O(5) has an angle of 115 ± 10°. The lower limit of 105° is that of normal sp^3-hybridized oxygen of H_2O. Any value higher than 105° suggests increased character toward sp^2. The acidity of hydrogens on O(5) will be increased with the s character of the hybrid, and the central oxygen will be available to participate in π bonding to the central metal. Thus, the Ti^{IV}–OH_2 bond appears to be predisposed toward formation of Ti=O as the pH of the solution is raised. This is in concert with the substitution chemistry of $[Ti(edta)(H_2O)]$, which as a species behaves as $TiO(edta)^{2-}$ above pH 2.[13]

Acknowledgment. The authors (R.E.S.) express appreciation for support of this study under National Science Foundation Grant No. CHE 802183. The Robert A. Welch Foundation and the NSF (Grant CHE-83-05046) have supported this study at Texas A&M University.

Registry No. $[Ti(edta)(H_2O)]$, 96055-83-3.

Supplementary Material Available: Listings of anisotropic temperature factors (Table VI) and observed and calculated *F* values (Table VII) (20 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Diffraction des Rayons X, Département de Chimie,
Université de Montréal, Montréal, Québec, Canada H3C 3V1, and Département de Chimie,
Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

Preparation and Crystal Structure of the Seven-Coordinate Compound Bis(trifluoroacetato)dicarbonyltris(trimethylphosphine)molybdenum(II)

ANDRÉ L. BEAUCHAMP,*[1a] FRANCINE BELANGER-GARIEPY,[1a] and SAMIR ARABI[1b]

Received July 23, 1984

The $Mo(CO)_2(PMe_3)_3(CF_3COO)_2$ complex, obtained by stirring $[HMo(CO)_3(PMe_3)_3]^+CF_3COO^-$ in dichloromethane, was characterized by X-ray diffraction and by NMR and IR spectroscopy. The crystals belong to the monoclinic space group $P2_1/c$ with $a = 11.835$ (5) Å, $b = 14.542$ (4) Å, $c = 14.893$ (6) Å, $\beta = 90.29$ (3)°, and $Z = 4$. The structure was solved by the heavy-atom method, and anisotropic refinement of all non-hydrogen atoms on 2067 nonzero Mo Kα reflections converged to $R = 0.054$. The Mo(II) atom is seven-coordinated, and its environment is best described in terms of a capped trigonal prism. The capping position is occupied by a monodentate $CF_3CO_2^-$ ion. The quadrangular plane contains two cis PMe_3 molecules and one CO ligand, with the remaining $CF_3CO_2^-$ ion also acting as a monodentate group. The remaining edge contains one CO and one PMe_3 molecule. In spite of the fact that the present CF_3CO_2 complex has a capped-trigonal-prism geometry whereas $MoBr_2(CO)_2(PMe_2Ph)_3$ is a capped octahedron, the structures of these molecules are actually very similar.

Introduction

The carboxylate ions are known to be highly versatile in binding to metal ions. They can behave as mono- or bidentate donors to a single metal ion or give rise to a variety of more complicated patterns by acting as bridging groups.[2] The specific case of the CF_3COO^- ion has been reviewed by Garner and Hughes.[3]

We have recently undertaken a series of studies on $M(CO)_kL_l(CF_3CO_2)_m$ systems (M = Mo, W; L = PMe_3, PEt_3, $P(OMe)_3$), in order to assess the influence of the two parameters M and L on the trifluoroacetate binding mode. We present in this report the preparation and X-ray structure determination of $Mo(CO)_2(PMe_3)_3(CF_3CO_2)_2$.

Experimental Section

Preparation of $Mo(CO)_2(PMe_3)_3(CF_3COO)_2$. $Mo(CO)_3(PMe_3)_3$ was protonated by a method described previously.[4] A 1-g (2.45 mmol) portion of $Mo(CO)_3(PMe_3)_3$ was stirred in 20 mL of CH_2Cl_2. To the clear colorless solution was added an excess (0.5 mL, 5.7 mmol) of CF_3COOH, whereupon the reaction solution immediately turned blue-green. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 and stirred for 24 h under nitrogen. Filtration gave a yellow solution from which the solvent was removed under vacuum. The residue was dissolved in methanol, and cooling to −20 °C yielded yellow crystals of the title compound (30% yield based on the $Mo(CO)_3(PMe_3)_3$ starting material). Anal. Calcd for $C_{15}H_{27}F_6MoO_6P_3$: H, 4.49; C, 29.72. Found: H, 4.29; C, 30.41.

^1H NMR (CD_2Cl_2, 300 K, vs. Me_4Si (δ 0)): δ 1.57 (d, $J_{PH} = 11$ Hz), 1.26 (d, $J_{PH} = 8$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 300 K, vs. 85% H_3PO_4 (δ 0)): δ 27.60, −8.97. IR wavenumbers (cm^{-1}, KBr): 1930 m, 1845 vs, 1720 m, 1660 s.

Crystal Data: $C_{15}H_{27}F_6MoO_6P_3$, fw = 606.23, monoclinic, $P2_1/c$, $a = 11.835$ (5) Å, $b = 14.542$ (4) Å, $c = 14.893$ (6) Å, $\beta = 90.29$ (3)°, $V = 2563.1$ Å^3, $D_{calcd} = 1.570$ g cm^{-3}, $Z = 4$, λ(Mo K$\bar{\alpha}$) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 7.5 cm^{-1}, $T = 293$ K, crystal dimensions 0.10 mm $(001–00\bar{1})$ × 0.13 mm $(1\bar{1}0–\bar{1}10)$ × 0.30 mm $(20\bar{1}–\bar{2}01)$.

Crystallographic Measurements and Structure Resolution. The yellow crystals isolated as described above were suitable for X-ray work. The specimen was mounted in a Lindemann capillary filled with nitrogen. Cell dimensions, space group, and intensity data were determined with an Enraf-Nonius CAD4 diffractometer. A list of 25 reflections was generated by using the automatic search procedure of the CAD4 software. These reflections were centered, and the reduced triclinic cell was calculated. This cell was checked by recording a long-exposure oscillation photograph about each of the axes. They showed the correct layer line spacing and the expected symmetry (mirror for oscillation about *b* only). The Niggli parameters[5] clearly showed that the crystal cannot be described with a lattice of higher symmetry. Space group $P2_1/c$ was uniquely determined by inspection of the full data set ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$).

A set of 4516 unique $\bar{h}kl$ and $\bar{h}k\bar{l}$ reflections ($2\theta \leq 50°$, Mo K$\bar{\alpha}$) was collected as described elsewhere.[6] A total of 2067 reflections significantly above background ($I \geq 3\sigma(I)$) was retained for structure resolution. These data were corrected for the effect of Lorentz, polarization, and absorption effects (Gaussian integration, grid 8 × 8 × 8, transmission range 0.82–0.86).

The structure was solved by the heavy-atom method and refined on $|F_o|$ by full-matrix least squares in the early stages. Isotropic refinement

---

(1) (a) Université de Montréal. (b) Université de Sherbrooke.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 170. Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 232.

(3) Garner, C. D.; Hughes, B. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 1–47.

(4) Arabi, M. S.; Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1976**, *104*, 323–330.

(5) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, pp 534–535.

(6) Bélanger-Gariépy, F.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 3461–3464.

0020-1669/85/1324-1860$01.50/0

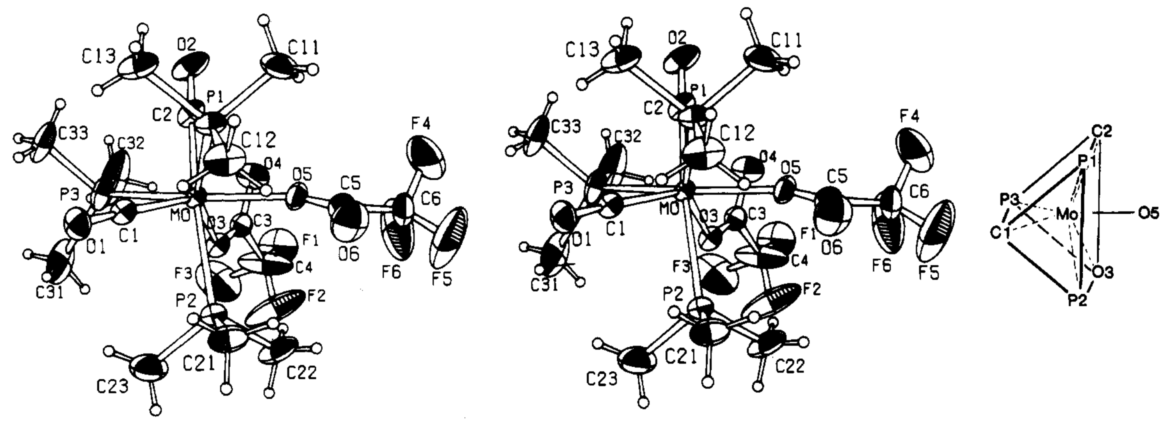
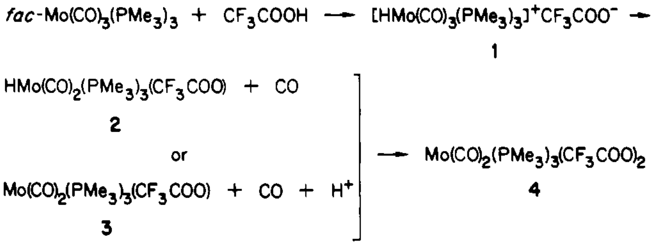


Figure 1. Left: Stereoview of the $Mo(CF_3CO_2)_2(CO)_2(PMe_3)_3$ molecule. Right: Line drawing of the capped trigonal prism around Mo.

Scheme I



of all non-hydrogen atoms converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.120$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.176$. The difference Fourier map contained electron density for at least one hydrogen atom of each methyl group. These positions were used to calculate ideal coordinates for all methyl hydrogens (C–H = 0.95 Å, angles 109.5°, $B = 10$ Å^2). Hydrogen parameters were not refined, but their coordinates were recalculated after each least-squares cycle. Anisotropic refinement of all non-hydrogen atoms by block-diagonal least squares converged to $R = 0.054$ and $R_w = 0.067$ (goodness-of-fit ratio 2.37). The final difference Fourier map had a general background below ±0.3 e/Å^3 and a few peaks in the range ±(0.4–0.6) e/Å^3, near Mo and F.

The scattering curves and anomalous dispersion coefficients of Mo and P were from standard sources.[7] The programs used are listed elsewhere.[8] The coordinates are listed in Table I.

Results and Discussion

The protonation of the four-coordinate $Ni[P(OR)_3]_4$, five-coordinate $Fe[P(OMe)_3]_5$, and six-coordinate $M(CO)_2(PR_3)_4$ (M = Mo, W) complexes proceeds only by addition to the metal center, forming $[HNi[P(OR)_3]_4]^+$, $[HFe[P(OMe)_3]_5]^+$, and $[HM(CO)_2(PR_3)_4]^+$, respectively.[4,9,10] In the case of $Mo[P(OMe)_3]_6$,[11] protonation gives the seven-coordinate $[HMo[P(OMe)_3]_6]^+$ hydride only in low yield (~5%), and the main reaction sequence[12] is outlined in eq 1. $HMo[P(OMe)_3]_4(O_2CCF_3)$

$$H^+ + Mo[P(OMe)_3]_6 \rightarrow [Mo[P(OMe)_3]_5P(OMe)_2]^+ + MeOH \quad (1)$$

was also obtained[12] by extended reaction of CF_3CO_2H with $Mo[P(OMe)_3]_6$. Reacting CF_3COOH with $[Mo(CCH_2\text{-}t\text{-}Bu)[P(OMe)_3]_2(\eta^5\text{-}C_5H_5)]$ was found to lead to protolytic cleavage of the carbyne fragment, and the reaction product was $[Mo(OCOCF_3)(CF_3CO_2H)[P(OMe)_3]_2(\eta^5\text{-}C_5H_5)]$.[13] The authors suggested the formation of an intermediate with only one CF_3COO group attached to molybdenum.

Table I. Refined Fractional Coordinates (×10^4; for Mo, ×10^5)

atom	x	y	z
Mo1	21998 (5)	40437 (4)	30654 (4)
P1	174 (2)	4091 (1)	2637 (2)
P2	2697 (2)	5641 (1)	3758 (1)
P3	2878 (2)	2830 (2)	4102 (2)
F1	6428 (6)	3755 (6)	1719 (6)
F2	6009 (6)	4895 (6)	2348 (10)
F3	6347 (6)	3828 (10)	2943 (6)
F4	2322 (9)	5334 (8)	−78 (5)
F5	2510 (13)	6544 (6)	386 (8)
F6	3669 (8)	5636 (11)	595 (7)
O1	795 (5)	4136 (4)	4814 (4)
O2	1714 (6)	2199 (4)	2038 (5)
O3	4037 (4)	4148 (3)	2933 (3)
O4	4303 (5)	3246 (5)	1752 (5)
O5	2399 (5)	4793 (4)	1809 (4)
O6	1298 (8)	6021 (5)	1677 (6)
C1	1317 (6)	4071 (5)	4155 (5)
C2	1917 (7)	2852 (5)	2423 (6)
C3	4605 (7)	3798 (6)	2334 (5)
C4	5797 (8)	4081 (9)	2266 (9)
C5	2061 (8)	5502 (7)	1444 (6)
C6	2637 (11)	5779 (8)	618 (7)
C11	−100 (8)	3970 (8)	1456 (7)
C12	−637 (7)	5094 (7)	2930 (7)
C13	−675 (8)	3168 (7)	3134 (8)
C21	1588 (8)	6468 (7)	3907 (7)
C22	3744 (10)	6289 (7)	3147 (9)
C23	3274 (11)	5628 (9)	4868 (8)
C31	3510 (10)	3223 (10)	5140 (9)
C32	3964 (12)	2115 (9)	3669 (11)
C33	1854 (11)	2022 (8)	4511 (9)

In the present case, the protonation of fac-$Mo(CO)_3(PMe_3)_3$ gives complex **1** (Scheme I), which was formulated on the basis of ^1H NMR and IR results.[4] The Mo center is then attacked by the $CF_3CO_2^-$ ion, probably forming a Mo–carboxylate species **2** or **3**, which would then give **4**. Unfortunately, direct evidence for **2** or **3** is still missing, and further work is under way to find the intermediates. Complex **4**, $Mo(CO)_2(PMe_3)_3(CF_3COO)_2$, is formulated on the basis of the following X-ray diffraction study.

The crystals of **4** contain discrete monomeric molecules in which Mo is seven-coordinated (Figure 1). The coordination sphere is best described in terms of a capped trigonal prism. The capping position is occupied by the O5 atom of a monodentate $CF_3CO_2^-$ ion. The quadrangular plane contains two cis PMe_3 molecules (P1 and P2) and one CO ligand (C2), with the remaining $CF_3CO_2^-$ ion also acting as a monodentate ligand through O3. The

---

(7) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104–109. Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17–23. Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(8) Authier-Martin, M.; Beauchamp, A. L. *Can. J. Chem.* **1977**, *55*, 1213–1217.

(9) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *2*, 4217–4222.

(10) Muetterties, E. L.; Rathke, J. W. *J. Chem. Soc., Chem. Commun.* **1974**, 850–851.

(11) Mathieu, R.; Poilblanc, R. *C.R. Seances Acad. Sci., Ser. C* **1974**, *279*, 1113–1114.

(12) Muetterties, E. L.; Kirner, J. F. Evans, W. J.; Watson, P. L.; Abdel-Meguid, S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056–1059.

(13) Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 493–495.

Table II. Interatomic Distances and Bond Angles

	Distances, Å		
Mo–P1	2.479 (2)	C4–F3	1.253 (15)
Mo–P2	2.608 (2)	C5–O5	1.231 (12)
Mo–P3	2.476 (3)	C5–O6	1.228 (13)
Mo–C1	1.935 (7)	C5–C6	1.466 (15)
Mo–C2	2.007 (8)	C6–F4	1.276 (14)
Mo–O3	2.190 (5)	C6–F5	1.174 (15)
Mo–O4	3.379 (7)	C6–F6	1.240 (16)
Mo–O5	2.179 (6)	P1–C11	1.796 (11)
Mo–O6	3.696 (8)	P1–C12	1.801 (10)
C1–O1	1.166 (9)	P1–C13	1.835 (10)
C2–O2	1.134 (10)	P2–C21	1.795 (10)
C3–O3	1.230 (10)	P2–C22	1.806 (12)
C3–O4	1.233 (11)	P2–C23	1.786 (13)
C3–C4	1.474 (12)	P3–C31	1.807 (14)
C4–F1	1.205 (14)	P3–C32	1.777 (14)
C4–F2	1.216 (15)	P3–C33	1.797 (13)
	Angles, deg		
P1–Mo–P2	107.1 (1)	C2–Mo–O5	92.3 (3)
P1–Mo–P3	119.4 (1)	O3–Mo–O5	77.1 (2)
P1–Mo–C1	71.9 (2)	Mo–C1–O1	176.5 (7)
P1–Mo–C2	75.1 (2)	Mo–C2–O2	176.6 (7)
P1–Mo–O3	159.2 (1)	Mo–O3–C3	125.7 (5)
P1–Mo–O5	82.8 (2)	Mo–O5–C5	139.6 (7)
P2–Mo–P3	108.5 (1)	Mo–P1–C11	114.8 (4)
P2–Mo–C1	76.8 (2)	Mo–P1–C12	118.4 (3)
P2–Mo–C2	174.0 (2)	Mo–P1–C13	114.0 (3)
P2–Mo–O3	75.6 (1)	C11–P1–C12	102.9 (5)
P2–Mo–O5	82.5 (2)	C11–P1–C13	103.1 (5)
P3–Mo–C1	70.5 (2)	C12–P1–C13	101.6 (5)
P3–Mo–C2	74.6 (2)	Mo–P2–C21	118.8 (3)
P3–Mo–O3	77.7 (1)	Mo–P2–C22	114.8 (4)
P3–Mo–O5	148.8 (2)	Mo–P2–C23	116.2 (4)
C1–Mo–C2	109.2 (3)	C21–P2–C22	102.5 (5)
C1–Mo–O3	127.9 (3)	C21–P2–C23	99.7 (5)
C1–Mo–O5	140.5 (3)	C22–P2–C23	102.2 (6)
C2–Mo–O3	100.4 (3)	Mo–P3–C31	116.1 (5)
Mo–P3–C32	115.1 (5)	O5–C5–O6	128.9 (10)
Mo–P3–C33	117.4 (4)	O5–C5–C6	116.7 (10)
C31–P3–C32	101.4 (7)	O6–C5–C6	114.4 (9)
C31–P3–C33	101.2 (6)	C5–C6–F4	114.0 (10)
C32–P3–C33	103.3 (6)	C5–C6–F5	116.6 (11)
O3–C3–O4	128.4 (8)	C5–C6–F6	116.1 (11)
O3–C3–C4	117.5 (8)	F4–C6–F5	101.8 (11)
O4–C3–C4	114.1 (8)	F4–C6–F6	100.2 (11)
C3–C4–F1	122.2 (10)	F5–C6–F6	106.0 (12)
C3–C4–F2	117.5 (10)		
C3–C4–F3	110.9 (10)		
F1–C4–F2	108.8 (11)		
F1–C4–F3	96.2 (10)		
F2–C4–F3	95.7 (11)		

remaining edge contains one CO (C1) and one PMe_3 (P3) molecule, the latter occupying the site more remote from the other two PMe_3 molecules.

The geometry found in the solid state is fully consistent with the structure in solution as deduced from spectroscopic data. The IR spectrum in CH_2Cl_2 shows absorptions due to monodentate CF_3CO_2 groups at ca. 1720 and 1660 cm^{-1}. The ^1H NMR spectrum shows two resonances at δ 1.57 and 1.26 with intensities in a 1:2 ratio, indicating two types of phosphine environments, in agreement with the $^{31}P\{^1H\}$ NMR spectrum consisting of two resonances at δ 27.60 and −8.97 also in a 2:1 ratio.

Description of the Structure. The interatomic distances and bond angles are listed in Table II. The Mo–C2 distance to the CO molecule in the quadrangular face (2.007 (8) Å) is longer than the other (Mo–C1 = 1.935 (7) Å). Differences are also noted in the Mo–P distances, the Mo–P2 bond (2.608 (2) Å) being longer than the other two Mo–P bonds (2.478 (3) Å). The long Mo–C and Mo–P bonds involve ligands trans to each other (174.0 (2)°), and this effect, also noted in analogous structures,[14-16] is presumably due to mutual trans influence. As to the Mo–O distances (average 2.184 (6) Å), they compare well with those found in other Mo(II) compounds.[17-19]

The C–O bonds (average 1.150 (10) Å) in the $C\equiv O$ molecules are similar to those observed in other Mo–carbonyl complexes.[14,15,17,18] The P–C distances in PMe_3 (average 1.800 (12) Å) are normal, and the usual difference is noted between the Mo–P–C and C–P–C angles (average 116.2°, 101.9°, $\sigma = 0.6°$, respectively).[20] The $CF_3CO_2^-$ ions behave as monodentate groups, since the distances from Mo to the "free" carbonyl oxygens are 3.379 (7) Å for O4 and 3.696 (7) Å for O6. Coordination of $CF_3CO_2^-$ sometimes produces a short C–O(free) bond and a long C–O(metal) bond. In the present case, the two types of C–O bonds show no significant differences. A similar situation was recently described.[18] The possibility that these ligands might be protonated, as observed by Green et al.,[13] was considered but not retained, because there was no residual electron density near O4 and O6 in the difference Fourier map and no nearby hydrogen-bond acceptors. Furthermore, the spectroscopic results did not support this assumption.

Choice of the Ideal Polyhedron. The stereochemistry of seven-coordinate compounds is customarily discussed in terms of three ideal polyhedra: pentagonal bipyramid (**P**, C_{5v}), capped octahedron (**O**, C_{3v}), and capped trigonal prism (**T**, C_{2v}).[21-23] Actual structures seldom match these polyhedra perfectly, and unless the deviations are very small, which is not the case here, the choice of the best ideal polyhedron is not obvious. The problem encountered can be envisaged in two steps. First, before the extent of departure from ideal symmetry is determined, the orientation of the actual structure with respect to the ideal polyhedron must be optimized. Second, **T** possesses three angles whose values are not fixed by symmetry, and **O** has two such angles. Thus, except for the **P**, some values for these adjustable angles have to be found as well.

The first part of the problem can be solved by a method described by Drew,[21] whereby the relative orientation of the polyhedra is optimized by a least-squares procedure derived by Dollase.[24] The best orientation is the one minimizing $\sum_i d_i^2$, where d_i is the distance between the ith apices in the actual and ideal polyhedra, respectively, and the summation is carried out over the seven apices. In order to focus on bond directions and minimize the effect of bond length disparity, apex positions based on bond lengths normalized to 1 Å are used. Tests were made with each metal–ligand bond initially occupying the unique position (axial in **P**, capped in **O** and **T**). If all angles were fixed by symmetry, the best polyhedron for any given structure could be immediately identified from its lowest final residual $R' = [\sum_i d_i^2/7]^{1/2}$. However, for **C** and **T**, angles not fixed by symmetry must be allowed to adjust as well. Using starting values suggested from Table II, the above procedure was repeated after varying these angles independently about the starting values (several steps of 1° and then of 0.1°). The minimum R' value was retained for each ideal polyhedron. This way, the best values for the adjustable angles are obtained, and the value of R' is a measure of the extent

---

(14) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1977**, 194–197. *Ibid.* **1974**, 1654–1658. Drew, M. G. B.; Wolters, A. P., Tomkins, I. B. *Ibid.* **1977**, 974–978.

(15) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1977**, 557–560.

(16) Arabi, S. Thèse de Doctorat d'état, Université Paul Sabatier, Toulouse, France, 1978.

(17) Beck, J. A.; Knox, S. A. R.; Riding, G. H.; Taylor, G. E.; Winter, M. J. *J. Organomet. Chem.* **1980**, *202*, C49–C52.

(18) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398–405.

(19) Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935–940.

(20) Capelle, B.; Beauchamp, A. L.; Dartiguenave, M.; Dartiguenave, Y.; Klein, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 3891–3897.

(21) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67–207. Drew, M. G. B.; Rix, C. J. *J. Organomet. Chem.* **1975**, *102*, 467–480.

(22) Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 41–144.

(23) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511–522.

(24) Dollase, W. A. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 513–517.

(25) Mawby, A.; Pringle, G. E. *J. Inorg. Nucl. Chem.* **1972**, *34*, 517–524.

Table III. Fit of Ideal Polyhedra to Observed Geometry for $MoX_2(CO)_3(phosphine)_3$ Compounds

	$MoCl_2(CO)_2$-$(PMe_2Ph)_3$ (ref 24)	$MoBr_2(CO)_2$-$(PMe_2Ph)_3$ (ref 14)	$Mo(CF_3CO_2)_2$-$(CO)_2(PMe_3)_3$ (this work)
Capped Octahedron (C_{3v})			
R',[a] Å, deg	0.055, 3.2	0.068, 3.9	0.117, 6.7
ϕ_B,[b] deg	71.8	73.0	72.7
ϕ_E, deg	128.8	125.0	125.8
capping site	C26	C1	C1
capped face	P1, P2, C25	P1, P2, P3	P1, P2, P3
uncapped face	P3, Cl1, Cl2	C2, Br1, Br2	C2, O3, O5
Capped Trigonal Prism (C_{2v})			
R', Å, deg	0.099, 5.7	0.101, 5.8	0.079, 4.5
ϕ_B, deg	81.1	82.2	83.7
θ_B, deg	50.5	51.5	52.1
ϕ_E, deg	143.1	144.2	145.3
capping site	Cl1	Br1	O5
quadrilat face	P2, P3, Cl2, C25	P1, P2, Br2, C2	P1, P2, O3, C2
opp edge	P1, C26	P3, C1	P3, C1
Pentagonal Bipyramid (C_{5v})			
R', Å, deg	0.263, 15.1	0.246, 14.1	0.224, 12.9
axial	Cl2, C25	P1, C2	P2, C2
equatorial	P1, P2, P3, Cl1, C26	P2, P3, Br1, Br2, C1	P1, P3, O3, O5, C1

[a] R' in degrees corresponds to the mean value for the angles between corresponding bond directions in the actual and ideal polyhedra, respectively, $[=2 \sin^{-1} (R'(\text{Å})/2)]$. [b] Angle symbols as in ref 21.

of fit with the actual structure.

This procedure was applied to three $MoX_2(CO)_2(phosphine)_3$ compounds and they are summarized in Table III. For the bromo compound in **O** geometry, the values are similar to those given by Drew,[21] the small differences probably arising from the fact that he used fixed standard values for the "adjustable" angles. As indicated by Drew,[21] the halide compounds are closer to the capped octahedral structure, the fit being ~2° better than in the trigonal-prism geometry. On the other hand, the present CF_3CO_2 complex is best described as a capped trigonal prism. At first sight, the fact that these structures are related to different ideal polyhedra could suggest that they differ considerably. However, the complexes of Br and CF_3CO_2 are actually very similar. When both compounds are described in terms of the same geometry, **O** for instance, the refined values of the adjustable angles are quite close. The capping position is occupied by a CO molecule and the capped face by three phosphines in both cases, whereas the CF_3CO_2 groups play the same role as the Br atoms in the uncapped face. A similar comparison can be made if both are envisaged as **T**. On the other hand, the chloro analogue is a different stereoisomer, in which the Cl atoms occupy the same sites as the Br or CF_3CO_2 groups, but one phosphine and one CO molecule are interchanged. Therefore, when described in **O** geometry, the Cl compound show a different distribution of CO and phosphine in the capped and uncapped sites. As a **T** structure, ligand distribution in the various sorts of sites remains the same, but the two phosphines in the quadrangular plane occupy trans, instead of cis, positions.

Hoffmann and co-workers[23] have discussed the distribution of ligands on the various sites of the seven-coordinate polyhedra. The compounds listed in Table III are found to follow these predictions quite well. For a d^4 Mo(II) system in **O** geometry, the preference for a π-donor ligand should follow the order uncapped face > capping site > capped face, whereas the opposite order would apply for a π acceptor. When described as capped octahedra, the three compounds have the best π donor (Br, Cl, O) in the uncapped face and a good π-acceptor CO molecule in capping position. When envisaged as capped trigonal prisms, these three molecules have a π-donor ligand in capping position. This is in good agreement with the order capping site > quadrangular face ~edge expected for π donors in a d^4 species with **T** geometry.

In summary, although the present CF_3COO complex is described as a capped trigonal prism, whereas the bromo analogue is a capped octahedron, these two compounds differ very little and their geometries could be interconverted by only small angular changes, which are likely to require only a very small amount of energy.[22,23]

Acknowledgment. We thank M. J. Olivier for collecting the X-ray data and D. Arbic for technical assistance. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. 4, 96211-74-4; *fac*-$Mo(CO)_3(PMe_3)_3$, 30513-05-4.

Supplementary Material Available: Listings of refined anisotropic temperature factors, calculated coordinates of hydrogen atoms, weighted least-squares planes, and observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.