A Neutral Organometallic Fluoro Complex Can Be a Good Ligand

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Abstract: The reaction of the complex [Mo(OTf)(η^3-C_3H_4-Me-2)$(CO)_2$(phen)] (**1**) (OTf = trifluoromethylsulfonate; phen = 1,10-phenanthroline) with tetrabutylammonium fluoride trihydrate afforded the fluoride complex [MoF(η^3-C_3H_4-Me-2)$(CO)_2$(phen)] (**2**). The IR spectrum and the oxidation potential of **2** reflect the fact that its metal center is more electron-rich than that of the chloro analogue [MoCl(η^3-C_3H_4-Me-2)$(CO)_2$(phen)]. Compound **2** reacted with **1** affording the homobinuclear complex [{Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)}$_2$(μ-F)][OTf] (**3**), with a fluoride bridge. Compound **2** also reacts with the species generated in situ by triflate abstraction from [M(OTf)$(CO)_3$('N−N')] (M = Mn, Re; 'N−N' = 2,2'-bipyridine (bipy), phen) using NaBAr'$_4$ (Ar' = 3,5-bis(trifluoromethyl)phenyl), affording the heterobinuclear complexes [{Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)}(μ-F){M$(CO)_3$('N−N')}][BAr'$_4$] (M = Mn, 'N−N' = bipy (**4**); M = Re, 'N−N' = phen (**5**)). All new compounds have been characterized by spectroscopic methods (IR and NMR) and, in the case of **1**, **2**, **3**, and **4**, also by means of X-ray diffraction analysis.

Keywords: carbonyl complexes · fluoro complexes · manganese · molybdenum · rhenium

Introduction

Owing to the small size and high electronegativity of the fluorine atom, fluoride is the archetypal hard ligand and hence it was once considered that complexes with a soft, low oxidation state transition-metal center and strong π-acceptor ligands, such as carbonyls, would be unstable. It is now recognized that this view is inadequate, and the fact that organometallic fluoro complexes are scarce in comparison with similar derivatives of the heavier halides is attributed more to synthetic difficulties.[1] Thus, although the number of known organometallic fluoro complexes has grown considerably in recent years, many of them, in particular the bi- or polymetallic complexes, have been serendipitously obtained as a result of fluoride abstraction from tetrafluoroborate or hexafluorophosphate anions by a highly electrophilic metal center.[1,2] Other polymetallic fluoro complexes are the products of self-assembly.[1c] Rational syntheses from mononuclear precursors, like those applied for the preparation of heterobimetallic compounds with chloride, bromide, or iodide bridges,[3] are, to the best of our knowledge, unknown. This may be due in part to the fact that the highly electronegative fluoride is the halide expected to show the lowest propensity to act as a bridge between metals.[4] We have endeavored to explore the synthesis of homo- and heterobinuclear carbonyl fluoro complexes from mononuclear precursors, and report our results herein.

Results and Discussion

The mononuclear precursor: We chose to study the simplest case, namely, the synthesis of binuclear complexes with a single fluoride as the only bridge between the two metals. Most stable complexes with bridging halide groups possess several bridging ligands, and complexes with a single halide or another anionic group with a single donor atom as the only bridge are often labile. However, two stable homobinuclear complexes of this type containing {Mo(η^3-

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allyl)(CO)$_2$('N–N')} fragments are known: the chloro derivative [{Mo(η^3-C$_3$H$_5$)(CO)$_2$(bipy)}$_2$(μ-Cl)][BF$_4$], unexpectedly isolated by Curtis and Fotinos as the product of the reaction of [MoCl(η^3-C$_3$H$_5$)(CO)$_2$(bipy)] with AgBF$_4$ in CH$_2$Cl$_2$,[5] and the hydroxo compound [{Mo(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(-phen)}$_2$(μ-OH)][BAr'$_4$], recently obtained by us from the reaction of [MoCl(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] with KOH in dry CH$_2$Cl$_2$.[6] Therefore, we chose a complex of the type [MoF(η^3-allyl)(CO)$_2$('N–N')] as our mononuclear precursor. Since complexes of the methallyl (2-methylallyl; η^3-C$_3$H$_4$-Me-2) group are somewhat more stable than those of unsubstituted allyl,[7] and it has been our experience that phenanthroline derivatives have better crystallinity than their bipy analogues, we targeted [MoF(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)].

Since [MoCl(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)],[8] the most convenient precursor for complexes of the {Mo(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)} fragment, reacted sluggishly with several fluoride sources, we decided to employ the more labile [Mo(OTf)(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] complex (**1**) as precursor. This triflato compound was synthesized in high yield by treatment of [MoCl(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] with silver triflate in dichloromethane, and was characterized by IR and NMR in solution (see Experimental Section) and by single-crystal X-ray diffraction analysis in the solid state (see Figure 1 and Table 1).

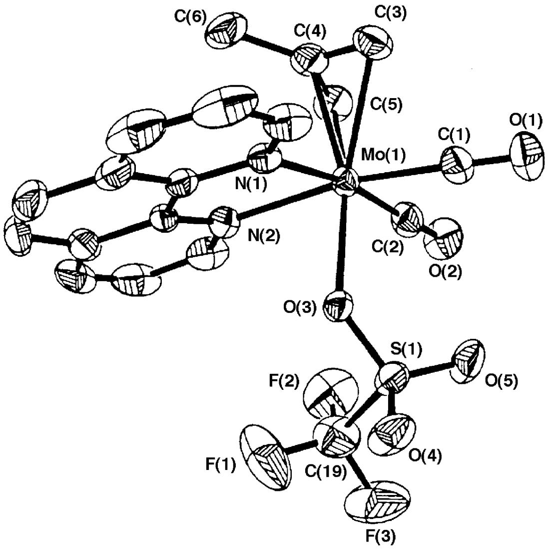
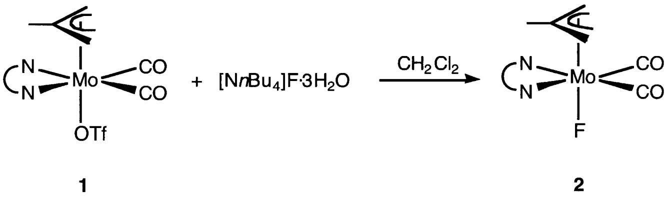


Figure 1. Structure of **1** (thermal ellipsoid (30%) plot).

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**.

Mo(1)–C(2)	1.965(5)	Mo(1)–N(1)	2.242(3)
Mo(1)–C(1)	1.965(5)	Mo(1)–N(2)	2.237(3)
Mo(1)–O(3)	2.203(2)	C(1)–O(1)	1.156(5)
Mo(1)–C(3)	2.314(4)	C(2)–O(2)	1.154(5)
Mo(1)–C(4)	2.239(5)	S(1)–O(3)	1.469(3)
Mo(1)–C(5)	2.302(4)		
C(2)-Mo(1)-C(1)	79.13(19)	C(2)-Mo(1)-O(3)	91.32(15)
C(1)-Mo(1)-O(3)	91.32(15)	N(2)-Mo(1)-N(1)	73.69(12)
C(1)-Mo(1)-N(1)	102.08(16)	O(3)-Mo(1)-N(1)	78.25(10)
C(2)-Mo(1)-N(2)	102.90(16)		

Complex **1** reacted with [N*n*Bu$_4$]F·3H$_2$O in the time of mixing, affording [MoF(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (**2**) as the single organometallic product (see Scheme 1), as indicated by monitoring the reaction by IR spectroscopy in the carbonyl stretching region and by ^{19}F NMR spectroscopy.[9] Unlike in several previous examples, the presence of water (since the fluoride reagent is a trihydrate) did not interfere in the synthesis of **2**.[1a,b]



Scheme 1. Preparation of the fluoro complex **2**.

Complex **2** was easily separated from the by-product [N*n*Bu$_4$]OTf,[10] taking advantage of the solubility of this salt in diethyl ether, in which the complex is insoluble. Thus, crystallization of the crude reaction product from dichloromethane/diethyl ether afforded a high yield of analytically pure **2**. The presence of the fluoride ligand in **2** was established by the observation of a singlet at $\delta = -204.8$ ppm in the ^{19}F NMR spectrum. Chemical shifts of $\delta = -214.7$ and $\delta = -266.0$ ppm have been reported for the complexes [MoF(η^2-MeHNC≡CNHMe)][BF$_4$][11] and [MoF(CO)$_2$(dppe)$_2$][PF$_6$],[12] respectively.

A medium intensity band at 446 cm^{-1} in the IR spectrum of solid **2** was assigned to the Mo–F stretch. M–F bands in the range 750–500 cm^{-1} are found in conventional metal fluorides,[13] that is, in medium or high valent, non-organometallic species with net π donation of electron density from F to M and, therefore, with some degree of multiple character of the M–F bond. On the other hand, a value as low as 413 cm^{-1} for the ν(Mo–F) band of the compound [NEt$_4$][MoF(CO)$_2$(S$_2$CNEt$_2$)$_2$] was taken as an indication of a weak Mo–F bond.[14]

The C_s-symmetric geometry of complex **2** depicted in Scheme 1 is consistent with the solution ^{1}H and ^{13}C NMR data, given in the Experimental Section, and with the results of a structure determination by means of X-ray diffraction, the results of which are displayed in Figure 2 and Table 2. The coordination environment of the molybdenum atom consists of two *cis* carbonyls and a phenanthroline chelate

Table 2. Selected bond lengths [Å] and angles [°] for complex **2**.

Mo(1)–F(1)	2.056(2)	Mo(1)–N(1)	2.255(3)
Mo(1)–C(2)	1.956(4)	Mo(1)–N(2)	2.246(3)
Mo(1)–C(1)	1.966(4)	C(1)–O(1)	1.156(4)
Mo(1)–C(3)	2.325(4)	C(2)–O(2)	1.162(4)
Mo(1)–C(4)	2.240(4)	Mo(1)–C(5)	2.320(4)
C(2)-Mo(1)-C(1)	82.99(15)	C(1)-Mo(1)-F(1)	90.26(13)
C(2)-Mo(1)-F(1)	90.46(12)	N(2)-Mo(1)-N(1)	74.05(11)
C(1)-Mo(1)-N(1)	98.77(13)	F(1)-Mo(1)-N(2)	77.11(9)
C(2)-Mo(1)-N(2)	102.20(13)	F(1)-Mo(1)-N(1)	80.13(9)

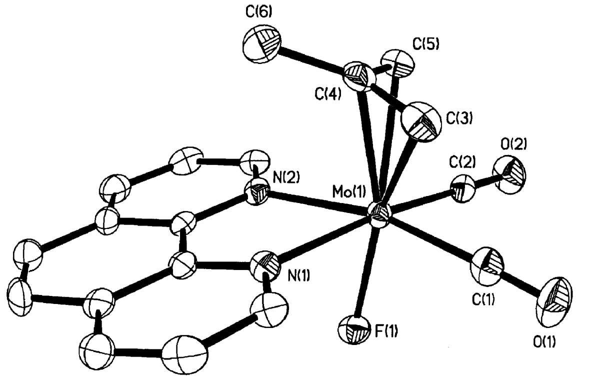
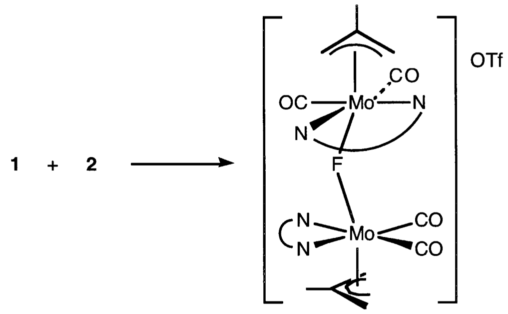


Figure 2. Structure of **2** (thermal ellipsoid (30 %) plot).



Scheme 2. Reaction between complexes **1** and **2** to generate the homobinuclear complex **3**.

defining an equatorial plane, on opposite sides of which lie the fluoro and η^3-methallyl ligands. This geometry has been found for most structurally characterized [MoX(η^3-allyl)(CO)$_2$('N−N')] (X = anionic ligand) compounds,[15] including the triflato complex **1**. The Mo−F distance in **2**, 2.056(2) Å, is comparable to those previously reported for other molybdenum carbonyl complexes containing a terminal fluoride ligand.[1a–c] Complex **2** is a covalent compound, fluoride dissociation from which is not facile. Thus, it does not react with trimethylphosphine (IR and ^{19}F NMR monitoring, two equivalents, 5 h, room temperature).[16]

Two ν(C−O) bands of similar intensity in the IR spectrum of the fluoro complex **2**, due to the *cis*-{Mo(CO)$_2$} fragment, occur at lower wavenumbers (1940 and 1858 cm^{-1}) than those of the chloro derivative [MoCl(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (1950 and 1872 cm^{-1}). This indicates that the metal center is more electron-rich in **2**, leading to a greater back-donation to the carbonyls in this complex. Accordingly, [MoF(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] and [MoCl(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] undergo electrochemical oxidations at potentials of 0.37 and 0.52 V, respectively.[17] Since the two complexes are isostructural, these differences reflect the different properties of the two halides. Intuitively, the higher electronegativity of F would be expected to lead to less electron density at the metal center of **2** and hence to higher ν(C−O) values and a higher oxidation potential, but the reverse is found. The same "inverse halide effect" has been found for several families of carbonyl fluoro complexes,[1a] and has been interpreted in terms of a superior π-donor character of fluoride over the heavier halides[1a,f] in combination with four electron repulsions[18] and, more recently, as resulting from the greater ionic character of the M−F bond.[19]

Binuclear compounds: Equimolar amounts of [Mo(OTf)(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (**1**) and [MoF(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (**2**) reacted instantaneously, as evidenced by a shift in the ^{19}F NMR signal from $\delta = -204.8$ to $\delta = -298.0$ ppm for the Mo-bonded fluoride. The reaction, shown in Scheme 2, involves the displacement of triflate by the fluoride ligand of **2**. Crystallization afforded a high yield of [{Mo(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)}$_2$(μ-F)][OTf] (**3**), which was characterized spectroscopically (see Experimental Section) and by X-ray diffraction analysis (Figure 3 and Table 3). The cation of **3** consists of two staggered {Mo(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)} moieties bridged by a single fluoride ligand. The two Mo−F distances, 2.100(3) and 2.121(3) Å, are slightly longer than that to the terminal fluoride of **2** (vide supra). The Mo-F-Mo angle, 150.46(15)°, is wider than the Mo-X-Mo angles in the compounds [{Mo(η^3-C$_3$H$_5$)(CO)$_2$(bipy)}$_2$(μ-Cl)][BF$_4$] (134.0(1)°)[5] and [{Mo(η^3-C$_3$H$_5$)(CO)$_2$(phen)}$_2$(μ-OH)][BAr'$_4$] (145.3(4)°),[6] reflecting

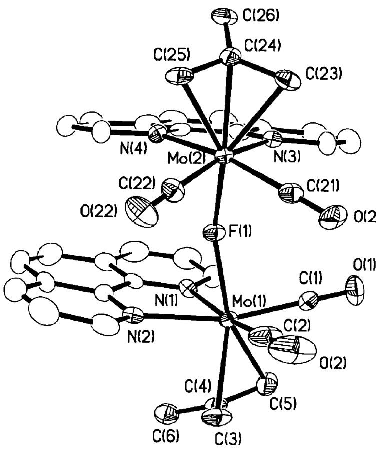


Figure 3. Structure of **3** (thermal ellipsoid (30 %) plot).

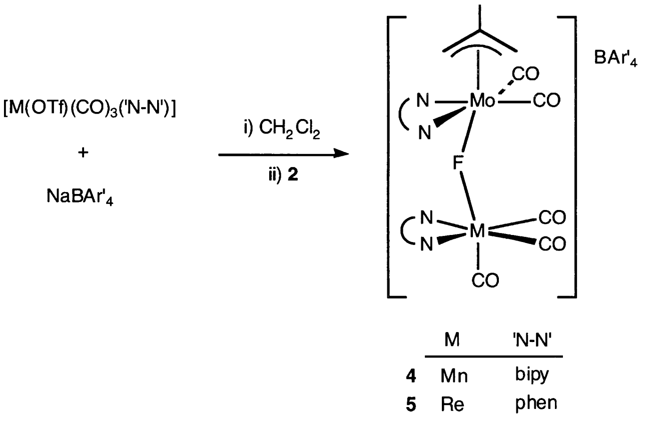
Table 3. Selected bond lengths [Å] and angles [°] for complex **3**.

Mo(1)−F(1)	2.100(3)	Mo(1)−N(1)	2.248(4)
Mo(2)−F(1)	2.121(3)	Mo(1)−N(2)	2.247(4)
Mo(1)−C(2)	1.953(6)	C(1)−O(1)	1.142(7)
Mo(1)−C(1)	1.972(6)	C(2)−O(2)	1.161(8)
Mo(1)−C(3)	2.311(6)	Mo(2)−C(21)	1.959(6)
Mo(1)−C(4)	2.233(6)	Mo(2)−C(22)	1.971(6)
Mo(1)−C(5)	2.314(6)	Mo(2)−C(24)	2.220(5)
Mo(2)−C(23)	2.301(5)	Mo(2)−N(3)	2.245(4)
Mo(2)−C(25)	2.319(6)	Mo(2)−N(4)	2.245(4)
Mo(1)-F(1)-Mo(2)	150.46(15)	F(1)-Mo(1)-N(1)	77.25(13)
C(2)-Mo(1)-C(1)	78.9(3)	N(2)-Mo(1)-N(1)	74.31(16)
C(2)-Mo(1)-F(1)	93.4(2)	F(1)-Mo(1)-N(2)	75.70(14)
C(1)-Mo(1)-F(1)	88.60(19)	C(21)-Mo(2)-C(22)	82.5(2)
C(21)-Mo(2)-F(1)	89.85(17)	C(22)-Mo(2)-F(1)	90.73(18)
F(1)-Mo(2)-N(4)	76.37(13)	F(1)-Mo(2)-N(3)	75.81(13)
N(4)-Mo(2)-N(3)	74.73(16)		

the smaller size of the fluoride bridge, but narrower than those in high oxidation state complexes in which net π-donation from fluoride to empty metal d orbitals is possible.[20]

Organometallic compounds with fluoride bridges between molybdenum atoms have been reported previously.[1a–c] However, **3** is the first example of a low-valent binuclear molybdenum compound with a single fluoride as the only bridge. Despite the absence of additional bridges, the binuclear cation of **3** is not labile; for instance, **3** is unreactive toward PMe_3 (5 h, room temperature).

In view of the facile synthesis of **3**, the preparation of fluoride-bridged heterobinuclear compounds was attempted in an analogous manner by the reactions of **2** with equimolar amounts of the triflato complexes $[M(OTf)(CO)_3('N{-}N')]$ (M = Mn, Re; 'N–N' = bipy, phen).[21] However, after several hours at room temperature, the IR and ^{19}F NMR data of the resulting solutions showed only the presence of the unchanged reagents, indicating insufficient lability of the triflato ligand in the group 7 complexes. Recently, we found that the triflate in $[Re(OTf)(CO)_3(bipy)]$ complexes could be easily abstracted by the salt $NaBAr'_4$ (Ar' = 3,5-bis(trifluoromethyl)phenyl).[22] The reaction takes place under very mild conditions and is driven by the low solubility of the product in dichloromethane, employed as solvent. This method allowed us to prepare several compounds $[Re(L)(CO)_3(bipy)][BAr'_4]$ with labile ligands L.[21] We found that by using the same method (now L = complex **2**; see Scheme 3 and Experimental Section), the formation of $[\{Mo(\eta^3\text{-}C_3H_4\text{-}Me\text{-}2)(CO)_2(phen)\}(\mu\text{-}F)\{M(CO)_3('N{-}N')\}][BAr'_4]$ took place in a few minutes for M = Mn, and in one hour for M = Re.



Scheme 3. Compound **2** acts as a metalloligand toward fragments $\{M(CO)_3('N{-}N')\}^+$ (M = Mn, Re).

The new heterobinuclear compounds were characterized spectroscopically and, in the case of **4**, by X-ray diffraction analysis (Figure 4 and Table 4). The cation of **4** consists of the $\{Mo(\eta^3\text{-}C_3H_4\text{-}Me\text{-}2)(CO)_2(phen)\}$ and $\{Mn(CO)_3(bipy)\}$ units bridged by a fluoride ligand, with an Mo-F-Mn angle of 145.80(18)°. The Mo–F and Mn–F distances (2.100(3) and 1.990(3) Å, respectively) are close to those found in **3** (identical, vide supra) and in the complex $[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}F)]$ (1.95(2) Å),[23] that is, within the range of Mn(μ-F)Mn distances.[1b] The similarity of the spectroscopic data indicate a similar structure for compound **5**. No signals attributable to the F ligands were observed in the ^{19}F NMR spectra of compounds **4** and **5**. Similar findings have been noted previously,[1a] and were attributed to the presence of water in the solvents used.[24] Like the homobinuclear compound **3**, heterobinuclear complexes **4** and **5** are stable with respect to dissociation, as shown by their lack of reactivity with PMe_3. This is noteworthy since even bimetallic compounds with several halide bridges are often labile. On the other hand, although anionic fluoro complexes have been found to display coordinating ability,[2c] we are not aware of any previous employment of a neutral fluoro complex as a ligand.

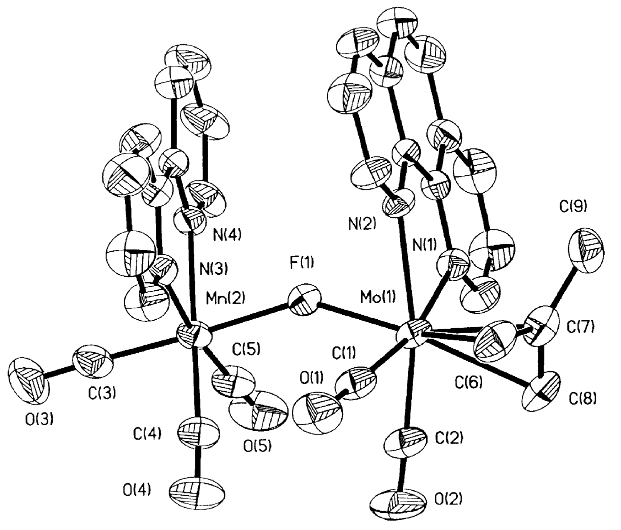


Figure 4. Structure of **4** (thermal ellipsoid (30 %) plot).

Table 4. Selected bond lengths [Å] and angles [°] for complex **4**.

Mo(1)–F(1)	2.100(3)	Mo(1)–N(1)	2.248(5)
Mn(2)–F(1)	1.990(3)	Mo(1)–N(2)	2.245(4)
Mo(1)–C(2)	1.969(7)	C(1)–O(1)	1.151(8)
Mo(1)–C(1)	1.950(8)	C(2)–O(2)	1.124(8)
Mo(1)–C(6)	2.333(8)	Mn(2)–C(3)	1.789(8)
Mo(1)–C(7)	2.235(7)	Mn(2)–C(4)	1.824(7)
Mo(1)–C(8)	2.319(6)	Mn(2)–C(5)	1.812(9)
Mn(2)–N(3)	2.042(5)	Mn(2)–N(4)	2.056(5)
Mo(1)-F(1)-Mn(2)	145.80(18)	F(1)-Mo(1)-N(1)	76.05(15)
C(2)-Mo(1)-C(1)	82.1(3)	N(2)-Mo(1)-N(1)	73.16(18)
C(2)-Mo(1)-F(1)	91.3(2)	F(1)-Mo(1)-N(2)	74.99(15)
C(1)-Mo(1)-F(1)	91.5(2)	C(5)-Mn(2)-C(4)	88.4(3)
C(3)-Mn(2)-F(1)	177.1(2)	C(5)-Mn(2)-F(1)	91.3(3)
C(4)-Mn(2)-F(1)	95.6(2)	C(3)-Mn(2)-C(5)	90.5(3)
F(1)-Mn(2)-N(3)	83.12(17)	F(1)-Mn(2)-N(4)	81.83(16)
N(3)-Mn(2)-N(4)	78.5(2)	C(3)-Mn(2)-C(4)	86.7(3)

In conclusion, we have found that the complex $[MoF(\eta^3\text{-}C_3H_4\text{-}Me\text{-}2)(CO)_2(phen)]$ (**2**), accessible in high yield in a straightforward manner from commercially available tetrabutylammonium fluoride trihydrate as fluoride source and $[Mo(OTf)(\eta^3\text{-}C_3H_4\text{-}Me\text{-}2)(CO)_2(phen)]$ (**1**), is a good ligand toward three different cationic metal fragments, thus allowing the rational synthesis of homo- and heterobimetallic fluoro-bridged compounds. Despite the absence of additional bridging ligands, the binuclear units of these bimetallic compounds are maintained in solution.

Experimental Section

General conditions have been reported elsewhere.[25]

For reference, the atom-numbering schemes for phen, bipy, and BAr'$_4$ are given in Figure 5.

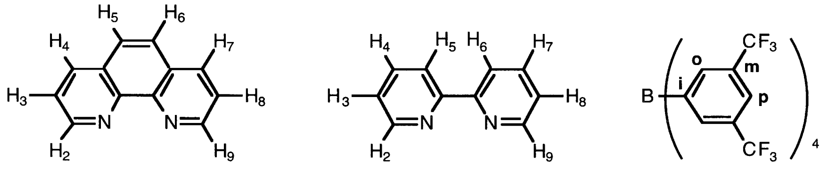


Figure 5. Atom-labelling schemes for phen, bipy, and BAr'$_4$.

Electrochemical studies were carried out using an EG&G model 273 A potentiostat, computer-controlled through the application of EG&G model 270 research electrochemistry software, in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum disc (1.6 mm diameter). The reference was an aqueous saturated calomel electrode separated from the test solution by a fine porosity frit and an agar bridge saturated with KCl. Solutions were 5.0×10^{-4} or 1.0×10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[NBu^n_4][PF_6]$ as the supporting electrolyte, in CH_2Cl_2. Under the conditions used, at a scan rate of 200 mV s^{-1}, $E^{\circ\prime}$ for the one-electron oxidation of $[Fe(\eta^5\text{-}C_5Me_5)_2]$, added to the test solutions as an internal calibrant, was −0.08 V (on this scale, the oxidation of $[Fe(\eta^5\text{-}C_5H_5)_2]$ occurs at 0.47 V).

General procedure for crystal structure determinations of compounds 1, 2, and 3:

A suitable crystal was attached to a thin glass fibre and transferred to a Bruker-Nonius MACH3 S diffractometer, and examined with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Unit cell determination and subsequent data collection were performed at 173(2) K. Unit cell constants were determined from a least-squares refinement of the setting angles of 25 machine-centered reflections in the range $10.19° < \theta < 18.07°$. Intensity data were collected using the $\omega/2\theta$ scan technique to a maximum 2θ of 49.94°. An absorption correction was applied based on azimuthal scans of several reflections, resulting in transmission factors ranging from 0.8581 to 1.0. A correction for crystal decay was not required. The data were corrected for Lorentz and polarization effects and converted to structure factors using the teXsan for Windows crystallographic software package.[26] Crystal and refinement data for **1**, **2**, and **3** are presented in Table 5.

Table 5. Crystal data and refinement details for complexes **1**, **2**, and **3**.

	1	**2**	**3**	
formula	$C_{19}H_{15}F_3MoN_2O_5S$	$C_{18}H_{15}FMoN_2O_2$	$C_{37}H_{30}F_4Mo_2N_4O_7S$	$C_{63}H_{35}BF_{25}MnMoN_4O_5$
formula weight	536.33	406.26	942.59	1564.64
crystal system	orthorhombic	triclinic	monoclinic	triclinic
space group	*Pbca*	P_1	*Cc*	*P*1
a [Å]	15.8772(8)	7.8749(5)	11.140(1)	11.724(3)
b [Å]	13.0846(9)	14.362(2)	18.432(1)	14.760(4)
c [Å]	20.125(1)	15.106(2)	18.355(1)	19.651(5)
α [°]	90	102.560(10)	90	81.180(5)
β [°]	90	98.687(8)	96.84(1)	76.903(4)
γ [°]	90	102.884(8)	90	89.312(5)
V [Å^3]	4180.9(4)	1589.5(3)	3742.1(4)	3272.2(14)
Z	8	4	4	2
T [K]	293(2)	173(2)	173(2)	299(2)
ρ_{calcd} [g cm^{-3}]	1.704	1.698	1.673	1.588
F(000)	2144	816	1888	1556
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073	0.71073	0.71073
crystal size [mm]	$0.40 \times 0.34 \times 0.34$	$0.36 \times 0.22 \times 0.08$	$0.30 \times 0.12 \times 0.10$	$0.15 \times 0.18 \times 0.26$
μ [mm^{-1}]	0.788	0.849	0.800	0.507
scan range [°]	$2.02 \leq \theta \leq 24.91$	$2.32 \leq \theta \leq 24.95$	$2.15 \leq \theta \leq 24.97$	$1.08 \leq \theta \leq 23.32$
refl. measured	3647	6009	6550	14758
independent refl.	3647	5566	6550	9359
data/restraints/parameters	3647/0/281	5566/0/435	6550/2/496	9359/0/902
goodness-of-fit on F^2	1.026	1.020	1.040	1.067
R_1/R_{w2} [$I > 2\sigma(I)$]	0.0384/0.0809	0.0321/0.0699	0.0359/0.0828	0.0665/0.1736
R_1/R_{w2} (all data)	0.0631/0.0907	0.0494/0.0758	0.0409/0.0855	0.1010/0.1996

Crystal structure determination of compound 4: A suitable crystal was attached to a glass fibre and transferred to a Bruker AXS SMART 1000 diffractometer, and examined with graphite-monochromated $Mo_{K\alpha}$ radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to 2θ = 48.6°. Raw frame data were integrated with the SAINT program.[27] The structure was solved by direct methods with SHELXTL.[28] A semiempirical absorption correction was applied with the program SADABS.[29] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. SHELXTL was used for all calculations and to generate the graphics. Crystal and refinement data for **4** are presented in Table 5.

CCDC-207047 (**1**), CCDC-207048 (**2**), CCDC-207049 (**3**), and CCDC-223966 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

[Mo(OTf)(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (1): AgOTf (0.062 g, 0.24 mmol) was added to a solution of $[MoCl(\eta^3\text{-}C_3H_4\text{-}Me\text{-}2)(CO)_2(phen)]$ (0.100 g, 0.24 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred in the dark for 30 min, and then the resulting orange solution was filtered through diatomaceous earth to remove AgCl. Concentration to a volume of 5 mL in vacuo and addition of hexane (20 mL) led to the precipitation of an orange microcrystalline solid, which was washed with hexane and dried in vacuo (0.110 g, 85 %). Crystals of X-ray quality were obtained by slow diffusion of hexane into a concentrated solution of **1** in CH_2Cl_2. Elemental analysis calcd (%) for $C_{19}H_{15}F_3MoN_2O_5S$: C 42.55, H 2.81, N 5.22; found: C 42.21, H 2.85, N 5.01; IR (CH_2Cl_2): $\tilde{\nu}$ = 1961 (ν(CO)) (vs), 1879 (ν(CO)) cm^{-1} (s); ^{1}H NMR (CD_2Cl_2): δ = 9.33 (d, $^3J_{H,H}$ = 4.27 Hz, 2H; $H_{2,9}$), 8.59 (d, $^3J_{H,H}$ = 7.90 Hz, 2H; $H_{4,7}$), 8.05 (s, 2H; $H_{5,6}$), 7.93 (dd, 2H; $H_{3,8}$), 3.16 (s, 2H; H_s), 1.38 (s, 2H; H_a), 0.84 ppm (s, 3H; η^3-$C_3H_4(CH_3)$-2); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 224.7 (CO), 152.6, 145.1, 139.1, 130.4, 127.7, 125.3 (phen), 80.5 (C^2, η^3-$C_3H_4(CH_3)$), 54.1 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 19.1 ppm (η^3-$C_3H_4(CH_3)$-2); ^{19}F NMR ($CDCl_3$): δ = −78.6 ppm.

[MoF(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (2): $[NnBu_4]F \cdot 3H_2O$ (0.151 g, 0.48 mmol) was added to a solution of **1** (0.250 g, 0.47 mmol) in CH_2Cl_2 (20 mL). The color changed from orange to red. After stirring for 15 min, the solution was filtered through diatomaceous earth. The volume was reduced to 5 mL by concentration in vacuo. Slow diffusion of Et_2O into the concentrated solution yielded deep-red crystals of **2** (0.175 g, 91 %). The crystal used for X-ray analysis was obtained by slow diffusion of hexane into a concentrated solution of **2** in CH_2Cl_2 at −20 °C. Elemental analysis calcd (%) for $C_{18}H_{15}FMoN_2O_2$: C 60.86, H 4.70, N 8.52; found: C 60.71, H 4.97, N 8.55; IR (CH_2Cl_2): $\nu_{CO} = 1940$ (vs), 1850 cm^{-1} (s); IR (KBr): $\tilde{\nu} = 1921$ (ν(CO)) (vs), 1846 (ν(CO)) (vs), 446 cm^{-1} (ν(Mo−F) (m); ^1H NMR (CD_2Cl_2): $\delta = 9.21$ (s, 2H; $H_{2,9}$), 8.45 (s, 2H; $H_{4,7}$), 7.88 (s, 2H; $H_{5,6}$), 7.79 (dd, 2H; $H_{3,8}$), 2.99 (s, 2H; H_s), 1.16 (s, 2H; H_a), 0.81 ppm (s, 3H; C_6H_4-CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 227.6$ (CO), 151.7, 145.2, 138.4, 130.5, 127.6, 125.1 (phen), 80.5 (C^2, η^3-$C_3H_4(CH_3)$), 59.2 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 19.9 ppm (η^3-$C_3H_4(CH_3)$-2); ^{19}F NMR (CD_2Cl_2): $\delta = -204.8$ ppm.

[{Mo(η³-C₃H₄-Me-2)(CO)₂(phen)}₂(μ-F)][OTf] (3): A solution of **1** (0.026 g, 0.049 mmol) and **2** (0.020 g, 0.049 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h. The resulting red solution was concentrated under reduced pressure to a volume of 5 mL, and then layered with hexane affording, after slow diffusion, red crystals of **3** (0.042 g, 91 %), one of which was used for X-ray analysis. Elemental analysis calcd (%) for $C_{37}H_{30}F_4Mo_2N_4O_7S$: C 47.14, H 3.20, N 5.94; found: C 47.01, H 3.39, N 6.01; IR (CH_2Cl_2): $\tilde{\nu} = 1960$ (ν(CO)) (sh), 1950 (ν(CO)) (vs), 1872 (ν(CO)) cm^{-1} (s); ^1H NMR (CD_2Cl_2): $\delta = 8.83$ (d, $^3J_{H,H} = 4.63$ Hz, 4H; $H_{2,9}$), 8.53 (d, $^3J_{H,H} = 8.09$ Hz, 4H; $H_{4,7}$), 7.94 (s, 4H; $H_{5,6}$), 7.72 (dd, 4H; $H_{3,8}$), 2.88 (s, 4H; H_s), 1.08 (s, 4H; H_a), 0.55 ppm (s, 6H; η^3-$C_3H_4(CH_3)$-2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 225.4$ (CO), 151.3, 143.9, 139.5, 129.9, 127.9, 125.3 (phen), 80.1 (C^2, η^3-$C_3H_4(CH_3)$), 53.7 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 19.2 ppm (η^3-$C_3H_4(CH_3)$-2); ^{19}F NMR (CD_2Cl_2): $\delta = -78.5$ (OTf), −298.0 ppm.

[{Mo(η³-C₃H₄-Me-2)(CO)₂(phen)}(μ-F){Mn(CO)₃(bipy)}][BAr′₄] (4): $NaBAr'_4$ (0.066 g, 0.075 mmol) was added to a solution of $[Mn(OTf)(CO)_3(bipy)]$ (0.033 g, 0.074 mmol) in CH_2Cl_2 (10 mL). After the mixture had been stirred for 5 min at room temperature, the IR spectrum showed ν_{CO} bands at 2049 (vs) and 1952 cm^{-1} (s). The mixture was filtered, through a cannula tipped with filter paper, onto a solution of **1** (0.030 g, 0.074 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred for 10 min. Following concentration in vacuo, addition of hexane caused the precipitation of **4** as a red microcrystalline solid (0.076 g, 89 %). Slow diffusion of hexane into a concentrated solution of **4** in THF at −20 °C yielded red crystals, one of which was used for a structure determination by X-ray diffraction analysis. Elemental analysis calcd (%) for $C_{65}H_{35}BF_{25}MnMoN_4O_5$: C 48.36, H 2.25, N 3.58; found: C 48.05, H 2.34, N 3.59; IR (CH_2Cl_2): $\tilde{\nu}= 2038$ (ν(CO)) (s), 1950 (ν(CO)) (vs), 1969 (ν(CO)) cm^{-1} (s); ^1H NMR (CD_2Cl_2): $\delta = 8.92$ (d, $^3J_{H,H} = 4.84$ Hz, 2H; $H_{2,9}$ phen), 8.64 (d, $^3J_{H,H} = 5.12$ Hz, 2H; $H_{2,9}$ bipy), 8.47 (dd, $^3J_{H,H} = 9.39$, 1.14 Hz, 2H; $H_{4,7}$ phen), 7.94 (d, $^3J_{H,H} = 6.26$ Hz, 2H; $H_{5,6}$ bipy), 7.88 (s, 2H; $H_{5,6}$ phen), 7.75 (dd, 2H; $H_{3,8}$ phen), 7.71 (m, 8H; C_o-H), 7.54 (s, 4H; C_p-H), 7.37 (m, 4H; bipy), 2.91 (s, 2H; H_s), 1.06 (s, 2H; H_a), 0.72 ppm (s, 3H; η^3-$C_3H_4(CH_3)$-2).

[{Mo(η³-C₃H₄-Me-2)(CO)₂(phen)}(μ-F){Re(CO)₃(phen)}][BAr′₄] (5): A solution of **2** (0.020 g, 0.05 mmol) and $[Re(CO)_3(phen)(THF)](BAr'_4)$ (0.070 g, 0.05 mmol) in CH_2Cl_2 (20 mL) was stirred for 2 h. The red solution obtained was concentrated in vacuo and then layered with hexane (20 mL), affording an orange microcrystalline solid, which was washed with hexane and dried in vacuo (0.070 g, 81 %). Elemental analysis calcd (%) for $C_{65}H_{35}BF_{25}MoN_4O_5Re$: C 45.39, H 2.05, N 3.25; found: C 45.57, H 1.88, N 3.49; IR (CH_2Cl_2): $\tilde{\nu} = 2031$ (ν(CO)) (s), 1952 (ν(CO)) (m), 1914 (ν(CO)) (vs), 1867 (ν(CO)) cm^{-1} (w); ^1H NMR (CD_2Cl_2): $\delta = 9.42$ (d, $^3J_{H,H} = 5.12$ Hz, 2H; $H_{2,9}$), 8.90 (d, $^3J_{H,H} = 6.64$ Hz, 2H; $H_{4,7}$), 8.83 (s, 2H; $H_{5,6}$), 8.62 (dd, 2H; $H_{3,8}$), 8.54 (d, $^3J_{H,H} = 7.97$ Hz, 2H; $H_{2,9}$), 8.41 (d, $^3J_{H,H} = 8.25$ Hz, 2H; $H_{4,7}$), 7.97 (s, 2H; $H_{5,6}$), 7.71 (m, 10H; C_o-H and 2H; bipy), 7.53 (s, 4H; C_p-H), 2.86 (s, 2H; H_s), 1.01 (s, 2H; H_a), 0.69 ppm (s, 3H; η^3-$C_3H_4(CH_3)$-2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 225.1$, 224.7 (Mo−CO), 196.4 (2 × Re−CO), 191.5 (Re−CO), 162.1 (q, $^1J_{C,B} = 49.6$ Hz; C_i), 153.1, 151.5, 146.7, 144.3, 139.8, 140.0, 139.2, 139.0 (phen), 135.2 (s; C_o), 129.2 (q, $^2J_{C,F} = 31.5$ Hz; C_m), 126.5 (q, $^1J_{C,F} = 272.4$ Hz; CF_3), 126.3, 126.7 (phen), 117.9 (s, C_p), 80.9 (C^2, η^3-$C_3H_4(CH_3)$), 59.4 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 19.4 ppm (η^3-$C_3H_4(CH_3)$-2); ^{19}F NMR (CD_2Cl_2): $\delta = -63.4$ ppm (BAr'_4).

[Mo(η³-C₃H₄-Me-2)(PMe₃)(CO)₂(phen)][BAr₄′]: $NaBAr'_4$ (0.104 g, 0.118 mmol) was added to a solution of $[MoCl(\eta^3$-C_3H_4-Me-2)$(CO)_2(phen)]$ (0.050 g, 0.118 mmol) in CH_2Cl_2 (10 mL), and the resulting mixture was stirred for 15 min at room temperature. The IR spectrum showed ν_{CO} bands at 1960 (vs) and 1880 cm^{-1} (s). The solution was filtered through a cannula tipped with filter paper, and PMe_3 (15 μL, 0.120 mmol) was added to the filtrate. After stirring for 5 min, concentration in vacuo, and the addition of hexane (20 mL), the phosphino complex $[Mo(\eta^3$-C_3H_4-Me-2)$(PMe_3)(CO)_2(phen)][BAr_4']$ was obtained as a red microcrystalline solid, which was dried in vacuo (0.135 g, 86 %). Elemental analysis calcd (%) for $C_{53}H_{36}BF_{24}MoN_2O_2P$: C 47.98, H 2.73, N 2.11; found: C 48.21, H 2.78, N 2.35; IR (CH_2Cl_2): $\tilde{\nu} = 1954$ (ν(CO)) (vs), 1877 (ν(CO)) cm^{-1} (s); ^1H NMR (CD_2Cl_2): $\delta = 8.99$ (d, $^3J_{H,H} = 3.70$ Hz, 2H; $H_{2,9}$), 8.58 (d, $^3J_{H,H} = 7.97$ Hz, 2H; $H_{4,7}$), 8.01–7.56 (m, 16H; $H_{5,6}$, $H_{3,8}$, BAr_4'), 3.27 (s, 2H; H_s), 2.15 (s, 2H; H_a), 0.73 (d, $^2J_{P,H} = 8.26$ Hz, 9H; PMe_3), 0.53 ppm (s, 3H; η^3-$C_3H_4(CH_3)$-2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 223.7$ (d, $^2J_{P,C} = 15.11$ Hz; CO), 162.2 (q, $^1J_{C,B} = 49.8$ Hz; C_i), 152.7, 144.6, 139.1 (phen), 135.2 (s; C_o), 131.1 (phen), 129.3 (q, $^2J_{C,F} = 31.2$ Hz; C_m), 128.5, 126.8 (phen), 124.9 (q, $^1J_{C,F} = 272.4$ Hz; CF_3), 117.9 (s; C_p), 89.6 (d, $^2J_{C,P} = 5.3$ Hz; C^2, η^3-$C_3H_4(CH_3)$), 59.5 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 17.3 (η^3-$C_3H_4(CH_3)$-2), 13.3 ppm (d, $^1J_{P,C} = 25.6$ Hz; PCH_3); ^{31}P NMR (CD_2Cl_2): $\delta = -11.4$ ppm.

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