Journal of Fluorine Chemistry, *48* (1990) 429–440

QUADRUPLY BONDED DIMOLYBDENUM COMPLEXES OF $PF_2S_2^-$. COMPARISON WITH COMPLEXES OF $PR_2S_2^-$ (R = Et, Me)

MOHAMMAD Q. ISLAM, WILLIAM E. HILL* and THOMAS R. WEBB*
Department of Chemistry
Auburn University, AL 36849-5312, (U.S.A.)

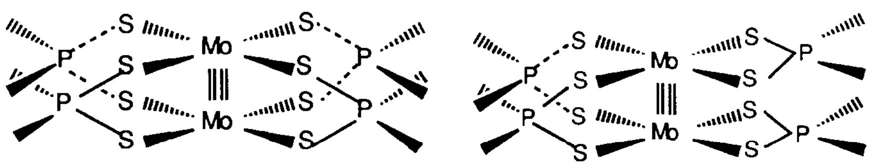
SUMMARY

Quadruply bonded dimolybdenum complexes $Mo_2(S_2PF_2)_4$, $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$, $Mo_2(S_2PF_2)_2(O_2CMe)_2$ and $Mo_2(S_2PMe_2)_4$ have been prepared by the stoichiometric reaction between molybdenum acetate or molybdenum trifluoroacetate and the ligand. The solid complexes have been characterized by elemental analyses, infrared spectroscopy, ^{19}F and ^{31}P nmr spectroscopy and mass spectrometry. Trifluoroacetate, $PF_2S_2^-$ and acetate act as bidentate bridging ligands in all of the complexes. Coordinating solvents such as acetonitrile, pyridine and dimethylsulfoxide rapidly displace $PF_2S_2^-$ but not the acetate or trifluoroacetate ligands. For $Mo_2(S_2PMe_2)_4$, two species have been observed by ^{31}P nmr in non-coordinating solvents. The major species is the all-ligand-bridged C_{4h} isomer; the minor species is the C_{2v} isomer in which two ligands bridge the Mo_2 core and two ligands chelate to one Mo.

INTRODUCTION

Mononuclear difluorophosphinate complexes, $M(S_2PF_2)_x$, have been reported for a number of metals [1]. Complexes of this ligand with the dinuclear Mo_2^{4+} core have not been reported; however, two $Mo_2(S_2PR_2)_4$ complexes have been reported. The rather insoluble diphenyldithiophosphinate, prepared by Steele and Stephenson [2], has not been fully characterized. The diethyldithiophosphinate, prepared by Burlitch [3], can exist as either the all-bridged form (Figure Ia) or a mixed isomer with two bridging and two chelating ligands (Figure Ib).

0022-1139/90/$3.50



Ia

Ib

Fig I. Observed Structures for $Mo_2(S_2PR_2)_4$

These isomers are in equilibrium in solution; equilibration is slow on the nmr time scale but rapid on the laboratory time scale. The equilibrium constant, K(= [Ia]/[Ib]), was found to depend modestly on the solvent polarity and Lewis basicity (in various media K ranged from 0 20 to 1 25) and not on temperature [3]. It is apparent that the two isomers are very closely balanced energetically (both in terms of Δ G and ΔH).

One possible influence on the isomeric structure adopted by the dithiophosphinate dimolybdenum complexes is the basicity of the $PR_2S_2^-$ ligand, which would be affected by the electronegativity of the R group We report here the preparation and characterization of $Mo_2(S_2PF_2)_4$, mixed carboxylate-S_2PF_2 complexes and $Mo_2(S_2PMe_2)_4$.

EXPERIMENTAL

Thiophosphoryl fluoride (PSF_3) [4], HS_2PF_2 [5,6], $Mo_2(O_2CMe)_4$ [7], $Mo_2(O_2CCF_3)_4$ [8] and $K_4Mo_2Cl_8$ [9] were prepared by reported procedures NaS_2PMe_2 was prepared from $Me_2P(S)P(S)Me_2$ [10] by adaptation of the procedure reported for NaS_2PEt_2 [11].

Physical Measurements. Elemental analyses were obtained from Atlantic Microlab, Inc. (Atlanta, GA) or Galbraith Laboratories, Inc. (Knoxville, TN) The ^{19}F and ^{31}P nmr spectra were recorded on a Bruker AM400 instrument at 376.5 MHz and 162.1 MHz respectively; the data are included in the results and discussion. IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer as Nujol or Fluorolube mulls. Mass spectra were obtained with a VG-7070 EHF mass spectrometer. Generally ion intensities less than 10% are not listed, and peaks below m/z 130 are not given. Samples were introduced into the ionization chamber as solids

Preparation of $Mo_2(S_2PF_2)_4$. $Mo_2(O_2CCF_3)_4$ (0.16 g, 0.025 mmol) was mixed with 10 mL benzene (Na-dried and distilled) in a 50-mL round-bottomed flask equipped with a magnetic stirring bar and a vacuum adapter. The flask was cooled to -196°C and evacuated. HS_2PF_2 (90 torr in 250mL, 1.1 mmol) was condensed into the flask. As the flask warmed to room temperature, the yellow solid turned orange and then blue. The flask was shaken well, and the contents were stirred for 12 hours (or until no orange or pink solid remained). The solvent and volatile materials were removed *in vacuo*, and the solid was pumped for three days to remove the last traces of trifluoroacetic acid produced in the reaction. $Mo_2(S_2PF_2)_4$ was obtained as a blue solid in quantitative yield. $Mo_2(S_2PF_2)_4$ was also synthesized from $Mo_2(O_2CMe)_4$ using this procedure with similar results.

Elemental analysis: Found, P 16.86, S 34.88; Calcd. P 17.12, S 33.36. IR (Nujol); 875(s), 800(w), 678(s), 392(s), 368(m), 335(m), 295(w) cm^{-1} Mass spectrum given as m/z(rel. int.), assignment: 724(13), $Mo_2(S_2PF_2)_4^+$, 655(100) $Mo_2S_8P_3F_6^+$; 586(28), $Mo_2S_8P_2F_4^+$; 573(18), $Mo_2S_7P_2F_5^+$; 554(42), $Mo_2S_7P_2F_4^+$; 517(17), $Mo_2S_8PF_2^+$; 472(20), $Mo_2S_6PF_3^+$, 457(15), $Mo_2S_3P_3F_4^+$; 438(10), $Mo_2S_3P_3F_3^+$; 403(18), $Mo_2S_6F^+$; 388(17), $Mo_2S_3P_2F_2^+$, 371(15), $Mo_2S_5F^+$; 356(18), $Mo_2S_2P_2F_2^+$; 339(13), $Mo_2S_4F^+$; 282(20), $Mo_2S_3PF_3^+$; 213(14), MoS_3F^+; 162(15), MoS_2^+; 130(17), MoS^+.

Preparation of $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$. This compound was synthesized from $Mo_2(O_2CCF_3)_4$ (0.32g, 0.50 mmol) and HS_2PF_2 (1.0 mmol) as described above; as the mixture warmed to room temperature, the solution turned orange, and an orange solid precipitated. After four hours of stirring, the mixture was filtered. The orange solid was dried for several hours, yield 79%. Reaction time is very important in obtaining the disubstituted product; if the mixture is stirred for longer times, the solution turns blue, indicating that some $Mo_2(S_2PF_2)_4$ has formed.

Elemental analysis: Found C 7.57, P 8.65, S 18.20; Calc. C 7.02, P 9.06, S 18.72. IR (Nujol); 1588(s), 1565(w), 1235(m), 1183(s), 890(s), 880(ms), 745(m), 740(m), 695(s), 550(w), 510(w), 390(s), 375(w), 365(w) cm^{-1}. Mass spectrum, m/z (rel. int.), assignment; 684(100), $Mo_2O_4S_4C_4P_2F_{10}^+$; 665(18), $Mo_2O_4S_4C_4P_2F_9^+$; 590(15), $Mo_2O_2S_4C_2P_2F_8^+$; 437(25), $Mo_2O_4C_4F_7^+$; 358(13) ; 343(32); 327(22); 311(10); 162(17), MoS_2^+, MoO_2S^+; 130(15), MoS^+, MoO_2^+. Due to considerable overlap of the isotopic patterns in the region m/z 250-400, assignments were not made there.

Preparation of $Mo_2(S_2PF_2)_2(O_2CMe)_2$. The procedure described above for $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$ was followed for the reaction of $Mo_2(O_2CMe)_4$ and HS_2PF_2 The product precipitated as a pink solid within half an hour The solid was filtered after one hour (or as the solution started to change from pink to blue). The solid was dried *in vacuo*, yield 70%

Elemental analysis Found C 8.23, H 1.09, S 21.75; Calcd. C 8.33, H 1.05, S 22.26. IR (Nujol): 1510(s), 1490(s), 1410(s), 885(s), 860(s), 700(s), 687(s), 630(w), 575(vw), 545(m), 388(s), 368(m) 358(m), 235(w) cm^{-1} Mass spectrum, m/z(rel. int.), assignment; 576(100), $Mo_2O_4S_4C_4P_2F_4H_6^+$; 502(12), $Mo_2O_2S_4CP_2F_4^+$; 465(15), $Mo_2O_4S_2C_3PF_4H_2^+$; 443(11), $Mo_2O_4S_2C_4PF_2H_6^+$, 383(11), 340(14); 321(12),289(11);162(10), MoS_2^+, $MoSO_2^+$; 130(10), MoS^+, MoO_2^+.

Preparation of $Mo_2(S_2PMe_2)_4$. NaS_2PMe_2 (0.30 g, 2.0 mmol) was dissolved in 50 mL of methanol in a 150-mL three-necked flask The solution was stirred under nitrogen for 15 minutes, and $Mo_2(O_2CCF_3)_4$ (0.29 g, 0.45 mmol) was added. The yellow solution changed to light green within seconds. The mixture was stirred under nitrogen for two hours; the green solid product was filtered, washed with methanol and dried *in vacuo*, yield 73% This complex could also be prepared from $K_4Mo_2Cl_8$ and NaS_2PMe_2 analogous to the Burlitch method for $Mo_2(S_2PEt_2)_4$ [3].

Elemental analysis: Found H 3.37, C 14 50, S 36.17; Calcd. H 3.45, C 13.87, S 36.99. IR (Nujol): 1280(m), 1025(w), 945(s), 905(m), 850(w), 730(s), 720(s), 590(m), 510(w), 500(w) cm^{-1}. The mass spectrum was obtained by desorption chemical ionization; only ions above m/z 450 are reported since ions at virtually every mass are observed below 450. Ions listed as m/z(rel. int. based on m/z 540), assignment; 692(28), $Mo_2S_8P_4C_8H_{24}^+$; 630(13), $Mo_2S_7P_4C_6H_{18}^+$, $Mo_2S_8P_3C_6H_{17}^+$; 599(19), $Mo_2S_7P_3C_6H_{18}^+$, 571(17), $Mo_2S_8P_2C_4H_{13}^+$; 556(11), $Mo_2S_8P_2C_3H_{10}^+$; 540(100), $Mo_2S_8P_2C_2H_6^+$; 521(28), $Mo_2S_6P_2C_3H_{15}^+$; 506(17), $Mo_2S_6P_2C_4H_{12}^+$; 473(45), $Mo_2S_5P_2C_4H_{11}^+$.

All of the complexes are air-sensitive as solids and in solution; the $PF_2S_2^-$ complexes are more air-sensitive than $Mo_2(S_2PMe_2)_4$ All of the $PF_2S_2^-$ complexes are moisture-sensitive, and also (*vide infra*) lose $PF_2S_2^-$ when dissolved in donor solvents. Further purification by chromatography was not attempted due to the high reactivity of the complexes.

RESULTS AND DISCUSSION

The molybdenum complexes of the $PF_2S_2^-$ ligand were prepared by the reaction of molybdenum acetate or trifluoroacetate with the stoichiometric amounts of HS_2PF_2 as shown in equation (1) & (2).

$$Mo_2(O_2CR)_4 + 2HS_2PF_2 \longrightarrow Mo_2(S_2PF_2)_2(O_2CR)_2 + 2RCO_2H \qquad (1)$$

$$Mo_2(O_2CR)_4 + 4HS_2PF_2 \longrightarrow Mo_2(S_2PF_2)_4 + 4\ RCO_2H \qquad (2)$$

$R = CH_3, CF_3$

Attempts to prepare $Mo_2(S_2PF_2)_{4-n}(O_2CR)_n$ (n = 1,3) by adjusting the ratio of molybdenum complex to acid were unsuccessful; only the di- and tetrasubstituted products were formed. Steele and Stephenson reported a mixed-ligand complex $[Mo(S_2PPh_2)(O_2CCH_3)]_x$ prepared from the reaction of $Mo_2(O_2CCH_3)_4$ and $S_2PPh_2^-$ but gave no further characterization [2]

$Mo_2(S_2PMe_2)_4$ was synthesized by the reaction of $Mo_2(O_2CCF_3)_4$ or $K_4Mo_2Cl_8$ with NaS_2PMe_2 in methanol under N_2 using a 1:4 mole ratio of reactants. Variation of the stoichiometric ratio led to a reduction in yield of $Mo_2(S_2PMe_2)_4$; no mixed-ligand complexes $Mo_2(S_2PMe_2)_n(O_2CR)_{4-n}$ (n = 1, 2, 3) could be prepared. We attribute this to the low solubility of $Mo_2(S_2PMe_2)_4$; mixed-ligand complexes disproportionate to give the insoluble complex.

All the molybdenum complexes reported here show molecular ions as a group of peaks with a characteristic isotopic pattern expected for a species containing two molybdenum atoms [12]. For $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$ and $Mo_2(S_2PF_2)_2(O_2CCH_3)_2$, these ions are the base peaks. For $Mo_2(S_2PF_2)_4$, the base peak occurs at m/e 655 corresponding to loss of a PF_2 group from the molecular ion. Other important fragment ions in the fragmentation of $Mo_2(S_2PF_2)_4$ occur at m/z 586 and 517 and correspond to successive loss of PF_2. Fragment ions at m/z 573 and 554 correspond to loss of F_2PSPF and PF_2SPF_2 from $Mo_2(S_2PF_2)_4$ or successive loss of SPF and SPF_2 from the m/z 655 fragment.

For the mixed-ligand complex, $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$, fragment ions at m/z 665 corresponding to loss of F and at m/z 590 corresponding to loss of CF_2CO_2 from the parent ion are observed. Similar losses have been reported for $Mo_2(O_2CCF_3)_4$ [8]. A number of ions arising from rearrangement are observed. The mass spectrum of $Mo_2(S_2PF_2)_2(O_2CCH_3)_2$ also contains ions produced by rearrangement. Loss of PF_2S_2 from the parent is observed at m/z 443.

Ions at m/z 162 corresponding to MoS_2^+ and/or MoO_2S^+ and at m/z 130 corresponding to MoS^+ and/or MoO_2^+ are observed for all of the complexes containing $PF_2S_2^-$.

For $Mo_2(S_2PMe_2)_4$, desorption chemical ionization (DCI) was required to see the molecular ion peak at m/z 692. Many of the fragment ions observed were produced by rearrangement. Among these are those observed at m/z 630 (loss of Me_2S or Me_2PH from the parent ion), and at m/z 616 (loss of PMe_3). Facile loss of PMe_3 requires migration of a CH_3 group from the phosphorus atom of one ligand to that of another. This is most likely when the ligands are in close proximity as would be the case in the structure containing both chelating and bridging ligands (Figure Ib).

Infrared spectra of the complexes are listed in the experimental section Two absorptions in the 800-890 cm^{-1} region, assigned to PF stretching vibrations, are observed, as expected [1], in all of the complexes

TABLE 1

The ^{31}P Nmr Data for the Molybdenum Complexes

Compound	Solvent	δ_P, ppm[a,b]	$^1J_{PF}$,Hz
$Mo_2(S_2PF_2)_4$	Benzene	86.7 t	1257
$Mo_2(S_2PF_2)_2(O_2CCF_3)_2$	Benzene	89.6 t	1245
	Acetone	92.7 t	1234
$Mo_2(S_2PF_2)_2(O_2CCH_3)_2$	Acetone	92.1 t (12)	1232
		119.4 t (1)	1150
$Mo_2(S_2PMe_2)_4$	Chloroform	103.9 (8)	
		98.6 (1)	
		72.5 (1)	
	Pyridine	99.3 (3)	
		51.8 (1)	

[a] Relative to 85% H_3PO_4 external reference. Downfield shifts have positive values, t = triplet.

[b] Numbers in parentheses are relative areas.

TABLE 2

The ^{19}F Nmr Data for the Molybdenum $PF_2S_2^-$ Complexes

Compound	Solvent	δ_P, ppm^a	$^1J_{PF}$(Hz)
$Mo_2(S_2PF_2)_4$	Benzene	-0.8 d	1258
	Acetone	-0.1(10) d	1248
		-3.9(1) d	1148
$Mo_2(S_2PF_2)_2(O_2CCF_3)_2$	Benzene	-0.8(2) d	1246
		-73.6(3)	
	Acetone	- 1.2(2) d	1235
		-73 4(3)	
$Mo_2(S_2PF_2)_2(O_2CCH_3)_2$	Acetonitrile	+1.0(1) d	1240
		-1.5(1) d	1234
		-3.8(5) d	1147

[a] Relative to trifluorotoluene (δ_F = -63.7 ppm relative to CCl_3F) internal reference. Relative area in parentheses. d = doublet.

containing the $PF_2S_2^-$ ligand. Phosphorus-sulfur stretching vibrations are observed in the range of 690-700 cm^{-1} for the $PF_2S_2^-$ complexes and at 720 and 730 cm^{-1} for the $PMe_2S_2^-$ complex. Bridging trifluoroacetate groups in $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$ are indicated by the strong band at 1588 cm^{-1} [8]. Strong bands observed in the 1600-1300 cm^{-1} region suggest that bridging bidentate acetate groups are also present in $Mo_2(S_2PF_2)_2(O_2CCH_3)_2$ [13].

^{31}P and ^{19}F nmr spectra are listed in Tables 1 and 2, respectively. The ^{19}F nmr spectrum of $Mo_2(S_2PF_2)_4$ in benzene consists of a doublet at -0.8 ppm ($^1J_{PF}$ = 1258 Hz). The coupling constant is much larger than that for free $PF_2S_2^-$ ion ($^1J_{PF}$ = 1148 Hz) indicating that the $PF_2S_2^-$ group is coordinated to the molybdenum centers. The ^{19}F nmr signals are sharp;

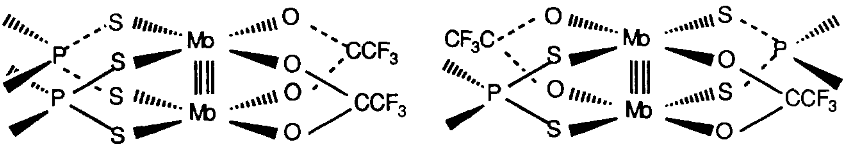
this indicates that the complex is diamagnetic, and therefore the quadruple metal-metal bond is retained. We assign the structure as the all bridged form (Ia) since only one signal is observed; the fluorines in

chelated ligands (as in Ib) could not be equivalent. In structures related to Ia, the Mo-Mo-X-Y-X rings are invariably non-planar [3, 14], again the substituents (F in this case) would be non-equivalent. However, ring inversion would lead to equivalence of the F atoms; presumably this process is fast on the nmr time scale. The ^{31}P nmr spectrum, a triplet at 86.5 ppm, is consistent with this assignment.

Addition of a Lewis base (acetonitrile, dimethylsulfoxide, or pyridine) to a benzene solution of $Mo_2(S_2PF_2)_4$, causes an immediate color change from blue to deep red. The ^{19}F spectra of these solutions consists of a doublet at -3.9 ppm (J_{PF} = 1148 Hz); the ^{31}P is a triplet at 119.7 ppm These resonances are characteristic of free $PF_2S_2^-$ [1a]. Thus, the added Lewis base has displaced the $PF_2S_2^-$ ligands, presumably producing the interesting $[Mo_2(solvent)_8]^{4+}$ cation, analogous to $Mo_2(OH_2)_8{}^{4+}$ [15]. A few partially substituted complexes have recently been reported [16].

In acetone the ^{19}F nmr spectrum of the fresh blue solution of $Mo_2(S_2PF_2)_4$ consists of two doublets in a 10:1 ratio [-0.1 ppm (J_{PF} = 1248 Hz), -3.9 ppm (J_{PF} = 1148 Hz)], the former assigned to coordinated $PF_2S_2^-$ and the latter to free ligand. Upon standing, the blue solution turns red; the -3.9 ppm doublet grows at the expense of the -0 1 ppm doublet, indicating that acetone slowly displaces the ligand.

The ^{19}F nmr spectrum of the mixed-ligand complex, $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$, in benzene consists of a doublet at -0.8 ppm ($^1J_{PF}$ = 1246 Hz), assigned to the bridging bidentate $PF_2S_2^-$ ligands, and a singlet at -73.6 ppm assigned to bridging bidentate trifluoroacetate ligands [17-19]. The relative area of the doublet and the singlet (2:3) confirms that two $PF_2S_2^-$ and two $CF_3CO_2^-$ ligands are present in the complex. The ^{31}P nmr spectrum of this mixed-ligand complex in benzene shows a triplet at 89.6 ppm Thus in benzene, one species is present in which both ligands are bridging bidentate. Two structures are possible for this mixed ligand complex containing only bridging bidentate ligands, a structure with cis $PF_2S_2^-$ ligands (Fig. 2a) or one with trans $PF_2S_2^-$ ligands (Fig. 2b)



2a

2b

Fig. 2. Possible Structures for $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$

Both cis [16, 20] and trans [19, 21] dimolybdenum complexes with bis-bridging carboxylates are known. Since all of the fluorines in the $PF_2S_2^-$ ligands are equivalent, we presume that the complex has the trans configuration (Fig 2b) In the cis isomer, the fluorine atoms in the $PF_2S_2^-$ ligand are not equivalent, since one is adjacent to a trifluoroacetate group while the other is near the other $PF_2S_2^-$ ligand.

In acetone solution, the ^{19}F nmr spectrum of $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$ initially consists of a doublet at -1.2 ppm ($^1J_{PF}$ = 1233 Hz) and a singlet at -73.4 ppm (relative areas 2:3). The ^{31}P spectrum consists of a triplet at 92.7 ppm. The ^{19}F spectrum was run at 1/2 hr intervals for several hours During this time the light red color deepened. The doublet at -1.2 ppm decreased in intensity while another doublet at -3.8 ppm ($^1J_{PF}$ =1148 Hz), assigned to free $PF_2S_2^-$, grew in The singlet at -73 4 ppm remained unchanged. These results indicate that acetone slowly displaces the $PF_2S_2^-$ ligands from the complex, but that trifluoroacetate is not replaced at or below room temperature. Variable-temperature nmr studies revealed that displacement of $PF_2S_2^-$ by acetone occurs at temperatures as low as -53°C. If the solution is warmed to 37°C, a new singlet appears at -77.3 ppm (assigned to monodentate or free $CF_3CO_2^-$) [17-19].

Addition of pyridine or dimethylsulfoxide to a freshly prepared solution of $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$ in benzene immediately gives a dark-red solution The ^{19}F spectrum consists of a doublet at -3.5 ppm ($^1J_{PF}$ = 1148 Hz) and a singlet at -73.6 ppm characteristic of anionic $PF_2S_2^-$ and bridging $CF_3CO_2^-$ groups respectively. Thus good donor solvents immediately displace the $PF_2S_2^-$ ligand.

The mixed-ligand complex, $Mo_2(S_2PF_2)_2(O_2CCH_3)_2$, was not soluble in benzene. The ^{31}P nmr spectrum of this complex in acetone consists of a triplet at 92.1 ppm ($^1J_{PF}$ = 1232 Hz), assigned to the bridging $PF_2S_2^-$ ligands, and a small triplet at 119.4 ppm ($^1J_{PF}$ = 1150 Hz), assigned to free $PF_2S_2^-$. The triplet for the coordinated ligand indicates that all fluorines are equivalent (consistent with a trans geometry). Over time the free-ligand signal grows at the expense of the bridging ligand peak. When the complex is dissolved in acetonitrile (a stronger Lewis base than acetone toward these complexes), the major peak in the ^{19}F nmr spectrum is a doublet (-3.8 ppm, $^1J_{PF}$ = 1150 Hz) characteristic of free $PF_2S_2^-$ As observed in the trifluoroacetate case, the $PF_2S_2^-$ ligand is more labile than the acetate.

The $^{31}P\{^1H\}$ nmr spectrum of $Mo_2(S_2PMe_2)_4$ in $CDCl_3$ consists of singlets at 103 8, 98.6 and 72.5 ppm (relative areas 7.9 :1.0 :1.0). The downfield peak is assigned to the isomer Ia (all bridging ligands); the others are assigned to the bridging and chelating ligands of isomer Ib, by analogy with Burlitch's work on $Mo_2(S_2PEt_2)_4$ [3]. The ^1H nmr spectrum of $Mo_2(S_2PMe_2)_4$ in $CDCl_3$ is consistent with the ^{31}P nmr results and consists of three doublets at 2 56, 2,48 and 2.39 ppm (relative to tetramethylsilane, J_{PH} = 13 Hz). The major doublet at 2.56 ppm is assigned to the all-bridged isomer (Ia) while the other two resonances are assigned to isomer 1b. The equilibrium constant relating these species can be calculated as the integral of the peak for structure Ia divided by the sum of the integrals for the peaks due to structure Ib. For $Mo_2(S_2PMe_2)_4$ in $CDCl_3$ at 25°C, K = [Ia]/[Ib] = 4 0; for $Mo_2(S_2PEt_2)_4$, K = 0 44 in $CHCl_3$ and 0.41 in toluene [3].

The $^{31}P\{^1H\}$ spectrum of a freshly prepared solution of $Mo_2(S_2PMe_2)_4$ in pyridine shows two peaks at 99.3 and 51.8 ppm (relative areas 3 · 1). The latter resonance is identical to that obtained for a solution of NaS_2PMe_2 in pyridine and is thus assigned to free $PMe_2S_2^-$. The major solution species has structure Ia. Pyridine displaces $PMe_2S_2^-$, albeit more slowly than observed for the replacement of $PF_2S_2^-$.

CONCLUSIONS

The nmr studies of the $Mo_2(S_2PF_2)_4$ and $Mo_2(S_2PF_2)_2(O_2CCF_3)_2$ complexes indicate that the $PF_2S_2^-$ ligand acts as a bridging bidentate ligand All of these complexes are quite reactive toward donor solvents, acetonitrile, pyridine and dimethylsulfoxide rapidly displace $PF_2S_2^-$, while acetone reacts more slowly. Based on nmr evidence, the probable species are solvated Mo_2^{4+} complexes. The trifluoroacetate and acetate bridging bidentates are not replaced by these solvents (or are replaced at a much slower rate).

It is noteworthy that the dimolybdenum complexes of xanthates [2, 22] and dithioacetate [23] form simple adducts with these donor solvents and the dithiocarboxylate ligands are not displaced. We therefore conclude that the $PF_2S_2^-$ (and $PMe_2S_2^-$) are weaker donors to the Mo_2^{4+} core than the dithiocarboxylates. Thus the order of reactivity of the bridging bidentate ligands is $PF_2S_2^-$ >$PMe_2S_2^-$ > trifluoroacetate > acetate> dithiocarboxylates.

In contrast to the observation that $PF_2S_2^-$ acts only as a bidentate bridging ligand, $PMe_2S_2^-$ acts as both a bridging bidentate and as a chelating ligand.

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