puckered structures necessary for the ineraction but is not so large as to fix the complex geometry in solution.[50]

Ligand Selectivity around Palladium(II). In accordance with the successful optical resolution of DL-A and DL-B via stereoselective incorporation of an enantiomer into the copper(II) complexes of L-B and L-A, respectively, the present experiment has confirmed the preferential incorporation of D enantiomers of A and B into the palladium(II) complexes Pd(A)(L-B)(H) and Pd(L-A)(B)(H), respectively (Table VIII). Use of D-A for resolution of DL-B affords Pd(D-A)(B)(H) abounding with the L enantiomer of B, which is consistent with the expectation based on the results for Pd(A)(L-B)(H).

Biological Significance of Ligand–Ligand Interactions. Reactions of metalloenzymes with the substrates certainly involve various enzyme–substrate interactions, which are regarded as ligand–ligand interactions around the central metal ion. As typically shown by the X-ray structure analysis of the carboxypeptidase A–substrate complex, hydrogen bonding and electrostatic and hydrophobic interactions are of utmost importance for enzymatic reactions.[3,51–54] The ligand–ligand interaction in the corresponding copper(II) complexes, which have hitherto received broad experimental support,[4–8] is reasonably substantiated by the evidence presented in this study for palladium(II) complexes, because both palladium(II) and copper(II) exhibit similar complexing properties preferring square-planar structures and nitrogen donors. Also, the apical bonding in copper(II) complexes does not seem to propound a problem regarding the interaction.

The effect of addition of methanol on the rotamer populations strongly suggests that hydrophobic environments in biological systems favor electrostatic interactions around copper(II) and other metal ions and make them an important driving force for placing a molecule in a proper orientation enabling biological reactions.

Based on this view, we may further expect to work out model systems which provide specific reaction pathways mimicking biological processes, if ligands are coordinated in a preferred configuration with favorable side-chain conformations by virtue of ligand–ligand interactions.

Acknowledgment. We are grateful to Professor Yoshio Sasaki of Osaka University for helpful comments and discussions and to Dr. Takashi Komorita of Osaka University for kindly supplying the computer program LGNCD. The program LAOCN-4A was obtained from the Quantum Chemistry Program Exchange, Indiana University. The computations have been performed at the Osaka University Computer Center. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

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Chemical and X-ray Structural Studies on the (Acetato)- and (Trifluoroacetato)pentacarbonylmetalates of Chromium and Molybdenum

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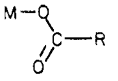
Abstract: The reaction of [PNP][Mo(CO)$_5$Cl], PNP = [Ph$_3$PNPPh$_3$]$^+$, with AgO$_2$CCH$_3$ and AgO$_2$CCF$_3$ in dichloromethane readily affords the complexes [PNP][Mo(CO)$_5$(O$_2$CCH$_3$)] (**1**) and [PNP][Mo(CO)$_5$(O$_2$CCF$_3$)] (**2a**) in good yield. The trifluoroacetate derivative of chromium (**2b**) is conveniently prepared in a similar manner. All three compounds crystallize in the triclinic space group $P\bar{1}$ with cell dimensions a = 10.563 (1) Å, b = 12.154 (2) Å, c = 17.047 (2) Å, α = 104.01 (1)°, β = 106.86 (1)°, and γ = 91.79 (1)° for **1**, a = 10.766 (2) Å, b = 12.210 (1) Å, c = 17.115 (2) Å, α = 104.10 (1)°, β = 106.59 (1)°, and γ = 92.77 (1)° for **2a**, and a = 10.715 (2) Å, b = 12.141 (2) Å, c = 17.070 (2) Å, α = 104.21 (1)°, β = 106.57 (1)°, and γ = 92.56 (2)° for **2b**. The structure of **1** was refined to values of R_1 = 0.069 and R_2 = 0.083 for 54 atoms (18 anisotropic) and 2860 reflections with $I > 3\sigma(I)$, while **2b** was refined to values of R_1 = 0.073 and R_2 = 0.089 for 57 atoms (21 anisotropic) and 3470 reflections with $I > 3\sigma(I)$. The structure of **2a** converged with R_1 = 0.050 and R_2 = 0.070 for 5338 reflections with $I > 3\sigma(I)$ and 57 anisotropic atoms. The most significant structural aspects are essentially equivalent (M)O—C and C=O bond lengths and short trans M—C(O) bond distances. Ligand substitutional processes involving displacement of either the acetate or carbonyl ligands in [PNP][Mo(CO)$_5$(O$_2$CCH$_3$)] are very facile, thus making them interesting and useful for preparing other compounds.

Introduction

The acetate and trifluoroacetate ions are known to bind to a variety of metals in one of three modes: monodentate (I), bidentate, or bridging (II).[1,2] Although the latter mode of carboxylate ion coordination is widely seen in metal dimers (e.g., Mo$_2$(O$_2$CR)$_4$),[3] monodentate binding of the trifluoroacetate ion has been noted recently in these species as well.[4] Other characterized molybdenum(II) complexes containing monodentate and bidentate carboxylates include the (C$_5$H$_5$)Mo(CO)$_3$O$_2$CCF$_3$[5] and (C$_6$H$_6$)Mo(C$_3$H$_5$)O$_2$CCH$_3$[6] derivatives. On the other hand little



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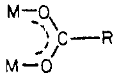

II

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0002-7863/81/1503-398$01.00/0

Table I. Infrared Spectra of Unidentate Acetate and Trifluoroacetate Derivatives[a]

	ν(CO), cm^{-1}			ν(CO$_2$), cm^{-1}		
compd	$A_1^{(1)}$	E	$A_1^{(1)}$	asym	sym	$\Delta\nu$(CO$_2$), cm^{-1}
[PNP][$Cr(CO)_5O_2CCH_3$]	2070	1921	1848	1588	1375	213
[PNP][$Cr(CO)_5O_2CCF_3$]	2065	1930	1858	1688	1421	267
[PNP][$Mo(CO)_5O_2CCH_3$]	2063	1923	1845	1593	1376	217
[PNP][$Mo(CO)_5O_2CCF_3$]	2069	1932	1855	1688	1423	265
[PNP][$Mo(CO)_5O_2{}^{13}CCH_3$]	2063	1923	1845	1548	1359	189

[a] Spectra taken in CH_2Cl_2 solution and are accurate to within ±2 cm^{-1}.

is known concerning the bonding of the acetate or trifluoroacetate ligands to group 6B metals in their zero oxidation states.[7a] We present in this report the preparations and X-ray structure determinations of the bis(triphenylphosphine)iminium carboxylate salts (^-O_2CR, R = CH_3 and CF_3) of chromium and molybdenum pentacarbonyls.

The reaction of molybdenum hexacarbonyl with acetic acid is apparently a complicated, multistep process culminating in formation of an array of trimer species containing bridging acetate ligands, in addition to $Mo_2(O_2CCH_3)_4$.[8] We have as a long-range goal a more thorough understanding of the complex reaction sequences. Hence an examination of the solution behavior of $Mo(CO)_5O_2CCH_3^-$, a possible precursor of these molybdenum acetate-containing dimer and trimer derivatives, has been initiated, and the results are reported herein.

Experimental Section

Materials. The carboxylates, AgO_2CCH_3 and AgO_2CCF_3, were obtained from Eastman Kodak Co. Bis(triphenylphosphine)iminium chloride, [PNP]Cl, and $M(CO)_6$ (M = Cr, Mo) were purchased from Alfa Products and Pressure Chemicals, respectively. Carbon monoxide enriched to >90% in ^{13}C was obtained from Prochem, B.O.C. Ltd., London, and ^{13}C acetic acid (90%) was supplied by KOR Isotopes. Dichloromethane was dried by refluxing with phosphorus pentoxide, followed by distillation. Hexane and tetrahydrofuran were dried by refluxing over Na/K alloy, followed by distillation. Similarly, diglyme was distilled from sodium. All reactions were carried out under an atmosphere of dry nitrogen in standard Schlenk ware.

Preparation of [PNP][$M(CO)_5Cl$] (M = Cr and Mo). A mixture of 1.81 g (6.91 mmol) of $Mo(CO)_6$ and 3.84 g (6.70 mmol) of [PNP]Cl was heated in 30 mL of freshly distilled diglyme at 120 °C for 2 h. The yellow solution was filtered hot under nitrogen. To the cooled filtrate was added 50 mL of dry hexane which resulted in the formation of a yellow-brown oil. When the oil was washed with hexane repeatedly, a yellow solid product was obtained. An infrared spectrum in CH_2Cl_2 solution afforded peaks at 2066, 1930, and 1855 cm^{-1} assignable to the $A_1^{(2)}$, E, and $A_1^{(1)}$ ν(CO) vibrational modes, respectively.

The chromium derivative was prepared in a completely analogous manner. The infrared spectrum in the ν(CO) region of this species exhibited bands at 2059, 1926, and 1854 cm^{-1}. These [PNP][$M(CO)_5Cl$] compounds are quite analogous to the well-known tetraethylammonium salts.[7b]

Preparations of [PNP][$M(CO)_5O_2CCH_3$] and [PNP][$M(CO)_5O_2CCF_3$] (M = Cr and Mo). All syntheses of these species were performed in a similar way. In a typical preparation the compound [PNP][$Mo(CO)_5Cl$] (1.59 g, 1.98 mmol) was dissolved in 30 mL of dichloromethane and AgO_2CCH_3 (0.425 g, 2.55 mmol) added. The solution was stirred for 10 min during which time silver chloride settled out of solution. The reaction mixture was filtered in nitrogen through Celite, and solvent was removed under reduced pressure to afford the bright yellow product in ca. 90% yield. Crystals suitable for X-ray analysis were obtained from THF/hexane at −10 °C. Anal. Calcd for [$Mo(CO)_5O_2CCH_3$]-[$(C_6H_5)_3P]_2N$: C, 61.95; H, 3.99; N, 1.68. Found: C, 62.08; H, 4.21; N, 1.79.

A sample of [PNP][$Mo(CO)_5O_2CCH_3$] labeled in ^{13}C at the carboxylic carbon atom was prepared from 90% enriched $AgO_2{}^{13}CCH_3$ (obtained from Ag_2O and $CH_3{}^{13}COOH$) and [PNP][$Mo(CO)_5Cl$]. Solution infrared data in the ν(CO) and $\nu(CO_2^-)$ regions on this and the other acetate and trifluoroacetate derivatives are given in Table I.

Infrared and ^{13}C NMR Spectra. The infrared spectra were recorded in matched NaCl-sealed cells on either a Perkin-Elmer 283B or Unicam SP 1100 spectrophotometer. The ^{13}C NMR spectra were measured on a JEOL FX60 spectrometer operated at 15.03 MHz with an internal deuterium lock. Samples were run in $CDCl_3$ solvent in 10-mm tubes.

X-ray Diffraction Studies. Crystals of all three compounds, [PNP][$Mo(CO)_5OCOCH_3$], **1**, [PNP][$Mo(CO)_5OCOCF_3$], **2a**, and [PNP][$Cr(CO)_5OCOCD_3$], **2b**, were examined by using the automatic search routine on an Enraf-Nonius CAD-4 diffractometer. The ω-scan peak profiles of several strong reflections indicated in each case that the crystals were of good quality. A least-squares analysis of the setting angles of 20 reflections for **1** and 25 reflections for **2a,b** [26° $\leq 2\theta \leq$ 32°], automatically located and centered, provided accurate unit cell parameters (Table II). The general procedures for data collection have been previously reported.[9] The variable CAD-4 parameters used in this study are presented in Table II. Standard Lorentz and polarization corrections were performed.

The refinement[10] of the structure of **1** proceeded as follows. A three-dimensional Patterson synthesis provided the position for the Mo atom. Three cycles of full-matrix least-squares refinement produced R_1 and R_2 values of 0.392 and 0.467, respectively, where

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2 \sum w|F_o|^2]^{1/2}$$

Alternating difference Fourier syntheses and least-squares calculations readily provided the position of all of the nonhydrogen atoms. Convergence of the isotropic model led to values of $R_1 = 0.081$ and $R_2 = 0.096$. The structure was refined further by 4 cycles of least squares by using anisotropic thermal parameters for all atoms in the anion as well as the phosphorus and nitrogen atoms in the cation. The final agreement factors as well as other pertinent parameters are listed in Table II.

The structure refinement for complex **2a** was simplified by the observation that **1** and **2a** are isomorphous. The atomic parameters were taken directly from the refinement of **1**, and least-squares refinement using isotropic thermal parameters for all atoms (exclusive of F atoms) was performed. A Fourier synthesis provided positional parameters for the three fluorine atoms, and three cycles of least squares led to convergence of the isotropic refinement. Anisotropic thermal parameters were introduced for all atoms, and five cycles of full-matrix least squares led to convergence of this model to $R_1 = 0.050$ and $R_2 = 0.070$.

Complex **2b** was also found to be isomorphous with **1** (and **2a**) and isostructural to **2a**. All positional parameters were obtained from the structure of **2a** as well as anisotropic thermal parameters for the atoms of the anion and the phosphorus and nitrogen atoms. Least-squares refinement of this model led rapidly to convergence with the final *R* values listed in Table II.

A listing of structure factor amplitudes for all structures is available as supplementary material (Tables III–V). Final positional and thermal parameters are tabulated in Tables VI–VIII.

Results and Discussion

Synthesis. Reaction of silver acetate and trifluoroacetate with methylene chloride solutions of [PNP][$M(CO)_5Cl$] (M = Cr, Mo, W) readily generates the [PNP][$M(CO)_5O_2CCH_3$] and [PNP][$M(CO)_5O_2CCF_3$] derivatives in high yields (eq 1). Because of the instability of the chromium and molybdenum carboxylates in solution with respect to reformation of the hexacarbonyls, it is necessary to isolate these species from solution

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(10) All crystallographic computing was performed on a PDP 11/45 or PDP 11/60 computer at the Molecular Structure Corporation, College Station, TX, employing the Enraf-Nonius structure determination package with local modifications.

Table **II**. Crystallographic Data and Enraf-Nonius CAD-4 Data Collection Parameters

	1	2	3
formula	$MoP_2O_7NC_{43}H_{33}$	$MoP_2F_3O_7NC_{43}H_{30}$	$CrP_2F_3O_7NC_{43}H_{30}$
M_r	833.6	887.6	843.7
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.563 (1)	10.766 (2)	10.715 (2)
b, Å	12.154 (2)	12.210 (1)	12.141 (2)
c, Å	17.047 (2)	17.115 (2)	17.070 (2)
α, deg	104.01 (1)	104.10 (1)	104.21 (1)
β, deg	106.86 (1)	106.59 (1)	106.57 (1)
γ, deg	91.79 (1)	92.77 (1)	92.56 (2)
V, Å^3	2019 (1)	2074 (1)	2047 (1)
Z	2	2	2
ρ_{calcd}, g cm^{-3}	1.37	1.42	1.37
cryst size, mm	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.4	0.2 × 0.3 × 0.3
μ(Mo Kα), cm^{-1}	4.52	4.57	4.38
radiatnq	graphite-monochromated Mo Kα ($\lambda \approx 0.71073$ Å)		
scan type	ω–2θ	ω–2θ	ω–2θ
scan width ($\Delta\omega$), deg	0.60 + 0.35 tan θ	0.60 + 0.35 tan θ	0.66 + 0.35 tan θ
aperature width, mm	1.5 + tan θ	1.5 + tan θ	1.5 + tan θ
prescan rejection limit	2.0 (0.5σ)	2.0 (0.5σ)	2.0 (0.5σ)
prescan acceptance limit	0.02 (50σ)	0.02 (50σ)	0.02 (50σ)
max scan speed, deg min^{-1}	20.12	20.12	20.12
max counting time, s	30	30	30
collectn range	$+h, \pm k, \pm l$, 4° $\leqslant 2\theta \leqslant$ 50°		
no. unique data	7081	7263	7135
no. data with $I > 3\sigma(I)$	2860	5338	3470
p	0.05	0.05	0.05
X-ray exposure time, h	49	57	54
cryst decomp	negligible	negligible	negligible
no. of variables	307	514	334
R_1	0.069	0.050	0.073
R_2	0.083	0.070	0.089
esd	1.83	2.07	2.21
largest parameter shift[a]	0.09	0.02	0.12
largest peak,[b] e Å^{-3}	0.29	0.27	0.31

[a] Final refinement cycle. [b] Largest peak in the final difference Fourier map.

rapidly. An alternative, more arduous preparation of the tungsten complexes

$$[PNP][M(CO)_5Cl] + AgO_2CCH_3 \xrightarrow[CH_2Cl_2]{25\ °C} [PNP][M(CO)_5O_2CCH_3] + AgCl \quad (1)$$

as well as the trifluoroacetato derivative of chromium, which involves oxidation of the appropriate $[PNP]_2[M_2(CO)_{10}]$ salt by the corresponding silver(I) or mercury(II) carboxylate,[7] has been reported previously.

Crystals of both the acetato and trifluoroacetato complexes are chemically stable with respect to oxidation by dioxygen over short exposure times. The infrared spectrum in the ν(CO) region displays the familiar three-band pattern consistent with C_{4v} symmetry about the $M(CO)_5$ moiety. Furthermore, the infrared spectrum in the $\nu(CO_2^-)$ region is congruous with those of other monodentate carboxylates,[1,2] consisting of a strong antisymmetric $\nu(CO_2^-)$ vibration at ~1688 (1590 cm^{-1}) and a somewhat weaker symmetrical $\nu(CO_2^-)$ at 1420 (1375 cm^{-1}) for the trifluoroacetate and acetate complexes, respectively. The assignments of the $\nu(CO_2^-)$ vibrations were confirmed by an infrared analysis of the specifically ^{13}C-labeled $Mo(CO)_5(O_2{}^{13}CCH_3)^-$ derivative (see Table I). The ^{13}C resonances, obtained on ^{13}C-enriched samples of $Mo(CO)_5O_2CCH_3^-$, were observed at 217.8 (axial CO), 205.9 (equatorial CO's), 177.4 (carboxylic carbon), and 23.7 ppm (methyl carbon).

Solid-State Structures. The three complexes $[PNP][M(CO)_5(O_2CCX_3)]$ (M = Mo, X = H or F; M = Cr, X = F) crystallize in the space group $P\bar{1}$ and, interestingly, all three are isomorphous. Although this feature would be expected for the chromium and molybdenum trifluoroacetato derivatives, it may seem surprising for trifluoroacetato and acetato analogues of molybdenum. An examination of the crystal packing (Figure 1) gives some insight into the reasons. The structures consist of an array of the two discrete ionic units, at normal van der Waals distances. However, the arrangement is dominated by the bulk of the bis(triphenylphosphine)iminium cations. These large, bent (141.2°) ions (Figure 2) define pockets that readily accommodate the smaller anions about equally well whether they contain the CH_3 or the CF_3 group.

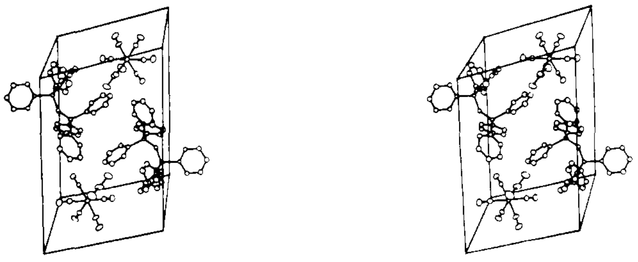

Figure 1. A stereoscopic view of the packing in **1** viewed approximately down the crystallographic a toward the origin.

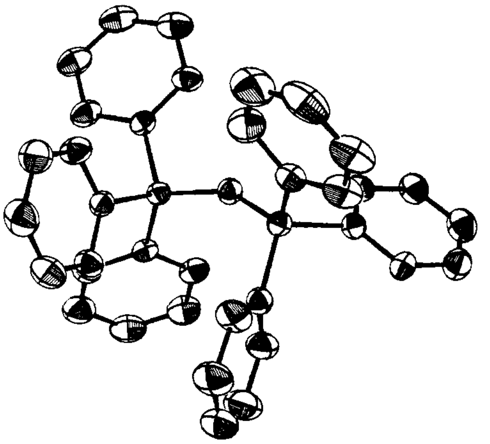

Figure 2. The $[(Ph_3P)_2N]^+$ cation in **2a** with thermal ellipsoids at the 40% probability level.

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[PNP][Mo(CO)_5(O_2CCH_3)]$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mo	0.2460 (1)	0.3489 (1)	0.81611 (7)	3.96 (4)	4.19 (5)	3.37 (4)	0.32 (4)	1.27 (3)	0.56 (4)
P(1)	0.3807 (3)	0.1941 (2)	0.3629 (2)	2.6 (1)	2.8 (1)	2.5 (1)	0.4 (1)	0.91 (9)	0.67 (9)
P(2)	0.3352 (3)	0.0504 (2)	0.1872 (2)	2.5 (1)	2.9 (1)	2.2 (1)	0.3 (1)	0.55 (9)	0.71 (9)
O(1)	0.4105 (8)	0.2061 (7)	0.7082 (5)	7.4 (4)	4.9 (4)	6.1 (4)	2.7 (4)	3.1 (3)	1.0 (4)
O(2)	0.4985 (9)	0.5340 (8)	0.9124 (6)	6.0 (5)	5.7 (5)	7.6 (5)	−1.6 (4)	1.4 (4)	0.4 (4)
O(3)	0.0775 (9)	0.4660 (10)	0.9333 (6)	7.8 (5)	10.2 (7)	7.8 (5)	−0.9 (5)	4.7 (3)	−2.6 (5)
O(4)	0.0282 (9)	0.1362 (8)	0.7291 (6)	4.4 (4)	6.8 (5)	8.4 (5)	−1.7 (4)	0.9 (4)	−0.2 (5)
O(5)	0.3724 (9)	0.2184 (8)	0.9501 (5)	6.6 (5)	9.3 (5)	6.3 (4)	1.2 (4)	1.9 (3)	4.7 (3)
O(6)	0.1707 (7)	0.4530 (7)	0.7262 (5)	4.4 (4)	5.8 (4)	6.1 (4)	1.4 (3)	2.2 (3)	2.2 (3)
O(7)	−0.0398 (10)	0.4229 (11)	0.7061 (8)	5.8 (5)	15.2 (8)	14.5 (7)	2.1 (6)	2.2 (5)	7.8 (6)
N	0.3209 (8)	0.0962 (7)	0.2788 (5)	2.9 (4)	2.8 (4)	2.7 (3)	−0.1 (3)	0.5 (3)	0.6 (3)
C(1)	0.350 (1)	0.2613 (9)	0.7443 (7)	5.3 (6)	2.5 (5)	4.8 (5)	0.7 (5)	2.1 (4)	0.8 (4)
C(2)	0.405 (1)	0.4725 (11)	0.8772 (7)	4.6 (6)	4.6 (7)	4.9 (6)	−0.2 (5)	1.3 (5)	0.8 (5)
C(3)	0.135 (1)	0.4297 (13)	0.8905 (8)	4.5 (5)	7.9 (9)	5.1 (6)	−1.3 (6)	3.0 (4)	−2.0 (6)
C(4)	0.099 (1)	0.2156 (11)	0.7553 (7)	3.7 (5)	6.2 (7)	4.7 (5)	0.3 (5)	1.4 (4)	1.4 (5)
C(5)	0.322 (1)	0.2657 (11)	0.9010 (7)	4.1 (5)	5.6 (7)	4.8 (5)	0.1 (5)	2.1 (4)	1.6 (5)
C(6)	0.057 (1)	0.4736 (15)	0.6953 (8)	1.9 (5)	14 (1)	6.3 (6)	0.3 (7)	1.8 (4)	2.1 (7)
C(7)	0.030 (2)	0.5541 (13)	0.6353 (9)	9.3 (9)	10.9 (8)	9.0 (7)	5.3 (7)	3.8 (7)	7.3 (6)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(110)	0.2572 (10)	0.2095 (9)	0.4178 (6)	2.9 (2)	C(210)	0.3089 (9)	−0.1036 (8)	0.1607 (5)	2.2 (2)
C(111)	0.2876 (11)	0.2883 (10)	0.4967 (7)	3.7 (3)	C(211)	0.2455 (10)	−0.1524 (9)	0.2074 (6)	3.1 (2)
C(112)	0.1921 (12)	0.3006 (10)	0.5409 (7)	4.7 (3)	C(212)	0.2185 (11)	−0.2721 (10)	0.1871 (7)	3.9 (3)
C(113)	0.0711 (12)	0.2305 (11)	0.5065 (7)	5.1 (3)	C(213)	0.2585 (11)	−0.3368 (10)	0.1223 (7)	4.4 (3)
C(114)	0.0436 (12)	0.1525 (11)	0.4282 (7)	4.9 (3)	C(214)	0.3246 (12)	−0.2877 (11)	0.0765 (7)	4.7 (3)
C(115)	0.1363 (11)	0.1415 (10)	0.3811 (7)	4.0 (3)	C(215)	0.3507 (10)	−0.1697 (9)	0.0947 (6)	3.6 (2)
C(120)	0.5303 (10)	0.1601 (9)	0.4318 (6)	2.8 (2)	C(220)	0.4951 (9)	0.0893 (9)	0.1781 (6)	2.7 (2)
C(121)	0.5585 (11)	0.0481 (9)	0.4174 (6)	3.7 (3)	C(221)	0.6016 (11)	0.0334 (9)	0.2141 (6)	3.7 (3)
C(122)	0.6728 (11)	0.0182 (10)	0.4706 (7)	4.4 (3)	C(222)	0.7293 (13)	0.0694 (11)	0.2121 (8)	5.5 (3)
C(123)	0.7555 (12)	0.1024 (11)	0.5370 (7)	4.8 (3)	C(223)	0.7486 (13)	0.1567 (12)	0.1756 (8)	5.5 (3)
C(124)	0.7312 (12)	0.2148 (10)	0.5533 (7)	4.5 (3)	C(224)	0.6405 (12)	0.2102 (11)	0.1398 (8)	5.3 (3)
C(125)	0.6171 (11)	0.2461 (10)	0.4988 (7)	4.0 (3)	C(225)	0.5128 (11)	0.1761 (10)	0.1403 (7)	4.1 (3)
C(130)	0.4183 (10)	0.3317 (9)	0.3467 (6)	3.1 (2)	C(230)	0.2133 (10)	0.1014 (9)	0.1109 (6)	3.0 (2)
C(131)	0.5382 (10)	0.3559 (9)	0.3332 (6)	3.7 (3)	C(231)	0.1912 (11)	0.0568 (10)	0.0246 (7)	4.4 (3)
C(132)	0.5553 (12)	0.4573 (11)	0.3094 (7)	4.8 (3)	C(232)	0.0988 (13)	0.1034 (11)	−0.0341 (8)	5.6 (3)
C(133)	0.4556 (12)	0.5283 (11)	0.2991 (7)	4.8 (3)	C(233)	0.0380 (13)	0.1897 (12)	−0.0053 (8)	6.0 (3)
C(134)	0.3345 (12)	0.5027 (11)	0.3117 (7)	5.1 (3)	C(234)	0.0495 (14)	0.2349 (13)	0.0793 (9)	7.2 (4)
C(135)	0.3165 (11)	0.4021 (10)	0.3363 (7)	3.8 (3)	C(235)	0.1434 (12)	0.1890 (11)	0.1410 (8)	5.3 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$ where *a*, *b*, and *c* are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

The $[PNP]^+$ ions refine as well-behaved units and the dimensions of the P–C, P–N, and C–C bonds (Tables IX and X)[11] are similar to those observed[12,13] in other structures in which they are contained. The average P–N bond length of 1.576 (5) Å is the same as the value of 1.575 (2) Å reported as the average of numerous determinations of bent $[PNP]^+$ ions.[12] The P–N–P angle of 141.2 (3)° is also well within the range of reported data. The observed P–C and C–C bond distances and N–P–C, C–P–C, and C–C–C bond angles average 1.802 (5) Å, 1.394 (8) Å, 111.1 (2)°, 107.9 (3)°, and 120.0 (7)°, respectively, and are, therefore, as expected.[14]

In general, the dimensions of the anionic species are comparable to those found in other monosubstituted chromium and molybdenum carbonyls.[15] As would be expected from their isomorphism, the three anions are isostructural in broad stereochemical terms, being readily described as octahedral ligand geometries around metal centers. The metal–carbon, metal–oxygen, and carbonyl–oxygen bond lengths represent normal observations. The acetate groups, excepting the H or F atoms, are planar, and these planes are perpendicular to the plane of the equatorial carbonyl groups. These acetate planes bisect the angle between two CO units with the carbonyl group pointing down between two of these ligands (Figure 3). In **2a,b** the fluorine atoms reside at positions indicative of a single well-behaved trifluoromethyl group with no evidence of any disorder. The average C–F bond length is 1.323 (7) Å.

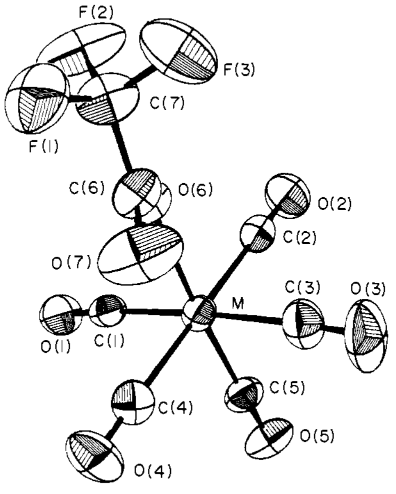

Figure 3. The $M(CO)_5(O_2CCF_3)^-$ anion (**2a,b**) drawn with 40% probability thermal ellipsoids.

The most intriguing aspect of the structures are the dimensions of the monodentate acetate groups. The metal–oxygen and carbon–carbon bond distances of 2.211 (7), 2.236 (2), and 2.133 (4) Å and 1.56 (1), 1.518 (6), and 1.565 (9) Å for **1**, **2a**, and **2b**,

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(11) Table X, a list of all bond distances and bond angles for the PNP^+ groups is included as supplementary material.

(12) Kirtley, S. W.; Chanton, J. P.; Love, R. A.; Tipton, D. L.; Sorrel, T. N.; Bau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3451.

(13) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 7601.

(14) None of the three structures has bond distances or bond angles which differ significantly from these averages.

(15) Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. H. submitted for publication in *Inorg. Chem.*

Table VII. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[PNP][Mo(CO)_5(O_2CCF_3)]$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mo	0.25637 (4)	0.34222 (3)	0.82065 (2)	3.59 (1)	3.92 (2)	3.09 (1)	0.36 (1)	1.20 (1)	0.95 (1)
P(1)	0.3833 (1)	0.19464 (9)	0.36454 (6)	2.68 (4)	2.73 (4)	2.69 (3)	0.46 (3)	1.05 (3)	0.80 (3)
P(2)	0.3332 (1)	0.05001 (9)	0.18883 (6)	2.88 (4)	2.98 (4)	2.46 (3)	0.36 (3)	0.89 (3)	0.76 (3)
F(1)	0.0076 (4)	0.6470 (3)	0.6987 (3)	7.6 (2)	6.0 (2)	13.6 (3)	2.3 (2)	3.0 (2)	1.7 (2)
F(2)	0.1388 (3)	0.5818 (3)	0.6311 (2)	6.6 (2)	14.8 (2)	15.2 (2)	4.9 (1)	6.9 (1)	11.8 (1)
F(3)	−0.0623 (4)	0.5155 (4)	0.5874 (2)	7.9 (2)	11.0 (2)	6.7 (2)	2.2 (2)	−0.0 (2)	3.4 (2)
O(1)	0.4179 (4)	0.2073 (3)	0.7096 (2)	6.4 (2)	5.0 (2)	6.1 (2)	1.7 (1)	3.2 (1)	1.5 (1)
O(2)	0.5027 (4)	0.5320 (4)	0.9150 (3)	7.0 (2)	6.1 (2)	6.2 (2)	−1.9 (2)	1.1 (2)	0.5 (2)
O(3)	0.0937 (4)	0.4518 (5)	0.9437 (3)	8.9 (2)	10.9 (3)	7.8 (2)	−0.5 (2)	5.7 (1)	−2.1 (2)
O(4)	0.0351 (4)	0.1322 (4)	0.7309 (3)	4.8 (2)	5.9 (2)	9.0 (2)	−1.4 (2)	1.5 (2)	0.2 (2)
O(5)	0.3812 (4)	0.2088 (3)	0.9496 (2)	6.2 (2)	8.0 (2)	5.6 (1)	1.1 (2)	2.1 (1)	4.0 (1)
O(6)	0.1805 (3)	0.4506 (3)	0.7338 (2)	3.7 (1)	5.4 (1)	4.6 (1)	1.3 (1)	1.7 (1)	2.1 (1)
O(7)	−0.0321 (4)	0.4106 (5)	0.7102 (3)	4.1 (2)	13.4 (3)	12.4 (3)	0.2 (2)	1.6 (2)	7.5 (2)
N	0.3226 (3)	0.0953 (3)	0.2811 (2)	3.6 (1)	3.1 (1)	2.9 (1)	0.1 (1)	1.4 (1)	0.5 (1)
C(1)	0.3590 (5)	0.2599 (4)	0.7481 (3)	4.5 (2)	3.7 (2)	4.0 (2)	0.5 (2)	1.6 (1)	1.6 (1)
C(2)	0.4126 (5)	0.4672 (4)	0.8807 (3)	4.9 (2)	4.5 (2)	3.6 (2)	0.3 (2)	1.5 (1)	1.1 (1)
C(3)	0.1499 (5)	0.4165 (5)	0.8983 (3)	5.1 (2)	5.6 (3)	5.2 (2)	0.0 (2)	2.1 (2)	0.1 (2)
C(4)	0.1079 (5)	0.2094 (5)	0.7616 (3)	3.9 (2)	5.3 (2)	4.6 (2)	0.5 (2)	1.4 (2)	1.0 (2)
C(5)	0.3330 (5)	0.2574 (4)	0.9014 (3)	4.4 (2)	5.1 (2)	4.0 (2)	−0.1 (2)	1.6 (1)	1.6 (1)
C(6)	0.0659 (5)	0.4639 (5)	0.7059 (3)	3.8 (2)	6.6 (3)	4.9 (2)	1.1 (2)	1.9 (2)	2.1 (2)
C(7)	0.0397 (5)	0.5507 (5)	0.6548 (4)	4.1 (2)	7.3 (3)	7.7 (3)	2.1 (2)	2.0 (2)	3.7 (2)
C(110)	0.2654 (4)	0.2080 (3)	0.4214 (2)	3.2 (2)	3.1 (2)	2.9 (1)	0.7 (1)	1.2 (1)	1.0 (1)
C(111)	0.2951 (5)	0.2861 (4)	0.5012 (3)	4.3 (2)	5.1 (2)	3.4 (2)	1.2 (2)	1.7 (1)	0.9 (2)
C(112)	0.2043 (5)	0.2970 (5)	0.5447 (3)	5.5 (2)	6.1 (3)	4.6 (2)	1.6 (2)	3.0 (1)	1.3 (2)
C(113)	0.0861 (5)	0.2308 (5)	0.5105 (3)	4.9 (2)	7.2 (3)	5.9 (2)	1.9 (2)	3.2 (2)	2.2 (2)
C(114)	0.0535 (5)	0.1531 (5)	0.4313 (4)	4.0 (2)	6.6 (3)	6.5 (2)	0.8 (2)	2.6 (2)	1.6 (2)
C(115)	0.1456 (4)	0.1414 (4)	0.3860 (3)	3.4 (2)	4.2 (2)	4.8 (2)	0.4 (2)	1.9 (1)	1.6 (1)
C(120)	0.5328 (4)	0.1634 (4)	0.4312 (2)	3.1 (2)	3.4 (2)	3.1 (1)	0.8 (1)	1.2 (1)	1.0 (1)
C(121)	0.5563 (5)	0.0507 (4)	0.4188 (3)	4.3 (2)	3.6 (2)	4.5 (2)	1.2 (2)	1.9 (1)	1.8 (1)
C(122)	0.6692 (5)	0.0237 (4)	0.4712 (3)	4.7 (2)	5.3 (2)	5.1 (2)	1.6 (2)	1.2 (2)	2.3 (2)
C(123)	0.7556 (5)	0.1082 (5)	0.5337 (3)	4.2 (2)	6.6 (2)	5.6 (2)	2.0 (2)	1.3 (2)	2.9 (2)
C(124)	0.7328 (5)	0.2208 (5)	0.5467 (3)	3.9 (2)	6.2 (3)	5.1 (2)	1.0 (2)	0.8 (2)	1.3 (2)
C(125)	0.6203 (5)	0.2490 (4)	0.4942 (3)	3.4 (2)	4.9 (2)	4.1 (2)	0.5 (2)	0.4 (2)	0.7 (2)
C(130)	0.4163 (4)	0.3309 (3)	0.3465 (2)	3.2 (2)	2.8 (2)	3.0 (1)	0.4 (1)	1.1 (1)	0.6 (1)
C(131)	0.5305 (4)	0.3573 (4)	0.3281 (3)	3.7 (2)	3.8 (2)	4.0 (2)	−0.1 (2)	1.5 (2)	1.1 (1)
C(132)	0.5460 (5)	0.4563 (4)	0.3027 (3)	4.7 (2)	4.7 (2)	5.6 (2)	−0.4 (2)	1.8 (2)	2.1 (2)
C(133)	0.4467 (6)	0.5267 (4)	0.2953 (3)	5.7 (2)	3.9 (2)	6.4 (2)	0.0 (2)	1.9 (2)	2.2 (2)
C(134)	0.3348 (5)	0.4997 (4)	0.3153 (3)	5.0 (2)	4.0 (2)	6.0 (2)	0.8 (2)	1.8 (2)	1.8 (2)
C(135)	0.3192 (4)	0.4027 (4)	0.3410 (3)	3.9 (2)	3.4 (2)	5.3 (2)	1.2 (2)	1.9 (1)	1.8 (1)
C(210)	0.3031 (4)	−0.1036 (4)	0.1623 (2)	3.1 (2)	3.1 (2)	2.7 (1)	0.2 (1)	0.7 (1)	0.6 (1)
C(211)	0.2405 (4)	−0.1528 (4)	0.2080 (3)	3.4 (2)	3.8 (2)	3.9 (2)	0.3 (2)	1.0 (1)	1.5 (1)
C(212)	0.2132 (5)	−0.2707 (4)	0.1870 (3)	4.4 (2)	3.7 (2)	4.5 (2)	0.2 (2)	0.9 (2)	1.5 (1)
C(213)	0.2483 (5)	−0.3384 (4)	0.1221 (3)	5.1 (2)	3.6 (2)	5.2 (2)	0.3 (2)	0.8 (2)	1.3 (2)
C(214)	0.3139 (5)	−0.2882 (4)	0.0773 (3)	5.2 (2)	3.9 (2)	4.8 (2)	0.8 (2)	1.3 (2)	0.4 (2)
C(215)	0.3417 (5)	−0.1716 (4)	0.0966 (3)	4.4 (2)	3.6 (2)	3.6 (2)	0.6 (2)	1.5 (1)	0.2 (2)
C(220)	0.4897 (4)	0.0866 (4)	0.1768 (2)	3.5 (2)	3.2 (2)	2.9 (1)	0.1 (1)	1.1 (1)	0.7 (1)
C(221)	0.5962 (5)	0.0360 (4)	0.2143 (3)	3.5 (2)	4.5 (2)	5.4 (2)	0.8 (2)	1.4 (2)	1.3 (2)
C(222)	0.7189 (5)	0.0683 (5)	0.2108 (4)	4.2 (2)	6.1 (3)	7.3 (3)	0.3 (2)	2.1 (2)	1.9 (2)
C(223)	0.7367 (5)	0.1510 (5)	0.1702 (4)	4.8 (2)	6.9 (3)	6.9 (3)	−0.8 (2)	3.0 (2)	0.7 (2)
C(224)	0.6313 (6)	0.2040 (5)	0.1353 (3)	5.8 (2)	6.3 (3)	6.3 (2)	−0.4 (2)	3.0 (2)	2.3 (2)
C(225)	0.5073 (5)	0.1721 (4)	0.1371 (3)	4.9 (2)	5.3 (2)	4.3 (2)	−0.3 (2)	2.1 (1)	2.0 (1)
C(230)	0.2133 (4)	0.1006 (4)	0.1138 (3)	3.2 (2)	3.6 (2)	3.7 (2)	0.3 (1)	0.7 (1)	1.4 (1)
C(231)	0.1923 (5)	0.0591 (5)	0.0274 (3)	4.2 (2)	6.9 (3)	3.7 (2)	0.4 (2)	0.8 (2)	2.4 (2)
C(232)	0.1020 (5)	0.1002 (5)	−0.0302 (3)	4.4 (2)	7.8 (3)	5.0 (2)	−0.0 (2)	0.5 (2)	3.5 (2)
C(233)	0.0358 (6)	0.1868 (5)	−0.0006 (4)	4.5 (3)	7.7 (3)	6.6 (2)	−0.8 (2)	−0.7 (2)	4.3 (2)
C(234)	0.0526 (6)	0.2296 (5)	0.0858 (5)	5.1 (3)	6.4 (3)	8.9 (3)	1.9 (2)	0.0 (3)	3.1 (2)
C(235)	0.1422 (6)	0.1855 (5)	0.1444 (4)	4.9 (2)	5.4 (2)	6.1 (3)	1.8 (2)	0.6 (2)	1.9 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$ where *a*, *b*, and *c* are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

respectively, are similar to those observed for both monodentate and bridging acetate and trifluoroacetate groups in molybdenum and chromium complexes.[16,17] It is the relationship between the two carbon–oxygen bond lengths that constitutes the unusual structural feature. The distances from the carboxyl carbon to the bound oxygen are 1.23 (1), 1.224 (4), and 1.196 (7) Å for **1**, **2a**, and **2b**, respectively. The distances between this same carbon atom and the free oxygen atom, classically expected to be a C–O double bond, are, in fact, longer at 1.26 (1), 1.243 (5), and 1.200 (7), respectively, for **1**, **2a**, and **2b**. There are few structures reported for the acetate group in this mode of linkage; however, the examples presently appearing in the literature adopt the more classical configuration. For instance, the monodentate acetate groups in $Mo_2(\mu\text{-}O_2CCF_3)_2(PEt_2Ph)_2(O_2CCF_3)_2$[17] have bond lengths of 1.273 (5) and 1.202 (5) Å for the (M)O—C and C=O bonds, respectively. We have also determined[18] the structure of $Mn(CO)_5(O_2CCF_3)$, isoelectronic with the anion in **2b**, and initial results indicate that the trifluoroacetate group has dimensions consistent with the classical representation as an M—O—C(R)=O unit. There are several possible explanations for the

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[16] Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161.

[17] Cotton, F. A.; Lay, D. G., unpublished work.

[18] Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.*, in press.

Table VIII. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[PNP][Cr(CO)_5(O_2CCF_3)]^a$

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cr	0.2530 (1)	0.3433 (1)	0.82169 (7)	4.17 (5)	4.50 (6)	3.36 (5)	0.48 (5)	1.05 (4)	0.89 (4)
P(1)	0.3836 (2)	0.1947 (2)	0.3637 (1)	2.96 (7)	2.72 (7)	2.54 (6)	0.43 (6)	0.95 (5)	0.59 (6)
P(2)	0.3341 (2)	0.0496 (2)	0.1876 (1)	3.02 (7)	3.10 (8)	2.45 (6)	0.33 (7)	0.69 (6)	0.76 (6)
F(1)	0.0084 (6)	0.6431 (5)	0.7013 (4)	9.0 (3)	6.4 (3)	12.9 (4)	2.9 (3)	3.3 (3)	1.5 (3)
F(2)	0.1417 (5)	0.5773 (5)	0.6339 (4)	6.6 (3)	13.8 (3)	15.7 (3)	4.3 (2)	5.4 (2)	11.0 (2)
F(3)	−0.0585 (6)	0.5108 (6)	0.5886 (4)	7.5 (3)	12.1 (4)	7.7 (3)	1.8 (3)	0.1 (3)	4.0 (3)
O(1)	0.4078 (6)	0.2130 (5)	0.7156 (3)	7.4 (3)	4.5 (3)	5.9 (3)	1.5 (2)	2.5 (2)	1.2 (2)
O(2)	0.4866 (6)	0.5286 (6)	0.9122 (4)	7.3 (3)	6.9 (3)	6.0 (3)	−1.5 (3)	0.9 (3)	0.7 (3)
O(3)	0.0971 (7)	0.4512 (7)	0.9388 (4)	8.6 (3)	10.4 (5)	7.4 (3)	0.1 (4)	4.8 (2)	−1.7 (3)
O(4)	0.0412 (6)	0.1416 (6)	0.7360 (4)	5.0 (3)	6.4 (3)	9.6 (4)	−0.8 (3)	1.4 (3)	0.9 (3)
O(5)	0.3744 (6)	0.2163 (5)	0.9477 (3)	6.3 (3)	8.2 (3)	5.9 (2)	1.1 (3)	1.4 (2)	4.0 (2)
O(6)	0.1811 (5)	0.4462 (4)	0.7377 (3)	4.1 (2)	5.7 (3)	4.5 (2)	1.2 (2)	1.4 (2)	2.1 (2)
O(7)	−0.0304 (6)	0.4095 (7)	0.7129 (4)	4.8 (3)	12.4 (4)	11.5 (4)	1.1 (3)	2.1 (3)	6.7 (3)
N	0.3224 (5)	0.0957 (5)	0.2792 (3)	3.8 (2)	3.4 (3)	2.4 (2)	−0.0 (2)	1.2 (2)	0.3 (2)
C(1)	0.3485 (7)	0.2681 (6)	0.7535 (5)	4.5 (3)	3.5 (3)	4.6 (3)	1.0 (3)	1.9 (3)	1.1 (3)
C(2)	0.3973 (8)	0.4615 (7)	0.8765 (5)	4.7 (4)	5.0 (4)	4.2 (3)	0.6 (3)	1.4 (3)	1.1 (3)
C(3)	0.1534 (8)	0.4135 (8)	0.8945 (5)	5.2 (4)	6.2 (5)	4.5 (3)	−0.1 (4)	1.9 (3)	0.7 (3)
C(4)	0.1168 (8)	0.2220 (8)	0.7668 (5)	3.9 (4)	6.8 (5)	6.0 (4)	0.8 (4)	1.6 (3)	2.0 (3)
C(5)	0.3259 (7)	0.2658 (7)	0.8983 (4)	4.0 (3)	6.2 (4)	3.7 (3)	−0.5 (3)	1.4 (3)	1.6 (3)
C(6)	0.0679 (7)	0.4568 (8)	0.7095 (5)	2.6 (3)	7.3 (5)	5.5 (4)	−0.0 (3)	1.9 (3)	1.2 (3)
C(7)	0.0421 (8)	0.5481 (8)	0.6579 (6)	4.0 (4)	8.0 (5)	7.9 (4)	2.1 (4)	1.7 (3)	4.1 (4)

atom	x	y	z	B, $Å^2$	atom	x	y	z	B, $Å^2$
C(110)	0.2650 (6)	0.2085 (6)	0.4203 (4)	3.0 (1)	C(210)	0.3045 (6)	−0.1048 (5)	0.1609 (4)	2.7 (1)
C(111)	0.2962 (7)	0.2859 (7)	0.5000 (5)	4.2 (2)	C(211)	0.2415 (7)	−0.1542 (6)	0.2067 (4)	3.3 (1)
C(112)	0.2017 (8)	0.2962 (7)	0.5448 (5)	5.4 (2)	C(212)	0.2155 (7)	−0.2728 (7)	0.1862 (5)	4.2 (2)
C(113)	0.0835 (9)	0.2293 (8)	0.5095 (5)	5.6 (2)	C(213)	0.2515 (8)	−0.3406 (7)	0.1217 (5)	4.7 (2)
C(114)	0.0519 (9)	0.1522 (8)	0.4294 (5)	5.6 (2)	C(214)	0.3163 (8)	−0.2915 (7)	0.0756 (5)	4.8 (2)
C(115)	0.1432 (7)	0.1413 (7)	0.3835 (5)	4.2 (2)	C(215)	0.3434 (7)	−0.1730 (6)	0.0955 (4)	3.9 (2)
C(120)	0.5344 (6)	0.1633 (6)	0.4306 (4)	3.0 (1)	C(220)	0.4910 (6)	0.0869 (6)	0.1760 (4)	2.9 (1)
C(121)	0.5569 (7)	0.0478 (6)	0.4180 (4)	3.9 (2)	C(221)	0.5954 (8)	0.0358 (7)	0.2134 (5)	4.6 (2)
C(122)	0.6711 (8)	0.0205 (7)	0.4688 (5)	5.0 (2)	C(222)	0.7251 (9)	0.0698 (8)	0.2118 (5)	5.9 (2)
C(123)	0.7590 (8)	0.1056 (7)	0.5339 (5)	5.0 (2)	C(223)	0.7398 (8)	0.1533 (7)	0.1701 (5)	5.5 (2)
C(124)	0.7362 (8)	0.2190 (8)	0.5467 (5)	5.3 (2)	C(224)	0.6349 (9)	0.2037 (8)	0.1341 (5)	5.7 (2)
C(125)	0.6199 (7)	0.2497 (7)	0.4943 (7)	4.3 (2)	C(225)	0.5076 (8)	0.1703 (7)	0.1361 (5)	4.4 (2)
C(130)	0.4174 (6)	0.3322 (6)	0.3462 (4)	2.9 (1)	C(230)	0.2134 (7)	0.1007 (6)	0.1121 (4)	3.3 (1)
C(131)	0.5314 (7)	0.3581 (6)	0.3282 (4)	3.9 (2)	C(231)	0.1912 (8)	0.0562 (7)	0.0259 (5)	4.8 (2)
C(132)	0.5465 (8)	0.4591 (7)	0.3019 (5)	5.1 (2)	C(232)	0.0981 (9)	0.1043 (8)	−0.0323 (5)	5.8 (2)
C(133)	0.4481 (8)	0.5278 (5)	0.2961 (5)	5.1 (2)	C(233)	0.0360 (9)	0.1899 (8)	−0.0036 (5)	6.0 (2)
C(134)	0.3337 (8)	0.5020 (7)	0.3141 (5)	5.2 (2)	C(234)	0.0513 (10)	0.2329 (9)	0.0832 (6)	7.2 (3)
C(135)	0.3183 (7)	0.4036 (7)	0.3405 (5)	4.3 (2)	C(235)	0.1444 (8)	0.1854 (7)	0.1421 (5)	5.1 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$ where a, b, and c are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

unusual mode of linkage in **1**, **2a**, and **2b**, and experiments are presently in progress to clarify these.

The geometry and coordination of the carbonyl ligands also exhibit chemically interesting features. In **1**, the equatorial carbonyl groups form a square array with an average C–M–C angle for adjacent carbonyls of 89.9 (4)° and a M–C distance of 2.05 (1) Å. The largest distortion from the square arrangement is the compression of the C(1)–M–C(4) angle (Figure 4) to 85.5 (4)°. This distortion is probably due to the orientation of the acetate group which places the carboxyl oxygen, O(7), directly over the C(3)–M–C(4) quadrant. Concomitant with this is a small shift of the equatorial plane toward the axial CO group (average C–M–C(5) angle of 88.7 (4)°). Also, the OC(C)O framework bends slightly away from the C(3)–M–C(4) quadrant to accommodate this orientation of the acetate group, producing a C(5)–M–O(6) bond angle of 175.9 (4)°. The average C–O bond lengths of 1.13 (1) Å show no distinct trends either for orientation toward or away from O(7) or, for that matter, for equatorial vs. axial environment.[19] However, the variations in the metal–carbon bond distances do show an interesting pattern. While the M–C(eq) distances average 2.05 (1) Å (comparable to the M–C distance of 2.06 (2) Å in $M(CO)_6$),[20] the axial M–C(5) bond length is considerably shorter at 1.96 (1) Å. This shift of 0.09 Å is a significantly larger difference than any previously observed. For instance, in $Mo(CO)_5(PPh_3)$, the difference between the equatorial distance (2.046 (4) Å) and the axial distance (1.995 (3) Å) is only

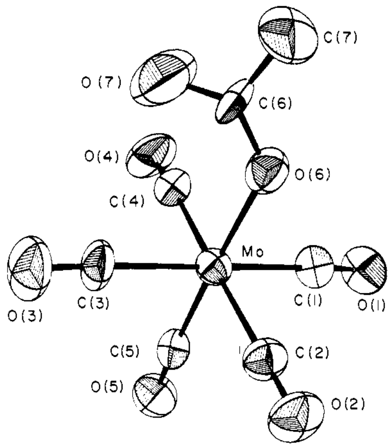

Figure 4. An ORTEP plot of the $Mo(CO)_5(O_2CCH_3)^-$ anion in **1** (40% thermal ellipsoids).

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[19] The C(3)–O(3) distance in **1** and the C(4)–O(4) distance in **2** are considerably shorter than the average values in each structure. However, the large thermal parameters for the oxygen atoms suggest that these deviations are crystallographic artifacts and corrected C–O distances would have to be calculated taking this large thermal motion into account. (Cf. Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.)

[20] Brockway, L. O.; Ewens, R. V. G.; Lister, L. *Trans. Faraday Soc.* **1938**, *34*, 1350.

Table IX. Bond Distances (Å) and Bond Angles (Deg) with Esd's

	1	2a	2b
	Distances		
M-C(1)	2.02 (1)	2.014 (4)	1.865 (6)
M-C(2)	2.06 (1)	2.053 (4)	1.909 (7)
M-C(3)	2.07 (1)	2.070 (4)	1.931 (7)
M-C(4)	2.05 (1)	2.058 (4)	1.878 (8)
M-C(5)	1.96 (1)	1.947 (4)	1.815 (7)
M-O(6)	2.211 (7)	2.236 (2)	2.133 (4)
C(1)-O(1)	1.14 (1)	1.148 (4)	1.153 (6)
C(2)-O(2)	1.13 (1)	1.134 (4)	1.142 (6)
C(3)-O(3)	1.10 (1)	1.133 (5)	1.123 (7)
C(4)-O(4)	1.11 (1)	1.109 (5)	1.149 (7)
C(5)-O(5)	1.14 (1)	1.152 (4)	1.170 (6)
C(6)-O(6)	1.23 (1)	1.224 (4)	1.196 (7)
C(6)-O(7)	1.26 (1)	1.243 (5)	1.200 (7)
C(6)-C(7)	1.56 (1)	1.518 (6)	1.565 (9)
C(7)-F(1)		1.350 (6)	1.334 (8)
C(7)-F(2)		1.316 (5)	1.311 (7)
C(7)-F(3)		1.308 (5)	1.317 (8)
P(1)-N	1.570 (6)	1.576 (3)	1.580 (4)
P(2)-N	1.579 (7)	1.581 (3)	1.568 (4)
P(1)-C(av)	1.805 (8)	1.802 (3)	1.803 (5)
P(2)-C(av)	1.799 (8)	1.801 (3)	1.802 (5)
	Angles		
M-C(1)-O(1)	174.3 (9)	175.3 (3)	173.0 (5)
M-C(2)-O(2)	174 (1)	176.5 (4)	176.2 (6)
M-C(3)-O(3)	174 (1)	175.4 (5)	177.0 (7)
M-C(4)-O(4)	171 (1)	174.5 (4)	174.0 (6)
M-C(5)-O(5)	176.8 (9)	178.3 (3)	179.1 (5)
M-O(6)-C(6)	129.9 (8)	125.7 (3)	124.5 (4)
C(1)-M-C(2)	90.6 (4)	89.5 (2)	89.3 (3)
C(1)-M-C(3)	176.6 (5)	175.9 (2)	176.8 (3)
C(1)-M-C(4)	85.5 (4)	88.0 (2)	88.2 (3)
C(1)-M-C(5)	87.8 (4)	86.9 (2)	88.1 (3)
C(1)-M-O(6)	93.0 (3)	93.6 (1)	92.2 (2)
C(2)-M-C(3)	92.1 (4)	92.6 (2)	92.3 (3)
C(2)-M-C(4)	175.0 (4)	176.3 (2)	177.2 (3)
C(2)-M-C(5)	88.0 (4)	88.7 (2)	88.9 (3)
C(2)-M-O(6)	88.0 (4)	86.9 (1)	86.1 (2)
C(3)-M-C(4)	91.7 (4)	89.7 (2)	90.0 (3)
C(3)-M-C(5)	90.2 (5)	89.6 (2)	89.2 (3)
C(3)-M-O(6)	89.3 (4)	90.1 (1)	90.7 (2)
C(4)-M-C(5)	88.8 (4)	88.4 (2)	89.7 (3)
C(4)-M-O(6)	95.3 (4)	95.9 (1)	95.4 (2)
C(5)-M-O(6)	175.9 (4)	175.6 (1)	174.9 (2)
O(6)-C(6)-O(7)	120 (1)	127.8 (4)	131.8 (7)
O(6)-C(6)-C(7)	120 (1)	116.1 (4)	114.5 (6)
O(7)-C(6)-C(7)	119 (1)	116.0 (4)	113.6 (6)
C(6)-C(7)-F(1)		111.5 (4)	111.8 (6)
C(6)-C(7)-F(2)		114.4 (3)	114.0 (6)
C(6)-C(7)-F(3)		112.3 (4)	111.2 (6)
F(1)-C(7)-F(2)		106.4 (4)	108.2 (7)
F(1)-C(7)-F(3)		103.4 (4)	104.4 (6)
F(2)-C(7)-F(3)		108.1 (4)	106.7 (7)
P(1)-N-P(2)	141.2 (5)	140.9 (2)	141.4 (3)

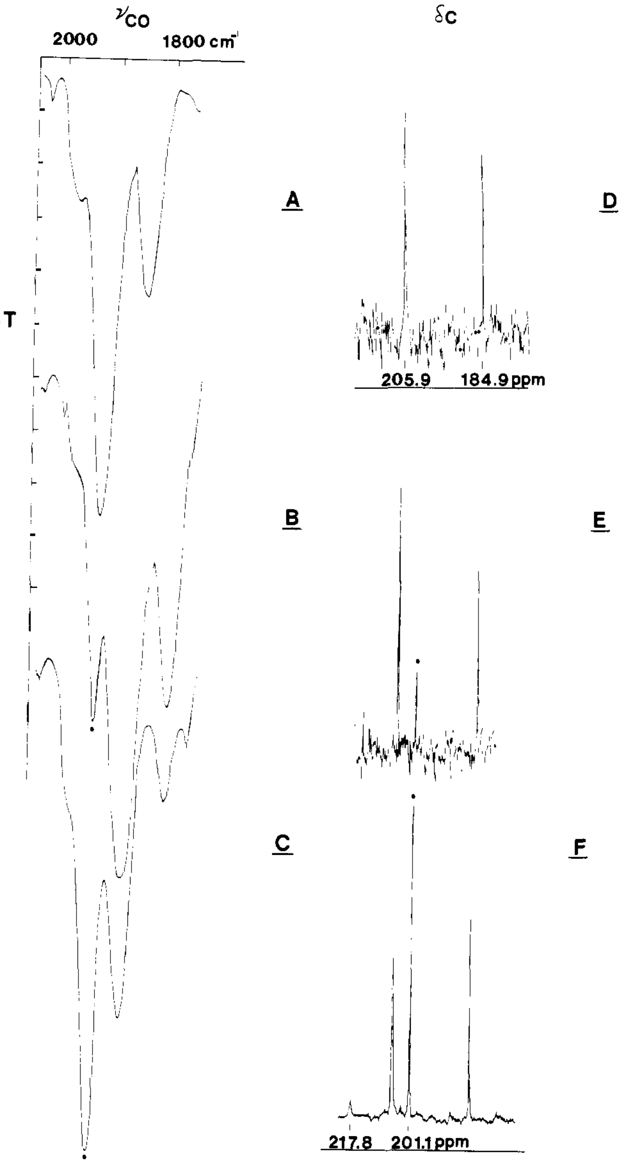

Figure 5. Infrared (ν(CO)) and ^{13}C NMR monitoring of the ^{13}CO-exchange reaction with [PNP][Mo(CO)$_5$O$_2$CCH$_3$]: A, initial IR of [Mo(CO)$_5$O$_2$CCH$_3$][PNP] in CH$_2$Cl$_2$; B, after 1 h in a ^{13}CO atmosphere at room temperature (peak marked by asterisk due to Mo(^{13}CO)$_6$); C, after 18 h at room temperature; D, initial ^{13}C NMR of [PNP][Mo(CO)$_5$O$_2$CCH$_3$] in the presence of ^{13}CO in CDCl$_3$ (peak at 184.9 ppm due to free CO); E, after 1 h at room temperature (peak marked by asterisk due to Mo(CO)$_6$); F, after 18 h at room temperature. The broadness of the ^{13}C resonances of the CO groups in [PNP][Mo(CO)$_5$O$_2$CCH$_3$] is due to axial–equatorial ^{13}C–^{13}C coupling (J = 3.4 Hz).

0.051 Å.[15] This large trans effect for the acetate group indicates that, in this complex, this ligand acts essentially as a σ donor and that there is little or no π component to the M–O bond.

The structure of the (trifluoroacetato)molybdenum anion, **2a**, shows no significant variation from that of **1**. The C–O and M–C(eq) bond lengths are 1.135 (5) and 2.049 (4) Å, respectively. The metal–oxygen distance of 2.236 (2) Å is slightly longer than that determined for **1**. Again, there is a slight distortion of the equatorial plane and of the C(5)–Mo–O(6) angle to accommodate the carboxylate ligand. Significantly, the M–C(ax) distance of 1.947 (4) Å is 0.102 Å shorter than the average equatorial M–C bond length, indicating that the CF$_3$CO$_2^-$ ligand (as in the CH$_3$CO$_2^-$ case) is acting solely as a donor (σ) of electrons.

The structure of the chromium analogue, **2b**, is similar. The main differences are accountable in terms of the smaller radius of this metal. The average M–C(eq) and M–O(6) distances of 1.896 (7) and 2.133 (4) Å, respectively, are normal. Again, the difference in axial vs. equatorial metal–carbon bond length is quite dramatic. This difference, 0.081 Å, is significantly larger than that in most of the structures reported in the literature. Only the complex Cr(CO)$_5$(SPMe$_3$)[21] exhibits a trans effect this large. In that report, the SPMe$_3$ ligand was considered as being solely a σ-donor group, not unlike the case we are describing here.

Solution Studies of the Pentacarbonyl(acetato)molybdenum Anion. In general the [PNP][M(CO)$_5$O$_2$CCH$_3$] and [PNP][M(CO)$_5$O$_2$CCF$_3$] (M = Cr, Mo) derivatives are found to be unstable in solution, eventually affording the parent hexacarbonyl species. This is a common mode of decomposition for many anionic and neutral group 6B metal–pentacarbonyl derivatives containing labile

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[21] Baker, E. N.; Reay, B. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2205.

ligands, e.g., halides or amines. Nevertheless, dissociative loss of carbon monoxide is observed to be the most facile reaction of these species in solution as demonstrated by their rapid exchange with free carbon monoxide according to eq 2.

$$Mo(CO)_5O_2CCH_3^- + {}^{13}CO \rightarrow Mo(CO)_{5-n}({}^{13}CO)_nO_2CCH_3^- + CO \quad (2)$$

The $Mo(CO)_5O_2CCH_3^-$ ion undergoes extensive ligand exchange with ^{13}CO at ambient temperature prior to formation of any appreciable quantity of $Mo(CO)_6$, thus yielding highly ^{13}CO-enriched molybdenum hexacarbonyl (see Figure 5).[22] The stereochemistry of this and related reactions will be discussed in detail in a later paper in this series. Hence the acetate ion can be categorized as a CO-labilizing ligand comparable with the chloride ion[23,24] and alkylphosphine oxides.[25] In addition to the factors favoring cis labilization discussed by Atwood and Brown,[24] the carboxylate ions may also be capable of conferring added stability on the five-coordinate intermediate or transition state resulting from CO dissociation by metal interaction with the free carboxylic oxygen atom.

The fact that CO substitution in $Mo(CO)_5O_2CCH_3^-$ is more facile than acetate displacement is also manifested in phosphine substitutional processes. The $Mo(CO)_5O_2CCH_3^-$ anion is found to react with excess Ph_3P or Et_3P to afford the *cis*-$Mo(CO)_4L_2$ species under conditions where $Mo(CO)_5L$ are substitutionally inert (eq 3).

$$\begin{array}{l} Mo(CO)_5O_2CCH_3^- + PPh_3 \rightarrow Mo(CO)_4[PPh_3]O_2CCH_3^- + CO \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow PPh_3 \qquad\qquad (3) \\ \qquad\qquad\qquad\qquad cis\text{-}Mo(CO)_4[PPh_3]_2 + CH_3CO_2^- \end{array}$$

The cis stereochemistry of the product in eq 3 was established by comparison of the infrared spectrum with that of an authentic sample.[26] Indeed, it is possible to synthesize highly ^{13}C-enriched *cis*-$Mo(CO)_4[phosphine]_2$ derivatives by equilibration of $Mo(CO)_5O_2CCH_3^-$ with ^{13}CO prior to addition of the phosphine. When reaction is carried out with the more stable tungsten acetate analogue, the $[PNP][W(CO)_4[PPh_3]O_2CCH_3]$ is isolable.[7]

During the carbonyl ligand-exchange process described in eq 1 no incorporation of ^{13}CO into the acetate moiety occurs according to either the $\nu(CO_2^-)$ infrared (Table I) or ^{13}C NMR spectra (carboxylic carbon resonance at 177.4 ppm). Conversely, when the $Mo(CO)_5O_2{}^{13}CCH_3^-$ is allowed to decompose in solution, no ^{13}C enrichment is observed in the $Mo(CO)_6$ thus formed. These negative results are not surprising, of course. The experiments were done and the negative results explicitly noted here because of their relevance to studies of the formation of trinuclear acetato complexes.[27]

Summary

The solid-state structure of (acetato)pentacarbonylmolybdenum revealed several interesting features, including an approximate equality of the formally single Mo(O—C) and double C=O bond lengths and a short trans Mo—CO bond. We felt these observations deserved further study in order to examine their generality. Hence the structures of the (trifluoroacetato)chromium and -molybdenum pentacarbonyls were determined, and they have been found to exhibit analogous structural characteristics. The particularly short trans M—CO bond is also evident from solution spectroscopic measurements, namely, a large ^{13}C downfield chemical shift for the axial CO ligand in the $Mo(CO)_5O_2CCH_3^-$ anion.[28] On the other hand $\nu(CO_2^-)$ vibrational modes did not show a great deal of sensitivity to M(O—C) and C=O bond length changes, for these occur at very similar frequencies in the complexes herein described and in $Mn(CO)_5O_2CCF_3$ (a species which exhibits significantly different Mn(O—C) and C=O bond lengths).

Finally carbon monoxide ligand substitution processes in solution evince reactivity patterns open to these anionic acetate derivatives which are not apparent from ground-state structural parameters; i.e., the monodentate-bonded acetate group is a strongly labilizing ligand.

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Supplementary Material Available: Tables III, IV, and V, listings of observed and calculated structure factors for the three complexes, and Table X, a listing of bond distances and bond angles for the $[PNP]^+$ cations (55 pages). Ordering information is given on any current masthead page.

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[22] CO exchange occurs initially stereoselectively at equatorial CO sites; however, the ^{13}C label eventually occupies both axial and equatorial sites. A more definitive discussion of the stereoselectivity of the ^{13}CO incorporation process must await investigations on the thermally more stable tungsten analogue where concomitant acetate displacement is less likely.

[23] Allen, A. D.; Barrett, P. F. *Can. J. Chem.* **1968**, *46*, 1655.

[24] Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

[25] Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1213.

[26] Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

[27] Unpublished work by A. Bino, F. A. Cotton, Z. Dori, and B. W. S. Kolthammer.

[28] The reported chemical shift values in $[Mo(CO)_5I][n\text{-}Bu_4N]$ are 214.4 (C_{trans}) and 202.4 ppm (C_{cis}). Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

[29] **Note Added in Proof**: It has just come to our attention that Doyle (*J. Organomet. Chem.* **1975**, *84*, 323) has previously published the preparation of pentacarbonylcarboxylate anions of the group 6B metals from the corresponding $M(CO)_5Cl^-$ and thallium(I) or silver(I) carboxylates.