have previously suggested that the transient generation of "I^+" in the presence of ICl leads to the formation of the $[I_3Cl_2]^+$ cation.[25] If $[IBr]^+$ is produced in the oxidation of IBr, our inability to obtain $[IBr][Sb_2F_{11}]$ or similar salts is most likely due to the greater stability of its decomposition products under the conditions prevailing in our preparation.

We also attempted to prepare $[IBrCl][SbCl_6]$ according to the method of Shamir and Lustig.[9] However, the material that we obtained has the composition $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ as we have established X-ray crystallography. The Raman spectrum of this material is shown in Figure 5 and the principal bands are given in Table VII. After assignment of the anion bands, the number of bands remaining is too great for the presence of only the simple $[IBrCl]^+$ cation, which should have only three bands. Indeed X-ray crystallography shows the cation composition to be $[IBr_{0.75}Cl_{1.25}]^+$, i.e., is a disordered mixture of probably all of the following cations: $[IBr_2]^+$, $[ICl_2]^+$, and $[IBrCl]^+$. Two I–Cl and two I–Br vibrations are clearly visible in our spectrum, which can be assigned to the appropriate modes of the $[ICl_2]^+$ and $[IBr_2]^+$ cations, respectively. We are unable to uniquely assign any bands to the $[IBrCl]^+$ cation, but these would occur in the same regions of the spectrum as the other cations and be obscured by these bands. The similarity between our spectrum and that of Shamir and Lustig,[9] whose preparation we followed, is close, although the relative intensities of the bands in the two spectra are not the same. It is not clear why we were unable to obtain pure $[IBrCl][SbCl_6]$ or even to change the composition of our disordered cation by repeated sublimation. Other workers[3] who isolated $[IBrCl][SO_3F]$ from the reaction between $[IBr_2][SO_3F]$ and $[ICl_2][SO_3F]$ were unable to decide unequivocally that they had prepared a true compound of $[IBrCl]^+$. Their reaction also could have resulted in a disordered bent cation as we have found.

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Registry No. $[IBr_2][Sb_2F_{11}]$, 56664-97-2; $[IBr_{0.75}Cl_{1.25}][SbCl_6]$, 85421-80-3; $[ICl_2][SbCl_6]$, 38656-81-4; $[ICl_2][AlCl_4]$, 42813-30-9; $[I_3][AsF_6]$, 59555-19-0.

Supplementary Material Available: A plot of scattering factor curves and listings of observed and calculated structure factor amplitudes, bond angles, and anisotropic thermal parameters (49 pages). Ordering information is given on any current masthead page.

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[24] Pohl, S.; Saak, W. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem.* **1981**, *36B*, 3.

[25] Birchall, T.; Myers, R. D. *Inorg. Chem.* **1982**, *21*, 213.

Contribution from the Molecular Structure Center and the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Addition of Carboxylic Acids to $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ and the Molecular Structure of $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$

MARK E. NOBLE, J. C. HUFFMAN,* and R. A. D. WENTWORTH*

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The addition of CF_3CO_2H to solutions of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ in CH_2Cl_2 results in $[Mo(NC_6H_4CH_3)(S_2OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$, which crystallizes in the monoclinic space group $P2_1/a$, with $a = 23.569$ (9) Å, $b = 17.162$ (6) Å, $c = 10.050$ (3) Å, $\beta = 111.88$ (1)°, and $Z = 4$ at -165 °C. The bridging sulfhydryl ligand is bent away from the terminal, multiply bound arylimido ligands. A comparison with other carboxylic acids indicates that the equilibrium constants for the addition of the acids follows the order $CF_3CO_2H \sim CCl_3CO_2H > CHCl_2CO_2H > CH_2ClCO_2H > CH_3CO_2H$. In contrast, no reaction was observed between $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$ and CF_3CO_2H. Evidence for the existence of the conjugate bases, $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)^-$, has also been accumulated.

Introduction

The existing analogy between the structures of mononuclear oxo and arylimido compounds of molybdenum[1] suggests the likelihood of a similar analogy with certain dinuclear compounds. Thus, the authenticated structure[2] of $[MoO(\mu\text{-}S)(S_2P(O\text{-}i\text{-}C_3H_7)_2)]_2$ would suggest the existence of a similar compound with terminal arylimido ligands. The isolation[3] of the structurally characterized,[4] cubane-like tetranuclear compound $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ (**T**) was then totally unexpected. The formation of this compound from the expected dinuclear fragments of $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$ (**D**), as shown by the equilibrium in eq 1, was recognized and verified experimentally. The equilibrium

$$2\mathbf{D} \rightleftarrows \mathbf{T} \tag{1}$$

constant for this reaction was found to be about 10^4 in CH_2Cl_2. Clearly, substitution of arylimido ligands for oxo ligands has caused either enhanced Lewis acidities for the metal atoms (possibly due to a lessened trans effect), enhanced Lewis basicities for the bridging sulfur atoms, or both.

Although an enhanced Lewis basicity for a bridging sulfur atom will not necessarily be accompanied by an enhanced susceptibility to protonation, we elected to examine the reactions of **T** with a series of substituted acetic acids. The goals of this study were to delineate the site of protonation (if, indeed, protonation occurs), to determine if the apparent basicity of this site is in qualitative agreement with the acidities of the carboxylic acids, and to compare the ease of protonation of **T** with that of $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$.

Experimental Section

Reagents and Procedures. Manipulations performed under nitrogen were done by using standard vacuum-line techniques and solvents that

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[1] Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063. Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1055.

[2] Atovmyan, L. O.; Tkachev, V. V.; Shchepinov, S. A. *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1978**, *4*, 460.

[3] Edelblut, A. W.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1110.

[4] Edelblut, A. W.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1981**, *103*, 1927.

0020-1669/83/1322-1756$01.50/0

had been dried and distilled under vacuum. The azide, $p\text{-}CH_3C_6H_4N_3$, was prepared by the reaction of NaN_3 with the diazonium salt obtained from the reaction of $p\text{-}CH_3C_6H_4NH_2$ with $NaNO_2$. The azide was stored and used as a cyclohexane solution (~2 M). All but one of the carboxylic acids were used as received while CCl_3CO_2H was dried under vacuum prior to use.

Physical and Analytical Methods. ^1H NMR spectra were recorded on either a Varian HR 220 or Nicolet NT 360 spectrometer. ^{31}P NMR spectra were obtained on a Varian XL 100 spectrometer at 40.5 MHz using ^1H decoupling and are listed as downfield shifts from external 85% H_3PO_4. ^{19}F NMR spectra were done with the Nicolet NT 360 spectrometer at 339.7 MHz and are listed as downfield shifts from external, neat CF_3CO_2H. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Model 283 spectrophotometer. Elemental analyses were conducted by Galbraith Laboratories, Inc., Knoxville, TN.

Equilibrium processes were investigated by ^{31}P NMR after admixture of the necessary components, including dry CH_2Cl_2 solvent, under N_2 in an NMR tube fitted with a septum cap. Subsequent additions were then made as necessary by using a needle and syringe.

$\mathbf{[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4}$ **(T).** A slurry of $Mo(CO)_6$ (28.9 mmol), $p\text{-}CH_3C_6H_4N_3$ (43.3 mmol), S (28.9 mmol), $HS_2P(OC_2H_5)_2$ (46.4 mmol), and THF (~30 mL) was refluxed under N_2 for 16 h. Following filtration, the solution was reduced to an oil under vacuum. Opened to air, methanol was added, slowly giving the product, which was collected, washed (methanol), and dried. Recrystallization from CH_2Cl_2/methanol afforded crystals (41%). Physical and spectroscopic properties of this product (IR; ^1H and ^{31}P NMR) are identical with those for the tetramer prepared by the previously reported procedure.[3]

$\mathbf{[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)}$ **(D·H,CF_3CO_2).** A solution of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ (0.64 mmol) in methylene chloride (4 mL) was aerially treated with excess CF_3CO_2H (0.25 mL), giving a deep orange color. Addition of 1% (v/v) CF_3CO_2H in petroleum ether (100 mL) slowly gave orange crystals, which were collected, washed (1% CF_3CO_2H/petroleum ether), and dried (82%). Anal. Calcd for $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$: C, 30.3; H, 3.7; N, 2.9. Found: C, 30.3; H, 3.8; N, 3.3. ^1H NMR ($CDCl_3$): δ 6.58 (4 H, m, aryl H), 4.13 (4 H, m, OCH_2), 2.11 (3 H, s, aryl CH_3), 1.30 and 1.24 (6 H, 2t, $OCCH_3$). ^{31}P NMR ($CDCl_3$): δ 114.1. ^{19}F NMR (CH_2Cl_2): δ 0.84. Selected IR bands (cm^{-1}): 2970 (m), 2456 (w), 1640 (s), 1465 (m), 1199 (vs), 1173 (m), 1161 (s), 1002 (vs), 961 (vs), 948 (vs), 815 (s), 640 (m), 631 (m).

$\mathbf{[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2}$. A solution of $Na_2MoO_4\cdot 2H_2O$ (41 mmol) in water (100 mL) acidified with H_2SO_4 (2.3 mL) was treated with excess $HS_2P(OC_2H_5)_2$ (41 mL) in the air. The resulting purple mixture was heated to a brief boil. After the mixture was allowed to cool, the aqueous portion was decanted, and the gummy residue was extracted with water followed by 1:1 and 4:1 ethanol/water. A 1:1 ethanol/petroleum ether extraction afforded a slurry of yellow powder, which was collected, washed (1:1 ethanol/petroleum ether), and dried. Recrystallization from 1,2-$C_2H_4Cl_2$/(1:1 ethanol/petroleum ether) gave yellow-orange crystals (50%). Anal. Calcd for $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$: C, 14.6; H, 3.1. Found: C, 14.3; H, 3.4. ^1H NMR ($CDCl_3$): δ 4.66 (4 H, m, OCH_2), 3.91 (4 H, m, OCH_2), 1.57 (6 H, t, CH_3), 1.29 (6 H, t, CH_3). ^{31}P NMR ($CDCl_3$): δ 111.6. Selected IR bands (cm^{-1}): 2972 (m), 1467 (m), 1155 (m), 1054 (s), 998 (vs), 964 (vs), 790 (s), 637 (m), 627 (m), 341 (m), 328 (m).

When this compound (0.61 mmol) in tetrahydrofuran (10 mL) was treated with a solution of $Na(S_2CN(C_2H_5)_2)\cdot 3H_2O$ (1.2 mmol) in methanol (5 mL) a yellow powder was obtained (93%) whose infrared spectrum was identical with that of $[MoO(\mu\text{-}S)(S_2CN(C_2H_5)_2)]_2$.[5] The ^{31}P NMR spectrum of the filtrate revealed a single peak corresponding to $Na(S_2P(OC_2H_5)_2)$.

X-ray Crystallography. Data Collection. A well-formed orange crystal of D·H,CF_3CO_2 was cooled to −165 °C on a Picker goniostat for characterization and data collection. The diffractometer, low-temperature apparatus, and data reduction techniques have been described previously.[6] A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima that could be indexed as monoclinic, space group $P2_1/a$ (an alternate setting of $P2_1/c$). Crystal data are given in Table I.

Table I. Crystal Data

space group	$P2_1/a$
temp, °C	−165
a, Å	23.569 (9)
b, Å	17.162 (6)
c, Å	10.050 (3)
β, deg	111.88 (1)
V, Å^3	3772.1
d_{calcd}, g/cm^3	1.674
Z	4
cryst size, mm	0.036 × 0.10 × 0.176
radiation	Mo Kα (0.71069 Å)
no. of unique data	4959
no. of data with $F > 2.33\sigma(F)$	2982
linear abs coeff	11.092
max abs	0.872
min abs	0.964
$R(F)$	0.090
$R_w(F)$	0.072
goodness of fit	1.171
largest Δ/σ	0.05

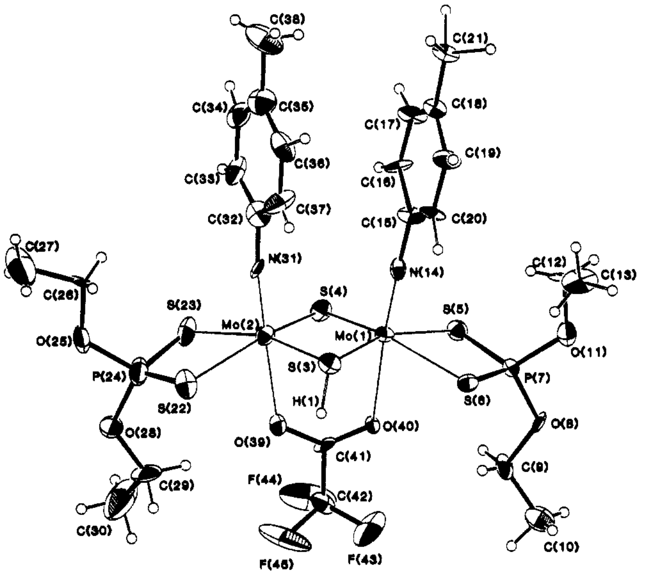

Figure 1. ORTEP drawing of $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$ with thermal ellipsoids at the 50% probability level for non-hydrogen atoms.

Data were collected by using standard moving crystal–moving detector techniques with a scan rate of 4° min^{-1} over a range of 2θ of 2° plus a dispersion correction. Five-second stationary background counts were recorded at the extreme of each scan. The source-to-sample and sample-to-detector distances were 23.5 and 22.5 cm, respectively. All data for $\pm h,+k,\pm l$ in the range $5° \leq 2\theta \leq 50°$ were collected and converted to intensities by using Lorentz, polarization, and absorption corrections. Of the 4959 unique data thus obtained, 2982 had $I \geq 2.33\sigma(I)$ and were considered observed.

Solution and Refinement of the Structure. Direct methods were used to locate all atoms with $Z \geq 15$, and a Fourier synthesis phased on these atoms located all remaining non-hydrogen atoms. A difference Fourier phased on the refined non-hydrogen atoms was used to locate all hydrogen atoms. In the final refinement, non-hydrogen atoms were assigned anisotropic thermal parameters and all positional parameters were allowed to vary while the isotropic thermal parameters of the hydrogen atoms were fixed.

As seen in Figure 1, several atoms possess large anisotropic motion. This is especially true of the fluorine atoms of the trifluoroacetate group and two of the ethoxy groups. Examination of a final difference Fourier synthesis gave no indication of a disorder, with the largest peaks of 1.2 and 1.3 e/Å^3 lying near the two molybdenum atoms. Several of the hydrogen atoms converged to positions that deviate significantly from "idealized" geometries, especially those attached to the ethoxy groups, which exhibited large thermal motion.

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(5) Schultz, F. A.; Ott, V. R.; Rolison, D. S.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1978**, *17*, 1758.

(6) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table II. Final Positional ($\times 10^4$) Parameters for Non-Hydrogen Atoms

atom	x	y	z
Mo(1)	902 (1)	1499 (1)	6120 (2)
Mo(2)	−68 (1)	2585 (1)	4978 (2)
S(3)	−118 (2)	1354 (3)	6162 (5)
S(4)	919 (2)	2662 (3)	4915 (5)
S(5)	1904 (2)	1227 (3)	5866 (5)
S(6)	1046 (2)	55 (3)	6716 (5)
P(7)	1840 (2)	130 (3)	6458 (5)
O(8)	1917 (6)	−483 (6)	5365 (11)
C(9)	1552 (9)	−414 (12)	3815 (19)
C(10)	1578 (10)	−1181 (13)	3147 (21)
O(11)	2395 (5)	−155 (7)	7817 (13)
C(12)	2527 (10)	227 (12)	9206 (19)
C(13)	2311 (11)	−244 (12)	10136 (20)
N(14)	1195 (6)	1798 (8)	7897 (15)
C(15)	1475 (9)	2046 (11)	9294 (17)
C(16)	1795 (9)	2735 (9)	9678 (19)
C(17)	2043 (8)	2939 (11)	11091 (20)
C(18)	1970 (8)	2522 (12)	12179 (17)
C(19)	1638 (10)	1819 (11)	11761 (19)
C(20)	1352 (8)	1583 (10)	10332 (18)
C(21)	2216 (8)	2782 (10)	13659 (17)
S(22)	−1227 (2)	2634 (3)	4006 (6)
S(23)	−276 (3)	3706 (3)	3264 (6)
P(24)	−1166 (3)	3529 (3)	2816 (6)
O(25)	−1509 (6)	4285 (8)	3009 (14)
C(26)	−1339 (9)	4627 (14)	4454 (19)
C(27)	−1780 (14)	5337 (20)	4212 (28)
O(28)	−1543 (7)	3421 (8)	1164 (13)
C(29)	−1423 (13)	2767 (14)	412 (24)
C(30)	−1488 (17)	3032 (17)	−1047 (31)
N(31)	69 (7)	3100 (8)	6545 (15)
C(32)	258 (8)	3468 (12)	7850 (20)
C(33)	486 (10)	4221 (11)	7968 (22)
C(34)	696 (9)	4581 (12)	9292 (22)
C(35)	672 (10)	4225 (13)	10498 (24)
C(36)	427 (9)	3481 (14)	10327 (20)
C(37)	200 (11)	3112 (12)	9032 (23)
C(38)	924 (12)	4663 (15)	11934 (22)
O(39)	−278 (5)	1829 (7)	3011 (12)
O(40)	488 (5)	961 (6)	3914 (11)
C(41)	44 (8)	1273 (10)	2957 (19)
C(42)	−111 (9)	929 (11)	1425 (19)
F(43)	109 (11)	259 (10)	1443 (14)
F(44)	77 (7)	1381 (10)	660 (14)
F(45)	−712 (7)	869 (11)	720 (14)

Final values of the positional parameters for the non-hydrogen atoms are given in Table II.

Results and Discussion

Reactions. The preparation of **T** was accomplished by employing a new one-pot method, which utilizes $Mo(CO)_6$, elemental sulfur, $HS_2P(OC_2H_5)_2$, and p-$CH_3C_6H_4N_3$. Yields of approximately 40% were realized. Spectroscopic data for the compound obtained by this method agreed with previously published[3] results in every respect.

We were not able to even attempt to prepare $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$ according to existing directions[2] for $[MoO(\mu\text{-}S(S_2P(O\text{-}i\text{-}C_3H_7)_2)]_2$ because the description is inadequate at best and affords no useful information. The desired compound was obtained from the reaction of MoO_4^{2-} and $HS_2P(OC_2H_5)_2$ in aqueous solution. In addition to providing the necessary bidentate ligands, $HS_2P(OC_2H_5)_2$ also provides the required reducing equivalents as well as sulfur for the bridges. As usual, it was not possible to observe ν(MoO) unambiguously because of the dominant absorptions due to the bidentate ligand. Proof of the presence of the oxo ligand as well as the entire $[MoO(\mu\text{-}S)]_2$ core was obtained from the metathetical reaction with $Na[S_2CN(C_2H_5)_2]$, which afforded the known[5] compound $[MoO(\mu\text{-}S)(S_2CN(C_2H_5)_2)]_2$ in 93% yield. The infrared spectrum agreed with the published spectrum in every detail.

Table III. Selected Bond Distances (Å)

Mo(1)-Mo(2)	2.839 (2)	Mo(2)-S(23)	2.506 (5)
Mo(1)-S(3)	2.434 (5)	Mo(2)-N(31)	1.73 (1)
Mo(1)-S(4)	2.342 (5)	Mo(2)-O(39)	2.26 (1)
Mo(1)-S(5)	2.511 (5)	O(39)-C(41)	1.23 (2)
Mo(1)-S(6)	2.542 (5)	O(40)-C(41)	1.25 (2)
Mo(1)-N(14)	1.74 (1)	C(41)-C(42)	1.56 (3)
Mo(1)-O(40)	2.26 (1)	F(43)-C(42)	1.26 (2)
Mo(2)-S(3)	2.449 (5)	F(44)-C(42)	1.28 (2)
Mo(2)-S(4)	2.354 (5)	F(45)-C(42)	1.33 (2)
Mo(2)-S(22)	2.538 (6)	S(3)-H(1)	1.2 (2)

Table IV. Selected Bond Angles (deg)

S(3)-Mo(1)-S(4)	107.7 (2)	S(4)-Mo(2)-S(22)	157.0 (2)
S(3)-Mo(1)-S(5)	162.8 (2)	S(4)-Mo(2)-S(23)	83.1 (2)
S(3)-Mo(1)-S(6)	86.6 (2)	S(4)-Mo(2)-O(39)	84.6 (3)
S(3)-Mo(1)-O(40)	84.6 (3)	S(4)-Mo(2)-N(31)	98.4 (5)
S(3)-Mo(1)-N(14)	91.6 (5)	S(22)-Mo(2)-S(23)	78.6 (2)
S(4)-Mo(1)-S(5)	84.8 (2)	S(22)-Mo(2)-O(39)	80.2 (3)
S(4)-Mo(1)-S(6)	157.8 (2)	S(22)-Mo(2)-N(31)	98.1 (5)
S(4)-Mo(1)-O(40)	85.7 (3)	S(23)-Mo(2)-O(39)	85.2 (3)
S(4)-Mo(1)-N(14)	101.8 (5)	S(23)-Mo(2)-N(31)	99.0 (5)
S(5)-Mo(1)-S(6)	78.2 (2)	O(39)-Mo(2)-N(31)	175.1 (6)
S(5)-Mo(1)-O(40)	84.4 (3)	Mo(1)-S(3)-Mo(2)	71.1 (1)
S(5)-Mo(1)-N(14)	97.6 (5)	Mo(1)-S(4)-Mo(2)	74.4 (1)
S(6)-Mo(1)-O(40)	78.7 (3)	Mo(1)-N(14)-C(15)	175 (1)
S(6)-Mo(1)-N(14)	94.5 (5)	Mo(2)-N(31)-C(32)	172 (1)
O(40)-Mo(1)-N(14)	172.4 (6)	O(39)-C(41)-O(40)	131 (2)
S(3)-Mo(2)-S(4)	106.8 (2)	O(39)-C(41)-C(42)	115 (2)
S(3)-Mo(2)-S(22)	88.6 (2)	O(40)-C(41)-C(42)	115 (1)
S(3)-Mo(2)-S(23)	164.5 (2)	Mo(1)-S(3)-H(1)	111 (8)
S(3)-Mo(2)-O(39)	84.0 (3)	Mo(2)-S(3)-H(1)	99 (8)
S(3)-Mo(2)-N(31)	91.4 (5)	S(4)···S(3)···H(1)	107 (8)

The reaction between **T** and CF_3CO_2H in CH_2Cl_2 is accompanied by an instantaneous color change from red-green to orange. The presence of the trifluoroacetate ligand in the orange, crystalline compound (**D**·H,CF_3CO_2) was confirmed from the infrared spectrum (ν(CO) at 1640 and 1465 cm^{-1} and ν(CF_3) at 1200 and 1160 cm^{-1}) and the ^{19}F NMR spectrum (δ 0.84). The presence of the dithiophosphate and arylimido ligands in the correct ratio was apparent from the ^{1}H NMR spectrum. Evidence for the bound hydrogen atom was obtained initially from an absorption at 2456 cm^{-1} in the infrared spectrum. Although this atom was not detected in the ^{1}H NMR spectrum at 15 °C, its effects were eventually found in spectra obtained at low temperatures. These effects will be discussed in a subsequent paragraph.

On the other hand, no color change occurs when CF_3CO_2H is added to a solution of $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$ in CH_2Cl_2. Moreover, the ^{31}P NMR spectrum of this complex remains unchanged after the addition of CF_3CO_2H, indicating the absence of a reaction.

Structure. The structural characterization of the adduct proved unambiguously that **D**·H,CF_3CO_2 is $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$ as shown in Figure 1. The location and refinement of all of the hydrogen atoms including the one associated with the sulfhydryl ligand provide ample evidence that the structure is well determined in spite of the large thermal amplitudes of several atoms.

Bond distances and angles within the alkyl portions of the bidentate ligands and the aryl portions of the imido ligands are within the expected ranges and merit no further comment. The remainder of the bond distances and angles can be found in Tables III and IV.

The average distance from the metal atoms to the bridging sulfur atom is 2.348 (9) Å[7] while the average distance to the

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(7) Standard deviations for average bond lengths have been calculated from the difference between individual bond lengths and the average bond length. Estimated standard deviations for sums and difference have been obtained from standard procedures for the propagation of errors.

bridging sulfur atom of the sulfhydryl ligand is 2.442 (11) Å. The difference, 0.094 (14) Å, is statistically significant and would readily distinguish these sulfur atoms even if the bound hydrogen atom had not been located.

The S(3)–H(1) bond length of 1.2 (2) Å and the sum of the covalent radii (1.32 Å[8]) agree within experimental error. Although the Mo(1)–S(3)–H(1) and Mo(2)–S(3)–H(1) bond angles were found to be 111 (8) and 99 (8)°, respectively, a structure in which these angles are equal is not excluded by the magnitude of the experimental error. However, the experimental error in the S(4)–S(3)–H(1) angle of 107 (8)° definitely excludes a structure in which H(1) lies in a plane defined by the Mo(1), Mo(2), and S(3) atoms. As a result, this hydrogen atom is definitely in the vicinity of O(39) and O(40). Significant hydrogen bonding can not occur, however, since the distance are 2.8 (2) and 2.9 (2) Å, respectively.

The Mo(1)–O(40) and Mo(2)–O(39) bond distances are identical at 2.26 (1) Å. These distances suggest either a trans effect[9] due to each multiply bound arylimido ligand or a compromise that results from the acetate ligand bridging two metal atoms separated by 2.839 (2) Å while avoiding undue compression of the bond angles about each molybdenum atom. The CO distances within the trifluoroacetate ligand are identical within experimental error with an average value of 1.24 (1) Å. This distance is close to the average distance of 1.26 (1) Å found[10] in $[Mo(O_2CCF_3)_2]_2$ and the average distance of 1.26 (2) Å found[11] in $[Mo(O_2CCF_3)_2(NC_5H_5)]_2$. The C(41)–C(42) bond distance of 1.56 (3) Å is virtually identical with the distance of 1.565 (9) Å in $Cr(CO)_5(O_2CCF_3)^-$ [12] but somewhat longer than the distances of 1.41 (8) (average), 1.52 (4) (average), and 1.518 (6) Å found in $[Mo(O_2CCF_3)_2]_2$, $[Mo(O_2CCF_3)_2(NC_5H_5)]_2$, and $Mo(CO)_5(O_2CCF_3)^-$,[12] respectively. The planarity of the carbon and oxygen atoms in this ligand in evident since the sum of the bond angles around C(41) is 361 (3)°. Finally, the large anisotropy in the fluorine thermal ellipsoids and the direction of this anisotropy (Figure 1) suggest a rotational disorder in the CF_3 group. Similar problems have been encountered by others[10,11] with this ligand.

Conformational Duality in Solution. Although a resonance due to the hydrogen atom of the bridging sulfhydryl ligand can not be observed in the ^1H NMR spectrum of **D**·H,CF_3CO_2 at about 15 °C, evidence for this atom was found at −47 °C in $CDCl_3$. At this temperature, resonances due to this atom appear at δ 1.44 and 2.60 with an intensity ratio of about 9:1. Two overlapping resonances due to the hydrogen atoms of the aryl methyl group can also be seen at δ 2.12 and 2.16 with the upfield peak having the predominant intensity. No other doubling can be detected in this spectrum nor can it be detected in the ^{31}P NMR spectra recorded at low temperatures.

Evidence that indicates that this phenomenon is not due to the slow (NMR time scale) dissociation of $CF_3CO_2^-$ will be presented in a subsequent paper, which includes conformational isomerism of *S*-alkyl derivatives. It will be shown there that the doubling is due to conformational isomerism of the sulfhydryl ligand. While complete delineation of these isomers is not possible, it is likely that one of them corresponds, at least approximately, to the conformation shown in Figure 1. It is also likely, as we will show, that this is the preferred conformation. The other conformation may be one in which the hydrogen atom of the sulfhydryl group and the arylimido ligands are on the same side of the plane described by the Mo(1), Mo(2), and S(3) atoms. Increased steric hindrance coupled with the loss of any weak attractive interactions between H(1) and the carboxylate oxygen atoms would then account for the disparate populations.

Table V. Estimated Equilibrium Constants[a] for the Formation of D·H,RCO_2

R	*K*	δ	R	*K*	δ
CF_3	$>10^5$	113.7	$CHCl_2$	6.9×10^3	114.1
CCl_3	$>10^5$	114.5	CH_2Cl	11	114.1
			CH_3	$<10^{-4}$	

[a] From ^{31}P NMR spectroscopy in CH_2Cl_2 at 35 °C. Initial concentrations of T differed slightly for each carboxylic acid, but all were near 0.025 M.

Another set of conformations, albeit unattractive, can be envisioned if the Mo(1)–S(3)–H(1) and Mo(2)–S(3)–H(1) bond angles are truly unequal. These conformations would arise if H(1) can occupy equilibrium positions on either side of a plane described by S(3), S(4), and C(41). However, this alternative offers no adequate reason for the differing populations.

Comparison of Carboxylic Acids. The reactions between T and CF_3CO_2H, CCl_3CO_2H, $CHCl_2CO_2H$, CH_2ClCO_2H, and CH_3CO_2H in CH_2Cl_2 were studied at 35 °C with ^1H-decoupled ^{31}P NMR spectroscopy. In the absence of a carboxylic acid, the spectrum consists of a single resonance at δ 110.8. Upon the addition of CF_3CO_2H, the intensity of this resonance diminishes while a new resonance due to **D**·H,CF_3CO_2 appears at δ 113.7. A stoichiometric quantity of CF_3CO_2H results in a ratio of the intensities of the signals due to **D**·H,CF_3CO_2 and **T** that is too large to measure accurately. Nevertheless, the ratio indicates that [**D**·H,CF_3CO_2]/[T] is greater than 50. Similar results were also obtained with CCl_3CO_2H, but measurable ratios were obtained with $CHCl_2CO_2H$ and CH_2ClCO_2H. No reaction was observed with CH_3CO_2H. Estimates of the equilibrium constants for the reaction in eq 2, which are based on these results, are given

$$\mathbf{T} + 2RCO_2H \rightleftharpoons 2\mathbf{D}\cdot H,RCO_2 \qquad (2)$$

in Table V along with other pertinent data. Insofar as we can determine from the available data, the trend in these constants follows the trend in the aqueous acidities of the carboxylic acids.[13]

We have also shown the formation of **D**·H,RCO_2 can be retarded by solvent effects even in the presence of excess CF_3CO_2H. For example, [**D**·H,CF_3CO_2]/[T] is only 0.81 in tetrahydrofuran when 3 times the stoichiometric quantity of the carboxylic acid has been added. Moreover, this ratio is also extremely sensitive to salt effects. The addition of an equimolar quantity of $[(C_2H_5)_3NH]O_2CCF_3$ to **D**·H,CF_3CO_2 in CH_2Cl_2 results in a ratio of only 1.5. Since no other resonances appear in the spectrum, substitution of a trifluoroacetate ligand for a dithiophosphate ligand is not the cause of the sharply curtailed ratio. In fact, there is no evidence in hand that points to any direct reaction between the salt and **D**·H,CF_3CO_2. Unless conflicting evidence is obtained in the future, we must assume that the effect is due solely to the perturbation of the solvent environment of **D**·H,CF_3CO_2 by the salt. This effect is not limited to this salt alone since identical experiments with $[(C_2H_5)_3NH]Cl$ and $[(n\text{-}C_4H_9)_4N]I$ led to ratios of 1.1 and 2.9, respectively.

Conjugate Base of D·H,CF_3CO_2. The existence of $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)_2(\mu\text{-}O_2CCF_3)^-$ (**D**·$CF_3CO_2^-$), the conjugate base of **D**·H,CF_3CO_2, was discovered by

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(8) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 117.

(9) While trans effects have not been found previously in Mo(VI) complexes containing near-linear arylimido ligands,[1] this phenomenon has been observed in a mononuclear complex of Mo(V) that contains this ligand. See: Noble, M. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1982**, *21*, 2101.

(10) Cotton, F. A.; Norman, J. G. *J. Coord. Chem.* **1972**, *1*, 161.

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

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

(13) Korbüm, K.; Vogel, W.; Andrussov, K. *Pure Appl. Chem.* **1960**, *1*, 241, 295.

observing the ^{1}H-decoupled ^{31}P NMR spectrum of solutions of **T** in CH_2Cl_2 containing increasing quantities of the salt $[(C_2H_5)_3NH]O_2CCF_3$. In general, these spectra consist of a resonance due to **T** and another assigned to $\mathbf{D}\cdot CF_3CO_2^-$ at about δ 115.7.[14] When the stoichiometric ratio of reagents, [salt]/[**T**] = 2.0, is present, the $[\mathbf{D}\cdot CF_3CO_2^-]/[\mathbf{T}]$ ratio is only 0.60. Increased quantities of the salt cause this ratio to experience a smooth, nonlinear enhancement until this ratio becomes 15 at [salt]/[**T**] = 8.0. Since only a trace of a resonance apparently due to $(C_2H_5O)_2PS_2^-$ was observed in the spectrum under these drastic conditions, the principal reaction is undoubtedly described by the equilibrium in eq 3.

$$\mathbf{T} + 2CF_3CO_2^- \rightleftharpoons 2\mathbf{D}\cdot CF_3CO_2^- \qquad (3)$$

The existence of $\mathbf{D}\cdot CF_3CO_2^-$ and an entire series denoted by $\mathbf{D}\cdot RCO_2^-$ is substantiated by another observation. When $[(C_2H_5)_3NH]O_2CCH_3$ is substituted for $[(C_2H_5)_3NH]O_2CCF_3$ under stoichiometric conditions, $[\mathbf{D}\cdot CH_3CO_2^-]/[\mathbf{T}]$ is 6.7, a dramatic increase from $[\mathbf{D}\cdot CF_3CO_2^-]/[\mathbf{T}]$ = 0.60 in the previous experiment. These results are explicable in terms of the better ligating ability of the acetate ligand because of the electron-withdrawing substituents on the trifluoroacetate ligand. Yet another indication of the existence of $\mathbf{D}\cdot CF_3CO_2^-$ was found during studies of the alkylation of $\mathbf{D}\cdot H,CF_3CO_2$ with alkyl halides. Since these reactions proceed more rapidly when $(C_2H_5)_3N$ is present, it is clear that the alkylation of the conjugate base is more facile than the direct alkylation of $\mathbf{D}\cdot H,CF_3CO_2$. These results will be reported in a subsequent paper.

No serious attempt to examine the protonation of $\mathbf{D}\cdot CF_3CO_2^-$ by ^{31}P NMR spectroscopy has been undertaken because of the salt effects mentioned in an earlier paragraph.

Significance. To our knowledge, $\mathbf{D}\cdot H,CF_3CO_2$ is the first compound in which the sulfhydryl ligand results from the direct addition of an acid to a compound containing a bridging sulfur ligand. Bound sulfhydryl ligands have been obtained previously by methods that include metathetical reactions,[15] sulfur abstraction from episulfides by metal hydrides,[16] hydrogenation of bridging sulfur atoms,[17] and reaction of nonmetal hydrides with those atoms.[18] In addition, only five sulfhydryl compounds appear to have been characterized previously by X-ray methods.[19] Although indications of residual electron density due to the hydrogen atom of the sulfhydryl ligand have usually been found in these investigations, the most convincing evidence for the location of this atom occurs in the structural characterization of $\mathbf{D}\cdot H,CF_3CO_2$.[20]

The formation of this compound by way of the addition of CF_3CO_2H to **T** is apparently a direct result of the presence of the arylimido ligands since the addition of CF_3CO_2H to $[MoO(\mu\text{-}S)(S_2POC_2H_5)_2)]_2$ does not occur. Moreover, the estimated equilibrium constants for the formation of $\mathbf{D}\cdot H,RCO_2$ follow the trends of the aqueous acidities of the carboxylic acids. This trend and relative stabilities of $\mathbf{D}\cdot CF_3CO_2^-$ and $\mathbf{D}\cdot CH_3CO_2^-$ indicate the importance of the energetics of breaking the O–H bonds of the acids in the stabilities of the adducts containing the sulfhydryl ligand.

Only a few studies of the acidities of bridging sulfhydryl ligands have been reported previously.[18,21] In contrast to $\mathbf{D}\cdot H,RCO_2$, low acidities have required strong bases for deprotonation. Since the compounds used in those studies contained low-valent transition metals, the enhanced acidity of this ligand in $\mathbf{D}\cdot H,RCO_2$ would appear to be due to the increased formal oxidation states of the metal atoms.

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Registry No. T, 73037-71-5; $\mathbf{D}\cdot H,CF_3CO_2$, 85166-52-5; $\mathbf{D}\cdot H,CCl_3CO_2$, 85185-06-4; $\mathbf{D}\cdot H,CHCl_2CO_2$, 85166-54-7; $\mathbf{D}\cdot H,CH_2ClCO_2$, 85166-55-8; $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$, 85166-53-6; $Mo(CO)_6$, 13939-06-5; $p\text{-}CH_3C_6H_4N_3$, 2101-86-2; Na_2MoO_4, 7631-95-0.

Supplementary Material Available: Listings of positional parameters for hydrogen atoms, all thermal parameters, observed and calculated structure amplitudes, and all bond distances and angles (42 pages). Ordering information is given on any current masthead page.

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[14] This chemical shift is not entirely constant since it varies from δ 115.3 at [salt]/[**T**] = 2.0 to δ 116.0 at [salt]/[**T**] = 8.0.

[15] Kopf, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 953.

[16] Beck, W.; Danzer, W.; Hofer, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 77. Beck, W.; Danzer, W.; Thiel, G. *Ibid.* **1973**, *12*, 582. Kury, R.; Vahrenkamp, H. *J. Chem. Res., Miniprint* **1982**, 401.

[17] Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

[18] Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.

[19] DiVaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 1518; **1978**, *17*, 816. Cragel, J.; Pett, V. B.; Glick, M. D.; DeSimone, R. E. *Ibid.* **1978**, *17*, 2885. DeSimone, R. E.; Glick, M. D. *Ibid.* **1978**, *17*, 3574.

[20] After the completion of this paper, another preparative method for a sulfhydryl compound came to our attention. The addition of COS to $RhH(P(C_6H_5)_3)_4$ results in the formal insertion of sulfur into the metal–hydride bond with the formation of the structurally characterized compound, $Rh(SH)(CO)(P(C_6H_5)_3)_2$. The sulfhydryl hydrogen atom was located on the final difference electron density map but was not refined. See: Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2857.

[21] Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604.