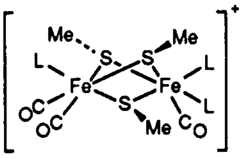
when we found that the new compounds were formed in a reaction of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$ and an additional ligand. Furthermore in this reaction a third species was also detected. The reaction (CH_3CN solution at reflux, 24 h) was

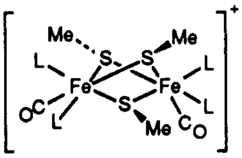
$$[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4 + L \rightarrow [Fe_2(\mu\text{-}SMe)_3(CO)_3(L)_3]BF_4 + [Fe_2(\mu\text{-}SMe)_3(CO)_2(L)_4]BF_4 + CO$$

Carbonyl displacement by a ligand is a reasonable and expected reaction in this situation, so the new species, predictably, have the formulas $[Fe_2(\mu\text{-}SMe)_3(CO)_{4-n}(L)_{2+n}]BF_4$ (n = 1, 2).

Unfortunately, the mixtures of products along with starting materials proved very difficult to separate, so that analytically pure products were not obtained. However, ^1H NMR data provided unequivocal characterizations. For example, the ^1H NMR spectrum of $[Fe_2(\mu\text{-}SMe)_3(CO)_3(PMe_3)_3]BF_4$ consisted of three doublets for the three chemically different phosphines, plus a singlet, doublet, and triplet for the three SCH_3 groups. The multiplicity of these latter resonances result from coupling to zero, one, and two phosphines located trans to the methyl group. The $^{31}P\{^1H\}$ NMR spectrum was also in accord with this formulation, since it contained three resonances that were doublets of doublets, the splitting due to ^{31}P–^{31}P couplings. These spectra uniquely fit the structure



The ^1H and ^{31}P NMR spectra of the third compound $[Fe_2(\mu\text{-}SMe)_3(CO)_2(PMe_3)_4]BF_4$ showed only one type of phosphine. The ^1H NMR spectrum contained one doublet for the phosphine methyl protons, along with two SCH_3 resonances in a 2:1 intensity ratio. The ^{31}P NMR spectrum was a singlet. These data uniquely identify this species as



Knowing the identities of these compounds allows comment on their formation in the electrochemical experiments. Several factors seem to be in evidence. The first is that the presence of water seems to promote this reaction. Water can be present, of course, from the calomel reference electrode. Second, most of the original electrochemical runs were on solutions that had been made up some time earlier and stored for periods up to several days. Control experiments indicated that this is sufficient time for some ligand redistribution to take place. Finally, electrochemical oxidation would presumably give product species that are quite labile, so that free phosphine would likely be generated in these solutions. In this context, note that oxidation products of isoelectronic $[Mn_2(\mu\text{-}SMe)_3(CO)_6]^-$ were found to rapidly decompose. Further we tried, without success, to isolate the products of oxidation of these compounds. All efforts gave only products of decomposition. Decomposition of an oxidation product means that free phosphine is expected to be present in these solutions. The presence of free phosphine also promotes this process.

It is appropriate to add a brief comment on the electrochemistry. The oxidation potential data, given in tabular form (Table I) show predictable trends. A trend in $E_{1/2}$ values is seen on the basis of the nature of the phosphine. This small variation is predictable on the basis of donor ability of the phosphines PMe_3 > PEt_2Ph or PMe_2Ph > PPh_3. Increasing the numbers of phosphines makes it easier to oxidize the complex, again as predicted since phosphines are better electron donors than CO.

Acknowledgment. We thank Dr. Ilene Locker and Dr. Bruce Adams for obtaining the 500-MHz ^1H NMR spectrum and the National Science Foundation for providing partial support for this work (Grant CHE-8615255 to Professor D. H. Evans for support for L.J.L.).

Synthesis and Molecular Structure of a Molybdenum Difluorocarbene Complex, $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OSO_2CF_3$

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Received July 16, 1990

Treatment of $(\eta^5\text{-}C_5R_5)Mo(CO)_3CF_3$ (R = H, Me (**3**)) with Me_3SiOTf in benzene solution at ambient temperature results in precipitation of the corresponding carbene triflate salts $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CF_2)]OTf$ (**1**) and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OTf$ (**4**) in high yield. The solid-state structures of **4** and its trifluoromethyl precursor **3** have been determined. In addition to being the first example of a structurally characterized group VI dihalocarbene complex, the observed lateral orientation of the planar CF_2 carbene moiety with respect to the basal plane in **4** is unprecedented for $CpML_3$(carbene) systems. Crystal data for **3**: orthorhombic, $P2_1cn$, with a = 9.208 (1) Å, b = 9.822 (1) Å, c = 17.176 (2) Å, V = 1553.4 (3) Å^3, Z = 4, R_F = 2.49%, and R_{wF} = 3.52%. Crystal data for **4**: tetragonal, $P4_2/mbc$, with a = 17.895 (2) Å, c = 12.040 (2) Å, V = 3855.5 (10) Å^3, Z = 8, R_F = 3.86%, and R_{wF} = 3.78%.

Introduction

Transition-metal dihalocarbene complexes constitute an unusual subclass of carbene compounds which may exhibit either electrophilic reactivity, as observed for classic heteroatom-substituted "Fischer-type" systems, or nucleophilic reactivity that is normally associated with "Schrock-type" alkylidenes.[1] In addition to addressing

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[1] (a) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (b) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293 and references therein.

fundamental questions concerning carbene structure and bonding, the demonstrated substitutional lability of halide substituents suggests a considerable potential for utilizing dihalocarbenes as metalated carbon atom synthons "$L_nM{=}C$" in organometallic C1 chemistry.[2-4] Despite these considerations, the chemistry of dihalocarbene complexes remains relatively limited in scope and is very much restricted to the late transition metals, particularly those of the iron triad.

In 1978 Reger and Dukes reported that treatment of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)CF_3$ (L = CO, PPh_3) with SbF_5 at −78 °C in liquid SO_2 afforded the thermally unstable hexafluoroantimonate salts $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)(CF_2)]SbF_6$.[5] These complexes are notable for being both the first reported examples of transition-metal difluorocarbenes and the only known examples of dihalocarbene coordination to a d^4 metal center. In retrospect, a comparison of this system with the later metal d^6 dihalocarbene complexes subsequently prepared by Roper,[2] Mansuy,[6] and Shriver[4] would clearly be desirable; however, all attempts to isolate these compounds resulted in decomposition to form $[(\eta^5\text{-}C_5H_5)Mo(CO)_4]^+$ as the sole identifiable product.

We have been interested in exploiting the lability of dihalocarbenes as a route to new bimetallic C1-bridged complexes, particularly those that incorporate both early- and late-metal centers. During the course of our initial work we chose to reexamine the stability of Reger's system. In accordance with his observations, we find that most common fluoride-abstracting reagents (BF_3, CPh_3^+) yield the tetracarbonyl cation as the only isolable major product. However, when $(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_3$ or $(\eta^5\text{-}C_5Me_5)Mo(CO)_3CF_3$ (**3**) was treated with $Me_3SiOSO_2CF_3$ in benzene solution, the carbene triflate salts $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(CF_2)]OSO_2CF_3$ (R = H (**1**), Me (**4**)) precipitated in near-quantitative yield. In this paper we report the characterization of carbene complexes **1** and **4**, the crystal structures of both **4** and its trifluoromethyl precursor **3**, and some brief observations concerning the reactivity of **4**. The solid-state structure of **4** is of particular interest due to the unprecedented lateral orientation of the planar carbene fragment in the four-legged piano-stool basal plane.

Results and Discussion

Complexes $(\eta^5\text{-}C_5R_5)Mo(CO)_3CF_3$ (R = H, Me (**3**)) react cleanly with a 2-fold excess of $Me_3SiOSO_2CF_3$ (TMSOTf) in benzene at room temperature to give the corresponding orange-yellow difluorocarbene salts $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(CF_2)]SO_3CF_3$ (R = H (**1**), Me (**4**)) in high yield according to eq 1. The reaction is complete within a few minutes.

$$(\eta^5\text{-}C_5R_5)Mo(CO)_3CF_3 \xrightarrow[C_6H_6,\ \text{room temp}]{\text{TMSOTf}} [(\eta^5\text{-}C_5R_5)Mo(CO)_3(CF_2)]OTf + TMSF \quad (1)$$
$$R = H, Me$$

One of the keys to the success of this reaction is the use of a nonpolar solvent to precipitate the products as they form, since rapid decomposition occurs in CH_2Cl_2 solution at 20 °C to regenerate $(\eta^5\text{-}C_5R_5)Mo(CO)_3CF_3$ as the major identifiable product. The exact nature of the fluoride-abstracting agent used also appears to be essential; treatment of $(\eta^5\text{-}C_5R_5)Mo(CO)_3CF_3$ with excess $BF_3{\cdot}Et_2O$, $[Ph_3C]BF_4$, or $[Ph_3C]PF_6$ resulted primarily in the formation of tetracarbonyl cations under identical reaction conditions,[7] whereas no reaction was observed between **3** and other potential trimethylsilyl sources, $Me_3SiOC(O)CF_3$ and Me_3SiOSO_2Ph. The reaction of **3** with 1 equiv or more of Me_3SiCl or Me_3SiI gave uncharacterized insoluble precipitates and Me_3SiF. Although the stabilities of **1** and **4** are comparable in the solid state, the solution stability of the permethylated derivative is substantially greater in CH_2Cl_2, with decomposition occurring on the time scale of days for **4** at −20 °C versus just hours for **1**.

^{19}F and ^{13}C NMR spectroscopic data for carbene complexes **1** and **4** in SO_2 solution are in accord with values reported by Reger for the hexafluoroantimonate salt of **1**. Resonances for the CF_2 fluorines appear as singlets at 163.7 (cf. δ 163.6 for $[CpMo(CO)_3(CF_2)]SbF_6$)[5] and 143.3 ppm, respectively, shifted considerably downfield from values for the parent trifluoromethyl complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_3$ (δ 12.3)[8] and **3** (δ 0.7). The resonance for the triflate CF_3 group appears far upfield at −78.9 ppm. The essentially identical chemical shifts observed for both the triflate and SbF_6 salts of $[CpMo(CO)_3(CF_2)]^+$ suggest that there is little or no significant anion interaction with the difluorocarbene ligand for these complexes in solution, consistent with the observed solid-state structure of **4** (vide infra). The ^{13}C NMR spectra of **1** and **4** are particularly diagnostic, with low-field CF_2 carbons appearing as binomial triplets at δ 272.8 ($^1J_{CF}$ = 472 Hz) and 271.8 ($^1J_{CF}$ = 465 Hz). In each complex one of the two carbonyl carbon signals observed is split into a triplet (J = 9 Hz) due to three-bond coupling to the carbene fluorines. For comparison, a quartet with $^3J_{CF}$ = 6 Hz is found for one of the carbonyl carbon resonances of **1**. In contrast to well-known trends correlating ^2J magnitudes with coordination stereochemistry, insufficient literature precedent exists to assign the observed carbonyl resonances as cis or trans based on ^3J values.[9] However, careful integration of the ^{13}C carbonyl resonances for **1** reveals that the fluorine-coupled resonance is due to the cis carbonyls; on the basis of this result the carbonyl resonances for **1** and **4** are similarly assigned.

A comparison of ν(CO) infrared data for **1** and **4** with those for other $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(L)]^+$ complexes supports the conclusion made earlier for d^8 metal systems[1] that the net π-acceptor ability of difluorocarbenes is exceptionally high. ν(CO) values for $[CpMo(CO)_3(CF_2)]^+$ (2105, 2015 cm^{-1}) are substantially higher than those reported for the phosphine and phosphite complexes $[CpMo(CO)_3(PPh_3)]PF_6$ (2025, 1995 cm^{-1})[10] and $[CpMo(CO)_3(P(OMe)_3)]PF_6$ (2070, 1998, 1976 cm^{-1})[11] and are shifted 25 cm^{-1} relative to values reported for the donor-substituted carbene $[CpMo(CO)_3(CH(OMe))]PF_6$ (2081, 1990 cm^{-1}).[12]

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(7) Analysis of product distributions was most conveniently carried out by ^{13}C NMR spectroscopy. $^{13}C\{^1H\}$ NMR (SO_2, 0 °C) data for $[(\eta^5\text{-}C_5Me_5)Mo(CO)_4]^+$: δ 220.07 (CO), 112.58 ($C_5(CH_3)_5$), 11.10 ($C_5(CH_3)_5$).

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Table I. Summary of Crystallographic Data for $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OTf$ (4) and $(\eta^5\text{-}C_5Me_5)Mo(CO)_3CF_3$ (3)

	$C_{15}H_{15}F_5O_6SMo$	$C_{14}H_{15}F_3O_3Mo$
cryst size, mm	0.36 × 0.56 × 0.94	0.54 × 0.60 × 0.74
cryst syst	tetragonal	orthorhombic
space group	$P4_2/mbc$	$P2_1cn$
temp, °C	−100	24
a, Å	17.895 (2)	9.2083 (11)
b, Å		9.8220 (13)
c, Å	12.040 (2)	17.176 (2)
V, Å^3	3855.5 (10)	1553.4 (3)
Z	8	4
ρ_{calc}, g/cm^3	1.772	1.643
wavelength, Å	0.71073	0.71073
mol wt	514.28	384.21
μ, cm^{-1}	8.41	8.59
T_{max}/T_{min}	0.126/0.096	0.128/0.096
2θ range, deg	4.0–46.0	4.0–58.0
scan type	ω	$\omega/2\theta$
scan range, deg	2.2	2.0
no. of rflns measd	5823	4533
no. of unique rflns	1420	4161
no. of rflns with $F > 6.0\sigma(F)$	1252	3469
R_F, %	3.86	2.49
R_{wF}, %	3.78	3.52
goodness of fit	2.44	1.04

ν(CF) values have also been used as an indicator of CF_2 acceptor ability among similar compounds, with low-energy bands being correlated with long C–F bonds and electrophilic carbene reactivity.[1] For both **1** and **4**, bands appear at 1270 and 1032 cm^{-1} that are readily assigned to the triflate counteranion. Assignment of one of the two remaining bands at 1195, 1155 cm^{-1} for **1** and 1142, 1133 cm^{-1} for **4** to the CF_2 unit is uncertain due to the presence of a third triflate mode that appears to be sensitive to the nature of the associated cation.[13] However, all these bands are in the middle of the range observed previously for difluorocarbenes (980–1233 cm^{-1}).[1b]

No changes in the ^{19}F NMR spectra for **1** and **4** are observed down to −70 °C. Thus, the single fluorine resonances observed are consistent with either a lateral ground-state orientation of the CF_2 moiety in the piano-stool basal plane or a low barrier to rotation about the Mo–carbene bond on the NMR time scale. Since low carbene rotational barriers have been observed for both $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(CF_2)]BF_4$[4b] and $[(\eta^5\text{-}C_5H_5)Mo(PPh_3)(CO)_2(CH_2)]OSO_2CF_3$,[14] the crystal structure of **4** was carried out to determine the difluorocarbene orientation in the solid state and to compare CF_2 bonding parameters with metrical data reported for d^6 transition-metal dihalocarbene coordination. The trifluoromethyl complex **3** has also been structurally characterized and provides the first direct comparison of a dihalocarbene with its trihalomethyl precursor.[15]

Crystallographic Studies. Crystal and data collection parameters for compounds **3** and **4** are summarized in Table I. Atomic coordinates and selected structural parameters are given in Tables II–IV. ORTEP representations are given in Figures 1 and 2. The overall coordination

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $(\eta^5\text{-}C_5Me_5)Mo(CO)_3CF_3$ (3)

atom	x	y	z	U^a
Mo	2656	2300 (1)	1467 (1)	35 (1)
C(1)	2370 (3)	314 (3)	1259 (2)	49 (1)
O(1)	2284 (4)	−819 (3)	1117 (2)	77 (1)
C(2)	3628 (4)	1432 (4)	2370 (2)	50 (1)
O(2)	4205 (4)	946 (3)	2891 (2)	79 (1)
C(3)	1511 (4)	2980 (4)	2385 (2)	56 (1)
O(3)	892 (4)	3405 (4)	2902 (2)	88 (1)
C(4)	336 (6)	2175 (5)	1066 (3)	56 (1)
F(1)	158 (3)	1750 (3)	314 (2)	76 (1)
F(2)	−405 (3)	3369 (3)	1077 (2)	79 (1)
F(3)	−542 (3)	1317 (4)	1476 (2)	84 (1)
C(11)	4714 (4)	3640 (4)	1374 (2)	47 (1)
C(12)	4861 (5)	2536 (4)	842 (3)	43 (1)
C(13)	3755 (4)	2690 (3)	261 (2)	47 (1)
C(14)	2961 (3)	3889 (4)	440 (2)	55 (1)
C(15)	3542 (4)	4469 (3)	1123 (3)	57 (1)
C(11M)	5762 (5)	3942 (5)	2019 (3)	75 (2)
C(12M)	6036 (4)	1486 (5)	833 (3)	63 (1)
C(13M)	3595 (6)	1842 (6)	−461 (2)	75 (2)
C(14M)	1863 (5)	4552 (6)	−83 (3)	90 (2)
C(15M)	3138 (6)	5809 (4)	1479 (3)	92 (2)

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

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OTf$ (4)

atom	x	y	z	U^a
Mo	4928 (1)	2155 (1)	10000	36 (1)
C(1)	4071 (4)	2273 (4)	8885 (6)	70 (2)
O(1)	3594 (3)	2364 (3)	8310 (5)	119 (3)
C(3)	5292 (9)	1402 (9)	8841 (13)	74 (4)
O(3)	5538 (7)	997 (8)	8157 (12)	128 (4)
C(2)	4943 (8)	1208 (7)	10828 (12)	72 (5)
F(1)	4648 (5)	1047 (5)	11798 (8)	111 (4)
F(2)	5362 (6)	611 (5)	10715 (11)	160 (7)
C(11)	6160 (4)	2534 (4)	10000	39 (2)
C(12)	5813 (2)	2847 (3)	9047 (4)	35 (1)
C(13)	5259 (2)	3368 (2)	9411 (4)	33 (1)
C(11M)	6841 (4)	2031 (5)	10000	60 (3)
C(12M)	6062 (3)	2760 (3)	7864 (4)	58 (2)
C(13M)	4833 (3)	3896 (3)	8688 (4)	43 (2)
S	3084 (1)	5179 (1)	10000	43 (1)
O(4)	3368 (2)	5499 (2)	11000 (3)	69 (1)
O(5)	3021 (3)	4374 (3)	10000	66 (2)
C(20)	2129 (5)	5476 (6)	10000	74 (4)
F(3)	2097 (4)	6231 (4)	10000	142 (4)
F(4)	1757 (2)	5242 (3)	10875 (4)	125 (2)

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

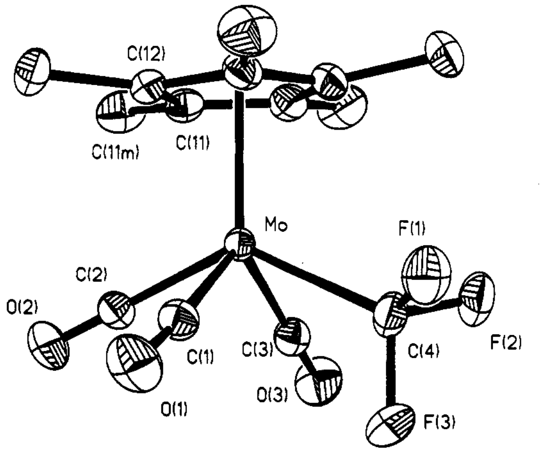

Figure 1. ORTEP view of $(\eta^5\text{-}C_5Me_5)Mo(CO)_3CF_3$ (3) with atom-labeling scheme. Ellipsoids are drawn at the 30% probability level.

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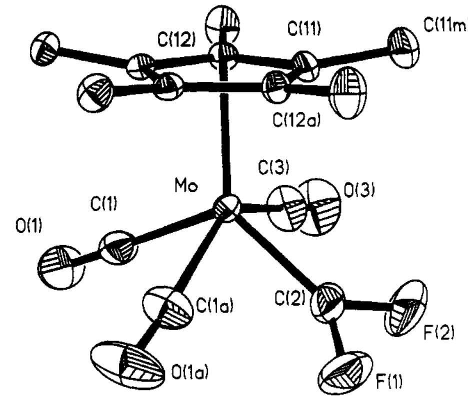

Figure 2. ORTEP view of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OTf$ (4) with atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. The triflate counteranion has been omitted for clarity.

geometry of both 3 and 4 is that of a normal four-legged piano-stool complex or Cp-capped square pyramid. No close (<3.28-Å) intermolecular contacts were observed between $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]^+$ and the triflate counteranion. Mo–C(ring) distances for 3 (2.309 (5)–2.372 (4) Å, average 2.338 Å) and 4 (2.307 (7)–2.360 (4) Å, average 2.321 Å) do not differ significantly from the range of values found for other Mo(II) pentamethylcyclopentadienyl complexes (2.320–2.372 Å).[16] A clear difference in the ring rotational conformation is evident when both molecules are viewed along the Mo–ring centroid axis (Figure 3). Whereas 3 adopts the commonly observed configuration for $CpM(CO)_3X$ molecules, having the CF_3 group eclipsed with one ring carbon and the trans carbonyl bisecting the opposite bond, the reverse is true for 4. Since it has been inferred from prior work that the best π-acceptor assumes the bisecting position,[17] one might be tempted to conclude that the CF_2 group in 4 has a comparable π-acceptor ability with CO. This inference taken by itself is entirely circumstantial but is nevertheless consistent with IR data and further structural observations discussed below.

An additional significant point of departure between the two structures 3 and 4 concerns the trans angles, L–Mo–CO. For 3, the angles for trans CF_3–Mo–CO (130.2°) and trans CO–Mo–CO (113.3°) fall within the normal ranges observed for $CpM(CO)_3L$ structures (L–M–CO, 125–133°; CO–M–CO, 105–117°).[17,18] In the difluorocarbene complex 4 the relative magnitudes for L–Mo–CO are reversed with the angle for trans CF_2–Mo–CO (115.6°) being considerably more acute relative to that of CO–Mo–CO (138.9°). Calculations by Hoffmann[17] on $CpMo(CO)_3Me$ and more recent work by Poli[18] indicate that the increase in the L–Mo–CO angle may be attributed to the loss of metal d(xy) and d(z^2) π-acceptor interactions relative to $CpMo(CO)_4^+$. These observations again would appear to reflect substantial carbene π-acceptor behavior for 4. It should be noted that although a crystallographically imposed disorder between the CF_2 group and the C(3)–O(3) carbonyl group by a bisecting mirror plane (see Experimental Section) should result in a secondary disorder for the remaining C(1)–O(1) group due to an averaging of the different geometrical constraints imposed by the two different trans groups, no such disorder is in fact observed.[19] This fortuitous result would seem to indicate that the "angular trans influences"[18] of CF_2 and CO ligands in this molecule either are very similar or are masked by solid-state effects.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-}C_5Me_5)Mo(CO)_3CF_3$ (3) and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OTf$ (4)

	$(\eta^5\text{-}C_5Me_5)$-$Mo(CO)_3CF_3$	$[(\eta^5\text{-}C_5Me_5)$-$Mo(CO)_3(CF_2)][OTf]$
	Bond Distances	
Mo–C(1)	2.001 (3)	2.049 (7)
Mo–C(2)	1.983 (4)	1.965 (13)
Mo–C(3)	2.010 (4)	2.046 (16)
Mo–C(4)	2.248 (5)	
Mo–C(11)	2.312 (3)	2.307 (7)
Mo–C(12)	2.309 (5)	2.316 (4)
Mo–C(13)	2.338 (3)	2.360 (4)
Mo–C(14)	2.372 (4)	
Mo–C(15)	2.357 (4)	
C(11)–C(12)	1.424 (5)	1.421 (6)
C(12)–C(13)	1.434 (6)	1.430 (6)
C(13)–C(14)	1.420 (5)	
C(14)–C(15)	1.409 (6)	
C(15)–C(11)	1.419 (5)	
C(13)–C(13A)		1.419 (9)
C(11)–C(11M)	1.499 (6)	1.514 (10)
C(12)–C(12M)	1.494 (6)	1.500 (7)
C(13)–C(13M)	1.500 (6)	1.493 (6)
C(14)–C(14M)	1.501 (6)	
C(15)–C(15M)	1.498 (6)	
C(1)–O(1)	1.141 (4)	1.110 (9)
C(2)–O(2)	1.145 (5)	
C(3)–O(3)	1.135 (5)	1.182 (21)
C(4)–F(1)	1.368 (5)	
C(4)–F(2)	1.357 (6)	
C(4)–F(3)	1.363 (6)	
C(2)–F(1)		1.313 (17)
C(2)–F(2)		1.313 (16)
CNT-Mo[a]	2.001	1.993
	Bond Angles	
C(1)–Mo–C(2)	77.3 (1)	115.6 (5)
C(1)–Mo–C(3)	113.3 (1)	81.9 (5)
C(1)–Mo–C(4)	76.5 (2)	
C(2)–Mo–C(3)	76.5 (2)	77.0 (6)
C(2)–Mo–C(4)	130.2 (2)	
C(3)–Mo–C(4)	76.1 (2)	
C(1)–Mo–C(1A)		81.9 (4)
C(1)–Mo–C(3A)		138.9 (5)
C(2)–Mo–C(1A)		76.5 (5)
Mo–C(1)–O(1)	175.9 (3)	176.7 (6)
Mo–C(2)–O(2)	179.0 (3)	
Mo–C(3)–O(3)	177.6 (4)	175.9 (14)
Mo–C(4)–F(1)	114.8 (3)	
Mo–C(4)–F(2)	115.2 (3)	
Mo–C(4)–F(3)	116.0 (3)	
Mo–C(2)–F(1)		129.4 (10)
Mo–C(2)–F(2)		131.1 (11)
F(1)–C(4)–F(2)	102.5 (4)	
F(1)–C(4)–F(3)	103.2 (4)	
F(2)–C(4)–F(3)	103.2 (4)	
F(1)–C(2)–F(2)		98.2 (11)
CNT-Mo-C(1)	121.7	114.5
CNT-Mo-C(2)	114.3	129.8
CNT-Mo-C(3)	125.0	106.6
CNT-Mo-C(4)	115.5	

[a] CNT-centroid of cyclopentadienyl ring.

No exceptional differences in trifluoromethyl ligation are noted between complex 3 and other crystallographically

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(17) Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

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(19) No unusual elongation of the anisotropic thermal parameters for C(1) and O(1) attributable to variation in the CO–Mo–L angle are observed; see Figures 2 and 3.

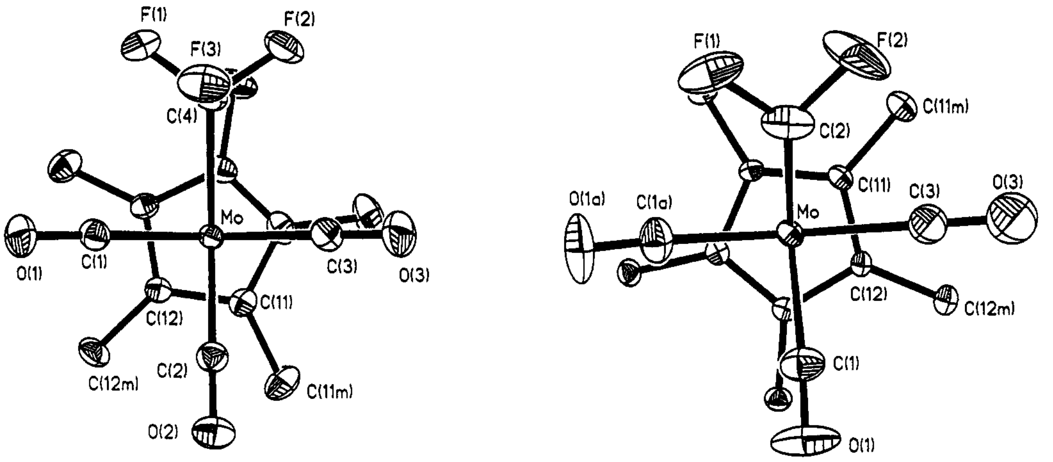
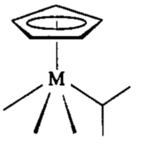


Figure 3. ORTEP view of molecules 3 (left) and 4 (right) in views down the Mo–(ring centroid) axes.

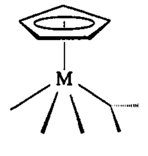
characterized Mo(II) fluoroalkyls. The observed Mo–C(4) distance of 2.248 (5) Å is intermediate between the reported values for $CpMo(^tBuNC)(\eta^4\text{-}^tBuN\overline{C(C(CF_3))_3C}\text{-}(CF_3))$ (2.27 (2), 2.22 (2) Å)[20] and $CpMo(CO)_3(C_3F_7)$ (2.28 (1) Å).[21] No significant distortion of Mo–C(4)–F angles or unusual lengthening of any of the C(4)–F bonds are apparent that would suggest the presence of incipient carbene character in the CF_3 moiety.

Although disorder between the CF_2 and C(3)–O(3) groups in 4 lowers the precision of metrical parameters obtained for the carbene group, the values obtained compare favorably with the small number of reported difluorocarbene structures.[1a,4b,15,22] Consistent with trends previously noted for other difluorocarbene complexes, the Mo–C(2) carbene bond distance of 1.965 (13) Å is 0.08 Å less than the Mo–carbonyl distances and almost 0.28 Å shorter than the Mo–CF_3 distance found for 3. Short M–difluorocarbene bonds have been previously attributed to multiple bonding derived from dπ–pπ interactions and/or hybridization effects (Bent's rule).[1b,4b] Since any Mo–CF_2 bond shortening due to fluorine substitution in 4 should be at least matched by an analogous shortening of the Mo–CF_3 bond in 3, the observed 0.28-Å difference between the two complexes cannot be simply accounted for by carbon hybridization differences ($C(sp^3) - C(sp^2) \approx 0.03$ Å)[23] and may be attributed to a substantial multiple bonding component between molybdenum and the difluorocarbene unit. The presence or absence of any π-donation between the fluorine and the carbene center in 4 as well as in other difluorocarbene complexes cannot be addressed due to the limited precision and number of data sets available for comparison.

The most unique feature in the structure of 4 is the disposition of the CF_2 group with respect to the $(\eta^5\text{-}C_5Me_5)Mo(CO)_3$ fragment. The observed angles for F(1)–C(2)–F(2), Mo–C(2)–F(1), and Mo–C(2)–F(2) (98.2 (11), 129.4 (10), and 131.1 (11)°, respectively, sum 358.7°) show that the carbene unit is essentially planar and symmetrical with respect to the Mo–C(2) axis. However, in contrast to all structurally characterized examples of four-legged piano-stool structures with single-faced π-acceptor ligands, which adopt an "upright" ligand orientation as in structure A,[24] complex 4 adopts the alternative lateral carbene orientation B with an angle of 80° between the carbene plane and the plane defined by Mo, C(2), and the ring centroid. This conformation preference is evidently not steric in origin, since $CpML_3$(carbene) complexes with both larger (*trans*-$CpMo(CO)_2(GePh_3)(C(OEt)Ph)$)[24a] and smaller ([*trans*-$CpW(CO)_2(PR_3)(CH_2)]^+$)[14] carbene substituents exhibit the ground-state geometry A. Hoffmann has analyzed conformation preferences for $CpML_3$(carbene) systems in terms of effective overlap between a ligand orbital of pπ symmetry and dπ orbitals d(xy) and d(z^2).[17] In his analysis maximum overlap for d(xy) occurs at θ = 90° (proportional to sin θ) and at θ = 45 and 135° for d(z^2) (proportional to sin 2θ), where θ is the centroid–M–ligand angle. Consistent with these predictions, overlap for $CpMo(GePh_3)(CO)_2(C(OEt)Ph)$, with $\theta \approx 114°$, was found to be more optimal for d(xy), in accord with the observed geometry A. Since θ = 130° for 4, it seems reasonable that in this instance the optimal overlap is obtained with the d(z^2) orbital by adopting the lateral geometry B.



A



B

Although our initial goal of accessing isolable group VI difluorocarbene systems has been realized, a preliminary survey of the reactivity of 4 with a range of substrates is disappointing. No identifiable products were observed in the reaction of 4 with potential nucleophiles and/or metathesis agents such as $Na[(Bu)(^iBu)_2AlH]$, $Li[Et_3BH]$, MeLi, or PhLi. Attempts to form μ-CF_2 bimetallic compounds via reactions with $(C_5H_4Me)Mn(CO)_2(THF)$, $((Cy)_3P)_2Pt$, or $(Ph_3P)_2Pt(C_2H_4)$ were similarly unsuccessful. The only moderately clean reaction observed thus far for 4 is with excess $HOCH_2CH_2OH$ in CH_2Cl_2 to give a 3:1 mixture of products, the minor component being the tetracarbonyl cation $[(\eta^5\text{-}C_5Me_5)Mo(CO)_4]^+$. The major component in this reaction is tentatively identified as the

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cyclic carbene complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_3(\overline{\text{COCH}_2\text{CH}_2\text{O}})]^+$ (see Experimental Section).

The lack of clean derivative chemistry for carbene complexes 1 and 4 is not very surprising in view of their pronounced solution thermal sensitivity and unusual counteranion specificity. However, the enhanced stability of the more electron-rich permethylated complex 4 compared to that of 1 is notable and suggests that further increasing the electron density via the incorporation of donor phosphine substituents may yield stable difluorocarbene systems more amenable to study. Efforts along these lines as well as further investigations of the parent systems are currently in progress.

Experimental Section

General Considerations. All manipulations were conducted under an atmosphere of nitrogen by using Schlenk, high-vacuum-line and/or glovebox techniques.[25] Glassware utilized in the synthesis of carbene complexes 1 and 4 was flame-dried under high vacuum prior to use in order to minimize hydrolysis side reactions. DME and benzene were stored over sodium–benzophenone ketyl and vacuum-distilled prior to use. CH_2Cl_2, SO_2, and $(CF_3CO)_2O$ were dried and vacuum-distilled from P_2O_5. $Me_3SiOSO_2CF_3$ (Aldrich) was used as received and stored under nitrogen. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on a Mattson Cygnus 100 FTIR instrument as Nujol mulls unless otherwise noted. NMR spectra were obtained with a JEOL GSX-400 instrument. Spectra taken in liquid SO_2 were locked and referenced to acetone-d_6 sealed in a capillary. ^{19}F spectra were referenced to $CFCl_3$ as an external standard with downfield chemical shifts taken to be positive. $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{CF}_3$ was prepared by following a literature procedure.[8]

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3(\text{CF}_2)]\text{OSO}_2\text{CF}_3$ (1). A solution of $CpMo(CO)_3CF_3$ (0.100 g, 0.31 mmol) in 20 mL of benzene was treated with $Me_3SiOSO_2CF_3$ (0.133 g, 0.60 mmol) via syringe at room temperature. Within 5 min yellow crystalline 1 began to precipitate. After the mixture was stirred for 1 h, the solid was filtered off, washed with benzene, and dried under vacuum. Complex 1 may be stored in the solid state at room temperature for several days without significant decomposition and may be stored indefinitely at −20 °C under nitrogen. 1 decomposes rapidly in dichloromethane solution within 1–2 h at −20 °C but may be kept in liquid SO_2 at 0 °C for several days without any noticeable spectroscopic changes. IR (Nujol, cm^{-1}): 2105 m, 2015 s, 1270 s, 1195 m, 1155 m, 1032 m. ^1H NMR (SO_2, 0 °C): δ 6.42 (s). ^{19}F NMR (SO_2, 0 °C): δ 163.7 (s; $\text{C}\mathit{F}_2$), −77.8 (s; $\text{OSO}_2\text{C}\mathit{F}_3$). ^{13}C NMR (SO_2, 0 °C): δ 272.8 (t, $^1J_{CF}$ = 472 Hz; $\mathit{C}\text{F}_2$), 209.4 (t, $^3J_{CF}$ = 9 Hz; CO's cis to CF_2), 207.9 (s; CO trans to CF_2), 117.2 (q, $^1J_{CF}$ = 319 Hz; $\text{OSO}_2\mathit{C}\text{F}_3$), 93.0 (dt, $^1J_{CH}$ = 186 Hz, $^3J_{CH}$ = 6 Hz; $\mathit{C}_5\text{H}_5$).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_3(\text{C(O)CF}_3)$ (2). A mixture of 1.35 g (5.1 mmol) of $Mo(CO)_6$ and 0.70 g (4.9 mmol) of $[C_5Me_5]Li$ was refluxed in 150 mL of DME for 12 h. Evolution of CO was observed during this time, and a dark orange-yellow solution resulted. The solution was cooled to −78 °C, and 2.10 g of (trifluoromethyl)acetic anhydride (10.0 mmol) was added by vacuum transfer. Upon addition, the solution turned red and was slowly warmed to room temperature and stirred overnight. After removal of volatiles under vacuum, the resulting residue was extracted with several portions of petroleum ether until the extracts were colorless. Concentrating the combined extracts and cooling to −78 °C yielded 1.50 g (71%) of crystalline orange-yellow product (mp 64–65 °C). The compound may be briefly exposed to air in the solid state and is best stored under nitrogen. Anal. Calcd for $C_{15}H_{15}F_3MoO_4$: C, 43.71; H, 3.67; F, 13.83. Found: C, 43.72; H, 3.65; F, 14.11. IR (Nujol, cm^{-1}): 2016 s, 1949 vs, 1637 m, 1221 m, 1172 m, 1128 m, 833 m, 710 m. ^1H NMR ($CDCl_3$): δ 1.97 (s). ^{19}F NMR ($CDCl_3$): δ −80.5 (s).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_3\text{CF}_3$ (3). The solid-state thermal decarbonylation of 2 under nitrogen was monitored by ^{19}F NMR spectroscopy. After 4–6 h at 110 °C, decarbonylation is virtually quantitative to give the yellow trifluoromethyl complex 3 in a purity suitable for most purposes. An analytical sample was recrystallized from petroleum ether (mp 165–167 °C dec). Like 2, 3 may be exposed to air for brief periods. Due to photosensitivity, compound 3 is best stored under nitrogen in the dark. Anal. Calcd for $C_{14}H_{15}F_3MoO_3$: C, 43.77; H, 3.94; F, 14.83. Found: C, 43.59; H, 3.82; F, 14.58. IR (Nujol, cm^{-1}): 2032 s, 1946 s, 1926 s, 1047 s, 993 sh, 981 s. ^1H NMR (C_6D_6): δ 1.65 (s). ^{19}F NMR (C_6D_6): δ 0.7 (s). ^{13}C NMR (C_6D_6): δ 242.47 (s; CO trans to CF_3), 232.26 (q, $^3J_{CF}$ = 6 Hz; CO's cis to CF_3), 154.31 (q, $^1J_{CF}$ = 368 Hz; $\mathit{C}\text{F}_3$), 108.49 (s; $\mathit{C}_5(\text{CH}_3)_5$), 11.40 (q, $^1J_{CH}$ = 128 Hz; $\text{C}_5(\mathit{C}\text{H}_3)_5$).

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_3(\text{CF}_2)]\text{OSO}_2\text{CF}_3$ (4). Carbene complex 4 was synthesized by a procedure analogous to that used for carbene 1. The yield starting from 0.340 g (0.89 mmol) of 3 after washing and drying under vacuum was 0.400 g (0.78 mmol, 87%) of orange-yellow crystalline solid, which could be stored at −20 °C under nitrogen for several months without noticeable decomposition. Solutions of 4 in CH_2Cl_2 at −20 °C showed little spectroscopic change after 1 week; SO_2 solutions at 0 °C can be stored for longer periods. Recrystallization from CH_2Cl_2 at −55 °C afforded large orange prisms suitable for crystallographic analysis. IR (Nujol, cm^{-1}): 2099 s, 2040 vs, 1272 vs, 1225 w, 1142 s, 1133 s, 1032 s. ^1H NMR (SO_2, 0 °C): δ 2.53 (s). ^{19}F NMR (SO_2, 0 °C): δ 143.3 (s; $\text{C}\mathit{F}_2$), −77.8 (s; SO_3CF_3). ^{13}C NMR (SO_2, 0 °C): δ 270.5 (t, $^1J_{CF}$ = 465 Hz; $\mathit{C}\text{F}_2$), 216.0 (t, $^3J_{CF}$ = 9 Hz; CO's cis to CF_2), 213.3 (s; CO trans to CF_2), 121.1 (q, $^1J_{CF}$ = 320 Hz; $\text{SO}_3\mathit{C}\text{F}_3$), 112.2 (s, $\mathit{C}_5(\text{CH}_3)_5$), 11.2 (q, $^1J_{CH}$ = 130 Hz; $\text{C}_5(\mathit{C}\text{H}_3)_5$).

Reaction of 4 with Ethylene Glycol. A 100-mg amount of carbene complex 4 in ca. 3 mL of CH_2Cl_2 was treated with 15 μL of $HOCH_2CH_2OH$ at −78 °C. When this mixture was warmed to ambient temperature, a homogeneous light yellow solution was obtained. After removal of the volatiles, ^{13}C NMR analysis of the crude product revealed a 3:1 mixture of two products, the minor product being the tetracarbonyl cation $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_4]^+$. The main product has been tentatively identified as the cyclic carbene complex $[\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_3(\overline{\text{COCH}_2\text{CH}_2\text{O}})]\text{OTf}$. ^{13}C NMR of major product (CD_2Cl_2, 25 °C): δ 245.37 (s; $\mathit{C}(\text{OCH}_2\text{CH}_2\text{O})$), 232.73 (s; CO), 226.65 (s; CO), 109.41 (s; $\mathit{C}_5(\text{CH}_3)_5$), 74.27 (t, $^1J_{CH}$ = 161 Hz; $\text{O}\mathit{C}\text{H}_2\mathit{C}\text{H}_2\text{O}$), 10.88 (q, $^1J_{CH}$ = 131 Hz; $\text{C}_5(\mathit{C}\text{H}_3)_5$).

Crystal Structure Determinations. X-ray data were collected on a Nicolet R3m/V automated diffractometer system with a dedicated Micro VAX II computer system and fitted with an LT-2 low-temperature device. The radiation used was Mo Kα monochromatized by a highly-ordered graphite crystal. The parameters used during collection of diffractometer data for complexes 3 and 4 are summarized in Table I. All computations used the SHELXTL PLUS (Version 3.4) program library (Nicolet Corp., Madison, WI).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Mo(CO)}_3\text{CF}_3$ (3). A large light yellow block (0.54 × 0.60 × 0.74 mm) grown from benzene by slow evaporation was sealed in a glass capillary under nitrogen. Orthorhombic unit cell dimensions were derived from a least-squares fit of 46 random strong reflections ($22° \le 2\theta \le 30°$). A total of 4161 unique reflections were collected in the range $4 \le 2\theta \le 58°$ with indices $+h,+k,+l$ by using the $\omega/2\theta$ scan technique with a variable scan rate of 3.0–30.0° min^{-1}. Systematic absences for the total data set were consistent with either space group *Pmcn* or $P2_1cn$. Subsequent successful refinement in $P2_1cn$ (an alternative setting of $Pna2_1$ (No. 33), related by $(x, y, z) \rightarrow (z, y, -x)$) indicated that the acentric space group with $Z = 4$ and no crystallographically imposed molecular mirror plane was the correct choice. Three standard reflections monitored after every 100 data collected showed no systematic variation. Data were corrected for absorption with use of an empirical ellipsoidal model based on φ scans for 12 reflections with $10° \le 2\theta \le 44°$.

The structure of 3 was solved with use of SHELXTL PLUS direct-methods software, which revealed almost all the non-hydrogen atoms on the initial *E* map. All remaining non-hydrogen atoms were located in subsequent difference Fourier maps and were refined anisotropically. Hydrogen atom positions were added in ideal calculated positions (d(C–H) = 0.96 Å) with methyl hydrogens refined as a rigid group. All hydrogen isotropic thermal parameters were set to approximately 1.2 times the isotropic equivalent of the associated carbon atom. Full-matrix least-

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[25] All reactions were carried out under a reduced ambient pressure of approximately 590 Torr (7200-ft elevation).

Organometallics 1991, *10*, 597–608 597

squares refinement gave an R value of 0.025 (R_w = 0.035) for 3469 data with $I > 3\sigma(I)$. The final Fourier difference map showed no peaks greater than ±0.49 e/Å^3.

[(η^5-C_5Me_5)Mo(CO)$_3$(CF_2)]SO_3CF_3 (4). An orange prism of 4 measuring 0.36 × 0.56 × 0.94 mm was obtained by slow cooling of a CH_2Cl_2 solution to −55 °C. Mounting in a glass capillary under nitrogen and cooling to −100 °C for alignment and data collection was carried out quickly in order to minimize decay of the thermally sensitive compound. Random centering on 48 strong reflections (22° ≤ 2θ ≤ 30°) suggested a tetragonal unit cell; 4/*mmm* Laue symmetry was confirmed by examination of ±*h*,±*k*,±*l* and ±*k*,±*h*,±*l* equivalent reflections. A total of 5823 redundant data were collected with use of a variable ω scan rate of 6.0–30.0° min^{-1} with indices ±*h*,±*k*,±*l*, giving 1420 unique reflections (R_{int} = 0.016). Three standard reflections monitored after every 100 data collected showed no systematic variation. The data were corrected for absorption by using the semiempirical φ-scan method. Systematic absences were consistent with either $P4_2/mbc$ or $P4_2bc$. A direct-methods solution in $P4_2/mbc$ followed by a series of difference Fourier maps placed all non-hydrogen atoms. Although full anisotropic refinement in $P4_2bc$ with all hydrogen atoms placed in idealized positions gave a low final R value of 0.034, the η^5-C_5Me_5 ring and the C(3)–O(3) carbonyl group were highly distorted. In the alternative centrosymmetric space group $P4_2/mbc$, a crystallographically imposed mirror plane bisects both the molybdenum complex and the triflate counteranion and requires disorder between the difluorocarbene and the C(3)–O(3) carbonyl ligands. Nevertheless, full refinement in this space group yielded a structure with no significant distortions and indicated that $P4_2/mbc$ was the correct choice. Due to moderate correlation between the anisotropic thermal coefficients of F(2) and O(3), both C(3) and O(3) were made isotropic for the final stages of refinement, which gave a final R value of 0.039 by use of 1252 reflections with $I > 3\sigma(I)$. The final Fourier difference map revealed a residual peak of 1.13 e/Å^3 associated with the triflate counteranion, with no other peak greater than 0.51 e/Å^3.

Acknowledgment. This work has been supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the NSF EPSCoR program (Grant No. RII-8610680). We would like to thank Drs. J. Korp and B. Santarsiero for valuable assistance and discussions concerning the crystallography of 4.

Supplementary Material Available: Tables of complete data collection parameters (Tables S1 and S5), bond angles (Tables S2 and S6), anisotropic thermal parameters (Tables S3 and S7), and hydrogen atom coordinates and isotropic thermal parameters (Tables S4 and S8) (13 pages); listings of calculated and observed structure factors (Tables S9 and S10) (20 pages). Ordering information is given on any current masthead page.

Sterically Crowded Aryloxide Compounds of Aluminum: Electronic and Steric Effects

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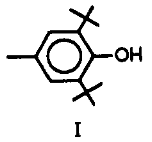
Received July 11, 1990

The mononuclear, four-coordinate aluminum compounds $AlR_2(BHT)L$ and $AlR(BHT)_2L$ [R = Me, Et; BHT = 2,6-di-*tert*-butyl-4-methylphenoxide; L = 2-Mepy, 4-Mepy, 2,6-Me_2py, CH_3CN, $N(C_2H_4)_3CH$, $HNEt_2$, HN^iBu_2, H_2N^tBu, H_2N^nBu, NH_3, py·O] are obtained when AlR_3 is treated with the correct molar equivalent of BHT–H and the appropriate Lewis base. The aluminum–methyl ^{13}C NMR chemical shift for the monoaryloxide compounds $AlMe_2(BHT)L$ is dependent primarily on the steric bulk of the Lewis base. The reaction of $AlMe_3$ with pentafluorophenol yields $[Me_2Al(\mu\text{-}OC_6F_5)]_2$. Cleavage of the phenoxide-bridged dimer by $N(C_2H_4)_3CH$ leads to the formation of the Lewis acid–base complex. The molecular structures of $AlMe_2(BHT)(2,6\text{-}Me_2py)$ (**4**), $AlEt_2(BHT)(H_2N^tBu)$ (**16**), $AlEt_2(BHT)(py{\cdot}O)$ (**19**), $AlMe(BHT)_2(py{\cdot}O){\cdot}{}^1/_2CH_2Cl_2$ (**20**), and $AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$ (**23**) have been determined by X-ray crystallography. The relationship between Al–O bond distances, Al–O–C bond angles, and the presence of Al–O π-bonding is discussed. Crystal data for **4**: monoclinic, $P2_1/n$, a = 9.994 (2) Å, b = 21.647 (4) Å, c = 10.822 (2) Å, β = 93.74 (2)° (198 K), Z = 4, R = 0.058, R_w = 0.066. Crystal data for **16**: monoclinic, $P2_1/n$, a = 9.025 (2) Å, b = 13.862 (2) Å, c = 19.339 (4) Å, β = 96.60 (1)° (183 K), Z = 4, R = 0.060, R_w = 0.068. Crystal data for **19**: monoclinic, $P2_1/n$, a = 9.630 (2) Å, b = 18.232 (4) Å, c = 13.980 (3) Å, β = 101.62 (2)° (173 K), Z = 4, R = 0.055, R_w = 0.055. Crystal data for **20**: monoclinic, $C2/c$, a = 25.025 (4) Å, b = 16.877 (3) Å, c = 19.261 (5) Å, β = 117.59 (2)° (193 K), Z = 8, R = 0.073, R_w = 0.077. Crystal data for **23**: triclinic, $P\bar{1}$, a = 6.9822 (6) Å, b = 9.4896 (8) Å, c = 12.7230 (9) Å, α = 93.140 (6)°, β = 94.650 (6)°, = 102.580 (7)° (183 K), Z = 2, R = 0.039, R_w = 0.044.

Introduction

Recent work in our laboratories has been concerned with the synthesis and characterization of aluminum aryloxide compounds derived from 2,6-di-*tert*-butyl-4-methylphenol (I) (BHT–H from the trivial name butylated hydroxytoluene).[2–4] The use of this sterically hindered aryloxide ligand allows for the isolation of monomeric four-coordi-



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