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Carbonyldinitrosyltris(fluorosulfato)tungstate(II) and -Molybdate(II) Anions: Synthesis, Spectroscopy, and Density Functional Theory Calculations

Qiang Xu,*[a, b] Nobuko Tsumori,[a, c] Ling Jiang,[a, b] Masanobu Kondo,[d] and Ryuichi Arakawa[d]

Abstract: Carbonyldinitrosyltris(fluorosulfato)tungstate(II) and -molybdate(II) anions, [*fac*-$M(CO)(NO)_2(SO_3F)_3]^-$ ($M = W$, Mo), which are novel weakly coordinating anions that contain a metal carbonyl/nitrosyl moiety, have been generated in fluorosulfonic acid and completely characterized by multinuclear NMR, IR, and Raman spectroscopy as well as ESI mass spectrometry. ESI MS measurements performed for the first time on a superacidic solution system unambiguously reveal the formation of the monoanionic, mononuclear W and Mo complexes formulated as $[M(CO)(NO)_2(SO_3F)_3]^-$ ($M =$ W, Mo). Multinuclear NMR spectroscopic studies at natural abundance and ^{13}C and ^{15}N enrichment clearly indicate the presence of one CO ligand, two equivalent NO ligands, and two types of nonequivalent SO_3F^- groups in a 2:1 ratio. The IR and Raman spectra reveal that the two equivalent NO ligands have a *cis* conformation, thus indicating a *fac* structure. Density functional calculations at the B3LYP level of theory predict that these anions have a singlet ground state ($^1A'$) with a C_s symmetry along with C–O and N–O vibrational frequencies that are in agreement with the experimental observations. Mulliken population analysis shows that the monovalent negative charge is dispersed on the bulky sphere, the surface of which is covered by all the negatively charged O and F atoms with charge densities much lower than SO_3F^-, suggesting that [*fac*-$M(CO)(NO)_2(SO_3F)_3]^-$ ($M = W$, Mo) are weakly nucleophilic and poorly coordinating anions.

Keywords: carbonyl ligands · molybdenum · nitrosyl ligands · superacidic systems · tungsten

Introduction

Strong acids and superacids[1,2] are employed both in industrial applications and in academic research as reaction media for the generation, stabilization, and synthetic application of highly electrophilic and frequently very reactive organic, inorganic, and selected metal–organic cations.[2–7] The weakly nucleophilic conjugate-base ions are formed in the autoprotolysis equilibria for a Brönsted superacid,[1,2] such as HSO_3F,[2,4,8] the protonic acid of choice in this study [Eq. (1)], or for conjugated metal superacids in fluorosulfonic acid, such as the HSO_3F–$Au(SO_3F)_3$, HSO_3F–$Pt(SO_3F)_4$, HSO_3F–$Sn(SO_3F)_4$, and HSO_3F–$Sb(SO_3F)_5$ systems [Eq. (2)],[9] which are closely related to the system in this study. Notably, in all the conjugated metal superacids in fluorosulfonic acid, the metal center is coordinated by only SO_3F^-.

$$2HSO_3F \rightleftharpoons H_2SO_3F^+(solv) + SO_3F^-(solv) \qquad (1)$$

$$2HSO_3F + Au(SO_3F)_3 \rightleftharpoons H_2SO_3F^+(solv) + Au(SO_3F)_4{}^-(solv) \qquad (2)$$

In solution, the superacids stabilize these otherwise short-lived species by virtue of their high acidities or acidium ion

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[a] Prof. Dr. Q. Xu, Prof. Dr. N. Tsumori, L. Jiang
National Institute of Advanced Industrial Science and Technology (AIST)
Ikeda, Osaka 563-8577 (Japan)
Fax: (+81) 72-751-9629
E-mail: q.xu@aist.go.jp

[b] Prof. Dr. Q. Xu, L. Jiang
Graduate School of Science and Technology
Kobe University
Nada Ku, Kobe, Hyogo 657-8501 (Japan)

[c] Prof. Dr. N. Tsumori
Toyama National College of Technology
13 Hongo-machi, Toyama 939-8630 (Japan)

[d] M. Kondo, Prof. Dr. R. Arakawa
Department of Applied Chemistry
Kansai University
3-3-35 Yamate-cho, Suita, Osaka 564-8680 (Japan)

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concentrations and the low nucleophilicity of the conjugate-base ions. Among the stabilized species, a number of new homoleptic σ-bonded metal carbonyl cations and their derivatives from Groups 6–12,[5–7] including $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$[10] and $[\{Mo(CO)_4\}_2(\mathit{cis}\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$,[11] have been developed in the past 15 years. The majority of the metal carbonyl cations known are considered to be superelectrophilic. Fluorosulfonic acid, HSO_3F, is an excellent solvent for the synthesis of metal carbonyl cations and their derivatives. The derivatives are generally formed by substitution of CO by anionic monodentate ligands (SO_3F^-, SbF_6^-, and Cl^-). As attempts to prepare the HCO^+ ion by protonation of CO in the conjugated superacid $HSO_3F\text{–}Au(SO_3F)_3$ resulted instead in the reductive carbonylation of $Au(SO_3F)_3$ to form the first noble-metal carbonyl cation $[Au(CO)_2]^+$,[5,12] it seems that the coordination ability of the metal center to CO, the electrophilicity of the potential metal carbonyl cations, and the nucleophilicity of the metal conjugated acids act as competitive factors for determining the final products. The formation of $[Pt(CO)_2(SO_3F)_2]$ from $Pt(SO_3F)_4$ via the intermediate $[Pt(CO)_4][Pt(SO_3F)_6]$ in HSO_3F with increasing SO_3F^- concentration is very interesting; after all the Pt^{IV} species has been reduced and converted into $[Pt(CO)_4]^{2+}$, nucleophilic substitution by SO_3F^- occurs.[13] Notably, the σ-bonded metal carbonyls known thus far exist as cations with weakly nucleophilic anions or as neutral derivatives such as metal carbonyl fluorosulfates, but no such mainly σ-bonded M–CO moieties have been found in anions.

A preliminary communication revealed the formation, together with some spectroscopic data, of complexes with a σ-bonded carbonyldinitrosyltungsten(II) or -molybdenum(II) moiety ($M(CO)(NO)_2$; M = W, Mo) in fluorosulfonic acid.[14] These σ-bonded $M(CO)(NO)_2$ moieties may be highly electrophilic, and the three unoccupied sites at the metal centers have the potential to be coordinated by the solvent molecules. As the isolation of these novel compounds was unsuccessful, we performed ESI mass spectrometry on the superacid solution system and found that the $M(CO)(NO)_2$ moieties are coordinated by three SO_3F groups to form $[\mathit{fac}\text{-}M(CO)(NO)_2(SO_3F)_3]^-$ (M = W, Mo). This is significant because these complexes represent a new type of conjugated metal–superacid anion that contains a σ-bonded metal carbonyl/nitrosyl moiety. DFT calculations show that in these anions the monovalent negative charge is dispersed on the bulky sphere, the surface of which is covered by all the negatively charged O and F atoms with charge densities much lower than SO_3F^-; therefore, these anions should be weakly nucleophilic.[15]

Results and Discussion

Synthesis

The polymeric $[\{Mo(CO)_4\}_2(\mathit{cis}\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ complex was isolated by the oxidation of molybdenum hexacarbonyl, $[Mo(CO)_6]$, by antimony(V) fluoride, SbF_5, at 60 °C in an excess of liquid SbF_5.[10,11] In contrast, the reaction of tungsten hexacarbonyl, $[W(CO)_6]$, with SbF_5 in the conjugate Brønsted–Lewis superacid $HF\text{–}SbF_5$ at 40 °C produced the salt $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ as the main product.[10] This salt is stable up to 100 °C; further heating resulted in partial elimination of CO and SbF_5 to produce $[\{W(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x$, the analogue of $[\{Mo(CO)_4\}_2(\mathit{cis}\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$.[10,11]

In this study, we found that the dissolution of $[M(CO)_6]$ (M = W, Mo) in HSO_3F led to the release of 2 mol of CO per mol of $[M(CO)_6]$ to produce $[W^{II}(CO)_4(L)_3]$ (**1**) and $[Mo^{II}(CO)_4(L)_3]$ (**2**) (L = solvent molecule, probably HSO_3F or its conjugate base SO_3F^-, or a closely related species), respectively [Eq. (3)], which contain $M(CO)_4$ moieties similar to those reported.[10,11] This reaction involves an oxidation of M^0 to M^{II}, for which the protons in the superacidic solution may be considered the oxidizer.[16c]

$$[M(CO)_6] \xrightarrow[-2CO]{HSO_3F} \underset{\substack{M = W\ \mathbf{1}\\ Mo\ \mathbf{2}}}{[M^{II}(CO)_4(L)_3]} \xrightarrow[+2NO,\,-3CO]{HSO_3F} \underset{\substack{M = W\ \mathbf{3}\\ Mo\ \mathbf{4}}}{[\mathit{fac}\text{-}M(CO)(NO)_2(SO_3F)_3]^-} \qquad (3)$$

Some tungsten and molybdenum nitrosyl cations with weakly coordinating anions have previously been reported. The reaction of tungsten or molybdenum hexacarbonyls with 2 equivalents of $NOBF_4$ in acetonitrile produced $[M(NO)_2(MeCN)_4](BF_4)_2$ (M = W, Mo).[17] Structurally characterized tungsten complexes $[W(CO)_3(NO)(L)(FSbF_5)]$ (L = Me_2PhP or Cy_3P; Cy = cyclohexyl) were synthesized by the reaction of $[LW(CO)_5]$ with $NOSbF_6$ in CH_2Cl_2 with loss of 2 equivalents of CO.[18] It was reported that the complexes $[M(CO)_4(diphos)]$ (M = W, Mo; diphos = 1,2-bis(diphenylphosphanyl)ethane) and $NOPF_6$ react in methanol/toluene to afford $[M(CO)_3(NO)(diphos)]PF_6$.[19] Halogen-containing tungsten carbonyl nitrosyl derivatives such as $[W(CO)_4(NO)Cl]$ were also reported.[20]

In this study, we found that upon exposure to NO, **1** and **2** are readily transformed into $[\mathit{fac}\text{-}W(CO)(NO)_2(SO_3F)_3]^-$ (**3**) and $[\mathit{fac}\text{-}Mo(CO)(NO)_2(SO_3F)_3]^-$ (**4**), respectively [Eq. (3)]. This involves replacement of three CO by two NO ligands in the superacid medium HSO_3F, which resulted in the formation of the anions carrying the $M(CO)(NO)_2$ moiety and three SO_3F groups (Figure 1), in contrast to the formation of the cationic complexes described above. In the superacidic solution, the proton is considered to be the countercation for the anionic complexes **3** and **4**. Compound **3** was stable under Ar atmosphere or vacuum, but gradually changed into $[W^{II}(NO)_2(L)_4]$ (L = solvent molecule, probably HSO_3F or its conjugate base SO_3F^-, or a closely related species) (**5**) upon heating at 60 °C (>5 h).

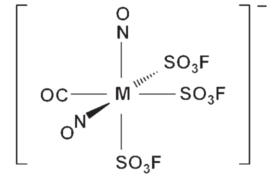

Figure 1. Structure of $[\mathit{fac}\text{-}M(CO)(NO)_2(SO_3F)_3]^-$ (M = W (**3**), Mo (**4**)).

Compound **4** was stable in HSO_3F under CO atmosphere even without gas-phase NO, but gradually changed into $[Mo^{II}(NO)_2(L)_4]$ (**6**) (L = solvent molecule) under NO or Ar atmosphere in the absence of CO (>2 days). The solution of **6** was indefinitely stable under Ar atmosphere. The stability of **3** was higher than that of **4** in the absence of CO, indicating that CO is much more strongly coordinated to W in **3** than to Mo in **4**. A similar tendency was observed in the reaction of $[M(CO)_3(MeCN)_3]$ (M = W, Mo) with $NOPF_6$.[21] It was reported that treatment of $[Mo(CO)_3(MeCN)_3]$ with $NOPF_6$/MeCN gives *cis*-$[Mo(NO)_2(MeCN)_4][PF_6]_2$, which contains no CO ligands, whereas the corresponding reaction of $[W(CO)_3(MeCN)_3]$ affords *cis*-$[W(CO)(NO)_2(MeCN)_3][PF_6]_2$.

ESI Mass Spectra

The relatively low viscosity of HSO_3F (2.384 cP), which is less than 1/10 of that of H_2SO_4 (24.2 cP) and is comparable with that of H_2O (0.89 cP),[22] enabled the ESI MS measurements of the solutions of **3** and **4** in HSO_3F. As shown in Figure 2, in the negative-ion ESI mass spectrum of HSO_3F, the SO_3F^- and $HSO_3F{\cdot}SO_3F^-$ ions were observed with only medium intensities.[23] As the electrospray was performed under an atmosphere of air, hydrolysis of HSO_3F by the moisture in air gave the products H_2SO_4 and HF, resulting in the formation of $H_2SO_4{\cdot}HSO_4^-$, $H_2SO_4{\cdot}SO_3F^-$, $2H_2SO_4{\cdot}HSO_4^-$, and $2H_2SO_4{\cdot}SO_3F^-$, which were observed as the dominant peaks along with small peaks for oligomeric species of higher weights with *m*/*z* values up to 493. Oligomeric species including HF were also observed with low intensities.

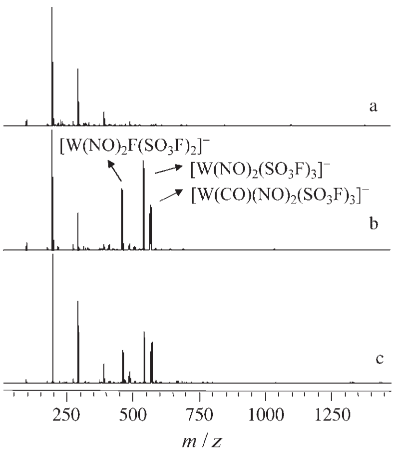

Figure 2. Negative-ion ESI mass spectra of a) HSO_3F, b) **3** at natural abundance in HSO_3F, and c) **3** at 99 % ^{15}NO enrichment in HSO_3F.

Besides the signals due to HSO_3F solvent, the ESI mass spectrum of **3** exhibits species with the tungsten isotope pattern[22,24] characterized by the intensity ratio $^{182}W:^{183}W:^{184}W:^{186}W = 26:14:31:28$ with corresponding *m*/*z* differences of 1, 1, and 2, respectively (i.e., $\Delta(m/z)(^{183}W-^{182}W)$, $\Delta(m/z)(^{184}W-^{183}W)$, and $\Delta(m/z)(^{186}W-^{184}W)$, respectively), thus indicating the presence of a monoanionic, mononuclear tungsten complex that can be formulated as $[W(CO)(NO)_2(SO_3F)_3]^-$ (Figures 2 and 3).[23] The three dominant species correspond to the parent ion **3**, [**3**−CO], and [**3**−CO−SO_3]. The [**3**−SO_3] and [**3**−CO−2SO_3] species were observed with medium and low intensities, respectively. The [**3**−2NO] species was observed with very low intensity, and the [**3**−NO] species could not be observed, probably due to its low intensity and overlap with the intense [**3**−CO] peak.

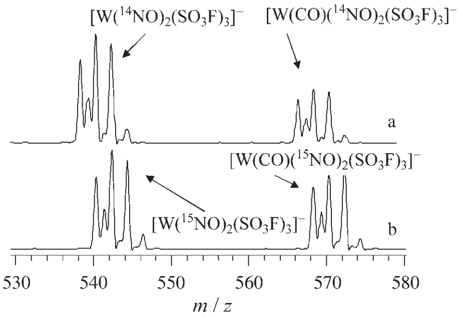

Figure 3. Negative-ion ESI mass spectra (*m*/*z* = 530–580) of **3** in HSO_3F at a) natural abundance and b) 99 % ^{15}NO enrichment.

Compared to the ESI mass spectrum of **3** at natural abundance, the mass spectrum of **3** at 99 % ^{15}NO enrichment (Figures 2c and 3b) exhibits high-weight shifts by *m*/*z* = 2 for **3**, [**3**−CO], [**3**−SO_3], [**3**−CO−SO_3], and [**3**−CO−2SO_3], whereas no shift is observed for [**3**−2NO], which supports the formulation of **3** as including two NO ligands.

In the ESI mass spectra of **3** at both natural abundance and 99 % ^{15}NO enrichment, all the dominant species contain two NO ligands, and only a trace amount of NO-free species [**3**−2NO] was observed, indicating that the two NO ligands are tightly bonded to W. In contrast, [**3**−CO] exhibits an intensity slightly larger than **3**, indicating that CO is more weakly bonded to W than NO, in agreement with the observation of the slow loss of CO from **3** and the slow transformation into **5** by heating at 60 °C.

The ESI mass spectrum of **4** exhibits species all with the molybdenum isotope pattern[22] characterized by the intensity ratio $^{92}Mo:^{94}Mo:^{95}Mo:^{96}Mo:^{97}Mo:^{98}Mo:^{100}Mo = 15:9:16:17:10:24:10$, with corresponding *m*/*z* differences of 2, 1, 1, 1, 1, and 2, respectively, thus indicating the presence of a monoanionic, mononuclear molybdenum complex that can be formulated as $[Mo(CO)(NO)_2(SO_3F)_3]^-$ (Figure 4).[23] The dominant species corresponds to [**4**−CO]. The species [**4**−CO−SO_3] and [**4**−CO−2SO_3] were observed with medium and low intensities, respectively. Notably, in contrast to **3**, only a trace amount of **4** was observed, indicating that CO is much more weakly coordinated to Mo in **4** than to W in **3**, in agreement with the observations of the lower stability of **4** in the absence of CO atmosphere.

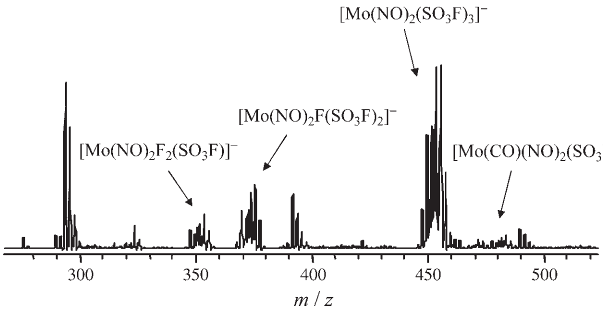

Figure 4. Negative-ion ESI mass spectrum of **4** in HSO_3F.

^{183}W, ^{13}C, ^{15}N, and ^{19}F NMR Spectroscopy

The ^{183}W and ^{13}C NMR spectroscopic studies at natural ^{13}C abundance and ^{13}CO enrichment indicate that **1** contains a $W(CO)_4$ moiety (Table 1).[14,23] Compound **1** at natural ^{13}C abundance shows a single ^{183}W resonance at −1119.5 ppm, which was split into a quintuplet with approximately 1:4:6:4:1 relative intensities ($^1J_{W,C}=115$ Hz) for the ^{13}CO-enriched sample prepared by repeating the substitution with 99% ^{13}CO, thus indicating the presence of four equivalent CO ligands coordinating to W. A ^{13}C resonance was observed at 204.6 ppm along with a satellite doublet with 1:12:1 relative intensities due to coupling ($^1J_{W,C}=115$ Hz) to ^{183}W (14% natural abundance, $I=\frac{1}{2}$).[23] The $W(CO)_4$ moiety was reported in $[\{W(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x$,[10] which is an analogue of the structurally well-defined seven-coordinate Mo^{II} complex $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$.[11]

The formulation of **3** with a $W(CO)(NO)_2$ moiety resulted from ^{183}W, ^{13}C, and ^{15}N NMR spectroscopic studies at natural abundance and ^{13}CO and 99% ^{15}NO enrichment, as partially reported in the preliminary communication.[14,23] Well-resolved spectra were obtained for **3** at ambient temperature, indicating that the structure is rigid on the NMR timescale. The single ^{183}W resonance at −1317.7 ppm was split into a doublet with $^1J_{W,C}=180$ Hz for the ^{13}CO-enriched sample and was further split into two triplets with $^1J_{W,N}=108$ Hz for the ^{13}CO- and ^{15}NO (99%)-enriched sample, indicating the presence of one CO and two magnetically equivalent NO ligands coordinating to W. These observations are consistent with the ^{13}C and ^{15}N NMR spectroscopic measurements[25] on the natural and ^{15}N-enriched complexes of **3**.[23] Single ^{13}C and ^{15}N resonances were observed at 190.7 and 70.3 ppm, respectively, and characteristic satellites due to the ^{183}W–^{13}C and ^{183}W–^{15}N couplings were observed with $^1J_{W,C}=180$ Hz and $^1J_{W,N}=108$ Hz. No C–N coupling ($^2J_{C,N}$) was observed. The observation of the two magnetically equivalent NO ligands by NMR spectroscopy excludes the structure of $[mer,cis\text{-}W(CO)(NO)_2(SO_3F)_3]^-$. Only limited ^{183}W NMR data have been reported thus far for related carbonyl- and nitrosyltungsten complexes. ^{183}W chemical shifts for **1** (−1119.5 ppm) and **3** (−1317.7 ppm) were downfield relative to $[W(CO)_6]$ (−3486 ppm).[26] The tungsten–carbon coupling constant, $^1J_{W,C}$, was higher for **3** (180 Hz) than for **1** (115 Hz), reflecting stronger M–C σ-bonding in **3**. For comparison, $^1J_{W,C}$ values were 126 Hz for $[W(CO)_6]$,[27] 166 and 139 Hz for the *trans*-to-MeCN CO and *trans*-$(CO)_2$, respectively, in $[mer,cis\text{-}W(CO)_3(NO)(MeCN)_2][SbF_6]$, and 178 Hz for $[fac\text{-}W(CO)_2(NO)(MeCN)_3][SbF_6]$;[18d] all the $^1J_{W,C}$ data available fall within a narrow range.

In the ^{19}F NMR spectrum of pure HSO_3F (Figure 5), a very intense peak at 41.9 ppm, along with a weak high-field satellite due to the ^{34}S isotope shift,[28] was observed. This peak did not change when **1** (0.3 M) was dissolved in HSO_3F. No additional ^{19}F signals were observed for **1**, suggesting rapid fluxionality or ligand exchange. Introduction of NO into HSO_3F led to high-field shift of the ^{19}F resonance. Besides the intense peak shifted high-field to 41.3 ppm, **3** in HSO_3F produced two sharp peaks with 2:1 relative intensities at 40.1 and 38.6 ppm, indicating the presence of two types of magnetically nonequivalent SO_3F groups in a 2:1 ratio. The ^{19}F resonance at 40.1 ppm is attributed to the two

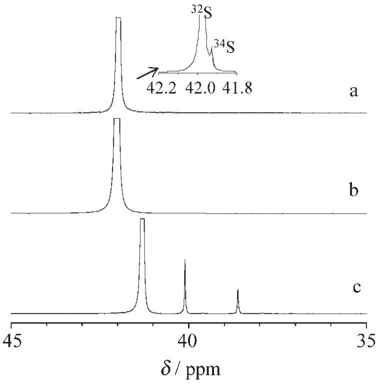

Figure 5. ^{19}F NMR spectra (376.05 MHz) of a) HSO_3F, b) **1** in HSO_3F (0.3 M), and c) **3** in HSO_3F. For HSO_3F, the main peak due to F on ^{32}S is observed along with a weak high-field satellite due to F on ^{34}S.

Table 1. ^{13}C, ^{15}N, ^{183}W, and ^{19}F NMR data of **1**, **3**, and related complexes.

Compound	$\delta(^{13}CO)$ [ppm]	$\delta(^{15}NO)$ [ppm]	$\delta(^{183}W)$ [ppm]	$\delta(^{19}F)$ [ppm]	$^1J_{W,C}$ [Hz]	$^1J_{W,N}$ [Hz]	Reference
1[a]	204.6		−1119.5		115		this work
3[a]	190.7	70.3	−1317.7	40.1,[b] 38.6[c]	180	108	this work
$[W(CO)_6]$[d]	191.9		−3486		126		[26, 27]
$[mer,cis\text{-}W(CO)_3(NO)(MeCN)_2][SbF_6]$[e]	204.2,[f] 195.0[g]				166,[f] 139[g]		[18]
$[fac\text{-}W(CO)_2(NO)(MeCN)_3][SbF_6]$[e]	213.0				178		[18]

[a] In HSO_3F. [b] SO_3F *trans* to NO. [c] SO_3F *trans* to CO. [d] In $CHCl_3$. [e] In CD_2Cl_2. [f] CO *trans* to MeCN. [g] *trans*-$(CO)_2$.

equivalent SO$_3$F groups *trans* to the equivalent NO ligands, and the resonance at 38.6 ppm to the SO$_3$F group *tran*s to CO. The observation of two ^{19}F NMR signals at room temperature argues against rapid fluxionality or ligand exchange in **3** as opposed to the case of **1**, in agreement with the expectation of more-facile fluxionality or ligand exchange for a seven-coordinate complex than for an octahedral one.

Similar ^{13}C and ^{15}N NMR spectroscopic results were obtained for the molybdenum analogues **2** and **4**. Compound **2** exhibits a ^{13}C resonance at 214.1 ppm, downfield from the neutral [Mo(CO)$_6$] (204.1 ppm).[27] Compound **4** shows a ^{13}C resonance at 189.9 ppm and a single ^{15}N resonance at 83.3 ppm due to the two magnetically equivalent NO ligands. A downfield ^{15}N resonance was observed at 115.1 ppm for **6**.

Vibrational Spectra

The IR and Raman spectra of **1** and **2** exhibit band distributions in the CO stretching range similar to those reported for [{W(CO)$_4$}$_2$(F$_2$SbF$_4$)$_3$]$_x$[Sb$_2$F$_{11}$]$_x$,[10] formed as the decomposition product of [W(CO)$_6$(FSbF$_5$)][Sb$_2$F$_{11}$],[10] and [{Mo(CO)$_4$}$_2$(cis-μ-F$_2$SbF$_4$)$_3$]$_x$[Sb$_2$F$_{11}$]$_x$,[11] respectively (Tables 2 and 3).[23] We believe that, as observed in [{Mo(CO)$_4$}$_2$(cis-μ-F$_2$SbF$_4$)$_3$]$_x$[Sb$_2$F$_{11}$]$_x$, the tungsten and molybdenum ions in **1** and **2** are similarly seven-coordinate, with a pyramidal M(CO)$_4$ group and the three other coordination sites occupied by solvent ligands.

The IR spectrum of **3** shows a CO stretching band at 2150 cm^{-1} along with its corresponding Raman counterpart at 2151 cm^{-1}.[23,29] Two NO IR stretching bands were observed at 1845 and 1763 cm^{-1}, along with their Raman counterparts at 1848 and 1764 cm^{-1}, respectively. The IR bands shifted to 1810 and 1729 cm^{-1} (Figure 6c) and their Raman counterparts to 1813 and 1732 cm^{-1}, respectively, with ^{15}NO (Table 2). Furthermore, two sets of triplet bands were observed at 1845, 1830, 1810 and 1763, 1735, 1729 cm^{-1} in the mixed ^{14}NO + ^{15}NO (1:1) isotope IR spectrum (Figure 6b), and at 1848, 1830, 1813 and 1764, 1736, 1732 cm^{-1} in the corresponding Raman spectrum. The isotopic spectra indicate that the two N–O stretching bands belong to a dinitrosyl species, and their IR and Raman activities indicate that the two NO ligands have a *cis* conformation.[30] As ESI MS, which revealed that **3** has a formulation of [W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$, and multinuclear NMR spectroscopy, which indicated that the two NO ligands are magnetically equivalent, exclude the structure of [mer,cis-W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$, the *cis* conformation for the two NO groups according to the vibrational spectra rules out the [$mer,trans$-W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$ structure, thus leading to the conclusion of a *fac* structure for **3**. The observed higher-frequency IR band along with its Raman counterpart is assigned to the

Table 2. C–O and N–O stretching vibrational frequencies (cm^{-1}) for **1**, **3**, **5**, and related complexes.[a]

Compound	Isotope	IR		Raman		Reference
		ν(CO)	ν(NO)	ν(CO)	ν(NO)	
1[b]	(^{12}CO)$_4$	2131 (s), 2062 (sh), 2040 (vs)		2133 (s), 2060 (s), 2044 (sh)		this work
	(^{13}CO)$_4$	2081 (s), 2011 (sh), 1995 (vs)		2082 (s), 2011 (s), 1996 (sh)		
3[b]	(^{12}CO)(^{14}NO)$_2$	2150 (s)	1845 (s), 1763 (s)	2151 (vs)	1848 (s), 1764 (m)	this work
	(^{12}CO)(^{14}NO)(^{15}NO)	2149 (s)	1830 (s), 1735 (s)	2148 (vs)	1830 (s), 1736 (m)	
	(^{12}CO)(^{15}NO)$_2$	2148 (s)	1810 (s), 1729 (s)	2149 (vs)	1813 (s), 1732 (m)	
	(^{13}CO)(^{14}NO)$_2$	2100 (s)	1842 (s), 1759 (s)	2100 (vs)	1843 (s), 1760 (m)	
	(^{13}CO)(^{15}NO)$_2$	2100 (s)	1807 (s), 1726 (s)	2099 (vs)	1807 (s), 1726 (m)	
5[b]	(^{14}NO)$_2$		1810 (w), 1707 (w)			this work
	(^{15}NO)$_2$		1773 (w), 1676 (w)			
[W(CO)$_6$][c]		1980		2121, 2015		[27]
[W(CO)$_6$(FSbF$_5$)][Sb$_2$F$_{11}$][d]		2125[e]		2125[e]		[10]
[mer-W(CO)$_3$(NO)(Me$_2$PhP)(FSbF$_5$)][f]		2102, 2012	1690			[18]
[fac-W(CO)$_2$(NO)(MeCN)$_3$][SbF$_6$][f]		2027, 1946	1685			[18]
cis-[W(CO)(NO)$_2$(MeCN)$_3$][PF$_6$]$_2$[g]		2164	1861, 1776			[21]
[W(NO)$_2$Cl$_2$]$_n$[h]			1800, 1680			[31]
[fac-W(CO)$_3$Cl$_3$][h]			1933, 1794, 1773			[32]

[a] s = strong, m = medium, w = weak, sh = shoulder, v = very. [b] In HSO$_3$F. [c] In CHCl$_3$. [d] In the solid state. [e] Average stretching frequency. [f] In CH$_2$Cl$_2$. [g] In MeCN. [h] In nujol.

Table 3. C–O and N–O stretching vibrational frequencies (cm^{-1}) for **2**, **4**, **6**, and related complexes.[a]

Compound	Isotope	IR		Raman		Reference
		ν(CO)	ν(NO)	ν(CO)	ν(NO)	
2[b]	$(^{12}CO)_4$	2140 (s), 2085 (sh), 2063 (vs)		2142 (s), 2084 (s), 2063 (sh)		this work
	$(^{13}CO)_4$	2091 (s), 2034 (sh), 2017 (vs)		2092 (s), 2037 (s), 2021 (sh)		
4[b]	$(^{12}CO)(^{14}NO)_2$	2171 (m)	1879 (s), 1787 (s)	2171 (vs)	1878 (s), 1788 (m)	this work
	$(^{12}CO)(^{15}NO)_2$	2170 (m)	1844 (s), 1755 (s)	2170 (vs)	1842 (s), 1756 (m)	
	$(^{13}CO)(^{14}NO)_2$	2122 (m)	1878 (s), 1786 (s)	2121 (vs)	1878 (s), 1788 (m)	
6[b]	$(^{14}NO)_2$		1853 (s), 1746 (s)		1854 (s), 1746 (m)	this work
	$(^{15}NO)_2$		1813 (s), 1706 (s)		1814 (s), 1708 (m)	
$[Mo(CO)_6]$[c]		1985		2119, 2022		[27]
$[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$[d]		2156, 2105, 2092, 2086		2156, 2105, 2088, 2085		[11]
cis-$[Mo(NO)_2(MeCN)_4][PF_6]_2$[e]			1863, 1761			[17, 21]
$[Mo(NO)_2Cl_2]_n$[f]			1805, 1690			[31]
$[Mo(CO)(NO)(H_2CPz'_2)(PMe_3)_2]BF_4$[g]		1914	1634			[35]

[a] s = strong, m = medium, w = weak, sh = shoulder, v = very. [b] In HSO_3F. [c] In $CHCl_3$. [d] In the solid state. [e] In MeCN. [f] In nujol. [g] In CH_2Cl_2.

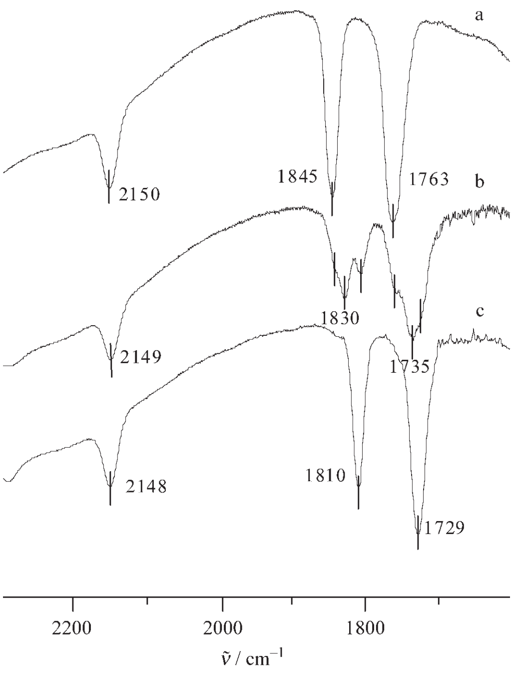

Figure 6. IR spectra of the carbonyl and nitrosyl regions of **3** in HSO_3F with isotopic NO. a) ^{14}NO; b) 50% ^{14}NO + 50% ^{15}NO; c) ^{15}NO.

symmetric NO stretching mode, and the lower-frequency band along with its Raman counterpart to the asymmetric NO stretching mode. Compounds **3** and **5** (IR: 1810 and 1707 cm^{-1}) were compared with the polymeric $[W(NO)_2Cl_2]_n$ (IR: 1800 and 1680 cm^{-1})[31] and its derivative [*fac*-$W(NO)_3Cl_3$] (IR: 1933, 1794, 1773 cm^{-1}),[32] as well as the related tungsten dinitrosyl cations $[W(CO)(NO)_2(MeCN)_3]^{2+}$ and $[W(NO)_2(MeCN)_4]^{2+}$, which are stabilized by the electron-donating MeCN ligands and exhibit nitrosyl bands at 1730–1870 cm^{-1} and a single carbonyl band, if a CO ligand is present, at around 2160 cm^{-1}.[17,21] Other related complexes include $[W(CO)_3(NO)(L)(FSbF_5)]$ (IR: L = Me_2PhP: 2102, 2012, 1690 cm^{-1}; L = Me_3P: 2102, 2010, 1690 cm^{-1})[18a] and [*fac*-$W(CO)_2(NO)(MeCN)_3][SbF_6]$ (IR: 2027, 1946, 1685 cm^{-1}).[18d] Notably, the CO stretching frequency for **3** is higher than the average CO stretching frequency of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ (2125 cm^{-1}),[10] and the NO stretching frequencies are comparable to those of the cationic complexes mentioned above, suggesting that the present $W(CO)(NO)_2$ moiety has less π-backbonding character and is relatively σ-bonded[5–7] while it is involved in the anion.

The IR and Raman spectra for **4** (Table 3)[23] are similar to those for **3**. The CO stretching wavenumbers observed at 2171 (IR) and 2171 cm^{-1} (Raman) are to our knowledge the highest for any molybdenum carbonyl species. The ν(NO) values in **4** (IR: 1879 and 1787 cm^{-1}) are higher than those of the polymeric $[Mo(NO)_2Cl_2]_n$ (IR: 1805 and 1690 cm^{-1})[31] and are close to those of the related molybdenum dinitrosyl cation $[Mo(NO)_2(MeCN)_4]^{2+}$ (IR: 1863 and 1761 cm^{-1}), which is stabilized by the electron-donating MeCN ligands and the PF_6^- anion.[21] Similar to **3**, the present $Mo(CO)(NO)_2$ moiety has relatively less π-backbonding character and is largely σ-bonded while it is involved in the anion.

The CO stretching wavenumbers observed at 2150 (IR) and 2151 cm^{-1} (Raman) for **3** and at 2171 (IR) and 2171 cm^{-1} (Raman) for **4** are much higher than those of the corresponding $M(CO)_4$ complexes (**1**: $\nu(CO)_{av}$ = 2078 (IR), 2079 cm^{-1} (Raman); **2**: 2096 (IR), 2096 cm^{-1} (Raman)) and indicate a much greater positive charge on the central metal, M, in **3** and **4** than in **1** and **2**, respectively, thus suggesting a charge transfer from M to NO. This is supported by Mulliken population analyses at the B3LYP level, which predict a positive charge on the CO ligand (+0.1035 in **3**, +0.1236 in **4**) and a negative charge on each NO ligand

(−0.1311 in **3**, −0.062 in **4**) (see below) and is consistent with the observation of ν(NO) values lower than 1876 cm^{-1}, the value for free NO.[33] The ν(NO) values for the present tungsten and molybdenum nitrosyl complexes **2**–**6** are much lower than those for [$Cu^{II}(NO)(L)_3$] in strong acids and superacids (e.g., 1933 (IR) and 1936 cm^{-1} (Raman) in HSO_3F);[34] a similar trend was observed for metal carbonyl cations in that late transition metals have much higher ν(CO) values than early transition metals.[5–7]

It was found in $^{12}CO\leftrightarrow^{13}CO$ and $^{14}NO\leftrightarrow^{15}NO$ isotope-exchange experiments monitored by IR spectroscopy that CO and NO are much more strongly coordinated to W in **3** than to Mo in **4**, in agreement with ESI MS measurements. Significant $^{12}CO\leftrightarrow^{13}CO$ and $^{14}NO\leftrightarrow^{15}NO$ exchanges with free CO and NO were not observed for **3** but were for **4**.

Table 4. Ground electronic states, point groups, and IR frequencies (cm^{-1}) and intensities (km mol^{-1}) of [*fac*-$M(CO)(NO)_2(SO_3F)_3$]$^-$ (M = W (**3**), Mo (**4**)) calculated at the B3LYP/D95*-SDD level, and observed IR frequencies (cm^{-1}) and scale factors.

Species	Elec. state	Point group	Stretching mode	$\tilde{\nu}_{calcd}$ (intensity, mode)	$\tilde{\nu}_{obs}$	Scale factor ($\tilde{\nu}_{obs}/\tilde{\nu}_{calcd}$)
3	$^1A'$	C_s	N–O asym. str.	1811 (1209, A″)	1763	0.973
			N–O sym. str.	1888 (659, A′)	1845	0.977
			C–O str.	2167 (469, A′)	2150	0.992
4	$^1A'$	C_s	N–O asym. str.	1836 (1197, A″)	1787	0.973
			N–O sym. str.	1916 (637, A′)	1879	0.980
			C–O str.	2182 (400, A′)	2171	0.995

Density Functional Theory Calculations

The geometries of **3** and **4** were optimized at the B3LYP level of theory, which are predicted to have a singlet ground state ($^1A'$) with C_s symmetry (Figure 7). For [*fac*-$W(CO)(NO)_2(SO_3F)_3$]$^-$ (**3**), the antisymmetric N–O, symmetric N–O, and C–O vibrational frequencies were calculated to be 1811 (A″), 1888 (A′), and 2167 cm^{-1} (A′) at the B3LYP/D95*-SDD level, which give scale factors (observed/calculated) of 0.973, 0.977, and 0.992, respectively (Table 4). The calculated intensity ratio of the antisymmetric/symmetric N–O stretching bands is 1209/659, in agreement with the observed value (100/55). Similarly, the corresponding frequencies are predicted to be 1820, 1896, and 2166 cm^{-1} with scale factors of 0.969, 0.973, and 0.993, respectively, at the B3LYP/D95*-LANL2DZ level. Hereafter, mainly the B3LYP/D95*-SDD results are presented for discussion. Our present calculations show that the singlet [*fac*-$W(CO)(NO)_2(SO_3F)_3$]$^-$ molecule lies 31.45 kcal mol^{-1} lower in energy than the triplet, which has an imaginary frequency at 655.3*i* cm^{-1}. We also performed DFT calculations on other isomers and found that the [*mer,cis*-$W(CO)(NO)_2(SO_3F)_3$]$^-$ and [*mer,trans*-$W(CO)(NO)_2(SO_3F)_3$]$^-$ molecules lie 7.71 and 31.92 kcal mol^{-1} higher in energy than the [*fac*-$W(CO)(NO)_2(SO_3F)_3$]$^-$ molecule, respectively. Similar results were obtained for the Mo analogue. For [*fac*-$Mo(CO)(NO)_2(SO_3F)_3$]$^-$ (**4**), the antisymmetric N–O, symmetric N–O, and C–O vibrational frequencies were calculated to be 1836 (A″), 1916 (A′), and 2182 cm^{-1} (A′) at the B3LYP/D95*-SDD level, which give scale factors (observed/calculated) of 0.973, 0.980, and 0.995, respectively (Table 4). The calculated intensity ratio of the antisymmetric/symmetric N–O stretching bands is 1197/637, in agreement with the observed value (100/50).

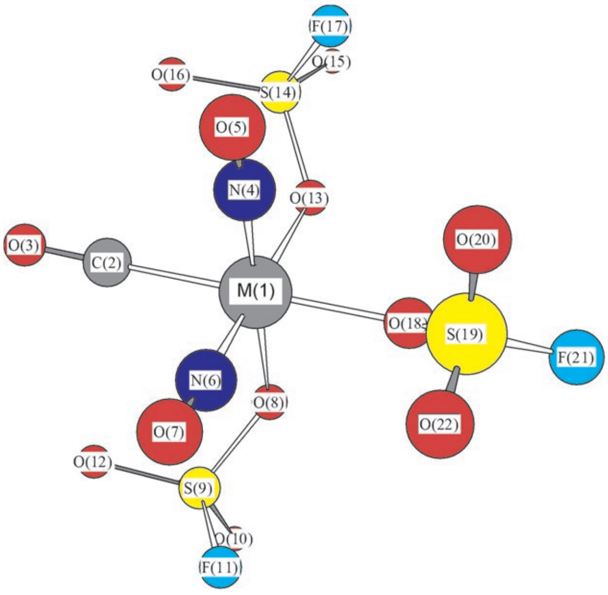

Figure 7. Optimized structure of [*fac*-$M(CO)(NO)_2(SO_3F)_3$]$^-$ (M = W (**3**), Mo (**4**)) calculated at the B3LYP/D95*-SDD level.

For **3**, the W(1)–C(2) and two equivalent W–N bond lengths (W(1)–N(4) and W(1)–N(6)) are predicted to be 2.117 and 1.857 Å, respectively (Figure 7).[23] For comparison, the W–C bonds in [$W(CO)_6(FSbF_5)$][Sb_2F_{11}] are 1.996–2.150 Å,[10] the W–C and W–N bonds in [$W(CO)_3(NO)(Me_2PhP)(FSbF_5)$] are 2.052–2.092 Å and 1.795 Å, respectively,[18a] and the N–O bonds in [*fac*-$W(NO)_3Cl_3$] are 1.88–1.92 Å long.[32b] The two W–O bonds *trans* to the NO ligands (W(1)–O(8) and W(1)–O(13)) are equivalent with a bond length of 2.131 Å, which is slightly longer than the W–O bond *trans* to the CO ligand (W(1)–O(18), 2.112 Å). The two W–N–O angles are equivalent with a value of 176.59°, indicating a nearly linear W–NO coordination. Similarly, for the Mo analogue **4**, the Mo(1)–C(2) and two equivalent Mo–N bond lengths (Mo(1)–N(4) and Mo(1)–N(6)) are predicted to be 2.129 and 1.845 Å, respectively (Figure 7).[23] For comparison, the Mo–C bonds in [{$Mo(CO)_4$}$_2$(*cis*-μ-$F_2SbF_4)_3$]$_x$[Sb_2F_{11}]$_x$ are 2.021–2.052 Å,[11] whereas short Mo–C (1.847 Å) and Mo–N (1.823 Å) bonds were observed in [$Mo(CO)(NO)(H_2CPz'_2)(PMe_3)_2$]$BF_4$ (Pz′ = 3,5-dimethylpyrazol-1-yl), which exhibits low C–O and N–O stretching frequencies at 1914 and 1634 cm^{-1}, respectively.[35] The two Mo–O bonds *trans* to the NO ligands (Mo(1)–O(8) and

Mo(1)−O(13)) are equivalent with a bond length of 2.138 Å, which is slightly longer than the W−O bond *trans* to the CO ligand (Mo(1)−O(18), 2.118 Å). The two Mo−N−O angles are equivalent with a value of 176.92°, indicating a nearly linear Mo–NO coordination. Notably, the C−O and N−O bond lengths in **4** are slightly shorter than in **3**, which corresponds to the slightly higher C−O and N−O stretching frequencies in **4** relative to **3**.

Figure 8 illustrates the representative molecular-orbital diagrams of singlet [*fac*-W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$ (**3**). The highest occupied molecular orbital (HOMO) is the π orbital delocalized to the W−CO−(NO)$_2$ subunit. HOMO-1 is the delocalized π orbital that involves mainly the W−CO−(NO)$_2$−O(18) subunit, whereas HOMO-2 is the delocalized π orbital that involves mainly the W−(NO)$_2$−O(8)−O(13) subunit. HOMO-3 is the delocalized π orbital that involves mainly the W−(NO)$_2$−O(8)−O(13)−O(18) subunit. These orbitals are primarily responsible for the stabilization of this anionic molecule. Similar molecular orbitals were obtained for the Mo analogue **4**.

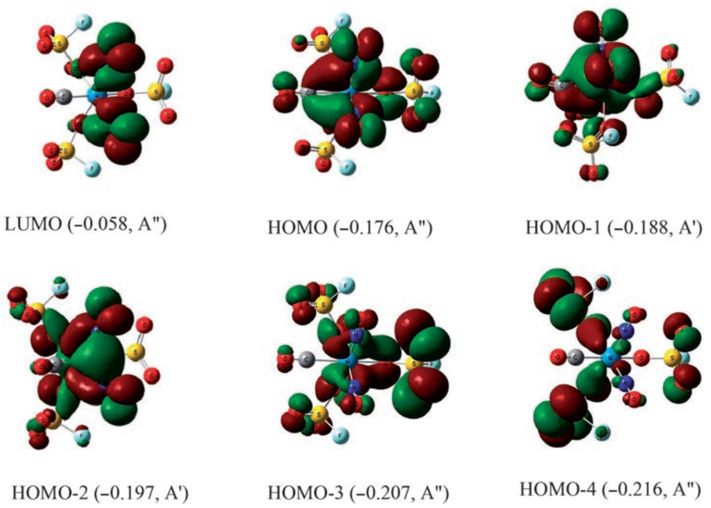

Figure 8. Molecular-orbital diagrams of singlet [*fac*-W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$ (**3**), showing the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) down to the fourth valence molecular orbital from the HOMO.

Mulliken population analysis for **3** showed that the W atom carries a positive charge of 0.8522.[23] The summation of the charge on the CO ligand is +0.1035, in agreement with the observation of the C−O vibration (2150 cm^{-1}) at slightly higher frequency than for free CO (2143 cm^{-1}),[36] as a result of carrying a slight positive charge as reported previously.[5–7] The summation of the charge on each NO ligand is −0.1311, that on each SO$_3$F ligand *trans* to the NO ligand is −0.5666, and that on the SO$_3$F ligand *trans* to the CO ligand is −0.5604. Similar results for Mulliken population analysis were also obtained for the [*fac*-Mo(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$ molecule.[23] Notably, **3** and **4** are covered by a bulky sphere consisting of all negatively charged O and F atoms. For comparison, we performed DFT calculations on SO$_3$F$^-$ at B3LYP/D95* level, and the salient results are shown in the Supporting Information.[23] The SO$_3$F$^-$ ion is predicted to have a singlet ground state (^{1}A′) with C_s symmetry. The three O−S bond lengths are all 1.481 Å, and the three O−S−O angles are 115.93, 115.94, and 115.94°. Mulliken population analysis for SO$_3$F$^-$ showed that the three O atoms carry charges of −0.6227, −0.6227, and −0.6226, respectively, and the charge on the F atom is −0.4400. By comparing the negative charges on the O and F atoms of SO$_3$F$^-$, it is clear that the negative charges on the O and F atoms of **3** and **4** are significantly reduced, suggesting that the bulky sphere of **3** and **4** covered by the negatively charged O and F atoms with lower charge density most likely has lower nucleophilicity than SO$_3$F$^-$.

Conclusions

Dissolution of [M(CO)$_6$] (M = W, Mo) in fluorosulfonic acid followed by exposure to NO allowed the generation of carbonyldinitrosyltris(fluorosulfato)tungstate(II) and -molybdate(II) anions, [*fac*-W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$ and [*fac*-Mo(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$. The new complexes are the first well-characterized weakly coordinating anions that contain a metal carbonyl/nitrosyl moiety, in contrast with the formation of a number of metal carbonyl cations in strong acids and superacids.

The formulation of [*fac*-W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$ resulted from multinuclear (^{183}W, ^{13}C, ^{15}N, and ^{19}F) NMR, IR, and Raman spectroscopy as well as ESI mass spectrometry. At room temperature, its structure is rigid on the NMR timescale. ^{183}W, ^{13}C, ^{15}N, and ^{19}F NMR studies at natural abundance and ^{13}C and ^{15}N enrichment clearly indicated the presence of one CO ligand, two equivalent NO ligands, and two types of magnetically nonequivalent SO$_3$F groups in a 2:1 ratio coordinating to W. The $^1J_{\mathrm{W,C}}$ and $^1J_{\mathrm{W,N}}$ values are 180 and 108 Hz, respectively. The relatively low viscosity of HSO$_3$F makes ESI MS measurements of the new complex in HSO$_3$F solution possible. The negative-mode ESI MS measurements at natural abundance and ^{15}N enrichment, which exhibit the characteristic pattern for tungsten isotopes at natural abundance, unambiguously revealed the formation of a monoanionic, mononuclear W complex that can be formulated as [W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$. The IR and Raman spectra in the CO and NO stretching regions showed that the two equivalent NO ligands have a *cis* conformation, indicating a *fac* structure. The C–O stretching frequency of 2150 cm^{-1}, which is higher than the value of 2143 cm^{-1} for free CO, along with the relatively high N–O stretching frequencies (1845 and 1763 cm^{-1}) suggest that the present W(CO)(NO)$_2$ moiety has less π-backbonding character and is relatively σ-bonded while it is involved in the anion.

DFT calculations on [*fac*-W(CO)(NO)$_2$(SO$_3$F)$_3$]$^-$ at the B3LYP level of theory predict that this anion has a singlet ground state (^{1}A′) with C_s symmetry along with C–O and N–O vibrational frequencies that are in agreement with experimental observations. Mulliken population analysis showed that the monovalent negative charge is dispersed on the bulky sphere, the surface of which is covered by all the negatively charged O and F atoms with charge densities much lower than SO_3F^-, thus suggesting that [*fac*-$W(CO)(NO)_2(SO_3F)_3$]$^-$ is a weakly nucleophilic and poorly coordinating anion.

Similar experimental and theoretical results were obtained for the tungsten and molybdenum analogues [*fac*-$W(CO)(NO)_2(SO_3F)_3$]$^-$ and [*fac*-$Mo(CO)(NO)_2(SO_3F)_3$]$^-$. These new complexes represent a new type of conjugated metal–superacid anion that contains a relatively σ-bonded metal carbonyl/nitrosyl moiety. The present findings also suggest that strong acids and superacids could be used to generate a number of new metal nitrosyl complexes, as in the successful preparation of a series of metal carbonyl cations over the last 15 years.

Experimental Section

Syntheses

[$W(CO)_6$] (97 %, Kanto Chemical Co.), [$Mo(CO)_6$] (98 %, Kanto Chemical Co.), HSO_3F (Wako Pure Chemicals), CO (99.95 %, Japan Fine Products Co.), ^{13}CO (^{13}C enrichment 99 %, ICON), NO (99.8 %, Sumitomo Seika), and ^{15}NO (^{15}N enrichment 99 %, Shoko Co. Ltd.) were used without further purification.

For compound preparation, use was made of equipment similar to that previously described.[16] Mixtures of [$W(CO)_6$] (1 mmol) or [$Mo(CO)_6$] (1 mmol) and HSO_3F (3 mL) were stirred in 30-mL three-necked flasks for 3–5 h under CO or Ar, whereupon the solution became clear yellow due to the formation of **1** and **2**. ^{13}CO-enriched complexes of **1** and **2** were prepared by repeating the substitution with 99 % ^{13}CO. Compounds **1** and **2** were rapidly transformed into **3** and **4** (≈30 min) upon exposure to NO atmosphere, producing a green solution. ^{13}C- and ^{15}N-enriched complexes of **3** and **4** were similarly prepared from the ^{13}CO-enriched complexes of **1** and **2**, respectively, by using 99 % enriched ^{15}NO instead of NO. All the resulting solutions were moisture-sensitive. Standard cannula-transfer techniques were used for all sample manipulations for the spectroscopic measurements. IR spectra were recorded with time to monitor the changes of the compounds during the reactions.

Instrumentation

NMR spectra were recorded at room temperature by using a JEOL JNM-AL400 spectrometer. For the ^{183}W NMR measurements (16.5 MHz), saturated Na_2WO_4 in D_2O prepared by using the substitution method[37] was contained as an external reference and a lock in sample tubes (10 mm o.d.), in which coaxial inserts containing liquid samples were placed. The ^{183}W chemical shifts (δ) are given in parts per million (ppm) downfield from Na_2WO_4. For the ^{13}C (100.4 MHz) and ^{15}N (40.4 MHz) NMR measurements, CD_3CN ($^{13}CD_3$, 1.3 ppm; $C^{15}N$, −134 ppm) was contained as an external reference and a lock in 5-mm o.d. sample tubes, in which coaxial inserts containing liquid samples were placed. ^{13}C and ^{15}N chemical shifts are given in δ units (parts per million) downfield from TMS and $NH_4{}^{15}NO_3$, respectively. For the ^{19}F (376.05 MHz) NMR measurements, a mixture of CD_3CN and C_6H_5F (^{19}F, −112.8 ppm) was contained as an external reference and a lock in sample tubes (5 mm o.d.), in which coaxial inserts containing liquid samples were placed. ^{19}F chemical shifts are given in ppm downfield from $CFCl_3$.

ESI mass spectra were obtained by using a QP8000α single-stage quadrupole mass spectrometer (Shimadzu Corp., Kyoto) connected to a laboratory-made ESI interface.[38] The operating conditions were: flow rate 1–2 μL min^{-1}, capillary temperature 200 °C, spraying voltage 3.5 kV. The sample solutions were made up to 0.3 M in HSO_3F and electrosprayed in the negative-ion mode by using a 500-μL syringe (Hamilton) with a stainless-steel needle of 32 gauge. The direction of the needle and the distance between the needle and the counterelectrode (nearly 1 cm) were adjusted to avoid electric discharge.

IR spectra were obtained on thin films between two silicon discs on a BIORAD FTS-6000e spectrometer by using a DTGS detector with a spectral range of 5000–400 cm^{-1} and a spectral resolution of 2 cm^{-1}. Raman spectra were recorded at room temperature on a Nicolet FT-Raman 960 spectrometer with a range of 4000–100 cm^{-1} and a spectral resolution of 2 cm^{-1} by using the 1064-nm excitation line (≈800 mV) of a Nd/YAG laser (Spectra Physics, USA). Liquid Raman samples were contained in an NMR tube (5 mm o.d.).

Computational Methods

Quantum chemical calculations were performed to predict the structures and vibrational frequencies of the potential reaction products by using the Gaussian 03 program.[39] The Becke three-parameter hybrid functional with Lee–Yang–Parr correlation corrections (B3LYP) was used.[40] The D95* basis set was used for C, N, O, F, and S atoms, and the SDD and the Los Alamos ECP plus DZ (LANL2DZ) set for W and Mo atoms.[41,42] Geometries were fully optimized, and vibrational frequencies were calculated with analytical second derivatives.

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