(1)° to the least-squares plane of the acac ring.

Bond distance between the α and β carbons of the naphthalene ring are shorter than the β–β bonds observed in other naphthalene derivatives.[10] The naphthalene ring inclines slightly as the benzo group approaches N(2), and their dihedral angle is 87.6 (1)° to the least-squares plane of the acac ring. Since the inclination of the aromatic ring results in only a slight change in the direction of polarization, it seems to contribute little to the rotational strength of these complexes in the present series.[6]

Acknowledgment. This research was supported in part by a Scientific Research Grant from the Ministry of Education to which the authors' thanks are due.

Registry No. I·2BF$_4$·2H$_2$O, 80327-54-4.

Supplementary Material Available: A listing of observed and calculated structure factors and tables of thermal parameters (Table III), observation of Bijvoet pairs (Table IV), possible hydrogen bonds (Table V), interatomic distances outside of the molecule (Table VI), nonessential bond lengths and angles (Table VIII) (24 pages). Ordering information is given on any current masthead page.

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[10] Harata, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2747. Ferraris, G.; John, D. W.; Yerkess, J.; Bartle, K. D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1628 and literature cited in these references.

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Crystal Structure of the Axial (Orange-Yellow) Isomer of Bis(methyldiphenylphosphine)tetrakis(trifluoroacetato)dimolybdenum

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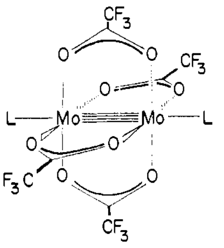
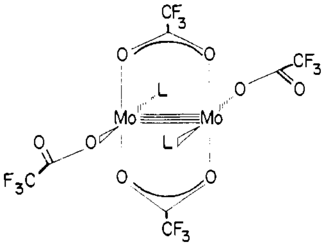
The X-ray crystal structure of the orange-yellow isomer of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ confirms that it possesses a class I (axial) structure as previously deduced spectroscopically. Accordingly, $PMePh_2$ is capable of forming both class I and class II (equatorial) adducts with $Mo_2(O_2CCF_3)_4$. NMR studies show that an equilibrium between the two isomers is established in solution. Crystal data: space group $P2_1/c$; a = 9.923 (1) Å, b = 22.517 (2) Å, c = 18.735 (3) Å, β = 99.18 (1)°; V = 4132 (2) Å^3; Z = 4; R = 4.43%, R_w = 6.63%; Mo–Mo = 2.128 (1) Å, Mo–P = 2.988 ± 0.024 Å, Mo–Mo–P = 166.15 ± 0.16°.

We have recently shown that tetrakis(trifluoroacetato)dimolybdenum yields 2:1 coordination complexes, $Mo_2(O_2CCF_3)_4(PR_3)_2$, with various tertiary phosphines.[1] Two general classes of complexes were isolated, referred to as class I and class II, as judged by infrared and NMR spectroscopy. Class I complexes were those in which the phosphine ligands were coordinated to axial sites (A), while class II complexes were those in which the phosphine ligands were coordinated to equatorial sites, one isomer of which is shown (B). On the basis of a cone angle vs. basicity graph, we showed that class II complexes were formed only by the smallest and most basic phosphines.[1]



A



B

A subsequent article has demonstrated that the crystal structures of $Mo_2(O_2CCF_3)_4(PPh_3)_2$ and $Mo_2(O_2CCF_3)_4(PEt_2Ph)_2$ are in complete accord with our findings, viz., that the former is a class I complex while the latter is a class II complex.[2] The structure of the latter is a testament to the predictive value of our cone angle and basicity criteria, since $Mo_2(O_2CCF_3)_4(PEt_2Ph)_2$ had not been previously prepared by us nor structurally characterized by spectroscopic studies.

In our original publication, we described the preparation of an orange-yellow complex, $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, which was assigned a class I (axial) structure.[1] However, Cotton and Lay were unable to prepare this compound by our published method and instead synthesized a compound of the same stoichiometry by a different route. Its color was reported to be red-orange, and crystallographic analysis revealed a class II (equatorial) structure.[2]

Table I. Crystal Data

space group: $P2_1/c$	V = 4132 (2) Å^3
a = 9.923 (1) Å	Z = 4
b = 22.517 (2) Å	mol wt = 1044.38
c = 18.735 (3) Å	d_{calcd} = 1.679 g cm^{-3}
β = 99.18 (1)°	μ_{calcd} = 7.8 cm^{-1}
$\alpha = \gamma$ = 90°	size = 0.27 × 0.31 × 0.45 mm

diffractometer: Enraf-Nonius CAD-4
radiation: Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.710 73 Å
monochromator: highly oriented graphite
scan range, type: $3 \leqslant 2\theta \leqslant 45°$, θ–2θ
scan speed, width: 0.6–6.7° min^{-1}, $\Delta\theta = (0.6 + 0.347 \tan\theta)°$
rflctns: 5926, 5393 unique, 4273 with $I > 3\sigma(I)$

R = 4.43%	variables = 523
R_w = 6.63%	GOF = 3.01

In view of this discrepancy, we have prepared $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ as originally described, with the exception that the solution volume was ca. 5 mL rather than ca. 10 mL. Herein we report its X-ray crystal structure and show that it is indeed a class I, axial diadduct. Some spectroscopic comparisons and preparative details involving the orange-yellow and red-orange isomers are also described.

Results and Discussion

An ORTEP[3] drawing of the orange-yellow isomer of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ (Figure 1) is that of a class I structure, as deduced previously by spectroscopic analysis.[1] Bond lengths and angles involving the molybdenum atoms are given in Table III. Most of the molecular features are quite normal, except for the large anisotropic thermal motion of the fluorine atoms

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[1] Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805–810.

[2] Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935–940.

[3] Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

0020-1669/82/1321-1318$01.25/0

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo1	0.26101 (5)	0.47374 (2)	0.27584 (3)	C6	−0.1358 (8)	0.4975 (4)	0.1432 (5)
Mo2	0.27183 (5)	0.55784 (2)	0.22528 (3)	C7	0.3534 (6)	0.4606 (3)	0.1404 (3)
P1	0.1871 (1)	0.36898 (7)	0.35724 (8)	C8	0.4080 (6)	0.4306 (3)	0.0787 (3)
P2	0.3194 (2)	0.65951 (7)	0.12784 (9)	C11	0.1566 (5)	0.2994 (3)	0.3083 (3)
F1	0.7499 (5)	0.4944 (3)	0.3200 (4)	C12	0.0327 (6)	0.2727 (3)	0.2930 (4)
F2	0.6974 (6)	0.5140 (3)	0.4143 (3)	C13	0.0176 (8)	0.2208 (3)	0.2519 (5)
F3	0.7226 (5)	0.5843 (2)	0.3506 (4)	C14	0.1234 (7)	0.1942 (4)	0.2294 (4)
F4	−0.0030 (4)	0.5900 (3)	0.4208 (3)	C15	0.2479 (8)	0.2216 (4)	0.2427 (4)
F5	0.1887 (5)	0.5829 (3)	0.4866 (2)	C16	0.2686 (7)	0.2755 (4)	0.2801 (4)
F6	0.1397 (6)	0.6568 (2)	0.4259 (3)	C17	0.2977 (6)	0.3462 (3)	0.4396 (3)
F7	−0.1352 (6)	0.4851 (4)	0.0754 (3)	C18	0.4036 (7)	0.3830 (4)	0.4667 (4)
F8	−0.2007 (5)	0.4533 (3)	0.1679 (4)	C19	0.4896 (9)	0.3665 (6)	0.5313 (4)
F9	−0.2075 (5)	0.5437 (3)	0.1444 (4)	C110	0.4736 (10)	0.3153 (5)	0.5651 (4)
F10	0.5300 (5)	0.4374 (3)	0.0807 (3)	C111	0.3799 (14)	0.2786 (5)	0.5364 (5)
F11	0.4033 (7)	0.3734 (2)	0.0814 (3)	C112	0.2804 (13)	0.2951 (4)	0.4751 (5)
F12	0.3460 (6)	0.4416 (3)	0.0200 (2)	C113	0.0237 (6)	0.3845 (3)	0.3871 (4)
O1	0.4658 (4)	0.4808 (2)	0.3273 (2)	C21	0.1977 (6)	0.6680 (3)	0.0459 (3)
O2	0.4790 (4)	0.5682 (2)	0.2752 (2)	C22	0.2354 (9)	0.6775 (5)	−0.0231 (4)
O3	0.1938 (4)	0.5157 (2)	0.3654 (2)	C23	0.1335 (10)	0.6830 (6)	−0.0842 (5)
O4	0.2050 (4)	0.6039 (2)	0.3116 (2)	C24	−0.0002 (10)	0.6778 (5)	−0.0783 (5)
O5	0.0565 (4)	0.4624 (2)	0.2246 (2)	C25	−0.0464 (10)	0.6668 (5)	−0.0072 (5)
O6	0.0698 (4)	0.5516 (2)	0.1726 (2)	C26	0.0609 (8)	0.6629 (4)	0.0524 (4)
O7	0.3278 (4)	0.4284 (2)	0.1905 (2)	C27	0.3354 (5)	0.7345 (3)	0.1669 (3)
O8	0.3401 (4)	0.5151 (2)	0.1362 (2)	C28	0.3297 (7)	0.7854 (3)	0.1210 (3)
C1	0.5277 (6)	0.5272 (3)	0.3142 (3)	C29	0.3468 (7)	0.8413 (3)	0.1555 (4)
C2	0.6739 (7)	0.5323 (3)	0.3495 (4)	C210	0.3675 (7)	0.8475 (3)	0.2280 (4)
C3	0.1807 (6)	0.5722 (3)	0.3617 (3)	C211	0.3713 (7)	0.7970 (3)	0.2716 (4)
C4	0.1244 (7)	0.5995 (3)	0.4264 (3)	C212	0.3558 (6)	0.7402 (3)	0.2389 (3)
C5	0.0096 (6)	0.5049 (3)	0.1838 (3)	C213	0.4856 (7)	0.6501 (4)	0.0973 (4)

Table III. Principal Bond Distances and Angles for Axial $Mo_2(O_2CCF_3)_4(PMePh_2)_2$

		Dist, Å			
Mo1-Mo2	2.128 (1)	Mo1-O1	2.111 (2)	Mo2-O2	2.131 (2)
Mo1-P1	2.964 (1)	-O3	2.124 (2)	-O4	2.115 (2)
Mo2-P2	3.012 (1)	-O5	2.117 (3)	-O6	2.093 (3)
av	2.988	-O7	2.092 (2)	-O8	2.128 (2)
		av	2.111	av	2.117
		Angles, Deg			
Mo2-Mo1-P1	166.31 (2)	O1-Mo1-O3	90.36 (9)	Mo2-Mo1-O1	91.34 (6)
Mo1-Mo2-P2	165.99 (2)	-O7	89.23 (9)	-O3	90.01 (7)
av	166.15	O3-Mo1-O5	90.73 (10)	-O5	91.07 (8)
O1-Mo1-O5	177.35 (10)	O5-Mo1-O7	89.56 (10)	-O7	92.83 (7)
O3-Mo1-O7	177.14 (10)	O2-Mo2-O4	90.52 (9)	Mo1-Mo2-O2	90.88 (7)
O2-Mo2-O6	176.90 (10)	-O8	89.32 (10)	-O4	92.95 (7)
O4-Mo2-O8	177.53 (10)	O4-Mo2-O6	90.02 (10)	-O6	92.14 (8)
av	177.23	O6-Mo2-O8	90.01 (10)	-O8	89.52 (7)
		av	89.97	av	91.34

and some of the carbon atoms of the phenyl groups.

The molecular geometry is very similar to that found for $Mo_2(O_2CCF_3)_4(py)_2$, py = pyridine,[4] except that the axial ligands are substantially farther away from the molybdenum atoms in the phosphine complex. The difference, Mo–P = 2.988 Å vs. Mo–N = 2.548 Å, can be ascribed either to the larger tetrahedral covalent radius of phosphorus (1.10 Å) relative to nitrogen (0.70 Å)[5] or to the larger cone angle of $PMePh_2$ (136°) relative to pyridine (132°).[1,6] The Mo–Mo distance, 2.128 Å, is identical within experimental error in the two complexes.

The terminal phosphine ligands are situated slightly off-axis from the Mo–Mo vector, with the Mo–Mo–P angle equal to 166.15° (Figure 2). The disposition of the phosphine groups appears to be dominated by external packing forces rather than covalent interaction with the dimolybdenum units. A similar situation was encountered in $Mo_2(O_2CCF_3)_4(py)_2$, where the Mo–Mo–N angle was 171.0°. The very weak bond between $Mo_2(O_2CCF_3)_4$ and the axial ligands had been indicated previously from NMR data, which suggested that extensive or complete dissociation occurred in solution.[1]

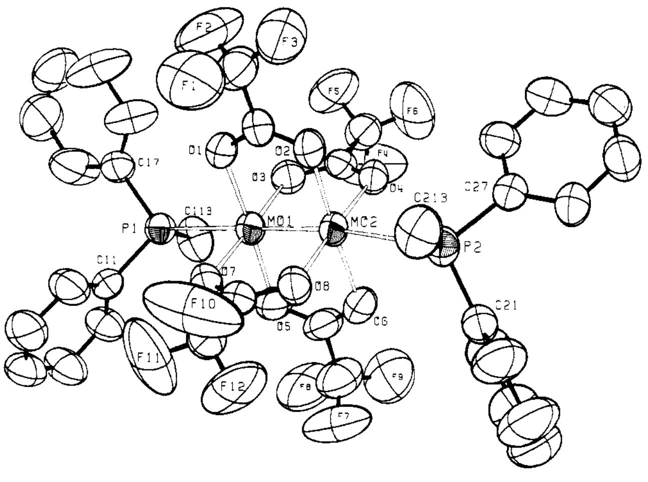

Figure 1. ORTEP[3] drawing of axial $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ showing the labeling scheme. Ellipsoids represent 50% probability surfaces.

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(4) Cotton, F. A.; Norman, J. G. *J. Am. Chem. Soc.* **1972**, *94*, 5697–5702.

(5) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 246.

(6) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

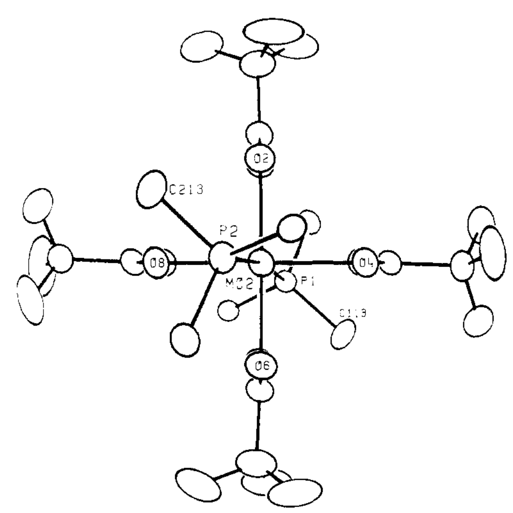

Figure 2. View down the Mo1→Mo2 vector, showing disposition of the $PMePh_2$ ligands with respect to the carboxylate planes.

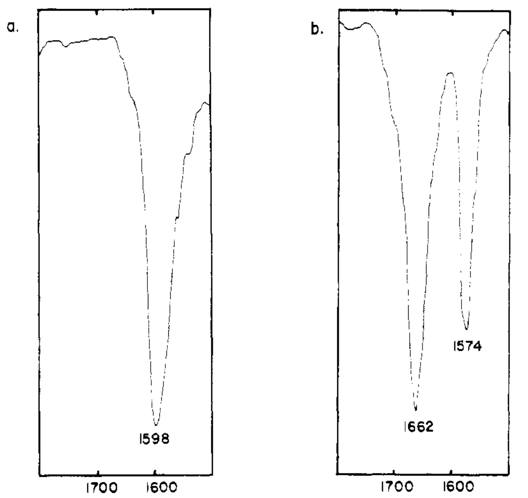

Figure 3. Solid-state infrared spectra of the (a) axial and (b) equatorial isomers of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$.

Thus, it is established that two isomers of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ exist: one with a class I (axial) structure and one with a class II (equatorial) structure.[7] This is not surprising, since $PMePh_2$ lies very close to the class I/class II boundary in our cone angle vs. basicity graph.[1]

We have investigated the conditions under which pure samples of the two isomers may be obtained. The synthesis of the axial isomer in diethyl ether is described in our original paper.[1] It is important that the diethyl ether solution of $Mo_2(O_2CCF_3)_4$ and $PMePh_2$ be concentrated until it changes color from yellow to orange and orange-yellow needles begin to appear. Crystals of the axial diadduct appear when the solution volume is ca. 5 mL. If the solution is not sufficiently concentrated, the bis(diethyl ether) adduct is obtained instead.[2] No crystals of the equatorial isomer were ever isolated from diethyl ether solution. The axial isomer may also be obtained as the first crop of crystals from a 1:2 molar ratio of $Mo_2(O_2CCF_3)_4$:$PMePh_2$ in toluene by cooling a saturated solution to −10 °C. However, subsequent crops of crystals from this solution are orange and consist entirely of the equatorial isomer of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ (see Experimental Section for details).

Each of the isomers gives an infrared spectrum characteristic of its class (Figure 3). For the axial isomer, all the O_2CCF_3 groups are clearly bidentate,[1] as shown by the single asymmetric CO_2 vibration at 1598 cm^{-1}. In contrast, the equatorial isomer exhibits strong bands at 1662 and 1574 cm^{-1} due to monodentate and bidentate O_2CCF_3 groups, respectively.[1,8] This infrared spectrum is rather different from that reported by Cotton and Lay for the equatorial isomer,[2] and it is likely that their bulk sample was largely the *axial* isomer.

We have also investigated the ^{19}F and $^{31}P\{^1H\}$ NMR spectra of the two compounds. Interestingly, pure samples of the axial and equatorial isomers dissolve in $CDCl_3$ to give identical spectra. At −50 °C, the $^{31}P\{^1H\}$ NMR spectra have as their major feature a broadened ($\nu_{1/2}$ = 100 Hz) peak at δ −29 due to the axial isomer of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$.[1] In addition, small peaks occur at δ +12, +8, and +7, resulting from various equatorially substituted isomers. (See ref 1 for the solution behavior of class II adducts.) The integrated intensities of the peaks at δ −29, +12, +8, and +7 are 100:23:18:19. Thus, the major species in solution is the axial isomer. Upon warming of the solution, the small peaks disappear, and the large peak shifts until at 25 °C only a single resonance ($\nu_{1/2}$ = 90 Hz) at δ −20 remains. It is apparent that a rapid equilibrium exists in solution between the axial and various equatorial isomers on the NMR time scale at room temperature.

The ^{19}F NMR spectra mirror the $^{31}P\{^1H\}$ observations. At −50 °C, a broad resonance ($\nu_{1/2}$ = 120 Hz) at δ −72.3 is observed due to the axial isomer. In addition, two sharp resonances at δ −71.4 and −74.5 result from bidentate and monodentate O_2CCF_3 groups of the equatorial isomers. The area ratios of the peaks at δ −72.3, −71.4, and −74.5 are 100:20:28, and again the axial isomer is seen to be the predominant species in solution. Upon warming of the solution to 25 °C, the sharp peaks broaden and disappear, yielding a single resonance ($\nu_{1/2}$ = 15 Hz) at δ −72.5. These ^{19}F chemical shifts are fully consistent with literature values for O_2CCF_3 ligands.[1,9] However, the chemical shifts reported by Cotton and Lay for $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ are different from these results.[2]

Experimental Section

Axial $Mo_2(O_2CCF_3)_4(PMePh_2)_2$. This isomer was prepared as previously described, with the exception that the final volume is ca. 5 mL.[1] For additional comments, see the text of this paper.

Equatorial $Mo_2(O_2CCF_3)_4(PMePh_2)_2$. Methyldiphenylphosphine (0.27 mL, 0.0015 mol) was added to $Mo_2(O_2CCF_3)_4$ (0.47 g, 0.00073 mol) in toluene (15 mL) under argon. After stirring for 1 h, the solution was filtered and concentrated to ca. 5 mL. Cooling to −10 °C yielded 0.15 g (20%) of the axial isomer (identified by IR spectroscopy) as orange-yellow needles, mp 107 °C. The mother liquors were recooled to −10 °C. Over a period of 1 day, a mixture of axial and equatorial isomers of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ was obtained. Subsequent crops of the pure equatorial isomer crystallized over several days at −10 °C as orange prisms, mp 116–118 °C. Total yield of the equatorial isomer was 0.42 g, 55%. Anal. Calcd: C, 39.1; H, 2.51; P, 5.90. Found: C, 39.5; H, 2.69; P, 5.70.

X-ray Data. Large needles of the compound were cut to size and mounted in thin-wall glass capillaries in air. The capillaries were then flushed with nitrogen and flame-sealed.

Preliminary precession photographs yielded rough cell dimensions and showed monoclinic Laue symmetry and systematic absences consistent with space group $P2_1/c$. A suitable crystal was then transferred to a diffractometer, and standard peak search and au-

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(7) Only one other example of crystallographically characterized structural isomers in dimolybdenum chemistry is known: Arenivar, J. D.; Mainz, V. V.; Andersen, R. A.; Zalkin, A.; Ruben, H., submitted for publication.

(8) In addition, the equatorial isomer may be recognized by doubling of the bands at 886, 775, and 690 cm^{-1} in the axial isomer to give bands at 895, 886, 789, 774, 696, and 690 cm^{-1}. Other features of the two infrared spectra are superimposable.

(9) King, R. B.; Kapoor, R. N. *J. Organomet. Chem.* **1968**, *15*, 457–469. Mitchell, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, *102*–107. Creswell, C. J.; Dobson, A.; Moore, D. S.; Robinson, S. D. *Inorg. Chem.* **1979**, *18*, 2055–2059. Teramoto, K.; Sasaki, Y.; Migita, K.; Iwaizumi, M.; Saito, K. *Bull, Chem. Soc. Jpn.* **1979**, *52*, 446–451.

tomatic indexing procedures gave cell dimensions in agreement with the photographic work. Least-squares refinement of the cell dimensions with higher angle reflections yielded the values given in Table I.

Data were collected in one quadrant of reciprocal space $(+h,+k,\pm l)$ by using measurement parameters given in Table I. Systematic absences consistent only with space group $P2_1/c$ occurred at $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. Corrections for absorption or decay were unnecessary. Systematically absent reflections were eliminated, and symmetry-equivalent reflections were averaged to yield the set of unique reflections. Only those data with $I > 3\sigma(I)$ were used in the least-squares refinement.

The structure was solved by normal heavy-atom methods, hindered slightly by near-special heavy-atom coordinates. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, and a p factor of 0.03 for intense reflections was used throughout refinement. The analytical forms for the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[10] Hydrogen atoms were not located. In the final cycle, all atomic positions and anisotropic thermal parameters were included in the full-matrix least-squares refinement. Final refinement parameters are given in Table I. All peaks in the final difference Fourier map had intensities of less than 0.31 e Å^{-3}, and the largest were located near fluorine atom positions or the phosphine methyl groups.

Acknowledgment. The crystal structure analysis was performed by Dr. F. J. Hollander, staff crystallographer at the University of California at Berkeley X-ray Crystallographic Facility (CHEXRAY). We thank the NSF for departmental grants used to purchase the NMR and X-ray spectrometers employed in this work and Chevron for a fellowship (G.S.G). We also thank Professors E. L. Muetterties and K. N. Raymond for advice.

Registry No. $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, axial, 72453-45-3; $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, equatorial, 76036-79-8; $Mo_2(O_2CCF_3)_4$, 36608-07-8.

Supplementary Material Available: Figure 4 showing a stereopair packing diagram of the unit cell contents, Figure 5 giving the numbering scheme for the O_2CCF_3 ligands, Table IV giving thermal parameters, and Table V giving structure factors (27 pages). Ordering information is given on any current masthead page.

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(10) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

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and University of Florida, Gainesville, Florida 32611

Structures of and Bonding in η^1-Cycloheptatrienylidene Complexes of Iron

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The crystal structures of the PF_6^- salts of two η^1-cycloheptatrienylidene complexes of iron of the form $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-CHT})Fe(CO)_2]PF_6$, in which CHT = C_7H_6 (**1**) or $C_{11}H_8$ (**7**), have been determined by single-crystal X-ray diffraction techniques with three-dimensional data gathered at −35 °C by counter methods. Yellow-orange crystals of **1** form as irregular blocks in triclinic space group $P\bar{1}$ with unit cell constants (at −35 °C) a = 7.981 (4) Å, b = 14.378 (3) Å, c = 7.133 (1) Å, α = 98.52 (1)°, β = 100.75 (1)°, and γ = 93.33 (1)°. The calculated density of 1.728 g cm^{-3}, with the assumption of two formula weights of **1** per unit cell, agrees with the measured value of 1.70 g cm^{-3}. Dark red crystals of **7** form as irregular hexagonal prisms in space group $P\bar{1}$ with unit cell constants (at −35 °C) a = 8.2086 (6) Å, b = 15.238 (2) Å, c = 7.4361 (8) Å, α = 90.509 (7)°, β = 104.396 (5)°, and γ = 94.676 (6)°. The calculated density of 1.691 g cm^{-3}, with the assumption of two formula weights of **7** per unit cell, agrees with the measured value of 1.68 g cm^{-3}. Full-matrix least-squares refinements of the structures have converged with conventional R indices (on $|F|$) of 0.057 and 0.041 for **1** and **7**, respectively, with use of (in the same order) the 4042 and 4414 symmetry-independent reflections with $I_o/\sigma(I_o) > 2.0$. Aside from the difference in the η^1-CHT rings, the molecular geometries of **1** and **7** are virtually identical, although the shorter Fe–C_{carb} bond (by 0.017 Å) in **1** suggests stronger Fe–carbene back-bonding in **1** than in **7**. In addition, from carbonyl stretching frequencies and ^1H and ^{13}C NMR data, it is concluded that, despite the existence of these CHT ligands in the carbene form, metal back-bonding with these η^1 ligands is less important than in similar nonheteroatom-stabilized carbene complexes such as $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-CH(Ph)})Fe(CO)_2](CF_3SO_3)$. It is noteworthy that the orientation of the CHT rings is ~90° from that observed in one Fe=CH_2- and two Ta=CHR-containing complexes.

Introduction

Transition-metal–carbene complexes, or more specifically methylene complexes, have long been considered as intermediates in olefin metathesis,[1–4] cyclopropanation,[4–7] polymerization, and other reactions.[6,8] Though their existence, however transitory, had thus often been inferred,[4–9] the first species to be isolated were the prototypical heteroatom-stabilized complexes MeC(OMe)W(CO)$_5$, PhC(OMe)W(CO)$_5$, and MeC(OMe)Cr(CO)$_5$, which were prepared by Fischer[10] and characterized structurally by Mills.[11] Since singlet carbene carbon atoms (C_{carb}) possess an unshared pair of electrons and an empty p orbital (i.e., sp^2 hybridization), the bonding between metal and ligand is potentially similar to that between a transition metal and a CO ligand (i.e., synergistic).[12] However, since the electrophilic C_{carb} atoms in Fischer-type complexes are bonded directly to a heteroatom which possesses

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