₂O	24b
69	60	48	Ph₃CLi	24d

[a] Chromium-complexed rings.

Significance of Torsional Angles. To place these structural and variable-temperature NMR data in perspective, we note that a number of Ph₃SiO–Z molecules have been crystallographically characterized.[19] These include systems containing such Z substituents as ClO₃, SiPh₃, C₂H₅, U(C₅H₅)₃, CrO₃SiPh₃, and Si[CH=CH₂]₃ (see Table VII). Of particular relevance is the pioneering study of Dunitz et al., in which it was shown that the O–P–C_{ipso}–C_{ortho} dihedral angles taken from the X-ray crystal structures of a large number of Ph₃PO–Z molecules could be used to visualize the most probable pathways for stereoisomerization.[20] For these Ph₃PO–Z systems, Dunitz noted that "the equilibrium structure of an isolated Ph₃P–Z fragment is close to a symmetric propeller shape with all three phenyl rings rotated from the respective C–P–Z planes in the same sense and by approximately the same amount, about 40°".[20] The stereoisomerization is thought to proceed by rotation of one ring toward a 90° torsion angle with concomitant rotation of the other phenyl rings in the opposite sense (i.e. toward 0°) so as to produce a conformation in which the torsion angles are approximately +90, +10, and –10°. Continued rotation leads eventually to a propeller of opposite chirality. Clearly, all three rings do not rotate at the same rate, and this should be reflected in the crystallographic results, which capture a series of snapshots of the Ph₃P fragment in many different environments.[21] This crystallographically derived picture of the stereoisomerization pathway is complemented by force field calculations and variable-temperature NMR data on related Ar₃CH systems which also favor the "two-ring flip" mechanism.[22]

The Ph₃SiO–Z systems we have found in the literature (see Table VII) as well as the three we have reported herein, i.e., 9–11, all possess the propeller structure in which the three rings are rotated in the same sense. Even in the cases where one phenyl group is aligned at 90° to the Si–O axis, the two remaining rings are oriented in the same direction. Typically, in Ph₃SiOClO₃, the torsion angles are 90, 28, and 35°.[19a] When the molecules have a 3-fold axis, as in the clathrate complexes of hexaphenyldisiloxane with benzene or piperidine, the dihedral angles are approximately 30°.[19b] When the phenyls each bear a relatively bulky π-bonded Cr(CO)₃ substituent, as in (Ph₃SiOH)[Cr(CO)₃]₃ (11), these angles open up to 40°.

Interestingly, a comparison of these data for Ph₃SiO–Z systems with those for Ph₃CO–Z molecules reveals that, although triarylmethanes bearing bulky ortho substituents adopt a propeller-type conformation in the solid state,[23] many trityl fragments do not.[24] Instead, a favored structure appears to be one in which one phenyl lies almost perpendicular to the pseudo 3-fold axis while the remaining rings adopt small dihedral angles of opposite sign. Typically, in Ph₃C–O–CHMeC₆H₄Cl, the torsion angles are +93, +28, and –19°.[24a] This conformation represents a relatively high-energy point approximately halfway along the trajectory of the two-ring flip mechanism which interconverts enantiomers of Ph₃C–Z. Clearly, the solid-state conformations of this class of molecules merit a more comprehensive study, and to this end, we are currently compiling structures from the Cambridge Crystallographic Database.

Chromium-Stabilized Benzylic Cations. Despite early failures to generate chromium-stabilized cations by treatment of carbinol complexes with HClO₄,[17a] it is now well established that benzylic cations are noticeably stabilized by the presence of a tricarbonylchromium moiety.[25] Recently, we have succeeded in obtaining NMR spectra of a series of primary benzylic cations each bearing a Cr(CO)₃ group.[26] In the present case, since the free triphenylmethyl cation is sufficiently stable to have been subjected to X-ray crystallographic structural determination,[27] one might hope to be able to isolate the corresponding Cr(CO)₃ complex, 13, in crystalline form. Protonation of 12 with CF₃SO₃H or with HBF₄/ether yields immediately a green solution of the cation [(Ph₃C)Cr-(CO)₃]⁺ (13), which can be left in air at room temperature for several hours with only minor decomposition. Interestingly, a solution which had been left overnight turned red but addition of water regenerated the yellow color of the starting material 12. (We note that Pettit's early attempts to generate [(Ph₃C)Cr(CO)₃]⁺ were reported to

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(25) (a) Acampora, M.; Ceccon, A.; Dal Farra, M.; Giacometti, G.; Rigatti, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 483. (b) Seyferth, D.; Merola, J. S.; Eschbach, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 4124. (c) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591.

(26) Downton, P. A.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1992**, *11*, 3281. (b) The cation [(Ph₃C)Cr(CO)₃]⁺ has been prepared independently, and the barrier to tripodal rotation has been determined: Siegel, J. S., personal communication. Calculations to elucidate the charge density distribution in this cation will be the subject of a manuscript describing our joint efforts in this area.

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Table VIII. ^{1}H and ^{13}C NMR Data for Ph₃COH, for [Ph₃C]⁺, for the Cr(CO)₃ Complexes 12 and 13, and for [(Ph₃C)Cr(CO)₃]⁻ [a]

	Ph₃COH	(Ph₃COH)-Cr(CO)₃ (12)	[Ph₃C]⁺	[(Ph₃C)-Cr(CO)₃]⁺ (13)	[(Ph₃C)-Cr(CO)₃]⁻
H-*ortho*	7.49 (d)	7.49 (d)	7.69 (d)	7.40 (d)	7.17
H-*meta*	7.54 (t)	7.54 (m)	7.90 (t)	7.60 (t)	7.01
H-*para*	7.54 (t)	7.54 (m)	8.29 (t)	7.97 (t)	6.73
C-*ipso*	135.1	145.5	140.28	130.6	147.4
C-*ortho*	135.0	127.4	143.09	135.1	131.3
C-*meta*	127.9	128.2	130.89	129.9	128.1
C-*para*	130.2	127.8	143.78	137.1	122.4
H-*ortho*		5.65 (d)		6.42 (d)	4.41
H-*meta*		5.35 (t)		5.87 (t)	4.84
H-*para*		5.76 (t)		6.82 (t)	4.53
C-*ipso*		119.05		102.7	133.5
C-*ortho*		96.59		104.9	73.1
C-*meta*		89.39		97.3	99.9
C-*para*		96.06		97.4	73.5
benzylic C	82.00	79.71	211.22	185.8	97.7
Cr–CO		233.3		229.3	241.1

[a] Data for [(Ph₃C)Cr(CO)₃]⁻ in THF-d_8 taken from: Ceccon, A.; Gambaro, A.; Romanin, A. M.; Venzo, A. *J. Organomet. Chem.* **1983**, *254*, 199; **1984**, *275*, 209.

^{1}H

^{13}C
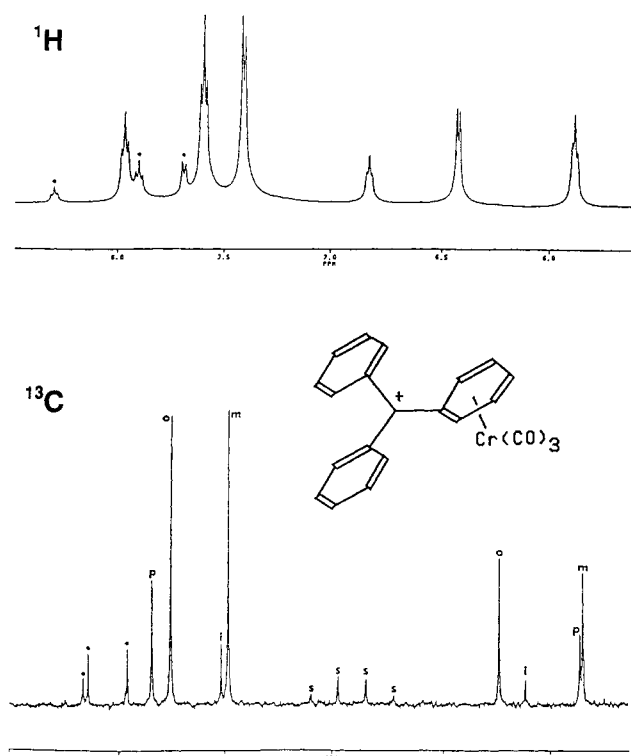
Figure 11. 500-MHz ^{1}H NMR and 125.7-MHz ^{13}C NMR spectra of the cation [(Ph₃C)Cr(CO)₃]⁺ (13) in CD₂Cl₂ solution, showing the *ipso, ortho, meta,* and *para* environments. Peaks marked with a dot (•) are attributable to uncomplexed triphenylmethyl cation. The triflic acid used for protonation gives rise to the fluorine-coupled quartet labeled s.

yield a green solution. However, the work was discontinued, as it was assumed that decomposition to Cr(III) had occurred.[17a] The ^{1}H and ^{13}C NMR data are collected in Table VIII, and the spectra of 13 are shown in Figure 11; they are entirely analogous to the spectra of the chromium-stabilized cations previously reported. In particular, the benzylic carbon in 13 which formally bears the positive charge is deshielded by 106 ppm relative to its resonance position in the alcohol 12. This compares favorably with Olah's report that conversion of (C₆H₅-CMe₂OH)Cr(CO)₃ to [(C₆H₅CMe₂)Cr(CO)₃]⁺ takes the

benzylic carbon ^{13}C NMR resonance from 71.4 ppm in the alcohol to 170.9 ppm in the cation.[28] It has been noted previously that both experimental data and EHMO calculations suggest that for [(benzyl)Cr(CO)₃]⁺ systems a tertiary cation requires much less anchimeric assistance from the neighboring metal than does a primary cationic center.[26] Thus, a tertiary cation need not bend toward the metal as is observed, for example, in ferrocenyl cations.[29] Such a concept is buttressed by X-ray crystallographic data[30,31] on the molybdenum-stabilized alkynyl cations 14 and 15, whereby the Mo–C⁺ distance is 2.44 Å in the primary cation 14 but lengthens to 2.74 Å in the tertiary cation 15. We are currently attempting to obtain X-ray-quality crystals of 13 to clarify this point.
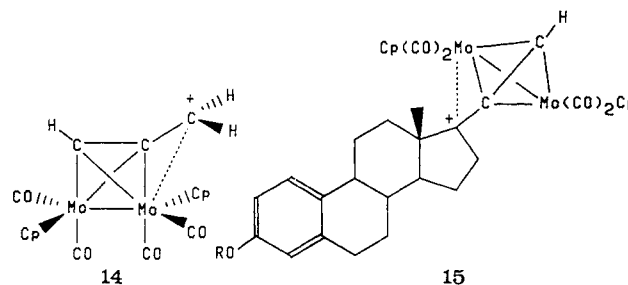
There has been a lively controversy[32] concerning the existence of free silicenium cations, and one might imagine that the presence of a tricarbonylchromium unit might help stabilize a positively charged silicon center. Protonation of the complexed silanols 9–11 brings about a small deshielding of the ring protons and carbons, but we have not yet detected a ^{29}Si signal: indeed, both Olah[33] and Lambert[34] have noted difficulties in obtaining ^{29}Si data on the proposed silicenium ions, which, by analogy to the ^{13}C shifts of carbenium ions, one might expect to be drastically deshielded.[35] In the present case, we believe that, upon acidification, the chromium complexes 9–11 do not eliminate water and are merely protonated silanols.[36] The problem may be that the silicon–oxygen bond is too strong to be broken in these systems. We also attempted (unsuccessfully) to generate a silicenium ion by abstraction of hydride from (Ph₃SiH)Cr(CO)₃; such an approach has been discussed extensively for the case of ferrocenyldimethylsilane.[37,38] We note that very recent attempts to isolate organosilicenium ions have used tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as the coun-

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(36) The variation in the ^{29}Si chemical shift of Ph₃SiOH in solvents of different acidity has been noted: Williams, E. A.; Cargioli, J. D.; LaRochelle, R. W. *J. Organomet. Chem.* **1976**, *108*, 153.

(37) Despite early claims, this system apparently does not yield a ferrocenyl-stabilized silicenium ion.[38]

(38) (a) Corey, J. Y.; Gust, D.; Mislow, K. *J. Organomet. Chem.* **1975**, *101*, C7. (b) Barton, T. J.; Hovland, A. K.; Tully, C. R. *J. Am. Chem. Soc.* **1976**, *98*, 5695. (c) Corriu, R. J. P.; Larcher, F.; Royo, G. *J. Organomet. Chem.* **1976**, *104*, 293.

teranion.[39] Current work in this laboratory involves the preparation of suitable precursors with a view to exploring the possible generation of silicenium ions stabilized by metal clusters.

Experimental Section

All syntheses were carried out under a dry nitrogen atmosphere utilizing conventional benchtop and glovebag techniques. Solvents were dried and distilled according to standard procedures.[40] ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded in CD_2Cl_2 on a Bruker AM-500 spectrometer operating at 500, 125.7, and 99.33 MHz, respectively. Infrared spectra were recorded on a Perkin-Elmer 283 instrument using NaCl plates. Fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB-E spectrometer. 3-Nitrobenzyl alcohol was used as the sample matrix, and xenon was the bombarding species (8 keV). Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario, Canada.

(Ph₃SiOH)Cr(CO)₃ (9) and (Ph₃SiOH)[Cr(CO)₃]₂ (10). A 250-mL round-bottom flask was charged with triphenylsilanol (5.54 g, 20.0 mmol), $Cr(CO)_6$ (4.62 g, 21.0 mmol), dry n-butyl ether (130 mL), and dry THF (15 mL). This mixture was heated under reflux for 2 days, after which time the solution was cooled and filtered under vacuum and the solvent removed. The yellow residue was flash chromatographed on silica gel using 1:1 ether/hexane as the eluent to yield, as the first yellow fraction, 9 (1.47 g, 3.57 mmol, 18%): mp 115–116 °C; IR (CH_2Cl_2) ν_{CO} at 1971 and 1896 cm^{-1}; mass spectrum (FAB+): m/z (%) 412 (8) ([M]$^+$, $C_{21}H_{16}$-$CrSiO_4$) 328 (32) ([M – 3CO]$^+$, $C_{18}H_{16}CrSiO$), 199 (45) [($C_{12}H_{11}$-SiO]$^+$). Anal. Calcd for $C_{21}H_{16}CrSiO_4$: C, 61.16; H, 3.91. Found: C, 61.20; H, 3.95. The second yellow fraction gave 10 (0.26 g, 0.47 mmol, 4.7%): mp 170–171 °C; IR (CH_2Cl_2) ν_{CO} at 1972 and 1900 cm^{-1}; mass spectrum (FAB+): m/z (%) 548 (5) ([M]$^+$, $C_{24}H_{16}Cr_2SiO_7$), 464 (18) ([M – 3CO]$^+$), 436 (8) ([M – 4CO]$^+$), 412 (15) ([M – $Cr(CO)_3$]$^+$), 328 (100) ([$C_{18}H_{16}CrSiO$]$^+$), 199 (48) ([$C_{12}H_{11}SiO$]$^+$). Anal. Calcd for $C_{24}H_{16}Cr_2SiO_7$: C, 52.55; H, 2.94. Found: C, 52.80; H, 2.90. Recrystallization of 9 and 10 from CH_2Cl_2 yielded samples suitable for X-ray crystallography.

(Ph₃SiOH)[Cr(CO)₃]₃ (11). A mixture of 9 (2.076 g, 5.04 mmol) and $Cr(CO)_6$ (1.262 g, 5.74 mmol) in dry n-butyl ether (50 mL) and dry THF (5 mL) was heated under reflux for 2 days. After cooling, filtration under vacuum, and removal of solvent, the yellow residue was purified twice by flash column chromatography on silica gel by using, successively, 1:4 ether/hexane and then 1:1 ether/hexane as the eluent. The third yellow band gave 11 (0.218 g, 0.319 mmol, 12%). Recrystallization from ether/hexanes yielded yellow needles: mp 190–191 °C; IR (CH_2Cl_2) ν_{CO} at 1974 and 1904 cm^{-1}; mass spectrum (FAB+) m/z (%) 684 (5) ([M]$^+$), 600 (10) ([M – 3CO]$^+$), 516 (7) ([M – 6CO]$^+$), 488 (6) ([M – 7CO]$^+$), 548 (12) ([M – $Cr(CO)_3$]$^+$), 464 (35) ([M – $Cr(CO)_3$ – 3CO]$^+$), 436 (15) ([M – $Cr(CO)_3$ – 4CO]$^+$), 380 (13) ([M – $Cr(CO)_3$ – 6CO]$^+$), 328 (100) ([M – $2Cr(CO)_3$ – 3CO]$^+$). Anal. Calcd for $C_{27}H_{16}Cr_3SiO_{10}$: C, 47.37; H, 2.36. Found: C, 47.19; H, 2.08.

Protonation of (Ph₃SiOH)[Cr(CO)₃]₃. 11 (50 mg, 0.07 mmol) was dissolved in CD_2Cl_2 (1 mL) in an NMR tube. The sample was cooled to –70 °C in a dry-ice/acetone bath and then protonated with 3–4 drops of triflic acid. Unlike the analogous carbinol systems, there was no immediate color change. The ^{1}H and ^{13}C NMR spectra were recorded at –70 °C but showed merely somewhat broadened peaks slightly deshielded by 1–2 ppm from those of the silanol 11.

Attempted Reaction of (Ph₃SiH)Cr(CO)₃ with Trityl Cation. As described elsewhere,[41] (Ph₃SiH)Cr(CO)₃ was prepared by the reaction of triphenylsilane with $Cr(CO)_6$. A CD_2Cl_2 solution of (Ph₃SiH)Cr(CO)₃ in an NMR tube was treated with trityl fluoroborate, but there was no color change and the NMR spectrum showed only the presence of starting materials.

(Ph₃COH)Cr(CO)₃ (12). A 250-mL round-bottom flask was charged with triphenylcarbinol (1.224 g, 4.7 mmol), $Cr(CO)_6$ (5.171 g, 23.5 mmol), dry n-butyl ether (100 mL), and dry THF (25 mL). This mixture was heated under reflux for 3 days, after which time the solution was cooled and filtered under vacuum and the solvent removed. The yellow residue was flash-chromatographed on silica gel using 5:95 ether/hexane as the eluent to yield, as the first yellow fraction, 12 (1.60 g, 4.04 mmol, 85%): mp 143 °C (lit.[17b] mp 145 °C). X-ray-quality crystals were grown by slow cooling of a dichloromethane solution of 12.

Protonation of (Ph₃COH)[Cr(CO)₃]₃. 12 (75 mg, 0.19 mmol) was dissolved in CD_2Cl_2 (1 mL) in an NMR tube. The sample was cooled to –70 °C in a dry-ice/acetone bath and then protonated with 3–4 drops of triflic acid, whereupon there was an immediate color change from yellow to deep green. The sample was transferred to the spectrometer and the ^{1}H NMR spectra recorded at –50 °C. The data are collected in Table VIII.

X-ray Crystallography. X-ray crystallographic data were collected on a Siemens P4 diffractometer with a rotating anode and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The background measurements were obtained by using a stationary crystal and stationary counter at the beginning and end of the scan, each for 25.0% of the total scan time. The scan type used for complexes 9–11 was θ–2θ, while an ω scan was used for complex 12. In each case a variable scan speed was used, 1.50–14.65°/min in ω for 9 and 10, 1.50–15.00°/min in ω for 11, and 3.00–60.00°/min in ω for 12. Three standard reflections which were measured after every 97 reflections showed no instrument instability and only minor crystal decay. The three silanol complexes were solved by using the direct methods contained in the SHELXTL-Plus program library.[42] The chromium atom in the carbinol complex 12 was found by the Patterson method, and the rest of the non-hydrogen atoms were found by phase expansion. The riding model of hydrogen atoms with fixed isotropic U values is employed for all solutions. The method of refinement was full-matrix least squares in each case. Crystal data collection parameters are listed in Table I. The scattering factors were taken from ref 43.

Supplementary Material Available: Tables of positional parameters for H atoms, thermal parameters, and bond lengths and angles for molecules 9–12 (16 pages). Ordering information is given on any current masthead page.

OM930016G

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